Electrochemical impedance spectroscopy (EIS) is a fast, in-situ, and non-destructive technique for characterizing aging in lithium-ion batteries (LiBs). The impedance is expressed as a ratio of the voltage response to a current perturbation and is typically obtained over a range of frequencies. Impedance data are represented in formats to provide insight into governing physical processes and allow for a separation of time constants for multiple physical processes based on the frequency of measurement. However, several processes with similar time constants exist in cells which complicate the interpretation of impedance spectra.

Interpretation of impedance measurements are most commonly resolved by equivalent circuit analogs.\(^1\)–\(^4\) These analogs require assumption of the physics of the processes involved, potentially leading to multiple interpretations during data fitting. Resistors, capacitors, and artificial circuit elements are useful for evaluating trends in the impedance response of the system. Often, the circuit elements are sufficient in fitting the data. However, there remains difficulty in expressing the chosen circuit elements as measurable physical parameters for a quantitative assessment.

Physics-based impedance models offer a more fundamental method to interpret experimental impedance data. These physics-based electrode models are convenient in relating the measured impedance response to fundamental physical parameters and can be easily modified to capture non-ideal impedance responses. In some cases, the models are used for parametric studies, to distinguish the overlapping physical processes that influence the impedance response. In other cases, the models are utilized to fit experimental impedance spectra, to elucidate the causes of cell degradation.

Two of the most frequently referenced models were developed by Doyle et al. and Meyers et al.\(^5\)–\(^6\) Doyle et al. used a porous electrode model to describe variation in kinetic and transport parameters for a lithium polymer chemistry. The individual responses of each electrode were found to be linked to the physical parameters chosen to describe lithium kinetics and mass transport. They concluded that solid-phase lithium diffusivities are measurable from the low-frequency response. However, the interpretation of the low-frequency portion of impedance spectra can be complicated by overlapping time constants from electrode processes. Because of the overlapping processes, the solid-phase diffusivity requires impedance data at low enough frequencies such that that process is the dominating impedance at the measured frequencies. Meyers et al. developed an entirely analytical porous electrode model that incorporated a particle size distribution and a surface film. The model ignored electrolyte-phase concentration gradients. An important conclusion from their work was that contributions from particle size distributions influence the curvature of the low-frequency impedance response. Both Doyle et al. and Meyers et al. assumed the existence of a steady-state solution, around which the system was perturbed. By allowing for a small perturbation in each variable, the solution exhibited linearity. The linear system of equations was transformed from the time domain to the frequency domain, leaving a set of ordinary differential equations, from which the impedance was readily calculated. This approach to obtaining the impedance response has been replicated by many authors.

An extension of these two works has allowed several groups to focus on investigating the low-frequency impedance response by developing physics-based models. Devan et al. presented the analytical solution of the impedance response of a single porous electrode with linear kinetics and electrolyte-phase concentration gradients present.\(^7\) The analytical expression indicated that electrolyte-phase concentration gradients manifest at low frequencies. More recently, Gambhire et al. developed a model that incorporated particles that underwent phase transitions.\(^8\) They found that phase transitions caused changes to the low-frequency impedance response, creating a finite length Warburg impedance element at low frequencies. This unique feature was determined useful in estimating the battery state of charge. Chen et al. generated an artificial porous electrode with various active material morphologies and constructed microstructures.\(^9\) The generated microstructures were then defined in terms of their physical properties and parameterized as impedance model inputs. They found that the coupled effect of particle shape and electrode microstructure caused additional curvature in the impedance response at mid and low frequencies. Most qualitative analyses have found multiple processes influence the mid- and low-frequency impedance response of the cell, which supports the need for a physics-based fitting approach.

Several investigators have attempted to validate physical models using experimental impedance spectra,\(^4\)–\(^10\) with some microstructural analysis of either positive or negative electrode to support the proposed model.\(^11\)–\(^12\) For example, Dees et al. investigated the post-cycling impedance response of an LiNi\(_{0.89}\)Co\(_{0.10}\)Al\(_{0.01}\)O\(_2\) (LiNCA) positive electrode.\(^13\) Microscopic imaging of cycled secondary particles indicated the presence of a core-shell particle structure. The shell was primarily of nickel that formed during cycling. The features of the simulated impedance responses better agreed with the experimental impedance measurements after incorporating a core-shell structure for the positive electrode particles. Abraham et al. developed a model to obtain physical parameters for a LiNCA cathode.\(^14\) They fit lithium diffusion coefficients in the solid phase and kinetic exchange-current densities at states of charge between 3 and 4.7 V vs. Li/Li\(^+\). The trends in the fitted diffusion coefficients were qualitatively supported by changes in electrode microstructure structure observed by in-situ X-ray diffraction measurements. To obtain improved experimental data fits, they introduced a tri-modal particle size distribution. The tri-modal distribution improved low-frequency agreement of the simulated response with experiment. Zavalis et al.
investigated both calendar aging and cycling in LiFePO₄ mesocarbon microbead (MCMB) pouch cells at 22°C. Cycling was found to cause a significant loss in capacity and increase in impedance, whereas calendar aging effects were less extensive. Scanning electron microscopy (SEM) micrographs of cycled electrodes indicated significant structural changes in the LiFePO₄ electrode causing a lessening of the electrode porosity. Parameter estimates obtained by fitting the impedance responses supported a changing porosity hypothesis, consistent with SEM observations.

In this work, we attempt to validate a physics-based model based on the work of Fuller et al. for a graphite|LiNi₀.₃₃Mn₀.₃₃Co₀.₃₄O₂ (LiNMC) cell. Our objective is to gain an understanding of the effect of structural changes in the electrodes due to high-temperature calendar aging on the mid- and low-frequency impedance response. The model includes multiple particles in each electrode, a two-layered positive electrode particle, and uses an additional free parameter to describe electrolyte transport. The model is validated using experimental EIS data and post-mortem micrographs. A discussion on the impact of calendar aging on the impedance spectra is presented.

**Experimental**

Calendar aging experiments were conducted using commercial electrodes. The negative electrode used was graphite. The positive electrode used was LiNMC. The electrolyte