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Practical Second Harmonic Nonlinear Electrochemical Impedance Spectroscopy for Lithium-Ion Batteries

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Abstract

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Lithium-ion batteries (LIBs) are intrinsically nonlinear electrochemical devices with two highly reactive electrodes separated by microns. Understanding the complex chemical and physical interaction between, and within, electrodes of practical LIBs requires *in-situ* and non-destructive characterizations to advance the field. Electrochemical impedance spectroscopy (EIS) is widely used for this purpose, but the method relies on linear approximations of nonlinear processes, leading to loss of information and model degeneracy. Second harmonic nonlinear electrochemical impedance spectroscopy (2nd-NLEIS), when measured simultaneously with EIS, is shown to address the challenges of model degeneracy and loss of information found in EIS. In this work, we provide a practical pathway for characterizing LIBs using 2nd-NLEIS, from simplified physics-

based models and experimental data validation methods to quantitative 2nd-NLEIS analysis strategies and open-source software tools.

Simplified physics-based models for 2nd-NLEIS consider the nonlinear contribution from Butler-Volmer kinetics and Warburg-like solid-state transport and thermodynamics. Analytical theories for 2nd-NLEIS in planar (Randles circuit) and macro-homogeneous porous electrodes are examined to fill the gap between complex full-physics modeling and the needs for practical physical parameter extraction from experimental data. For experiments involving aged LiBs, transmission line models (TLMs) extended to include the second harmonic response provide the flexibility needed to describe complex core-shell particles in the aged cells. Extended TLMs capture the evolution of EIS and 2nd-NLEIS spectra as commercial NMC|C cells age.

We show that 2nd-NLEIS spectra comply with Kramers–Kronig (KK) relations, enabling data quality tests that evaluate the stationarity and causality of EIS, and through this work, 2nd-NLEIS experiments. A nonlinear measurement model (MM) test coupled with measured total harmonic distortion (THD) of less than 1% is shown to be a foundation for ensuring data quality and a suitable perturbation amplitude required for simultaneous EIS and 2nd-NLEIS analysis. The practical implementation of these strategies is included in *nleis.py*, an open-source Python package, to ensure the reproducibility of the simultaneous EIS and 2nd-NLEIS analysis.

EIS and 2nd-NLEIS have complementary parity signals. In a full-cell measurement, the full-cell EIS signal is from the sum of the two half-cell signals whereas full-cell 2nd-NLEIS signals arise from the difference between the two half-cell signals. The summative EIS signals are denoted *positive parity* whereas the subtractive nature of 2nd-NLEIS is denoted *negative parity*, and when fit simultaneously to a common physics-based model, enable the first definitive impedance-based quantification of the evolving charge transfer symmetry for the NMC cathode during aging.

Combining differential voltage analysis with simultaneous EIS and 2nd-NLEIS analysis, we have successfully quantified the growth of asymmetric charge transfer, especially at low states of charge (SOC). By varying SOC, it was observed that the cathode approaches symmetric charge transfer at intermediate SOC (50% SOC). This phenomenon perfectly aligns with the direction of lattice strain reduction given the formation of Ni-rich rocksalt surface layers on NMC particles, providing a non-invasive probe to the surface reconstruction of NMC cathode.

The last piece of this thesis focuses on the real-world impact of the advancements in 2nd-NLEIS. The importance of considering asymmetric charge transfer in time domain application (i.e., SOC estimation) was demonstrated using the full physics pseudo-two-dimensional (P2D) model. We also generated 10228 pairs of unique EIS and 2nd-NLEIS spectra using the full-physics P2D model to support data science assisted parameter estimation and the determination of the domain of applicability for simplified models in the future.

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DEDICATION

To my family, girlfriend, and friends,

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Chapter 1.

INTRODUCTION

Transportation electrification and clean energy storage demand the rapid advancement of battery materials to improve their energy density and longevity. [1,2] Lithium-ion battery (LIB) systems dominate the market with their comparatively high energy density, which makes it one of the most studied and mature battery systems for these applications. [1,3–5] Most recent advancements in LIBs emerge in the materials side (i.e., cathode and anode materials), where experiments and characterizations are performed in half-cells to understand their crystal structures and potential aging mechanisms. [3,6–9] Naïvely, a whole-cell battery is a stack of cathode, separator, and anode filled with electrolyte in a sealed cell container, making the cell structure engineering a focus for whole-cell advancements. [10–12] However, the performances of the individual electrodes in an engineered whole-cell do not exactly follow their half-cell performances due to the interaction between the cathode and anode. [13–15] For example, the transition metal dissolution from the metal oxide cathode can catalyze the decomposition of the stable solid electrolyte interface (SEI) on the graphite anode, leading to detrimental effects on the performance of the cells. [15–17] The result of transition metal dissolution can be probed by invasive methods like XRD, SEM, or ssNMR, but these techniques cannot easily capture the dynamic interaction between electrodes as they usually require cell opening and can only focus on individual electrodes. [3,18,19] In contrast, electrochemical techniques can be used to probe these interactions noninvasively. [14,15] For instance, lithium plating can be identified with differential voltage analysis, which is good at probing slow bulk thermodynamics but not fast dynamics at the electrode interface. [20] Most battery degradation happens at the electrochemical interface, which urges the application and

advancement of noninvasive characterization techniques that can probe the interfacial dynamics. [21–23]

Electrochemical impedance spectroscopy (EIS) is a powerful noninvasive characterization technique used to study aging and electrode interactions in LIBs. [24–27] Chemical and physical characteristics can be learned from frequency domain measurement with EIS and applied to time domain applications like state estimation and battery diagnostics. [28–31] One major challenge for impedance analysis is the linearity requirement for EIS, where measurements are well-controlled so that the system response can be linearized, though the electrochemical processes in LIBs are intrinsically nonlinear. Information loss is unavoidable during linearization, while the problem of model degeneracy arises at the same time. [32–35] Nonlinear electrochemical impedance spectroscopy (NLEIS), on the other hand, is designed to account for the intrinsic nonlinearity of the battery system. Early attempts of NLEIS aimed to measure and analyze the strong nonlinear response of the electrochemical system. [33,36–39] Under strong nonlinear dynamics, challenges emerge from experimentation and modeling. Experimentally, the strong perturbation, though it improves the signal-to-noise ratio, [40] can corrupt the linear signal acquisition. [41] Theoretically, physics modeling is even more challenging. One key consequence of the large perturbation is the inapplicability of Taylor and Volterra series approximations of the highly nonlinear response given the large deviation from the equilibrium. [42] Equally important, when the perturbation is large enough, the validity of Butler-Volmer kinetics is questionable and more complicated charge transfer mechanisms like Marcus Theory are required to describe the system. [43]

Second harmonic nonlinear electrochemical impedance spectroscopy (2nd-NLEIS) is a specialized form of NLEIS, the leading order nonlinear response, when an electrochemical interface is driven into a weakly nonlinear regime. The potential value of 2nd-NLEIS was first

explored by Murbach et al., and they have shown experimentally and mathematically that the first (linear) and second harmonic (nonlinear) impedance response can be acquired simultaneously under the weakly nonlinear regime. [26,34] Electrochemical processes that cannot be seen in linearized EIS measurements are now acquired in the second harmonic response (i.e., asymmetry of the charge transfer reaction). Moreover, simultaneous EIS and 2nd-NLEIS analysis introduces a mathematical advantage, complementary parity, that can facilitate much greater self-consistency in parameter extraction. That is, the full cell EIS signal is the sum of cathode and anode response (*positive parity*), and the full cell 2nd-NLEIS is the difference of cathode and anode response (*negative parity*). [35,44–46] Though 2nd-NLEIS introduces many complementary benefits to EIS alone, the practical application of 2nd-NLEIS remains challenging due to the lack of tools to validate and analyze the experimental data. This thesis addressed these 2nd-NLEIS challenges by providing simplified physics-based models, effective data validation methods, and software tools for data analysis. [34,35,44,47]

1.1 LINEAR AND SECOND-HARMONIC NONLINEAR ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Electrochemical impedance spectroscopy (EIS), or linear EIS, is an electrochemical characterization technique achieved by introducing either current (G-EIS) or voltage (P-EIS) perturbation and measuring the corresponding voltage or current response in the frequency domain. [48] In practice, G-EIS is usually better for engineered LIBs as they generally experience less impedance and a larger current perturbation is easier control, making it easier to measure a small voltage response. [49] Additionally, as discussed in this dissertation, G-EIS ensures there is no state-of-charge drift during nonlinear experiments on the closed LIB system, whereas P-EIS cannot ensure this in LIBs.

G-EIS experiments impose a single frequency alternating current (AC) excitation to the electrochemical systems under study. For simplicity, the perturbation can be expressed in Euler's representation as,

$$I = \Delta I \exp(j\omega t) \quad (1.1)$$

where $j = \sqrt{-1}$, ΔI is the amplitude of the current modulation (*Amp*) with frequency ω (*radians/s*). A general rule of thumb for EIS is to find a current amplitude that generates a 5 mV voltage response. Under 5 mV perturbation, the voltage output (E_{EIS}) for a stationary system can be linearized and produces a modulated output voltage ($\tilde{E}_1$) at the excitation frequency ω .

$$E_{EIS} = \tilde{E}_1 \exp(j\omega t) + h.o.t. \quad (1.2)$$

where *h.o.t.* represents the nonlinear higher order terms that are ignored as small during linearization. The linear impedance ($\tilde{Z}_1$) of the system is then analogous to Ohm's Law in the DC systems and can be written as,

$$\tilde{Z}_1(\omega) = \frac{\tilde{E}_1}{\Delta I} \quad (1.3)$$

Second harmonic nonlinear electrochemical impedance spectroscopy (2nd-NLEIS) can be viewed as an extension to the linear EIS by slightly over-perturbing the system to the weakly nonlinear regime. For an appropriate excitation amplitude that drives the system to this regime, Murbach et al. demonstrated that the weakly nonlinear voltage response is a combination of the linear ($\tilde{E}_1$) and second ($\tilde{E}_2$) harmonic voltage response, [45]

$$\tilde{E}_{2nd-NLEIS} = \tilde{E}_1 \exp(j\omega t) + \tilde{E}_2 \exp(j2\omega t) + h.o.t. \quad (1.4)$$

where *h.o.t.* represents the additional nonlinear higher order term that are ignored when considering only the leading order nonlinearity. Do note, the Euler representation here can be related to its trigonometric equivalent by scaling $\tilde{E}_2$ by 1/2 if a sine or cosine wave is used to

perturb the system. Following the Volterra series development, the second harmonic nonlinear impedance ($\tilde{Z}_2$) response can be defined as

$$\tilde{Z}_2(\omega) = \frac{\tilde{E}_2}{(\Delta I)^2} \quad (1.5)$$

Importantly, **Equation 1.4** provides the theoretical foundation for the simultaneous data acquisition and analysis of linear and second harmonic nonlinear impedance response. [35,45]

A key source of nonlinearity in electrochemical systems is charge transfer at the electrified interface. **Figure 1.1** shows Butler-Volmer kinetics with different degrees of charge transfer asymmetry represented by the anodic (α_a) and cathodic (α_c) charge transfer coefficients. Under 5 mV (bounded by black dashed lines), the relationship between overpotential and current density can be linearized and is insensitive to the charge transfer coefficients; EIS is likewise insensitive to charge transfer symmetry in a stationary LIB measurement. On the other hand, the overpotential and current density follow a weakly nonlinear relationship when the overpotential resides between 5 mV and 20 mV (bounded by orange dashed lines), allowing one to discriminate between symmetric ($\alpha_a = \alpha_c$) or asymmetric ($\alpha_a \neq \alpha_c$) charge transfer; 2nd-NLEIS is likewise sensitive to charge transfer symmetry in a stationary LIB measurement.

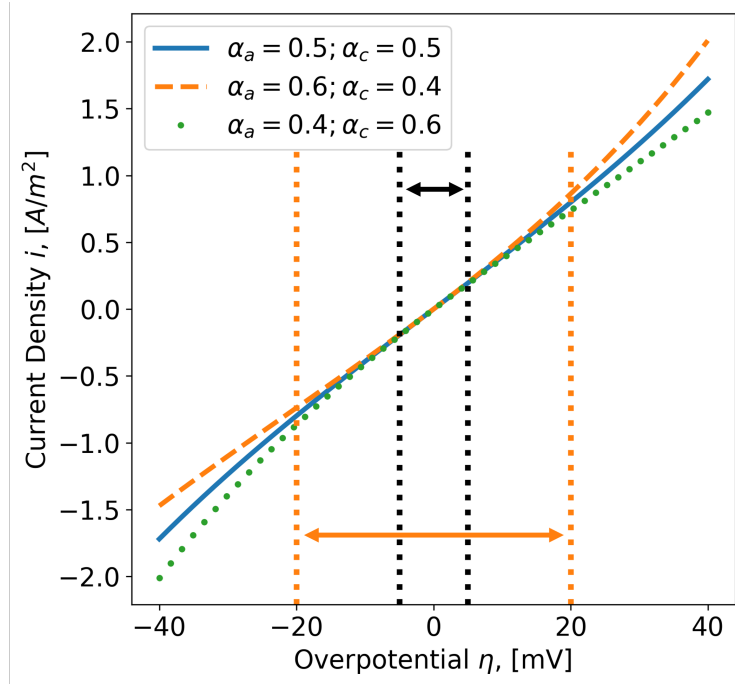


Figure 1.1. Butler-Volmer (BV) kinetics as a function of the overpotential from -40 to 40 mV. The black dashed line shows the approximate linear regime in the BV kinetics ($|\eta| \leq 5$ mV). The orange dashed line shows the weakly nonlinear regime in the BV kinetics ($|\eta| \leq 20$ mV). The anodic (α_a) and cathodic (α_c) charge transfer coefficient is varied with $\alpha_a + \alpha_c = 1$. A symmetric charge transfer is represented by $\alpha_a = \alpha_c = 0.5$. An asymmetric charge transfer that favors anodic (oxidation) reaction is represented by $\alpha_a > \alpha_c$, while cathodic (reduction) reaction is favored when $\alpha_a < \alpha_c$.

The schematics of a typical data acquisition process for EIS and 2nd-NLEIS are shown in **Figure 1.2**. A sinusoidal AC current with amplitude ΔI is shown in **Figure 1.2a**. The corresponding time domain oscillating voltage response is shown in **Figure 1.2b**. A phase shift is usually present in the time domain voltage response. Due to the intrinsic nonlinearity of the electrochemical system, the time domain voltage response is the superposition of all the harmonics generated by the system, which are challenging to distinguish in the time domain. Instead, the time domain data needs to be converted to the frequency domain using the Fourier Transform to separate the harmonic response of the stationary and causal system. In practice, Fast Fourier

Transforms (FFTs) are used to convert time domain data to the frequency domain. **Figure 1.2c-e** illustrates the frequency domain after FFT of the current input and voltage output described in **Figure 1.2a-b**. As demonstrated in **Figure 1.2c**, an ideal current input contains only the first harmonic and no higher harmonics, mirroring **Equation 1.1**, so that electrochemical nonlinearity is the only source of higher harmonics in the voltage response. The frequency domain voltage response is shown in **Figure 1.2d-e** for the first ten harmonics. With appropriate current perturbation amplitude ΔI , the system can be controlled to generate a dominant first harmonic voltage signals (EIS), measurable second harmonic voltage signal (2nd-NLEIS), and more modest third and higher harmonic signals, mirroring the form of **Equation 1.4**. This step aligns analysis with the EIS and 2nd-NLEIS experiments.

The presence of a second harmonics is system-symmetry dependent. In half cell experiments, the combination of symmetric charge transfer and the lack of curvature in the open circuit potential (at the state-of-charge being examined) results in an odd-harmonic spectrum **Figure 1.2d**. On the other hand, significant second harmonic signals can be measured if the system has asymmetric charge transfer, curvature in the open circuit potential, or both (**Figure 1.2e**). The art of 2nd-NLEIS is, thus, to optimize the perturbation amplitude and measure high quality first harmonic and second harmonic voltage responses without the complicating influence of higher harmonics. When experiments and analysis are aligned, the measured harmonic current and voltages at each frequency can be fed into **Equations 1.1-5** to calculate the full spectrum EIS and 2nd-NLEIS.

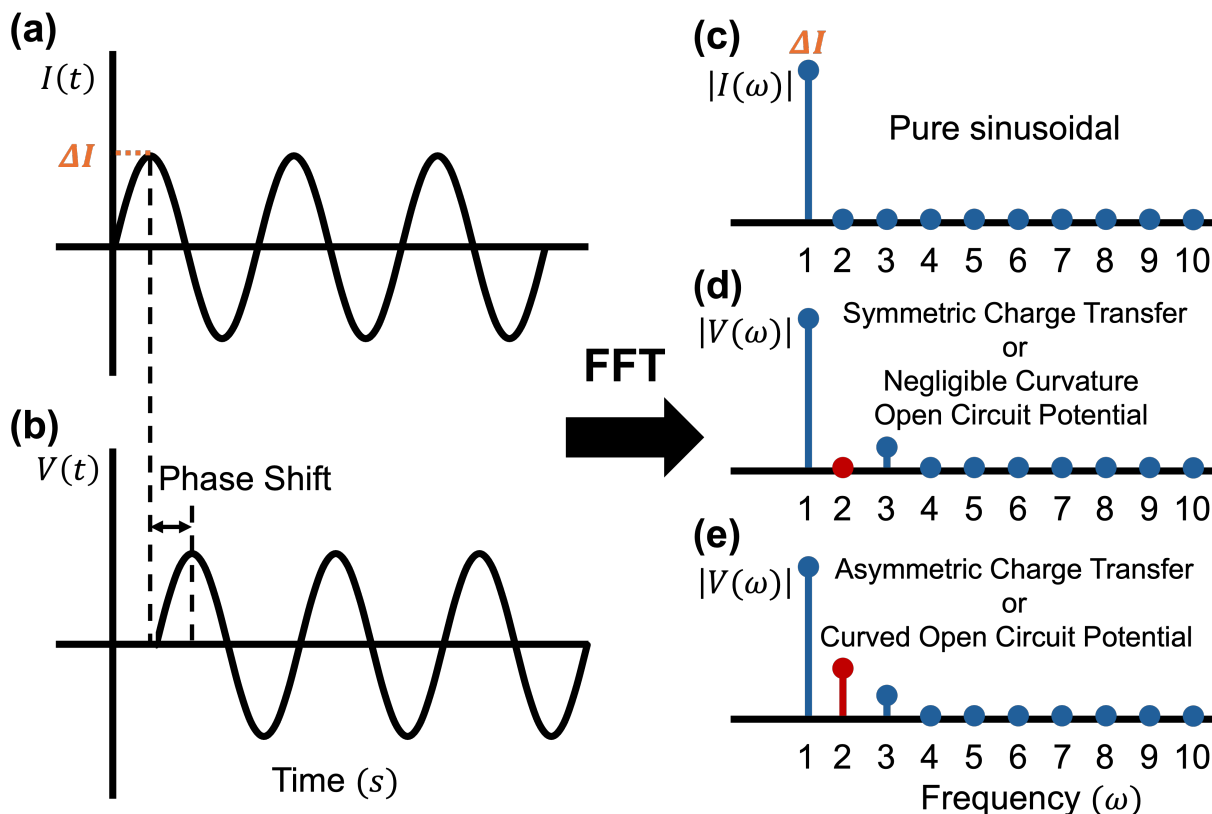


Figure 1.2. Schematic for a single frequency galvanostatic EIS and 2nd-NLEIS experiment in frequency and time domain. a) current perturbation and b) voltage response in the time domain. c) current harmonics, d) symmetric voltage harmonics, and asymmetric voltage harmonics in the frequency domain. The first 10 harmonics are shown in the frequency domain and the second harmonic voltage response is labeled in red.

The frequency dependence of EIS and 2nd-NLEIS makes them a unique electrochemical technique that can distinguish ohmic, charge transfer, and diffusion processes in the battery system. These processes possess separated time scales, making the separation of electrochemical processes possible in a wide range of sweeping frequencies. [50] Mathematically, the 2nd-NLEIS response is driven by the EIS response, so the 2nd-NLEIS response inherits all the linear characteristics from EIS response and adds unique nonlinear characteristics of the system. [35] **Figure 1.3** shows a pair of typical whole-cell EIS and 2nd-NLEIS data in Nyquist plot representations for LIBs. As shown

in **Figure 1.3a**, the EIS spectrum can be separated into five different regions. At high frequencies, inductance appears as a measurement artifact from the electrical contacts, which is usually ignored for the impedance analysis. The high frequency response also shows the ohmic characteristic of the LIBs, where no imaginary component is present. As the frequency is reduced, the impedance response is dominated by the charge transfer and capacitive character of each electrode interface, as shown in **Figure 1.3a**. Though shown separately in the illustration, real battery measurements usually exhibit less distinct separation between the two electrode processes. At low frequencies, solid state diffusion and thermodynamics become important as the lithium ions insert within the electrode and interfacial thermodynamic equilibrium dominates the diffusion response. This leads to the widely observed Warburg-like diffusion tail shown in **Figure 1.3a**. Overall, the whole-cell EIS spectrum is obtained from the summation of the impedance contribution from these five regions. This is a characteristic of *positive parity* signals, where individual electrode responses are summed to provide a whole-cell response. On the other hand, 2nd-NLEIS possesses a *negative parity* signal, where the impedance response is the difference between the cathode and anode. Furthermore, each electrode's 2nd-NLEIS response inherits its linear characteristics. **Figure 1.3b** shows a schematic of 2nd-NLEIS spectrum. The example 2nd-NLEIS response is in three quadrants of the Nyquist plot, but the actual response in batteries can spread all four quadrants as a consequence of the subtraction between two electrodes, making it sensitive to the changes in each electrode. In all our formulations of 2nd-NLEIS, the second harmonic signal inherits all the same characteristic time scale as the corresponding EIS; no new timescales are introduced. The second harmonic nonlinear charge transfer response at high frequencies always “spirals” into the origin as the LIB response becomes purely resistive (a true linear state). At intermediate frequencies where interfacial charge transfer is seen in EIS, 2nd-NLEIS also displays a charge transfer loop if

there is an electrode with asymmetric charge transfer. Finally, similar to the linear response, the nonlinear diffusion and thermodynamics reside in the low frequency region and exhibit a tail shape as well. The EIS and 2nd-NLEIS spectra together open a new perspective on LIB characterization. Advancements in the analytical theory and analysis strategies are indispensable for taking advantage of the additional physical information from 2nd-NLEIS.

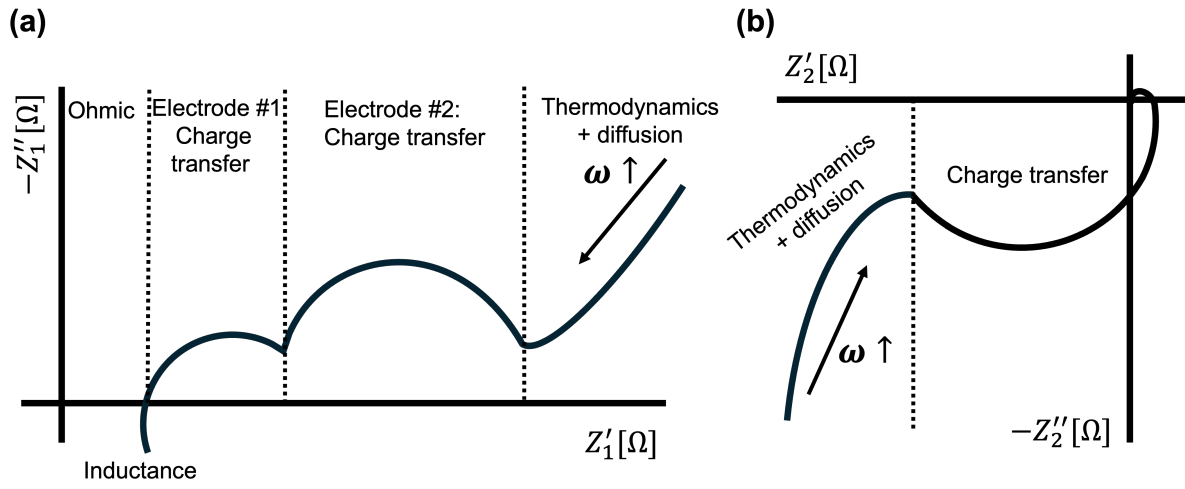


Figure 1.3. Schematic Nyquist plots of typical whole-cell a) EIS and b) 2nd-NLEIS spectra for LIB.

1.2 PHYSICS-BASED MODELING FOR EIS AND 2ND-NLEIS

Simultaneous data acquisition of both EIS and 2nd-NLEIS for lithium-ion batteries (LIBs) can be easily achieved with well-controlled experiments that drive the system to the weakly nonlinear regime using conventional EIS equipment. [26] The data analysis and interpretation of the 2nd-NLEIS remain the biggest challenge. Physics-based and equivalent circuit-based modeling are two major approaches that are well-established in the field of EIS. [45,50] A full physics model like Newman's pseudo-2-dimensional (P2D) model provides descriptions to most physics that happens in LIBs with the cost of substantial model complexity. [45] Equivalent circuit models (ECMs), on the other hand, employ simplified physics and (when done appropriately) a convenient physics-

informed visualization of the system to describe the apparent impedance of LIBs. [51] Unfortunately, the simplicity of ECMs comes with the risk of losing direct physical interpretability if the analyst is simply curve-fitting. [52] Despite this, the simplicity of ECMs makes them the most popular approach in EIS analysis. [27,53]

Though ECMs dominate the EIS data analysis, when extending to the weakly nonlinear dynamics, physics-based modeling is still essential for understanding and analyzing the weakly nonlinear responses. Early modeling works has focused on the P2D model. Murbach and Schwartz extended Newman's P2D model to include the nonlinear second and third harmonic response. [34] The weakly nonlinear P2D model is physics informative and has a total of 42 parameters (4 more parameters than the linear P2D model), but the complexity of the P2D model requires extensive computational power to numerically simulate a pair of EIS and 2nd-NLEIS spectra, making it inapplicable to real-time applications. [34] Moreover, the impedance response is insensitive to many of the individual 42 parameters, leading to redundancies in numerical simulations. [34,35] Model simplification is an emerging area for EIS and 2nd-NLEIS analysis. For example, Kirk et al. developed a nonlinear single particle (SPM) model that aims to resolve the issue of model complexity, but their model appears to be too simple to capture all the physics in commercial LIBs. [44] We have published nonlinear Randles circuit and porous electrode models. [35] Therefore, adapting a physics-based modelling approach with sufficient physics to connect experiments with interpretable ECMs will be crucial to encourage the adoption of the 2nd-NLEIS.

P2D model, though not efficient for parameter estimations, can further enrich the understanding of LIBs' weakly nonlinear response with the emergence of data science and machine learning approaches. Many experimental datasets for LIBs have been introduced in the past decades to encourage data-driven analysis. [54–56] Severson et al. published a dataset of 124

LFP cells to develop a machine learning model for the state of health (SOH) diagnosis of LIBs. [55] The experimental data acquisition requires significant investment in time and fixed capitals, which makes 124 LFP cells one of the largest publicly available datasets. A comprehensive experimental dataset for EIS and 2nd-NLEIS is even limited given the complexity of the experiments. As a result, numerical simulation is essential to advancing data-driven methods. The P2D model, with its comprehensive physics, is a perfect candidate for physical data generation. For example, Murbach and Schwartz have originated this process with a simulation of 38000 unique EIS spectra to facilitate parameter estimation using data science approaches, while a complementary 2nd-NLEIS data is still missing. [45] Consequently, a comprehensive dataset widely exploring the feasible space of both EIS and 2nd-NLEIS data is essential for advancing the field.

1.3 LITHIUM-ION BATTERY DIAGNOSIS AND PROGNOSIS

Diagnosis and prognosis of lithium-ion batteries (LIBs) is an active field of research for the development of engineered whole-cells. [14,26,46,55,57,58] As the interaction between electrodes becomes increasingly important during cycling, electrochemical characterization methods are ideal for non-invasively probing the exact physical environment in the cell. [14,24,25,46] For example, lithium plating can be observed by post-mortem characterization, but the observed lithium plating only accounts for a small portion of the plated lithium due to its reversibility during cycling in the electrolyte. [59,60] Derivative-based techniques, like differential voltage analysis, can provide bulk thermodynamic and chemical reaction information about the battery system. [14] For example, capacity slippage can be observed and used as a state of health (SOH) metric, [61] but these methods are less sensitive to the faster dynamics in the battery. Data-driven approaches are another popular direction for advanced battery diagnosis and prognosis.

Large experimental datasets are required to feed into machine learning models with the hope of finding the intrinsic correlation between cycling data and SOH. [55,62] Acquiring large battery aging datasets is expensive, so is largely limited to industrial organizations. Limited data availability makes data-driven analysis less intriguing than physics-informed analysis for academic research.

Electrochemical impedance spectroscopy (EIS), as noted above, is good at probing reaction kinetics, solid diffusion, and thermodynamics that occur at different characteristic time scales, [50] so is a key method to understanding the internal dynamics of whole-cell LIBs. Perhaps the most well-known characteristic of LIBs, especially those with NMC (nickel/manganese/cobalt oxide) cathodes, is their increasing cathode charge transfer resistance as they age. [24–26,63] As we show in this dissertation, 2nd-NLEIS provides a uniquely mechanism-sensitive view into the EIS observation of increasing charge transfer resistance.[26,35,46,64] Likewise, because 2nd-NLEIS is sensitive to the curvature of the equilibrium potential, we show that important new thermodynamic information about interfacial dynamics can be probed with 2nd-NLEIS that is not available in EIS.

1.4 REAL-TIME STATE ESTIMATION, DIAGNOSIS, AND CONTROL

Transportation electrification is one of the key application areas for lithium-ion batteries (LIBs). In many popular electric vehicles (EVs), thousands of cylindrical LIBs are packed into a battery pack to store and release energy. A battery pack in the EV is, thus, a source of energy analogous to the fuel tank filled with gas in the conventional gasoline-based vehicle. [65] The limited range of contemporary EVs coupled with the lack of charging infrastructure, as compared to gasoline-based vehicles, raises the range anxiety for drivers. [66] While the amount of energy remaining in the fuel tank is easily and reliably measured, the amount of energy stored (lithium ion in each electrode) in the battery system cannot be measured directly in a sealed battery pack,

introducing a challenging state estimation problem. [67] Current battery state estimation (fuel gauge) algorithms are dominated by integration-based and model-based approaches. [68] Coulombic counting is one of the simplest integration-based approaches that relies heavily on the accuracy of the current sensor. [69] In a perfect world, a battery's state of charge (SOC) can be accurately estimated with the integration of the current throughput over time. However, real world applications are full of noise and errors, requiring complicated methods to achieve an outcome that seems straightforward. [70] As a result, integration-based methods are usually coupled with voltage-based methods to recalibrate the algorithm or used as a precursor for model-based methods to provide a more accurate state estimation. [69,71–73] Model-based approaches, on the other hand, require accurate cell models that can be integrated with an optimal Kalman filter to eliminate the effect of noisy current measurement and to recalibrate SOC estimation with the voltage measurement. [71–74] Equivalent circuit models (ECMs) are normally chosen over full physics model owing to their simplicity and additivity. An additional correction circuit element can be easily added to the existing model to introduce new physics without significantly increasing the model complexity or complicating the algorithm. [75] In general, ECMs can capture most of the variance in the battery system. [76] A major limitation of ECMs is that the models are derived from the linearization of nonlinear battery system responses. [26,35] The linearization of the nonlinear system response not only leads to information loss, but also fails to capture the system responses when the system behaves nonlinearly under large power requirements. [77] For example, the asymmetric behavior in the charge transfer reaction is completely ignored from linearization, even in more sophisticated models. [78–81] Many recent publications have demonstrated the emergence of asymmetric charge transfer behavior, [26,35,64,82] which is, thus, a necessary component for cell models to achieve a reliable full range (0 to 100%) state estimation.

1.5 THESIS ROADMAP

From half-cell physics to full cell characterization, this thesis provides a practical pathway to utilize 2nd-NLEIS to gain more physical insight about lithium-ion batteries (LIBs) non-invasively. To achieve these goals, comprehensive theoretical, experimental, and software development are conducted to advance 2nd-NLEIS in LIB research. This thesis is then organized as the follows: **Chapter 2** describes the analytical theory (planar and macro-homogeneous porous electrode) for 2nd-NLEIS, paving the foundation for this thesis; **Chapter 3** extends the analytical theory and builds numerical transmission line models to enrich the tools available for 2nd-NLEIS analysis; **Chapter 4** introduces a nonlinear measurement model approach to enable the validation of 2nd-NLEIS experiments; **Chapter 5** proposes a data analysis pipeline for the simultaneous analysis of EIS and 2nd-NLEIS and points out multiple areas of future researches; **Chapter 6** focuses on the state of health (SOH) diagnosis with the EIS and 2nd-NLEIS for commercial LIBs, providing connection between the breakdown of charge transfer symmetry and the growth of lattice strain during aging of Ni-rich NMC cathodes; **Chapter 7** introduces *nleis.py* as a robust open-source software tool to support the 2nd-NLEIS data processing and analysis; Lastly, **Chapter 8** concludes the thesis and brings up the area of future research on 2nd-NLEIS and their potential impacts from state estimation and data science perspectives.

Chapter 2.

SECOND-HARMONIC NONLINEAR ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY: I. ANALYTICAL THEORY AND EQUIVALENT CIRCUIT REPRESENTATIONS FOR PLANAR AND POROUS ELECTRODES

Note: this chapter was published as an article

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Abstract

Analytical theory for second harmonic nonlinear electrochemical impedance spectroscopy (2nd-NLEIS) of planar and porous electrodes is developed for interfaces governed by Butler-Volmer kinetics, a Helmholtz (mainly) or Gouy-Chapman (introduced) double layer, and transport by ion migration and diffusion. A continuum of analytical EIS and 2nd-NLEIS models is presented, from nonlinear Randles circuits with or without diffusion impedances to nonlinear macrohomogeneous porous electrode theory that is shown to be analogous to a nonlinear transmission-line model. EIS and 2nd-NLEIS for planar electrodes share classic charge transfer RC and diffusion time-scales, whereas porous electrode EIS and 2nd-NLEIS share three characteristic time constants. In both cases, the magnitude of 2nd-NLEIS is proportional to nonlinear charge transfer asymmetry and thermodynamic curvature parameters. The phase behavior of 2nd-NLEIS is more complex and model-sensitive than in EIS, with half-cell NLEIS spectra potentially traversing all four quadrants of a Nyquist plot. We explore the power of simultaneously analyzing the linear EIS and 2nd-NLEIS spectra for two-electrode configurations, where the full-cell linear EIS signal arises from the sum of the half-cell spectra, while the 2nd-NLEIS signal arises from their difference.

2.1 INTRODUCTION

Electrochemical impedance spectroscopy (EIS) is a widely used electroanalytical technique for studying fundamental and applied aspects of corrosion, [83,84] biosensors, [85,86] fuel cells, [87,88] and batteries. [89,90] EIS probes the linear frequency response of electrochemical interfaces. Yet, electrochemical interfaces are inherently nonlinear, so the mathematics that underpins EIS analysis is an approximation that holds in the limit of infinitesimal current or voltage modulations, where nonlinearity-generated higher-order responses can be ignored. In practice, a rule of thumb for experiments is that interfacial modulations under 5 mV are sufficiently small for linear analysis, though tests are available to ensure real data meets linearity and stationarity assumptions. [91,92] Linearization of a nonlinear system results in a loss of information and introduces the potential for degeneracy in both equivalent circuit-based and physics-based analysis, sometimes limiting the mechanistic discriminating power of EIS. [32,33] Two distinct approaches have emerged to explore the frequency response of electrochemical interfaces beyond the infinitesimal linear response limit, namely, probing the weakly nonlinear response with modulations just larger than the linear limits [51] or strongly nonlinear responses from large modulations that drive complex nonlinear system dynamics. [40] Here we focus on weak nonlinearity as it has the discriminating power of nonlinear analysis while maintaining moderate amplitude modulations that are less likely to damage the electrochemical interface(s) under test.

Perhaps the most studied weakly nonlinear electroanalytical technique is faradaic rectification, a method that relies on moderate amplitude current modulations of the electrochemical interface to generate measurable frequency-dependent shifts of the mean voltage under conditions of zero mean current. [93,94] As with linear EIS, practitioners of faradaic rectification have identified tests for whether current modulations are sufficient to excite 2nd-order

nonlinear processes without over driving the system (thereby complicating analysis); a rule of thumb is that current modulations should produce under 20 mV of voltage oscillation. [95] Other examples of weakly nonlinear frequency response methods in electrochemistry include more specialized techniques such as nonlinear hydrodynamic modulation voltammetry (HNV). [96,97] In HNV, experiments and theory can measure and explain frequency-dependent limiting current behaviors that result from second-order Reynolds stress rectification of flow, creating an HNV-analog of faradaic rectification, [98] as well as probe and understand complex magnitude and phase behaviors of oscillating limiting current harmonics that occur in second- and higher-order nonlinear processes. [99] Faradaic rectification and nonlinear HNV are mainly applied to fairly simple electroanalytical half-cell configurations with planar interfaces, where transport is neglected or carefully controlled via a rotating disc electrode.

Probing the weakly nonlinear response of more complex porous electrode configurations, such as those used in electrochemical energy applications, is a rather new extension of linear EIS. Wilson et al. looked at third harmonic nonlinear electrochemical impedance spectroscopy (3rd-NLEIS) to qualitatively discriminate among multiple oxygen reduction mechanisms in symmetric cells with two identical porous solid oxide fuel cell (SOFC) electrodes. [33] Murbach et al. showed the power of second harmonic NLEIS (2nd-NLEIS) when using two dissimilar electrodes in a battery configuration, which produced full-cell responses with both even and odd harmonic NLEIS spectra. [26] Physics-based analysis showed that 2nd-NLEIS provides access to interfacial processes not measurable with linearized EIS and, importantly, the presence of a 2nd-NLEIS signal need not alter the analysis of traditional EIS, as long as the driving current modulation amplitude is small enough to avoid third-order nonlinear processes. [34] In practice, this means selecting a current modulation that produces a measurable second harmonic in the output voltage spectrum

without also generating measurable third- or higher-harmonics. [26] While the most direct way to assess the appropriate current modulation amplitudes for 2nd-NLEIS is through analysis of the voltage spectrum, a rule of thumb is that input current modulations should produce voltage modulations above 5 mV (the typical linear limit) and below 20 mV (the typical faradaic rectification limit) to avoid over-driving nonlinear processes and corrupting the linear response. [26]

As Wilson, et al. [33] and Murbach et al. [26,34] have shown, physics-based NLEIS modeling and complementary experiments provide powerful mechanistic discrimination and insights for porous electrodes in complex electrochemical configurations, but these complex models have not been useful for parameter estimation from datasets. Recently, a nonlinear single particle model (SPM) has been developed by Kirk et al. to quantitatively analyze 2nd-NLEIS spectra for commercial Li-ion batteries; this represents, to the best of our knowledge, the first model-based analysis of 2nd-NLEIS data. [44] The battery datasets fit by Kirk et al. showed the classical EIS depressed interfacial charge transfer behavior that is attributable to co-limiting ohmic and charge transfer within the porous battery electrodes; [44] co-limiting physics is not captured by SPM models where no ohmic variation or current density variation is allowed to occur in the porous electrode. In short, the P2D-based models in Murbach et al. were too complex for quantitative analysis of battery EIS and 2nd-NLEIS data, whereas Kirk et al. demonstrated the power of parameter estimation with simple models, but the specific model used excluded essential physics seen in the battery dataset.

In this work, we seek to develop a continuum of increasingly sophisticated modeled physics—from nonlinear Randles circuits and nonlinear SPMs to simplified nonlinear porous electrodes—in order to explore the essential drivers of 2nd-NLEIS, and the ways linear EIS and

2nd-NLEIS complement one another. We also explore the implications of a subtle point made by Murbach et al., [26] namely, the “parity rules” for NLEIS response when two half-cells are combined into a two-electrode cell. Specifically, the odd-harmonic NLEIS signals from half-cells add to produce the full-cell odd-harmonic NLEIS response, whereas even-harmonic NLEIS signals from two half-cells get subtracted to produce the full-cell even-harmonic NLEIS response. Here, we further elaborate on the impact of two-electrode cells having additive “positive parity” first harmonic (linear) EIS spectra and complementary subtractive “negative parity” 2nd-NLEIS spectra. One consequence of these harmonic “parity rules” can be seen in the symmetric two-electrode experiments reported by Wilson et al., [33] where only odd-harmonics were present in the NLEIS spectrum; in a symmetric cell, the identical 2nd-NLEIS half-cell signals nullify at all frequencies.

Overall, our goal here is to simplify the physics, analysis, and equivalent circuit representation of 2nd-NLEIS to chart a tractable and easy to implement quantitative analysis pathway that can be viewed as a natural extension of EIS for planar and porous electrode half-cells, as well as their combination into two-electrode configurations. This paper is accompanied by Part II, an experimental study to show model implementation.

2.2 GOVERNING PHYSICS FOR THE DYNAMICS OF WEAKLY NONLINEAR PLANAR AND POROUS ELECTRODES

A key driver for the nonlinear response of an electrochemical interface is the charge transfer reaction. For a weakly nonlinear electrochemical interface, the faradaic current density (i_f) is expressed using a two-term Taylor series expansion of the Butler–Volmer equation for small but finite overpotentials, i.e., $f(E - E_n) \ll 1$, yielding

$$i_f \approx i_0 f(E - E_n) + \varepsilon i_0 f^2(E - E_n)^2 + h.o.t. \quad (2.1)$$

where i_0 is the exchange current density (A/m^2), $E = \phi_s - \phi_i$ is the interfacial potential difference (V) between the solid electrode and the ion-conducting electrolyte, $E_n = (\phi_s - \phi_i)^{eq}$ is the equilibrium interfacial potential difference (V), and $f = \frac{nF}{RT}$ (V^{-1}). The parameter ε is a measure of charge transfer asymmetry (dimensionless) such that the anodic and cathodic charge transfer coefficients are $\alpha_a = 0.5 + \varepsilon$ and $\alpha_c = 0.5 - \varepsilon$, respectively, with $\varepsilon = 0$ representing symmetric charge transfer. Finally, *h.o.t.* denotes the higher order terms of the Taylor series which we ignore here, but can be included in the description of the weakly nonlinear electrochemical interface as it is increasingly perturbed from equilibrium. Non-faradaic current (i_{nf}) is treated with a simple (linear) constant-coefficient Helmholtz model:

$$i_{nf} = c_{dl} \frac{dE}{dt} \quad (2.2)$$

where c_{dl} is the double layer capacitance per unit interfacial area (F/m^2). Consequently, a planar electrochemical interface of area A (m^2) has a total current (I) given by the sum of **Equations 2.1** and **2.2** in the weakly nonlinear regime

$$\frac{I}{A} = i_0 f(E - E_n) + \varepsilon i_0 f^2(E - E_n)^2 + c_{dl} \frac{dE}{dt}. \quad (2.3)$$

Next, we formulate the weakly nonlinear governing equation for a porous electrode of thickness d (m) on a current collector of area A (m^2), where we denote the internal interfacial area per unit volume of the porous electrode as S_c (m^{-1}). Per the schematic in **Figure 2.1**, bulk electrolyte contacting the electrolyte-filled porous electrode is located at $x = 0$ and the current collector is at $x = d$. The weakly nonlinear behavior we explore here is a straightforward extension of the macrohomogeneous porous electrode theory developed by Paasch et al., [100] except we use the two-term quadratic form of **Equation 2.1** instead of the single term linear

response. Because most porous electrodes utilize a low resistivity solid relative to the ionic resistivity of the electrolyte in the pores, we simplify our formulation of Paasch's equations using a constant solid potential $\phi_s = \text{const}$. The resulting macrohomogeneous governing equation for charge conservation in the porous electrode domain, extended to the weakly nonlinear regime using **Equation 2.1**, is

$$\frac{1}{\rho_i} \frac{\partial^2 E}{\partial x^2} = S_c c_{dl} \frac{dE}{dt} + S_c i_0 f(E - E_n) + S_c \varepsilon i_0 f^2(E - E_n)^2, \quad (2.4)$$

where ρ_i is the effective ionic resistivity of electrolyte ($\Omega \cdot m$) from volume-averaging the electrode pore-space.

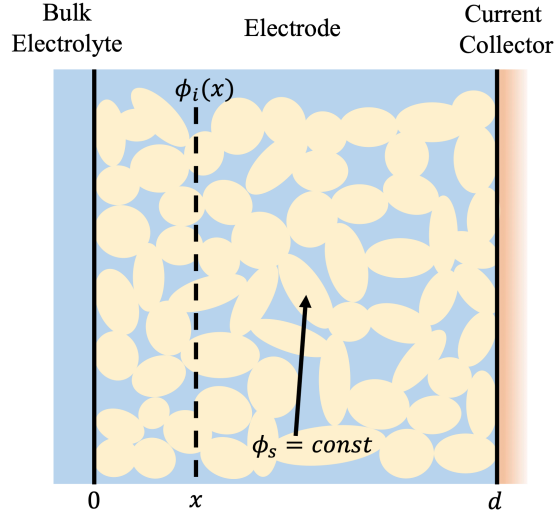


Figure 2.1. Two-dimensional schematic of a porous electrode with zero resistivity solid (yellow regions) and interconnected pores filled with an ion-conducting electrolyte phase (blue regions).

2.2.1 Casting the Governing Equations into a Weakly Nonlinear Impedance Formalism

Electrochemical impedance spectroscopy (EIS) experiments impose a single frequency alternating current excitation to the electrode under study, represented here as

$$I = \Delta I \exp(j\omega t), \quad (2.5)$$

where $j = \sqrt{-1}$, ΔI is the amplitude of the current modulation (*Amp*) with frequency ω (*radians/s*) For sufficiently small excitation amplitude ΔI , the voltage output for a stationary system is dominated by the linear response of the interface and produces a modulated voltage at the excitation frequency ω . Murbach et al. has shown theoretically, [34] and validated experimentally, [26] that moderately larger amplitude single-frequency current excitations can generate a weakly nonlinear modulated voltage response of the form

$$E = \tilde{E}_1 \exp(j\omega t) + \tilde{E}_2 \exp(j2\omega t) + h.o.t. \quad (2.6)$$

where the voltage output is at the excitation frequency ω and the second harmonic 2ω . To be consistent with **Equation 2.1**, we ignore higher order terms generated at increasingly large current modulation amplitudes, but can direct the interested reader elsewhere for the formal solution structure for *h.o.t.* [33,101,102] As we have shown previously, [26] the linear and second harmonic impedances from the voltage spectrum represented by **Equation 6** are

$$\tilde{Z}_1(\omega) = \frac{\tilde{E}_1}{\Delta I} \quad (2.7)$$

and

$$\tilde{Z}_2(\omega) = \frac{\tilde{E}_2}{\Delta I^2} \quad (2.8)$$

where $\tilde{Z}_1$ is the complex frequency-dependent (linear) EIS and $\tilde{Z}_2$ is the complex frequency-dependent second harmonic nonlinear EIS (2nd-NLEIS) function.

Mathematically, the EIS function $\tilde{Z}_1(\omega)$ computed in **Equation 2.7** is identical to the comparable (linear) EIS spectrum when **Equation 2.6** represents the voltage spectrum; practically, we have shown that achieving **Equation 2.6** experimentally is straightforward.[26] In contrast, when the current amplitude is large enough to generate half-cell voltage spectra with three, four, or higher multiples of the excitation frequency, then $\tilde{Z}_1(\omega)$ computed in **Equation 2.7** will have

additional nonlinear contributions that deviate from the traditional (linear) response. Here, we only consider moderate modulation amplitudes consistent with **Equation 2.6**.

2.3 RESULTS AND DISCUSSION

2.3.1 *The Weakly Nonlinear Randles Circuit*

A planar electrochemical interface with time-invariant and uniform concentrations throughout the solid and electrolyte phases is governed by **Equation 2.3** with constant E_n . For simplicity, we set $E_n = 0$ and re-write **Equation 2.3** in terms of physically interpretable parameters common to a Randles circuit analysis, namely,

$$I = \frac{E}{R_{ct}} + \frac{\varepsilon f E^2}{R_{ct}} + C_{dl} \frac{dE}{dt} \quad (2.9)$$

where $R_{ct} = \frac{1}{Ai_0 f}$ is the interfacial charge transfer resistance (Ω), and $C_{dl} = Ac_{dl}$ is the double layer capacitance of the interface (F). Since current generated through faradaic and non-faradaic processes are additive in **Equation 2.9**, it represents parallel paths across the interface, akin to a Randles circuit but with an extra nonlinear charge transfer term that scales with the charge transfer symmetry parameter $\frac{\varepsilon f}{R_{ct}}$.

To find $\tilde{Z}_1(\omega)$ and $\tilde{Z}_2(\omega)$ for this weakly nonlinear Randles circuit, we insert **Equations 2.5** and **2.6** into **Equation 2.9**, separate the equations into first harmonic (linear) terms multiplied by $\exp(j\omega t)$, second harmonic terms multiplied by $\exp(j2\omega t)$, and ignore any higher harmonic terms. With algebraic manipulation, the governing equation for the complex interfacial voltage fluctuations at the excitation frequency ω is,

$$(1 + \omega^* j) \tilde{E}_1 = R_{ct} \Delta I \quad (2.10)$$

and the second harmonic interfacial voltage at a frequency of 2ω is

$$(1 + 2\omega^*j)\tilde{E}_2 = -\varepsilon f \tilde{E}_1^2 \quad (2.11)$$

where $\omega^* = \omega R_{ct} C_{dl}$ is the dimensionless frequency commonly used in Randles circuit analysis. Note that **Equation 2.11** shows that the second harmonic potential response ($\tilde{E}_2$) depends on the solution at the excitation frequency ($\tilde{E}_1$). Algebraic manipulation of **Equation 2.10**, along with the use of **Equation 2.7**, provides the classic linear Randles EIS frequency response at the first harmonic,

$$\tilde{Z}_1 = \frac{R_{ct}}{1 + \omega^*j} \quad (2.12a)$$

with real and imaginary parts given as

$$Re(\tilde{Z}_1) = \tilde{Z}'_1 = \frac{R_{ct}}{1 + \omega^{*2}} \quad (2.12b)$$

And

$$Im(\tilde{Z}_1) = \tilde{Z}''_1 = -\frac{\omega^* R_{ct}}{1 + \omega^{*2}}. \quad (2.12c)$$

To find the weakly nonlinear 2nd-NLEIS response, **Equation 2.10** is rearranged and inserted into **Equation 2.11**, then solved for $\tilde{E}_2$. Using **Equation 2.8** provides the 2nd-NLEIS for the nonlinear Randles circuit,

$$\tilde{Z}_2 = \frac{-\varepsilon f R_{ct}^2}{1 + 4\omega^*j - 5\omega^{*2} - 2\omega^{*3}j} \quad (2.13a)$$

which can be written as real and imaginary terms

$$Re(\tilde{Z}_2) = \tilde{Z}'_2 = \frac{-\varepsilon f (\tilde{Z}_1'^2 - \tilde{Z}_1''^2 + 4\omega^* \tilde{Z}_1' \tilde{Z}_1'')}{1 + 4\omega^{*2}} \quad (2.13b)$$

and

$$Im(\tilde{Z}_2) = \tilde{Z}''_2 = \frac{\varepsilon f [2\omega^* (\tilde{Z}_1'^2 - \tilde{Z}_1''^2) - 2\tilde{Z}_1' \tilde{Z}_1'']}{1 + 4\omega^{*2}}. \quad (2.13c)$$

Equation 2.13 shows the size of the 2nd-NLEIS response is directly proportional to the charge transfer asymmetry parameter (ε), with the same characteristic $R_{ct}C_{dl}$ time constant as is found in the linear EIS response.

Figure 2.2 shows Nyquist plots for the first harmonic (linear) EIS and 2nd-NLEIS response of a weakly nonlinear Randles circuit for a series of different charge transfer asymmetry parameters (ε). As expected, the first harmonic linear EIS response in **Figure 2.2a** is a classic Randles semi-circle of width R_{ct} and characteristic frequency (top of the semi-circle) of $\omega = \frac{1}{R_{ct}C_{dl}}$. The linear EIS response is not sensitive to the charge transfer asymmetry parameter. In contrast, the 2nd-NLEIS signal in **Figure 2.2b** is characterized by a frequency-dependent spiral toward the origin, starting from a real-axis DC limit of $\tilde{Z}_2(\omega \rightarrow 0) = -\varepsilon f R_{ct}^2$. Each 2nd-NLEIS spiral enters three of the four Nyquist plot quadrants. The 2nd-NLEIS response for a half-cell vanishes at all frequencies when charge transfer is symmetric with $\varepsilon = 0$.

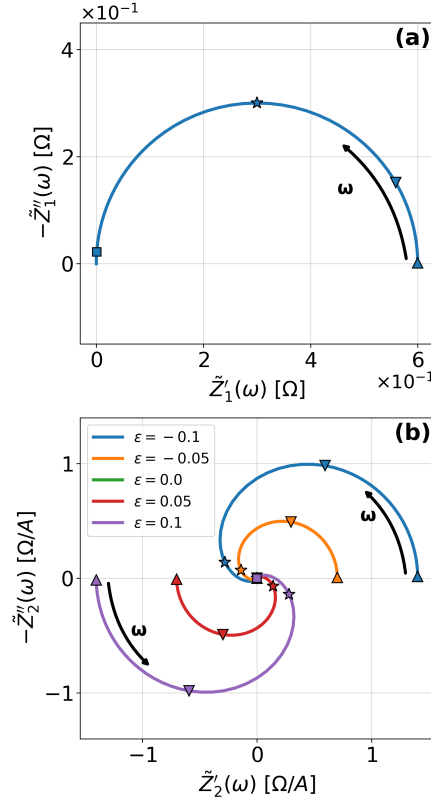


Figure 2.2. Example Nyquist plots for the weakly nonlinear Randles circuit with various charge transfer asymmetry parameters ε : (a) First harmonic (linear) EIS and (b) 2nd-NLEIS. The EIS response in (a) does not depend on ε . Arrows show the direction of increasing frequency with markers for 1 mHz ($\triangle$), 100 mHz (∇), 10 Hz ($\square$), and $\omega^* = 1$ ($\star$). Fixed parameters: $R_{ct} = 0.6 \, \Omega$ and $C_{dl} = 0.72 \, \text{F}$.

Circuit drawings enable easy visualization of the structure and elements of a linear EIS formulation. Our weakly nonlinear Randles circuit arose from parallel interfacial current paths determined from a two-term nonlinear representation of Butler-Volmer charge transfer (faradaic path) and linear representation of a constant capacitance Helmholtz double layer (non-faradaic path). We illustrate this physics with the nonlinear Randles equivalent circuit drawing shown in **Figure 2.3**, where the charge transfer resistance has a second parallel dashed line to denote the second-order nonlinearity used in the weakly nonlinear expansion. In the two-term expansion of charge-transfer, we now have two physicochemical parameters describing the linear charge

transfer resistance and the charge transfer asymmetry. Had we used higher order terms in **Equation 2.1** and added higher order harmonics to **Equation 2.6**, we would have added extra dashed lines accordingly. A classic capacitor symbol denotes the conventional (linear) non-faradaic current path.

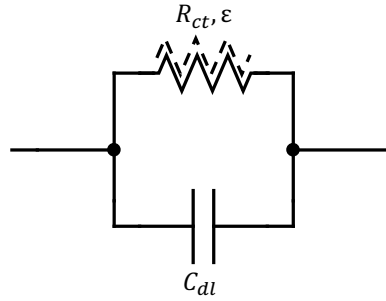


Figure 2.3. Equivalent circuit representation of a simple electrochemical interface under the weakly nonlinear conditions of a two-term expansion of the charge transfer pathway. The three unique parameters describing the nonlinear circuit are also given.

2.3.2 A Porous Electrode with no Concentration Effects in Solution or Solid

As discussed above, E_n can be treated as zero when all concentrations are time-invariant and uniform, allowing **Equation 2.4** to be rewritten with common parameters used in analysis:

$$\frac{d^2}{R_{pore}C_{dl}} \frac{\partial^2 E}{\partial x^2} = \frac{dE}{dt} + \frac{E}{C_{dl}R_{ct}} + \frac{\epsilon f E^2}{C_{dl}R_{ct}} \quad (2.14)$$

where $R_{pore} = \frac{\rho_i d}{A}$ is the effective electrolyte resistance across the entire porous electrode (Ω),

$C_{dl} = AS_c c_{dl} d$ is the double layer capacitance of the porous interface (F), $R_{ct} = \frac{1}{AS_c i_0 f d}$ is the

charge transfer resistance of the porous electrode (Ω). Paasch, et al. [100] has shown that the continuous form of **Equation 2.14** can be represented by a transmission-line equivalent circuit, as shown in **Figure 2.4**, though here we have substituted N weakly nonlinear Randles elements for the classic linear transmission line, as elaborated above. In the **Supplementary materials**, we demonstrate the equivalency of **Equation 2.14** and **Figure 2.4** for the two-term weakly nonlinear

porous electrode. [103] Likewise, we expect that replacing linear elements with the appropriate nonlinear elements in any sort of sophisticated transmission line model (TLM), such as the 3D TLM proposed by Moškon et al., [104,105] mono-rail TLM by Solchenbach et al., [106] and multi-rail TLM by Siroma et al., [107] should generate the appropriate 2nd-NLEIS signal.

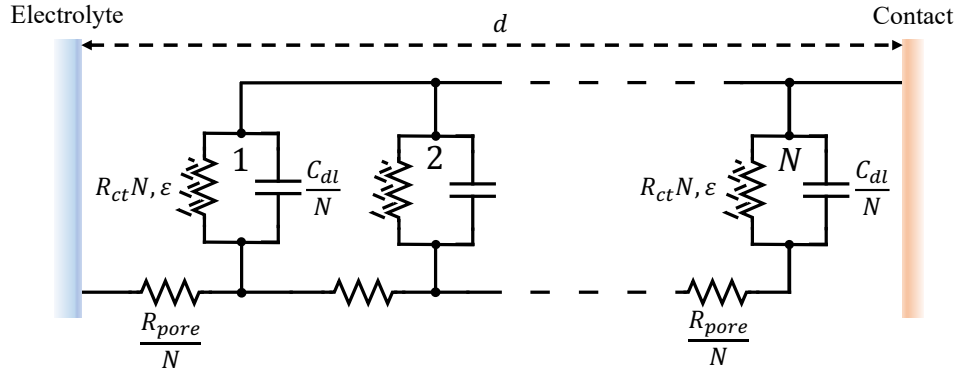


Figure 2.4. Transmission line representation of a porous electrode under weakly nonlinear conditions.

Substituting **Equation 2.6** into **Equation 2.14**, and separating into first and second harmonic terms, again ignoring any higher-order terms, we find a first harmonic governing equation that is identical to the Paasch model (in the limit of zero solid resistivity),

$$\frac{d^2}{C_{dl} R_{pore}} \frac{\partial^2 \tilde{E}_1}{\partial x^2} = \left(j\omega + \frac{1}{C_{dl} R_{ct}} \right) \tilde{E}_1. \quad (2.15a)$$

with boundary conditions dictated by the current excitation conditions imposed at the current collector and electrolyte edge of the porous electrode,

$$\frac{\partial \tilde{E}_1}{\partial x} \Big|_{x=0} = -\frac{R_{pore}}{d} \Delta I \quad (2.15b)$$

and

$$\frac{\partial \tilde{E}_1}{\partial x} \Big|_{x=d} = 0. \quad (2.15c)$$

The second harmonic governing equation at twice the excitation frequency (2ω) is written as

$$\frac{d^2}{C_{dl}R_{pore}} \frac{\partial^2 \tilde{E}_2}{\partial x^2} = \left(j2\omega + \frac{1}{C_{dl}R_{ct}} \right) \tilde{E}_2 + \frac{\varepsilon f \tilde{E}_1^2}{C_{dl}R_{ct}}, \quad (2.16a)$$

where we note the non-homogeneous term involving E_1^2 requires the solution to **Equation 2.15**.

The homogeneous boundary conditions for the second harmonic are

$$\frac{\partial \tilde{E}_2}{\partial x} \Big|_{x=0} = 0 \quad (2.16b)$$

and

$$\frac{\partial \tilde{E}_2}{\partial x} \Big|_{x=d} = 0 \quad (2.16c)$$

where **Equations 2.16b** and **2.16c** ensure that no second harmonic current exists at the current collector or bulk electrolyte boundary. This is a requirement in our impedance formulation because the excitation current has a single frequency, as in **Equation 2.5**. However, the inhomogeneous term in **Equation 2.16a** will generate internal second harmonic currents within the electrode interfaces when charge transfer is asymmetric, i.e., $\varepsilon \neq 0$.

The solution of **Equation 15** is,

$$\tilde{E}_1 = \Delta I \cdot R_{pore} \frac{\cosh\left(\beta_1 \frac{(d-x)}{d}\right)}{\beta_1 \sinh(\beta_1)} \quad (2.17a)$$

with the parameter

$$\beta_1 = \left(j\omega C_{dl}R_{pore} + \frac{R_{pore}}{R_{ct}} \right)^{\frac{1}{2}}. \quad (2.17b)$$

The linear EIS response for the weakly nonlinear porous electrode is found by taking **Equation 2.17** at the electrolyte interface ($x = 0$) and dividing by the current excitation amplitude, i.e.,

$$\tilde{Z}_1(\omega) = \frac{R_{pore} \coth(\beta_1)}{\beta_1}, \quad (2.18)$$

which is identical to the linear Paasch model in the limit of zero solid resistivity.

Equation 2.17b shows there are two relevant time constants in this porous electrode formulation, yielding two dimensionless frequencies, $\omega^* = \omega C_{dl} R_{ct}$ and $\omega^\dagger = \omega C_{dl} R_{pore}$. The ratio between these frequencies ($\frac{R_{pore}}{R_{ct}}$) dictates how accessible the electrode pore structure is to current, namely, if it is a “thin” uniformly accessible electrode ($R_{pore} \ll R_{ct}$), a “thick” electrode with a poorly accessible interfacial area ($R_{pore} \gg R_{ct}$), or somewhere in-between. The D.C. limit for the electrode impedance makes the implications of “thin” or “thick” limits clearer on the width of the impedance arc:

$$\tilde{Z}_1(\omega \rightarrow 0) = \frac{R_{pore}}{\sqrt{\frac{R_{pore}}{R_{ct}}}} \coth\left(\sqrt{\frac{R_{pore}}{R_{ct}}}\right). \quad (2.19)$$

The solution for **Equation 2.16** is

$$\begin{aligned} \tilde{E}_2 &= \tilde{C}_1 \sinh\left(\beta_2 \frac{x}{d}\right) + \tilde{C}_2 \cosh\left(\beta_2 \frac{x}{d}\right) \\ &- \frac{\varepsilon f R_{pore}^3 (\Delta I)^2}{R_{ct} (\beta_1 \sinh(\beta_1))^2} \left[\frac{\cosh\left(2\beta_1 \frac{(d-x)}{d}\right)}{2(\beta_2 - 2\beta_1)(\beta_2 + 2\beta_1)} + \frac{1}{2\beta_2^2} \right] \end{aligned} \quad (2.20a)$$

where

$$\tilde{C}_1 = -\frac{\varepsilon f R_{pore}^3 (\Delta I)^2}{R_{ct} (\beta_1 \sinh(\beta_1))^2} \left[\frac{\beta_1 \sinh(2\beta_1)}{\beta_2 (\beta_2 - 2\beta_1)(\beta_2 + 2\beta_1)} \right], \quad (2.20b)$$

$$\tilde{C}_2 = -\tilde{C}_1 \coth(\beta_2), \quad (2.20c)$$

and

$$\beta_2 = \left(j2\omega C_{dl} R_{pore} + \frac{R_{pore}}{R_{ct}} \right)^{\frac{1}{2}} \quad (2.20d)$$

Setting **Equation 2.20** to its value at $x = 0$, the electrolyte boundary, and dividing by $(\Delta I)^2$ yields the 2nd-NLEIS response:

$$\tilde{Z}_2(\omega) = \frac{\varepsilon f R_{pore}^3}{R_{ct} (\beta_1 \sinh(\beta_1))^2} \left[\left[\frac{\beta_1 \sinh(2\beta_1)}{\beta_2(\beta_2 - 2\beta_1)(\beta_2 + 2\beta_1)} \right] \coth(\beta_2) - \left[\frac{\cosh(2\beta_1)}{2(\beta_2 - 2\beta_1)(\beta_2 + 2\beta_1)} + \frac{1}{2\beta_2^2} \right] \right]. \quad (2.21)$$

The functional forms of β_1 and β_2 suggest the 2nd-NLEIS response shares the same dimensionless frequencies as the linear system, namely, $\omega^* = \omega C_{dl} R_{ct}$ and $\omega^\dagger = \omega C_{dl} R_{pore}$. The magnitude for the 2nd-NLEIS spiral is set by the D.C. limit,

$$\tilde{Z}_2(\omega \rightarrow 0) = -\frac{\varepsilon f R_{ct} R_{pore}}{\sinh^2\left(\sqrt{\frac{R_{pore}}{R_{ct}}}\right)} \left[1 + \frac{1}{3} \sinh^2\left(\sqrt{\frac{R_{pore}}{R_{ct}}}\right) \right]. \quad (2.22)$$

Figure 2.5 shows the Nyquist plots for the first harmonic (linear) EIS response given by **Equation 18** and the 2nd-NLEIS response given by **Equation 21** for a “thick” porous electrode where $R_{pore} = 10 R_{ct}$. The first harmonic response shown in **Figure 2.5a** is characterized by a “semi-teardrop” shape that is characteristic for thick electrodes with poor utilization of internal interfacial area. In the thick electrode limit, the frequency at the top of the EIS curve (maximum imaginary impedance) is $\omega^* = \sqrt{3}$. Though not shown, “thin” porous electrodes ($R_{pore} \ll R_{ct}$) retain the classic shape of a Randles semi-circle except at extremely high frequencies. The 2nd-NLEIS response shown in **Figure 2.5b** has a spiral-like character akin to the weakly nonlinear Randles circuit, but with subtle differences in shape. An example of the subtle shape difference is that the 2nd-NLEIS curves in **Figure 2.5b** only traverse two of the four Nyquist plot quadrants, whereas the Randles case in **Figure 2.2b** had a three-quadrant spiral. As is always true for the 2nd-NLEIS, the half-cell response is proportional to the charge transfer asymmetry parameter and has a null response for symmetric charge transfer.

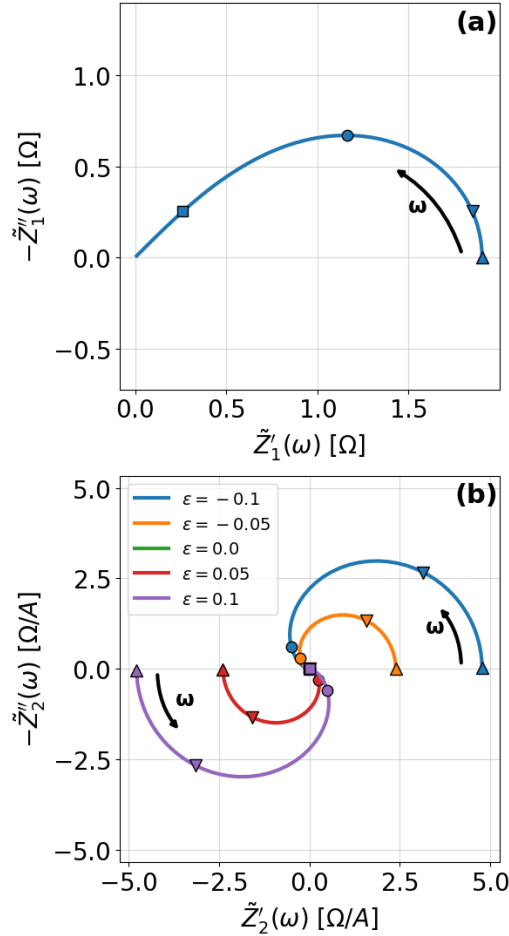


Figure 2.5. Example Nyquist plots for the weakly nonlinear response of a porous electrode with various charge transfer asymmetry parameters ϵ : (a) First harmonic (linear) EIS and (b) 2nd-NLEIS. The EIS response in (a) does not depend on ϵ . Arrows show the direction of increasing frequency with markers for 1 mHz (△), 100 mHz (▽), 10 Hz (□), and $\omega^* = \sqrt{3}$ (○). The parameters used to compute the curves, $R_{pore} = 6 \Omega$, $R_{ct} = 0.6 \Omega$, and $C_{dl} = 0.72 \text{ F}$, are characteristic of a thick electrode with poorly accessible internal surface area.

2.3.3 Weakly Nonlinear Diffusion Impedance Contributions to Planar Interfaces and Porous Electrodes

Diffusion dynamics in the solid or electrolyte phase of an electrochemical system can give rise to a weakly nonlinear Warburg-like diffusion impedance. Here we expand the analysis above to include solid-state bounded diffusion in the nonlinear Randles and porous electrode impedance responses. The archetypical problem considered here involves Li-ion insertion materials, where

the equilibrium potential is a function of the concentration of lithium ions inserted into the solid electrode (denoted c_s). A Taylor series expansion can be used to define the second order processes that describe the nonlinear oscillating equilibrium potential ($\tilde{E}_n$) of a fully relaxed non-hysteretic system,

$$\tilde{E}_n = \left(\frac{\partial E_n}{\partial c_s} \right) \Big|_{SoC} \tilde{c}_s + \frac{1}{2} \left(\frac{\partial^2 E_n}{\partial c_s^2} \right) \Big|_{SoC} \tilde{c}_s^2 + h.o.t. \quad (2.23)$$

where $\tilde{c}_s$ is the oscillating concentration of inserted ions at the solid interface, $\left(\frac{\partial E_n}{\partial c_s} \right) \Big|_{SoC}$ and $\left(\frac{\partial^2 E_n}{\partial c_s^2} \right) \Big|_{SoC}$ are the slope and curvature of the equilibrium potential at the given state of charge (SoC) for the insertion material. To be consistent with prior results and the two-term expansion in **Equation 2.23**, the weakly nonlinear solid state surface concentration fluctuations are expected to follow

$$\tilde{c}_s = \tilde{c}_{s,1} \exp(j\omega t) + \tilde{c}_{s,2} \exp(j2\omega t) \quad (2.24)$$

where $\tilde{c}_{s,1}$ and $\tilde{c}_{s,2}$ are the first and second harmonic coefficients for the fluctuating insertion concentrations at the solid surface. Substituting **Equation 2.24** into **2.23** and ignoring higher harmonics yields the weakly nonlinear oscillating equilibrium potential:

$$\tilde{E}_n = \left(\frac{\partial E_n}{\partial c_s} \right) \Big|_{SoC} \tilde{c}_{s,1} \exp(j\omega t) + \left[\left(\frac{\partial E_n}{\partial c_s} \right) \Big|_{SoC} \tilde{c}_{s,2} + \frac{1}{2} \left(\frac{\partial^2 E_n}{\partial c_s^2} \right) \Big|_{SoC} \tilde{c}_{s,1}^2 \right] \exp(j2\omega t) \quad (2.25)$$

An oscillating faradaic current of the form

$$I_f = \tilde{I}_{f,1} \exp(j\omega t) + \tilde{I}_{f,2} \exp(j2\omega t) \quad (2.26)$$

is consistent with our prior solutions for both planar and porous electrodes, even though the total current represented by **Equation 2.5** has no second harmonic component entering or leaving the

electrode. The transfer function relating oscillating surface concentration to oscillating faradaic current is known as the diffusion impedance ($\tilde{Z}_D$), which we write as [108]

$$\tilde{Z}_{D,1}(\omega) = \tilde{Z}_D(\omega) = \left(\frac{\partial E_n}{\partial c_s} \right) \Big|_{SoC} \frac{\tilde{c}_{s,1}|_{x=l}}{\tilde{I}_{f,1}} \quad (2.27a)$$

and

$$\tilde{Z}_{D,2}(\omega) = \tilde{Z}_D(2\omega) = \left(\frac{\partial E_n}{\partial c_s} \right) \Big|_{SoC} \frac{\tilde{c}_{s,2}|_{x=l}}{\tilde{I}_{f,2}}. \quad (2.27b)$$

Inserting **Equations 2.27** into **Equation 2.25** produces a compact form of the oscillating equilibrium potential

$$\tilde{E}_n = \tilde{Z}_{D,1} \tilde{I}_{f,1} \exp(j\omega t) + \left[\tilde{Z}_{D,2} \tilde{I}_{f,2} + \kappa (\tilde{Z}_{D,1} \tilde{I}_{f,1})^2 \right] \exp(j2\omega t) \quad (2.28)$$

where we have defined a new differential voltage parameter κ (V^{-1})

$$\kappa = \frac{\left(\frac{\partial^2 E_n}{\partial c_s^2} \right) \Big|_{SoC}}{2 \left(\frac{\partial E_n}{\partial c_s} \right)^2 \Big|_{SoC}} \quad (2.29)$$

that scales with the curvature of the open circuit potential at a given SoC. Charge transfer-driven diffusion nonlinearities occur at frequencies relevant to diffusive timescales set via $\tilde{Z}_D$. Expressions for the bounded diffusion impedance $\tilde{Z}_D(\omega)$ have been calculated for a variety of insertion material geometries and are summarized in **Table 2-I**. [109–111]

The first and second harmonic faradaic current modulations can be found through algebraic manipulation of **Equations 2.1, 2.6, 2.26, and 2.28** to identify the coefficients multiplying $\exp(j\omega t)$, that is,

$$I_{f,1} = \frac{\tilde{E}_1}{\tilde{Z}_{D,1} + R_{ct}} \quad (2.30a)$$

and, likewise, the coefficient multiplying $\exp(j2\omega t)$ is:

$$I_{f,2} = \frac{[\tilde{E}_2 - \kappa(\tilde{Z}_{D,1} I_{f,1})^2] + \varepsilon f[\tilde{E}_1 - \tilde{Z}_{D,1} I_{f,1}]^2}{\tilde{Z}_{D,2} + R_{ct}}. \quad (2.30b)$$

These expressions hold for both the planar and the porous electrode.

Table 2-I. Bounded diffusion impedance for different insertion material geometries. The diffusion timescale $\tau = \frac{l^2}{D}$ (s) is tied to the insertion material characteristic dimension l (m) and inserted ion diffusion coefficient D (m^2/s). Bounded diffusion impedance scales with $A_w = \left(-\frac{\partial E_n}{\partial c_s}\right) \left(\frac{l}{nFA_i}\right)$, where A_i is the interfacial area of the electrode. The functions I_0 and I_1 denote the modified Bessel functions of zero and first order, respectively.

	Planar	Cylindrical	Spherical
$\tilde{Z}_D(\omega)$	$\frac{A_w \coth(\sqrt{j\omega\tau})}{\sqrt{j\omega\tau}}$	$\frac{A_w I_0(\sqrt{j\omega\tau})}{\sqrt{j\omega\tau} I_1(\sqrt{j\omega\tau})}$	$\frac{A_w \tanh(\sqrt{j\omega\tau})}{\sqrt{j\omega\tau} - \tanh(\sqrt{j\omega\tau})}$

2.3.4 Weakly Nonlinear Response of a Planar Insertion Electrode with Bounded Solid Diffusion

Equation 2.3 provides the template for treating a weakly nonlinear planar electrode when faradaic charge transfer is accompanied by diffusion of inserted ions, that is, when **Equations 2.28** and **2.30** are used with **Equation 2.3**. The resulting nonlinear equivalent circuit diagram is represented by **Figure 2.6**.

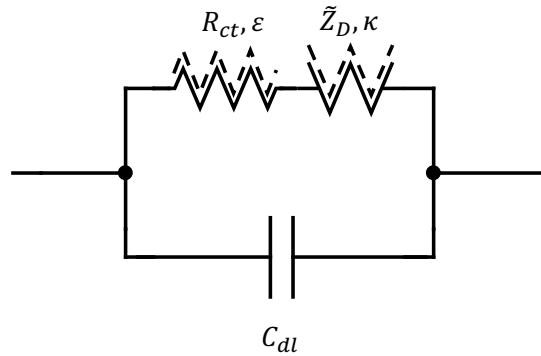


Figure 2.6. Equivalent circuit representation for a planar electrochemical interface with weakly nonlinear representation of charge transfer and the accompanying diffusive transport processes.

Substituting **Equations 2.6, 2.28, and 2.30** into **Equation 2.3** followed by algebraic manipulation and separation of equations into first and second harmonics produces expressions for $\tilde{E}_1$ and $\tilde{E}_2$.

Equation 2.7 is used with the $\tilde{E}_1$ solution to write the first harmonic (linear) EIS response

$$\tilde{Z}_1 = \frac{R_{ct}}{\frac{R_{ct}}{R_{ct} + \tilde{Z}_{D,1}} + j\omega^*} \quad (2.31)$$

while solutions to $\tilde{E}_2$ are used with **Equation 8** to write the second harmonic NLEIS response

$$\tilde{Z}_2 = \frac{R_{ct}}{\left(j2\omega^* + \frac{R_{ct}}{\tilde{Z}_{D,2} + R_{ct}}\right)} \frac{\left[\kappa \left[\frac{\tilde{Z}_{D,1}}{\tilde{Z}_{D,1} + R_{ct}}\right]^2 - \varepsilon f \left[\frac{R_{ct}}{\tilde{Z}_{D,1} + R_{ct}}\right]^2\right]}{\tilde{Z}_{D,2} + R_{ct}} \left(\frac{R_{ct}}{\frac{R_{ct}}{R_{ct} + \tilde{Z}_{D,1}} + j\omega^*}\right)^2 \quad (2.32)$$

Equations 2.31 and 2.32 enable the simulation of the full spectrum linear EIS and 2nd-NLEIS response for a planar thin film of insertion material on a current collector substrate. **Figure 2.7a** shows a Nyquist plot for linear EIS, where a Randles charge transfer semi-circle at higher frequencies is seen to merge into a 45-degree diffusive impedance at intermediate frequencies and, ultimately, the chemical capacitance of the bounded thin film is observed at sufficiently low frequencies. The corresponding 2nd-NLEIS response is explored as a function of the charge transfer asymmetry parameter (ε) in **Figure 2.7b** and as a function of the voltage curvature parameter (κ) in **Figure 2.7c**. **Figure 2.7b** shows the same three-quadrant 2nd-NLEIS charge transfer spiral as the weakly nonlinear Randles circuit presented in **Figure 2.2**, but as the frequency becomes low enough to activate diffusive processes, the weakly nonlinear bounded diffusion impedance terms in **Equation 2.32** becomes apparent. **Figure 2.7c** shows the effect of κ on the nonlinear second harmonic response. As shown in the Nyquist plot, the direction and magnitude of the weakly nonlinear diffusion response are governed by the κ . For the parameters shown here, the case of κ equal to zero is close to the pure charge transfer behavior with **Equation 2.32** reverting to the pure charge transfer DC limit. One could imagine when the charge transfer time scale and diffusion

time scale are comparable to each other, a larger deviation from pure charge transfer reaction might displayed even when κ is zero. The direction-sensitive features of 2nd-NLEIS — where realistic charge transfer and diffusion parameters can produce signals in all four quadrants of a Nyquist plot — significantly boost the mathematical discriminating power of 2nd-NLEIS over conventional one-quadrant linear EIS. We discuss this parameter sensitivity as an especially important feature for full-cell studies in the Implications and Concluding Remarks section.

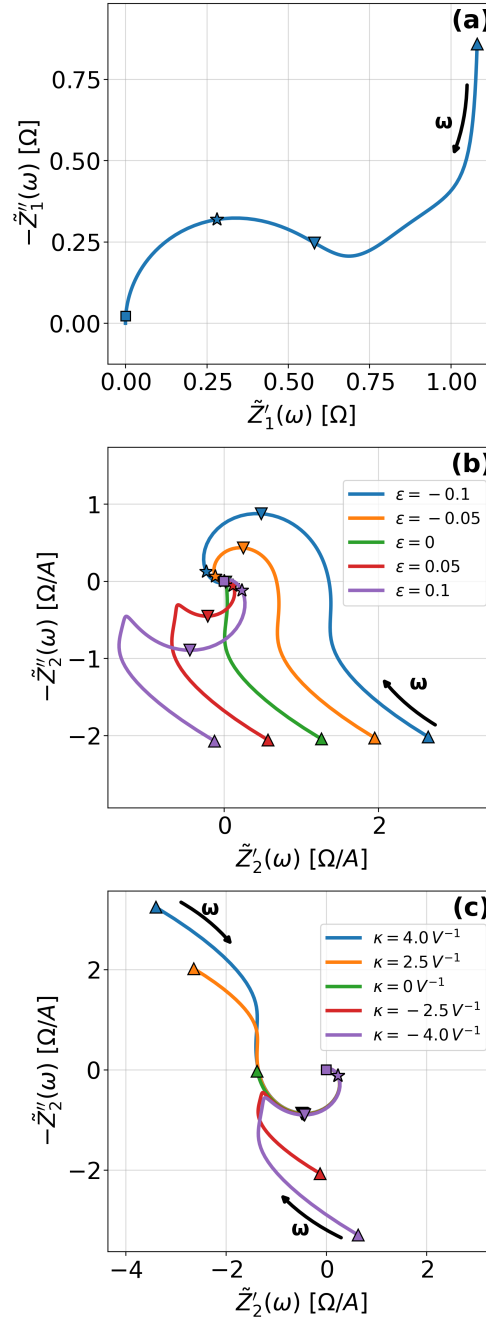


Figure 2.7. Example Nyquist plots for the weakly nonlinear response of a planar thin film insertion electrode with varying charge transfer asymmetry (ϵ) and differential voltage (κ) parameters. (a) First harmonic (linear) EIS is independent of ϵ and κ . (b) The 2nd-NLEIS spectrum as a function of ϵ for $\kappa = -2.5$ V $^{-1}$. (c) The second harmonic NLEIS spectrum as a function of κ for $\epsilon = 0.1$. Arrows show the direction of increasing frequency with markers for 1 mHz ($\triangle$), 100 mHz (∇), 10 Hz ($\square$), and $\omega^* = 1$ ($\star$). The parameters used to compute the curves are $R_{ct} = 0.6$ Ω, $C_{dl} = 0.72$ F, $A_w = 1.5$ Ω, and $\tau = 300$ s.

2.3.5 Weakly Nonlinear Response of a Porous Insertion Electrode with Bounded Solid Diffusion

Equation 2.4 is the starting point for describing a porous insertion electrode with solid-state diffusive transport. The corresponding weakly nonlinear equivalent circuit representation of such a porous electrode is shown in **Figure 2.8**.

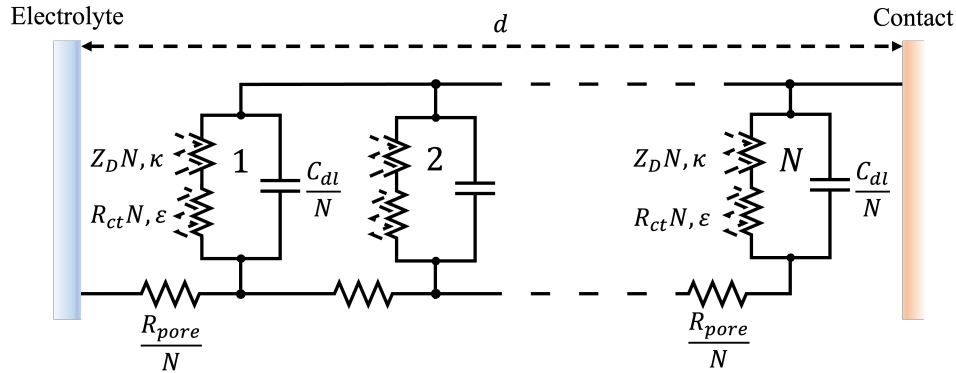


Figure 2.8. Equivalent circuit representation of a weakly nonlinear porous electrode with diffusive transport limitation under the weakly nonlinear condition.

Substituting **Equations 2.5, 2.28, and 2.30** into **Equation 2.4** and separating terms into first and second harmonic equations, while ignoring higher order harmonics, yields the first harmonic (linear) governing equation:

$$\frac{d^2}{C_{dl} R_{pore}} \frac{\partial^2 \tilde{E}_1}{\partial x^2} = \left[j\omega + \frac{1}{C_{dl}(\tilde{Z}_{D,1} + R_{ct})} \right] \tilde{E}_1 \quad (2.33)$$

with identical boundary conditions to **Equations 2.15b and 2.15c**. The solution to **Equation 2.33** is identical to **Equation 2.17a**, but with **Equation 2.17b** replaced by the diffusion impedance modified parameter

$$\beta_1^D = \left(j\omega C_{dl} R_{pore} + \frac{R_{pore}}{\tilde{Z}_{D,1} + R_{ct}} \right)^{\frac{1}{2}} \quad (2.34)$$

yielding the linear EIS impedance

$$\tilde{Z}_1^D(\omega) = \frac{R_{pore} \coth(\beta_1^D)}{\beta_1^D} \quad (2.35)$$

Formulating the second harmonic porous electrode response when solid state bounded diffusion effects are included yields a governing equation and boundary conditions identical in form to **Equation 2.16**, resulting in a solution having an identical form to **Equation 2.20** and 2nd-NLEIS response

$$\tilde{Z}_2^D(\omega) = \frac{R_{pore}^3 k^D}{R_{ct} [\beta_1^D \sinh(\beta_1^D)]^2} \left[\left[\frac{\beta_1^D \sinh(2\beta_1^D)}{\beta_2^D (\beta_2^D - 2\beta_1^D) (\beta_2^D + 2\beta_1^D)} \right] \coth(\beta_2^D) - \left[\frac{\cosh(2\beta_1^D)}{2(\beta_2^D - 2\beta_1^D) (\beta_2^D + 2\beta_1^D)} + \frac{1}{2\beta_2^{D^2}} \right] \right] \quad (2.36)$$

with the diffusion impedance modified parameters

$$\beta_2^D = \left(j2\omega C_{dl} R_{pore} + \frac{R_{pore}}{\tilde{Z}_{D,2} + R_{ct}} \right)^{\frac{1}{2}} \quad (2.37a)$$

and

$$k^D = \frac{\left[-R_{ct} k \left[\frac{\tilde{Z}_{D,1}}{\tilde{Z}_{D,1} + R_{ct}} \right]^2 + R_{ct} \varepsilon f \left[\frac{R_{ct}}{\tilde{Z}_{D,1} + R_{ct}} \right]^2 \right]}{\tilde{Z}_{D,2} + R_{ct}} \quad (2.37b)$$

being the only differentiating factor between **Equation 2.36** and **Equation 2.21**.

Equations 2.35 and **2.36** enable the simulation of the full spectrum linear EIS and 2nd-NLEIS response for a porous insertion electrode on a current collector substrate. **Figure 2.9a** shows a Nyquist plot for linear EIS, where a typical “thick” porous electrode charge transfer teardrop shape is seen at frequencies above 100 mHz, akin to what is seen in **Figure 2.5a** without any diffusion effects. At frequencies below 100 mHz, the effect of diffusive transport becomes evident as the 45-degree diffusive impedance transitions to a chemical capacitance behavior in the bounded thin film at the lowest frequencies shown. Here we assume the porous electrode was built from planar (platelet-like) particles, hence the “planar” functional form is used for the diffusion impedance in **Table 2-I**. The corresponding 2nd-NLEIS response is explored as a function of the

charge transfer asymmetry parameter (ε) in **Figure 2.9b** and as a function of the potential curvature parameter (κ) in **Figure 2.9c**. **Figure 2.9b** shows the same two-quadrant 2nd-NLEIS charge transfer spiral at frequencies above 100 mHz as we saw in **Figure 2.5**, but as the frequency becomes lower, the weakly nonlinear bounded diffusion impedance terms in **Equation 2.36** and **2.37** becomes apparent. **Figure 2.9c** shows the effect of κ on the scaling and quadrants where the low frequency nonlinear second harmonic diffusion processes appear. In contrast to the planar electrode, there is a distinct weakly nonlinear diffusion response for the porous electrode even when κ equals to zero, which is primarily due to the inhomogeneity of the current distribution with the presence of pore electrolyte.

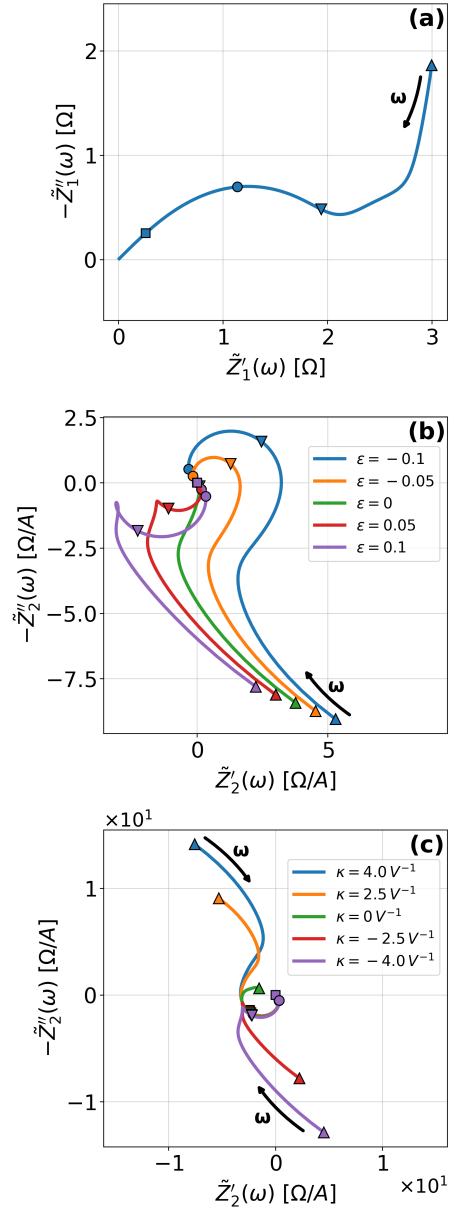


Figure 2.9. Example Nyquist plots for the weakly nonlinear response of a porous insertion electrode with varying charge transfer asymmetry (ϵ) and differential voltage (κ) parameters. (a) First harmonic (linear) EIS is independent of ϵ and κ . (b) The 2nd-NLEIS spectrum as a function of ϵ for $\kappa = -2.5 \text{ V}^{-1}$. (c) The 2nd-NLEIS spectrum as a function of κ for $\epsilon = 0.1$. Arrows show the direction of increasing frequency with markers for 1 mHz ($\triangle$), 100 mHz (∇), 10 Hz ($\square$), and $\omega^* = \sqrt{3}$ ($\circ$). The particles making up the porous insertion electrode are assumed to be planar (platelet-like) particles (**Table 2-I**), with the parameters used $R_{pore} = 6 \text{ } \Omega$, $R_{ct} = 0.6 \text{ } \Omega$, $C_{dl} = 0.72 \text{ F}$, $A_w = 2 \text{ } \Omega$, and $\tau = 200 \text{ s}$.

2.4 IMPLICATIONS AND CONCLUDING REMARKS

2.4.1 *Signal Parity and Second Harmonic NLEIS (2nd-NLEIS) for Two-Electrode Cells*

Linearization used in traditional EIS techniques leads to half-cell model degeneracy with both physics-based models [33] or equivalent circuit models. [32] The challenge of half-cell degeneracy is compounded when analyzing two-electrode cells. The origin of this compounding impact is that a two-electrode cell has an EIS response that is the sum of half-cell EIS signals; thus, two-electrode linear EIS is a “**positive parity**” signal owing to the additive trait of half-cells. This positive parity trait makes it even more difficult to assign the physicochemical contributions to the EIS signal to a particular electrode.

2nd-NLEIS is effective at addressing the challenge of model degeneracy in half-cell measurements.[33] Perhaps more importantly, the two-electrode 2nd-NLEIS signal arises from the difference between the half-cell 2nd-NLEIS responses; [26] thus, two electrode 2nd-NLEIS is a “**negative parity**” signal owing to subtractive traits of half-cells. The complementary parity between EIS and 2nd-NLEIS, when analyzed with a common physics-based model, makes assigning half-cell physicochemical processes from two-electrode measurements much more feasible.

To demonstrate the importance of using complementary parity signals to assign physicochemical process, we use the half-cell modeling above to build four different two-electrode models that each fairly closely represent the linear EIS response from two-electrode battery data presented by Murbach et al. [26] The four distinct models were built by simply “swapping” charge transfer and diffusion-related physicochemical parameters systematically among the positive and negative electrodes, creating the four parameter sets summarized in **Table 2-II**. **Figure 2.10** shows the simulated Nyquist plots for each two-electrode linear EIS model. The positive parity additive

response makes it difficult to assign the charge transfer and diffusion properties to one electrode or another. Though not truly degenerate (there are subtle differences among the four cases), the two-electrode EIS responses are practically indistinguishable. The Nyquist plots for the four corresponding two-electrode 2nd-NLEIS models are shown in **Figure 2.10b**. In contrast to **Figure 2.10a**, each negative-parity NLEIS model for the two-electrode cells has a highly distinct response that is sensitive to the assignment of specific physicochemical parameters to specific electrodes. In short, the complementary parity between linear EIS and 2nd-NLEIS in a two-electrode configuration provides the discriminating power needed to assign half-cell processes in a two-electrode configuration that lacks a separate reference measurement.

The implications for the half-cell and two-electrode cell analysis given here, when combined with our prior work on the experimental accessibility of two-harmonic measurements, is that 2nd-NLEIS is a truly complementary measurement that should be added to the EIS toolbox in order to take advantage of the discriminating power described above. To build confidence in 2nd-NLEIS based methods, adoption of the advanced quality assurance and analysis methods that have become fairly routine in the linear EIS community [91] need to be advanced to the second harmonic. A key question that underpins the efficient adoption of 2nd-NLEIS is how to systematically test that an experimental modulation is adequate to excite the second-order weakly nonlinear effects analyzed here, without over-driving the system into third-order (and higher) nonlinear processes that will distort the linear EIS signals, avoiding the need to use more sophisticated series analysis to extract any meaningful parameters (e.g., see analysis in Murbach et al's work [34]). In the experiments we've reported previously, modulated voltages of roughly 10-15 mV (at frequencies that activate charge transfer and diffusion processes) appear to nicely

drive second-order (two term, two harmonic) responses without overly exciting higher-order distortions. [26]

Table 2-II. Parameters of first and second harmonic impedance simulation for four nearly degenerated linear first harmonic models and their corresponding nonlinear second harmonic models.

Physicochemical Parameter			Model 1	Model 2	Model 3	Model 4
Cathode	Charge Transfer	$R_{pore,c} [\Omega]$	0.0198	0.0198	0.00860	0.00860
		$R_c [\Omega]$	0.00749	0.00749	0.00214	0.00214
		$C_c [F]$	5.03	5.03	0.390	0.390
	Diffusion	$A_{W,c} [\Omega]$	0.138	0.143	0.138	0.143
		$\tau_c [s]$	3547	13595	3547	13595
	NLEIS	$\kappa_c [V^{-1}]$	9.05	9.05	39.5	39.5
	Parameters	$\varepsilon_c []$	0.0598	0.0598	0	0
Anode	Charge Transfer	$R_{pore,a} [\Omega]$	0.00860	0.00860	0.0198	0.0198
		$R_a [\Omega]$	0.00214	0.00214	0.00749	0.00749
		$C_a [F]$	0.390	0.390	5.03	5.03
	Diffusion	$A_{W,a} [\Omega]$	0.143	0.138	0.143	0.138
		$\tau_a [s]$	13595	3547	13595	3547
	NLEIS	$\kappa_a [V^{-1}]$	39.5	39.5	9.05	9.05
	Parameters	$\varepsilon_a []$	0	0	0.0598	0.0598

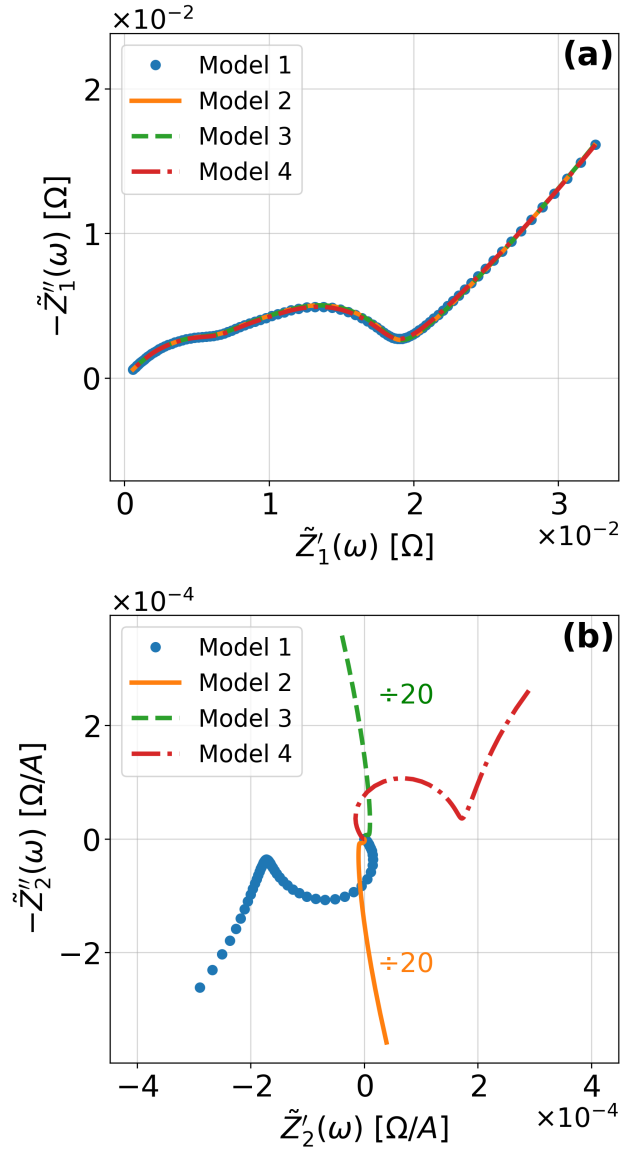


Figure 2.10. Simulated Nyquist plots for (a) four nearly degenerated linear models and (b) the corresponding nonlinear second harmonic responses. The real and imaginary nonlinear second harmonic responses for models 2 and 3 are divided by 20 to place them on the same scale as the other 2nd-NLEIS responses.

2.4.2 Equivalent Circuit Representations, and Further Generalization

As shown above, building the second harmonic nonlinear impedance response from two-term (weakly nonlinear) expansions of interfacial and transport models creates a mathematical structure that is consistent with the parallel and series circuit element additivity rules of linear circuits. We

formally introduced the consequences of two-term expansions of the Butler-Volmer charge transfer model and solid-state bounded diffusion. In contrast, we chose a constant coefficient Helmholtz model for the double layer which avoids nonlinear contributions to the non-faradaic current; this allowed us to show that mixing linear and nonlinear elements is easily accomplished and it also aligned the work here with previous nonlinear pseudo-2-D modeling of porous insertion electrodes. [34]

For completeness, we note that more general descriptions of the electrochemical double layer require a replacement of **Equation 2.2**, given that interfacial capacitance is no longer a constant:

$$i_{nf} = c_{dl} \frac{dE}{dt} + E \frac{dc_{dl}}{dt}. \quad (2.38a)$$

Most double-layer models represent the double layer capacitance as a complex function of interfacial potential E . Because 2nd-NLEIS perturbs the interface from its equilibrium state with small but finite modulations, it is reasonable to use a two-term Taylor series expansion for the capacitance, yielding a universal “local” form for the capacitance of

$$c_{dl} = c_{dl,n} [1 + \theta f(E - E_n)], \quad (2.38b)$$

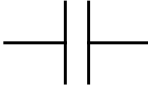
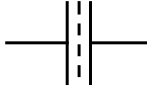
where $c_{dl,n}$ is the capacitance of the interface at the equilibrium potential and θ is a model-dependent nondimensional constant. The combination of **Equation 2.38a** and **2.38b** creates a direct replacement for **Equation 2.2** that introduces second order nonlinearity into the governing equation for non-faradaic currents. Had **Equation 2.38** been used throughout this paper, the linear EIS response would be unchanged, but the 2nd-NLEIS response would have many extra terms and an extra parameter θ in the solutions for each specific case studied.

The selection of a particular double layer structure yields a detailed interpretation of the model-dependent constant θ . For example, a Gouy-Chapman double layer with monovalent ions yields $\theta = 0.5 * \tanh[0.5f(E_n - E_{pzc})]$, where E_{pzc} is the potential of zero charge (PZC) for the interface. For the Gouy-Chapman model, interfacial capacitance has a local minimum at the PZC with $\theta = 0$, resulting in no 2nd-NLEIS contribution from the double layer. More broadly, nonlinear double layer contributions to 2nd-NLEIS spectra are likely to only be important at highly polarizable interfaces and at high frequencies where faradaic charge transfer contributions are negligible. In short, though not used here, non-faradaic currents can contribute to 2nd-NLEIS through the second-order nonlinearity generated by a non-constant double layer capacitance. The form of the contribution, **Equation 2.38b**, is universal but the interpretation of the new nonlinear parameter θ is dependent on the interfacial structure of models. For electrochemical energy systems we mostly study, facile charge transfer is a key feature of the electrochemical interface, so the impact of weak double-layer nonlinearity is diminished.

Shown in **Table 2-III** is a visual representation of the linear and two-term weakly nonlinear elements that underpin all the analysis above. We adapt traditional linear EIS circuit element representations and add a parallel dashed line to represent the second-order nonlinear form of each linear circuit element. Adding a parallel dashed line conveys the use of a two-term expansion to represent the second-order nonlinear electrochemical processes being analyzed. As shown in **Figure 2.3**, **Figure 2.4**, **Figure 2.6**, and **Figure 2.8**, one can mix and match linear and second-order impedance elements to visualize the mix of physical assumptions that underpin the linear and second harmonic response of the corresponding Nyquist plots. Such development of visual representation emphasizes the ability to substitute linear circuit elements with appropriate nonlinear element circuits to take advantage of the existing TLM models [104,105,105–107,112]

in describing different electrochemical processes, while obtaining additional insights about reaction kinetics and thermodynamics with the complementary 2nd-NLEIS analysis.

Table 2-III. Circuit element representations for the first and second harmonic impedance response when a two-term expansion is used to represent a nonlinear electrochemical process.

Circuit Elements	Linear EIS	2nd Harmonic NLEIS
Resistor		
Capacitor		
Diffusion element		

To conclude, second harmonic nonlinear electrochemical impedance spectroscopy (2nd-NLEIS) is a powerful tool for probing complementary information to traditional electrochemical impedance spectroscopy (EIS), extracting meaningful non-linear contributions to charge transfer, mass transports, and thermodynamics of the electrochemical systems. However, the application of the 2nd-NLEIS has been hampered by the lack of simple models able to extract meaningful parameters. To resolve this problem, we systematically developed simple physics-based models for planar electrochemical interfaces and porous electrodes that are governed by a Helmholtz double layer, Butler–Volmer kinetics, and solid-state bounded Fickian diffusion. The limiting cases and dependences of the second harmonic impedance response on charge transfer asymmetry and thermodynamics are explored. The importance of using the complementary parity between linear EIS and 2nd-NLEIS as a strategy to separate half-cell parameters for two-electrode measurements is discussed. For completeness, the nonlinear double-layer response for non-faradaic current is briefly introduced for the interested reader. Lastly, we try to depict a sensible

visual representation of second order nonlinear circuit elements as a shorthand way to identify the mathematical underpinning and structure of the analysis, helping bridge the gap between model-based analysis, experiments, and the intuition needed for the physical interpretation of EIS and 2nd-NLEIS data.

2.5 LIST OF VARIABLES

i_f	Faradaic current density ($\frac{A}{m^2}$)
i_{nf}	Non-faradaic current density ($\frac{A}{m^2}$)
i_0	Exchange current density ($\frac{A}{m^2}$)
α_a	Anodic charge transfer coefficient
α_c	Cathodic charge transfer coefficient
ε	Charge transfer symmetry parameter
n	Number of electrons involved per electrochemical reaction
F	Faraday constant ($C \cdot mol^{-1}$)
R	Gas constant ($J \cdot K^{-1} \cdot mol^{-1}$)
T	Temperature (K)
$E, \tilde{E}$	Measured overpotential (V)
ϕ_s	Solid phase potential (V)
ϕ_i	Ionic conducting phase potential (V)
$E_n, \tilde{E}_n$	Equilibrium polarization (V)
f	Reciprocal of thermal voltage ($\frac{1}{V}$)
c_{dl}	Double layer capacitance per unit area ($\frac{F}{m^2}$)

A	Interfacial area (m^2)
d	Thickness of the electrode (m)
S_c	Area of the pores per unit volume on which the double layer can be formed (m^{-1})
ρ_i	Resistivity of pore electrolyte ($\Omega \cdot m$)
I	Imposed current (A)
ΔI	Amplitude of the imposed current (A)
ω	Frequency of imposed current (s^{-1})
$\tilde{E}_1$	Complex magnitude of measured overpotential at ω (V)
$\tilde{E}_2$	Complex magnitude of measured overpotential at 2ω (V)
$\tilde{Z}_1$	First harmonic impedance coefficient (Ω)
$\tilde{Z}_2$	Second harmonic impedance coefficient ($\frac{\Omega}{A}$)
R_{ct}	Charge transfer resistance of the interface or porous electrode (Ω)
C_{dl}	Double layer capacitance of the interface or porous electrode (F)
ω^*	Dimensionless frequency related to charge transfer resistance
R_{pore}	Effective pore electrolyte resistance across the entire porous electrode (Ω)
$\omega^\dagger$	Dimensionless frequency related to pore electrolyte resistance
$\tilde{c}_s$	Ion concentration in the solid phase ($\frac{mol}{m^3}$)
I_f	Faradaic current (A)
$\tilde{Z}_D$	Bounded diffusion impedance (Ω)
κ	Thermodynamic parameter ($\frac{1}{V}$)
τ	Diffusion time constant (s)
l	Characteristics length scale for diffusion (m)

D	Diffusion coefficient of the electroactive species ($\frac{m^2}{s}$)
A_w	Bounded diffusion impedance coefficient (Ω)
A_i	Interfacial area of the electrode (m^2)
e	Electron charge (C)

Chapter 3.

EXTENDING TRANSMISSION LINE MODELS TO SECOND-HARMONIC NONLINEAR ELECTROCHEMICAL IMPEDANCE SPECTRA

Note: this chapter will be submitted and published as an article

Abstract

Transmission line models (TLMs) are finite algebraic representations of continuous porous electrodes that provide extra flexibility to include materials physics that can make traditional porous electrode analysis intractable. We provide an algebraic framework for extending traditional linear TLMs to second harmonic nonlinear TLMs (2nd-nTLMs). Solutions to the algebraic framework are validated against analytical porous electrode theory developed previously. To demonstrate the flexibility of 2nd-nTLMs to depict materials physics found in engineered battery materials, we introduce core-shell particles into the porous electrodes and explore their EIS and 2nd-NLEIS response. The ratio between pore electrolyte resistance and interfacial charge transfer resistance (R_{pore}/R_{ct}) determines the TLMs' finite discretization and convergence criterion. Increasing R_{pore} drives current non-uniformity and hence requires finer discretization (more elements). The discriminating power of 2nd-NLEIS in half-cell experiments is explored using TLMs/2nd-nTLMs with core-shell structured particles over a range of RC time constants for the core and the shell. The 2nd-NLEIS responses amplify small difference in parameters under conditions where EIS is insensitive. Parameter identifiability is further evaluated for two identical and overlapping RC time constants by curve fitting with 1-RC models. Overall, simultaneous EIS and 2nd-NLEIS analysis cannot discern core-shell particles with two identical time constants, but can identify inapplicable models when overlapping time constants are present.

3.1 INTRODUCTION

Electrochemical impedance spectroscopy (EIS) is widely used to characterize electrochemical interfaces, materials, and devices. [50,91,113,114] The parameters derived by fitting data to equivalent circuit models (ECMs) are used to track and interpret the physics, chemistry, and performance of the electrochemical system under test. [52,53,79] For example, the growth of charge transfer resistance signals an overall decline in interfacial charge transfer rates. Extraction of parameters like charge transfer resistance from a complex electrochemical device is a useful way to parameterize the device, and track changes quantitatively, but how such information should be physically interpreted and used can be obscured by the degeneracy often found in linearized models used for EIS. [32,34,35,115]

Even a simple semi-circle-shaped EIS Nyquist plot for a two electrode cell has an ambiguous signal; is it dominated by one or both electrodes (with overlapping time constants)? [27,53] The distribution of relaxation time (DRT) method can potentially help with this challenge when multiple reactions hold overlapping, but different, time constants associated with a measurement. [116,117] However, DRT can be insensitive to the system response and provide a non-unique reconstruction of time constant distribution. [117] Physical interpretation can be further impacted by the ease of fitting many different systems using a constant phase element (CPE). [118] For example, CPE can be interpreted as a nonideal capacitive behavior driven by microscopic rough solid electrodes' surface. [119,120] However, CPE elements are often used to fit the depressed semicircle of porous electrodes in batteries, where the physical origin of the EIS signal is often the nonuniform current distribution in the porous electrode, not a distribution of reaction or capacitive time constants. [79] In porous electrodes, the impedance is heavily affected by the resistance of the electrolyte and its interaction with the interfacial charge transfer resistance

of the electrode internal surface area, allowing EIS Nyquist plot charge transfer features to range from semi-circular to “teardrop” shapes that resemble the CPE response. [35,121] Many implementations of CPE in battery impedance analysis fit the data well but may obscure the underlying physical parameters.

Second-harmonic nonlinear electrochemical impedance spectroscopy (2nd-NLEIS) can combine with linear EIS to address many of the issues associated with model selection, degeneracy, and parameter interpretation. 2nd-NLEIS involves driving the electrochemical system to the weakly nonlinear regime with a slightly larger perturbation than EIS. [26] Under the weakly nonlinear regime, the co-existence of the first (EIS) and second (2nd-NLEIS) harmonic response introduces complementary parity between the two half-cell responses, which can effectively break full-cell model degeneracy. [34,35,46] Moreover, 2nd-NLEIS relies on the square of the corresponding half-cell EIS so it further addresses the challenges of half-cell model degeneracy by amplifying the difference between individual electrochemical reactions’ responses in a half-cell. [35]

As an emerging technique, 2nd-NLEIS analysis is still limited by the availability of practical physics-based models to analyze experimental data. We have developed nonlinear full-physics P2D models, [34] along with analytical planar and porous electrode models, [35] whereas Kirk et al. developed a single particle model (SPM). [44] Each of these half-cell models only consider single time constant interfacial charge transfer, which is fine for a limited set of analyses, but in more complex situations, like aging batteries, materials transformations lead to more complex behaviors. For example, in nickel-rich NMC materials, surface reconstruction results in a rocksalt shell on the original primary particle, leading to an increased charge transfer resistance and introducing a new charge transfer time constant. [60,122,123]

Transmission line models (TLMs) provide an algebraic representation of analytical porous electrode theory [100,124,125] while offering extraordinary flexibility to include materials insights such as the surface reconstruction and dendrite growth within the porous electrode. [126] Moreover, TLMs are already used in the field of lithium-ion battery (LIB) research for EIS analysis. [104,105,107,126–129] The addition of second-harmonic nonlinear TLMs (2nd-nTLMs) can thus take advantage of the discriminating power of 2nd-NLEIS while introducing a key new physics-based modeling tool for EIS and 2nd-NLEIS analysis.

In this work, we seek to provide an algebraic framework to extend any linear TLMs developed for EIS to 2nd-nTLMs. The 2nd-nTLM framework takes advantage of the analytical nonlinear Randles circuit we developed in our previous work. [35] Overall, we aim to provide a simple and complete framework for researchers to leverage the power of 2nd-NLEIS to obtain self-consistent parameter estimation in both half-cell and full-cell experiments.

3.2 MATHEMATICAL FORMULATION

We have previously detailed the experimental and mathematical formulation for weakly nonlinear 2nd-NLEIS. [26] Here, we briefly review key requirements that underpin the weakly nonlinear assumption. In 2nd-NLEIS experiments, a pure single-frequency sinusoidal alternating current (I) modulation is applied to the electrochemical system under study,

$$I = \Delta I \exp(j\omega t), \quad (3.1)$$

where $j = \sqrt{-1}$, ΔI is the amplitude of the current modulation (*Amp*) with frequency ω (*radians/s*). For a well-controlled experiment that drives a voltage response greater than 5 mV but less than 20 mV (the upper voltage cutoff can be tuned based on the system investigated to optimize signal quality), a second harmonic (2ω) voltage response can be obtained simultaneously with the first harmonic (ω) response and negligible higher order terms (*h. o. t.*) as,

$$E = \tilde{E}_1 \exp(j\omega t) + \tilde{E}_2 \exp(j2\omega t) + h.o.t. \quad (3.2)$$

The EIS and 2nd-NLEIS response can then be described as follows,

$$\tilde{Z}_1(\omega) = \frac{\tilde{E}_1}{\Delta I}, \quad (3.3)$$

and

$$\tilde{Z}_2(\omega) = \frac{\tilde{E}_2}{(\Delta I)^2}. \quad (3.4)$$

Equation 3.1 enforces a zero-second-harmonic-current condition at the current collector and at the bulk electrolyte end of the transmission line, implying second harmonic currents generated within interior elements of the transmission line must nullify at the ends of the TLM. The general framework for developing physically meaningful TLMs and 2nd-nTLMs of porous electrodes starts with discretization of the porous electrode into N identical interfacial impedance elements as shown in **Figure 3.1a**. We simplify the analysis by assuming zero solid resistivity, as described in [35], and then ascribe the electrolyte-filled pore resistance across the thickness as R_{pore} . Under the macro-homogeneous assumption, each discretized element is identical, allowing insertion of elements such as **Figure 3.1b** or **Figure 3.1c** into the TLM framework. Note, here we use the 2nd-NLEIS equivalent circuit representations defined previously to show nonlinear charge transfer and Warburg elements.[35] **Figure 3.1b** and **Figure 3.1c** represent circuit elements that can be directly compared to the analytical theory as described in the previous work. [35]

The TLM or 2nd-nTLM with ECM shown in **Figure 3.1b** is described by three linear parameters: pore electrolyte resistance (R_{pore}), charge transfer resistance at the bulk electrode interface (R_{ct}), and double layer capacitance at the bulk electrode interface (C_{dl}), each scaled with respect to N . The corresponding 2nd-nTLM requires an additional nonlinear parameter (ϵ) that describes the un-scaled nonlinear reaction charge transfer asymmetry. Similarly, a TLM/2nd-nTLM with diffusion-hindered charge transfer reaction (**Figure 3.1c**) requires a scalable linear diffusion

impedance ($\tilde{Z}_D$) and un-scaled nonlinear differential voltage parameters (κ). The corresponding scalable parameters are defined as follows,

$$R_{pore,N} = \frac{R_{pore}}{N} \quad (3.5)$$

$$R_{ct,N} = R_{ct}N \quad (3.6)$$

$$C_{dl,N} = \frac{C_{dl}}{N} \quad (3.7)$$

$$\tilde{Z}_{D,N} = \tilde{Z}_D N \quad (3.8)$$

where $\tilde{Z}_D$ can be calculated using **Table 2-I** in **Chapter 2** for planar, cylindrical, or spherical insertion materials geometry. [35] It is also important to note that these scalable parameters are directly correlated to the surface area of the current collector as well as the actual interfacial area of the electrolyte/electrode interface, which is also detailed in our previous work. [35] The final converged solution for a TLM/ 2^{nd} -nTLM network is realized when increasing N no longer changes the impedance for a given set of parameters.

The solution of the proposed TLM framework involves three major steps to set-up the algebraic equations and perform an efficient matrix calculation: step 1 defines the EIS response of the TLM; step 2 finds the linear current distribution within the discretization of the TLM; step 3 solves the second harmonic current distribution within the TLM (with zero second harmonic current boundary conditions), which enables the calculation of 2^{nd} -NLEIS response for the 2^{nd} -nTLM.

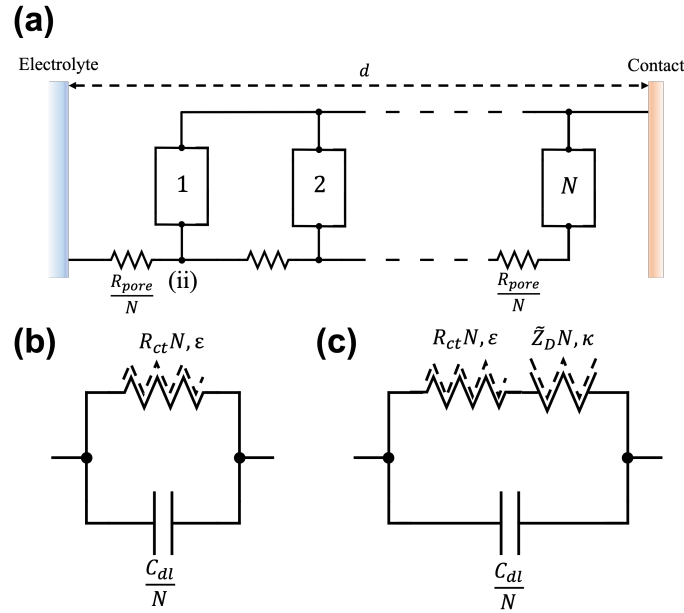


Figure 3.1. a) Generalized equivalent circuit representation for a N -element TLM and 2nd-nTLM with zero solid resistivity. Example repeating ECM for b) a simple charge transfer reaction and c) a diffusion-hindered charge transfer reaction.

3.2.1 Step 1: Linear Impedance of the Transmission Line Model (TLM)

The linear impedance of the N -element transmission line model (TLM) can be determined with Kirchhoff's law and Ohm's law given the impedance for each branch ($\tilde{Z}_{1,b}^{(N)}$) and the discretized pore electrolyte resistance as follows,

$$\tilde{Z}_1^{(N)} = R_{pore,N} + \frac{1}{\frac{1}{\tilde{Z}_{1,b}^{(N)}} + \frac{1}{R_{pore,N} + \frac{1}{\frac{1}{\tilde{Z}_{1,b}^{(N)}} + \frac{1}{R_{pore,N} + \dots}}}}, \quad (3.9)$$

where ... will be substituted by $\frac{1}{\frac{1}{\tilde{Z}_{1,b}^{(N)}} + \frac{1}{R_{pore,N} + \dots}}$ until $N - 1$ iterations are performed and will be

filled with $\tilde{Z}_{1,b}^{(N)}$ for the last iteration. Practical implementation will be initialized with the last $\tilde{Z}_{1,b}^{(N)}$ and performs calculations reversely. Importantly, the branched formulation enables generalization to any physical situation in a porous electrode. For example, **Figure 3.1b** can be used to describe

the interfacial charge transfer reaction in the porous electrode, which has the following impedance expression,

$$\tilde{Z}_{1,b}^{(N)} = \frac{1}{\frac{1}{R_{ct,N}} + j\omega C_{dl,N}} \quad (3.10)$$

A more interesting situation considered a core-shell structured particle (i.e., the growth of the surface layer on top of the bulk electrode) can be described by a series of two Randles circuits as shown in **Figure 3.2a**. The charge transfer impedance in each branch can then be described as,

$$\tilde{Z}_{1,b}^{(N)} = \frac{1}{\frac{1}{R_{ct,N}} + j\omega C_{dl,N}} + \frac{1}{\frac{1}{R_{s,N}} + j\omega C_{s,N}}. \quad (3.11)$$

In general, $\tilde{Z}_{1,b}^{(N)}$ can be any physically meaningful element. We show several physically meaningful ECMs in **Figure 3.2** with analytical linear and nonlinear Randles responses to represent charge transfer and diffusion impedances in core-shell primary particles that get agglomerated into a porous electrode.

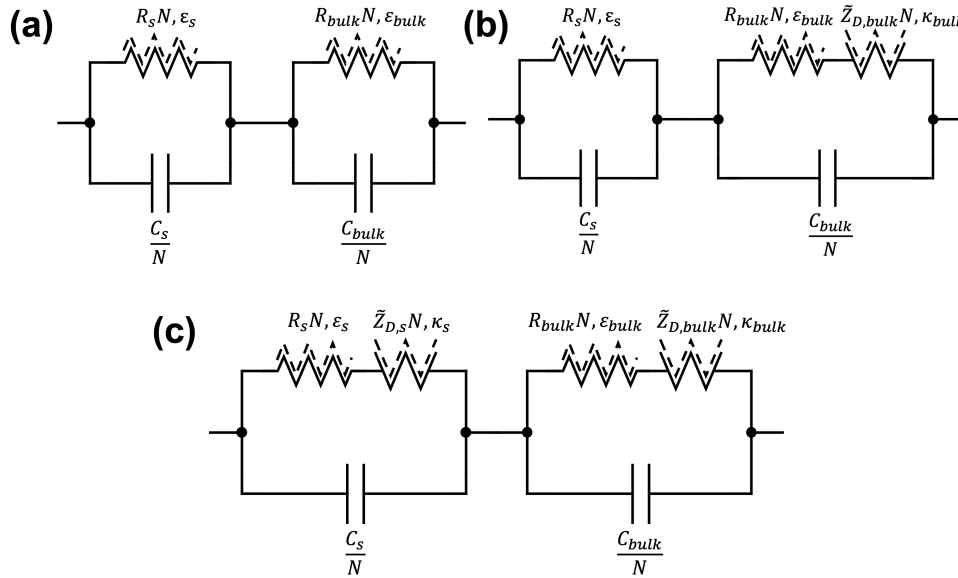


Figure 3.2. Physical ECMs that can be used to develop TLM and 2nd-nTLM for a porous electrode that has distinct surface and bulk behavior: a) simple charge transfer reaction in bulk electrode and surface film; b) simple charge transfer reaction in the surface film and diffusion hindered charge transfer reaction in the bulk electrode; c) diffusion hindered charge transfer reaction in both surface film and bulk electrode.

3.2.2 Step 2: Linear Current Distribution Through the Transmission Line Model (TLM)

Transmission line modeling not only provides physical insights into the shape of impedance spectra but also the A.C. current distribution within the electrode. D.C. current distribution within a porous electrode was first explored analytically by Euler and Nonnenmacher, and Newman and Tobias in the 1960s, [130,131] and can provide key insights into the performance of lithium-ion batteries (LIBs). [121]

In this formulation, the normalized current distribution can be obtained as the fraction of current passing through each TLM branch. When the current modulation information is provided, the exact current passing through each branch can also be determined. Here, we demonstrate the mathematical formulation for the current fraction calculation that follows Kirchhoff's current and voltage laws. Given the input current described by **Equation 3.1**, Kirchhoff's current law requires the total current passing through the electrode (ΔI) as the sum of the current passing through each branch ($\tilde{I}_{1,i}$),

$$\Delta I = \sum_{i=1}^N \tilde{I}_{1,i}. \quad (3.12)$$

The Kirchhoff's voltage law also requires voltage conservation. A voltage balance can then be established between the solid and solution phase over each branch, where the voltage drop considers both the electrolyte resistance and impedance of each branch. The linear voltage response calculated from the first N (≥ 1) branches can then be generalized as follows,

$$\tilde{E}_1^{(N)} = N \times R_{pore,N} \times \Delta I - R_{pore,N} \times \left(\sum_{i=1}^N (N - i) \times \tilde{I}_1^{(i)} \right) + \tilde{Z}_{1,b}^{(N)} \times \tilde{I}_1^{(N)}. \quad (3.13)$$

With **Equations 3.3, 3.12, and 3.13**, a $N \times N$ matrix that defines the fraction of current distribution can be established for a N -element TLM,

$$\tilde{Z}_1^{(N)} \begin{bmatrix} 1 \\ \vdots \\ 1 \end{bmatrix} = R_{pore,N} \begin{bmatrix} 1 & 1 & \cdots & 1 \\ 2 & 2 & \cdots & 2 \\ \vdots & \vdots & \ddots & \vdots \\ N & N & \cdots & N \end{bmatrix} \times \begin{bmatrix} \tilde{\theta}_1^{(1)} \\ \vdots \\ \tilde{\theta}_1^{(N)} \end{bmatrix} +$$

$$\begin{bmatrix} \tilde{Z}_{1,b}^{(N)} & 0 & \cdots & \cdots & 0 \\ -R_{pore,N} & \tilde{Z}_{1,b}^{(N)} & 0 & \cdots & 0 \\ -2R_{pore,N} & -R_{pore,N} & \ddots & 0 & 0 \\ \vdots & \vdots & -R_{pore,N} & \tilde{Z}_{1,b}^{(N)} & 0 \\ -(N-1)R_{pore,N} & -(N-2)R_{pore,N} & \cdots & -R_{pore,N} & \tilde{Z}_{1,b}^{(N)} \end{bmatrix} \times \begin{bmatrix} \tilde{\theta}_1^{(1)} \\ \vdots \\ \tilde{\theta}_1^{(N)} \end{bmatrix}, \quad (3.14)$$

where $\tilde{Z}_1^{(N)}$ is the total impedance of the N elements TLM calculated from **Equation 3.9**, and

$\tilde{\theta}_1^{(i)} = \tilde{I}_1^{(i)} / \Delta I$ is the fraction of linear current ($\tilde{I}_1^{(i)}$) passing through the i^{th} branch. **Equation 3.14**

has a form of $Ax = b$, which provides a fast linear algebra solution for $\begin{bmatrix} \theta_1^{(1)} \\ \vdots \\ \theta_1^{(N)} \end{bmatrix}$.

3.2.3 Step 3: Impedance of Second-Harmonic Nonlinear Transmission Line Model (2nd-nTLM)

The development of the second harmonic nonlinear transmission line model (2nd-nTLM) relies on the linear TLM, the fraction of current distribution, and the analytical nonlinear Randles circuit. The whole process relies on the charge conservation within the electrode for the second harmonic current. The 2nd-NLEIS experiment requires zero current boundary conditions (no second harmonic current entering and exiting the system), while not constraining the internal second harmonic current generation. This suggests the following charge conservation for the second harmonic current,

$$\sum_{i=1}^N \tilde{I}_{2,i}^{(N)} = 0, \quad (3.15)$$

where $\tilde{I}_{2,i}^{(N)}$ is the second harmonic current generated at each branch and will nullify within the electrode.

The second harmonic nonlinear voltage drop can then be established over each branch through the thickness direction of the TLM. At the bulk electrolyte interface, the electrolyte only contributes to linear EIS but not the 2nd-NLEIS. Within the electrode, the second harmonic voltage has nonlinear (quadratic) contributions from the current flowing at the fundamental frequency, and linear contributions from current flowing at twice the fundamental frequency (denoted by @2 ω subscript). The voltage balance can then be obtained at the intersection (ii) as shown in **Figure 3.1a**, which provides the following $N \times N$ matrix for the second harmonic voltage response at each branch,

$$\begin{aligned} \tilde{E}_2^{(N)} \begin{bmatrix} 1 \\ \vdots \\ 1 \end{bmatrix} &= \tilde{Z}_{1@2\omega,b}^{(N)} \times I_d \times \begin{bmatrix} \tilde{I}_2^{(N)} \\ \vdots \\ \tilde{I}_2^{(1)} \end{bmatrix} + \tilde{Z}_{2,b}^{(N)} \times I_d \times \begin{bmatrix} \tilde{I}_1^{(N)^2} \\ \vdots \\ \tilde{I}_1^{(1)^2} \end{bmatrix} \\ &+ R_{pore,N} \begin{bmatrix} N-1 & N-2 & N-3 & \cdots & 2 & 1 \\ N-2 & N-2 & N-3 & \cdots & 2 & 1 \\ N-3 & N-3 & N-3 & \cdots & 2 & 1 \\ \vdots & \vdots & \vdots & \ddots & \vdots & 1 \\ 1 & 1 & \cdots & \cdots & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \times \begin{bmatrix} \tilde{I}_2^{(N)} \\ \vdots \\ \tilde{I}_2^{(1)} \end{bmatrix} \end{aligned} \quad (3.16)$$

where $\tilde{Z}_{2,b}^{(N)}$ can be obtained with the nonlinear Randles circuit and I_d is the identity matrix. [35]

For example, under a cosine wave perturbation, $\tilde{Z}_{2,b}^{(N)}$ in a macro homogenous porous electrode with only one charge transfer reaction (**Figure 3.1b**) is of the form,

$$\tilde{Z}_{2,b}^{(N)} = \frac{-0.5\varepsilon_{bulk}fR_{ct,N}^2}{1+4\omega_{bulk}^*j-5\omega_{bulk}^{*2}-2\omega_{bulk}^{*3}j}, \quad (3.17a)$$

where $\omega_{bulk}^* = \omega R_{ct,N} C_{dl,N}$ is the dimensionless characteristic frequency for the bulk charge transfer reaction and ε_{bulk} is the charge transfer asymmetry parameter for the bulk electrode. Note that a factor of 1/2 is introduced in **Equation 3.17a** vs. our original model in [35], to recognize

factor the use of a trigonometric (cosine) perturbation here vs Euler circular function in [35]. If a surface layer is formed on top of the porous electrode (**Figure 3.2a**), $\tilde{Z}_{2,b}^{(N)}$ is of the form,

$$\tilde{Z}_{2,b}^{(N)} = \frac{-0.5\varepsilon_{bulk}fR_{ct,N}^2}{1+4\omega_{bulk}^*j-5\omega_{bulk}^{*2}-2\omega_{bulk}^{*3}j} + \frac{-0.5\varepsilon_sfR_{ct,N}^2}{1+4\omega_s^*j-5\omega_s^{*2}-2\omega_s^{*3}j}, \quad (3.17b)$$

where $\omega_s^* = \omega R_{s,N}C_{s,N}$ is the dimensionless characteristic frequency for the surface charge transfer reaction and ε_s is the charge transfer asymmetry parameter for the surface film. This approach can easily be generalized with other physical ECMs that satisfy the linear and nonlinear TLM framework.

The fraction distribution of second harmonic currents can then be obtained by solving **Equation 3.16** with **Equation 3.15**. To do that, the first row of the matrix will be subtracted from the rest of the matrix to form a $(N - 1) \times N$ matrix as a result of identical second harmonic voltage responses at the intersection (ii) (**Figure 3.1a**) for each discretization branch. The $(N - 1) \times N$ matrix can be combined with **Equation 3.15** to form a $N \times N$ matrix that describes the second harmonic current distribution in the TLM with zero flux boundary condition,

$$\begin{aligned} -\tilde{Z}_{2,b}^{(N)} \begin{bmatrix} \{\tilde{\theta}_1^{(N)}\}^2 - \{\tilde{\theta}_1^{(1)}\}^2 \\ \{\tilde{\theta}_1^{(N)}\}^2 - \{\tilde{\theta}_1^{(2)}\}^2 \\ \vdots \\ \{\tilde{\theta}_1^{(N)}\}^2 - \{\tilde{\theta}_1^{(N-1)}\}^2 \\ 0 \end{bmatrix} &= \tilde{Z}_{1@2\omega,b}^{(N)} \begin{bmatrix} 1 & 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & -1 & 0 \\ \dots & \dots & \dots & \dots & \dots \\ 1 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \tilde{\theta}_2^{(N)} \\ \tilde{\theta}_2^{(N-1)} \\ \vdots \\ \tilde{\theta}_2^{(1)} \end{bmatrix} \\ + R_{pore,N} \begin{bmatrix} N-1 & N-2 & \dots & 1 & 0 \\ N-2 & \vdots & 1 & 0 & 0 \\ \vdots & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \tilde{\theta}_2^{(N)} \\ \tilde{\theta}_2^{(N-1)} \\ \vdots \\ \tilde{\theta}_2^{(1)} \end{bmatrix} &+ \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots \\ 1 & 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} \tilde{\theta}_2^{(N)} \\ \tilde{\theta}_2^{(N-1)} \\ \vdots \\ \tilde{\theta}_2^{(1)} \end{bmatrix}, \quad (3.18) \end{aligned}$$

where $\tilde{\theta}_2^{(i)} = \tilde{I}_2^{(i)} / (\Delta I)^2$ is the fraction of second harmonic current ($\tilde{I}_2^{(i)}$) passing through i^{th} branch.

Equation 3.18 can be solved with matrix multiplication, providing the solution of

$\begin{bmatrix} \tilde{\theta}_2^{(N)} \\ \tilde{\theta}_2^{(N-1)} \\ \vdots \\ \tilde{\theta}_2^{(1)} \end{bmatrix}$. The 2nd-NLEIS response of the 2nd-nTLM can be obtained with the last row of **Equation**

3.16, which provides a voltage drop over the first discretization branch. Following the impedance definition of **Equation 3.4**, the 2nd-NLEIS of the 2nd-nTLM is then of the form,

$$\tilde{Z}_2^{(N)} = \tilde{Z}_{2,b}^{(N)} \times \left\{ \tilde{\theta}_1^{(1)} \right\}^2 + \tilde{Z}_{1@2\omega,b}^{(N)} \times \tilde{\theta}_2^{(1)}. \quad (3.19)$$

Overall, any physical TLMs that satisfy the boundary condition described by **Equation 3.15** can be solved using this framework and provide the correct 2nd-NLEIS response with **Equation 3.19**.

3.2.4 Practical Implementation and Code Availability

Implementing these algebraic equations without a standardized platform can be challenging. Importantly, the TLM framework can only be fully utilized when combined with other physics-based models to characterize porous electrodes and extract physical parameters. Fortunately, we have previously developed `nleis.py`, [47] an open-source Python package, that provides a platform to perform 2nd-NLEIS analysis with several lines of code as well as many built-in physics-based models. The TLM framework has been built into `nleis.py` and is fully modularized with circuit element described by **Figure 3.2b**. This integration facilitates easy generalization to other physical TLMs by slightly altering the existing framework. Together with an extensive library of models, the TLM framework can be easily built into cell models to perform individual and simultaneous analysis of EIS and 2nd-NLEIS using `nleis.py`. Lastly, the jupyter notebooks developed in this work are archived in GitHub and Zenodo. [132]

3.3 RESULTS AND DISCUSSION

3.3.1 *Validation of TLM and 2nd-nTLM with Analytical Macro-Homogeneous Porous Electrode Model*

Porous electrode theories and Transmission line models (TLMs) have been demonstrated to provide equivalent views into porous electrode response. In fact, TLMs provide a discrete algebraic representation of the analytical porous electrode theories while providing additional flexibility in describing complex physics. In our previous work, [35] an analytical macro-homogeneous porous electrode model for EIS and 2nd-NLEIS has been developed that follows Paasch's analytical framework. [100] In our previous work, we briefly demonstrated the convergence between our analytical solution and its equivalent 2nd-nTLM with a simple charge transfer reaction, but did not dive into details with the presence of solid-state diffusion. In this work, we will reevaluate the convergence criterion for simple 2nd-nTLM with our analytical theories. A macro-homogeneous porous electrode with diffusion-hindered interfacial charge transfer at the surface of spherical particles is considered to further validate the generalized TLM and 2nd-nTLM framework.

As noted from our previous work and Morasch et al., [35,121] the ratio (R_{pore}/R_{ct}) is a critical parameter that characterizes the impedance response and the current accessibility of the electrode while determining the convergence criterion for the TLM/2nd-nTLM with respect to the analytical theories. **Figure 3.3** shows the comparison between TLMs/2nd-nTLMs and analytical solution with R_{pore}/R_{ct} of 0.1, 1, 10, and 100 for a N value of 1, 10, 100, and 1000. The choice of R_{pore}/R_{ct} is designed to cover uniformly (electrochemically “thin”) and non-uniformly accessible (electrochemically “thick”) porous electrodes. The case of $R_{pore}/R_{ct} = 0.1$ (**Figure 3.3a**) shows a rapid convergence between the TLM and the analytical solution even at $N = 1$.

Effectively, $R_{pore,N}$ is so small (or alternatively, R_{ct} is so large) that the current will almost uniformly pass through each discretized branch and lead to the equivalent of a simple Randles circuit response that can be represented with a single element TLM. As R_{pore}/R_{ct} increases (**Figure 3.3c,e,g**), the current distribution becomes more nonuniform and the conventional porous electrode response emerges with the 45-degree tilt at high frequency to form a teardrop shaped response. The emergence of porous electrode features also requires a more refined discretization (larger N) to ensure the convergence of TLMs with the analytical solution. In these cases, the presence of significant $R_{pore,N}$ drives more current to the discretized branches adjacent to the bulk electrolyte while leaving the rest of the discretized branches inaccessible. Therefore, finer discretization is required to fully capture the current distribution and provide a correct description of the electrode impedance.

The 2nd-nTLMs responses (**Figure 3.3b, d, f, and h**) with different R_{pore}/R_{ct} follow similar convergence trends as their corresponding TLMs, where finer discretization is required with a larger ratio of R_{pore}/R_{ct} . It is worth noting that the 2nd-nTLM generally converges faster than the TLM. This is mainly attributed to the fact that $R_{pore,N}$ only propagates the second harmonic current while not generating additional nonlinear responses. Finer discretization, thus, significantly improves the accuracy of the electrolyte contribution to the nonlinear response, leading to faster convergence of the 2nd-NLEIS response.

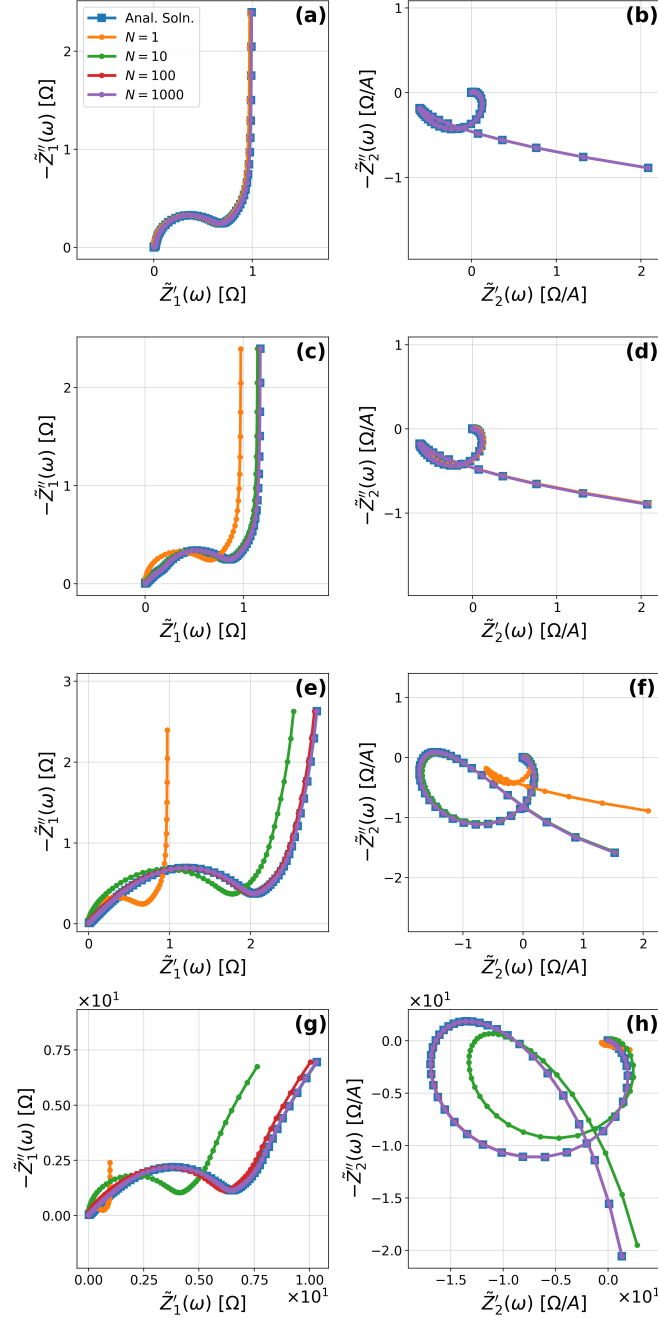


Figure 3.3. Convergence criterion for TLM and 2nd-nTLM with analytical solution for a macro homogeneous porous electrode with diffusion hindered interfacial charge transfer in spherical particles (Anal. Soln.) for different ratio (R_{pore}/R_{ct}) of R_{pore} and R_{ct} . a-b) $R_{pore}/R_{ct} = 0.1$, c-d) $R_{pore}/R_{ct} = 1$, e-f) $R_{pore}/R_{ct} = 10$, and g-h) $R_{pore}/R_{ct} = 100$. The fixed parameters used to compute the responses are $R_{ct} = 0.6 \, \Omega$, $C_{dl} = 0.72 \, F$, $A_w = 2 \, \Omega$, $\tau = 400 \, s$, $\kappa = -1 \, V^{-1}$, and $\varepsilon = 0.1$. A total of 100 log-spaced points are used for frequency from 1×10^{-3} to 1×10^4 Hz.

3.3.2 *Electrode Utilization and Electrochemical Characteristics of Porous Electrode Revealed by TLM*

Understanding the current distribution within the porous electrode is critical to optimizing the electrode performance. In the example of lithium-ion battery (LIB) applications, the interaction between electrolyte and electrode dictates the battery's power and energy performance. A uniform accessible (electrochemically "thin") electrode provides a uniform current distribution and better power capability, while a non-uniform accessible (electrochemically "thick") electrode has a current distribution focused at the interface of the bulk electrolyte and porous electrode, limiting its power performance. These design characteristics have been well-demonstrated in the commercial LIBs. [133,134] Modeling the impedance response of the porous electrodes with TLMs, thus, provides a unique visualization of the frequency-dependent current distribution within the electrode.

A typical porous electrode can be separated into three categories (electrochemical thin, intermediate, and thick) based on its electrochemical properties, which are determined by the ratio between the effective pore electrolyte resistance and the effective interfacial charge transfer resistance (R_{pore}/R_{ct}), when the solid phase resistance is small compared to both. $R_{pore}/R_{ct} = 0.1, 1$, and 10 are chosen to describe electrochemical thin, intermediate, and thick electrodes respectively. Based on the convergence criterion shown in the previous section, N is set to 100 to provide sufficient discretization for all these cases. Their corresponding characteristic impedance responses are normalized with their DC impedance and are shown in **Figure 3.4a**. As shown in **Figure 3.4a**, normalization reveals the differences in the characteristic shape. That is, an electrochemical thin electrode exhibits a classic semi-circle impedance response, while an electrochemical thick electrode shows a teardrop impedance response with a 45-degree tilt at high

frequency. The 45-degree behavior is driven by the electrolyte distribution within the porous electrode, which limits the utility of the electrode for high-power applications. The corresponding current distributions under the DC limit for these three cases are summarized in **Figure 3.4b**. The electrochemical thin electrode shows the most uniform current distribution, which provides the highest electrode utility. On the other hand, an electrochemical thick electrode will have current clustered at the electrode-electrolyte interface ($x = 0$), reducing its electrode utilization. Moreover, the non-uniform current distribution will lead to non-uniform energy consumption, which can further complicate the performance optimization of porous electrodes. Therefore, under the practical limitation of battery electrolyte, R_{pore}/R_{ct} can be easily optimized for high-power and high-energy applications by tuning the thickness and tortuosity of the electrode. Meanwhile, searching for higher conductivity electrolytes will always be beneficial for the performance optimization of contemporary batteries, as it can effectively reduce the overall impedance.

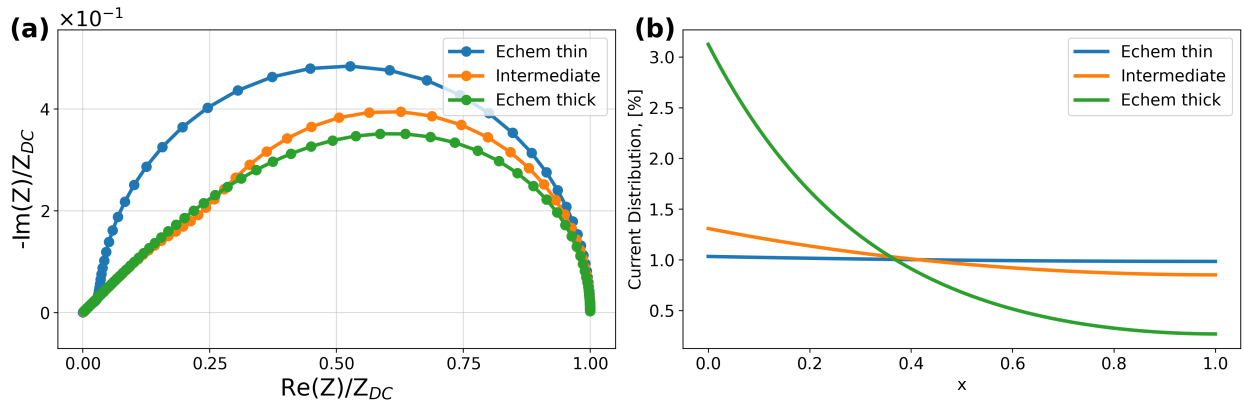


Figure 3.4. a) Normalized Nyquist plot of electrochemical thin ($R_{pore}/R_{ct} = 0.1$), intermediate ($R_{pore}/R_{ct} = 1$), and thick ($R_{pore}/R_{ct} = 10$) porous electrode ($N = 100$), and b) their corresponding current distribution within the electrode under the DC limit (1×10^{-3} Hz). The fixed parameters used to compute the curves are $R_{ct} = 1 \Omega$, $C_{dl} = 1 F$. A total of 100 log-spaced points are used for frequency from 1×10^{-3} to 1×10^4 Hz.

3.3.3 *Parameter Identifiability with TLM and 2nd-nTLM for a Porous Electrode with Core-Shell Structured Particles*

It is well known that the aging of lithium-ion batteries can lead to the growth of cell impedance, especially for the NMC cathode. [24,60,122] This impedance growth has usually been measured by EIS and analyzed with equivalent circuit models (ECMs). [24,60] Numerous physical and a-physical ECMs have been proposed to describe the cathode impedance growth. [53] Experimentally, it has been found that aging can lead to the formation of a Ni-rich surface layer on top of the bulk NMC cathode materials (i.e., a core-shell structured particle). [135,136] This extra layer has been considered the main contributor to NMC impedance growth. [60,136] We have shown in our previous work that 2nd-NLEIS can significantly improve the parameter identifiability in a full cell setup with one charge transfer reaction at each electrode. The fact that the nonlinear response relies on the square of the linear response also provides better model and parameter identifiability in half-cell experiments. To demonstrate that, three scenarios containing core-shell particles with two RC time constants are simulated using the 2-RC TLM/2nd-nTLM models selected from the circuit elements shown in **Figure 3.2**. The simulated results are compared with single RC time constant particles in TLM/2nd-nTLM (a normal porous electrode model as shown in [35]), showcasing the discriminating power of 2nd-NLEIS. The 2-RC model considered here includes cases comprised of identical, overlapping, and distinct RC time constants. The shell is deemed thin so only solid-state diffusion is accounted for in the spherical particle core. This physical description covers a range of conditions that may describe an NMC cathode particles age; it is represented by the nonlinear ECM in **Figure 3.2b**. The parameters used to simulate the three different cases are summarized in **Table 3-I**, where the total equivalent charge transfer resistance and the degree of asymmetry are kept the same for each pair of 1-RC and 2-RC models. In all

simulations, N is set to 100 to provide sufficient discretization. The simulation results are summarized in **Figure 3.5**.

Table 3-I. Parameters for 2-RC core-shell and 1-RC equivalent TLM/2nd-nTLM model.

	Case 1		Case 2		Case 3	
Model	2-RC	1-RC	2-RC	1-RC	2-RC	1-RC
$R_{pore} [\Omega]$			6			
$R_{ct,b} [\Omega]$	0.6	1.2	1.2	1.8	0.6	1.2
$C_{dl,b} [F]$	1.44	0.72	0.72	0.72	0.72	0.72
$A_w [\Omega]$	2	2	2	2	2	2
$\tau_d [s]$	400	400	400	400	400	400
$\kappa [1/V]$	-1	-1	-1	-1	-1	-1
$\varepsilon_b [-]$	0.1	0.1	0.1	0.1	0.1	0.1
$R_{ct,s} [\Omega]$	0.6	-	0.6	-	0.6	-
$C_{dl,s} [F]$	1.44	-	7.2	-	7.2	-
$\varepsilon_s [-]$	0.1	-	0.1	-	0.1	-

Case 1 describes a situation where the shell and core possess the same RC time constant and overall charge transfer resistance. In this case, the situation is degenerate with a 1-RC TLM with the same effective charge transfer resistance but half the effective double layer capacitance; **Figure 3.5a** shows that the EIS responses of a 1-RC and 2-RC TLM are indistinguishable. This can be a practical challenge when doing EIS analysis, as the linearized system response can be described by the summation of any linearized ECMs. The 2nd-NLEIS (**Figure 3.5b**), on the other hand, can distinguish the physics between a single electrochemical process and multiple electrochemical processes when the charge transfer processes have asymmetry, even when the core and shell have identical asymmetry. Case 2 considers a scenario where the two electrochemical reactions have overlapping, but not identical, time constants. Given the parameters provided, they can be distinguished in both EIS and 2nd-NLEIS (**Figure 3.5c-d**). Lastly, case 3 describes a situation where the two electrochemical reactions possess distinct time constants, which shows the

clearest distinction between a single time constant particle and the two time constant particles for both EIS and 2nd-NLEIS (**Figure 3.5e-f**).

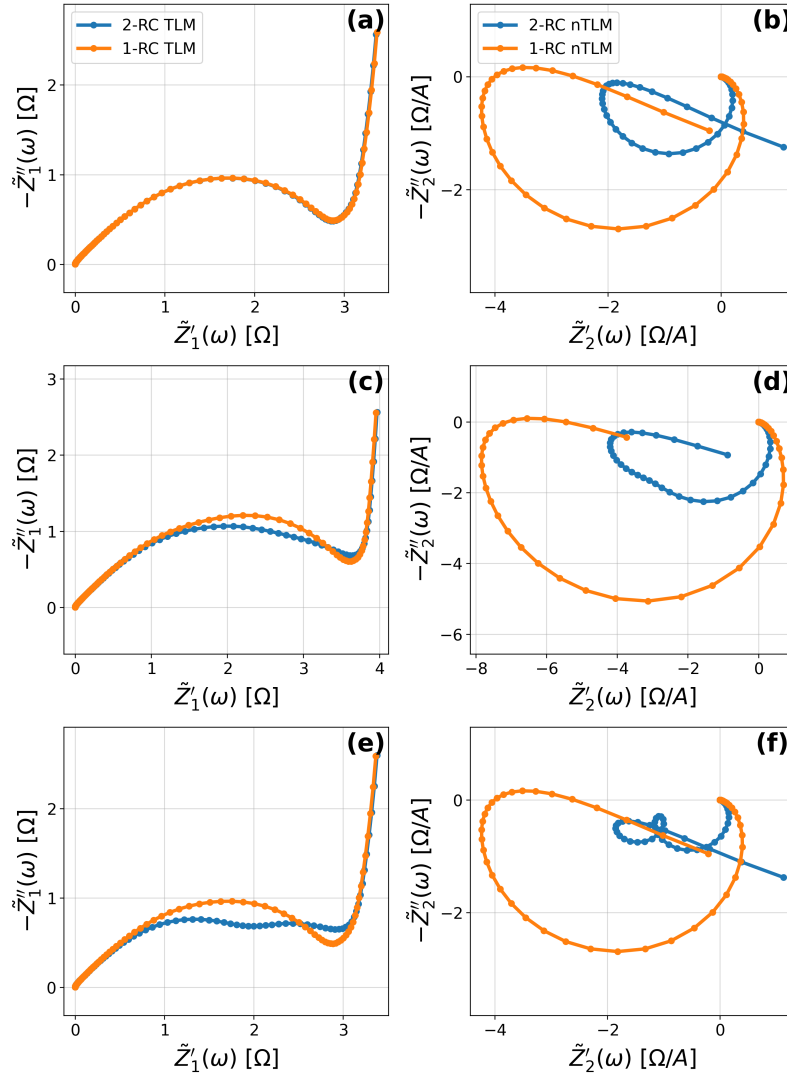


Figure 3.5. Simulated 2-RC core-shell and 1-RC equivalent TLM/2nd-nTLM for the three cases described in **Table 3-I**. In all three cases, the equivalent charge transfer resistance is kept the same between the 1-RC and 2-RC models. a-b) case 1; c-d) case 2; e-f) case 3. A total of 100 log-spaced points are used for frequency from 1×10^{-3} to 1×10^4 Hz.

These simulations provide direct insight into parameter identifiability with *a posteriori* knowledge of the system. For practical impedance data analysis, model fitting is usually performed to extract physical parameters without *a posteriori* knowledge. As a result, the ability to distinguish

among fitting models is an indispensable benefit of 2nd-NLEIS, if possible. From the three cases introduced in **Table 3-I** and **Figure 3.5**, only case 3, with a clear separation of the 2 RC time constants, is easily distinguished from the 1-RC model. EIS in cases 1 and 2 is more ambiguous. Therefore, cases 1 and 2 are further explored to assess the discriminating power of 2nd-NLEIS to identify correct or incorrect modelled physics when data with known physics is fit by an inappropriate (but reasonable) model. Specifically, we perform EIS-only and simultaneous EIS/2nd-NLEIS fitting of two-time constant simulated data with a (physically incorrect) 1-RC models. The EIS-only fitting of the two time constant simulated data is performed using `impedance.py` [137] and the simultaneous EIS/2nd-NLEIS fitting is performed using `nleis.py` [47] with equally weighted cost function for EIS and 2nd-NLEIS. The fitted parameters are shown in **Table 3-II** and the fitting results are shown in **Figure 3.6**.

As shown in **Figure 3.5a**, the EIS response of the 2-RC model is identical to a single RC porous electrode model when two electrochemical reactions share the same charge transfer resistance and RC time constants. So as expected, fitting 2-RC simulated data with a 1-RC model leads to a good fit, as shown in **Figure 3.6a**. The resulting parameters from our analytical porous electrode model are very close to the effective charge transfer resistance (1.2Ω) and double layer capacitance ($0.72 F$). By performing simultaneous analysis of the EIS and 2nd-NLEIS TLM data to our analytical porous electrode model, estimated parameters are further improved (**Figure 3.6b-c**). Because of the constraint of 2nd-NLEIS, the EIS parameters are fully refined, which almost perfectly aligns with the input model parameters. On the other hand, the estimated degree of asymmetry (ϵ) halved due to the increase in the effective charge transfer resistance. These suggest that it is impossible to distinguish two identical electrochemical reactions even with 2nd-NLEIS, though simultaneous fitting does help refine the parameter estimation. Moreover, if the degree of

asymmetry can be estimated prior to the experiments, irrational fitting results from the simultaneous analysis of EIS and 2nd-NLEIS can help inform the model selections.

Perhaps, the situation described in case 2 is more interesting for practical application. As shown in **Figure 3.5c**, two overlapping RC time constants cannot be effectively captured by a single RC time constant porous electrode model. However, the depressed semi-circle shape can be almost perfectly described by a Randles circuit with a constant phase element (CPE). **Figure 3.6d** shows the fitting of our 2-RC simulated data with a single Randles circuit containing a CPE element. An almost indistinguishable fit is obtained with inappropriate physics, which is common given the flexibility introduced with the CPE element. As shown in **Table 3-II**, the fitted parameters are completely off track from the underlying 2-RC simulated parameters. Thus, the high quality EIS-only fit by the CPE-containing model parameterizes the data as a fitting function, not a physics-aligned description. Simultaneously fitting EIS and 2nd-NLEIS can thus help to discern inappropriate physics from the correct underlying governing physics. This relies on the fact that the 2nd-NLEIS response is generated with the same underlying governing physics as EIS and is directly proportional to the square of the EIS signal. Although the CPE model can fit EIS data well, it fails to capture the 2nd-NLEIS system response when fit simultaneously, as shown in **Figure 3.6e-f**, which demonstrates the model discriminating power introduced through use of 2nd-NLEIS in the impedance analysis pipeline.

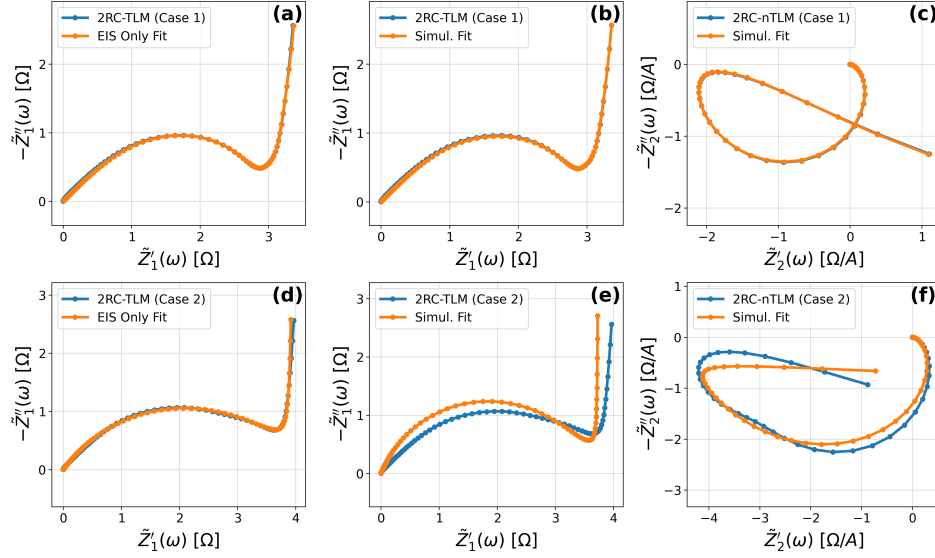


Figure 3.6. Curve fitting results with 2-RC TLM/nTLM model as experimental data for a-c) case 1 and d-f) case 2. For each case, EIS-only fitting and EIS/2nd-NLEIS simultaneous fitting are performed. Case 1: a) EIS-only fitting and b-c) simultaneous fitting with analytical porous electrode. Case 2: d) EIS-only fitting and e-f) simultaneous fitting with an R-CPE model. A total of 100 log-spaced points are used for frequency from 1×10^{-3} to 1×10^4 Hz. Equal weighting for EIS and 2nd-NLEIS is chosen following our previous work. [46]

Table 3-II. Extracted parameters from curve-fitting analysis with 2-RC TLM/nTLM model as experimental data.

Parameters	Case 1 (2RC vs. porous electrode model)			Case 2 (2RC vs. R-CPE model)		
	2-RC Model	EIS Fitting Results	Simultaneous Fitting Results	2-RC Model	EIS Fitting Results	Simultaneous Fitting Results
R_{pore} [Ω]	6	6.29	6.01	6	-	-
$R_{ct,b}$ [Ω]	0.6	1.13	1.17	1.2	4.05	3.58
$C_{dl,b}$ [F]	1.44	0.79	0.74	0.72	0.22	0.18
α_{dl} [-]	-	-	-	-	0.60	0.76
A_w [Ω]	2	1.82	1.95	2	0.50	1.13
τ_d [s]	400	372	395	400	92.0	200
κ [1/V]	-1	-	-0.98	-1	-	-1.09
ε [-]	0.1	-	0.05	0.1	-	0.019
$R_{ct,s}$ [Ω]	0.6	-	-	0.6	-	-
$C_{dl,s}$ [F]	1.44	-	-	7.2	-	-
ε_s [-]	0.1	-	-	0.1	-	-

3.4 CONCLUDING REMARKS

In this work, a generalized transmission line model framework (TLM/2nd-nTLM) was developed with linear and nonlinear Randles circuit as the primary building block for EIS and 2nd-NLEIS. As a discrete algebraic representation of analytical porous electrode theory, this framework provides extraordinary flexibility to extend and include additional physics into the porous electrode. For example, the impedance response of a porous electrode with core-shell structured particles can be easily modeled using this framework. The numerical solution involves a three-step algebraic and matrix solution by calculating EIS response and linear current distribution, nonlinear current distribution, and lastly 2nd-NLEIS response. The numerical solution was validated using analytical porous electrode theory. It was found that the interaction between the electrolyte resistance and charge transfer resistance (R_{pore}/R_{ct}) determines the discretization required to find a convergent solution. A finer discretization is required when the effective electrolyte resistance is much larger than the interfacial charge transfer resistance ($R_{pore}/R_{ct} \gg 1$). Effectively, the large electrolyte resistance concentrates the current at the bulk electrolyte interface, making the rest of the electrode inaccessible. On the other hand, coarser discretization can be used when the electrolyte resistance is comparable with or smaller than the charge transfer resistance ($R_{pore}/R_{ct} \leq 1$), reducing the computation power required. Physically, this improves the electrode utilization and makes the current evenly distributed through the electrode. The effects of R_{pore}/R_{ct} on the electrode utilization and impedance characteristics were further evaluated by considering electrochemical thick ($R_{pore}/R_{ct} = 10$), intermediate ($R_{pore}/R_{ct} = 1$), and thin electrode ($R_{pore}/R_{ct} = 0.1$). A transition from teardrop to semi-circle shape was observed in the impedance response. Meanwhile, it can be observed that the current distribution transitions from a non-uniform current distribution clustered at the bulk electrolyte interface to a uniform current distribution through the electrode.

The ratio between electrolyte resistance and interfacial charge transfer resistance (R_{pore}/R_{ct}) can then be used to improve the design and optimization of contemporary lithium-ion batteries.

In addition to model extensibility, the TLM/2nd-nTLM framework offers the potential to leverage the discriminating power of 2nd-NLEIS to address the EIS degeneracy in half-cells when multiple reaction time constants are present in the porous electrode (i.e., core-shell structured particles appeared because of battery aging). Three scenarios were considered, including two identical, overlapping, and distinct RC time constants. These scenarios were compared with their corresponding one RC time constant models. The model and parameter sensitivities of 2-RC models were further evaluated with curve fitting analysis using 1-RC models. It was found that the analytical porous electrode model can fit the 2-RC model well if the model has two identical RC time constants. The estimated parameters will be slightly off from the apparent values, which can be enhanced with simultaneous EIS and 2nd-NLEIS fitting. On the other hand, if the two RC time constants overlap and form a depressed semi-circle shape. The EIS can be easily fitted with a Randles circuit with a constant phase element (CPE), which results in significant deviation in parameter estimation. Simultaneous EIS and 2nd-NLEIS fitting shows the Randles circuit with constant phase element (CPE) is incapable of simultaneously describing the more complex physics. As a result, simultaneous EIS and 2nd-NLEIS, even in half-cells, can help discriminate nearly degenerate EIS models and help guide more self-consistent model selection. Overall, this work provides a practical way to extend linear TLM to second harmonic nonlinear TLM to leverage the power of 2nd-NLEIS when more complex electrochemical materials are used in porous electrodes. With the introduction of TLM and 2nd-nTLM, we complete the development of a practical 2nd-NLEIS toolbox with simplified physics-based models that facilitate self-consistent parameter estimation for complex porous electrode systems.

Chapter 4.

MEASUREMENT MODEL VALIDATION OF SECOND-HARMONIC NONLINEAR ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Note 1: this chapter will be submitted and published as an article.

Note 2: additional contributors include Rose Lee and Rebecca Vincent for data, and An-Hung Shih for initial exploration.

Abstract

Second harmonic nonlinear electrochemical impedance spectroscopy (2nd-NLEIS) is emerging as a powerful complement to traditional EIS, though a data workflow and validation method is required to improve its adoption. We present a data analysis workflow that utilizes conservative total harmonic distortion (THD) metrics in the input and output spectra to ensure adequate linearity for EIS analysis and adequate instrument performance for collecting 2nd NLEIS. We show that 2nd-NLEIS spectra satisfy Kramers–Kronig (KK) relations, which lets us develop strategies to validate the stationarity and causality assumptions that underpin both EIS and 2nd-NLEIS measurements. A measurement model (MM) test is developed based on the Kramers–Kronig (KK) compliance of 2nd-NLEIS spectra to facilitate data validation. Cost and confidence interval algorithms are used to automate MM fitting. These methods are evaluated with synthetic EIS and 2nd-NLEIS data, as well as experimental EIS and 2nd NLEIS data from a Samsung 18650 NMC||C cell, NMC||C pouch cells, and in-house Li||Cu coin cell. Overall, this work provides a robust way to validate and optimize the input modulation for simultaneous EIS and 2nd-NLEIS analysis, paving the way for more reliable model parameterization and error analysis.

4.1 INTRODUCTION

Electrochemical impedance spectroscopy (EIS) is a non-invasive characterization technique widely used to study electrochemical systems, [91,113,138] and is a key tool for diagnosing the coupled transport and chemistry in advanced batteries. [50,53,139] EIS relies on a linearized approximation for intrinsically nonlinear electrochemical systems, resulting in information loss and a reduced ability to discriminate among competing mechanistic interpretations of impedance data. [32,35,140] Second harmonic nonlinear electrochemical impedance spectroscopy (2nd-NLEIS) is emerging as a complementary technique to EIS that reduces some of these intrinsic linearization challenges. 2nd-NLEIS does not require additional instrumentation nor does it add experimental measurement time – EIS and 2nd-NLEIS datasets are collected simultaneously. [26,34,40,46,141,142] Simultaneously measuring and analyzing EIS and 2nd-NLEIS requires a careful evaluation and setting of the magnitude of the input modulation; too small a modulation degrades 2nd-NLEIS signal quality, whereas too large a modulation can degrade the linear approximation that underpins EIS. To date, there are no data quality tests for 2nd-NLEIS to assess how well the input modulation balance is achieved to optimally accommodate simultaneous EIS and 2nd-NLEIS analysis. The foundation for such a test is that 2nd-NLEIS, like EIS, requires measurements on a stationary and causal electrochemical system. When amplitude is properly selected, and the system is stationary and causal, simultaneous EIS and 2nd-NLEIS collection enables model-based analysis of both signals in a straightforward manner without linearization-related losses of information. [34,35] Developing a Kramers-Kronig-based approach for testing 2nd-NLEIS data for stationarity, causality, and assessing measurement noise is the purpose of this paper.

Physics-based models for 2nd-NLEIS have been developed for analyzing battery-relevant electrodes, [34,35,44] as well as more general models of electrochemical interfacial and transport processes in nonlinear Randles circuits and porous electrodes. [35] These models have been fit to EIS and 2nd-NLEIS experimental data to quantify both the linear and nonlinear parameters linked to battery performance and aging. [34,44,46] As noted above, none of the 2nd-NLEIS experimental data has been evaluated for stationarity and causality (though the corresponding EIS has), nor has experimental noise been assessed in the 2nd-NLEIS data. The omission of data quality tests is especially relevant for practical experimentation, given the small size of the second harmonic signal that underpins the nonlinear analysis.[26,44,46]

In addition to stationarity and causality, it is important to consider whether the linear assumption that underpins EIS experiments are likely to hold. To assess linearity, total harmonic distortion (THD) metrics, distortion of Lissajous plots, and Kramers–Kronig (KK) relations have been proposed as tests of nonlinear contributions that may be problematic for EIS experimental data. In practical applications, a THD of less than 5% of the linear signal is sometimes considered an acceptable level of nonlinear harmonic generations to meet the linear approximation. [143,144] Goh et al. have demonstrated experimentally the connection between Lissajous plots and THD, finding that $THD < 4\%$ was an acceptable quantitative metric for linear analysis of a particular system, the ferri-/ferro-cyanide redox system. [143] Goh et al.’s results showed that measurable nonlinear harmonics co-exist with a signal that adequately satisfies the linear approximation underpinning EIS. KK-relations are sometimes reported as a test for linearity, stationarity, and causality in data, though KK methods are actually insensitive to the linearity assumption and are mainly suitable for testing the stationarity and causality of the data. [143,145–147] The

development of fast computing LinKK [148,149] and/or measurement model testing of data [146,150] are now routinely implemented in software tools for EIS data quality evaluation.

Given the small intrinsic signal associated with second harmonic generation when $THD < 5\%$, it is especially important for data quality to be assessed to add confidence to the analysis. Since our first measurements of 2nd-NLEIS in batteries, we have implemented a stricter requirement for THD than those cited above, namely a $THD < 1\%$, owing to the complexity of battery systems and desire to ensure the linear assumptions that underpin EIS remain valid. [26] The resulting EIS spectra were tested to ensure they satisfy the KK-relations, but we had no 2nd-NLEIS tests. [26,46] Despite ensuring $THD < 1\%$, significant second harmonic signals were extracted and analyzed. [26]

Our restrictive use of $THD < 1\%$ is driven by the knowledge that the validity of the linear approximation depends on the actual perturbation (potential or current) and system under test. In potentiostatic EIS (PEIS), a voltage criterion such as $\Delta V < 5\text{ mV}$ is widely used to ensure linearity, but there is no comparable criterion for ensuring a high quality 2nd-NLEIS dataset that also satisfies linearity. [26,91] In fact, the magnitude of the electrochemical second harmonic (and higher order harmonics) is highly dependent on the nonlinear physics of the electrochemical interface(s) under test. For example, charge-transfer-kinetics dominated systems require asymmetry between the forward and backward reaction to generate any second harmonic, but will always generate a third harmonic (see derivations for Butler Volmer kinetics in **Supplementary Note 4.7.1** for galvanostatic perturbation). Ohmic-dominated electrochemical systems can appear linear up to very large modulation amplitudes. Consequently, fine-tuning of modulation is required to obtain high quality 2nd-NLEIS for each system.

In this work, we aim to provide a first-look at systematically validating galvanostatic 2nd-NLEIS experimental data using a KK-compliant nonlinear measurement model basis function so that optimal current perturbation amplitudes can be evaluated. We also revisit the data collection, validation, and analysis workflow of 2nd-NLEIS so it aligns with common EIS workflows. To accomplish these aims, we first review some high-level aspects of experimental methods, signal processing, and measurement model tests for the satisfaction of Kramers–Kronig relations.

4.2 REVISITING HARMONIC DISTORTION AND SECOND HARMONIC NONLINEAR ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY IN STATIONARY AND CAUSAL SYSTEMS

In typical electrochemical impedance spectroscopy (EIS) measurements, the system is perturbed with a sinusoidal alternating current (GEIS) or voltage (PEIS) modulation, and the corresponding system responses are measured. [91] Here, we consider a galvanostatic current perturbation of the form,

$$I = \Delta I \times \exp(j\omega t) \quad (4.1)$$

with modulation amplitude ΔI , frequency ω , and $j = \sqrt{-1}$. The leading order linear+nonlinear voltage output response from the modulated current can be represented as the series, [33,34,99]

$$V = \tilde{V}_1 \times \exp(j\omega t) + \tilde{V}_2 \times \exp(j2\omega t) + h.o.t. \quad (4.2)$$

for a weakly nonlinear causal and stationary system, where $\tilde{V}_1$ is the complex Fourier coefficient at frequency ω , $\tilde{V}_2$ is the complex Fourier coefficient at frequency 2ω , and *h.o.t.* denotes other higher order terms in the Fourier series. The first harmonic (linear EIS) and second harmonic (2nd-NLEIS) impedances ($\tilde{Z}_1$ and $\tilde{Z}_2$, respectively) are written as, [34]

$$\tilde{Z}_1 = \frac{\tilde{V}_1}{\Delta I} \quad (4.3)$$

$$\tilde{Z}_2 = \frac{\tilde{v}_2}{(\Delta I)^2} \quad (4.4)$$

The 2nd-NLEIS response is found using a Fast Fourier Transform (FFT) to convert time domain measurements to the frequency domain. The FFT of a single-sine input current modulation should produce a single frequency FFT with no harmonics per **Equation 4.1**. Performing an FFT on the output voltage for a stationary and causal nonlinear electrochemical system produces a spectrum with discrete integer harmonics and negligible baseline, i.e. an experimental representation of **Equation 4.2**. **Figure 4.1** provides a schematic of galvanostatic impedance measurements in the time domain (**Figure 4.1a-b**) and frequency domain (**Figure 4.1c-e**).

Figure 4.1c illustrates the FFT magnitude spectrum for an ideal input current modulation, showing a single input frequency and negligible baseline or harmonics. **Figure 4.1d,e** show two scenarios for the FFT magnitude spectrum of the output voltage when the nonlinear electrochemical system is stationary and causal. The key difference between **Figure 4.1d** and **Figure 4.1e** is whether there are observable even harmonic signals. As demonstrated in our previous work, [34,35] asymmetric charge transfer and/or curvature in the local thermodynamic function is required to generate a non-zero second harmonic signal in a typical electrochemical interface. The emergence of measurable harmonics in the output does not intrinsically indicate degradation of the linearity approximation in EIS. [26] Rather, the spectral signatures of note for possible nonlinear corruption of EIS and 2nd NLEIS are the size of third and fourth harmonic, respectively, in the output spectrum (see **Figure 4.1d** and **4.1e**). When 3rd and 4th harmonics in the output spectra are appreciable it is a sign the approximation in **Equation 4.2** may improperly ignore higher order terms.

There is no universal test for how large higher order harmonic contributions can be while preserving **Equations 4.2-4.4** as an adequate representation of the leading order EIS and 2nd-

NLEIS spectra. The sources of nonlinearity matter; we explore this issue systematically in **Supplementary Note 4.7.1** for the (nominally) simple case of nonlinear response caused by interfacial charge transfer. Total harmonic distortion (THD) is a metric widely used as a surrogate for assessing the degree to which nonlinearity may corrupt the interpretability of a (presumed linear) EIS measurement. THD is typically computed from the frequency domain input and output signals as,

$$THD = \frac{\sqrt{\sum_{n=2}^{10} Y_n^2}}{Y_1}, \quad (4.5)$$

where Y_n is the magnitude of the n th-harmonics in current or voltage ($n \geq 2$), and Y_1 is the magnitude of the fundamental (first) harmonic. For a simple ferri-/ferro-cyanide redox system, $THD < 4\%$ in the output current spectrum was deemed sufficiently low for PEIS experiments to be adequately linear for EIS analysis. [143] Likewise, instrument makers sometimes provide a rule of thumb that $THD < 5\%$ provides sufficiently linear response to perform uncorrupted EIS analysis. [144] In all these cases, the presence of a measurable THD spectrum means there is a nonlinear signal accompanying the signal used for linear analysis, i.e., the output spectra looks like **Figure 4.1d** or **Figure 4.1e** with the second and higher harmonics totaling less than a few percent of the fundamental first harmonic.

As a side note, it is important to align the experimental definition of ΔI with the mathematical Euler's formulations of our leading-order EIS and 2nd-NLEIS math, **Equations 4.1-2**. Specifically, there is a factor of two between modulations defined by a trigonometric circular function and that of the complex Euler circular function used here. Because EIS has a linear relationship between output and input modulations (**Equation 4.3**), EIS results are insensitive to this factor of 2. But the quadratic scaling of 2nd-NLEIS output voltage to input modulation can

lead to a factor of 1/2 error if alignment of the modeling and experimental scaling is not accounted for. In short, new details matter for 2nd-NLEIS; if ΔI is defined based on trigonometric circular functions in an experiment, our 2nd-NLEIS mathematics must be scaled by 1/2 so that nonlinear model fitting parameters are correct.

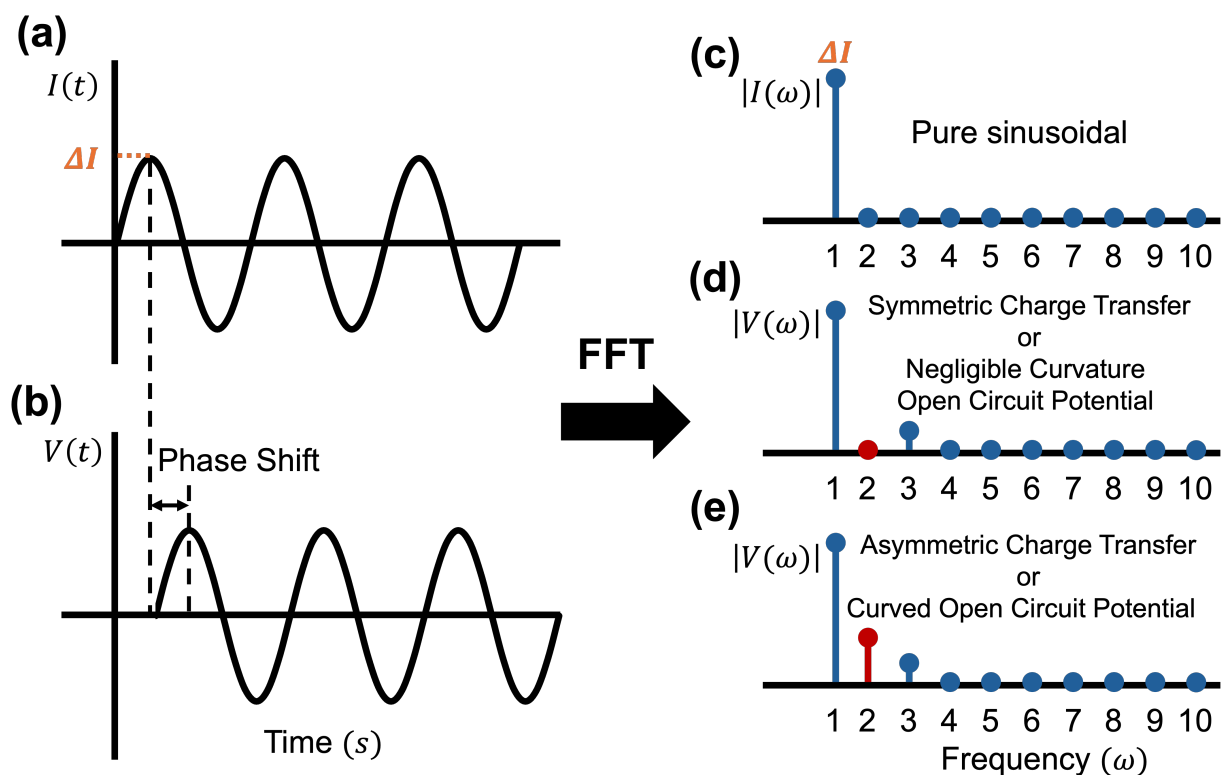


Figure 4.1. Schematic for a typical galvanostatic impedance measurement under the weakly nonlinear regime: a) current perturbation and b) voltage response in the time domain. c) current harmonics, d) symmetric voltage harmonics, and e) asymmetric voltage harmonics in the frequency domain. The first 10 harmonics are shown in the frequency domain and the second harmonic voltage response is labeled in red.

4.3 EXPERIMENTAL METHODS

4.3.1 Pouch Cells

Materials – 290 mAh Li-ion NMC||C pouch cells were purchased from TinyCircuits. Cell disassembly in an Ar glovebox, followed by energy dispersive X-ray spectroscopy, confirmed the cathode was NMC532.

Electrochemical testing – The pouch cells underwent galvanostatic cycling at 25 °C in a temperature-controlled chamber using a 96-channel Maccor cycler at a rate of C/10 for 5 cycles between the manufacturer recommended voltage limits of 2.45 V and 4.2 V. The cells were subsequently charged to 3.5 V, at which point the cells were held at a constant voltage of 3.5 V for 2 h, and then left to rest at open circuit for another 2 h.

Electrochemical impedance spectroscopy measurements were taken after this rest period using the frequency response analyzer module (FRA32) in the Autolab PGSTAT128N potentiostat. A frequency range of 10 kHz – 10 mHz with 10 points per decade and a current modulation amplitude of 50 mA were used, with at least 8 integration cycles per frequency.

4.3.2 In-House Coin Cells

Cell assembly – Electrolyte preparation and coin cell assembly were performed in an argon-filled glovebox from VTI (<0.01 ppm H₂O and O₂). Stainless steel CR2032 coin cell components from MTI Corporation were utilized to make lithium-copper half cells (Li || Cu). The Cu cathodes were prepared by making 16 mm diameter punches from a sheet of Cu foil (9 μm thickness). The Cu punches were then washed with DI water, etched with 1M hydrochloric acid, and rinsed with acetone to remove surface impurities. After drying overnight at 80 °C under vacuum, the Cu foils were transferred to the argon-filled glovebox for coin cell assembly. Li || Cu cells were assembled

with a 15.6 mm diameter Li chip (250 μm thickness), two 19 mm diameter polyethylene separators (16.0 μm thickness each, Nanoshel), and the etched Cu foil with 60 μL of electrolyte split between electrode layers. After crimping, the coin cells were removed from the glovebox for electrochemical testing.

The electrolyte was a local high concentration electrolyte (LHCE) prepared by dissolving lithium bis(fluorosulfonyl)imide (LiFSI, battery grade, Nippon Shokubai) in a mixture of 1,2-dimethoxyethane (DME, battery grade, Gotion, Inc.) and 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (TTE, battery grade, SynQuest) following a molar ratio of 1.0 LiFSI: 1.2 DME: 1.0 TTE. LiFSI and DME were used as received, while the TTE was dried with pre-activated molecular sieves prior to use.

Electrochemical testing – After resting at open-circuit potential for 8 hours, the Li || Cu cells were subjected to galvanostatic cycling at 25 $^{\circ}\text{C}$ in a temperature-controlled Neware cycler. Following a modified Aurbach protocol, [151,152] the cells initially went through a formation cycle by plating/stripping 4 mAh cm^{-2} of Li at a current density of 0.5 mA cm^{-2} . A Li reservoir of 4 mAh cm^{-2} was then plated onto the Cu foil at 0.5 mA cm^{-2} . A small fraction of this reservoir (0.5 mAh cm^{-2}) was cycled at 0.5 mA cm^{-2} , and after 10 shallow cycles, the remaining Li reservoir was exhaustively stripped from the Cu cathode, indicated by the sharp rise in voltage (cutoff 1.0 V).

EIS was utilized to evaluate interfacial evolution with cycling. Impedance measurements were taken after the initial plating of the Li reservoir (“0 cycles”), using the frequency response analyzer module (FRA32) in the Autolab PGSTAT128N potentiostat. A frequency range of 500 kHz – 10 mHz was used, with at least 8 integration cycles per frequency. Initially, a potentiostatic scan with an excitation signal of 3 mV AC was conducted to capture the linear behavior of the cell. Using the impedances from the linear data, the current required to target a weakly nonlinear

signal of 10 mV was calculated at each frequency. A galvanostatic scan was then performed, with the current amplitude manually adjusted at each frequency to yield the desired 10 mV weakly nonlinear response. To illustrate the value of the 2nd NLEIS measurement model tests developed here, we present a Li||Cu cell that failed the 2nd-NLEIS data quality tests (not a typical result).

4.4 RESULTS AND DISCUSSION

Measurement model tests are used in the impedance field to verify data satisfies Kramers–Kronig (KK) relations, enabling an evaluation of causality, stationarity, and noise in an experimental impedance spectrum. [146,150,153] The adoption of measurement model tests relies on the fact that a superposition of a KK-compliant circuit element is also KK-compliant. As a result, if the impedance spectrum can be fitted by a series of Voigt circuits (a KK-compliant element), the data is considered KK-compliant.

4.4.1 *Kramers-Kronig Relations in 2nd-NLEIS*

Kramers-Kronig (KK) relations, originally developed for optics applications, [154,155] have been extensively used to assess the quality of linear impedance spectra. [50,146,148,149,156,157] In most impedance literature, the satisfaction of the KK-relations is assumed to guarantee the satisfaction of the key assumptions that underpin EIS: linearity, stationarity, and causality. However, it has also been demonstrated experimentally and numerically that KK-relations are actually insensitive to the linearity assumption in the weakly nonlinear regime where simultaneous EIS and 2nd-NLEIS ideally operates. [143,145,147] In fact, we show below, 2nd-NLEIS data and functions are KK-transformable, further verifying that KK-based tests are not a suitable linearity test.

Mathematically, the Kramers-Kronig relations are bidirectional transforms that connect the real and imaginary parts of any complex function that is analytic in the upper half plane of the complex variable ω , which is the frequency for impedance spectroscopy. [158–161] The original formulation from Kramers and Kronig involves integration from $-\infty$ to ∞ . For practical application in impedance spectroscopy, it can be reformulated with integration from 0 to ∞ as, [149]

$$\text{Re}[\tilde{Z}(\omega)] = \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\omega' \cdot \text{Im}[\tilde{Z}(\omega')]}{\omega^2 - \omega'^2} d\omega' \quad (4.6)$$

$$\text{Im}[\tilde{Z}(\omega)] = \frac{-2}{\pi} \mathcal{P} \int_0^\infty \frac{\omega \cdot \text{Re}[\tilde{Z}(\omega')]}{\omega^2 - \omega'^2} d\omega' \quad (4.7)$$

where $\mathcal{P}$ is the Cauchy principal value. In theory, analyticity implies causality and stationarity, and vice versa. Linearity automatically ensures analyticity; however, the converse is not true: an analytic function need not be linear. Thus, a valid KK transformation of data can only guarantee the satisfaction of stationarity and causality, rather than the linearity, as demonstrated by Urquidí-Macdonald et al. [145] and Goh et al. [143] The fact that analyticity, rather than linearity, is required to evaluate stationarity and causality enables the generalization of KK relations and measurement model tests to 2nd-NLEIS.

The application of KK relations to 2nd-NLEIS relies on the fact that our formulation of the problem arises from second-order Taylor series expansions of nonlinear functions in the governing equations describing electrochemical processes. [34,35] This formulation applies to systems with no history-dependent behavior and automatically guarantees the analyticity in the upper half plane of frequency ω . As a result, KK-relations are mathematically capable of validating the stationarity and causality requirement for 2nd-NLEIS. This argument can be demonstrated with a Randles circuit (RC) that describes a simple electrochemical interface with a parallel charge transfer and

double layer. The EIS response of a RC ($\tilde{Z}_{1,RC}$) is well-known and the 2nd-NLEIS response ($\tilde{Z}_{2,RC}$) for the RC was developed in our previous work. The governing equation derived with a cosine perturbation is summarized in **Equations 4.8** and **4.9**, [35]

$$\tilde{Z}_{1,RC} = \frac{R_{ct}}{1+j\omega^*}, \quad (4.8)$$

$$\tilde{Z}_{2,RC} = \frac{-0.5\varepsilon f R_{ct}^2}{1+4j\omega^*-5(\omega^*)^2-2j(\omega^*)^3}, \quad (4.9)$$

where R_{ct} is the charge transfer resistance, $\omega^* = \omega R_{ct} C_{dl}$ is the dimensionless frequency, C_{dl} is the double layer capacitance, $f = \frac{nF}{RT}$, ε is the charge transfer asymmetry parameter, and $j = \sqrt{-1}$.

Figure 4.2 shows the results of the KK transform using **Equation 4.6**. A similar transformation using **Equation 4.7** is also performed as shown in **Figure S4.2**. We know the linear Randles circuit (RC) is KK transformable and, as argued above, the results show the weakly nonlinear Randles circuit (NLRC) is also KK transformable.

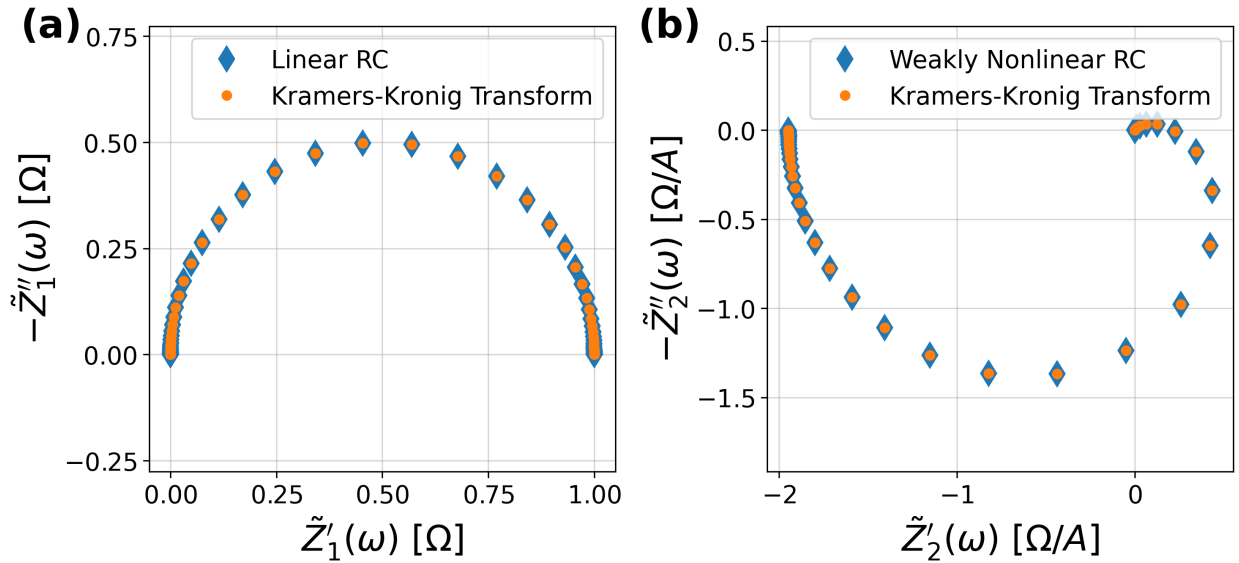


Figure 4.2. Simulated a) EIS and b) 2nd-NLEIS based on analytic Randles and weakly nonlinear Randles circuit and their corresponding KK transformation based on **Equation 4.6**. The parameters used are $R_{ct} = 1 \Omega$, $C_{dl} = 1 \text{ F}$, $\varepsilon = 0.1$. A total of 100 log-spaced points are used for frequency from 10^{-5} to 10^5 Hz.

4.4.2 Measurement Model Formulation for 2nd-NLEIS

The improper integrals required for Kramers-Kronig (KK) relations described in **Equations 4.6** and **4.7** are generally hard to perform for impedance data. [146,149] Measurement models tests introduced by Agarwal et al. provide an effective way to bypass the challenges of numerical integration. [146] Measurement models rely on the fact that the superpositions of KK compliant models are also KK compliant. The KK evaluation can then be converted to a curve fitting problem using a superposition of Voigt circuit, a re-parameterized form of **Equation 4.8**:

$$\tilde{Z}_1 = R_{ohmic} + \sum_{k=1}^N \frac{R_{1,k}}{1+j\omega\tau_{1,k}}, \quad (4.10)$$

where R_{ohmic} is the ohmic resistance, R_k is the resistance for each Voigt circuit, $\tau_k = R_k C_k$ is the corresponding time constant, C_k is the capacitance that corresponds to each resistance, and $j = \sqrt{-1}$. Similarly, it is natural to consider a 2nd-NLEIS measurement model using the complementary weakly nonlinear Randles circuit (NLRC), as shown in **Equation 4.9**,

$$\tilde{Z}_2 = \sum_{k=1}^M \frac{-0.5\varepsilon_k f R_{2,k}^2}{1+4j\omega\tau_{2,k}-5(\omega\tau_{2,k})^2-2j(\omega\tau_{2,k})^3}, \quad (4.11)$$

where, $f = \frac{nF}{RT}$, $R_{2,k}$ is the resistance, $\tau_{2,k} = R_{2,k} C_{2,k}$ is the time constants, $C_{2,k}$ is the capacitance, and ε_k is the asymmetry parameter for each NLRC. **Equation 4.11** is automatically KK-compliant since it is the superposition of the KK-compliant NLRC, as shown in **Figure 4.2**. Additionally, it can be seen that ε_k and $R_{2,k}$ are coupled with each other in the NLRC, so we reparameterize the numerator into a lumped single variable (denoted as $R_{2,k}^{eff}$), which gives the following two parameter 2nd-NLEIS measurement model,

$$\tilde{Z}_2 = \sum_{k=1}^M \frac{R_{2,k}^{eff}}{1+4j\omega\tau_{2,k}-5(\omega\tau_{2,k})^2-2j(\omega\tau_{2,k})^3}. \quad (4.12)$$

Equation 4.12 is the measurement model largely used to test for KK-compliance of 2nd-NLEIS data, though we also briefly explore use of the Voigt function as a KK-compliant basis for 2nd-NLEIS measurement models.

4.4.3 Automated Testing

The original measurement model test developed by Agarwal et al., adopted an automated curve fitting approach that iteratively added RC circuit elements while checking the confidence interval of the fitted parameters. [146,150] To avoid overfitting, RC elements were added until the 95% confidence interval of any fitted parameter included zero. The LinKK method introduced by Boukamp uses a fixed logarithmic distribution of time constants based on the measurement frequency and only fits the R values in the measurement model. [148] This method converted the nonlinear curve fitting problem to a linear algebra problem, improving the calculation efficiency, while also being prone to overfitting. To eliminate the problem of overfitting, Schönleber et al. proposed an overfitting parameter μ that compares the number of positive and negative resistance values obtained, with a higher ratio of negative values being a natural indicator of overfitting for most EIS data. [149] The nature of 2nd-NLEIS data — $R_{2,k}^{eff}$ can be positive or negative, and with two electrodes, the Nyquist plot can have loops and spirals through all four quadrants—suggests fitting models to data may demand greater flexibility in automating the fitting process. In that light, here we consider a cost function-based evaluation (cost algorithm) that compares the normalized cost function between each iteration of the automated fitting process:

$$Cost = \sum_{i=1}^N \left[\frac{\bar{Z}_2^{exp}(\omega_i) - \bar{Z}_2^{model}(\omega_i)}{\max(|\bar{Z}_2^{exp}|)} \right]^2. \quad (4.13)$$

Once the difference in cost ($\Delta Cost = Cost_i - Cost_{i+1}$) is below a tolerance value (5×10^{-4} is used here, based on preliminary trial and error), the fit is terminated. Tolerance provides a tunable

degree of freedom to fit the 2nd-NLEIS data and will be compared with the confidence interval method.

Another aspect of measurement model automation is the need for a robust curve fitting algorithm. While the linear algebra approach introduced in the LinKK method is computationally attractive, we choose to use nonlinear curve fitting with the best fit parameters from iteration (i) used along with the default initial guess parameters for the element added to iteration (i+1) prior to Cost minimization. At times, the cost function will increase from iteration (i) to (i+1), and when this happens, we terminate the fitting and seed a new initial guess to escape a local minimum. Lastly, we reproduced the confidence interval evaluation approach (conf algorithm) introduced by Orazem as a reference method. [150] The measurement model workflow is summarized in **Figure 4.3**.

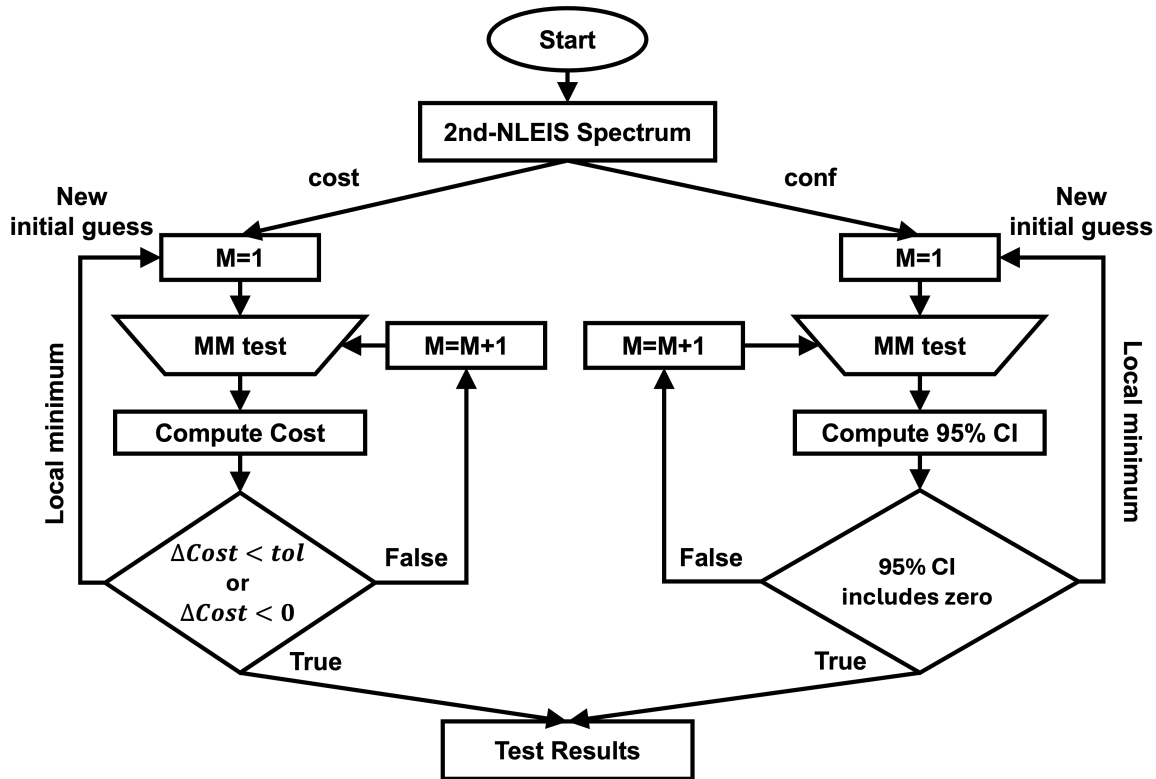


Figure 4.3. Process flow diagram for the proposed measurement model test with cost and conf algorithm.

4.4.4 Synthetic Data Generation and Error Evaluation

To gain insight into the performance of the proposed data validation approach, synthetic 2nd-NLEIS data ($\tilde{Z}_{2,model}$) are first generated using physics-based models developed in our previous work. [35] Noisy versions of the NLRC and porous electrodes model are considered. Noise was added using a magnitude-dependent random Gaussian with a 5% standard deviation ($\sigma = 5\%$) applied to the real and imaginary parts of the model impedance, creating simulated noisy data ($\tilde{Z}_{2,data}$). The actual distribution of error is shown in **Figure S4.3**. The noisy data are fed into the measurement model test to obtain the best fit to the data ($\tilde{Z}_{2,fit}$). We plot the residual errors between the data and the fit to capture the variance of the system:

$$real\ residual\ error = \frac{Re(\tilde{Z}_{2,data}) - Re(\tilde{Z}_{2,fit})}{abs(\tilde{Z}_{2,data})} \times 100, \quad (4.14)$$

$$imaginary\ residual\ error = \frac{Im(\tilde{Z}_{2,data}) - Im(\tilde{Z}_{2,fit})}{abs(\tilde{Z}_{2,data})} \times 100. \quad (4.15)$$

4.4.5 Code Availability

The numerical integration for KK evaluation is done with MATLAB 2024a on a Mac with an M1 pro chip. The nonlinear measurement model method is written in Python and built into the open-source nleis.py for easy implementation. [47] The package impedance.py (v1.7.1) [137] is used to perform the LinKK test and the measurement model program (v1.8) [162] is used to perform benchmark measurement model tests. All codes and supplementary Jupyter Notebooks have been archived in Zenodo and GitHub. [132]

4.4.6 Error Quantification with Noisy NLRC

In theory, any KK-compliant data can be assessed by any measurement model (MM) with a linear combination of KK-compliant basis functions. Hence, using Voigt functions or nonlinear Randles circuits as the bases for **Equations 4.10** and **4.12** can each represent valid MM in EIS or 2nd-NLEIS. However, not every KK-transformable basis function is expected to perform the same for a given data type. To illustrate this point, a noisy weakly-nonlinear Randles circuit (NLRC) was simulated (**Figure 4.4a**) to evaluate the use of **Equations 4.10** and **4.12** as measurement models via the two fitting algorithm pathways (confidence interval algorithm, “conf”, and cost function algorithm, “cost”) shown in **Figure 4.3**. The results are summarized in **Table 4-I**, while **Figure 4.4b-c** show the noise-free model compared to the MM for each basis function and fitting algorithm pathway. The measurement model built from a NLRC basis function (**Equation 4.12**) recovers the original model with a single element, as expected, with both fitting algorithms. On the other hand, using a Voigt function as the MM, while meeting the requirements for KK-compliance, fails to capture the correct line shape when using a 95% confidence interval fitting algorithm; the data is underfit when terminating with a single element. Given the multi-quadrant nature of even the simplest 2nd-NLEIS spectra, it takes more than 1 Voigt element to properly fit the data, but that requires a fitting algorithm less restrictive than the 95% confidence interval criterion. By relaxing the fitting algorithm constraints through the cost method with $tol = 5 \times 10^{-4}$, 3 Voigt elements capture the (3 quadrant) line shape of the data. These results suggest it is sensible to select the KK-compliant basis function that best reflects the simplest circuit element for the data under test—**Equation 4.10** for EIS and **Equation 4.12** for 2nd-NLEIS. **Figure 4.4d-e** shows the residual error of the fitting result using **Equation 4.12** for real and imaginary parts of

the noisy 2nd-NLEIS data, effectively reconstructing the introduced magnitude scaled Gaussian noise.

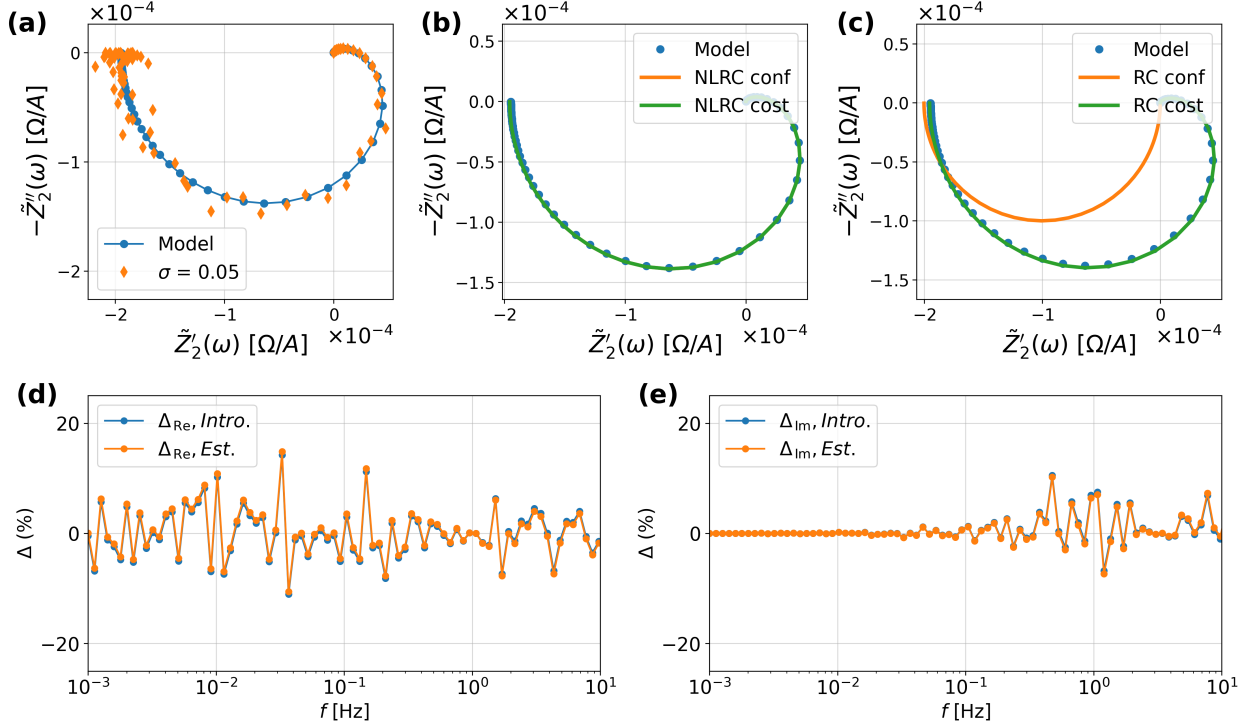


Figure 4.4. a) Simulated NLRC and its corresponding noise spectrum with $\sigma = 5\%$. The parameters used are $R_{ct} = 0.01 \Omega$, $C_{dl} = 7.2 \text{ F}$, $\varepsilon = 0.1$. A total of 100 log-spaced points are used for frequency from 10^{-3} to 10^2 Hz. Comparison between the ground truth model with MM-test result using b) NLRC and c) Voigt as the basis function. Introduced and estimated residual for d) real and e) imaginary part of the 2nd-NLEIS. The default guesses for the basis function are $R_{2,k}^{eff} = -0.01 \Omega/A$ and $\tau_{2,k} = 0.01 \text{ s}$.

Table 4-I. Settings and test results of noisy weakly nonlinear RC under four different conditions.

Basis Function	Method	Tolerance	# Elements	Error Recovery
Voigt Function (RC) (Eq. 4.10)	cost	5×10^{-4}	3	Good
	conf	95% CI	1	Failed
Nonlinear RC (NLRC) (Eq. 4.12)	cost	5×10^{-4}	1	Good
	conf	95% CI	1	Good

4.4.7 Error Quantification for a Noisy Porous Electrode with Solid State Diffusion

Porous electrodes account for most practical applications of 2nd-NLEIS in batteries. The impedance response of a porous electrode generally requires more MM basis functions to capture the behavior due to the interaction between electrolyte resistance and interfacial charge transfer. [163] A half-cell porous electrode model with solid state diffusion into plate-like particle is shown in **Figure 4.5**, with Gaussian distributed noise ($\sigma = 5\%$ of mean values) added to create a noisy porous electrode dataset from the underlying model. A MM test was performed using **Equation 4.12** and both fitting algorithm pathways (“conf” and “cost”) in **Figure 4.3**. The confidence interval pathway selected a 6-element fit whereas the cost function method with $tol = 5 \times 10^{-4}$ fits with 8 elements. The fitted results are shown in **Figure 4.5b-c**. Both fitting algorithms capture the general line shape of the spectrum, with discrepancy between the two results best seen in the residual plot shown in **Figure 4.5d-e**. The less-restrictive cost algorithm, with $tol = 5 \times 10^{-4}$, shows a small extension to high frequencies compared to the confidence interval method. Nevertheless, regardless of what fitting algorithm is used, the residual plots show that both fitting algorithms struggle to recover the actual noise spectrum at high frequencies because 2nd-NLEIS approaches the origin, where small errors can have large effects.

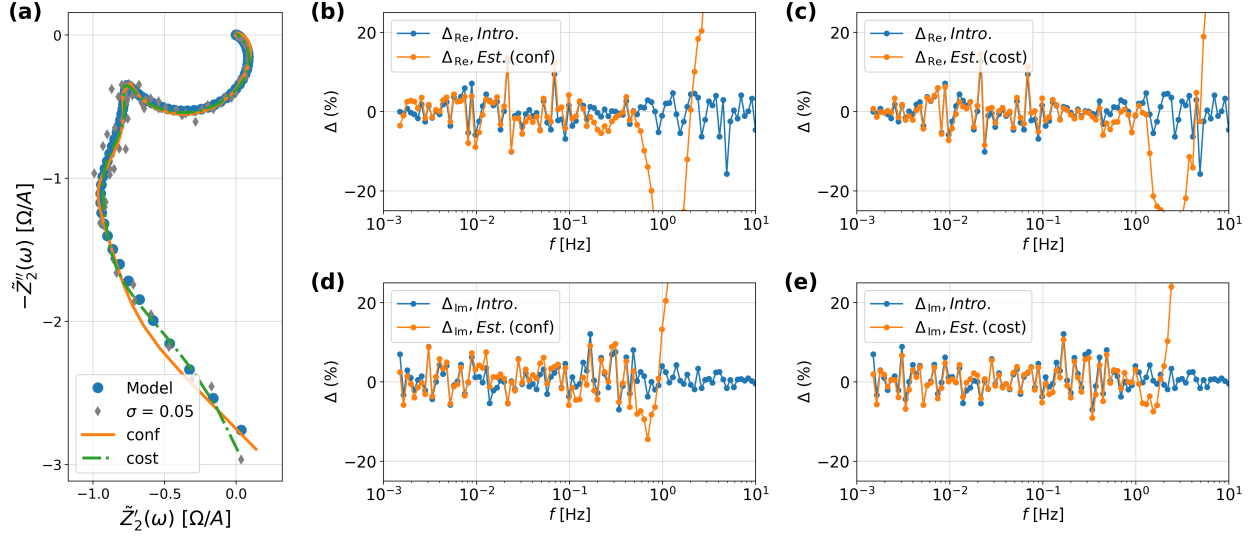


Figure 4.5. a) Simulated porous electrode with planar diffusion, its corresponding noise spectrum with $\sigma = 5\%$, and MM-test with conf and cost method. The parameters used are $R_{ct} = 6 \Omega$, $R_{ct} = 0.6 \Omega$, $C_{dl} = 0.72 \text{ F}$, $\varepsilon = 0.05$, $A_w = 2 \Omega$, $\tau_d = 200 \text{ s}$, and $\kappa = -2.5 \text{ V}^{-1}$. A total of 100 log-spaced points are used for frequency from 1.5×10^{-3} to 10 Hz . Introduced and estimated residual error for b-c) real, d-) imaginary part 2nd-NLEIS estimated with (b,d) the conf algorithm and (c,e) the cost algorithm. The tolerance used here is 5×10^{-4} for the cost algorithm. The default guesses for the basis function are $R_{2,k}^{eff} = -0.01 \Omega/A$ and $\tau_{2,k} = 0.01 \text{ s}$.

4.4.8 The Experimental Data Validation Workflow

Here we lay out the multi-step process we use to validate galvanostatic 2nd-NLEIS experiments. First, the total harmonic distortion (THD) spectrum for the input current modulation is analyzed to verify negligible input harmonics. The ideal THD spectrum for input current is identically zero at all frequencies, though all real instruments have noise, so input current THD ensures the equipment has expected behavior, namely, a low featureless (noise floor). We will see in our experimental results that THD of the input current modulation does not always behave ideally at high frequencies, leading to an instrument-based cut-off frequency where it is unwise to interpret 2nd-NLEIS due to instrument-generated harmonics.

Our next data validation step is to set a ceiling for THD in the output voltage spectrum. As discussed previously, we take a conservative approach and only simultaneously analyzed EIS and 2nd-NLEIS analysis if the output voltage $THD < 1\%$.

Finally, the 2nd-NLEIS measurement model test developed in this work is used to assess stationarity, causality, and the noise spectrum for the 2nd-NLEIS data. As with the LinKK test, a successful regression of the 2nd-NLEIS measurement model to the experimental data results in residual error centered on zero over the testing frequencies. In general, we find a 2nd-NLEIS residual error of less than 10% is can be used effectively in modeling.

4.4.9 *Experimental Data Validation Workflow: Reanalyzing Commercial 18650 Cell Data*

Our initial work in this area used Samsung commercial 18650 power cells, where we found the quality control and high cell-to-cell consistency ideal for the first application of 2nd-NLEIS. We now revisit the previously published [26] and archived [164] data using the data validation workflow developed here.

A set of typical input current THD spectra for the low impedance (~ 0.04 ohm) 18650 cells are presented in **Figure S4.4a** for three different current modulation amplitudes ($\Delta I = 0.3, 0.4$, and 0.5). All input THD spectra show fairly ideal behavior—a flat and featureless noise floor (well under 0.1% THD)—up to a frequency of roughly 100 Hz. But as frequency increases beyond 100 Hz, a sharply rising THD is seen in the input modulation. Despite the input THD rising, it remains under 1% for all frequencies, so the input harmonics are unlikely to be important for EIS measurements. Nonetheless, the rising input THD suggests the instrument is generating harmonic features that will be hard to distinguish from the battery under test, so we consider any data above 100 Hz as unsuitable for quantitative 2nd-NLEIS analysis. We draw a 100Hz line in **Figure S4.4a**

based on this first workflow evaluations. Below 100 Hz warrants further evaluation of EIS and 2nd NLEIS, whereas above 100 Hz is only useful for EIS analysis.

Next, we evaluate the output voltage THD spectrum (**Figure S4.4b**), where we see the entire spectrum is under 1% THD, thereby satisfying our conservative criterion for a suitable linear approximation for EIS. Note that the 100 Hz line shown in **Figure S4.4b** reaffirms that instrument generated harmonic signal above 100 Hz is comparable to, or larger than, nonlinear signal generated by the battery under test and is not suitable for subsequent NLEIS analysis.

Finally, we apply the MM-test using **Equation 4.12** and the two fitting algorithms to our previously published data to assess, for the first time, the stationarity, causality, and noise in the 2nd-NLEIS spectra. [26] As described in Murbach et al., [26] the EIS ($\tilde{Z}_1$) spectrum was obtained from the best fit of **Equation 4.3** to the three different ΔI values at each frequency from 10 kHz to 3.16 mHz (10 points per decade). The 2nd-NLEIS ($\tilde{Z}_2$) spectrum was obtained from the best fit of **Equation 4.4** to the three different ΔI values at each frequency from 100 Hz to 3.16 mHz; we truncated frequencies above 100 Hz based on the THD results above.

Figure 4.6a,d shows the resulting EIS data validation step using the LinKK method with $\mu = 0.85$. Successful fitting of the EIS spectrum with less than 1% residual errors for both real and imaginary components suggests high-quality EIS data that satisfies stationarity and causality. Having less than 1% THD in the input and output signals is good evidence that the data adequately meets the linearity assumption that underpins EIS. We have previously used a physics-based porous electrode model to fit and parameterize this EIS data. [46]

The 2nd-NLEIS data is evaluated with our MM-test in **Figure 4.6b-c**, where either 6 or 7 elements are fit, depending upon whether the more restrictive 95% confidence interval algorithm is used or the less restrictive cost algorithm is applied with $tol = 5 \times 10^{-4}$, respectively. In the

residual plots the highest frequency given is 10 Hz. Despite an adequate THD spectrum up to 100 Hz, the Nyquist plot shows that the 2nd-NLEIS signal is approaching the origin by 10 Hz and the residual plots show the data diverging from the measurement model. As with the synthetic data presented above, as the magnitude of the 2nd-NLEIS signal approaches zero, the residual errors grow unbounded. Thus, the measurement model shows the 2nd-NLEIS signal is useful below 10 Hz. One can also see the residual errors have a zero mean over much of the frequency spectrum shown, confirming stationarity and causality for the data. The tests also suggest that the noise of the measurement is less than 5% for most practical frequencies. In summary, the measurement model test provides a robust way to evaluate stationary, causality, and noise in the 2nd-NLEIS data, whether one chooses a cost-based algorithm or 95% confidence algorithm.

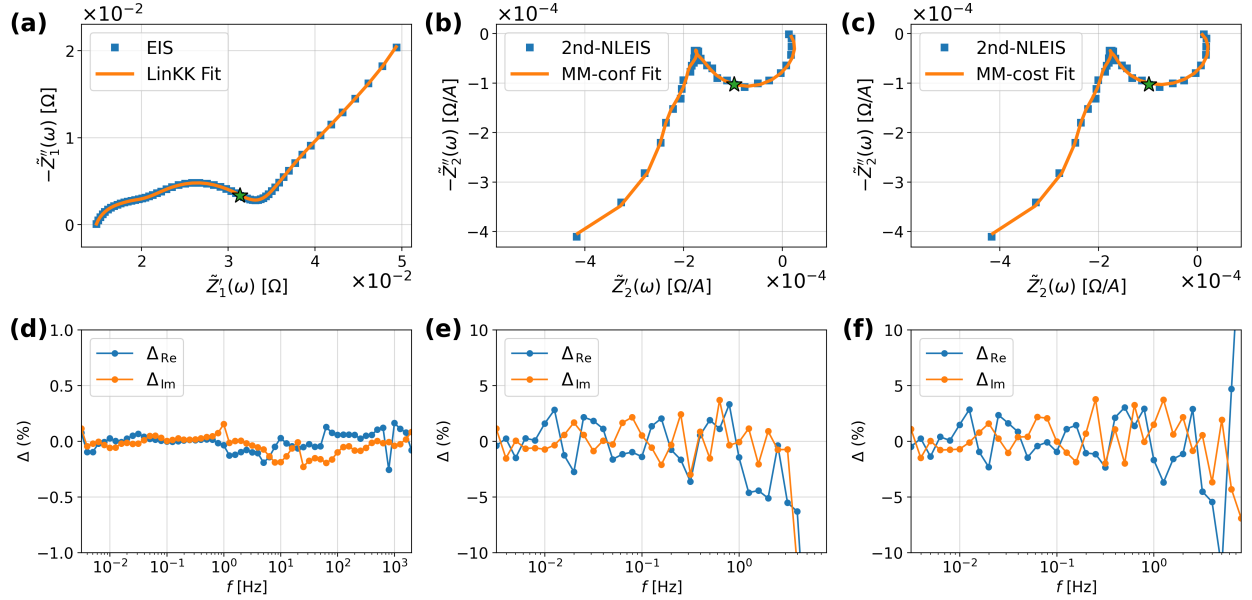


Figure 4.6. Kramers-Kronig test result using a,d) LinKK for EIS, and MM-test with conf (b,e) and cost (c,f) algorithm for 2nd-NLEIS collected with a commercial 18650 cell. a-c) Nyquist plot of experimental data and corresponding fitting results. d-f) The estimated residual error for both the real and imaginary parts of the impedance. The tolerance used here is 5×10^{-4} for the cost algorithm and the default guesses for the basis function are $R_{2,k}^{eff} = -0.01 \Omega/A$ and $\tau_{2,k} = 0.01 s$. The 1 Hz points are labeled as ☆ in a-c.

In practice, measurements with a single input modulation amplitude (rather than 3 as shown above) are generally adopted to save experimental time in EIS, so we consider the consequences of making measurements with individual values of $\Delta I = 0.3, 0.4$, and 0.5 A . LinKK was first performed on all three EIS spectra (**Figure S4.5a**) with less than 1% residual error observed (**Figure S4.6**) at each modulation amplitude. 2nd-NLEIS data was tested using the cost algorithm to evaluate the quality of each individual spectrum, with the measurement model results shown in **Figure 4.7**. For completeness, **Figure S4.5a,b** shows the overlay of the three individual EIS and 2nd-NLEIS spectra. Because 2nd-NLEIS signal grows quadratically with ΔI , the spectrum with $\Delta I = 0.3\text{ A}$ is noticeably noisier than the spectrum with $\Delta I = 0.5\text{ A}$ (**Figure 4.7a-c**). The MM-test allows us to quantify the noise spectrum through the residual error plots, where $\Delta I = 0.3\text{ A}$ data in **Figure 4.7d** has residuals roughly 3X larger than the $\Delta I = 0.5\text{ A}$ data in **Figure 4.7f**. Based on the results here, and the three-step workflow, we would choose $\Delta I = 0.5\text{ A}$ as our single modulation amplitude to ensure a suitable input and output THD for simultaneous EIS and 2nd-NLEIS analysis. The resulting EIS spectrum can be analyzed over the entire frequency range, but tests developed here suggested trustworthy 2nd-NLEIS data was only observed at frequencies below 10 Hz.

In supporting materials, the same analysis is performed using the conf algorithm with NLRC (**Figure S4.7**) and the measurement model program with RC (**Figure S4.8**), and the same conclusion can be drawn.

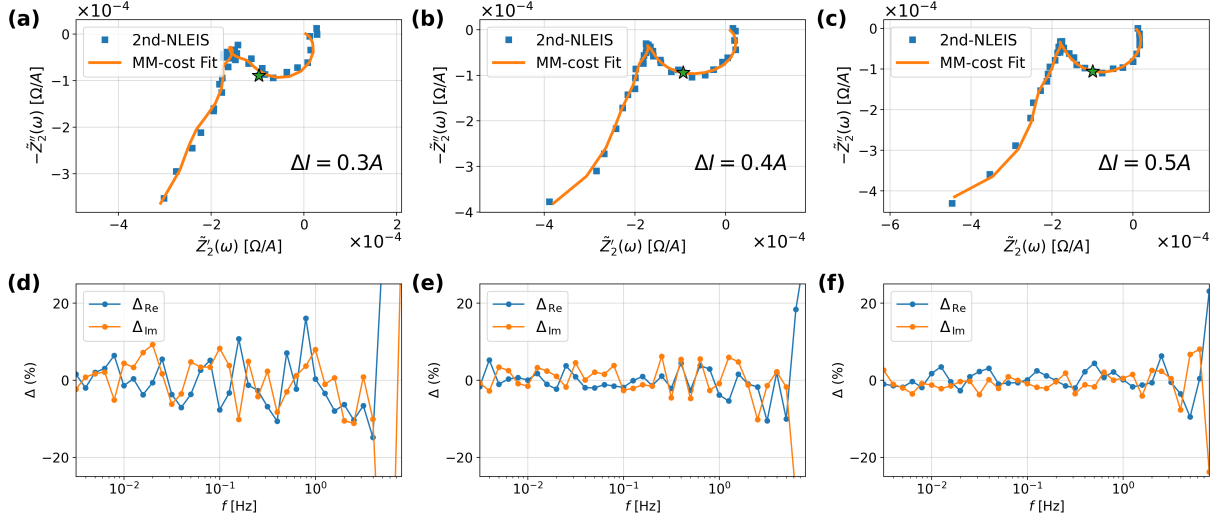


Figure 4.7. Measurement model test using cost algorithm for 2nd-NLEIS data collected with a current perturbation of a,d) 0.3 A, b,e) 0.4 A, and c,f) 0.5 A for a commercial 18650 cell. a-c) Nyquist plots of experimental data and corresponding fitting results. d-f) The estimated residual error for the real and imaginary parts of the 2nd-NLEIS data. The tolerance used here is 5×10^{-4} for the cost algorithm and the default guesses for the basis function are $R_{2,k}^{eff} = -0.01 \Omega/A$ and $\tau_{2,k} = 0.01 \text{ s}$. The 1 Hz points are labeled as ☆ in a-c.

4.4.10 Experimental Data Validation Workflow: 2nd-NLEIS on a Low-Cost Pouch Cell

Low cost pouch cells generally exhibit less manufacturing quality control in coating, formation, sorting, and grading than the 18650 cells just tested. [165] To demonstrate this point, we tested two NMC||C cells (purchased from the same manufacturer at the same time) at 3.5 V, where a second harmonic signal is expected. [46] Before the 2nd-NLEIS measurement, these cells underwent 5 break-in cycles to stabilize the battery. **Figure 4.8a-b** shows the EIS and 2nd-NLEIS data of two cells at 3.5 V. In the fresh state, both cells have roughly the same high frequency resistance, while the remaining EIS impedance features for pouch-1 are noticeably different in size and shape from pouch-2. It can also be observed in **Figure 4.8a** that pouch-1 has two clear “semi-circular” impedance features in the region characterized by charge transfer, while pouch-2 only has one apparent “semi-circular” feature. The variation between cells is further amplified in the

2nd-NLEIS spectra, where a larger “semi-spiral” is observed for pouch-2 than pouch-1 (**Figure 4.8b**).

To assess the quality of the EIS and 2nd-NLEIS data, the input current and output voltage THD spectra are first evaluated, as shown in **Figure S4.9**. The THD spectra for both cases are consistently less than 1% at all frequencies, suggesting the linearity approximation needed for robust EIS analysis is adequately satisfied. Again, the THD spectrum of the input current perturbation is low and featureless below 100 Hz but rises quickly above 100 Hz. As a result, the 2nd-NLEIS data is truncated at 100 Hz, while the full-spectrum EIS is analyzed. A LinKK test on EIS (**Figure S4.10**) shows less than 1% residual error, which indicates good stationarity and causality, and low measurement noise, for the impedance measurement. The 2nd-NLEIS data are next evaluated by the MM-test using the cost algorithm to fit the curve and extract residual errors (**Figure 4.8c-f**). As shown by **Figure 4.8c-d**, the automated MM-tests fit the data with 8 and 9 elements for pouch-1 and pouch-2 respectively. The test results show a consistent residual error of less than 10% for most practical frequencies less than 10 Hz. Above 10 Hz, larger residual errors have been observed, which are primarily due to the MM-test consistently failing near the origin. Here again, we show good measurement model fits with residuals of the 2nd-NLEIS fit around zero, supporting the notion this data is stationary, causal, and has suitable measurement noise to support quantitative analysis. In short, this data is suitable for EIS and 2nd-NLEIS modeling.

The same analysis is performed using the conf algorithm with NLRC (**Figure S4.11**) and the measurement model program with RC (**Figure S4.12**). For this specific dataset, we found 95 % confidence interval can be too restrictive to verify the experimental data validity.

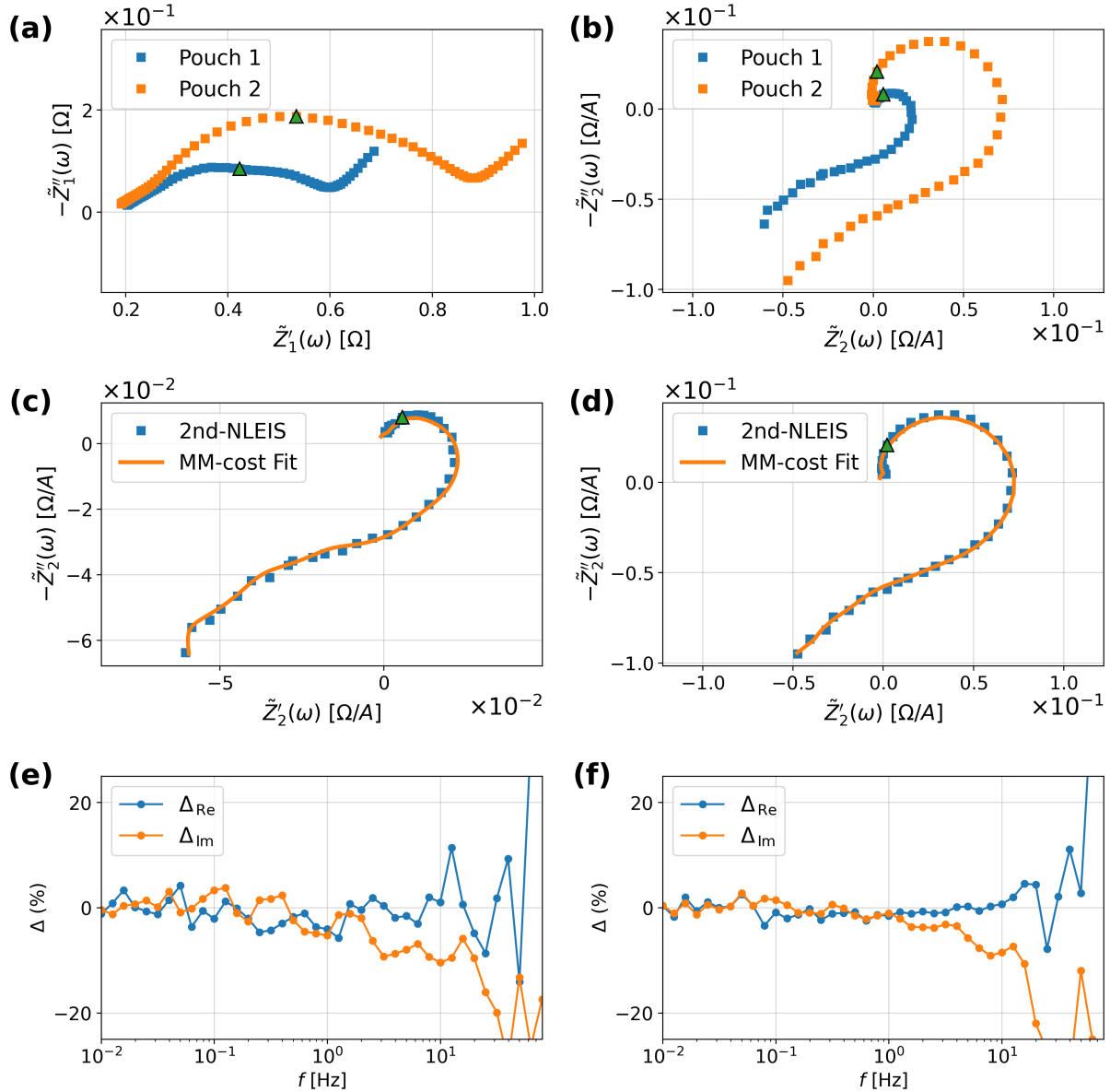


Figure 4.8. a) Full spectrum EIS and b) 2nd-NLEIS data (truncated at 100 Hz) collected for two 290 mAh pouch cell replicates with a current perturbation of 50 mA. c-f) measurement model test results with the cost algorithm. c-d) Nyquist plots of experimental 2nd-NLEIS data and corresponding fitting results. e-f) The estimated residual error for the real and imaginary parts of the 2nd-NLEIS data. The tolerance used here is 5×10^{-4} for the cost algorithm and the default guesses for the basis function are $R_{2,k}^{eff} = 0.001 \Omega/A$, $\tau_{2,k} = 0.01 s$ for pouch-1 and $\tau_{2,k} = 0.1 s$ for pouch-2. The 10 Hz points are labeled as $\triangle$ in (a) and (d).

4.4.11 *Experimental Data Validation Workflow: 2nd-NLEIS Data that Fails*

In-house coin cell measurements generally have larger cell-to-cell variation than mass manufactured cells and, therefore, especially warrant scrutiny for data quality. We are using 2nd-NLEIS to study Li||Cu coin cells to understand lithium metal interfaces. In theory, once bulk Li is plated on the copper electrode, one has a Li||Li|Cu cell that that should be symmetric and display no 2nd NLEIS signal at any frequency. **Figure 4.9a-b** shows the EIS and 2nd-NLEIS spectra for the plated Li||Li|Cu cell; the presence of 2nd-NLEIS signal suggests there is a difference in the performance of the Li foil and plated Li metal electrodes for the electrolyte under study. Following our workflow pattern, the input current THD spectrum is found to be under 1 % for all frequencies, but shows a steep rise from the noise floor at frequencies above 1000 Hz (**Figure S4.13**). The output voltage THD spectrum is below 1% at all frequencies. Therefore, the linearity approximations required for quantitative EIS analysis appear to be satisfied at all frequencies tested. Because of the rising input current THD above 1000 Hz, 2nd-NLEIS is only considered suitable for analysis at frequency under 1000 Hz due to instrument harmonic generation. To further evaluate the stationarity, causality, and noise of the EIS spectrum, LinKK was performed on the data with the fitting results and residual errors are shown in **Figure 4.9a** and **Figure 4.9c** respectively. This is the first example of a residual error exceeding 1% (between 0.1 and 10 Hz) and there is a systematic variation in the residual, rather something akin to a noise spectrum.

The charge transfer spiral observed in the 2nd-NLEIS spectrum, **Figure 4.9b**, has an unusual shape, and the MM-test shown in **Figure 4.9b** and **Figure 4.9d** fail to capture the data line-shape. In short, the unusual 2nd-NLEIS shape cannot be described by the measurement model using the cost fitting algorithm with $tol = 5 \times 10^{-4}$. The residual error shown in **Figure 4.9d** further confirms the abnormal nonlinear charge transfer response. The same conclusions can be

drawn using the conf algorithm (**Figure S4.14**) and measurement model program (**Figure S4.15**). Given the behavior of the LinKK results for the EIS data and clear failure of the 2nd-NLEIS MM tests, this is an experiment that has failed to demonstrate stationarity and causality, and should not be modeled.

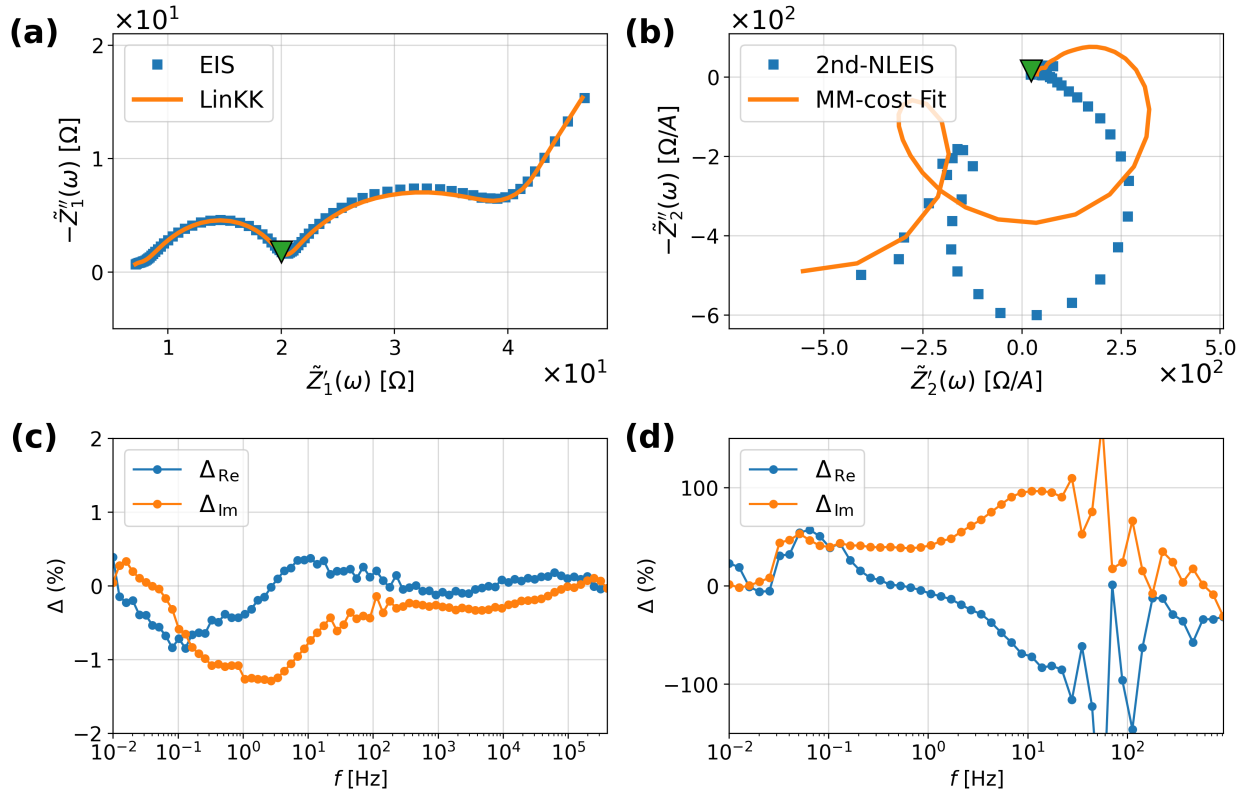


Figure 4.9. Measurement model test results with the cost algorithm for in-house coin-cell measurement. a-b) Nyquist plots of experimental a) EIS and b) 2nd-NLEIS data and their corresponding fitting results. c-d) The estimated residual error for both the real and imaginary parts of the c) EIS and b) 2nd-NLEIS data. The tolerance used here is 5×10^{-4} for cost algorithm and the default guesses for the basis function are $R_{2,k}^{eff} = 0.01 \text{ } \Omega/\text{A}$ and $\tau_{2,k} = 0.01 \text{ s}$. The 112.74 Hz points are labeled as ∇ in (a-b).

4.5 CONCLUSIONS

This work provided a complete pathway to collect, process, and validate 2nd-NLEIS measurements under the galvanostatic mode, while building confidence that the nonlinear signal is still within

well accepted limits for simultaneous EIS analysis. With in-depth harmonic analysis, it has been shown that a larger, but not too large, current perturbation can be selected by combining THD criteria with MM tests. We have adopted a conservative <1% total harmonic distortion (THD) metric to indicate a weakly nonlinear response that does not corrupt the underlying linear approximations for EIS analysis. Two different Kramers-Kronig (KK) compliant basis functions were evaluated in measurement models for 2nd-NLEIS, and two different automated algorithms the fitting process (cost function and confidence interval algorithms) were evaluated. Not surprisingly, using a basis function that represents a KK-compliant Voigt function worked better for EIS than 2nd-NLEIS, and similarly, a nonlinear Randle circuit generally captured the line shape of 2nd-NLEIS data in fewer fit circuit elements than the Voigt function. Overall, the data collection and validation pipeline introduced in this work paves the foundation for robust and compatible simultaneous collection and analysis of EIS and 2nd-NLEIS data, addressing key issues associated with using a linearized model alone for mechanistic insights and quantitative parameter estimation.

4.6 SUPPLEMENTARY NOTES

4.6.1 *Harmonic Generation Principle of Butler-Volmer Kinetics under Galvanostatic Perturbation*

Here we consider a general Butler Volmer (BV) equation that can be described as follows,

$$i_f = i_0 [\exp(\alpha_a f \eta) - \exp(-\alpha_c f \eta)]. \quad (4.S1)$$

where i is the electrode current density (A/m^2), i_0 is the exchange current density (A/m^2), $\alpha_a = 0.5 + \varepsilon$ and $\alpha_c = 0.5 - \varepsilon$ are anodic and cathodic charge transfer coefficients, $f = nF/RT$ (V^{-1}), and η is the overpotential (V). To explore the harmonic generation under the galvanostatic perturbation, it is essential to obtain an inverse BV equation, which describes the overpotential as

a function of applied current. Unfortunately, there is no general closed-form representation for the inverse Butler Volmer, except for a symmetric condition ($\varepsilon = 0$) and a highly asymmetric condition ($\varepsilon = \pm 0.5$). [44] In between symmetric and highly asymmetric scenarios, the analytical expression of the leading harmonic signal can be easily obtained based on the approach introduced in our previous work, [35] which can be verified by the limiting case of symmetric and asymmetric conditions. Moreover, only the first four harmonics in the response function are considered given the constraint of the weakly nonlinear condition. The emergence of fifth and higher harmonics can be a natural indicator of the breakdown of the weakly nonlinear assumption.

For simplicity, we first consider the derivation of the symmetric condition. The BV equation can be simplified to a hyperbolic sine function. As a result, the inverse BV takes an inverse sinh function that can be described as follows with the cosine current perturbation,

$$\eta = \frac{2 \sinh^{-1}\left(\frac{1}{2} \frac{\Delta I \times \cos(\omega t)}{i_0}\right)}{f}, \quad (4.S2)$$

With Taylor series expansion, the first and third harmonic signals for this special case can be derived as follows with the trigonometry identity shown in **Supplementary Note 4.7.2**,

$$V_1 = \frac{\Delta I}{i_0 f} + \frac{3}{96 f} \left(\frac{\Delta I}{i_0}\right)^3 + h. o. t, \quad (4.S3a)$$

$$V_3 = \frac{1}{96 f} \left(\frac{\Delta I}{i_0}\right)^3 + h. o. t, \quad (4.S3b)$$

where even harmonics are absent. As a result, the first harmonic signal is mainly affected by the third harmonics under the weakly nonlinear regime. The critical current that results in $\delta_1\%$ deviation in the leading first harmonic response can be written as follows,

$$\Delta I_{1,critical} = \frac{\sqrt{\frac{\delta_1}{3}}}{10}. \quad (4.S4)$$

The corresponding intensity ratio S_1/S_3 for the given deviation $\delta_1\%$ can be obtained as,

$$\frac{S_1}{S_3} = \frac{300}{\delta_1} + 3. \quad (4.S5)$$

On the other hand, under a highly asymmetric (i.e. $\varepsilon = \pm 0.5$) condition, the BV equation can be simplified to a single exponential function, where the results will be completely symmetric for the two extremes. Here, we review the case of $\varepsilon = 0.5$, where the inverse-BV can be written as the following with the cosine current perturbation,

$$\eta = \frac{\ln\left(\frac{\Delta I \times \cos(\omega t)}{i_0} + 1\right)}{f}, \quad (4.S6)$$

Equation 4.S6 can be expanded using Taylor series expansion and gives the following harmonic signals with the trigonometry identity shown in **Supplementary Note 4.7.2**,

$$V_1 = \frac{\Delta I}{i_0 f} + \frac{1}{4f} \left(\frac{\Delta I}{i_0}\right)^3 + h.o.t., \quad (4.S7a)$$

$$V_2 = -\frac{1}{4f} \left(\frac{\Delta I}{i_0}\right)^2 - \frac{1}{8f} \left(\frac{\Delta I}{i_0}\right)^4 + h.o.t., \quad (4.S7b)$$

$$V_3 = \frac{1}{12f} \left(\frac{\Delta I}{i_0}\right)^3 + h.o.t., \quad (4.S7c)$$

$$V_4 = -\frac{1}{32f} \left(\frac{\Delta I}{i_0}\right)^4 + h.o.t., \quad (4.S7d)$$

The critical current that results in $\delta_1\%$ deviation in the leading first harmonic response and $\delta_2\%$ deviation in the leading second harmonic response can be derived as follows,

$$\Delta I_{1,critical} = \frac{\sqrt{4 \times \delta_1 \times i_0^2}}{10}, \quad (4.S8a)$$

$$\Delta I_{2,critical} = \frac{\sqrt{2 \times \delta_1 \times i_0^2}}{10}. \quad (4.S8b)$$

The intensity ratio S_1/S_3 and S_2/S_4 can be obtained as

$$\frac{S_1}{S_2} = \frac{300}{\delta_1} + 3, \quad (4.S9a)$$

$$\frac{S_2}{S_4} = \frac{400}{\delta_2} + 4. \quad (4.S9b)$$

The limiting case results suggest an intrinsic harmonic generation principle, which can be described as follows,

$$S_1 = S_{1,1} + 3S_{3,3} + h.o.t, \quad (4.S10a)$$

$$S_2 = S_{2,2} + 4S_{4,4} + h.o.t, \quad (4.S10b)$$

$$S_3 = S_{3,3} + h.o.t, \quad (4.S10c)$$

$$S_4 = S_{4,4} + h.o.t. \quad (4.S10d)$$

That is, the third and fourth harmonic corrections to the first and second harmonics are directly proportional to the leading third and fourth harmonics. **Equation 4.S10** enables us to generalize the full spectrum expression for galvanostatic perturbation with only leading harmonic expressions, which can be solved analytically. To do that, a fourth-order Taylor series expansion of the BV equation is adopted as the follows,

$$i = i_0 \left[(\alpha_a^1 + \alpha_c^1) f\eta + \frac{(\alpha_a^2 - \alpha_c^2)(f\eta)^2}{2} + \frac{(\alpha_a^3 + \alpha_c^3)(f\eta)^3}{6} + \frac{(\alpha_a^4 - \alpha_c^4)(f\eta)^4}{24} \right]. \quad (4.S11)$$

For the simplicity of the calculation, we consider the voltage response that consists of the four leading order harmonic signals using Euler's representation,

$$\eta = V_1 \exp(i\omega t) + V_2 \exp(i2\omega t) + V_3 \exp(i3\omega t) + V_4 \exp(i4\omega t) + h.o.t., \quad (4.S12)$$

which can be easily converted to a cosine wave by substituting Euler's representation and considering the trigonometry identities shown in **Supplementary Note 4.7.2**. The governing equation for the first four harmonics can be obtained by plugging **Equation 4.S12** into **Equation**

4.S11. Rearrange given the current perturbation of the form of **Equation 4.1** gives the following algebraic equation for the first four leading harmonic signals.

$$\Delta I = i_0(\alpha_a^1 + \alpha_c^1)fV_1, \quad (4.S13a)$$

$$i_0 \left[(\alpha_a^1 + \alpha_c^1)fV_2 + \frac{(\alpha_a^2 - \alpha_c^2)}{2}f^2V_1^2 \right] = 0, \quad (4.S13b)$$

$$i_0 \left[(\alpha_a^1 + \alpha_c^1)fV_3 + \frac{(\alpha_a^2 - \alpha_c^2)}{2}f^2 2V_1V_2 + \frac{(\alpha_a^3 + \alpha_c^3)}{6}f^3V_1^3 \right] = 0, \quad (4.S13c)$$

$$i_0 \left[(\alpha_a^1 + \alpha_c^1)fV_4 + \frac{(\alpha_a^2 - \alpha_c^2)}{2}f^2(2V_1V_3 + V_2^2) + \frac{(\alpha_a^3 + \alpha_c^3)}{6}f^3 3V_1^2V_2 + \frac{(\alpha_a^4 - \alpha_c^4)}{24}f^4V_1^4 \right] = 0 \quad (4.S13d)$$

The harmonic coefficients $V_1 \dots V_4$ can then be solved algebraically to obtain the following leading harmonic signals.

$$V_1 = \frac{\Delta I}{i_0 f}, \quad (4.S14a)$$

$$V_2 = -\varepsilon f \left(\frac{\Delta I}{i_0 f} \right)^2, \quad (4.S14b)$$

$$V_3 = \left(\frac{9\varepsilon^2 - 0.25}{6} \right) f^2 \left(\frac{\Delta I}{i_0 f} \right)^3, \quad (4.S14c)$$

$$V_4 = \frac{(\varepsilon - 16\varepsilon^3)}{6} f^3 \left(\frac{\Delta I}{i_0 f} \right)^4. \quad (4.S14d)$$

To convert it back to the harmonic signal under the cosine wave, the trigonometry identities (**Supplementary Note 4.7.2**) converting $\cos^n(\omega t)$ need to be applied to the second and higher harmonic signals. The leading higher harmonics coefficient can then be written as,

$$V_2 = -\frac{\varepsilon f}{2} \left(\frac{\Delta I}{i_0 f} \right)^2, \quad (4.S15a)$$

$$V_3 = \left(\frac{9\varepsilon^2 - 0.25}{24} \right) f^2 \left(\frac{\Delta I}{i_0 f} \right)^3, \quad (4.S15b)$$

$$V_4 = \frac{(\varepsilon - 16\varepsilon^3)}{48} f^3 \left(\frac{\Delta I}{i_0 f} \right)^4. \quad (4.S15c)$$

The trigonometry identity also implies that the third harmonic correction to the first harmonic is three times the leading third harmonic signal and the fourth harmonic correction to the second harmonic is four times the fourth harmonic signal. As a result, the first four harmonics voltage response under the current perturbation can be written as follows,

$$V_1 = \frac{\Delta I}{i_0 f} + 3 \left(\frac{9\varepsilon^2 - 0.25}{24} \right) f^2 \left(\frac{\Delta I}{i_0 f} \right)^3, \quad (4.S16a)$$

$$V_2 = -\frac{\varepsilon f}{2} \left(\frac{\Delta I}{i_0 f} \right)^2 + 4 \frac{(\varepsilon - 16\varepsilon^3)}{48} f^3 \left(\frac{\Delta I}{i_0 f} \right)^4, \quad (4.S16b)$$

$$V_3 = \left(\frac{9\varepsilon^2 - 0.25}{24} \right) f^2 \left(\frac{\Delta I}{i_0 f} \right)^3, \quad (4.S16c)$$

$$V_4 = \frac{(\varepsilon - 16\varepsilon^3)}{48} f^3 \left(\frac{\Delta I}{i_0 f} \right)^4. \quad (4.S16d)$$

The validity of **Equation 4.S16** can be easily verified by taking the limit of $\varepsilon = 0$ and $\varepsilon = \pm 0.5$, which will reproduce **Equations 4.S3** and **4.S7** respectively. **Equation 4.S16** can, thus, guide us to determine the correct current perturbation to drive a valid impedance measurement under the weakly nonlinear condition. For a given deviation of $\delta_1\%$ and $\delta_2\%$, the critical current perturbation can be determined as,

$$\Delta I_{1,critical} = \frac{\sqrt{\left| \frac{8 \times \delta_1 \times i_0^2}{9\varepsilon^2 - 0.25} \right|}}{10}, \quad (4.S17a)$$

$$\Delta I_{2,critical} = \frac{\sqrt{\left| \frac{-6 \times \delta_1 \times i_0^2}{1 - 16\varepsilon^2} \right|}}{10}. \quad (4.S17b)$$

As suggested by **Equation 4.S17**, there are singularity points at $\varepsilon = \pm \sqrt{\frac{0.25}{9}}$ for the first harmonic signal and $\varepsilon = \pm 0.25$ for the second harmonic signal. The singularity behaviors make the determination of the optimal current perturbation tricky as divergent behaviors can easily appear.

As a result, the first and second harmonic signals must be considered simultaneously to ensure the singularities are well-behaved. Essentially, the singularity behavior helps maintain the signal quality when the perturbation gets larger. This makes it possible to use the minimum perturbation required to drive either the first or second harmonic signal to a given deviation δ_1 and δ_2 as the optimal perturbation. The optimal current perturbation can then be written as follows,

$$\Delta I_{opt} = \min (\Delta I_{1,critical}, \Delta I_{2,critical}). \quad (4.S18)$$

Here, we consider a valid first and second harmonic signal to have a maximum deviation of $\delta_1 = \delta_2 = 1\%$ to avoid significant corruption from the higher harmonics. For a unit exchange current density, the critical current can be determined using **Equations 4.S17** and **4.S18**. As shown in **Figure S4.1a**, the critical current for i_0 and ε has different singularities. By taking the minimum of the two, one can effectively avoid over-perturbing the system near the singularity and the maximum deviation is always determined by the worst signal and is capped at 1%. The corresponding critical voltage response is obtained by solving the inverse BV numerically with ΔI_{opt} , i_0 , and ε using `minimize_scalar` from `scipy.optimize`, which is shown in **Figure S4.1b**. Although the current input is purely symmetric with respect to the asymmetry parameter ε , it can be observed that the voltage response is highly asymmetric. This is the result of direction sensitive harmonic generation as demonstrated by **Equation 4.S16**. That is, $\varepsilon > 0$ can lead to a reduction in the measured voltage response, while $\varepsilon < 0$ can lead to a growth in the measured voltage response. Overall, this result further supports that the rule of thumb for the weakly nonlinear condition should be evaluated based on THD and measurement model tests rather than a rule of thumb for measured voltage response.

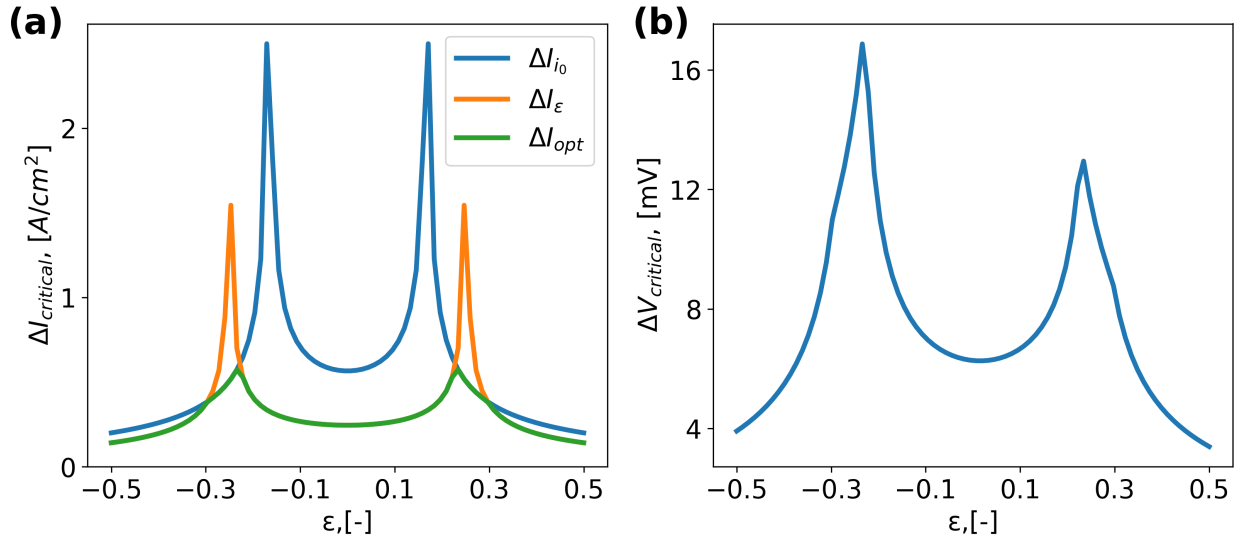


Figure S4.1. a) Critical current that drives 1% deviation in i_0 and ε estimation (first and second harmonic signal and their corresponding ΔI_{opt} with respect to the asymmetry parameter ε . b) The determined critical voltage based on ΔI_{opt} . The exchange current density used for this simulation is $1 A/cm^{-2}$.

4.6.2 Trigonometry Identities

$$\cos^2(\omega t) = \frac{1 + \cos(2\omega t)}{2}, \quad (4.S19a)$$

$$\cos^3(\omega t) = \frac{3 \cos(\omega t) + \cos(3\omega t)}{4}, \quad (4.S19b)$$

$$\cos^4(\omega t) = \frac{3 + 4 \cos(2\omega t) + \cos(4\omega t)}{8}, \quad (4.S19c)$$

4.7 SUPPLEMENTARY FIGURES

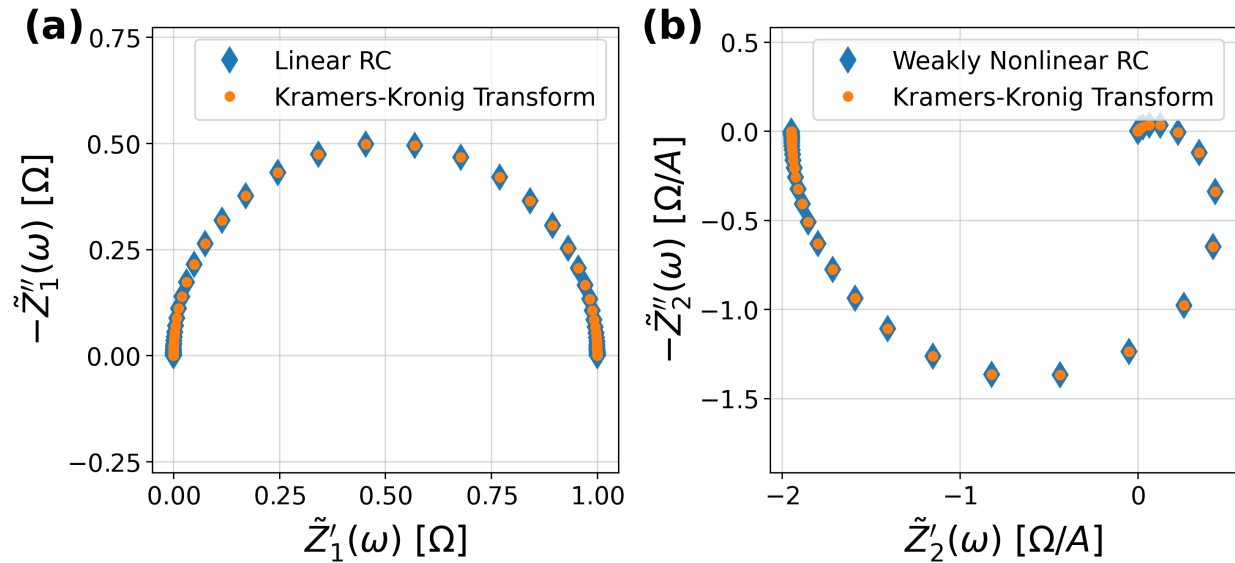


Figure S4.2. Simulated a) EIS and b) 2nd-NLEIS based on analytic Randles and weakly nonlinear Randles circuit and their corresponding KK transformation based on **Equation 4.7**. The parameters used are $R_{ct} = 1 \Omega$, $R_{dl} = 1 \text{ F}$, $\varepsilon = 0.1$. A total of 100 log-spaced points are used for frequency from 10^{-5} to 10^{-5} Hz.

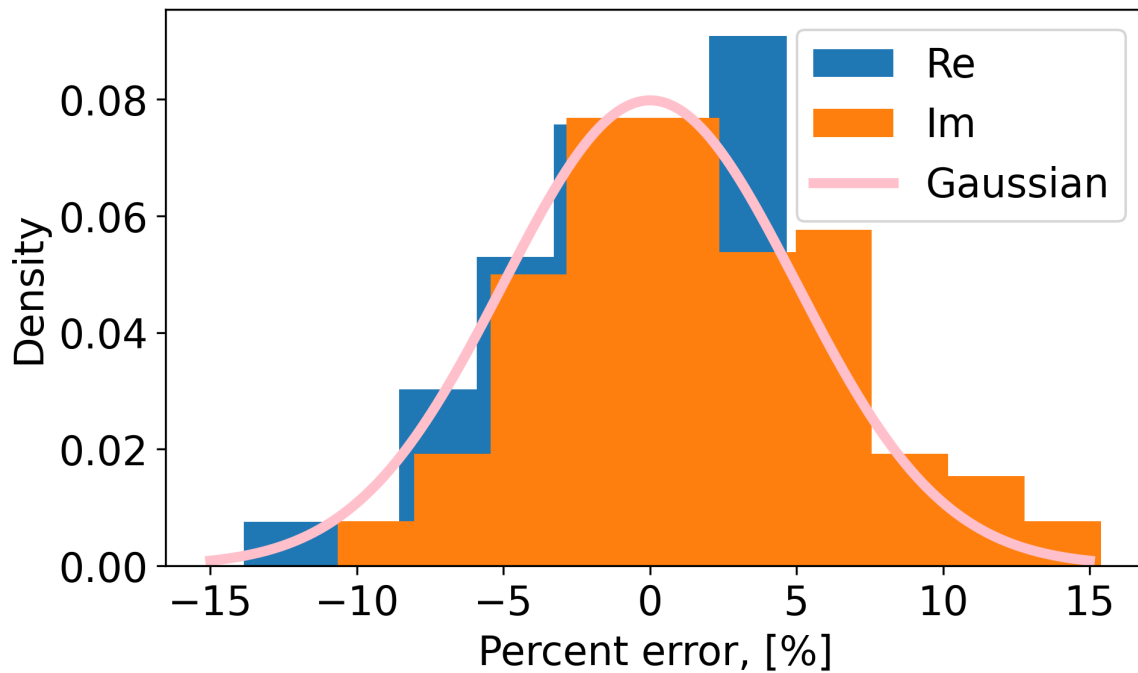


Figure S4.3. The Gaussian distribution of the introduced error with $\sigma = 5\%$ and its corresponding sampling for the real and imaginary parts of the impedance value.

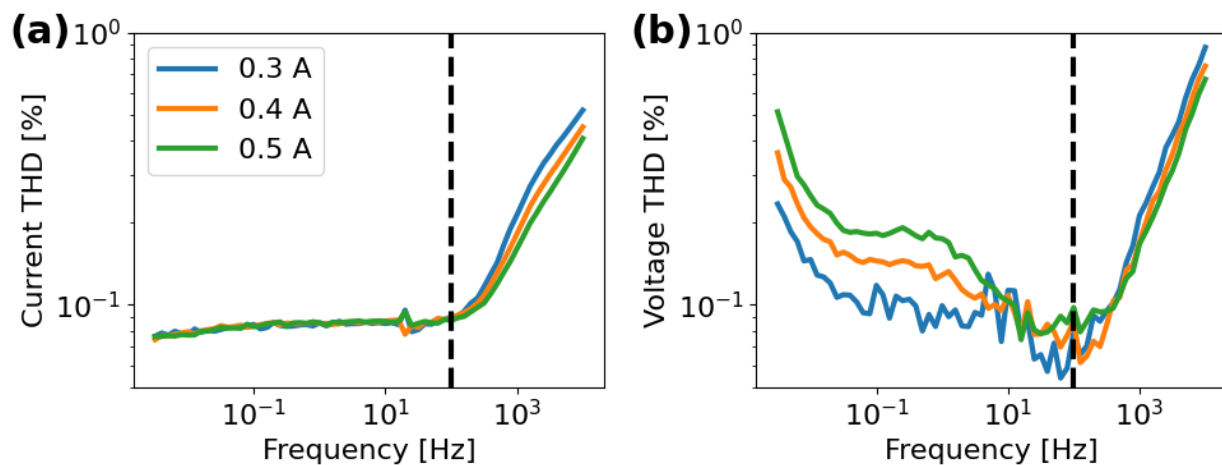


Figure S4.4. Total harmonic distortion (THD) of a) current perturbation, b) voltage response of a 1.5 Ah Samsung 18650 cell with 0.3, 0.4, 0.5 A current perturbation at 30 % SOC after 100 cycles of aging. The black dashed line indicates a cutoff frequency of 100 Hz.

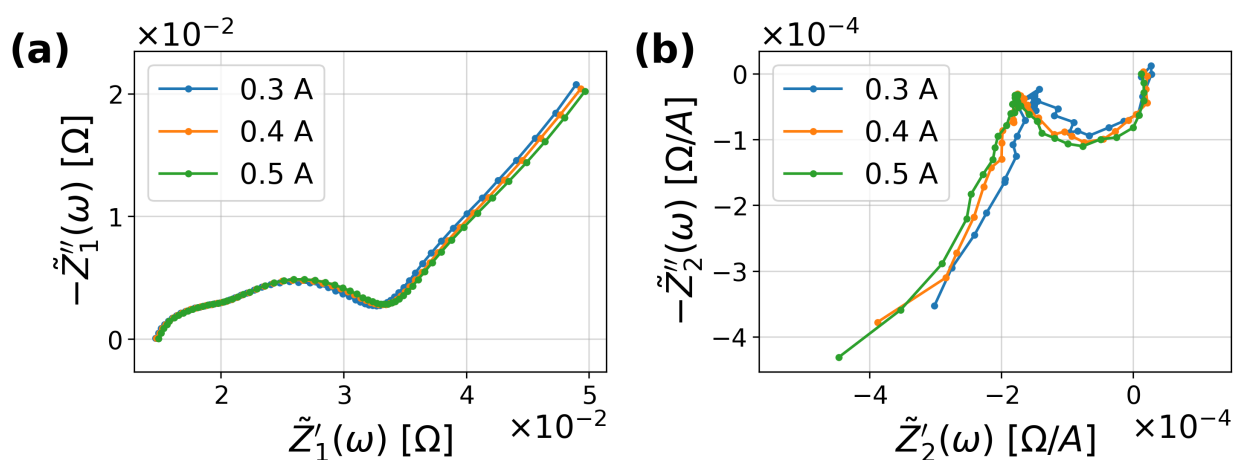


Figure S4.5. a) EIS and b) 2nd-NLEIS of a 1.5 Ah Samsung 18650 cell with 0.3, 0.4, 0.5 A current perturbation at 30 % SOC after 100 cycles.

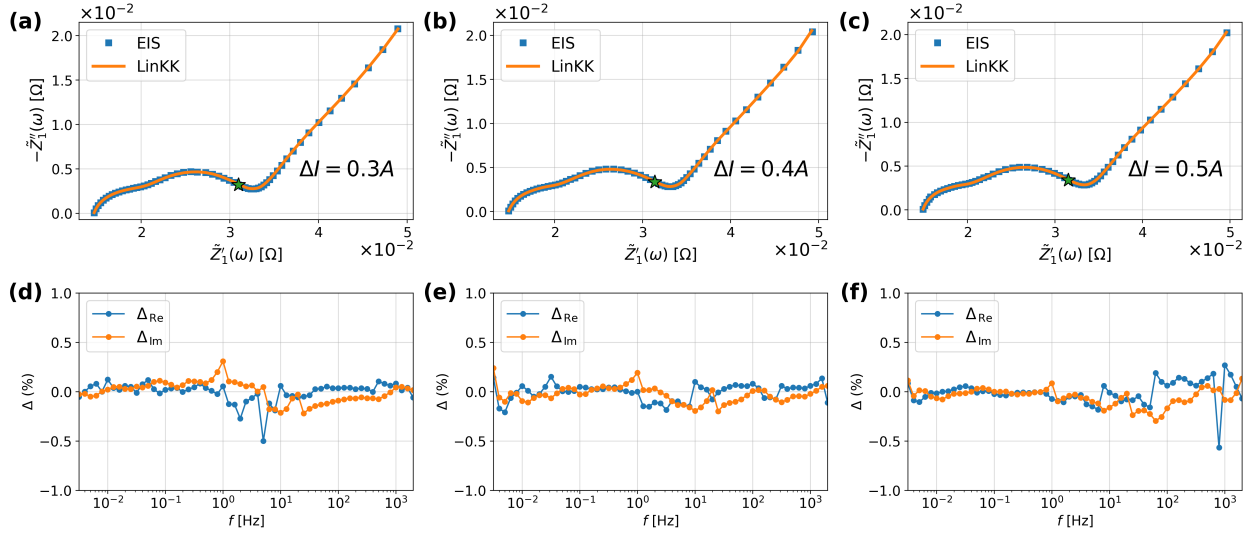


Figure S4.6. LinKK test for EIS data collected with a current perturbation of a,d) 0.3 A, b,e) 0.4 A, and c,f) 0.5 A for a 1.5 Ah Samsung 18650 cell at 30 % SOC after 100 cycles. a-c) Nyquist plots of experimental data and corresponding fitting results. d-f) The estimated residual error for both the real and imaginary parts of the EIS data. The 1 Hz points are labeled as ☆ in a-c.

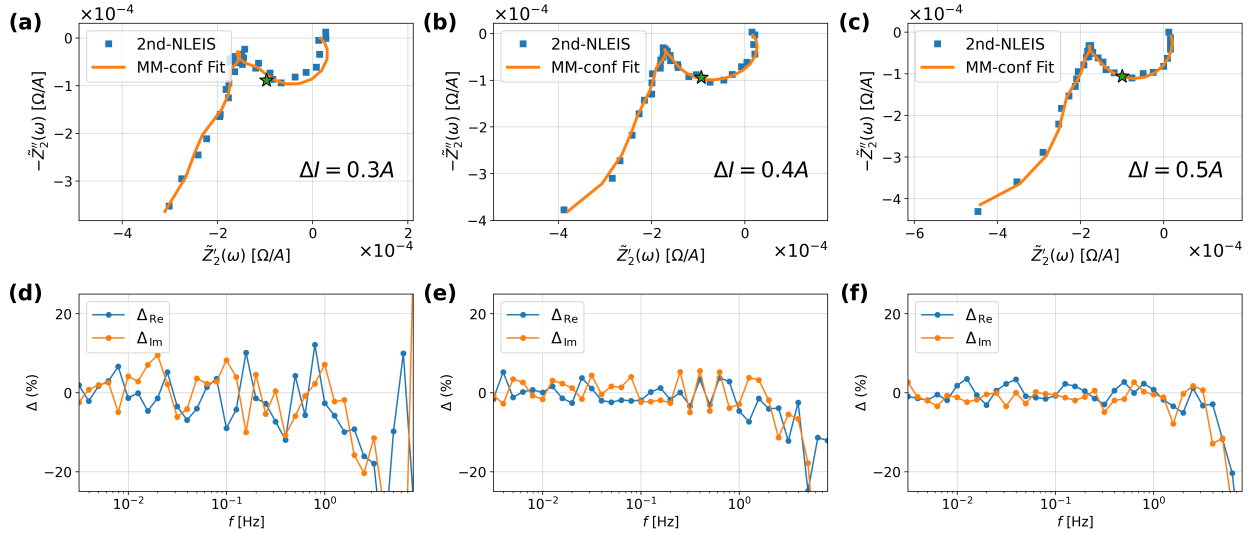


Figure S4.7. Measurement model test results with conf algorithm for 2nd-NLEIS data collected with a current perturbation of a,d) 0.3 A, b,e) 0.4 A, and c,f) 0.5 A for a 1.5 Ah Samsung 18650 cell at 30 % SOC after 100 cycles. a-c) Nyquist plots of experimental data and corresponding fitting results. d-f) The estimated residual error for both the real and imaginary parts of the 2nd-NLEIS data. The default guesses for the basis function are $R_{2,k}^{eff} = -0.01 \Omega/A$ and $\tau_{2,k} = 0.01 s$. The number of elements determined are 5, 6, and 6 for 0.3, 0.4, and 0.5 A respectively. The 1 Hz points are labeled as ☆ in a-c.

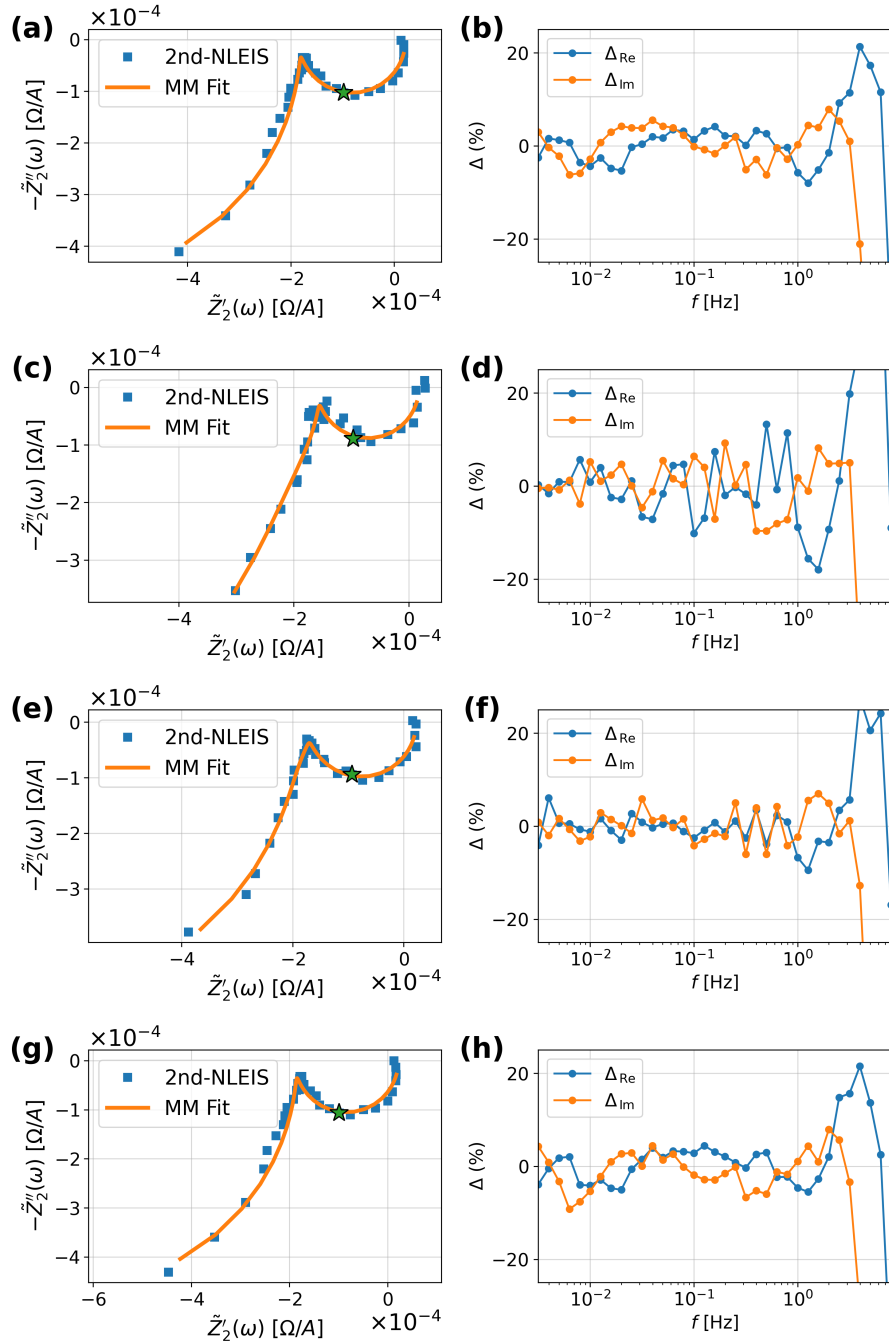


Figure S4.8. Measurement model program test results with Voigt as a basis function for a-b) extracted 2nd-NLEIS data and data collected with a current perturbation of c-d) 0.3 A, e-f) 0.4 A, and g-h) 0.5 A for a 1.5 Ah Samsung 18650 cell at 30 % SOC after 100 cycles. a, c, e, g) Nyquist plots of experimental data and corresponding fitting results. b, d, f, h) The estimated residual error for both the real and imaginary part of the 2nd-NLEIS data. The fitting was performed iteratively using the program without any weighting. The number of elements determined are 2, 3, 3, and 2 for extracted data, 0.3, 0.4, and 0.5 A data respectively. The 1 Hz points are labeled as ☆ in a-c.

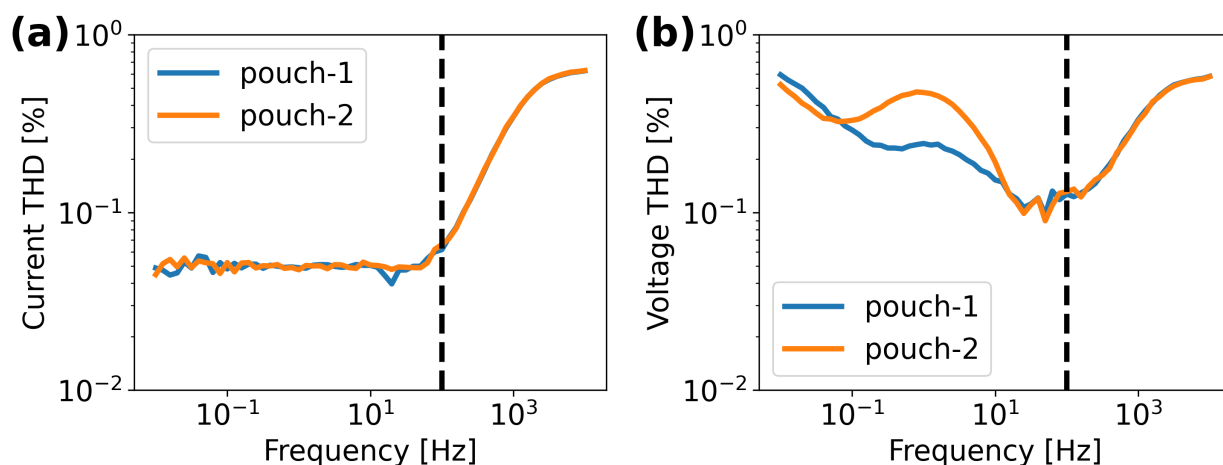


Figure S4.9. Total harmonic distortion (THD) of a) current perturbation, b) voltage response of 290 mAh NMC pouch cells. The black dashed line indicates a cutoff frequency of 100 Hz.

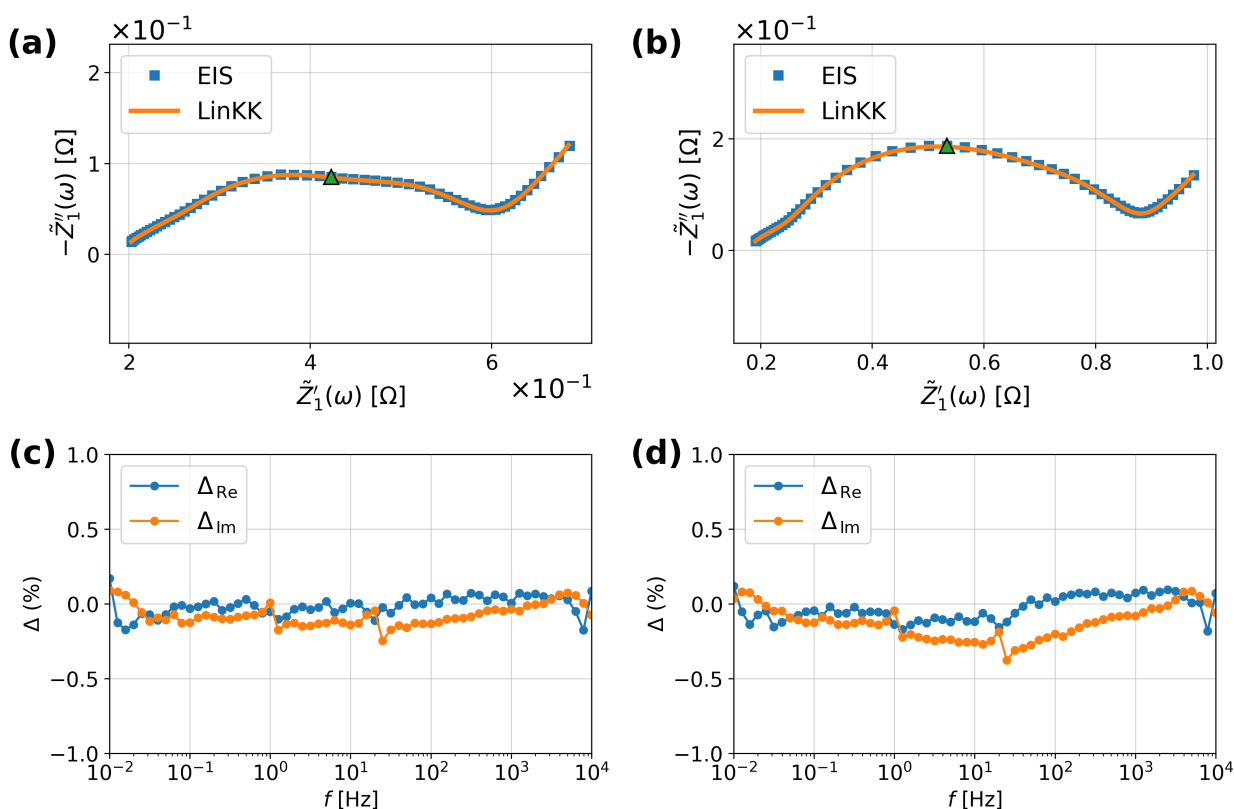


Figure S4.10. LinKK test for EIS data collected with a current perturbation of 50 mA for 290 mAh NMC pouch cells. a-b) Nyquist plots of experimental data and corresponding fitting results. c-d) The estimated residual error for both the real and imaginary parts of the EIS data. The 10 Hz points are labeled as $\triangle$ in a-b.

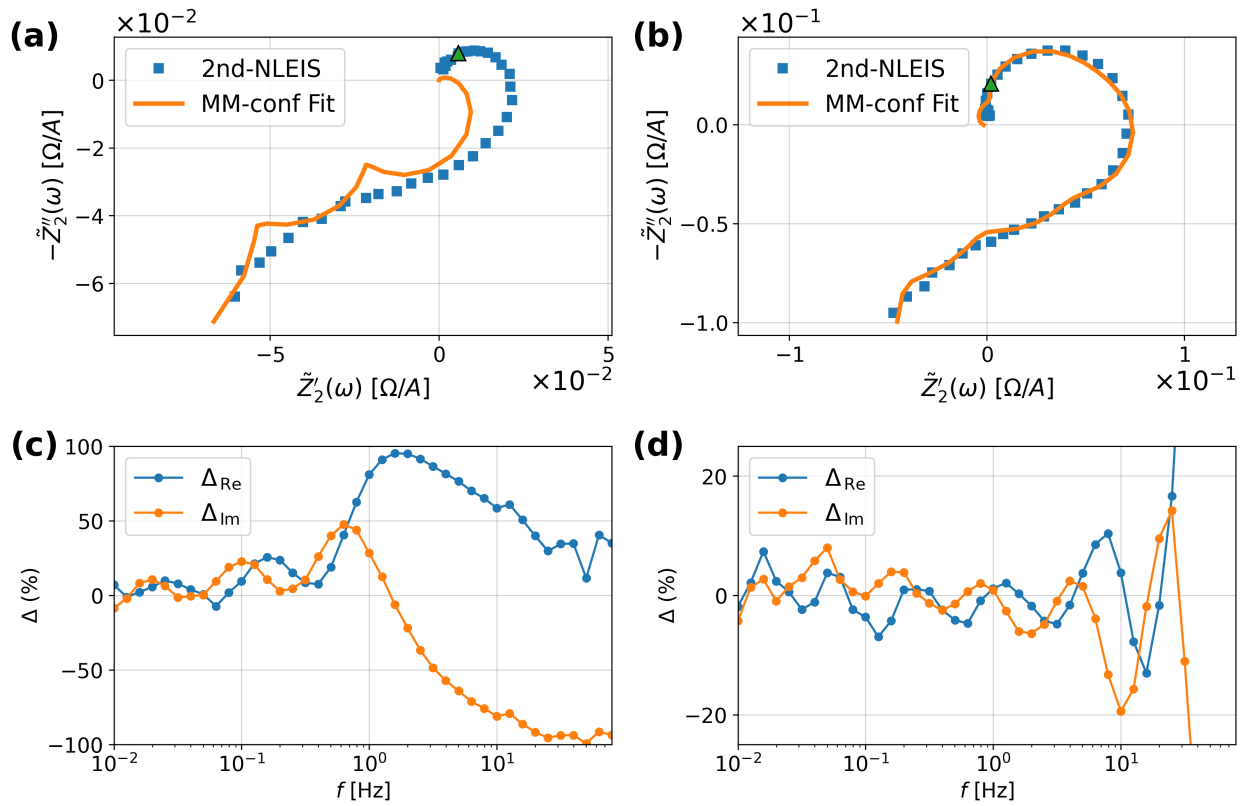


Figure S4.11. Measurement model test results with the conf algorithm for 2nd-NLEIS data collected with 290 mAh pouch cells and a current perturbation of 50 mA. a-b) Nyquist plots of experimental data and corresponding fitting results. c-d) The estimated residual error for both the real and imaginary parts of the 2nd-NLEIS data. The default guesses for the basis function are $R_{2,k}^{eff} = 0.001 \Omega/A$ and $\tau_{2,k} = 0.1 \text{ s}$. The number of elements determined are 3 and 6 for pouch-1 and -2 respectively. The 10 Hz points are labeled as $\triangle$ in (a-b).

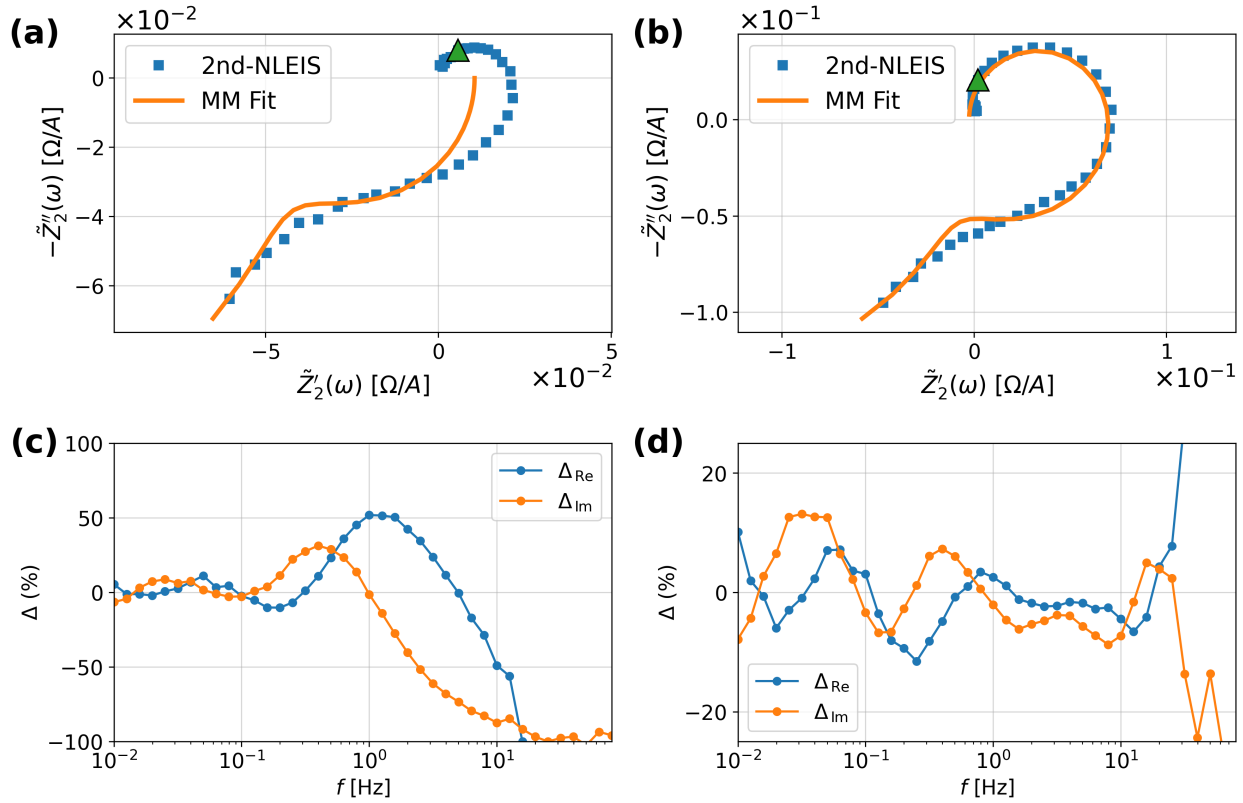


Figure S4.12. Measurement model program test results with Voigt as a basis function for 2nd-NLEIS data collected with 290 mAh pouch cells and a current perturbation of 50 mA. a-b) Nyquist plots of experimental data and corresponding fitting results. c-d) The estimated residual error for both the real and imaginary parts of the 2nd-NLEIS data. The fitting was performed iteratively using the program without any weighting. The number of elements determined are 2 and 3 for pouch-1 and -2 respectively. The 10 Hz points are labeled as $\triangle$ in (a-b).

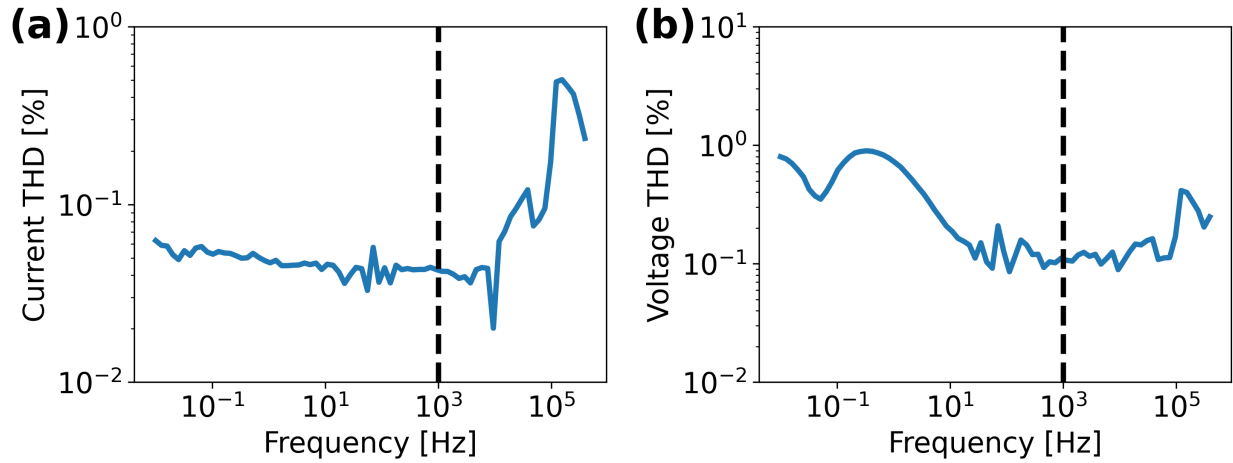


Figure S4.13. Total harmonic distortion (THD) of a) current perturbation, b) voltage response of in-house coin cell. The black dashed line indicates a cutoff frequency of 1000 Hz.

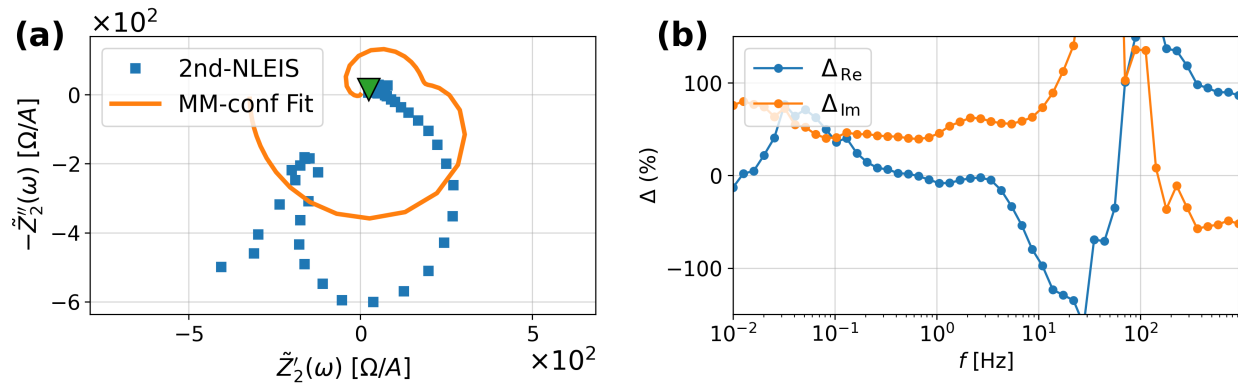


Figure S4.14. Measurement model test results with the conf algorithm for in-house coin-cell 2nd-NLEIS measurement. a) Nyquist plots of experimental data and corresponding fitting results. b) The estimated residual error for both the real and imaginary parts of the 2nd-NLEIS data. The default guesses for the basis function are $R_{2,k}^{eff} = 0.01 \text{ } \Omega/\text{A}$ and $\tau_{2,k} = 0.01 \text{ s}$. The number of elements determined is 2. The 112.74 Hz points are labeled as ∇ in (a).

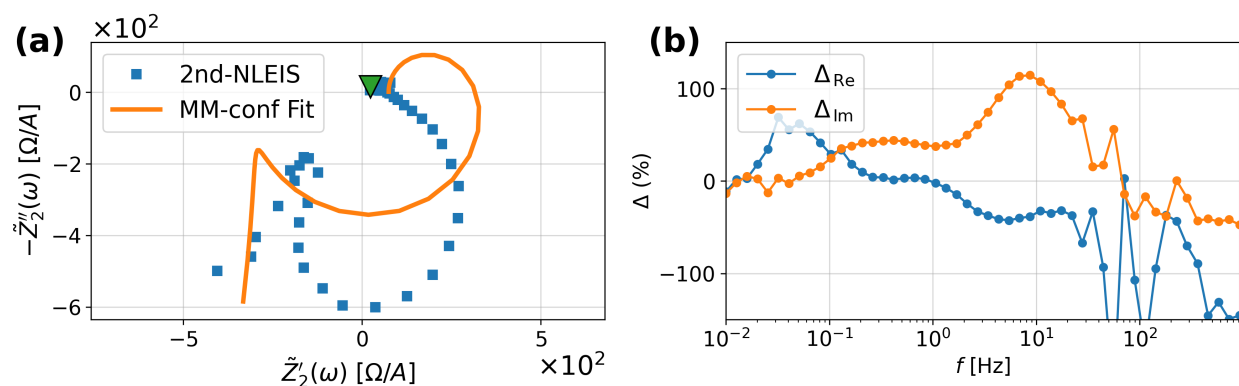


Figure S4.15. Measurement model program test results with Voigt as a basis function for in-house coin-cell 2nd-NLEIS measurement. a) Nyquist plots of experimental data and corresponding fitting results. b) The estimated residual error for both the real and imaginary parts of the 2nd-NLEIS data. The fitting was performed iteratively using the program without any weighting. The number of elements determined is 3. The 112.74 Hz points are labeled as ∇ in (a).

Chapter 5.

SECOND-HARMONIC NONLINEAR ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY: II. MODEL-BASED ANALYSIS OF LITHIUM-ION BATTERY EXPERIMENTS

Note: this chapter was published as an article

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Abstract

Quantitative analysis of electrochemical impedance spectroscopy (EIS) and 2nd-harmonic nonlinear EIS (2nd-NLEIS) data from commercial Li-ion batteries is performed using the porous electrode half-cell models developed in Part I. Because EIS and 2nd-NLEIS signals have opposite parity, the full-cell EIS model relies on the sum of cathode and anode half-cells whereas the full-cell 2nd-NLEIS model requires subtraction of the anode half-cell from the cathode. The full-cell EIS model produces a low error fit to EIS measurements, but importing EIS best-fit parameters into the 2nd-NLEIS model fails to ensure robust model-data convergence. In contrast, simultaneously fitting opposite parity EIS and 2nd-NLEIS models to the corresponding magnitude-normalized experimental data provides a lower total error fit, more internally self-consistent parameters, and better assignment of parameters to individual electrodes than EIS analysis alone. Our results quantify the extent that mild aging of cells (<1% capacity loss) results in substantial increases in cathode charge transfer resistance, and for the first time, a breakdown in cathode charge transfer symmetry at 30% and lower state-of-charge (SoC). New avenues for model-based analysis are discussed for full-cell diagnostic and we identify several open questions.

5.1 INTRODUCTION

The growing demand for lithium-ion (Li-ion) batteries is driven by clean energy storage and transportation applications in the rapidly electrifying global economy. [1] Experimental battery sciences are largely carried out using half-cells to isolate the behavior to a single electrode, [166,167] provide a thermodynamic reference potential, and more easily couple techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), and solid-state nuclear magnetic resonance spectroscopy (ssNMR). [3,168,169] In contrast, commercial Li-ion cells are engineered with two active electrodes separated by microns and wetted by minimal electrolyte; chemical interactions between the two electrodes and electrolyte play a key role in safety and performance over the entire battery's life cycle. [170,171] Improving non-invasive diagnostic techniques for extracting physicochemical insights into the evolution of engineered cells is critical to their safe use and reuse in the emerging battery electric economy.

Electrochemical impedance spectroscopy (EIS) is a key diagnostic approach for full-cell analysis of batteries, [50,172] offering insights into the formation of the solid electrolyte interface, [173,174] transport processes, [175,176] charge transfer kinetics, [177,178] and aging mechanisms [179–181] in lithium-ion cells. The implementation of EIS is now fairly routine, but the interpretation of EIS data remains an active area for physical and mathematical analysis that can extract deeper mechanistic and quantitative insights, non-destructively. [182–184] The most basic analysis approach is the use of equivalent circuit models (ECM) to analyze impedance data. ECM models are sometimes used to extract parameters from data without physical interpretation, [172] but that need not be true. Most ECM, including Randles circuits, [185] porous electrode models, [100,124,125] and transmission line (TLM) models, [105,126] derive from interpretable linearized governing physics describing the electrified interface and transport processes. [100,105,186,187]

Yet, lithium-ion batteries are complex nonlinear systems, and the application of linearized models contributes to model degeneracy, even in half-cells, where an EIS spectrum can be represented equally by different linear models. [32,33] Full cells, like an engineered battery, compound the challenge of EIS model discrimination and assignment of parameters to individual electrodes.

Second harmonic nonlinear electrochemical impedance spectroscopy (2nd-NLEIS) is an extension of EIS obtained by using moderately larger modulations of the electrochemical input to induce a weakly nonlinear response at twice the frequency of the input modulation, but no higher harmonics. [26,34,44,51] By measuring the weakly nonlinear response of a two-electrode cell, 2nd-NLEIS can break some of the degeneracy found in linearized EIS models, providing additional information about the cell, all without degrading the information contained in the accompanying EIS dataset. Different forms of NLEIS have been proposed and implemented in the field of corrosion, [36,188] fuel cells, [33,189] mass transport, [97,101,102] chemical sensing, [190,191] and lithium ion batteries, [26,44,192] though often these studies rely on exciting more strongly nonlinear behavior than just the 2nd harmonic signal analyzed here. The potential of 2nd-NLEIS in battery characterization was first shown by Murbach et.al experimentally, where they compared a pseudo-two-dimensional (P2D) battery model with EIS and 2nd-NLEIS measurements. [26] Kirk et.al was the first to quantitatively analyze experimental battery data based on a single particle model (SPM) for EIS and 2nd-NLEIS. [44] SPM models capture key interfacial capacitive and charge transfer processes, as well as the solid-state diffusion impedance, but exclude electrolyte-related losses. Because batteries almost universally rely on “electrochemically thick” porous electrodes (with internal ohmic drop and non-uniform current distributions), the SPM model did not capture the depressed semi-circular shape seen in the measured EIS data. In short, a P2D model

appears too complex for EIS and 2nd-NLEIS parameter estimation from battery experimental data, whereas the SPM model misses key physics that is clearly seen in experimental battery data.

In Part I, we developed a porous electrode half-cell model for EIS and 2nd-NLEIS that incorporated ohmic losses in electrolyte-filled pores (physics not in SPM) but excluded solid-state ohmic losses, binary electrolyte transport, and effective media traits that are part of P2D modeling. [35] Here, we build full-cell models from the EIS and 2nd-NLEIS half-cell representations of the porous anode and cathode and fit the model to full-cell experimental data. A key point in the full-cell model development, first noted by Murbach, [34] is that the EIS signal arises from the *sum* of the half-cell responses (i.e., the summative full-cell response has “positive parity”), whereas the 2nd-NLEIS signal arises from the *difference* between the half-cell responses (i.e., the subtractive response has negative parity). Another feature of the weakly nonlinear response shown in Part I is that, mathematically, the solution structure is hierarchical with the linearized EIS solution incorporated into the 2nd-NLEIS solution. The complementary parity and hierarchical solution structure suggest two strategies for parameter estimation when experimental EIS and 2nd-NLEIS datasets are acquired simultaneously. Sequential optimization (SO) first estimates 12 EIS model parameters by fitting to the EIS dataset, then fixes those parameters when fitting the 4 additional 2nd-NLEIS model parameters to data. Sequential-simultaneous optimization (SSO) uses the EIS best-fit parameters as initial guesses in a cost function that simultaneously fits all 16 parameters to the EIS and 2nd-NLEIS datasets.

Overall, this work seeks to clarify the path forward for model-data convergence in the use of 2nd-NLEIS and EIS for better full-cell diagnostics in two-electrode systems like Li-ion batteries. We show when naïve parameter estimation strategies fail and discuss the opportunities and limitations of combining EIS and 2nd-NLEIS measurements and modeling to enable model

discrimination, assignment of parameters to individual electrodes, and interpretation of changes to batteries as they are used and degraded.

5.2 METHODS AND PARAMETER ESTIMATION APPROACHES

5.2.1 *Experimental Procedures and Data Availability for the Lithium-Ion Batteries Under Test*

Here we reuse and quantitatively analyze, for the first time, the triplicate EIS and 2nd-NLEIS experimental datasets we have previously published [26] and archived. [164] The cells are 1.5 Ah Li NMC|C Samsung cells (INR 18650-15M) with mixed NMC 532/LMO cathodes and graphite anodes. [14]

Briefly, the datasets were acquired for fresh cells and modestly aged cells that were cycled 100 times at a 2C discharge, 2C CCCV charge, and controlled temperature of 25 °C between 4.2 V and 2.5 V. One hundred cycles produced an average reduction in capacity of 0.7% from the initial (fresh) cell values of approximately 1.48 Ah. Despite the modest change in the state of health (SoH), the EIS and 2nd-NLEIS datasets showed appreciable changes over the frequency range evaluated (3.16 mHz-10 kHz) for EIS and (3.16 mHz-10 Hz) for 2nd-NLEIS. The high frequency limit in 2nd-NLEIS reflected measurable signal to noise in our experimental datasets, as presented previously. [26,164]

EIS and 2nd-NLEIS data was acquired at several states-of-charge (SoC) for the fresh and modestly aged cells by setting a series of cell stopping voltages, see **Table A5-I**, followed by several hours of hold-time to allow current to relax. Other EIS and 2nd-NLEIS measurement procedures are detailed in our previous work, including the Kramer-Kronig analysis of triplicate EIS datasets. [26]

5.2.2 Linear and Nonlinear Response for Full-Cell Datasets

The full cell model used for data fitting has a linear resistor (R_0) and inductor (L_0) in series with two porous electrode half-cell models, as given in Part I. [35] The inductor and resistor capture high frequency experimental features not present in the porous electrode models (i.e., contact resistance, lead inductance, and separator resistance). The cathode EIS and 2nd-NLEIS model (given in Part I, Eqs (2.35) and (2.36)) assumes spherical primary particles and the anode assumes platelet-like particles. The resulting full-cell EIS model is,

$$\tilde{Z}_1^{model} = L_0 + R_0 + \tilde{Z}_1^{cath} + \tilde{Z}_1^{anode} \quad (5.1)$$

whereas the resulting full-cell 2nd-NLEIS model is

$$\tilde{Z}_2^{model} = \tilde{Z}_2^{cath} - \tilde{Z}_2^{anode} \quad (5.2)$$

We label **Equation 5.1** a positive parity full-cell response because the signal arises from the summation of anode and cathode responses, whereas **Equation 5.2** is a negative parity full-cell response because it arises from a difference in half-cells. A key premise emphasized in **Figure 2.10** of Part I is that the complementary parity of EIS and 2nd-NLEIS full-cell responses creates an opportunity for improved model discriminating power, allowing more clear assignment of half-cell parameters from full-cell measurements than is possible with EIS alone.

5.2.3 Parameter Estimation Approaches

All the EIS parameter estimation is performed using `impedance.py`, which is an open-source Python package for impedance analysis. [137] A 2nd-NLEIS toolbox based on `impedance.py` was built to support the 2nd-NLEIS parameter estimation (see **supplementary materials**, which are available on GitHub and Zenodo).[103] In both EIS and 2nd-NLEIS analysis, nonlinear least square

optimization is performed using the SciPy Curve fit module. Levenberg–Marquardt and trust region algorithms are implemented for unbounded and bounded optimization, respectively.

As shown in Part I, solutions to the governing equations have a hierarchical structure, with the linear EIS response solved first, and then subsequently used to determine the 2nd-NLEIS response. Because of this hierarchical structure, the vector of 12 parameters needed for the full-cell linear EIS response (denoted $\mathbf{p}_1$) are all included in the 2nd-NLEIS model, as well as 4 additional 2nd-NLEIS full cell parameters (denoted $\mathbf{p}_2$). The hierarchical nature of the solutions and the extensive literature on linear EIS parameter estimation make it natural to first consider sequential optimization, starting with fits of $\mathbf{p}_1$ to EIS experimental data, and then exporting the best-fit $\mathbf{p}_1$ parameters to the 2nd-NLEIS model, where fitting is limited to the $\mathbf{p}_2$ nonlinear parameter vector.

Mathematically, the sequential optimization (SO) scheme we employed is the minimization of the magnitude-normalized linear EIS cost function,

$$COST_1 = \sum_{i=1}^N \left[\frac{Z_1^{exp}(\omega_i) - Z_1^{model}(\omega_i; \mathbf{p}_1)}{\max(|Z_1^{exp}|)} \right]^2 \quad (5.3)$$

to identify the best-fit parameter set $\mathbf{p}_1$ using impedance.py.[137] Initial guesses for parameter estimation are guided by the shape and magnitude of the Nyquist plot features, with estimated timescales and magnitudes consistent with the frequencies, widths, and shapes of charge transfer arcs, shape and magnitude of diffusion impedance region, etc. We assume faster charge transfer and diffusion processes should be assigned to the anode, and slower processes to the cathode, consistent with the assignments made in prior EIS studies of NMC|C.[193] This process for seeding initial parameter values consistently leads to low error fits for all our EIS data.

Once a best-fit parameter set $\mathbf{p}_1$ is established, SO minimizes the magnitude-normalized 2nd-NLEIS cost function,

$$COST_2 = \sum_{i=1}^M \left[\frac{Z_2^{exp}(\omega_i) - Z_2^{model}(\omega_i; \mathbf{p}_2) | \mathbf{p}_1}{\max(|Z_2^{exp}|)} \right]^2 \quad (5.4)$$

using the $\mathbf{p}_2$ parameter set while holding the values of $\mathbf{p}_1$ fixed. Initial guesses for $\mathbf{p}_2$ are guided by the reference full-cell charge discharge profile and the presence (or absence) of a charge transfer asymmetry-driven moderate-to-high frequency NLEIS “loop” feature.

To evaluate the overall quality of the SO fit, the two magnitude-normalized *COST* functions are summed:

$$COST_{seq} = COST_1 + COST_2. \quad (5.5)$$

Sequential optimization can also be considered the first step in a two-step parameter estimation process we call Sequential-Simultaneous Optimization (SSO). The sequential optimization process cited above produces best-fit parameter set $[\mathbf{p}_1]_{seq}$ along with values for $[\mathbf{p}_2]_{seq}$ which we use as the initial guesses for a simultaneous estimation of all parameters against the single cost function,

$$COST_{simul} = \sum_{i=1}^N \left[\frac{Z_1^{exp}(\omega_i) - Z_1^{model}(\omega_i; \mathbf{p}_1)}{\max(|Z_1^{exp}|)} \right]^2 + \sum_{i=1}^M \left[\frac{Z_2^{exp}(\omega_i) - Z_2^{model}(\omega_i; \mathbf{p}_1, \mathbf{p}_2)}{\max(|Z_2^{exp}|)} \right]^2 \quad (5.6)$$

Equation 5.6 is equivalent to **Equation 5.5**, but with all parameters subject to fitting at one time. Simultaneous optimization means the final parameter set we report with SSO, $[\mathbf{p}_1, \mathbf{p}_2]_{simul}$, need not reside in a local or global minimum of **Equation 5.3**. Thus, **Equation 5.6** unleashes the discriminating power of 2nd-NLEIS models to select among a wide range of high-quality EIS fits. A future refinement of **Equation 5.6** would involve more sophisticated weighing schemes for the two terms, based on an assessment of data quality, as discussed later.

5.3 RESULTS AND DISCUSSION

5.3.1 *Parameter Estimation with Sequential Optimization (SO)*

Figure 5.1 presents typical EIS and 2nd-NLEIS experimental spectra collected with fresh and 100 cycle-aged cells at 10% state-of-charge (SoC), along with their corresponding sequentially-optimized (SO) model fits. **Figure 5.1a** and **1c** show that best-fit parameter set $[p_1]_{seq}$ (12 model degrees of freedom) produces good fidelity full-cell EIS model-data convergence. In particular, we see the two flattened interfacial charge transfer arcs are captured well by the EIS porous electrode models at intermediate and high frequencies, while solid state thermo-diffusion processes appear to be adequately represented by the low frequency Warburg-like diffusion impedances. In stark contrast, sequential fitting of the 2nd-NLEIS data by fixing the best-fit $[p_1]_{seq}$ parameters and optimizing the remaining parameter set p_2 (4 new model degrees of freedom) produces poor full-cell 2nd-NLEIS model-data convergence for fresh (**Figure 5.1b**) and aged (**Figure 5.1d**) cells, despite the high-quality fits $[p_1]_{seq}$ produced for the EIS spectra. **Figure 5.2** and **Figure 5.3** show a consistent pattern for all our SO fitting at each SoC studied, namely, high fidelity EIS model fits and poor 2nd-NLEIS fits to data.

The consistent failure of sequential optimization to produce adequate 2nd-NLEIS model fits can have multiple origins. Failure would be expected if the modeled physics was inadequate for capturing the key data features and timescales. Another, and seemingly more likely, failure mode for the poor fit of 2nd-NLEIS spectra can be seen in Part I (**Figure 2.10**), where parameter “swapping” within p_1 can produce nearly degenerate EIS spectra, but radically different 2nd-NLEIS results. SO fitting squelches the discriminating power of 2nd-NLEIS by constraining fitting degrees of freedom. For example, we find parameters needed to describe the linear EIS thermo-diffusion feature of these datasets are non-unique and produce high fitting uncertainty (see

Supplementary Materials). [103] Similar observations are also mathematically demonstrated in Kirk et. al's work with the SPM model. [44] Consequently, naïve SO fitting assumes the optimal fit for 2nd-NLEIS must derive from the lowest error fit of the EIS data, but this ignores the fact that high quality EIS fits can easily result from degenerate or nearly-degenerate parameter sets or misassigning parameters to the wrong electrode in a full cell measurement. The next section addresses the role of simultaneous optimization of all 16 parameters to address these issues.

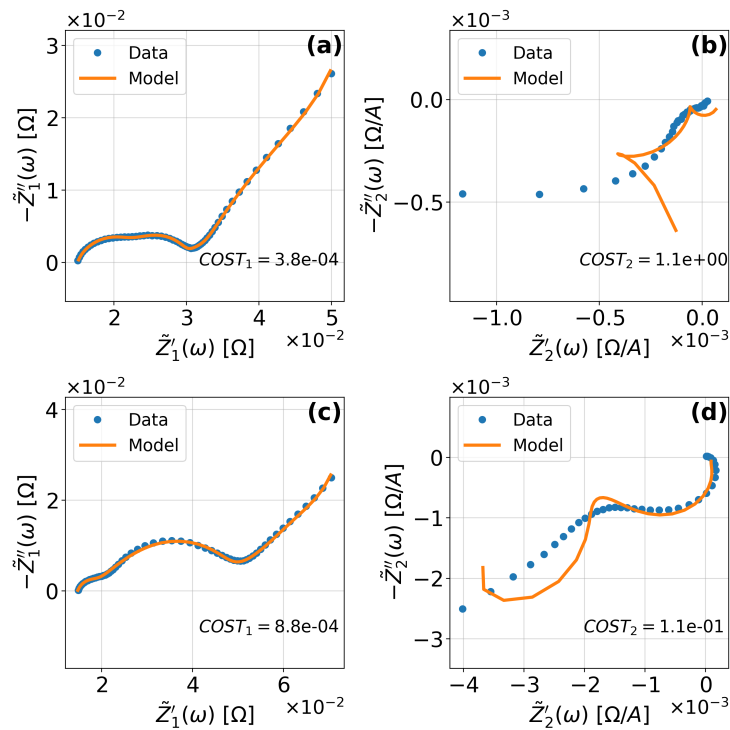


Figure 5.1. Nyquist plots of measured and sequentially optimized EIS (a,c) and 2nd-NLEIS (b,d) spectra for fresh (a,b) and aged cells (c,d) at 10% SoC.

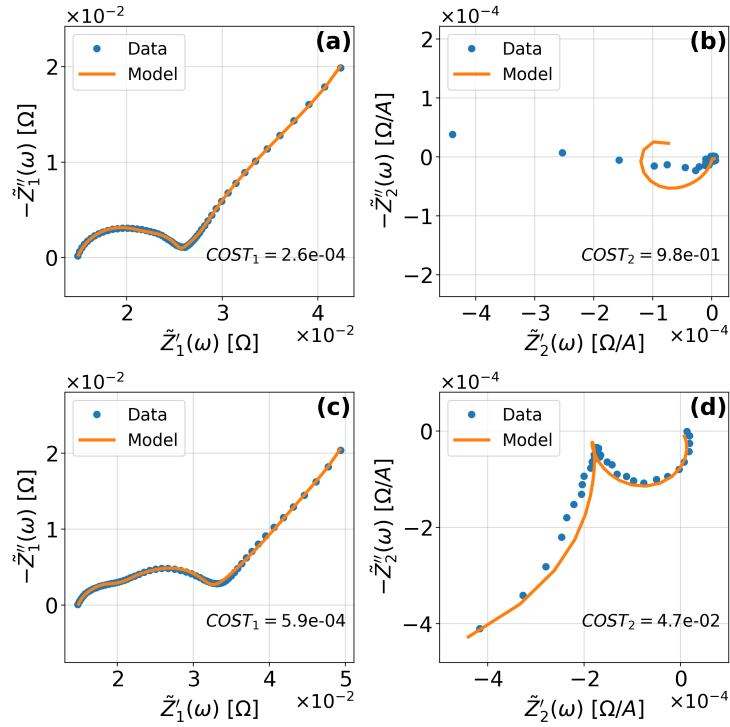


Figure 5.2. Nyquist plots of measured and sequentially optimized EIS (a,c) and 2nd-NLEIS (b,d) spectra for fresh (a,b) and aged cells (c,d) at 30% SoC.

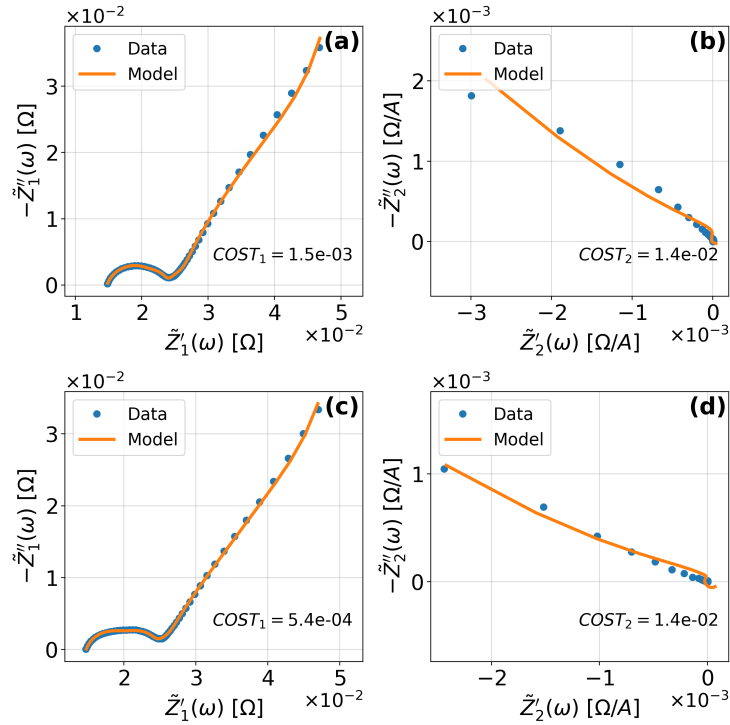


Figure 5.3. Nyquist plots of measured and sequentially optimized EIS (a,c) and 2nd-NLEIS (b,d) spectra for fresh (a,b) and aged cells (c,d) at 50% SoC.

5.3.2 Parameter Estimation with Sequential-Simultaneous Optimization (SSO)

Sequential-simultaneous optimization (SSO) analysis of EIS and 2nd-NLEIS takes advantage of the complementary parity of the respective spectra to obtain the most physically self-consistent set of parameters $[p_1, p_2]_{simul}$ for the battery under test. The SSO fits shown in **Figure 5.4 - Figure 5.6** use the corresponding SO fit parameters (presented in **Figure 5.1 - Figure 5.3**, respectively) as the initial guess for minimizing the cost function in **Equation 5.6** by simultaneously varying all model parameters. The SSO optimized parameters are given in **Table A5-II - Table A5-III** (see **Supplemental Materials** for additional results, including all fit confidence intervals for measurements at multiple SoCs). [103] A common set of trends are seen in comparing **Figure 5.1 - Figure 5.3** with **Figure 5.4 - Figure 5.6**. The SSO fits of EIS data retain a low error $COST_1$ function, but it is not quite as good as the SO method for the same data. In general, the SSO mid-frequency EIS charge transfer fits are well-defined while the SSO fitting quality of the low-frequency EIS thermo-diffusion regime is poorer compared to SO. On the other hand, SSO produces a significant improvement in the 2nd-NLEIS fit for all six spectra. In short, SSO balances a slightly-poorer EIS fit with a much-improved 2nd-NLEIS fit to produce a lower $COST_{simul}$ via a self-consistent set of parameters for the complementary datasets of opposite parities.

Although SSO fitting provides much-needed internal self-consistency in estimating physical parameters for the full-cell, there is still much to explore in the simultaneous analysis of EIS and 2nd-NLEIS data. For example, **Figure 5.4 - Figure 5.6** show that the SSO method produces an especially robust fit for aged cells that have well-defined and separated charge transfer timescales for each electrode in both the EIS and 2nd-NLEIS datasets. In contrast, fresh cells can sometimes display a bias toward excellent fits in the interfacial charge transfer region at the cost of poorer fits to the thermo-diffusion region, and vice versa, depending on details of the

experimental data set. For example, **Figure 5.4a-b** at low SoC show a fairly good fit of the EIS at higher frequencies but increasing deviation from the data as diffusion becomes more important. The porous electrode models presented in Part I show strong coupling between diffusion and charge transfer processes, especially for electrochemically “thick” electrodes like those studied here. Hence, the lack of clear timescale separation in one part of the curve can influence other parts; this is perhaps why the model fit in **Figure 5.4b** displays a small charge transfer loop near the origin, where there is little evidence of this in the data itself. Likewise, at higher states of charge, e.g., **Figure 5.6a-b**, one sees there are strongly overlapping charge transfer timescales for both electrodes and the lack of a 2nd-NLEIS charge transfer feature; consequently, this is a case where 2nd-NLEIS contributes little to improving the confidence and assignment of charge transfer parameters compared to EIS alone. Thus, the fitting in **Figure 5.4 - Figure 5.6** shows that SSO parameter estimation, as implemented here, has the greatest ability to discriminate processes when there is clear time-scale separation with distinct EIS and 2nd-NLEIS features in the charge transfer and thermo-diffusion processes, as one might expect.

The qualitative discussion of fitting provided above is reflected statistically through the sensitivity analysis. We show this for the 30% SoC data using Sobol sampling methods, see **Supplemental Materials: Sobol Sampling Notebook** for details. [103] In summary, Sobol sampling was used to produce 3400 initial parameter sets over the range of 50% to 150 % of the best fit-parameters we report here. [194,195] The sampling results show when the linear EIS full-cell timescales for charge transfer are overlapping and there is little nonlinear charge transfer response, a more complex minimization landscape results, with some very large outlier parameter estimates, are found. In contrast, local minima for aged cells at lower SoC values, where the linear EIS responses have distinctive timescales for each electrode and significant nonlinear charge

transfer signals, are all very close to (what appears to be) a global minimum. This further confirms that the presence of 2nd-NLEIS charge transfer features and well separated time constants help produce internally self-consistent parameter estimates and assignments for parameters to each electrode.

While we find clear evidence that parameters from SSO co-optimization are more internally self-consistent and well-assigned to each electrode than those found through SO fitting to EIS and 2nd-NLEIS data, there is also evidence that more sophisticated signal weighting schemes are needed, akin to what has developed with EIS parameter estimation, to balance the impact of data quality and feature magnitude on fit robustness.[91] However, to implement sophisticated data quality and weighing with two terms of the SSO fitting cost function, **Equation 5.6**, one must first develop parallel methods for data-quality assessment of EIS and 2nd-NLEIS. As discussed in the Conclusions and Implications section, we believe our parallel model development in Part I is foundational for this kind of future work.

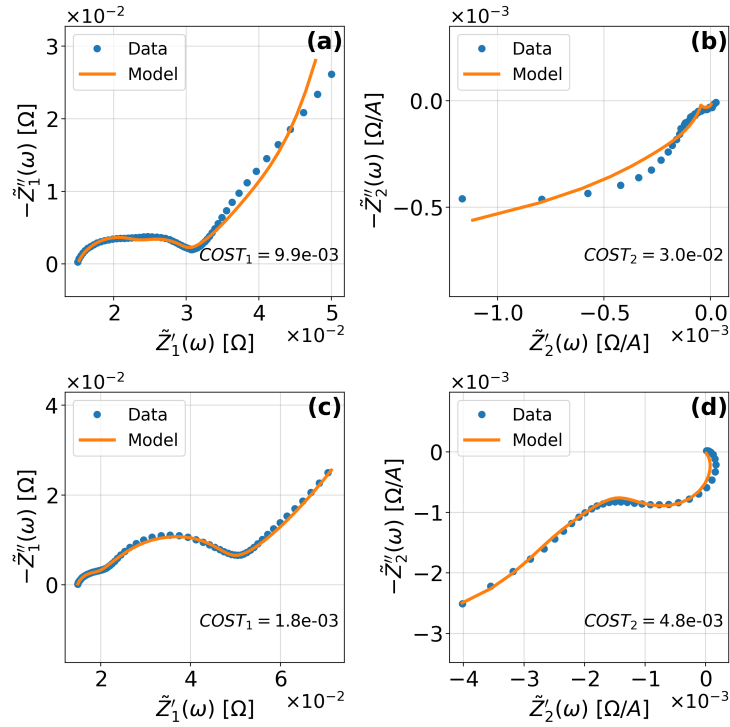


Figure 5.4. Nyquist plots of the measured and simultaneously optimized EIS (a,c) and 2nd-NLEIS (b,d) spectra for a 10% SoC (a,b) fresh and (c,d) aged cell.

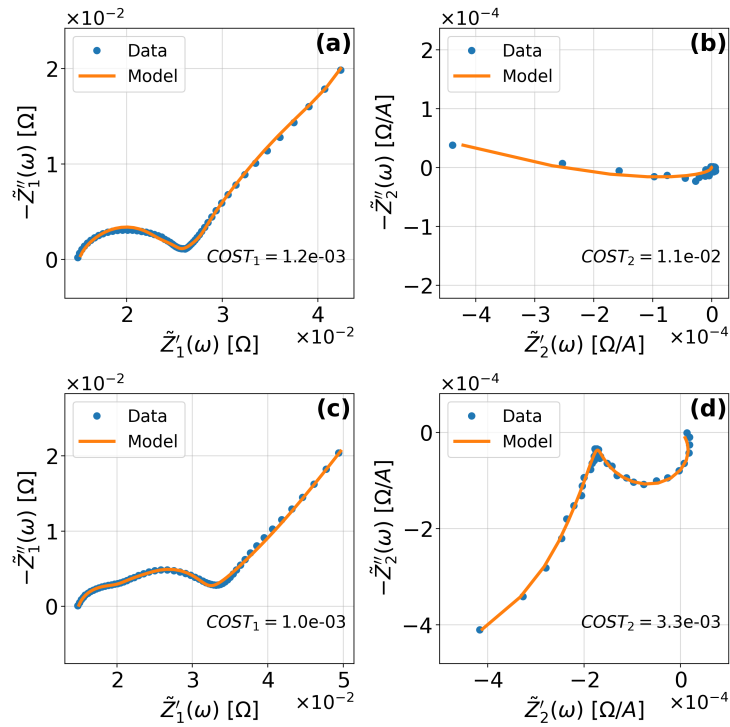


Figure 5.5. Nyquist plots of the measured and simultaneously optimized EIS (a,c) and 2nd-NLEIS (b,d) spectra for a 30% SoC (a,b) fresh and (c,d) aged cell.

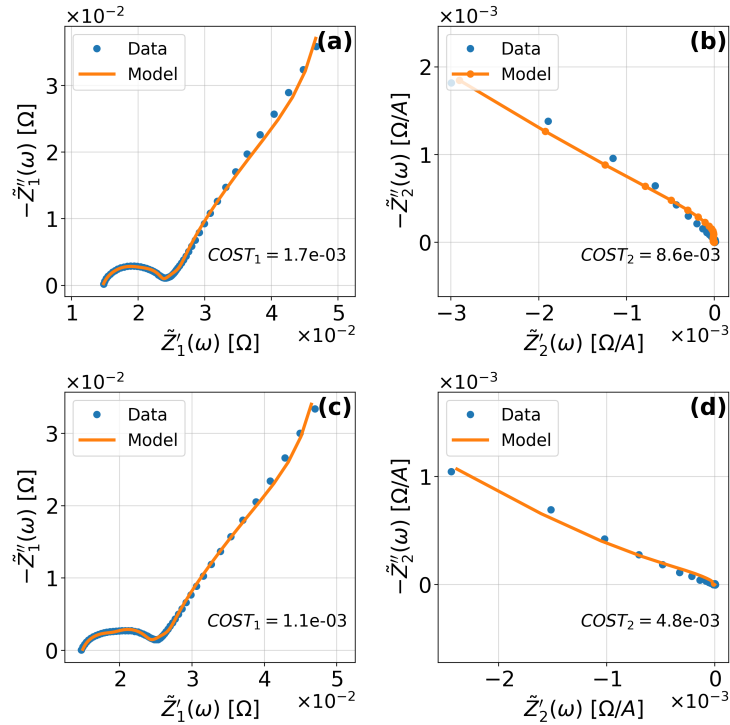


Figure 5.6. Nyquist plots of the measured and simultaneously optimized EIS (a,c) and 2nd-NLEIS (b,d) spectra for a 50% SoC (a,b) fresh and (c,d) aged cell.

5.3.3 Interpreting Aging-Related Charge Transfer Kinetic Information

Perhaps the most interesting and easily observed element of the combined EIS and 2nd-NLEIS data is the way it shows the state of health (SoH) and state of charge (SoC) dependence in the charge transfer resistance (R_{ct}) and the charge transfer asymmetry (ε) parameters for each electrode in the full-cell SSO fits. Aging-related evolution of charge transfer resistance has been widely studied for battery systems using EIS, [196–198] but this is the first time 2nd-NLEIS is being used to quantitatively estimate the impact of aging-related changes to reaction symmetry via the model parameter ε at the cathode and anode. Previously, we have shown (qualitatively) that the breaking of charge transfer symmetry on an electrode leads to a 2nd-NLEIS charge transfer arc in experimental data. [26,34]

To illustrate this breaking of charge-transfer symmetry, **Figure 5.7** overlays the experimental EIS and 2nd-NLEIS spectra for fresh and aged cells at 30% SoC. Recall, the aged cell is only mildly degraded, with a modest 0.7% decline in capacity. Despite the mild aging, the EIS data shows a slowing of interfacial charge transfer processes on one electrode, resulting in the clear separation of the two charge transfer arcs and growth of the overall charge transfer resistance. The emergence of a slower mid-frequency EIS arc is accompanied by the simultaneous emergence of a 2nd-NLEIS charge transfer arc over the same frequency regime. Qualitatively, the experimental data in **Figure 5.8** shows the growth of mid-frequency charge transfer arcs in EIS and 2nd-NLEIS primarily as SoC declines in these mildly aged cells. The distinct EIS charge transfer time scales and clear 2nd-NLEIS charge transfer loops for aged cells at 30% and 10% SoC, **Figure 5.7** and **Figure 5.8**, increases confidence in the charge-transfer parameter estimates. Quantitatively, **Table A5-II** and **Table A5-III** show the fit of the data in **Figure 5.8** having an aged cell cathode charge transfer asymmetry parameter that goes from $\varepsilon_c = 0$ at 50% SoC to $\varepsilon_c = 0.11$ at 10% SoC (aged), with $\varepsilon_c = 0.064$ at the intermediate SoC of 30% (aged). We believe this is the first time it has been shown that fresh cells have symmetric charge transfer over most of the SoC range, but that mild aging leads to a breaking of charge transfer symmetry that accompanies the well-known growth of charge transfer resistance in NMC cathodes. Moreover, based on the sign of ε_c , aged cathodes have a larger activation barrier for insertion of lithium ions than de-insertion, especially at low SoC. The physicochemical origin of aging-induced asymmetry in the low SoC transfer coefficient of these cells is not known, but the experimentally-observed 2nd-NLEIS data is a clear signature of mechanistic changes very early in the battery's aging lifecycle. Finally, though none of the 2nd-NLEIS experimental data for fresh cells have clear charge transfer features associated with asymmetry, our poorest fitting 2nd-NLEIS model (**Figure 5.4b**) seems to include an aphysical

2nd-NLEIS charge transfer feature, providing further motivation for continuing to develop robust post-processing and fitting routines for the analysis of 2nd-NLEIS data.

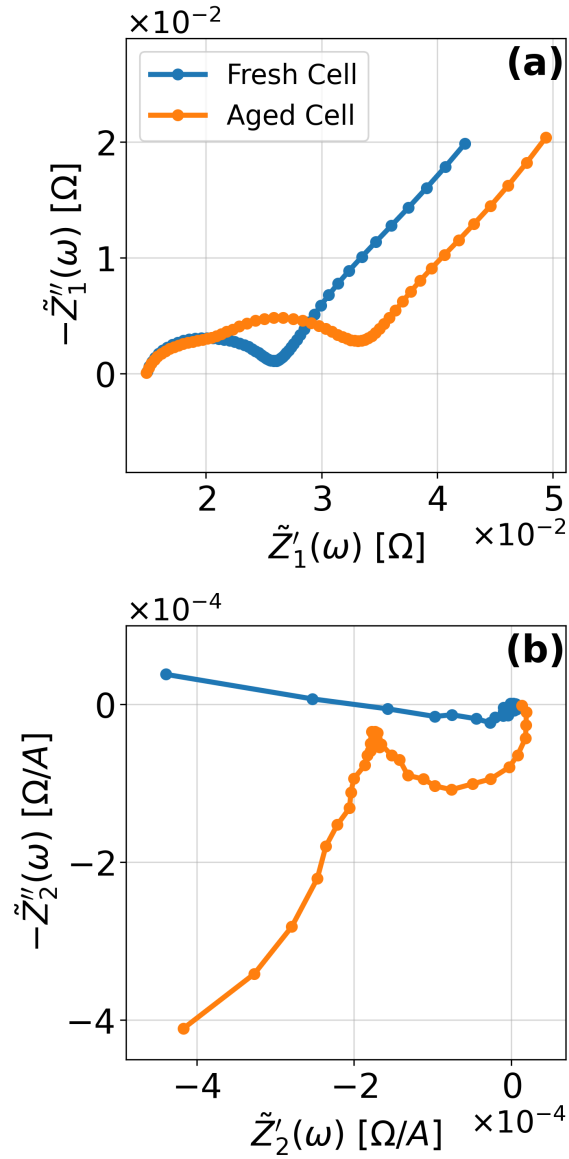


Figure 5.7. Nyquist plots of the measured (a) EIS and (b) 2nd-NLEIS spectra for fresh and aged cells at 30% SoC.

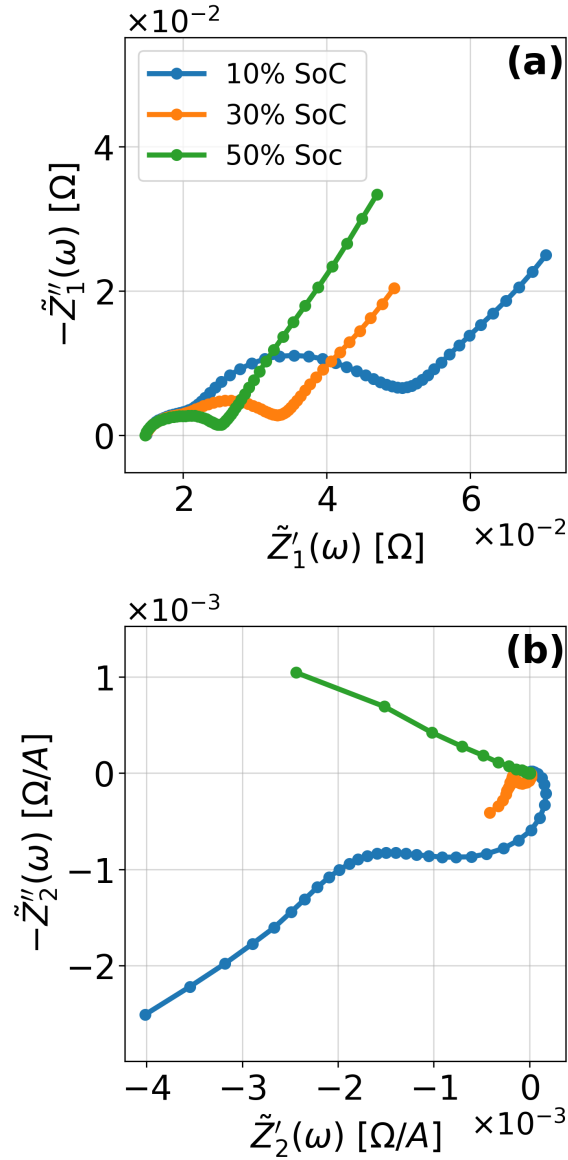


Figure 5.8. Nyquist plots of the measured (a) EIS and (b) 2nd-NLEIS spectra at 10%, 30%, and 50% SoC of cells aged for 100 cycles at 2C.

5.3.4 Cell-to-Cell Variation

Because this is a new technique, we have looked at cell-to-cell reproducibility in experimental measurements and model-based fitting. **Figure 5.9a** and **Figure 5.9b** show an overlay of triplicate fresh-cell EIS and 2nd-NLEIS experimental spectra at 30% SoC. Aside from a small ohmic offset seen among the EIS spectra at the highest frequencies (**Figure 5.9a**), presumably attributable to

variability in cell contact resistances, there is rather good data reproducibility among the Samsung cells. However, differences are clearly visible in the fresh cell 2nd-NLEIS datasets (**Figure 5.9b**) at the lowest frequencies where the spectra are dominated by thermo-diffusion processes. The absence of appreciable mid-frequency 2nd-NLEIS features in any of the fresh cells indicates symmetric charge transfer on both electrodes. For comparison, **Figure 5.9c-d** show triplicate aged-cell EIS and 2nd-NLEIS data at 30% SoC. Aside from small EIS ohmic variations in **Figure 5.9c**, the main differences among the triplicate measurements are, again, at the lowest frequencies in the 2nd-NLEIS spectra, where thermo-diffusion dominates. Unlike the fresh cells, aged cells (**Figure 5.9d**) show a significant and reproducible mid-frequency 2nd-NLEIS charge transfer loop, indicating that cycle aging of the cells systematically breaks the symmetry of charge transfer in the cathode at this SoC (30%), as noted above. The fact that low frequency 2nd-NLEIS shows appreciable variance among the fresh and aged datasets, whereas the EIS dataset simply shows an ohmic offset, is perhaps driven by the amplifying impact of the 2nd-NLEIS full-cell signal having negative parity, so small half-cell differences among two large signals get amplified when subtracting one from the other.

Figure 5.9e-p separate each triplicate EIS and 2nd-NLEIS dataset for fresh and aged cells and use SSO fitting to parameterize the experimental data. The optimized parameters are summarized in **Table A5-IV** and **Table A5-V** (see **Supplemental Materials** for corresponding parameter confidence intervals). [103] As expected from the experimental observations given above, the estimated parameters show good reproducibility for the high and mid frequency interfacial charge transfer features, especially when the charge transfer time scales are well separated and the data has a distinctive 2nd-NLEIS charge transfer loop, whereas the parameters from the low frequency thermo-diffusion region show more variations.

In general, we see the fitting parameters associated with interfacial charge transfer processes are more tightly clustered than parameters associated with thermodynamics and diffusion processes that dominate at low frequencies. The confidence intervals for the fitting, shown in the **Supplemental Materials**, [103] are aligned with this observation. In particular, the parameters derived from our diffusion impedance models have large fitting confidence intervals, meaning the parameters have high uncertainty, whereas the kinetic parameters derived from the porous electrode models tend to have narrower confidence intervals and represent more certain estimates. The replicate data shows that small changes in the measured spectra can lead to substantial variation in parameter estimates, again, pointing to the value of developing 2nd-NLEIS post-processing and fit weighting schemes that accounts for measurement error structure.

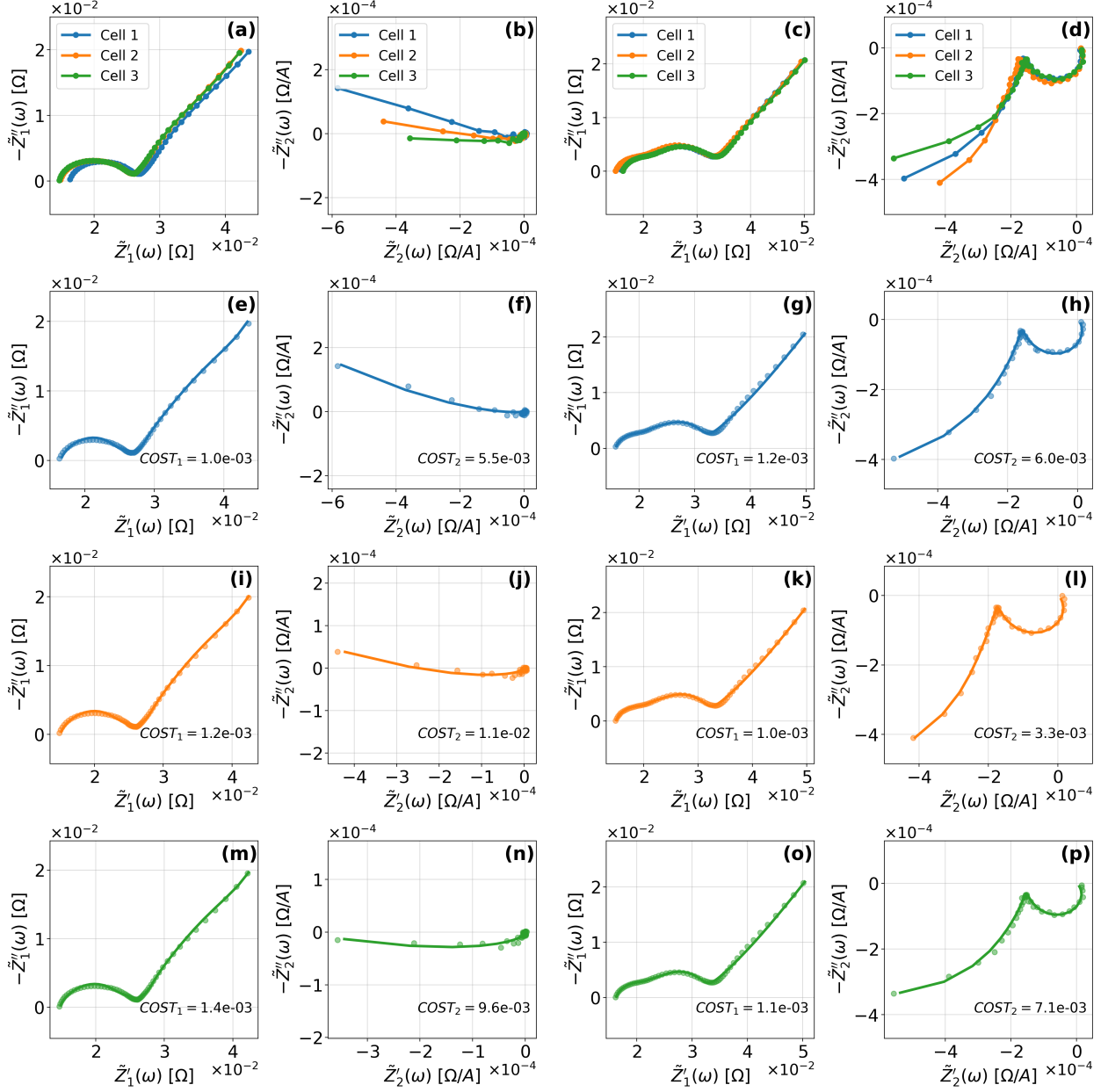


Figure 5.9. Triplicate measurements of EIS and 2nd-NLEIS are overlaid for 30% SoC fresh cells in (a) and (b), respectively, and mildly-aged cells in (c) and (d), respectively. The corresponding SSO best-fit models of the EIS and 2nd-NLEIS data are shown for: fresh cell 1 in (e,f); aged cell 1 in (g,h); fresh cell 2 in (i,j), aged cell 2 in (k,l); fresh cell 3 in (m,n), aged cell 3 in (o,p).

5.4 CONCLUSIONS AND IMPLICATIONS

In this paper we constructed full-cell analytical models and fit them to previously-reported experimental EIS and 2nd-NLEIS spectra acquired at various states of charge (SoC) for fresh and

mildly aged Samsung 18650 NMC/LMO|C cells. The full-cell EIS model and data have positive parity—the signal arises from the sum of the half-cells—whereas the full-cell 2nd-NLEIS model and data have negative parity—the signal arises from the difference between anode and cathode half-cells. The EIS full-cell model has 12 distinct parameters, whereas the 2nd-NLEIS full-cell model depends on all 12 EIS parameters plus 4 additional parameters unique to the 2nd-NLEIS model. Two distinct parameter estimation routines were used to fit models to data. Sequential optimization (SO) first fit the 12 EIS model parameters to the EIS data, then fixed the EIS parameters when fitting the remaining 4 parameters to the 2nd-NLEIS data. SO fitting largely failed to capture the features of 2nd-NLEIS data, despite high quality EIS fits. The Sequential-simultaneous optimization (SSO) method allowed all 16 parameters to be simultaneously fit, taking full advantage of the complementary parity of EIS and 2nd-NLEIS data to obtain internally self-consistent parameters across both datasets.

Perhaps the most significant new finding from quantitative SSO fitting of the experimental data is the fact that mild aging (a mere 0.7% decline in capacity) not only increases the charge transfer resistance of the cell appreciably, a process reported in the literature and attributed to the cathode surface layer formation, but degradation also breaks the cathode charge transfer symmetry at moderate and low SoC. This is a new result not easily ascertained for a battery without the methods shown here for the first time.

While this work shows the benefit of using SSO optimization to find the most internally self-consistent parameters across the opposite parity EIS and 2nd-NLEIS datasets, it also leaves many avenues for further exploration. For example, in the original work that generated the experimental data used here, data quality in the EIS spectra was assessed with a Kramers-Kronig

analysis, but there was no similar data quality assessment for the 2nd-NLEIS results. In short, 2nd-NLEIS has no parallel advanced fitting strategies comparable to EIS, such as the use of measurement models to assess the measurement error structure, nor weighting schemes that use this error structure in parameter estimation.[91] When using SSO to simultaneously fit EIS and 2nd-NLEIS spectra, sophisticated post-processing requires parallel strategies for both the EIS and 2nd-NLEIS spectra, so we have used none of these methods here. However, the model development shown in Part I is a promising foundation for developing parallel nonlinear data quality and weighting schemes that can take advantage of SSO fitting.

Throughout the paper we have noted confidence intervals for all parameters can be found in the **Supplementary Materials**. [103] Of special note has been the high uncertainty for parameters associated with thermo-diffusion. Extracting interpretable full-cell parameters from nonlinear diffusion impedance models will require a rethinking of the experimental measurements. In particular, we believe cell testing to much lower frequencies are needed to shift from the Warburg-like thermo-diffusion behavior to the more purely imaginary “chemical capacitance” dominated by the bulk insertion thermodynamics. With lower frequency data, the linear EIS fit will likely lead to a much clearer definition of the diffusion time scale for each electrode, and thereby improve our confidence in estimates of the linear response scaling factor (A_W) and nonlinear thermodynamic parameter (κ). High confidence determination of A_W and κ would provide a direct measure of interfacial thermodynamics that is complementary to the bulk insertion thermodynamics we have measured in these same cells with slow scan (<C/20) charge discharge profiles and fitting using the multi-species, multi-reaction (MSMR) model.[14]

Overall, this work has advanced the quantitative analysis of EIS and 2nd-NLEIS spectra acquired in two electrode cells. We show that a simple analytical EIS and 2nd-NLEIS model captures nearly all key traits of the experimental datasets while remaining tractable for parameter estimation. Nonetheless, it is worthwhile noting some of the simplifications used here compared to our previous P2D-based EIS and NLEIS models.[34] For example, here we assume the resistivity of the solid is negligible compared to the resistivity of the electrolyte, eliminating any ohmic losses from the solid. Moreover, the electrolyte-filled pores in the electrode are represented by a lumped effective electrolyte resistance as a single fitting parameter; in the P2D model intrinsic electrolyte resistivity and geometric factors associated with the porous electrode are defined individually. Likewise, no electrolyte concentration gradients were considered, wholly ignoring the nature of binary electrolyte theory where ohmic and diffusive transport are coupled. Finally, the fact that the experimental cell under test had a mixed cathode material was completely ignored in the analysis. In short, there are many experimental and analysis avenues opened up by this work, and many questions to answer on how best to perform, analyze, and extract information from complementary EIS and 2nd-NLEIS datasets.

5.5 APPENDIX

Table A5-I. Voltages for EIS and 2nd-NLEIS measurements.

State of Charge (SoC)	10%	30%	50%
Voltage	3.500	3.643	3.820

Table A5-II. Best fit parameters of EIS and 2nd-NLEIS for 10%, 30%, and 50% SoC fresh cells.

Physicochemical Parameter		10% SoC	30% SoC	50% SoC
Inductance	$L_0 \times 10^{-8} [\Omega]$	4.4	4.2	6.0
Ohmic region	$R_{ohmic} [\Omega]$	0.014	0.014	0.013
Cathode	$R_{pore,c} [\Omega]$	0.11	0.072	0.00087
	Charge Transfer	$R_{ct,c} [\Omega]$	0.00061	0.00015
		$C_{dl,c} [F]$	36.72	85.69
		$R_{ct,c} \times C_{dl,c} [s]$	0.022	0.013
	Diffusion	$A_{W,c} [\Omega]$	0.083	0.0014
		$\tau_c [s]$	9997	17.42
		$\kappa_c [V^{-1}]$	-3.4	-0.16
	NLEIS Parameters	$\varepsilon_c [-]$	0.09	0
		$R_{pore,a} [\Omega]$	0.0198	0.045
Anode	Charge Transfer	$R_{ct,a} [\Omega]$	0.0027	0.0014
		$C_{dl,a} [F]$	0.45	0.96
		$R_{ct,a} \times C_{dl,a} [s]$	0.0012	0.0013
		$A_{W,a} [\Omega]$	0.00016	0.000003
	Diffusion	$\tau_a [s]$	0.46	0.51
		$\kappa_a [V^{-1}]$	-2.33	-379.2
	NLEIS Parameters	$\varepsilon_a [-]$	0	0

Table A5-III. Best fit parameters of EIS and 2nd-NLEIS for 10%, 30%, and 50% SoC aged cells.

Physicochemical Parameter		10% SoC	30% SoC	50% SoC
Inductance	$L_0 \times 10^{-8} [\Omega]$	9.1	8.7	8.6
Ohmic region	$R_{ohmic} [\Omega]$	0.0135	0.0137	0.0137
Cathode	$R_{pore,c} [\Omega]$	0.0634	0.0197	0.0024
	$R_{ct,c} [\Omega]$	0.0124	0.00738	0.0043
	$C_{dl,c} [F]$	11.0	5.08	1.37
	$R_{ct,c} \times C_{dl,c} [s]$	0.14	0.043	0.0059
	$A_{W,c} [\Omega]$	0.112	0.095	0.027
	$\tau_c [s]$	1523.1	1877.9	388.4
	$\kappa_c [V^{-1}]$	5.69	2.32	21.5
	$\varepsilon_c [-]$	0.11	0.064	0
	$R_{pore,a} [\Omega]$	0.025	0.011	0.075
	$R_{ct,a} [\Omega]$	0.00065	0.0016	0.0003
Anode	$C_{dl,a} [F]$	1.14	0.58	3.12
	$R_{ct,a} \times C_{dl,a} [s]$	0.00074	0.00093	0.00094
	$A_{W,a} [\Omega]$	0.023	0.032	0.0012
	$\tau_a [s]$	534.3	614.8	3.71
	$\kappa_a [V^{-1}]$	97.9	13.0	4.38
	$\varepsilon_a [-]$	0	0	0

Table A5-IV. Best fit parameters of EIS and 2nd-NLEIS for Cell-to-Cell replicates. 30% SoC fresh cells.

Physicochemical Parameter		Cell 1	Cell 2	Cell 3		
Inductance		$L_0 \times 10^{-8}[\Omega]$	5.2	4.2	3.0	
Ohmic region		$R_{ohmic} [\Omega]$	0.015	0.014	0.014	
Cathode	Charge Transfer	$R_{pore,c} [\Omega]$	0.071	0.072	0.073	
		$R_{ct,c} [\Omega]$	0.00013	0.00015	0.00017	
		$C_{dl,c} [F]$	148.1	85.69	88.4	
		$R_{ct,c} \times C_{dl,c} [s]$	0.019	0.013	0.015	
		$A_{W,c} [\Omega]$	0.000923	0.0014	0.00014	
	Diffusion	$\tau_c [s]$	11.43	17.42	17.15	
		NLEIS	$\kappa_c [V^{-1}]$	-0.31	-0.16	-0.18
	Parameters	$\varepsilon_c [-]$	0	0	0	
	Anode	Charge Transfer	$R_{pore,a} [\Omega]$	0.075	0.045	0.048
			$R_{ct,a} [\Omega]$	0.00087	0.0014	0.0013
$C_{dl,a} [F]$			1.77	0.96	1.09	
$R_{ct,a} \times C_{dl,a} [s]$			0.0015	0.0013	0.0014	
$A_{W,a} [\Omega]$			0.000057	0.000003	0.0000014	
Diffusion		$\tau_a [s]$	10.6	0.51	0.42	
		NLEIS	$\kappa_a [V^{-1}]$	-302.3	-379.2	-947.6
Parameters		$\varepsilon_a [-]$	0	0	0	

Table A5-V. Best fit parameters of EIS and 2nd-NLEIS for Cell-to-Cell replicates. 30% SoC aged cells.

Physicochemical Parameter		Cell 1	Cell 2	Cell 3	
Inductance	$L_0 \times 10^{-8}[\Omega]$	14.1	8.7	11.7	
Ohmic region	$R_{ohmic} [\Omega]$	0.014	0.0137	0.015	
Cathode	$R_{pore,c} [\Omega]$	0.020	0.0197	0.018	
	Charge Transfer	$R_{ct,c} [\Omega]$	0.00678	0.00738	0.00718
		$C_{dl,c} [F]$	5.52	5.08	5.07
		$R_{ct,c} \times C_{dl,c} [s]$	0.037	0.037	0.036
	Diffusion	$A_{W,c} [\Omega]$	0.095	0.095	0.1
		$\tau_c [s]$	2000	1877.9	2000
	NLEIS	$\kappa_c [V^{-1}]$	4.39	2.32	4.01
	Parameters	$\varepsilon_c [-]$	0.065	0.064	0.061
	Anode	$R_{pore,a} [\Omega]$	0.010	0.011	0.009
		Charge Transfer	$R_{ct,a} [\Omega]$	0.0017	0.0016
$C_{dl,a} [F]$			0.55	0.58	0.51
$R_{ct,a} \times C_{dl,a} [s]$			0.00094	0.00093	0.0010
Diffusion		$A_{W,a} [\Omega]$	0.035	0.032	0.031
		$\tau_a [s]$	621.9	614.8	539.1
NLEIS		$\kappa_a [V^{-1}]$	16.7	13.0	17.2
Parameters		$\varepsilon_a [-]$	0	0	0

Chapter 6.

CONNECTING CHARGE TRANSFER ASYMMETRY TO SURFACE RECONSTRUCTION INDUCED LATTICE STRAIN IN AGED NI-RICH NMC||C CELLS

Note 1: this chapter will be submitted and published as an article

Note 2: additional contributors include Victor Hu, Erica Eggleton, and Linnette Teo for data

Abstract

Surface reconstruction is one of the key degradation mechanisms for Ni-rich NMC cathodes. The reconstructed surface pins the bulk NMC lattice and introduces lattice strain that alternates the electronic structure as well as the charge transfer mechanism of NMC particles. The physical connection between strain and charge transfer remains unclear. Non-invasive and *in-situ* electrochemical characterization of surface reconstruction is required to bridge the gap and provide physical interpretations. Here, we study an aging dataset collected with commercial NMC532||C cells for up to 1500 high C-rate cycles. Combining differential voltage analysis, EIS, and 2nd-NLEIS, a state of charge (SOC) and state of health (SOH) dependent asymmetric charge transfer ($\varepsilon_c > 0$) that favors oxidation (delithiation) reaction is observed for the bulk NMC particles. The degree of asymmetry grows with aging and decreases as the SOC of the cell increases from 10% to 50%, which aligns with the direction of lattice strain reduction and suggests a lattice strain growth induced asymmetric charge transfer. The electrochemical strategies introduced in this work, thus, provide a unique and non-invasive way to probe the surface reconstruction of NMC cathode as well as asymmetry parameters that can be measured and modeled to optimize the performance of commercial lithium-ion batteries.

6.1 INTRODUCTION

Transportation electrification, clean energy storage, and portable electronics have driven the advancement of lithium-ion batteries (LIBs) toward higher energy density, better rate performance, and longer cyclability.[199,200] Nickel-rich lithium nickel manganese cobalt oxide (NMC) is one of the most adopted high-energy-density chemistries (> 270 Wh/kg in full cell). [200–203] However, the higher energy density and capacity comes with diminished cycling stability, [135,136,204,205] evidenced by oxygen evolution and surface reconstruction found in post-mortem and operando half-cell experiments. [136,206,207]

Recent advances in the operando understanding of surface reconstruction in nickel-rich NMC materials is inspiring materials engineering strategies that can translate to the full-cell environment. For example, Xu et al. have identified an NMC fatigue mechanism that results from surface reconstruction and the formation of a Ni-rich rock salt surface phase. [135] Using operando XRD measurements, they observed that the active/fresh NMC particles can freely expand and contract in the *c*-lattice plane, while the fatigued NMC has restricted contraction and expansion due to the increased lattice strain introduced by the surface rocksalt phase. Their observations suggest that the fatigued bulk NMC is still electrochemically active but only to a maximum accessibility of $\sim 75\%$ delithiation. To mediate the lattice strain and surface reactivity induced fatigue, Wang et al. proposed a strain-retardant approach that introduces a coherent perovskite phase at the surface of Ni-rich NMC, which has been demonstrated to significantly reduce the lattice strain evolution during cycling with improved cycling stability. [208] Similarly, Liu et al. synthesized a compositional and structural dual-gradient NMC cathode with a disordered surface to prevent surface reconstruction and hence the growth of lattice strain. [123] Electrochemically, Zhang et al. have formed a conformal surface layer *in situ* with brief external electrical shorting,

which has been visualized using cryogenic electron microscopy. [19] They have observed improved coulombic efficiency and capacity retention with the presence of a conformal surface layer. Chemically, fluorine with higher electronegativity has been thought of as an optimal substitution for oxygen in Ni-rich NMC and Mn-rich disordered rocksalt (DRX) materials. [209–212] Sharma et al. show that surface coating of fluorine can effectively reduce the surface reactivity and hence improve the cyclability. [136]

In engineered batteries, degradation pathways can only be understood and managed in the context of the two-electrode cell configuration where cathode and anode are porous, separated by microns with little electrolyte inventory, and increasingly involve composite active materials such as Si/C anodes and mixed metal oxide cathodes. [213–219] Electroanalytical disaggregating and assigning changes in the electrochemical response to an individual electrode in a two-electrode experiment with both electrodes actively participating. This complication is further amplified by the heterogeneous porous electrodes and proprietary electrolytes used in high performance batteries, from mixed metal oxides on the cathode to composite Si/C anodes. [217–219]

To enable chemistry specific characterization in commercial LIBs, the complementary parity introduced by the direction-sensitive current experienced at each electrode must be investigated and utilized. That is, a single electrochemical measurement yields two pieces of information — the positive parity signal (+) arises from the sum, while the negative parity signal (-) takes the difference between positive and negative electrode responses. This holds for voltage profile (-) and its corresponding dV/dQ (+) for slow scan ($< C/20$) thermodynamics measurements, which can be used to anchor specific electrochemical reactions and states. The complementary parity also shows up in electrochemical impedance spectroscopy (EIS), where EIS holds positive parity (+) and the second harmonic nonlinear EIS (2nd-NLEIS) possesses negative parity (-).

As an excellent surface probe, the rate-sensitive charge transfer resistance (R_{ct} ; measured by EIS) and mechanism-sensitive charge transfer asymmetry parameter (ε ; measured by 2nd-NLEIS) can enable non-invasive and *in-situ* surface characterization for commercial LIBs. Specifically, the mechanistic sensitivity of 2nd-NLEIS can reveal structure-related degradation at the surface, such as surface reconstruction induced lattice strain growth. In this work, we demonstrate an electroanalytical framework that enables accurate and non-invasive full cell characterization with a mixed cathode of NMC532 and LMO through combined low C-rate (C/20) thermodynamic measurements, EIS, and 2nd-NLEIS with physics-based modeling. [14,26,34,35,46] The utilization of the well-characterized NMC532||graphite system enables analysis to focus only on full cell behavior with support from numerous half-cell literature. [24,220–222] The thermodynamic modeling ensures the accurate identification of specific NMC states, while EIS and 2nd-NLEIS analysis help to gain physical insight into the interfacial reactivity and lattice strain growth through the measurement of charge transfer resistances (R_{ct}) and asymmetry parameters (ε).

Upon aging, we have identified asymmetric charge transfer that favors the delithiation of NMC materials at low cell SOC. We propose and attribute the asymmetric behavior to the increased lattice strain induced by the surface reconstruction for the first 600 cycles of cycling, which has been widely observed in these Ni-rich NMC materials. [135,222–224] After 600 cycles, many other potential degradation mechanisms can affect the aging, which leads to variation in the charge transfer mechanism and requires further investigation. [225] Overall, our method provides a unique way to connect ex-situ and laboratory understanding of Ni-rich NMC to commercial LIBs characterization electrochemically. The ability to do *in-situ* characterization with commercial LIBs will be invaluable and can accelerate the optimization of Ni-rich NMC cathode commercially.

Lastly, our method is universal and can be easily generalized to other electrochemical systems that follow Butler-Volmer Kinetics to understand mechanistic evolution during operation.

6.2 METHODS

6.2.1 Battery Cycling

The batteries tested here are 1.5 Ah Li NMC|C Samsung cells (INR 18650–15 M). The detailed cycling protocol can be found in our previous work. [14] Briefly, these cells first experienced five C/2 break-in cycles from 2.5 to 4.2 V. Cycle aging was then performed for 300, 600, 900, and 1500 cycles with 2.67C (4A) CCCV charge to 4.2 V and CC discharge to 2.5V. After cycle aging, a C/20 charge-discharge profile was collected to support differential voltage analysis.

6.2.2 EIS and 2nd-NLEIS Measurements

EIS and 2nd-NLEIS measurements were performed after cycle aging, where the cells were first discharged to 2.5 V. The cells were then charged to 10% (3.5 V), 30% (3.64 V), and 50% (3.82 V) SOC respectively based on the open circuit voltage determined in previous work. [26] The exact perturbation was determined by driving the system to generate enough second harmonic signal, while avoiding measurable third harmonic signals. The general rule of thumb for this system is to have a voltage response greater than 5 mV but less than 20 mV.

6.2.3 Differential Voltage (dV/dQ) Analysis with Multi-Species, Multi-Reaction (MSMR) Model

Here, we adopted a fitting and optimization routine from our previous work to analyze the C/20 capacity check data using the Multi-Species, Multi-Reaction (MSMR) Model. [14] Briefly, the full cell voltage response at any cell capacity (Q) will be the difference between the potential of the

positive electrode (U^+) with a capacity Q^+ and the potential of negative electrode (U^-) with capacity Q^- ,

$$V_{cell} = U^+(Q^+) - U^-(Q^-). \quad (6.1)$$

On the other hand, the full cell differential voltage response ($\frac{dV_{cell}}{dQ_{cell}}$) is the sum between the positive electrode differential voltage response ($\frac{dU^+(Q^+)}{dQ^+}$) and negative electrode differential voltage response ($\frac{dU^-(Q^-)}{dQ^-}$),

$$\frac{dV_{cell}}{dQ_{cell}} = \frac{dU^+(Q^+)}{dQ^+} + \frac{dU^-(Q^-)}{dQ^-}. \quad (6.2)$$

The summation nature in **Equation 6.1** combined with the subtraction nature in **Equation 6.2** that rely on a set of self-consistent data is a complementary parity that can improve the parameter identifiability when analyzed simultaneously. The MSMR model is fitted within this framework to identify the individual electrode reaction and overall electrode slippage and provide physical insights to complement the impedance analysis.

The MSMR model was first proposed by Verbrugge et al. as a thermodynamic model that enables the identification and matching of individual electrochemical reactions within insertion electrodes. [226] It was first proposed as a half-cell model, while a combined full-cell analysis with a half-cell model for cathode and anode was adopted in this work. Experimentally, it has been identified that the Samsung cell contains a mix of LiNMC/LMO cathode and graphite anode. [14] Therefore, a total of 12 chemical reactions are used, which consist of 4 NMC reactions, 2 LMO reactions, and 6 graphite reactions. The parameter identification begins with physical parameters from Verbrugge et al., [226] which are summarized in **Table S6-I**. Mathematically, the MSMR model describes each insertion reaction using a fraction of lithium occupancy, which can be

directly converted to the extensive Li^+ capacity (Q) at each state of lithiation (SOL). The potential dependent Li^+ capacity for each insertion reaction (Q_k) can then be described as,

$$Q_k = \frac{Q_{k,tot}}{1 + \exp\left[\frac{f(U - U_k^0)}{\omega_k}\right]}, \quad (6.3)$$

where $Q_{k,tot}$ is the total capacity for reaction k , $f = \frac{F}{RT}$, U is the half-cell potential vs. Li/Li^+ , U_k^0 is the standard potential for reaction k vs. Li/Li^+ , and ω_k describes the nonideality of reaction k . The attractive, ideal, repulsive Nernstian behavior is described by $\omega_k < 1$, $\omega_k = 1$, and $\omega_k > 1$ respectively. The corresponding differential capacity can then be written as,

$$\frac{dQ_k}{dU}(U) = -\frac{Q_{k,tot}}{\omega_k} \frac{f \exp\left(\frac{f(U - U_k^0)}{\omega_k}\right)}{\left[1 + \exp\left(\frac{f(U - U_k^0)}{\omega_k}\right)\right]^2}. \quad (6.4)$$

By summing over the N insertion reaction, the half-cell capacity, differential capacity, and total insertion capacity can be obtained as follows,

$$Q(U) = \sum_{k=1}^N Q_k(U), \quad (6.5)$$

and

$$\frac{dQ}{dU}(U) = \sum_{k=1}^N \frac{dQ_k}{dU}(U), \quad (6.6)$$

and

$$Q_{tot} = \sum_{k=1}^N Q_{k,tot}. \quad (6.7)$$

Plugging **Equations 6.3-6.7** into **Equations 6.1** and **6.2** provides a lumped battery model that can describe the C/20 slow scan voltage profile. This model was optimized with the experimental data using the method described in [14]. Lastly, the slippage and parameter identification are done only for the charging profile to provide a self-consistent estimation with the impedance measurement.

6.2.4 Simultaneous EIS and 2nd-NLEIS Analysis

Simultaneous analysis of EIS and 2nd-NLEIS is enabled with well-controlled experiments as demonstrated in our previous work. [26] In short, a pure but slightly larger sinusoidal current perturbation (I) than normal EIS is required to drive the system to the weakly nonlinear regime, where the voltage response (V) is greater than 5 mV (EIS criterion) but less than 20 mV (2nd-NLEIS criterion) for the system under tests. Under this condition, the EIS (linear) and 2nd-NLEIS (nonlinear) responses can be obtained simultaneously given the nonlinear nature of charge transfer kinetics and thermodynamics in LIBs. Mathematically, the current response is of the form,

$$I = \Delta I \times \exp(j\omega t) \quad (6.8)$$

and,

$$V = \tilde{V}_1 \times \exp(j\omega t) + \tilde{V}_2 \times \exp(j2\omega t) + h.o.t. \quad (6.9)$$

where $j = \sqrt{-1}$, ΔI is the amplitude of the current modulation (Amp) with angular frequency ω (radians/s), $\tilde{V}_1$ and $\tilde{V}_2$ are the voltage outputs at the excitation frequency ω and the second harmonic 2ω respectively, and *h.o.t* is the negligible higher harmonic voltage responses. It is important to note that, if a cosine wave is used to perturb the system, $\tilde{V}_2$ should be scaled by 1/2 to reflect the correct trigonometry. The EIS ($\tilde{Z}_1$) and 2nd-NLEIS ($\tilde{Z}_2$) response can then be defined as the following,

$$\tilde{Z}_1(\omega) = \frac{\tilde{V}_1}{\Delta I} \quad (6.10)$$

and,

$$\tilde{Z}_2(\omega) = \frac{\tilde{V}_2}{(\Delta I)^2}. \quad (6.11)$$

Equations 6.10 and **6.11** describe EIS and 2nd-NLEIS response for each half-cell reaction, which can be used to obtain full-cell EIS and 2nd-NLEIS models. The corresponding half-cell definition in **Equation 6.10** suggests that the full-cell EIS is the sum of cathode impedance ($\tilde{Z}_1^+$) and anode impedance ($\tilde{Z}_1^-$). Additionally, the inductor (L_0) and resistor (R_0) are included to capture the high frequency response from lead inductance, contact resistance, and separator resistance.

$$\tilde{Z}_{1,cell} = L_0 + R_0 + \tilde{Z}_1^+ + \tilde{Z}_1^-. \quad (6.12)$$

On the other hand, **Equation 6.11** suggests that the full cell 2nd-NLEIS arises from the difference between the cathode ($\tilde{Z}_{2,+}$) and anode ($\tilde{Z}_{2,-}$). Because the inductance and ohmic resistance cannot generate any nonlinear response, the full cell 2nd-NLEIS can be written as,

$$\tilde{Z}_{2,cell} = \tilde{Z}_2^+ - \tilde{Z}_2^-. \quad (6.13)$$

Equations 6.8-6.13 pave the mathematical foundation for the simultaneous analysis of EIS and 2nd-NLEIS.

6.2.5 Analytical Porous Electrode and Numerical Transmission Line Model

To benchmark the degradation of individual electrodes, variations of the porous electrode model are developed. Here, a combination of the analytical porous electrode (APE) model [35] and numerical transmission line model (TLM) is adopted from our previous work. For a fresh cell or even a mildly aged cell, where the surface contribution is negligible, a simple porous electrode response is usually present. A transmission line representation can be adopted to describe it as shown in **Figure S6.1**, which accounts for the macrohomogeneity of the porous electrode. Through the electrode thickness (d), the porous electrode can be visualized as N parallel connections of interfacial electrochemical reaction in series with the pore electrolyte resistance. The interfacial electrochemical reaction typically includes charge transfer, double layer effects, and solid-state

diffusion, which can be described by a Randles circuit with solid-state diffusion. This model also ignores the solids phase resistance, which is negligible in typical LIB systems with conductive carbon coating. An analytical solution is available for this simple case for EIS and 2nd-NLEIS response. As the cell ages, the growth of the surface layer begins to contribute to the impedance response. An additional time constant is usually required to describe the impedance that arises from the surface reconstruction. As a result, the adoption of transmission line representation can easily describe the growth of the surface layer. This is done by adding another surface Randles circuit in series with the bulk Randles circuit (**Figure S6.1b**). Though this model requires minimum physical parameters to describe the surface layer contribution, the analytical solution of this model is unavailable. Instead, we have proposed a numerical transmission line framework to approximate the continuous solution for EIS and 2nd-NLEIS in **Chapter 3**. It is worth noting that the model described by **Figure S6.1b** can be reduced to the APE model shown in **Figure S6.1a** if the surface layer has minimal contribution to the overall impedance, which can be used to validate the transmission line framework. We have also shown in **Chapter 3** that the TLM model converges to the APE model with experimental data that does not show surface contribution. In this work, these two models are used interchangeably. Nevertheless, the APE model is mainly used for impedance data that does not show the surface contribution to reduce the model complexity, while the TLM model is used to capture significant surface contributions. A spherical particle geometry is assumed for the cathode and a platelet-like particle geometry is assumed for the anode to provide the best description of the solid-state diffusion behavior. We do note that diffusion response is not unique and generally comes with larger uncertainty.

Lastly, the reaction kinetics of the NMC cathode is assumed to follow the Butler-Volmer equation (**Equation 6.14**), which has also been confirmed by Park et al. using combined operando XRD, physics-based modeling, and EIS approach. [227]

$$i = i_0 \times \left\{ \exp\left(\alpha_a \frac{nF}{RT} \eta\right) - \exp(\alpha_c \frac{nF}{RT} \eta) \right\} \quad (6.14)$$

where i is electrode current density, i_0 is the exchange current density, $\alpha_a = 0.5 + \varepsilon$ is the anodic charge transfer coefficient, $\alpha_c = 0.5 - \varepsilon$ is the cathodic charge transfer coefficient, n is the number of electrons involved in the reaction, F is the Faraday constant, R is the gas constant, T is the temperature, $\eta = E - E_n$ is the overpotential, E is the measured electrode potential, and E_n is the equilibrium potential. As shown in **Equation 6.14**, the Butler-Volmer equation is determined by two main physical parameters: exchange current density i_0 and asymmetry parameter ε . Exchange current density describes the rate of charge transfer reaction, which is inversely related to the apparent charge transfer resistance. As a result, the spike in the charge transfer resistance from EIS measurements indicates a slowdown in the charge transfer rate. On the other hand, the asymmetry parameter probes the evolution in the charge transfer mechanism, which is highly sensitive to the changes in the electrochemical environment as the battery ages. For example, fresh NMC particles have been observed and demonstrated to behave symmetrically, while aged NMC particles exhibit an asymmetric charge transfer reaction. [46] The mechanism-sensitive nature of the asymmetry parameter (only probed with 2nd-NLEIS) can help to gain mechanistic insight into the NMC degradation, which will be discussed later.

6.3 ELECTROCHEMICAL CHARACTERIZATION OF COMMERCIAL 18650 CELLS

The proprietary design and optimization of commercial lithium-ion batteries (LIBs) make it challenging to replicate their exact chemical environments. Consequently, laboratory cell

dissection coupled with coin cell experiments are less representative of the actual LIB system. [228] Electrochemical tests, thus, play an indispensable role in the *in-situ* and *in-operando* characterization of these commercial cells. The segregation of individual electrode responses from two-electrode experiments remains challenging, especially with mixed active materials in the cathode and anode. Fortunately, the complementary parity introduced by the direction-sensitive current definition enables accurate parameterization of these full-cell experiments non-invasively. That is, a single measurement can generate two pieces of information, where one comes from the sum of positive and negative electrode responses and the other takes the difference between positive and negative electrode responses.

In thermodynamic measurements (C/20 cycling), the full cell voltage is the difference between positive and negative half-cell potentials, while the full cell dV/dQ arises from the sum between dU/dQ of positive and negative electrodes (**Methods**). The slow scan ($<C/20$) voltage profile can then be analyzed simultaneously with its corresponding dV/dQ to enable the extraction of electrode slippage information and dominant chemical reactions in the electrode with a multi-species, multi-reaction (MSMR) model. [14,226,229] Similarly, in impedance measurements, the linear EIS signal arises from the sum of positive and negative electrode responses, while the 2nd-NLEIS signal is the difference between positive and negative electrode responses. The combined analysis of EIS and 2nd-NLEIS can hence enable the extraction of rate (R_{ct}) and mechanism (ε) sensitive parameters respectively, where charge transfer response in the 2nd-NLEIS appears only when $\varepsilon \neq 0$. [35,46] Consequently, thermodynamic modeling can help to anchor the same NMC states for impedance analysis, while impedance analysis can help to gain physical insights about the interfacial charge transfer kinetics.

The cells tested here were 1.5 Ah Li NMC/LMO||C Samsung cells (INR 18650–15 M). These cells were cycled with a C-rate of 2.67 C at 25 °C for up to 1500 cycles. Impedance measurements were performed at 10%, 30%, and 50% full cell state of charge (SOC) at the end of 300, 600, 900, and 1500 cycles to evaluate the SOC and state of health (SOH) dependence. The two standard deviation capacity retention profiles at 2.67C along with apparent cell charge transfer resistance are shown in **Figure 6.1a**. The capacity degradation in these cells exhibits a sublinear behavior, which is usually attributed to the formation of a solid electrolyte interface (SEI). [230] The capacity degradation also comes with a growth of cell charge transfer resistance, especially at low SOC, which agrees with the literature. [24]

To gain further insights into the overall impedance growth and capacity degradation, **Figure 6.1b** shows example EIS spectra at 30% for fresh, 300, and 600 cycles along with the equivalent circuit model (ECM) required to describe the battery system, and **Figure 6.1c** shows the zoom-in view of high frequency EIS response. The overall impedance growth is mainly attributable to the medium to low frequency response (assigned to the cathode, as is routine in the literature [24,231,232]), while the high frequency response (assigned to the anode, as is routine in the literature [24,231–233]) exhibits negligible impedance growth. The stabilization of anode impedance (as suggested by the impedance above 100 Hz (Δ)) is likely due to the continuous growth of SEI as suggested by the sublinear capacity degradation (**Figure 6.1a**). [24,230] On the other hand, a slowdown in the reaction time scale with the emergence of another charge transfer time constant is observed for the cathode (as demonstrated by the shift of 100 Hz (Δ), 1 Hz ($\square$), and 10 mHz ($\star$) marker toward the left of impedance spectra). As a result, the cathode is responsible for the gradual deviation between 2.67 C and C/20 capacity retention such that the actual cathode gradually approaches a higher state of lithiation (SOL) at the end of the charge.

Overall, the description of these observations requires a simplified ECM with at least three charge transfer time constants and one diffusion time constant, along with essential ohmic resistance and inductance as shown in **Figure 6.1b**, though the key porous electrode response is not included.

To ensure accurate characterization of the exact NMC states using EIS and 2nd-NLEIS, the C/20 charging profile and its corresponding dV/dQ data are fitted and optimized using the MSMR model. The extracted thermodynamic parameters are summarized in **Table S6-II - Table S6-VI**. The mean absolute errors of the fitting are summarized in **Table S6-VII**. The individual half-cell potentials at each SOC for both cathode and anode are obtained and summarized in **Table S6-VIII**. The corresponding fitting and optimization results are shown in **Figure S6.2 - Figure S6.7**. The SOL for fresh, 600 cycles, and 1500 cycles are shown in **Figure 6.1d**. The SOL of the cathode and anode are shown from dark red/blue to light red/blue respectively for 10%, 30%, and 50% SOC. As the cell ages, a clear slippage in the individual half-cell voltage is observed, which highlights the shift to lower SOL. As shown in **Figure 6.1d**, the 10% and 30% SOC data directly reside in the first two dQ/dV peaks, which only correlate to NMC states. At 50% SOC, overlapping NMC and LMO responses are present, while the extracted thermodynamic parameters suggest the response is still dominated by NMC. These suggest that NMC aging is responsible for all the cathode impedance growth in these cells.

Overall, thermodynamics modeling enables the segregation of individual chemical reactions from these standard full-cell electrochemical tests and ensures consistent analysis for specific NMC states. This information, when further combined with 2nd-NLEIS analysis, can be a unique *in-situ* full cell probe for mechanism-sensitive degradation in the NMC cathode.

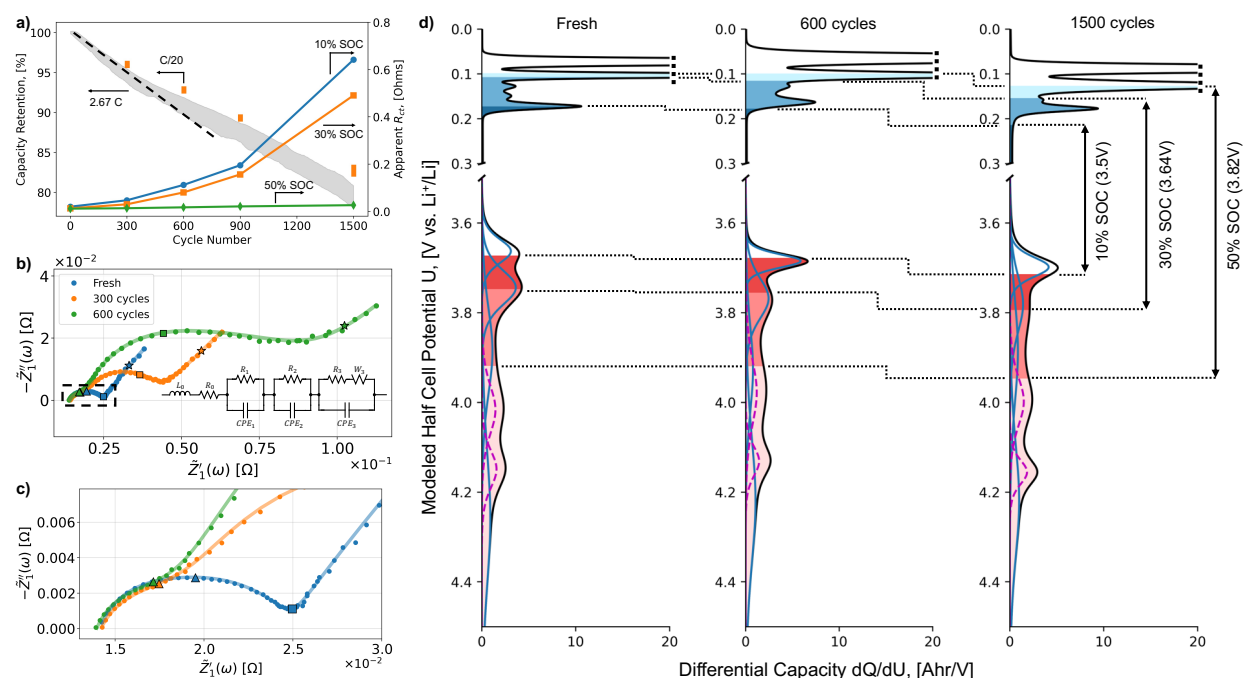


Figure 6.1. a) The two standard deviation capacity retention plot (gray) for cell replicates cycles with a current of 2.67 C at $T = 25^\circ\text{C}$. The orange squares represent the C/20 capacity retention check at the end of each stopping cycle. b) EIS spectra at 30% SOC for fresh, 300 cycles, and 600 cycles with the corresponding three-time constants equivalent circuit model. c) The enlarged high frequency impedance response. The 100 Hz ($\triangle$), 1 Hz ($\square$), and 10 mHz ($\star$) points are labeled in EIS for b) and c). d) State of lithiation for fresh, 600, and 1500 cycles. The blue line represents NMC states and purple dashed-line represents LMO states.

6.4 INTERFACIAL CHARGE TRANSFER KINETICS PROBED WITH COMBINED EIS AND 2ND-NLEIS ANALYSIS

The EIS and corresponding 2nd-NLEIS of 10%, 30%, and 50% SOC for the fresh, 300 cycles, and 600 cycles are shown in **Figure 6.2a-f**. For each SOC, the SOH dependence of EIS and 2nd-NLEIS is shown in **Figure S6.8**. Both EIS and 2nd-NLEIS exhibit strong SOC/SOL and SOH dependence for charge transfer dynamics, while the solid-state diffusion cannot be fully understood quantitatively with our data due to its dependence on equilibrium potential and the limited low frequency (<3 mHz) data. Therefore, interfacial charge transfer kinetics is the focus of this work.

The fresh cell EIS (**Figure 6.2a**) shows a gradual increase in the charge transfer resistance with the decrease of SOC (an increase of SOL) that agrees with the literature. [24] The fresh cell 2nd-NLEIS (**Figure 6.2d**) exhibits diffusion-sensitive features with a negligible nonlinear charge transfer response, indicating a symmetric charge transfer reaction. That is, lithiation and delithiation are equally favored on both the cathode and the anode.

As the cell has been cycle-aged for 300 cycles (<5% capacity loss), both the linear and nonlinear charge transfer dynamics begin to show stronger SOC dependence with reduced charge transfer rate (increasing charge transfer resistance), while the solid-state diffusion remains almost constant, signaling the negligible changes in the bulk diffusion behavior (**Figure 6.2b,e**). The aging, thus, has mostly impacted the interfacial kinetics, which can also be rationalized from the transition from a teardrop shape to a semi-circle shape charge transfer response in EIS. As reported in the literature, surface reconstruction happens throughout cycling, which progressively thickens the surface rocksalt layer. [222] That is, a relatively thin layer of rocksalt is expected to be present at an earlier stage of cycling (~ 300 cycles). The absence of a clear multiple time-constant charge transfer indicates the negligible contribution from the thin surface rocksalt to the interfacial charge transfer rate. However, the presence of semi-spirals in 2nd-NLEIS (**Figure 6.2g**) suggests a breakdown of charge transfer symmetry as a consequence of surface reconstruction and changes in the charge transfer mechanism. That said, the thin surface rocksalt layer is already affecting the charge transfer mechanisms at the bulk, even though it can barely be observed in normal EIS measurements.

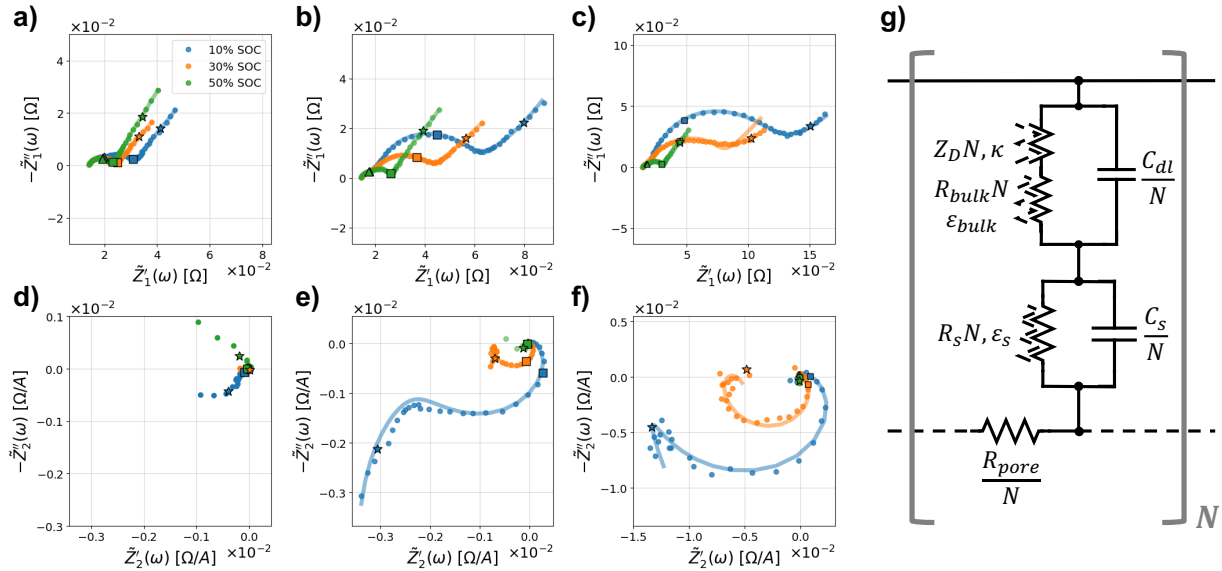


Figure 6.2. EIS (a-c) and 2nd-NLEIS (d-f) spectra at 10, 30, and 50% SOC for a,d) fresh, b,e) 300 cycles, and c,f) 600 cycles. The dots are EIS and 2nd-NLEIS measurements at each frequency, while the lines show the best-fit model used for parameterization. The 100 Hz (Δ), 1 Hz ($\square$), and 10 mHz ($\star$) points are labeled for both EIS and 2nd-NLEIS. g) The transmission line model that provides a physical description of the growth of cathode impedance.

For intermediate-aged cells that experienced 600 fast charge and discharge cycles, more aggressive growth in the charge transfer resistance is observed for 10% and 30% SOC (**Figure 6.2c**), which limits the appearance of the solid-state diffusion response in the frequency range probed. On the other hand, the solid-state diffusion responses remain almost unchanged at 50% SOC as compared to fresh cells (**Figure S6.8c**). Additionally, a flattening of the charge transfer semi-circle response is observed and is a signature of the growth of the surface contribution to the impedance at medium (30%) SOC. The 2nd-NLEIS results (**Figure 6.2f**) follow a similar trend with nonlinear charge transfer dominance for 10% and 30 % SOC. This again shows that the growth in the charge transfer resistance (slowdown in the charge transfer rate) is mainly due to the changes in the interfacial charge transfer mechanism characterized by the asymmetric charge transfer behavior. Moreover, although not clear at this point, it is emerging that the overall

impedance at 30% SOC is growing at a faster rate than 10% SOC, which indicates a surface-dominant interfacial charge transfer.

After the cells have been cycled for more than 900 cycles (**Figure S6.8**), the interfacial charge transfer is so sluggish that it significantly overlaps with the solid-state diffusion, which significantly complicates the quantitative analysis. Qualitatively, it can be observed that the rocksalt surface has a significant contribution to the charge transfer resistance especially at low SOC, while the charge transfer dynamics remain facile at 50% SOC. It is clear, at these stages, that aging is not limited to surface reconstruction. Other degradation can appear and contribute to the growth of the EIS and 2nd-NLEIS response. For example, for the first time, a crossover has been observed for nonlinear charge transfer response at 10% and 30% SOC (**Figure S6.8**), signaturing a distinct interfacial charge transfer dynamic that has evolved as the cell ages. As a result, quantitative analysis was limited to the first 600 cycles.

The quantitative analysis of the first 600 cycles data is done with the APE and TLM models introduced in the **Methods**. The representation transmission line model is shown in **Figure 6.2g**. To capture the surface contribution, our model considers charge transfer resistance and asymmetry parameters for both bulk and surface, while bulk properties are extracted for analysis. The best fit charge transfer resistance (R_{ct}) and asymmetry parameter (ϵ) for the bulk/surface interface for different SOH is shown in **Figure 6.3**. The extracted parameters confirm a significant growth of bulk charge transfer resistance for 10% and 30% SOC over aging, while minor growth has been observed for bulk at 50% SOC. Moreover, the experimentally observed and calculated bulk charge transfer resistances at 50% SOC are much smaller compared to other SOC. Such a facile charge transfer indicates that the electrochemical reaction is purely limited by the electrolyte conductivity at 50% SOC. On the other hand, the charge transfer is rate-limited for 10% and 30% SOC,

confirming that the changes in the charge transfer mechanism are responsible for the reduction of the charge transfer rate. This conclusion is also supported by the extracted asymmetry parameters. First, a similar increasing trend in the bulk symmetry parameter is observed for the first 600 cycles at 10% and 30% SOC, indicating that continuous symmetry breaking and changes in the charge transfer mechanism are responsible for a slowdown in the charge transfer rate. The symmetric charge transfer observed for 50% SOC verifies the persistence of the same charge transfer mechanism. The minor changes in the charge transfer resistance are likely due to the loss of active surface area rather than the mechanistic changes at the surface.

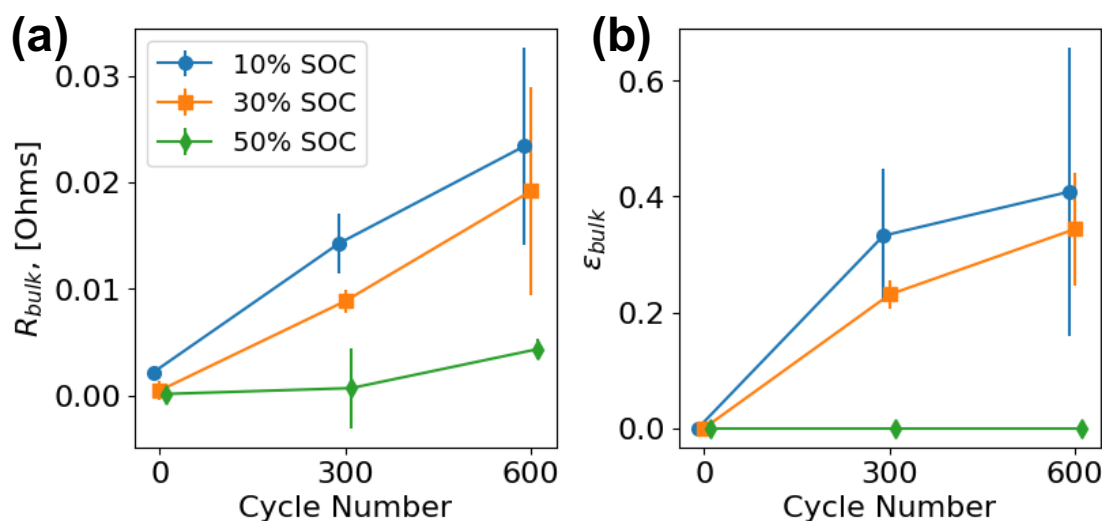


Figure 6.3. Identified a) bulk charge transfer resistance and b) bulk asymmetry parameter for the first 600 cycles. The error bar describes the confidence interval of the fitted parameter with respect to the data.

6.5 LATTICE STRAIN DRIVEN ASYMMETRIC CHARGE TRANSFER AT THE BULK ROCKSALT INTERFACE

Charge transfer resistance, as a surface-determined rate parameter, can increase with many possible physical degradation mechanisms. To provide a physical interpretation for the growth of charge transfer resistances and asymmetric charge transfer behavior, different degradation

mechanisms at the surface need to be explored first. Particle cracking and loss of contact are the most well-known degradation mechanisms that will lead to changes in the surface environments. These can reduce the active surface area and hence the effective charge transfer rate. However, these degradations only change the active surface area without altering the actual charge transfer mechanism (i.e., the charge transfer reaction remains the same). As a result, they cannot introduce a highly SOC/SOL sensitive charge transfer resistance as shown in **Figure 6.2**. Instead, mechanism changes are required to induce significant changes in the rate constant. In the literature, it has been proposed that Li/Ni antisite mixing in the bulk particles is responsible for the degradation of NMC. [234] However, this phenomenon is likely changing the bulk diffusion mechanism rather than the interfacial charge transfer. Of all possible degradation mechanisms, only surface reconstruction can lead to changes in the actual charge transfer mechanism and hence lead to an order of magnitude difference in charge transfer rate as the SOC/SOL changes.

The reconstructed surface appears as a Ni-rich rocksalt layer as NMC evolves oxygen. [223] It is usually assumed that the main component of this surface layer is NiO-like, which is responsible for the increase in the charge transfer resistance. [135] Understanding the actual composition of this Ni-rich layer is then essential to correlate it to the rate and mechanism changes. It has been demonstrated that the surface layer forms uniformly around the particle. [135] To enable charge transfer, the surface cannot be pure NiO in the rocksalt phase. That is, lithium transfer at the surface requires a vacant octahedral site and an intermediate tetrahedral site so that the lithium can enter the bulk electrode (o-t-o diffusion). [235,236] If pure NiO is present, surface charge transfer is impossible due to the lack of vacant sites; intercalation of lithium ions into the bulk NMC will be significantly limited, thus limiting the reversible capacity. The fact that lithium can continuously intercalate into bulk NMC indicates that the surface must have a solid solution

of Li^+ , Ni^{2+} , and O^{2-} that enables the lithium hopping between the interstitial octahedral and tetrahedral sites.

Owing to the fact that Li^+ ($r = 0.76 \text{ \AA}$) is similar in size to Ni^{2+} ($r = 0.69 \text{ \AA}$), [237] we propose that the Ni-rich surface layer is behaving like a disordered rocksalt (DRX) structure with randomly distributed Li^+ and Ni^{2+} in the structure. In fact, many recent works have demonstrated the formation of the disordered phase at the surface of LiCoO_2 and NMC811, which further supports the proposed Ni-rich DRX structure at the surface of Ni-rich NMC. [222,238] **Figure 6.4a** shows a schematic for the proposed structure evolution at the surface from layered oxide to DRX, and finally to NiO using tetrahedral clusters. In the fresh cell, lithium can only migrate through 1-TM channels by the o-t-o mechanism. [235,236] As the cell ages, Nickel at the surface can be reduced to 2+ by forming a rocksalt phase, which is accompanied by Li/Ni antisite mixing. A DRX structure can form at this stage, which is dominated by 0-TM, 1-TM, and L3-TM (highlighted in light green), while 2-TM, D3-TM, and 4-TM clusters gradually appear. Interfacial charge transfer can happen and Li^+ can easily migrate through a 0-TM site or a 1-TM site at the surface. As the cell further ages, a thicker and more reduced layer will form. The surface will then be dominated by 2-TM, D3-TM, and 4-TM (highlighted in light pink), which hinders the lithium migration within the surface and thus limits the surface charge transfer. Lastly, if NiO is uniformly formed (consisting of only 4-TM sites) at the surface, the particle is at the end of its life and charge transfer is not possible. Given that the surface layer is only nanometers thick at an early stage of cycling (<600 cycles), [222] the limited diffusion sites (4-TM site) are unlikely to dominate and affect cell capacity, and indeed highly reversible cycling behavior is demonstrated. However, these sites can significantly affect the surface structure, the charge transfer mechanism, and thus the charge transfer rate.

Structurally, operando-XRD results from Xu et al. and others have demonstrated that the c lattice parameter changes significantly for Ni-rich NMC during charge and discharge. [135,220] Specifically, upon charging (delithiation), the c lattice parameter will first increase due to the electrostatic repulsion between the oxide layers. [122] After reaching a maximum at around 50-70% SOC (50–30% SOL), depending on the composition of NMC, the oxide layers begin to contract, leading to a reduced c lattice parameter. This process is believed to be reversible for fresh cells with minimal lattice strain, as the lattice expansion and contraction are purely driven by electrostatic repulsion and attraction. As the cell ages and cycles to a higher voltage (low SOL), the formation of a Ni-rich rock salt surface layer is favored due to the reduction of $\text{Ni}^{3+/4+}$ to Ni^{2+} , which reconstructs the surface that can pin the bulk lattice. Due to the size similarity of Li^+ and Ni^{2+} , the lattice parameter of the surface rocksalt layer remains mostly unchanged during cycling. The pinned surface layer is then responsible for the growth of the lattice strain in Ni-rich NMC, which can be evaluated by the lattice mismatch in the c direction. Here, we adopted the nomenclature proposed by Xu et al., where the lattice strain/mismatch in the c direction can be described using **Equation 6.15**. [135]

$$\text{lattice strain} = \frac{d_{003} - d_{111} \times 6}{d_{111} \times 6} \times 100\%, \quad (6.15)$$

where d_{003} is the d spacing of the (003) lattice plane in NMC, and d_{111} is the d spacing of the (111) lattice plane in NiO, which is expected to be slightly smaller than the actual spacing with the presence of lithium. With **Equation 6.15**, the potential-dependent lattice strain for NMC532 with a reconstructed surface layer can be calculated with operando XRD from Weber et al. [220] As shown in **Figure 6.4b**, the cathode experiences a larger lattice strain at high SOL (low SOC) with the presence of the pinning rocksalt surface. This lattice strain reduces during delithiation, which reaches a minimum close to zero at around 70% SOC. This lattice strain is expected to be minimal

for fresh cells, while the growth in the thickness of the surface layer is expected to significantly increase the lattice strain by the pinning effects as introduced by Xu et al. [135] Combined with our observation in EIS and 2nd-NLEIS, the observed asymmetric charge transfer can be explained by the lattice strain induced by the surface rocksalt layer. We propose that the continuous growth in lattice strain due to the formation of a thick rocksalt layer is responsible for the growth in charge transfer resistance and asymmetry parameters for the first 600 cycles. First, negligible 2nd-NLEIS charge transfer response has been observed for fresh cells (**Figure 6.2d**), indicating that a symmetric charge transfer reaction is present in a strain-free state. As the cell ages, nonlinear charge transfer behavior emerges (**Figure 6.2e-f**). With the identified $\varepsilon_c > 0$ ($\alpha_a > 0.5$; $\alpha_c < 0.5$) for the cathode at low SOC (high SOL), the oxidation (delithiation) reaction is kinetically favored over the reduction (lithiation) reaction, which is well aligned with the direction of lattice strain reduction (**Figure 6.4b**). In other words, the transition from a high strain state to a low strain state is kinetically favored at low SOC (high SOL). As the cell is charged, the lattice strain is reduced and approaches zero at a medium SOC (50% SOC). A symmetric charge transfer reaction was observed at this stage, indicating a symmetric charge transfer reaction in this strain-free state. This SOC dependence is in excellent agreement with the trend in the proposed lattice strain. The growth in the asymmetry parameter (ε_c) for the first 600 cycles at each SOC further supports our lattice strain theory. Namely, the increased lattice strain at each SOC leads to an increased asymmetry in the charge transfer reaction. The lattice mismatch hinders the lithium migration from the surface to the bulk, hence limiting the charge transfer rate at the bulk. These together show that the growth of lattice strain is responsible for the direction-sensitive asymmetric charge transfer reaction and reduction of charge transfer rate for the bulk NMC electrode. We conclude that the charge transfer asymmetry, which has been heavily overlooked in the literature of electrochemical testing and

modeling, is an indicative and measurable physical parameter to probe the surface reconstruction and lattice strain evolution in Ni-rich NMC materials. The addition of the asymmetry parameter will further improve the modeling of the NMC-type LIBs and any battery system that follows Butler-Volmer kinetics.

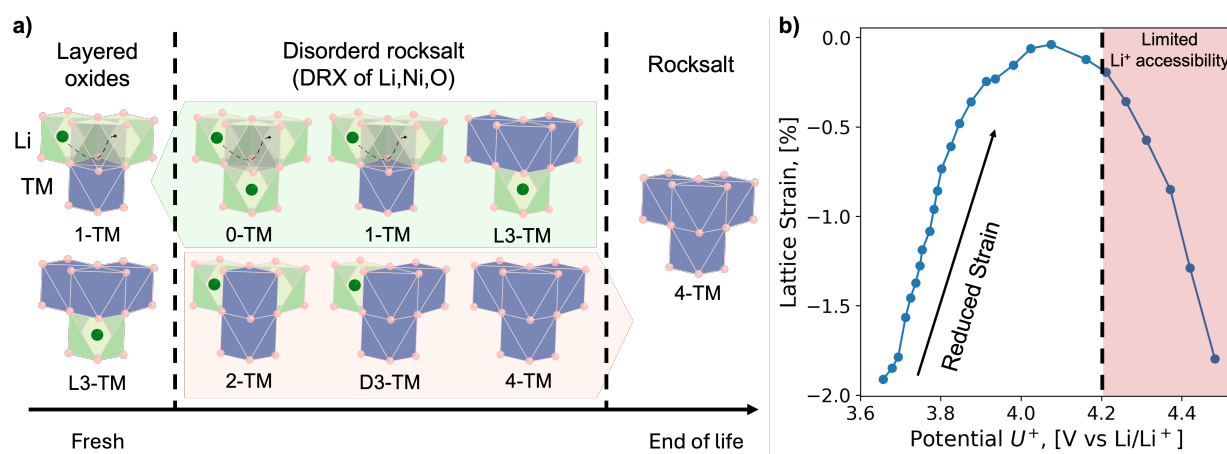


Figure 6.4. a) Evolution of possible tetrahedral clusters and their corresponding lithium mobility at the surface. [235] b) The calculated lattice strain for NMC532 based on **Equation 1**. The voltage dependent c lattice parameter is extracted from Weber et al. [220] for polycrystalline NMC532. d_{111} is assumed to be 2.41217 Å for NiO as suggested by Sasaki et al. [239]

6.6 CONCLUSION AND FUTURE OUTLOOKS

For a long time, the charge transfer kinetics have been assumed to be symmetric in the NMC cathode. Here, we have shown that aged NMC exhibits asymmetric charge transfer behavior that can be correlated to its structural evolution, which has been overlooked in the literature. The understanding of the asymmetric behavior is enabled by the simultaneous data collection and analysis of EIS and 2nd-NLEIS, where the rate (R_{ct}) and mechanism/asymmetry (ε) sensitive characterization can be obtained non-destructively. This information has been confidently extracted for the first 600 cycles, which can be directly correlated to the surface reconstruction of the NMC cathode. Aging can also arise from other degradation mechanisms after 600 cycles. The

asymmetric behavior will then have contributions from multiple aging sources. The asymmetry parameter (ε) at this point will lose direct mapping to one degradation mechanism but can still provide a physical and electrochemical representation of the overall degradation and the corresponding mechanism changes. Yet, the ability to correlate mechanistic changes to SOH will be extremely valuable for the modeling of NMC-based commercial LIBs.

Beyond the battery health characterization, accurate battery modeling is essential to optimize the performance and lifetime of LIBs. Simultaneous data collection and analysis of EIS and 2nd-NLEIS can also revolutionize the parameterization of Butler-Volmer Kinetics in LIBs with NMC cathode. That is, the EIS and 2nd-NLEIS can not only provide all essential physical parameters in Butler-Volmer Kinetics but also enhance the estimation accuracy with the complementary EIS and 2nd-NLEIS signal. Ultimately, the consideration of the symmetric information in the battery model can enable the development of better state estimation and control algorithms, which can operate in a feedback loop to optimize the performance and lifetime of LIBs.

6.7 APPENDIX

6.7.1 Supplementary Figures

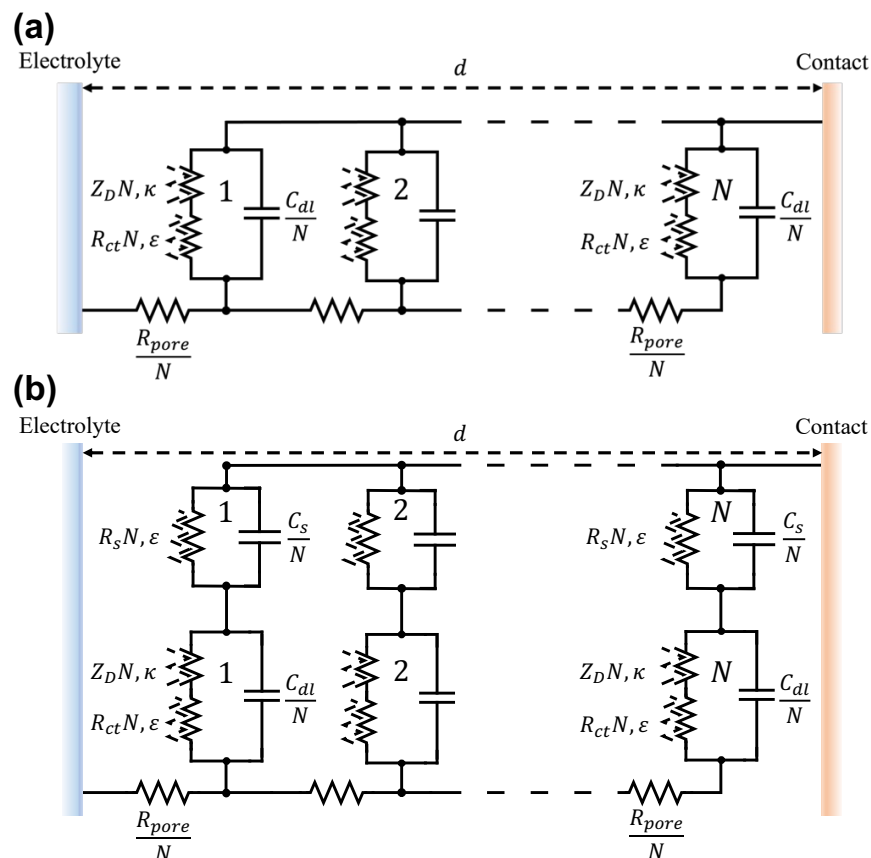


Figure S6.1. Transmission line representation for a) typical porous electrode without surface layer and b) porous electrode with surface layer. R_s is the surface charge transfer resistance, C_s is the surface capacitance, R_{ct} is the bulk charge transfer resistance, C_{dl} is the double layer resistance of the bulk, Z_D is the diffusion impedance, R_{pore} is the pore electrolyte resistance, κ is the differential voltage parameter, ε is the charge transfer asymmetry parameter, and N is the number of repeating elements over the thickness of d . When $N \rightarrow \infty$, a) and b) approach a continuous limit, where the analytical solution is available for a).

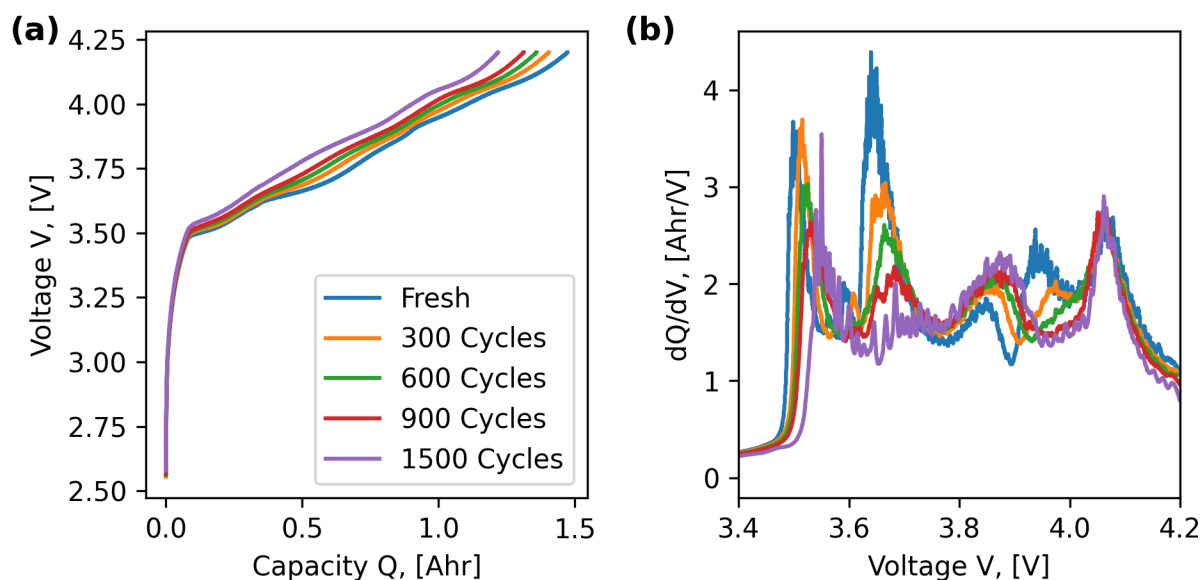


Figure S6.2. (a) C/20 charging profile and (b) its corresponding dQ/dV results at the end of cycling for fresh, 300 cycles, 600 cycles, 900 cycles, and 1500 cycles.

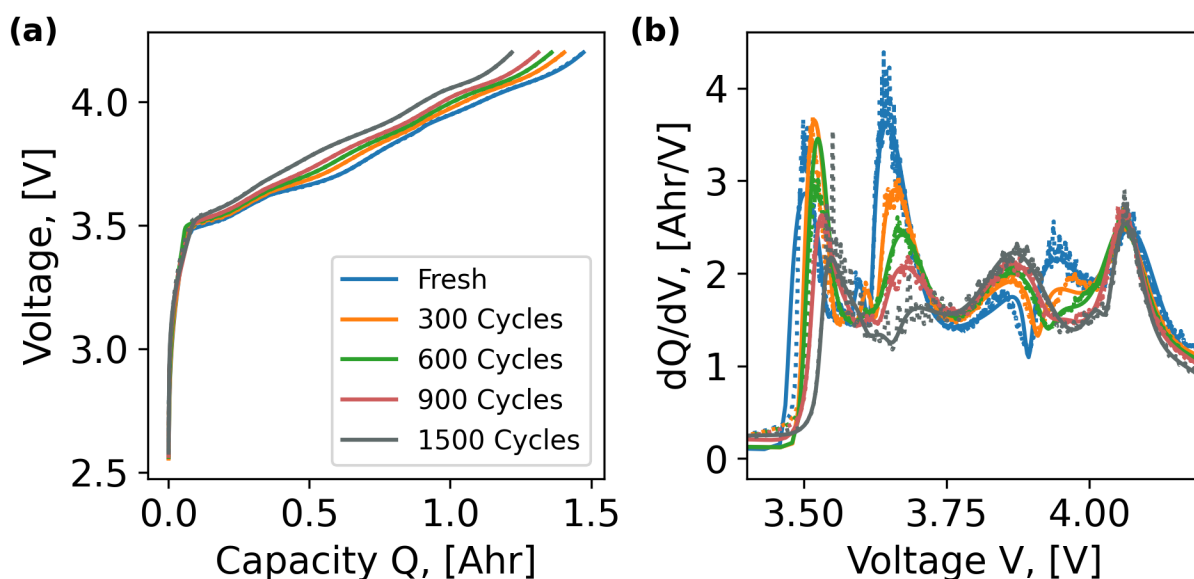


Figure S6.3. The optimized full-cell (a) charging profile and its corresponding (b) dQ/dV results at the end of cycling for fresh, 300 cycles, 600 cycles, 900 cycles, and 1500 cycles. The dots represent the experimental data, while the lines represent the fitted curves. The mean absolute errors (MAE) of the fitting results were summarized in **Table S6-VII**.

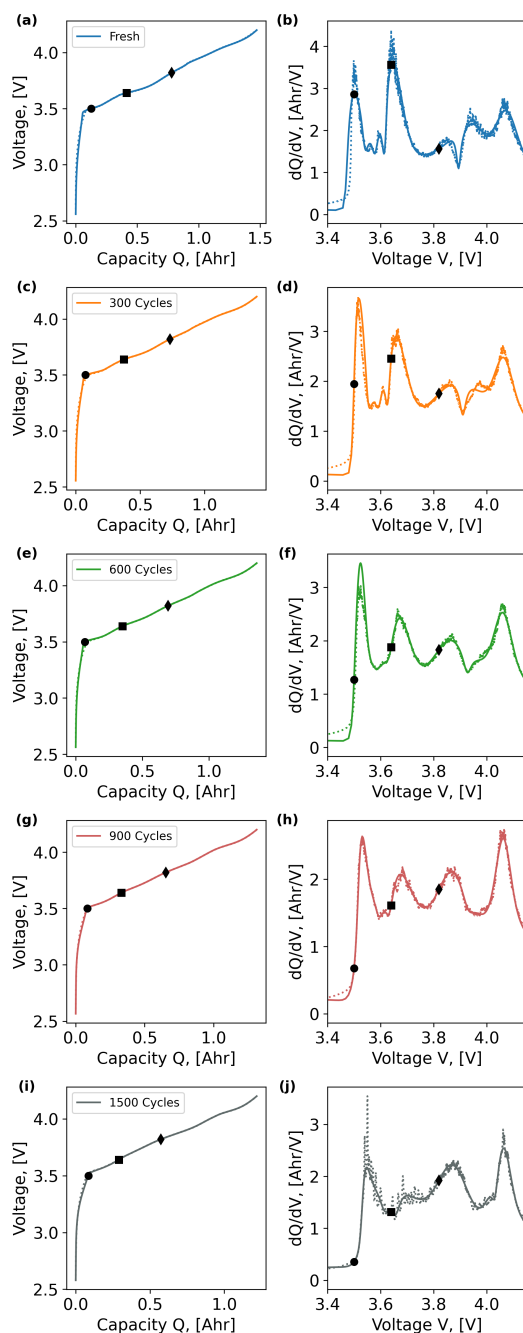


Figure S6.4. The individually optimized full-cell charging profile and its corresponding dQ/dV results at the end of cycling for (a-b) fresh, (c-d) 300 cycles, (e-f) 600 cycles, (g-h) 900 cycles, and (i-j) 1500 cycles. The dotted-lines represent unfiltered charging profile and dQ/dV , while the solid-lines represent the best fit results. The $\circ$, $\diamond$, and $\square$ are representing the measurements at 10% (3.5 V), 30% (3.64 V), and 50% (3.82 V) SOC respectively.

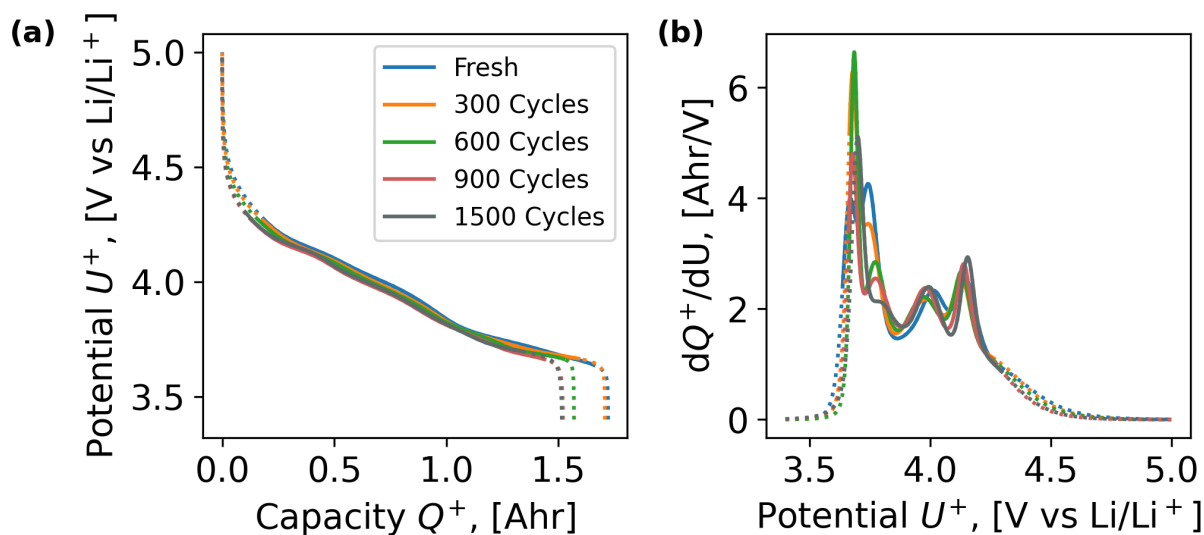


Figure S6.5. The optimized cathode half-cell (a) charging profiles and their corresponding (b) dQ^+/dU^+ results at the end of cycling for fresh, 300 cycles, 600 cycles, 900 cycles, and 1500 cycles. The dotted-lines represent the full voltage range half-cell potential obtained from curve fitting, while the solid-lines are the capacity range utilized to obtain the full-cell response.

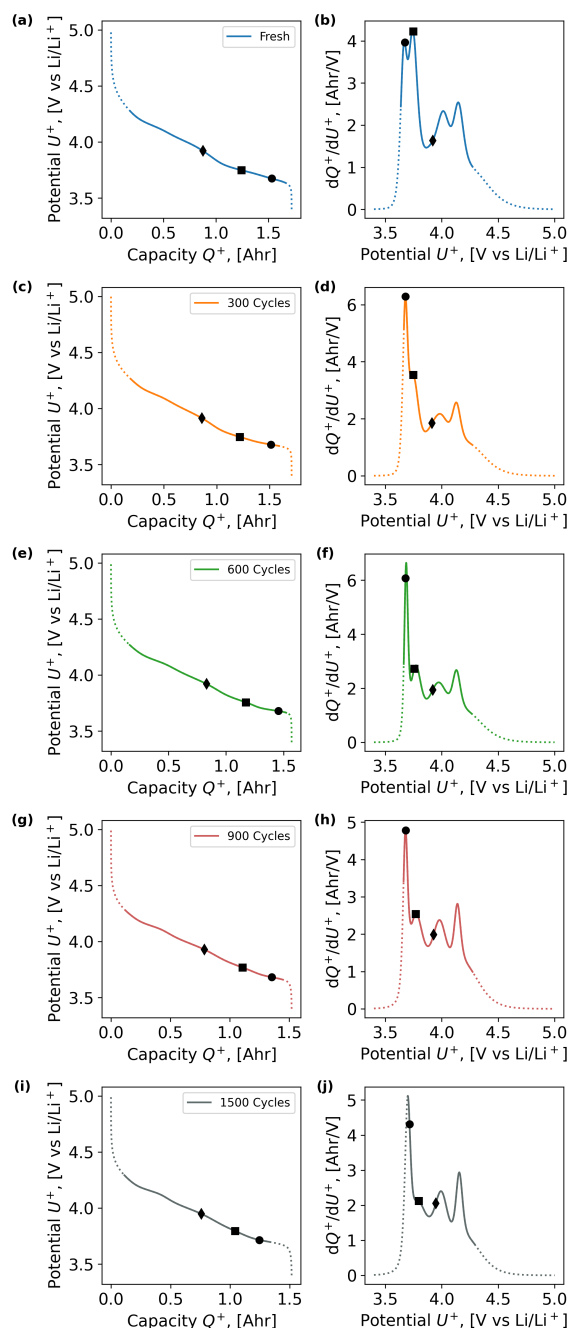


Figure S6.6. The individually optimized cathode half-cell charging profile and its corresponding dQ^+/dU^+ results at the end of cycling for (a-b) fresh, (c-d) 300 cycles, (e-f) 600 cycles, (g-h) 900 cycles, and (i-j) 1500 cycles. The dotted-lines represent the full voltage range half-cell potential obtained from curve fitting, while the solid-lines are the capacity range utilized to obtain the full-cell response. The $\circ$, $\diamond$, and $\square$ are representing the actual cathode half-cell potential that has been measured at 10% (3.5 V), 30% (3.64 V), and 50% (3.82 V) SOC respectively.

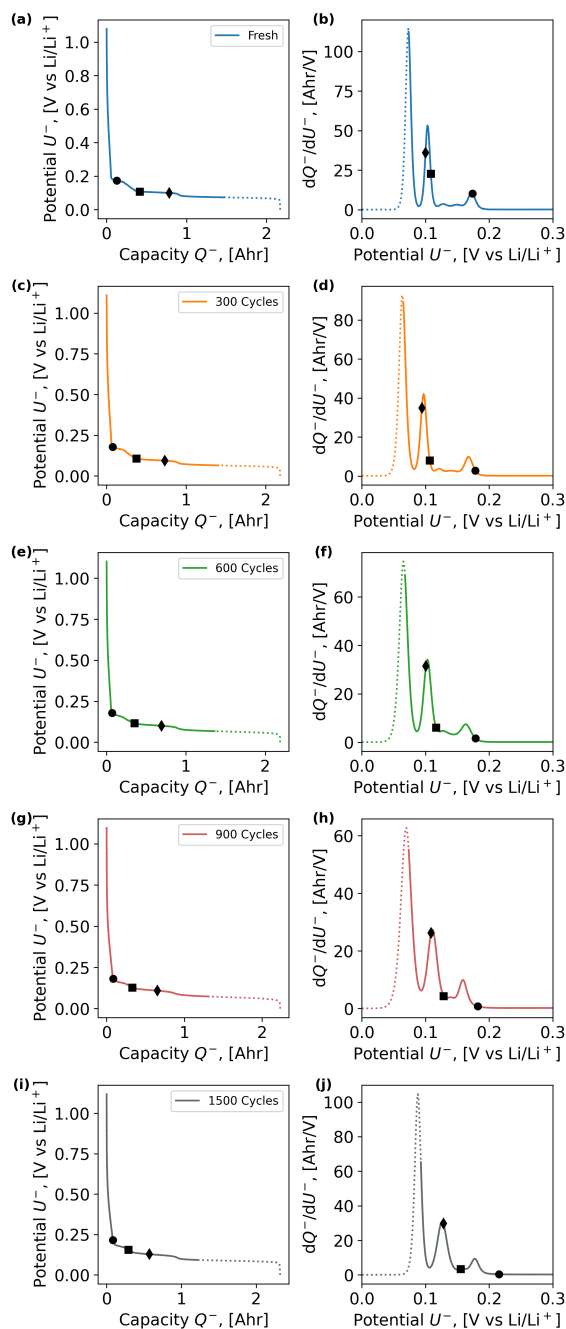


Figure S6.7. The individually optimized anode half-cell charging profile and its corresponding dQ/dU results at the end of cycling for (a-b) fresh, (c-d) 300 cycles, (e-f) 600 cycles, (g-h) 900 cycles, and (i-j) 1500 cycles. The dotted-lines represent the full voltage range half-cell potential obtained from curve fitting, while the solid-lines are the capacity range utilized to obtain the full-cell response. The $\circ$, $\diamond$, and $\square$ are representing the actual anode half-cell potential that has been measured at 10% (3.5 V), 30% (3.64 V), and 50% (3.82 V) SOC respectively.

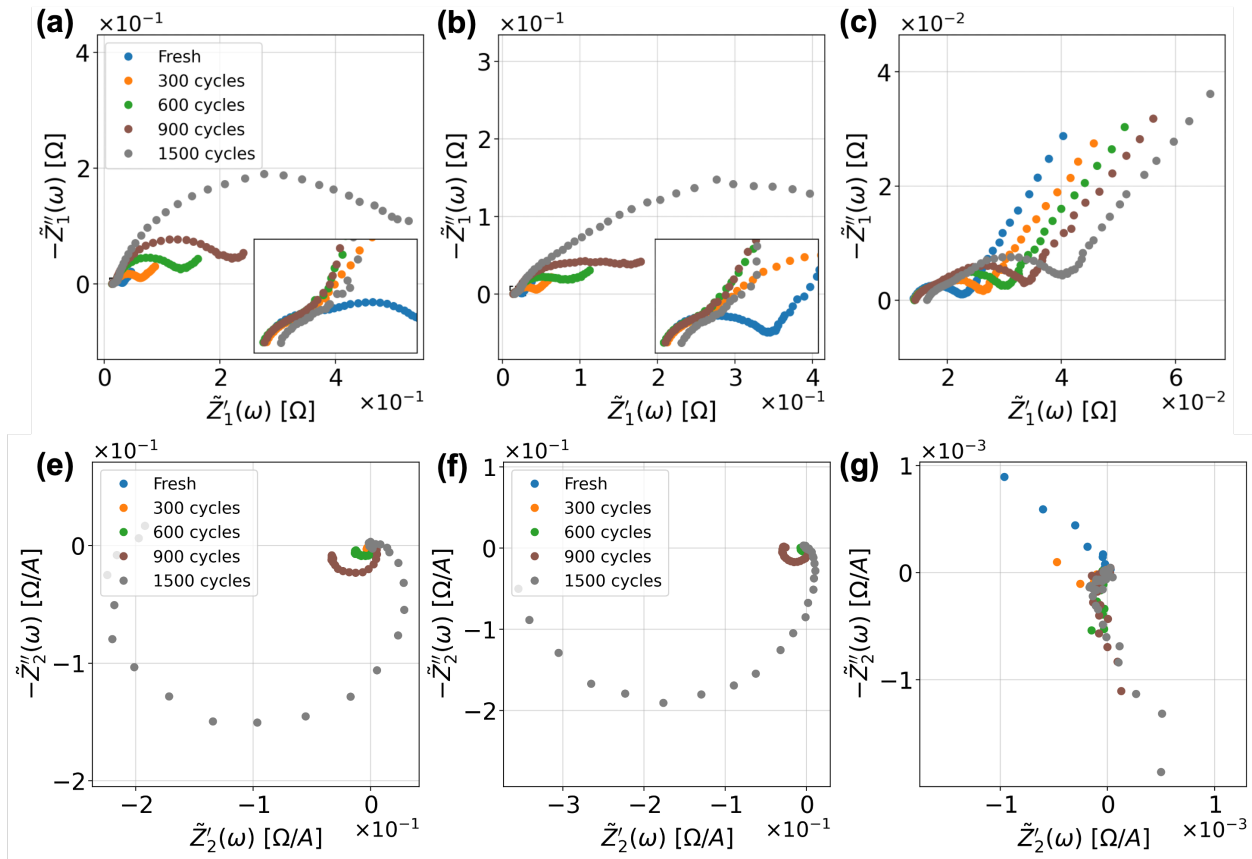


Figure S6.8. The SOH dependence of EIS (a-c) and its corresponding 2nd-NLEIS (e-g) spectra at a,e) 10%, b,f) 30, and c,g) 50% SOC from fresh to 1500 cycles. The dots are EIS and 2nd-NLEIS measurements at each frequency.

6.7.2 *Supplementary Tables***Table S6-I.** The MSMR parameters from Verbrugge et al. [226]

Reaction	U_k^0 vs. Li/ Li ⁺ (V)	$Q_{k,tot}$ (Ahr)	ω_k
NMC1	3.62 ₃	0.18 ₅	0.72 ₅
NMC2	3.74 ₆	0.40 ₇	1.07 ₂
NMC3	3.88 ₈	0.30 ₆	2.65 ₆
NMC4	4.23 ₀	0.45 ₄	5.52 ₈
LMO1	4.01 ₂	0.23 ₄	1.52 ₀
LMO2	4.14 ₉	0.19 ₁	0.93 ₀
GR1	0.08 ₈	0.85 ₈	0.08 ₆
GR2	0.12 ₈	0.47 ₅	0.08 ₀
GR3	0.14 ₃	0.29 ₇	0.72 ₅
GR4	0.17 ₀	0.10 ₈	2.53 ₃
GR5	0.21 ₅	0.13 ₄	0.09 ₅
GR6	0.36 ₃	0.10 ₈	5.97 ₄

Table S6-II. The fitted MSMR parameters for fresh cell.

Reaction	U_k^0 vs. Li/ Li ⁺ (V)	$Q_{k,tot}$ (Ahr)	ω_k
NMC1	3.66 ₃	0.23 ₁	0.72 ₅
NMC2	3.74 ₄	0.39 ₁	1.04 ₈
NMC3	3.88 ₆	0.30 ₈	2.62 ₉
NMC4	4.25 ₉	0.38 ₉	4.14 ₆
LMO1	4.01 ₆	0.22 ₂	1.48 ₃
LMO2	4.14 ₉	0.18 ₁	1.12 ₂
GR1	0.07 ₃	1.26 ₄	0.10 ₈
GR2	0.10 ₃	0.54 ₈	0.10 ₀
GR3	0.12 ₇	0.06 ₁	0.18 ₂
GR4	0.14 ₉	0.06 ₄	0.21 ₉
GR5	0.17 ₃	0.16 ₂	0.15 ₂
GR6	0.34 ₃	0.08 ₁	6.72 ₇

Table S6-III. The Fitted MSMR parameters for 300 cycles cell.

Reaction	U_k^0 vs. Li/ Li ⁺ (V)	$Q_{k,tot}$ (Ahr)	ω_k
NMC1	3.67 ₇	0.28 ₉	0.54 ₄
NMC2	3.74 ₈	0.36 ₃	1.17 ₁
NMC3	3.90 ₆	0.28 ₇	2.56 ₆
NMC4	4.23 ₉	0.41 ₉	3.83 ₉
LMO1	3.99 ₈	0.21 ₄	1.85 ₄
LMO2	4.13 ₁	0.13 ₆	0.94 ₉
GR1	0.06 ₄	1.28 ₄	0.13 ₅
GR2	0.09 ₇	0.53 ₉	0.12 ₅
GR3	0.12 ₁	0.04 ₇	0.15 ₄
GR4	0.14 ₁	0.07 ₀	0.27 ₃
GR5	0.16 ₈	0.16 ₁	0.16 ₄
GR6	0.32 ₃	0.09 ₂	6.72 ₀

Table S6-IV. The Fitted MSMR parameters for 600 cycles cell.

Reaction	U_k^0 vs. Li/ Li ⁺ (V)	$Q_{k,tot}$ (Ahr)	ω_k
NMC1	3.68 ₅	0.24 ₇	0.40 ₈
NMC2	3.76 ₈	0.31 ₄	1.24 ₅
NMC3	3.92 ₆	0.21 ₅	2.64 ₄
NMC4	4.21 ₉	0.42 ₂	3.86 ₄
LMO1	3.97 ₈	0.24 ₀	1.96 ₁
LMO2	4.13 ₁	0.13 ₁	0.88 ₂
GR1	0.06 ₅	1.29 ₀	0.16 ₈
GR2	0.10 ₃	0.54 ₃	0.15 ₆
GR3	0.12 ₇	0.05 ₇	0.19 ₃
GR4	0.14 ₀	0.08 ₁	0.34 ₂
GR5	0.16 ₄	0.14 ₂	0.20 ₅
GR6	0.30 ₃	0.08 ₈	6.53 ₇

Table S6-V. The Fitted MSMR parameters for 900 cycles cell.

Reaction	U_k^0 vs. Li/ Li ⁺ (V)	$Q_{k,tot}$ (Ahr)	ω_k
NMC1	3.67 ₈	0.20 ₃	0.51 ₀
NMC2	3.76 ₈	0.32 ₅	1.55 ₆
NMC3	3.90 ₆	0.26 ₉	3.23 ₈
NMC4	4.19 ₉	0.40 ₁	3.50 ₈
LMO1	3.98 ₃	0.21 ₀	1.51 ₈
LMO2	4.14 ₀	0.11 ₃	0.71 ₃
GR1	0.07 ₀	1.35 ₃	0.21 ₀
GR2	0.11 ₁	0.54 ₄	0.19 ₅
GR3	0.13 ₉	0.04 ₃	0.16 ₅
GR4	0.15 ₈	0.06 ₀	0.42 ₇
GR5	0.15 ₉	0.13 ₁	0.15 ₃
GR6	0.29 ₈	0.11 ₀	4.90 ₃

Table S6-VI. The Fitted MSMR parameters for 1500 cycles cell.

Reaction	U_k^0 vs. Li/ Li ⁺ (V)	$Q_{k,tot}$ (Ahr)	ω_k
NMC1	3.69 ₈	0.25 ₄	0.59 ₈
NMC2	3.78 ₁	0.25 ₀	1.71 ₈
NMC3	3.88 ₆	0.28 ₇	3.20 ₇
NMC4	4.21 ₉	0.36 ₀	3.49 ₇
LMO1	3.99 ₈	0.22 ₆	1.47 ₁
LMO2	4.15 ₆	0.13 ₉	0.73 ₇
GR1	0.08 ₈	1.35 ₂	0.12 ₆
GR2	0.12 ₆	0.63 ₂	0.20 ₁
GR3	0.15 ₈	0.04 ₂	0.17 ₈
GR4	0.17 ₂	0.04 ₅	0.53 ₄
GR5	0.17 ₈	0.13 ₀	0.15 ₃
GR6	0.27 ₈	0.13 ₄	4.90 ₃

Table S6-VII. The mean absolute errors (MAE) of the fitting results of voltage profile, dV/dQ , and dQ/dV for fresh, 300, 600, 900, and 1500 cycles.

	Voltage profile (V)	dV/dQ (V/Ahr)	dQ/dV (Ahr/V)
Fresh	0.004	0.023	0.091
300 cycles	0.003	0.022	0.082
600 cycles	0.003	0.019	0.067
900 cycles	0.002	0.012	0.037
1500 cycles	0.003	0.028	0.073

Table S6-VIII. Individual electrode potential at the full cell voltage designed for 10%, 30%, and 50% SOC. The calculations ensured that an error of $O(0.01\text{ V})$ between the measured and calculated full cell voltage.

	10% SOC (3.50 V)		30% SOC (3.64 V)		50% SOC (3.82 V)	
	Cathode	Anode	Cathode	Anode	Cathode	Anode
Fresh	3.67 ₄	0.17 ₄	3.74 ₈	0.10 ₈	3.92 ₀	0.10 ₀
300 Cycles	3.67 ₈	0.17 ₈	3.74 ₇	0.10 ₇	3.91 ₄	0.09 ₄
600 Cycles	3.67 ₉	0.17 ₉	3.75 ₇	0.11 ₇	3.92 ₁	0.10 ₁
900 Cycles	3.68 ₂	0.18 ₂	3.76 ₈	0.12 ₈	3.92 ₉	0.10 ₉
1500 Cycles	3.71 ₅	0.21 ₅	3.79 ₅	0.15 ₅	3.94 ₈	0.12 ₈

Chapter 7.

NLEIS.PY: A NONLINEAR ELECTROCHEMICAL IMPEDANCE ANALYSIS TOOLBOX

Note: this chapter was published as an article

- Yuefan Ji, Matthew D. Murbach, Daniel T. Schwartz, nleis.py: A Nonlinear Electrochemical Impedance Analysis Toolbox. Journal of Open Source Software, 10(105), 7424, <https://doi.org/10.21105/joss.07424>

Building on the growing adoption of impedance.py [137] as an open-source software tool within the electrochemical impedance spectroscopy (EIS) community, nleis.py is a toolbox for impedance.py that aims to provide an easily accessible tool to perform second harmonic nonlinear EIS (2nd-NLEIS analysis), with the ability to extend to higher harmonic analysis in the future. The toolbox is designed with impedance.py in mind to minimize the learning curve for users. It inherits the basic functionality of impedance.py, introduces paired linear and 2nd-harmonic nonlinear circuit elements, and enables the simultaneous analysis of EIS and 2nd-NLEIS. With this toolbox, one can choose to individually analyze an EIS or 2nd-NLEIS spectra or perform simultaneous parameter estimation of linear and nonlinear impedance data using an impedance.py workflow. Ultimately, the nleis.py toolbox will be integrated into impedance.py as adoption grows, while maintaining the standalone version of nleis.py as a platform to develop advanced features as the field matures.

7.1 BACKGROUND

Electrochemical impedance spectroscopy (EIS) is a widely accepted electroanalytical method that is often used to characterize engineered electrochemical systems like fuel cells [114] and lithium-ion batteries (LIBs). [50] EIS experiments and modeling require linearization of system response,

leading to unavoidable information loss and model degeneracy challenges in real-world nonlinear electrochemical processes. [32,91] Second-harmonic nonlinear electrochemical impedance spectroscopy (2nd-NLEIS) is emerging as a powerful and complementary tool to EIS in lithium-ion battery (LIB) research. 2nd-NLEIS uses a moderately larger input modulation than conventional EIS to drive the electrochemical system into the weakly nonlinear regime where the fundamental frequency continues to represent the linear system response, and a small additional 2nd-harmonic signal adds key new information about the nonlinear dynamics of the interfaces under study. [26] Analyzing a 2nd-NLEIS signal unavoidably complicates the mathematical modeling compared to linear system theory, but it also provides a sensible way to break EIS degeneracy and generate key new insights into charge transfer, transport, and thermodynamic parameters that are inaccessible to EIS alone. Early work with the pseudo-two-dimensional (P2D) LIB model provided the first physical insights into the potential value of 2nd-NLEIS signals for battery research, [34] whereas quantitative parameter estimation of 2nd-NLEIS experiments has required adoption of physically-insightful reduced order models, such as Kirk et al.'s work developing a nonlinear single particle model (SPM), [44] and our work defining nonlinear Randles circuit (RC) and porous electrode models (PEM). [35]

7.2 STATEMENT OF NEED

As an emerging technique requiring nonlinear dynamic modeling to analyze experimental data, 2nd-NLEIS method adoption is slowed by a lack of commercial or open-source software for parameter estimation from experiments, even though NLEIS experiments can be performed with EIS equipment offered by several vendors. [26] Within the linear EIS community, the adoption of an open-source impedance.py equivalent circuit modeling workflow has successfully facilitated reproducible, easy-to-use, and transparent impedance analysis that supports an active community

of users. By introducing nonlinear equivalent circuit modeling through `nleis.py`, we seek to enhance the accessibility of this powerful new technique with a streamlined data analysis pipeline that researchers are already familiar with, hence accelerating the co-development of theory and experiments. Moreover, there is neither a research nor industry standard platform available to measure and analyze 2nd-NLEIS. Consequently, we aim to use `nleis.py` as a starting point to establish 2nd-NLEIS measurements and analysis best-practices while working in concert with the `impedance.py` user community.

7.3 NAMING CONVENTIONS AND PARAMETER ASSIGNMENTS

The linear and second harmonic nonlinear circuit elements are defined in a pair with an addition of ‘n’ after the nonlinear circuit element to facilitate the simultaneous analysis of linear and nonlinear impedance response. Additionally, because of the nature of the nonlinear response, the simplest possible circuit element is a wrapper Randles circuit (RC) rather than the Resistor (R) and capacitor (C) element defined in `impedance.py`. For example, the linear and nonlinear Randles circuits are defined in pairs as RC and RCn respectively. For higher harmonics (>2) analysis not yet implemented here, there is no restriction for the circuit element definition, but a general consideration is to avoid numbers in the definition of raw circuit elements for future expansion. Lastly, parameter assignment should follow a convention that first defines the linear parameters of a model (p_1) then the nonlinear parameters (p_2). For the RC circuit as an example, RC should only take $[p_1]$ as parameter inputs, while RCn should take $[p_1, p_2]$ as parameter inputs, as described in [46].

7.4 CURRENT NLEIS.PY FUNCTIONALITIES

7.4.1 *Nonlinear Equivalent Circuit Fitting*

The 2nd-harmonic nonlinear Equivalent Circuit Fitting is accomplished with ‘NLEISCustomCircuit’. It inherits most features from the impedance.py ‘CustomCircuit’, but provides an extra level of flexibility for performing NLEIS specific tasks. Overall, the users should expect the same workflow as impedance.py.

7.4.2 *Simultaneous Equivalent Circuit Fitting of EIS and 2nd-NLEIS*

‘EISandNLEIS’ is the key feature of nleis.py that enables the simultaneous analysis of EIS and 2nd-NLEIS with equivalent circuit modeling. The visual representation of nonlinear equivalent circuit representation can be found in [35]. Everything works like impedance.py, but the users should provide the correct pair of linear and nonlinear circuit strings with a single initial guess that is consistent with both linear and nonlinear circuit features seen in the data. For EIS and 2nd-NLEIS data with known error structure or relative magnitudes, the users can also specify the optimization weighting and normalization method for the EIS and 2nd-NLEIS data parameter estimation process, as introduced in [44,46].

7.4.3 *Visualization*

The user can choose to use the plotting function in impedance.py or a customized plotting function for EIS (plot_first) and 2nd-NLEIS (plot_second) to get a correctly labeled Nyquist plot.

7.4.4 *Nonlinear Circuit Elements*

nleis.py supports a variety of linear and 2nd harmonic nonlinear circuit element pairs from simple Randles circuits to analytical porous electrode and numerical transmission line models. These

models all rely on the foundation of the analytical theory developed by [35] for Randles and porous electrodes. Just like `impedance.py`, `nleis.py` supports manual element definition. If you want your model to be included in future releases, create an issue on GitHub with your models to contribute to the project.

7.5 FUTURE NLEIS.PY FUNCTIONALITIES

7.5.1 *Data Processing*

There is only a simple data processing function for frequency domain data truncation now. We hope to include data processing and conversion from either time or frequency domain data in the future (i.e. FFT capability for time domain data). If you have equipment that allows you to perform 2nd-NLEIS and wish it to be compatible with `nleis.py`, create an issue with a sample file to help the advancement of 2nd-NLEIS.

7.5.2 *Data Validation*

Unlike EIS, which already has a set of well-established validation methods available, there is not yet a standard set of tools to quickly validate the causality and stationarity requirements of 2nd-NLEIS data. We are actively working on the development of such a data validation method, which will be incorporated in the future. If you have a new method for 2nd-NLEIS validation, we are also interested in including it in the future after it is peer reviewed and published. Create an issue or submit a pull request to initiate review for inclusion.

7.5.3 *Contribute to the Project*

In general, 2nd-NLEIS is a novel technique for electrochemical science and engineering research and development. Many areas familiar to EIS analysts are not fully developed for nonlinear

systems. If you are publishing theoretical or experimental work that is advancing the field and would like to disseminate it as software others can use as part of `nleis.py`, we encourage you to create an issue on GitHub and become a contributor to `nleis.py`.

7.6 SIDE-BY-SIDE COMPARISON BETWEEN IMPEDANCE.PY AND NLEIS.PY API

`nleis.py` comes with detailed documentation with examples and concepts for new users to get started. For existing `impedance.py` users, we expect this side-by-side comparison between `impedance.py` and `nleis.py` can reduce barriers for extending your impedance analysis to the weakly nonlinear regime.

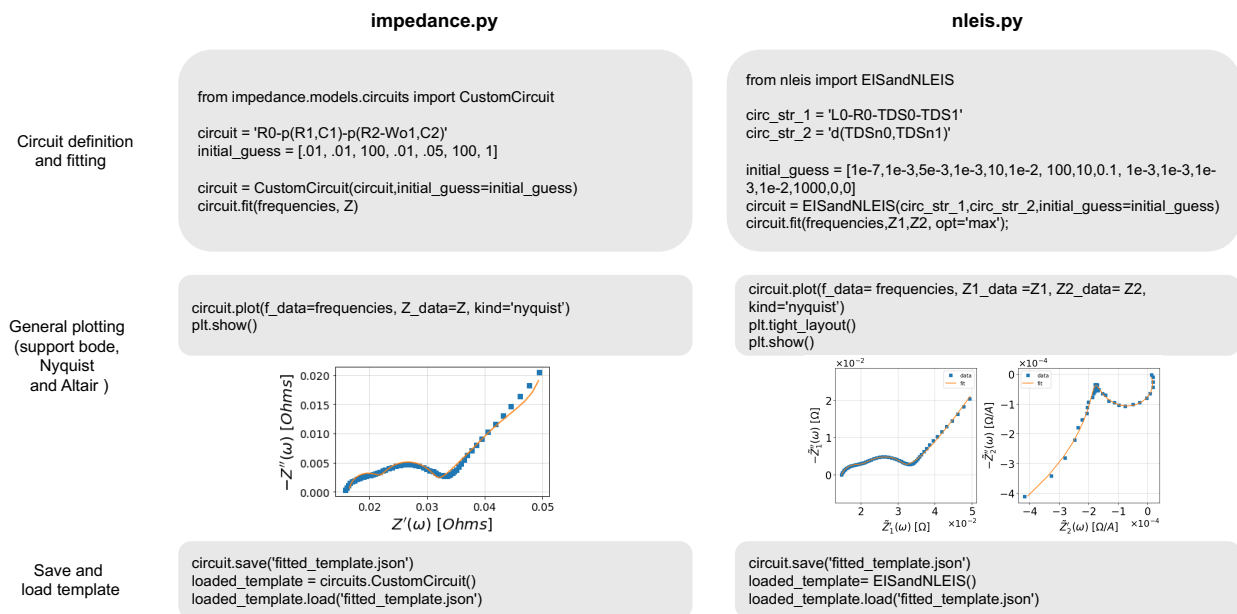


Figure 7.1. Side-by-side comparison between `impedance.py` and `nleis.py` API.

Chapter 8.

CONCLUSIONS AND DIRECTIONS OF FUTURE WORK

8.1 THESIS SUMMARY

Lithium-ion battery (LIB) research encompasses every aspect from materials level innovations to the pack level implementations. The understanding of the internal dynamics is essential for the advancement of battery materials for transportation electrification and energy storage. Electrochemical impedance spectroscopy (EIS) has been included as an indispensable characterization technique for LIB research, though limitations are still present with the application of this linearized method. Second harmonic nonlinear electrochemical impedance spectroscopy (2nd-NLEIS) is emerging as a complementary technique to EIS that enriches the information obtained from impedance analysis by extending the measurement to the weakly nonlinear regime. The merit of 2nd-NLEIS hasn't been fully elucidated due to the complexity of the original pseudo-two-dimensional (P2D) and recent single particle (SPM) model. Specifically, the nonlinear dynamics measured by 2nd-NLEIS are necessary for the understanding of the intrinsic nonlinearity of the LIB systems.

In this thesis, a continuous pathway has been established to support practical 2nd-NLEIS analysis, highlight the importance of the previously ignored nonlinear dynamics, and illuminate the area of potential future applications. First, analytical frameworks were developed to facilitate the understanding and analysis of 2nd-NLEIS, paving the foundation for this thesis. Randles circuit and porous electrode theory have been extended to include the weakly nonlinear response (**Chapter 2**). Nonlinear equivalent circuit representations were proposed to provide connections between EIS and 2nd-NLEIS. This also enables the extension of transmission line models (TLMs) to include nonlinear dynamics. A generalized TLM framework was developed to provide

flexibility to characterize the aging phenomenon observed in aged LIBs (**Chapter 3**). For example, A TLM that considers core-shell structured particles in the porous electrode has been developed to describe the surface reconstruction of the NMC cathode.

To facilitate the adoption of 2nd-NLEIS, a robust data validation method is required. Relying on the stationarity and causality requirement for 2nd-NLEIS, we found that the 2nd-NLEIS spectra satisfy the Kramers-Kronig relations, enabling the evaluation of data quality. Inspired by the widely adopted measurement model (MM) test in EIS, a nonlinear MM test was developed with a nonlinear Randles circuit as the basis function (**Chapter 4**). Coupled with a 1% total harmonic distortion (THD) requirement, the quality of 2nd-NLEIS can now be accessed prior to the data analysis and used to optimize the perturbation amplitude to 2nd-NLEIS.

Another aspect of this thesis focuses on interpreting the weakly nonlinear dynamics. Built on the theoretical foundation, a simultaneous data analysis pipeline has been developed to support quantitative data analysis. The application of the porous electrode model enables the first successful parameter identification of the charge transfer asymmetry with mildly aged NMC||C cells (**Chapter 5**). Specifically, aging causes a breakdown of charge transfer symmetry ($\varepsilon_c > 0$) on the cathode, while the anode remains intact. An increase in cathode charge transfer asymmetry (from $\varepsilon_c = 0$ at 50% SoC to $\varepsilon_c = 0.11$ at 10% SoC) has also been observed with a decrease in the state of charge (SOC). To further expand the *in-situ* characterization ability and the understanding of asymmetric charge transfer behavior, a larger aging dataset was analyzed to explore the aging phenomenon in the commercial NMC||C cells (**Chapter 6**). Combining differential voltage analysis with simultaneous EIS and 2nd-NLEIS analysis, we have successfully quantified a continuous growth of asymmetric charge transfer that favors delithiation ($\varepsilon_c > 0$) on the cathode during aging, especially at a low SOC. By varying SOC, it was observed that the cathode

approaches symmetric charge transfer at intermediate SOC (50% SOC). This phenomenon perfectly aligns with the direction of lattice strain reduction given the formation of Ni-rich rocksalt surface on NMC particles, providing a non-invasive probe to the surface reconstruction of NMC cathode.

The last piece of this thesis completes the practical implementation of 2nd-NLEIS by developing *nleis.py*, an open-source Python package inspired by the successful adoption of *impedance.py* in facilitating reproducible EIS analysis (**Chapter 7**). *nleis.py* includes the models, data validation method, and simultaneous EIS and 2nd-NLEIS analysis pipeline developed in this thesis and acts as a platform to ensure reproducible simultaneous EIS and 2nd-NLEIS analysis.

Overall, this thesis delivered a comprehensive toolbox for the practical implementation of 2nd-NLEIS for LIBs, paving the foundation for countless future research and applications that consider the nonlinear behavior of LIBs. For example, we hope to inspire DFT calculations to gain further structure and kinetics understanding of the relationship between lattice strain growth and asymmetric charge transfer behavior. This thesis also included two directions of future work to inspire readers. First, the importance of considering asymmetric charge transfer behavior in state estimation was demonstrated through P2D modeling. To initiate and spur future works on nonlinear state estimation and control, we proposed a Kalman filter based nonlinear state estimation with nonlinear equivalent circuits introduced in this thesis. The other direction emphasizes on the emerging popularity of data science approaches. We simulated 10228 pairs of unique EIS and 2nd-NLEIS spectra using the P2D model and introduced a potential strategy to determine the domain of applicability for simplified models. This dataset can also support data science assisted parameter estimation in the future.

8.2 THE IMPORTANCE OF CONSIDERING ASYMMETRIC BUTLER-VOLMER KINETICS IN BATTERY STATE ESTIMATION

8.2.1 *Introduction*

Electrochemical modeling plays an indispensable role in the design, optimization, and control of Lithium-ion batteries (LIBs) for transportation electrification. [240] Paired with carefully extracted or selected parameters, the voltage response of the battery can be modeled to provide insight about the energy and power performance. Perhaps, Newman's P2D model is the most well-known and implemented model for battery design and research, thanks to its comprehensive physics consideration. The P2D model considers interfacial charge transfer, Helmholtz double layer, Fickian solid state diffusion, binary electrolyte theory, and charge conservation between the solution phase and the solid phase in a volume averaged porous electrode. Butler-Volmer kinetics is usually adopted to describe interfacial charge transfer behavior in LIBs, especially with the NMC||C system. The Butler-Volmer kinetics is determined by two physical parameters: exchange current density (i_0 ; rate sensitive) and charge transfer coefficient/charge transfer asymmetry parameter ($\varepsilon = \alpha_a - 0.5$; mechanism sensitive). The exchanged current density is easy to measure with EIS and is one of the key parameters that will be carefully extracted experimentally for battery modeling. The asymmetry parameter, on the other hand, is usually overlooked and assumed to be 0 ($\alpha_a = \alpha_c = 0.5$) in literature. [79–81,241] As demonstrated through this thesis, the charge transfer behavior in the NMC cathode becomes asymmetric upon aging. It is also important to note that the actual concentration of lithium in each electrode is not measurable and the state of charge (SOC) of the battery must be estimated. [67] Ignoring the asymmetric behavior can, thus, lead to inaccurate state and energy estimation. In the

next section, we will demonstrate the importance of considering asymmetric charge transfer for state of charge (SOC) estimation using the P2D model.

8.2.2 *Evaluation of Publicly Available Parameters Sets*

Battery parameterization has been an important field of research, aiming to provide the most accurate parameters to feed the P2D model. [79–81,241] Even with carefully extracted parameters, building and tuning a P2D model can be challenging. Thanks to the open-source battery modeling software, PyBaMM, [242] creating a P2D model using publicly available parameter values is as simple as writing a multi-line code in Python. To demonstrate the importance of considering asymmetric charge transfer kinetics, we have evaluated three parameters sets available in PyBaMM. The details of cell type, chemistry, and parameters sets are summarized in **Table 8-I**. We systematically screened the asymmetric behavior during charge/discharge from $\varepsilon = -0.2$ to $\varepsilon = 0.2$ for cathode materials using PyBaMM. These simulated full cell experiments were first discharged at 1C for 1 hour and then charged at 1C for 1 hour to bring them back to the original state. As shown in **Figure 8.1**, the voltage responses of LCO systems show larger sensitivity to the asymmetry in the charge transfer kinetics, while the voltage profile remains indistinguishable for NMC systems at the fresh state. These suggest that NMC systems generally have much facile charge transfer kinetics than LCO systems in the publicly available parameter sets, making asymmetric behavior less apparent in the voltage response. The importance of considering asymmetric charge transfer behavior is, thus, system dependent and systems with sluggish interfacial charge transfer require more attention to the asymmetric behavior. For example, the mapped capacity can vary from ~ 0.25 Ah to ~ 0.55 Ah at the same dynamic voltage of 3.6 V in the LCO system described by parameters set Marquis2019. This can be a significant challenge to BMS development without considering asymmetric behavior. That is, contemporary BMS relies heavily

on the dynamic voltage reading and predicts the instantaneous open circuit voltage (OCV), which can be used to find accurate SOC with an accurate SOC-OCV relationship. However, the presence of asymmetric behavior can increase the error in the OCV estimation and hence the SOC estimation. The next section will introduce a potential framework to include asymmetric behavior in the Kalman filter based SOC estimation algorithm.

Table 8-I. Summary of the parameter sets used for simulation.

Parameters Set	Cell Type	Model Chemistry	Ref.
Marquis2019	Kokam SLPB78205130H	LCO graphite	[81]
Ai2020	Enertech SPB655060	LCO graphite	[80,241]
Chen2020	LG M50	NMC 811 graphite	[79]

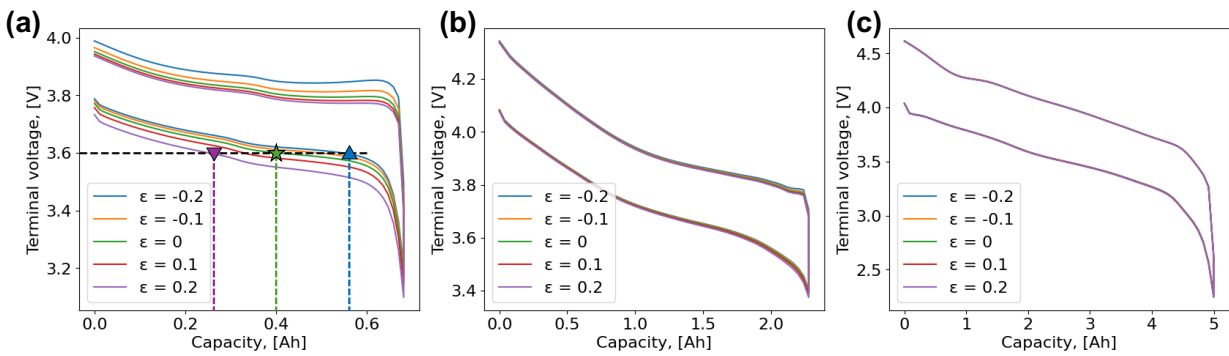


Figure 8.1. PyBaMM simulated 1C cycling profile using publicly available parameters sets: a) Marquis2019; b) Ai2020; c) Chen2020. The black dashed-line shows a constant voltage of 3.4 V in a), while the colored dashed-lines show its corresponding capacity mapping for $\varepsilon = 0.2$ (purple), $\varepsilon = 0$ (green), and $\varepsilon = -0.2$ (blue).

As demonstrated in **Chapters 5 and 6**, aging in the NMC cathode involves an increase in the charge transfer resistance and the breakdown of charge transfer symmetry. To demonstrate the effect of asymmetric charge transfer under aging, the charge transfer rate is manually reduced by 10-fold to represent an aged NMC electrode based on the parameters set in Chen2020. The asymmetry dependence under this condition is shown in **Figure 8.2**, which shows a clear discrepancy between symmetric and asymmetric behavior as compared to the fresh state. By

comparing the discharging power at 1C, a 3% power difference is observed between $\varepsilon = -0.2$ and $\varepsilon = 0.2$, which can be further amplified at higher C-rate application or higher degree of asymmetry. It can also be observed in **Figure 8.2** that the same voltage reading can map to drastically different state of charge (i.e., from ~ 2.2 Ah to ~ 3.1 Ah at 3.4 V) in this system, which could also introduce challenges in SOC estimation. Therefore, ignoring asymmetric behavior in aged batteries can significantly increase the variance in the SOC estimation and reduce the ability to precisely control the battery (i.e., the algorithm employed to prevent lithium plating).

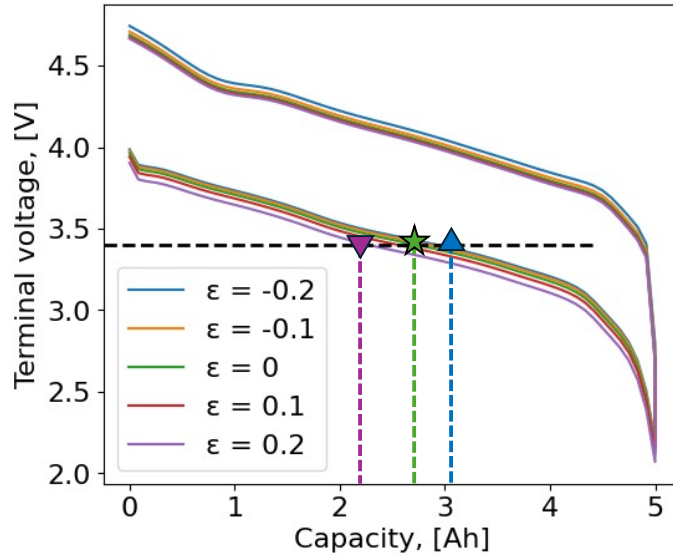


Figure 8.2. PyBaMM simulated 1C cycling profile using Chen2020 parameters set with reduced charge transfer rate to mimic observed aging behavior. The black dashed-line shows a constant voltage of 3.4 V, while the colored dashed-lines show its corresponding capacity mapping for $\varepsilon = 0.2$ (purple), $\varepsilon = 0$ (green), and $\varepsilon = -0.2$ (blue).

8.3 DEVELOPMENT OF KALMAN FILTER BASED NONLINEAR STATE ESTIMATION

8.3.1 Introduction

Electrochemical modeling provides a connection between the measurable current, voltage, and temperature with battery's internal state of charge (SOC), which is one of the key roles of the

contemporary battery management system (BMS). [68] Though lacks robustness, columbic counting with open circuit voltage calibration is the most widely used algorithm given its simplicity. [69] The growing demand for high performance EVs urges the shift from columbic counting to a more robust model-based method for SOC estimation. [76,243]

Kalman filter with an equivalent circuit model (ECM) provides opportunities to eliminate the effect of current sensor errors and provides dynamic calibration with the measured voltages. [70–75] Conventional ECMs are good at capturing the linear dynamics in the battery system. However, the nonlinear nature of the LIB system makes the nonlinear state estimation an intriguing field of research for a more accurate and robust SoC estimation algorithm. Nonlinear state estimation cannot only provide more accurate estimation results but also introduce additional dynamic parameters that are sensitive to the state of health (SOH) of a battery as discussed in **Chapters 5 and 6**. With the Kalman filter based algorithm these parameters can be estimated with a slight modification of the current framework. Additionally, the nonlinear dynamic parameters can also benefit the control of the battery during fast charging. For example, model predictive control can be implemented with the estimated parameters to prevent lithium plating or overcharging. It is important to note that state estimation and model predictive control are interconnected, where an accurate state estimation is the prerequisite for effective model predictive control. As a result, an accurate state estimation with a Kalman filter is crucial for future developments of model predictive control.

The formulation of 2nd-NLEIS provides an unparalleled advantage in measuring nonlinear parameters, facilitating the construction of weakly nonlinear cell models. In the next section, we will introduce the formulation of an extended Kalman filter for the nonlinear Randles circuit, laying the foundation for designing nonlinear state estimation.

8.3.2 Governing Equation for Kalman Filter Based Nonlinear State Estimation

Nonlinear state estimations and controls require the development of accurate cell models. Given the performance of conventional ECMs, nonlinear ECMs are promising in providing a more accurate estimation without over-complicating the dynamic equations. Here, we adopted a nonlinear Randles circuit and aim to solve for the discrete time domain governing equation to take advantage of the previously developed Kalman filter algorithm. Consider the time domain governing equation for a Randles circuit with nonlinear charge transfer dynamics,

$$R_{ct} * I(\tau) = E + \varepsilon f E^2 + \frac{dE}{d\tau} \quad (8.1)$$

where $\tau = t/(R_{ct}C_{dl})$ is the dimensionless time, R_{ct} is the charge transfer resistance, C_{dl} is the double layer capacitance, $I(t)$ is the current input, E is the voltage response, $f = \frac{nF}{RT}$ (V^{-1}), and ε is the charge transfer asymmetry parameter defined in **Chapter 2**. From initial inspection, it is noticed that the traditional discretization method with an analytical solution is not valid in this case. The analytical solution of the nonlinear Randles is ill-determined when $\varepsilon = 0$, emphasizing the need for an alternative discretization method. Numerical integration, on the other hand, cannot provide accurate discretization and take advantage of the previously established frameworks. The perturbation method is a well-suited method that lies in between the analytical and numerical methods with decent accuracy. An approximated solution to **Equation 8.1** can be found using a regular perturbation series of the form,

$$E = E_1 + \varepsilon E_2 + h. o. t. \quad (8.2)$$

when $\varepsilon \ll 1$, where E_1 is the linear voltage response and E_2 is the nonlinear voltage response. Inserting **Equation 8.2** into **Equation 8.1** results in a governing equation that aligns with the frequency domain development in **Chapter 2** with the form,

$$R_{ct} * I(\tau) = E_1 + \varepsilon E_2 + \varepsilon f(E_1 + \varepsilon E_2)^2 + \frac{d(E_1 + \varepsilon E_2)}{d\tau}. \quad (8.3)$$

The dynamic response can be separated into linear and nonlinear dynamics for E_1 and E_2 respectively. The governing equation for the linear dynamics resembles the response of a linear Randles circuit as follows,

$$R_{ct}I(\tau) = E_1 + \frac{d(E_1)}{d\tau} \quad (8.4)$$

The nonlinear dynamics (related to E_2) is then given as

$$0 = E_2 + f(E_1)^2 + \frac{d(E_2)}{d\tau} \quad (8.5)$$

The discrete time domain governing equation for **Equations 8.4** and **8.5** can then be obtained as follows with an integration factor e^τ ,

$$\begin{aligned} \begin{bmatrix} E_{1,k+1} \\ E_{2,k+1} \end{bmatrix} &= \begin{bmatrix} e^{-\Delta\tau} & 0 \\ 0 & e^{-\Delta\tau} \end{bmatrix} \begin{bmatrix} E_{1,k} \\ E_{2,k} \end{bmatrix} + \begin{bmatrix} R_{ct}(1 - e^{-\Delta\tau}) \\ 0 \end{bmatrix} I_k + \begin{bmatrix} 0 & 0 \\ -2fR_{ct}\Delta\tau e^{-\Delta\tau} & 0 \end{bmatrix} \begin{bmatrix} E_{1,k} \\ E_{2,k} \end{bmatrix} \\ &+ I_k \begin{bmatrix} 0 \\ -fR_{ct}^2(1 - e^{-2\Delta\tau}) + 2fR_{ct}^2\Delta\tau e^{-\Delta\tau} \end{bmatrix} I_k^2 + \begin{bmatrix} 0 & 0 \\ -f(1 - e^{-\Delta\tau})e^{-\Delta\tau} & 0 \end{bmatrix} \begin{bmatrix} E_{1,k}^2 \\ E_{2,k}^2 \end{bmatrix} \end{aligned} \quad (8.6)$$

The equation for $E_{1,k+1}$ is the well-known state space governing equation for the Randles circuit, while the equation for $E_{2,k+1}$ is the discrete time weakly nonlinear response in addition to the linear response. These two governing equations enable the development of a simplified battery cell model consistent with the experimental findings in **Chapters 5** and **6**. That is, the cathode is the major contributor to the weakly nonlinear response. A whole-cell equivalent circuit representation can be proposed as shown in **Figure 8.3**, where linear and nonlinear Randles circuits are used for the anode and cathode respectively.

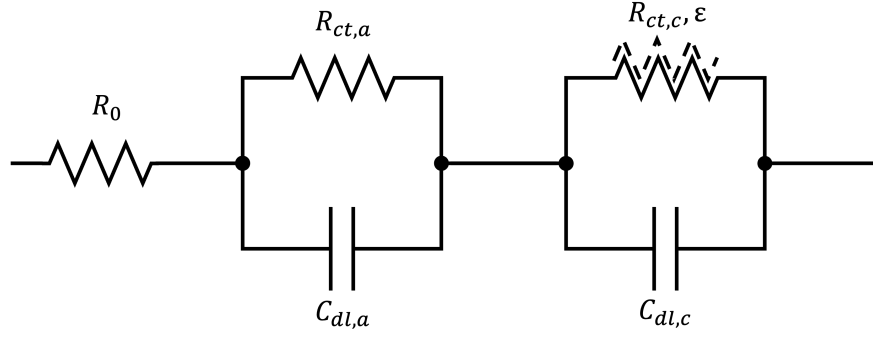


Figure 8.3. A whole-cell equivalent circuit model consists of internal resistance, linear Randles for the anode, and nonlinear Randles for the cathode.

The discrete time governing equation for a battery can then be written as follows,

$$SoC_{k+1} = SoC_k - \frac{\Delta t}{Q} \times I_k \quad (8.7a)$$

$$E_{1,a,k+1} = E_{1,a,k} e^{-\frac{\Delta t}{\tau_a}} + R_{a,ct} I_k \left[1 - e^{-\frac{\Delta t}{\tau_a}} \right] \quad (8.7b)$$

$$E_{1,c,k+1} = E_{1,c,k} e^{-\frac{\Delta t}{\tau_c}} + R_{c,ct} I_k \left[1 - e^{-\frac{\Delta t}{\tau_c}} \right] \quad (8.7c)$$

$$E_{2,c,k+1} = E_{2,c,k} e^{-\frac{\Delta t}{\tau_c}} - f R_{c,ct}^2 I_k^2 \left(1 - e^{-2\frac{\Delta t}{\tau_c}} \right)$$

$$-f \left\{ E_{1,c,k}^2 \left(1 - e^{-\frac{\Delta t}{\tau_c}} \right) + 2 R_{c,ct} I_k [E_{1,c,k} - R_{c,ct} I_k] \frac{\Delta t}{\tau_c} - 2 R_{c,ct} I_k E_{1,c,k} \left[\left(1 - e^{-\frac{\Delta t}{\tau_c}} \right) \right] \right\} e^{-\frac{\Delta t}{\tau_c}} \quad (8.7d)$$

$$\varepsilon_{k+1} = \varepsilon_k \quad (8.7e)$$

where Q is the capacity of the battery, and the state vector is of the form,

$$x(k) = [SoC(k) \quad E_{1,a}(k) \quad E_{1,c}(k) \quad E_{2,c}(k) \quad \varepsilon(k)]^T \quad (8.8)$$

Following the perturbation method described in **Equation 8.2**, the cell model described in **Figure 8.3** can be written as,

$$E_{cell}(k) = E_{OCV}(SoC(k)) - E_{1,a}(k) - E_{1,c}(k) - \varepsilon E_{2,c}(k) - R_0(SoC(k))I(k) \quad (8.9)$$

Kalman filter is well-known for performing estimation for linear systems. Here, we adopted an extended Kalman filter, a nonlinear version of the Kalman filter, to perform the nonlinear state estimation with the nonlinear whole-cell model described in **Figure 8.3**. Mathematically, the discrete time nonlinear state equation in **Equation 8.7** has the following form,

$$x(k+1) = g(x(k), u(k)) + w(k) \quad (8.10)$$

where $g(x(k), u(k))$ is the nonlinear state equation that depends on the state vector x and controlled vector u , and w is the process noise. The cell model described in **Equation 8.9** is of the form,

$$y(k) = h(k) + v(k) \quad (8.11)$$

where h is the nonlinear cell model, and v is the observation noise. The extended Kalman filter then relies on the linearization of the nonlinear state equation to perform the nonlinear state estimation. The state transition (F) and observation (H) metrics can be generated with the following Jacobians,

$$F_{k+1} = \frac{\partial f}{\partial x} \Big|_k = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & e^{-\frac{\Delta t}{\tau_a}} & 0 & 0 & 0 \\ 0 & 0 & e^{-\frac{\Delta t}{\tau_c}} & 0 & 0 \\ 0 & 0 & \frac{\partial E_{2,c}}{\partial E_{1,c}} \Big|_k & e^{-\frac{\Delta t}{\tau_c}} & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \quad (8.12)$$

and,

$$H = \begin{bmatrix} \frac{\partial E_{OCV}}{\partial SOC} & -1 & -1 & -\varepsilon & -E_{2,c}(k) \end{bmatrix} \quad (8.13)$$

where

$$\frac{\partial E_{2,c}}{\partial E_{1,c}} \Big|_k = -f \left\{ 2E_{1,c,k} \left(1 - e^{-\frac{\Delta t}{\tau_c}} \right) + 2R_{c,ct} I_k \frac{\Delta t}{\tau_c} - 2R_{c,ct} I_k \left[\left(1 - e^{-\frac{\Delta t}{\tau_c}} \right) \right] \right\} e^{-\frac{\Delta t}{\tau_c}} \quad (8.14)$$

The extended Kalman filter algorithm is shown in **Table 8-II**. This algorithm can be implemented with Simulink to develop the nonlinear state estimator. As mentioned in **Chapters 5** and **6**, the estimated charge transfer asymmetry ε can be an important indicator of the SOH of a battery system. More importantly, the dynamic information of the charge transfer asymmetry can provide additional information about the reaction kinetics in the battery system, paving the foundation for a fast-charging algorithm that utilizes this kinetics information for model predictive control.

Table 8-II. Extended Kalman filter algorithm.

Prediction
$\hat{x}_{k+1 k} = f(x_{k k}, u_k)$ $P_{k+1 k} = F(x_k, u_k)P_{k k}F^T(x_k, u_k) + Q_k$
Correction
$\tilde{y}_{k+1} = z_{k+1} - h(\hat{x}_{k+1 k})$ $S_{k+1} = H_{k+1}P_{k+1 k}H_{k+1}^T + R_{k+1}$ $K_{k+1} = P_{k+1 k}H_{k+1}^T S_{k+1}^{-1}$ $\hat{x}_{k+1 k+1} = \hat{x}_{k+1 k} + K_{k+1}\tilde{y}_{k+1}$ $\hat{P}_{k+1 k+1} = (I - K_{k+1}H_{k+1})P_{k+1 k}$

8.4 VALIDATION OF ANALYTICAL POROUS ELECTRODE MODEL WITH PHYSICS-BASED MODELING AND DATA SCIENCE APPROACH

8.4.1 Introduction

Lithium-ion batteries (LIBs) are complex nonlinear systems that involve the interaction between electrodes and electrolytes along with the movement of lithium-ions in the system. [244]

Nonlinear partial differential equations (PDEs) are required to describe the reaction kinetics, mass transports, and thermodynamics in the LIB system. [34,78,245] These nonlinear PDEs together build the foundation of the full physics model, for which the pseudo-two-dimensional (P2D) model is known. The P2D model considers the classic porous electrode theory with binary electrolyte theory and solid diffusion, which makes it one of the most accurate models for LIB systems. Though the P2D model excels at its rich physics information, the complexity is an unavoidable challenge for real time applications given the numerous computational powers required. [34,45] On the other hand, equivalent circuit models (ECMs) dominate the industrial application with the simplified physics that approximates LIBs. For example, Randles circuit is the most famous ECM that is used as a building block for most complicated ECMs, though it is usually too simple for LIBs. [104,105,107,185] The P2D model and ECMs represent the two extremes of the physics-based modeling for LIBs: either too complicated to be implemented effectively or too simple to describe all the physics. The analytical porous electrode (APE) model we developed in **Chapter 2** lies in between these two extremes, aiming to provide a model that balances model complexity and model applicability.

The development of the APE model relies on the simplification of the P2D model that considers only the major design aspects of commercial LIBs. For example, zero solid resistivity is assumed given the application of high-conductivity battery electrodes. Binary electrolyte theory is ignored given the concentrated electrolyte used in the battery system and the constant electrolyte concentration assumption. All these simplifications reduce the P2D model to a single PDE that can be solved analytically as described in **Chapter 2**. These simplifications can unavoidably lead to errors in describing the correct physics and show up in the parameter estimation with curve fitting analysis. In addition to the known simplification, it is also important to know the limitations

of our model in various applications. Given a measured data and a proposed model, a correlation matrix can be proposed as shown in **Figure 8.4**. There are four possible potential outcomes between fitted data and model as shown in the correlation matrix: 1. a good fit of data as a result of a good physics-based model; 2. a good fit of data as a result of an unrealistic physics-based model; 3. a bad fit of data due to a bad physics-based model; 4. a bad fit of data given the correct physics-based model.

The first condition is undoubtedly the desired outcome for the simplified APE model, but conditions 2 and 4 are also of interest in real applications. For example, the wide application of the well-known Randles circuit for battery modeling usually resides in condition 2. Though Randles circuit is a physics-based model that describes the reaction happening at a thin electrochemical interface, it has been used as a major building block for the development of contemporary battery management systems (BMSs) owing to its ability to capture most physical behavior in the battery systems with only two parameters. [73,74,76] The successful implementation of the Randles circuit does not mean it is the correct physics but demonstrates the need for a simple and informative model that can describe the system well. Condition 4, on the other hand, expresses the need for advanced data quality metrics so that the correct physics will not be buried by the bad data. For instance, the parameter estimation for an electrochemical interface can be messed up even with the known Randles circuit given the poorly measured experimental data. [246] Lastly, the least interested condition 3 can inform us of the applicability of our model. Therefore, it is important to identify the four conditions illustrated in **Figure 8.4** for the APE model developed in **Chapter 2**. Full physics-based modeling with the P2D model provides an excellent way to evaluate these conditions, as it provides the most comprehensive view of the LIB without the concern of the quality of the experimental data.

Good Fit	?	✓
Bad Fit	×	?
	Bad Physics	Good Physics

Figure 8.4. Correlation matrix that shows the relationship between modeled physics and expected fitting outcomes. The (✓) suggests the desired outcomes, the (?) suggests the interested outcomes, and the (×) suggests the unwanted outcomes.

8.4.2 *Physics Based Modeling and Data Science Approach*

To simulate enough EIS and 2nd-NLEIS spectra that represent the wide variety of potential electrode designs, upper bounds and lower bounds for the physical parameters used in the P2D model are first determined. Here, we begin from parameter ranges proposed by Murbach and Schwartz and enlarge the bounds related to solid and solution resistivity, charge transfer resistance, and double layer capacitance to test the extreme design and operating conditions in commercial LIBs, where our simplification could fail. [45] The modified bounds are summarized in **Table 8-III**. With the wide range of bounds, the Sobol sampling method is used to ensure the sample spaces are uniformly distributed. Sobol sampling is done with SALib to generate a total of 10228 sets of input parameters in the proposed ranges. These parameters are then fed into the P2D model developed by Murbach and Schwartz using COMSOL 6.2 with MATLAB live link on an iMac

with M1 chip and 16 GB RAM. [34] Frequencies are varied from 1 mHz to 100 kHz with 10 points per decade to provide enough data points. Each simulation of EIS and 2nd-NLEIS takes approximately 7 minutes that leads to a total time of about 2 months of simulation for all spectra. Though slightly smaller than the EIS data set proposed by Mrubach and Schwartz, this dataset provides the first comprehensive dataset for EIS and 2nd-NLEIS, which can be a foundation for data-science driven analysis in the future.

The applicability of the analytical porous electrode (APE) theory can be validated in three steps to comprehend the correlation matrix described in **Figure 8.4**. First, a direct parameters mapping can be explored between the P2D model and the APE model. The full cell P2D model has a total of 42 parameters and considers the impedance contribution from two electrodes and a separator. To describe this full cell response, an equivalent two-electrode APE model with a total of 15 parameters is developed and considers each electrode in the battery as a porous electrode. The separator and other ohmic processes are included in a resistor. The proposed APE model can be written mathematically as,

$$cell = resistor (R_0) + porous\ anode + porous\ cathode \quad (8.15)$$

The parameter mapping analysis shows that 31 out of 42 parameters from the P2D model can be lumped directly into the 15 parameters in the APE model without any simplification. The remaining 11 parameters are related to model simplifications. The actual parameters mapping is shown as follows,

$$\sigma_{eff,i} = \sigma_i \times (1 - \epsilon_i - \epsilon_{f,i})^{Brugg} [S/m] \quad (8.16)$$

$$k_{eff,i} = k_i \times \epsilon_i^{Brugg} [S/m] \quad (8.17)$$

$$a_i = \frac{3}{r_i} \times (1 - \epsilon_i - \epsilon_{f,i}) [m^2/m^3] \quad (8.18)$$

$$R_0 = \frac{l_{pos}}{\sigma_{eff,pos} + k_{eff,pos}} + \frac{l_{sep}}{k_{eff,sep}} + \frac{l_{neg}}{\sigma_{eff,neg} + k_{eff,neg}} [\Omega \cdot m^2] \quad (8.19)$$

$$R_{pore,i} = \frac{l_i}{k_{eff,i}} [\Omega \cdot m^2] \quad (8.20)$$

$$R_{ct,i} = \frac{1}{i_{0,i} \times \frac{nF}{RT} \times a_i \times l_i} [\Omega \cdot m^2] \quad (8.21)$$

$$C_{dl,i} = \frac{a_i \times l_i}{c_{dl,i}} [F/m^2] \quad (8.22)$$

$$A_{w,i} = -\frac{\partial U}{\partial C_s} \frac{r_i}{nF \times D_{s,i} \times a_i \times l_i} [\Omega \cdot m^2] \quad (8.23)$$

$$\tau_{d,i} = \frac{r_i^2}{D_{s,i}} [s] \quad (8.24)$$

$$\varepsilon_i = \alpha_{a,i} - 0.5 [-] \quad (8.25)$$

$$\kappa_i = \left(\frac{\frac{\partial^2 U}{\partial C_s^2}}{\frac{\partial U}{\partial C_s}} \right)_i [1/V] \quad (8.26)$$

where σ_i is the solid phase conductivity, k_i is the solution phase conductivity, ϵ_i is the void fraction, $\epsilon_{f,i}$ is the filler fraction, *Brugg* is the Bruggeman coefficient, $\sigma_{eff,i}$ is the effective solid phase conductivity, $k_{eff,i}$ is the effective solution phase conductivity, r_i is the radius of the particles, a_i is the specific interfacial area, l_{pos} is the thickness of the positive electrode, l_{sep} is the thickness of the separator, l_{neg} is the thickness of the negative electrode, $i_{0,i}$ is the exchange current density, $c_{dl,i}$ is the double layer capacitance, n is the number of electrons involved per electrochemical reaction, F is the Faraday constant, R is the gas constant, T is the temperature, $D_{s,i}$ is the solid state diffusion coefficient, $\frac{\partial U}{\partial C_s}$ is the first derivative of open circuit voltage, $\frac{\partial U}{\partial C_s}$ is the first derivative of the open circuit voltage, $\frac{\partial^2 U}{\partial C_s^2}$ is the second derivative of the open circuit

voltage, and $\alpha_{a,i}$ is the anodic charge transfer coefficient. **Equations 8.19-8.26** describe the key lumping parameters derived from the P2D model required to simulate an APE model introduced in **Chapter 2**. The direct parameters mapping shown in **Equations 8.19-8.26**, thus, enables the simultaneous simulation of the P2D model (42 parameters) and the APE model (15 parameters), which can then be compared directly using the following normalized cost function for EIS and 2nd-NLEIS,

$$COST = \sum_{i=1}^N \left[\frac{Z^{P2D}(\omega_i) - Z^{APE}(\omega_i)}{\max(|Z^{P2D}|)} \right]^2 \quad (8.27)$$

Figure 8.5 shows two typical outcomes from the direct comparison between P2D and APE models: namely, good match and bad match. **Figure 8.5a-b** shows the typical outcomes for condition 1, where the P2D model aligns with the APE model, suggesting the underlying physics is not affected by the simplification made in the APE model. On the other hand, **Figure 8.5c-d** shows typical results of incorrect physics that will be fed into the next step of analysis.

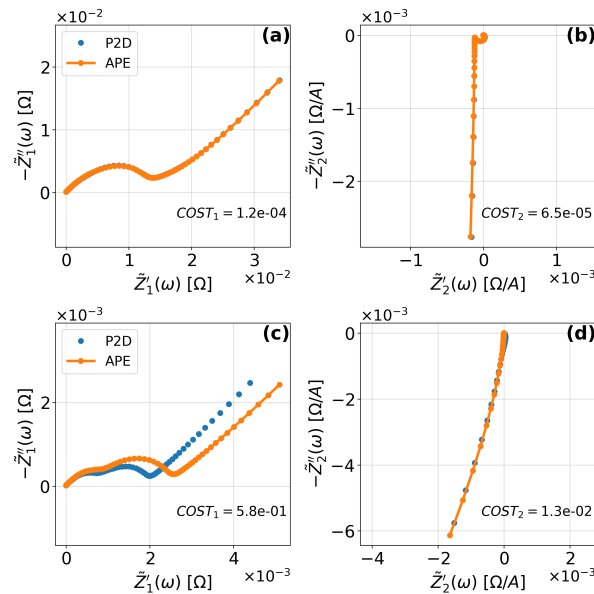


Figure 8.5. Typical linear (a,c) and second harmonic nonlinear (b,d) impedance response from direct mapping analysis. (a-b) demonstrate good and (c-d) demonstrate a bad match between the P2D and APE models.

The parameters set described by **Figure 8.5c-d** includes not only condition 2 but also condition 3. To distinguish between completely wrong physics and wrong but useful physics, a curve fitting analysis is performed. Here, we adopt the data analysis pipeline described in **Chapter 5** and simultaneously fit both EIS and 2nd-NLEIS results from the P2D simulation with the APE model. **Figure 8.6** shows two typical results from the curve fitting analysis, where the directly mapped parameters are used as initial guesses. For the same P2D result in **Figure 8.5c-d**, a perfect match between the P2D and APE model can be obtained with curve fitting as shown in **Figure 8.6 a-b**, which demonstrates a case that an unrealistic physics described by the APE model can still be used to analyze the underlying physics (condition 2), though special care is needed for the data interpretation. The results in **Figure 8.6c-d**, on the other hand, show the situation where the APE model fails to describe the P2D result even with curve fitting (condition 3). The physical parameters obtained for conditions 1, 2, and 3 can then be used to quantify the overall applicability of the APE model in analyzing the real battery impedance as well as its limitations given the simplification we made.

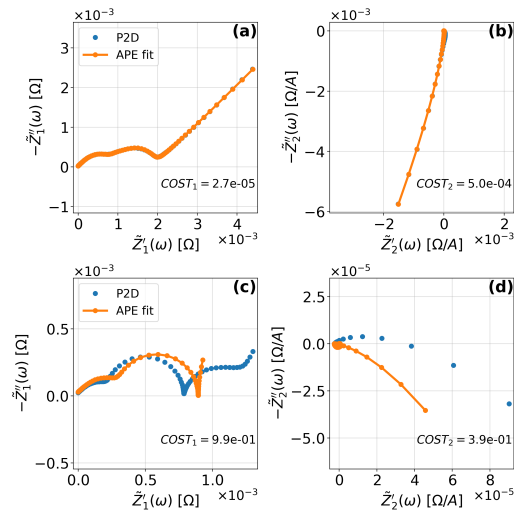


Figure 8.6. Typical linear (a,c) and second harmonic nonlinear (b,d) impedance response from curve fitting analysis. (a-b) demonstrate a good and (c-d) demonstrate a bad fit between the P2D and APE models for an initial bad match.

Lastly, parameters from conditions 1 and 2 are revisited to evaluate the sensitivity of the APE model to the measurement noise. Random noise ($\sigma = 5\%$ of the magnitude) proportional to the magnitude of the impedance is added to the simulated P2D result to mimic the situation that experimental data are poorly collected. **Figure 8.7** shows the curve fitting results for **Figure 8.5** after random noise is added to the P2D simulation. In both cases, the APE model demonstrates an excellent robustness to the measurement noise. Further exploration can be done to thoroughly examine the limitations of the model. These results will complete the last pieces of the correlation matrix (condition 4). Applicability of simplified physics-based models can then be understood with this data-science driven approach. Future exploration on this EIS and 2nd-NLEIS dataset can benefit from the growing popularity of data science approaches to improve the accuracy and confidence of parameter estimation, while leveraging the complementary parity of EIS and 2nd-NLEIS.

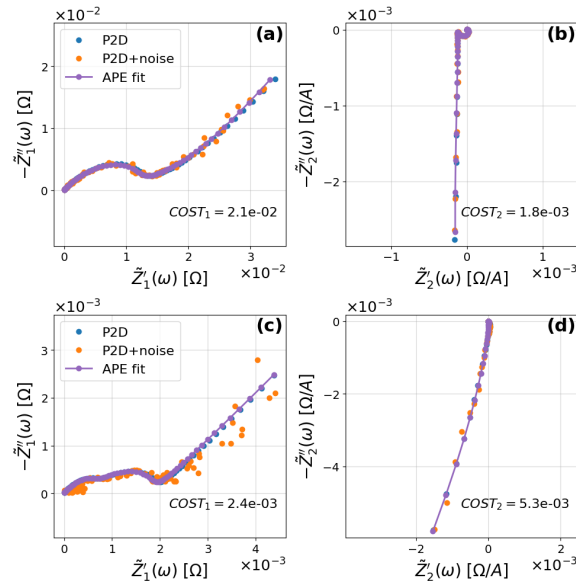


Figure 8.7. Linear (a,c) and second harmonic nonlinear (b,d) impedance response from curve fitting analysis with 5% random noise. (a-b) demonstrate the model sensitivity when correct physics is present (condition 1), and (c-d) demonstrate the model sensitivity when a wrong but usable physics is present (condition 2).

Table 8-III. Physicochemical and geometric parameters ranges.

Physicochemical Parameters			
Parameters	Lower Limit	Upper Limit	Units
$C_{dl,n}$	1	100	$\mu F / cm^2$
$C_{dl,p}$	1	2000	$\mu F / cm^2$
c_0	100	5000	mol / m^3
D	10^{-11}	10^{-9}	m^2 / s
$D_{s,n}$	10^{-19}	10^{-10}	m^2 / s
$D_{s,p}$	10^{-17}	10^{-10}	m^2 / s
$\frac{dU_n}{dc^s}$	10^{-2}	10^2	$V \cdot cm^3 / mol$
$\frac{dU_p}{dc^s}$	10^{-2}	10^2	$V \cdot cm^3 / mol$
$\frac{d^2U_n}{dc^{s^2}}$	10^{-2}	10^5	$V \cdot cm^6 / mol^2$
$\frac{d^2U_p}{dc^{s^2}}$	10^{-2}	10^5	$V \cdot cm^6 / mol^2$
$i_{0,n}$	1	20	A / m^2
$i_{0,p}$	0.1	200	A / m^2
t_+^0	0.2	0.99	—
$\alpha_{a,n}$	0.2	0.8	—
$\alpha_{a,p}$	0.2	0.8	—
κ	0.1	8	S / m
σ_n	30	4000	S / m
σ_p	1	200	S / m
Geometric Parameters			
l_n	15	1200	μm
l_s	8	40	μm
l_p	15	1200	μm
R_n	0.5	20	μm
R_p	1	15	μm
$\epsilon_{f,n}$	0.01	0.12	—
$\epsilon_{f,p}$	0.01	0.12	—
ϵ_n	0.2	0.5	—
ϵ_s	0.35	0.8	—
ϵ_p	0.2	0.5	—

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- Phosphate, and Layered Nickel-Manganese-Cobalt Oxide, *J. Electrochem. Soc.* 164 (2017) E3243. <https://doi.org/10.1149/2.0341708jes>.
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CURRICULUM VITAE

Yuefan Ji

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Education

University of Washington, Seattle GPA: 3.84/4.0 June 2025
 Ph.D. Chemical Engineering
 Thesis: *Practical Second Harmonic Nonlinear Electrochemical Impedance Spectroscopy for Lithium-Ion Batteries*
 M.S. Chemical Engineering with Data Science Option Dec. 2023
University of California, Santa Barbara GPA: 3.84/4.0 June 2021
 M.S. Materials Science
University of California, Santa Barbara GPA: 3.71/4.0
 B.S. Chemical Engineering & B.S. Mathematical Sciences, graduated with honors June 2020
 Dean's List: W17, S17, F17, S18, W19, S19, F19

Research Experience

Graduate Researcher, Schwartz Group, Chemical Engineering Department, UW Seattle
 January 2021 – Present

- Pioneered Li-ion battery characterization with second harmonic nonlinear electrochemical impedance spectroscopy (2nd-NLEIS)
- Developed porous electrodes model to improve data analysis accuracy and resolve model degeneracy in EIS.
- Investigated the SOC and SOH dependence of the nonlinear parameters, such as charge transfer asymmetry and thermodynamic curvature using 2nd-NLEIS.
- Implemented Pseudo-two-dimensional (P2D) model with COMSOL to enhance the understanding of complex EIS and 2nd-NLEIS spectra.
- Designed and built nleis.py, an open-source package supporting EIS and 2nd-NLEIS data analysis.

Graduate Researcher, Clément Group, Materials Department, UC Santa Barbara
 August 2020 – August 2021

- Synthesized novel disordered rock salt cathode materials via a high-energy ball mill, achieving a rechargeable capacity above 250 mAh/g.
- Characterized cathode materials using powder XRD and electrochemical methods (galvanostatic test, cyclic voltammetry, and differential capacity analysis).
- Designed a carbon anode pre-treatment protocol for methane pyrolysis-derived carbon to enable its application in Li-ion and Na-ion batteries as the anode or conductive additive.

Undergraduate Researcher, Clément Group, Materials Department, UC Santa Barbara.
 March 2019 – August 2020

- Analyzed methane pyrolysis-derived carbon anodes for lithium-ion battery applications.
- Prepared anodes, assembled coin cells, made measurements of cell performances, and did characterizations of the carbon.
- Assembled and tested coin cells to evaluate the electrochemical performance and material characteristics.
- Synthesized the novel lithium transition metal oxide via high-temperature solid-state synthesis.

Work Experience

Cell Engineering Intern, Tesla

Mar 2024 – June 2024

- Established EIS, GITT, ICI, and AMIDR methods to determine solid-state diffusion coefficients within the cathode and anode materials.
- Developed an EIS-based technique for battery electrode tortuosity determination.
- Improved exchange current density measurement and determination using EIS.
- Enhanced battery characterization and analysis algorithms in Python.
- Helped to optimize the development of fast-charging algorithms.

Battery Engineer Intern, Pure Watercraft

June 2023 – Sept 2023

- Developed a SOC estimation algorithm (Kalman filter + open circuit calibration) improving accuracy to $\pm 1\%$ using MATLAB/Simulink.
- Designed high/low-end SOC buffer systems to enhance user experience (better confidence in SOC reading).
- Implemented a coulomb counting framework enabling capacity calibration for SOH estimation.
- Developed validation test plans leading to the discovery of sensor calibration faults.
- Developed test plans to validate onboard DC internal resistance measurement capability, enhancing battery diagnostics.
- Automated data analysis pipelines in Python, reducing model development and validation time for SOC estimation.

Design Projects

EIS Cream, Data Science Capstone, UW Seattle

Jan 2021 – June 2021

- Led the development of a machine learning and data visualization package for battery research that enables fast data exploration and SOH prediction.
- Implemented random forest, gradient boosting, and neural networks for SOH prediction.
- Presented software in a poster session and engaged with stakeholders for feedback.

Ethyl Acetate Plant Design, Senior Capstone, UC Santa Barbara

March 2020 – June 2020

- Designed an ethanol dehydrogenation process, improving profitability with a multi-reactor system.
- Designed a process flow diagram including reactors, heat exchangers, and separation units.
- Simulated a conceptual design of the plant using MATLAB and designed a separation system that involves azeotropic solution via Aspen Plus.
- Simulated a process flow diagram using Aspen HYSYS and performed economic analysis.

Para-Xylene Plant Design, Senior Capstone, UC Santa Barbara

January 2020 – March 2020

- Designed a Para-xylene production via Toluene disproportionation reaction.
- Constructed a conceptual design of the plant via MATLAB simulation of a process flow diagram and simulated it in Aspen HYSYS

Honors and Awards

University of Washington, Seattle, Clean Energy Institute Graduate Fellow

Best Senior Design Project for 2019-2020, Department of Chemical Engineering, UC Santa Barbara

Skills

Battery Testing: EIS, 2nd-NLEIS, GITT, ICI, AMIDR, Arbin, and Bio-Logic

Battery Fabrication: Coin cell, PAT cell, and Swagelok cell

Materials characterization and synthesis: XRD, ICP-OES, TGA-MS, and high-energy ball mill

Computer Language: Python (pandas, NumPy, SciPy, Matplotlib), MATLAB, Simulink, COMSOL

Teaching Experience

Teaching Assistant

- CHEME 525 A - Chemical Engineering Thermodynamics (1 quarter at UW)
- CHEME 480 A - Process Dynamics and Control (1 quarter at UW)
- MCDB 108 A - General Biochemistry (1 quarter at UCSB)

Publications

Y. Ji, M.D. Murbach, D.T. Schwartz, nleis.py: A Nonlinear Electrochemical Impedance Analysis Toolbox. *JOSS*. (2025) <https://doi.org/10.21105/joss.07424>

R. Giovine, E. Yoshida, V. Wu, **Y. Ji**, M. Crafton; B. McCloskey, R. Clément, An experimental approach to assess fluorine incorporation into disordered rocksalt oxide cathodes. *Chem. Mater.* (2024) <https://doi.org/10.1021/acs.chemmater.3c03138>

Y. Ji, D.T. Schwartz, Second-Harmonic Nonlinear Electrochemical Impedance Spectroscopy: II. Experimental approach and analysis on lithium-ion battery experiments. *J. Electrochem. Soc.* (2024) <https://doi.org/10.1149/1945-7111/ad2596>

Y. Ji, D.T. Schwartz, Second-Harmonic Nonlinear Electrochemical Impedance Spectroscopy: I. Analytical theory and equivalent circuit representations for planar and porous electrodes. *J. Electrochem. Soc.* (2023) <https://doi.org/10.1149/1945-7111/ad15ca>.

Y. Ji, C. Palmer, E.E. Foley, R. Giovine, E. Yoshida, E. Sebti, A.R. Patterson, E. McFarland, R.J. Clément, Valorizing the carbon byproduct of methane pyrolysis in batteries, *Carbon*. 204 (2023) 26–35. <https://doi.org/10.1016/j.carbon.2022.12.044>.

Proposals

"Investigating the phase purity and long-range structure of disordered rocksalt cathodes through XRD", APS beamline 11-BM. Granted, November 2020

"Investigating the local structure and oxidation state of disordered rocksalt cathodes through XAS", APS beamline 20-BM-B. Granted, August 2021

Presentations

R. Vincent, **Y. Ji**, D. T. Schwartz, Nondestructive State-of-Health Evaluation of Li-Ion Batteries Using EIS and Nonlinear EIS. In: 2025 MRS Spring Meeting. Seattle, WA. Apr 10, 2025.

Y. Ji, D. T. Schwartz, Structural and Kinetic Understanding of the Surface Reconstruction in Ni-Rich NMC Using Second-Harmonic Nonlinear Electrochemical Impedance Spectroscopy. In: 2025 MRS Spring Meeting. Seattle, WA. Apr 8, 2025.

Y. Ji, D. T. Schwartz, Leveraging the Discriminating Power of Second-Harmonic Nonlinear Electrochemical Impedance Spectroscopy with Nonlinear Transmission Line Model. In: Electrochemical Society PRiME 2024. Honolulu, HI. Oct 9, 2024.

Y. Ji, A. H. Shih, D. T. Schwartz, Analyzing Experimental Data Validity and Error Structure for Second-Harmonic Nonlinear Electrochemical Impedance Spectroscopy. In: Electrochemical Society PRiME 2024. Honolulu, HI. Oct 9, 2024.

Y. Ji, D. T. Schwartz, Understanding the Interfacial Evolution of Lithium-Ion Batteries Using Second-Harmonic Nonlinear Electrochemical Impedance Spectroscopy. In: Electrochemical Society PRiME 2024. Honolulu, HI. Oct 9, 2024.

Y. Ji, D. T. Schwartz, The Evolution of Cathode Electrolyte Interphases Probed with Second-Harmonic Nonlinear Electrochemical Impedance Spectroscopy. In: 98th ACS Colloid & Surface Science Symposium. June 22, 2024.

Y. Ji, D. T. Schwartz, NMC Charge Transfer Symmetry Breaks during Cycle Aging of Lithium-Ion Cells. In: 245th Electrochemical Society Meeting. San Francisco, CA. May 28, 2024.

Y. Ji, D. T. Schwartz, Coupling Linear and Second-Harmonic Electrochemical Impedance Spectroscopy to Determine Half-Cell Physicochemical Processes from Measurements in Two-Electrode Cells. In: 243rd Electrochemical Society Meeting. Boston, MA. May 30, 2023.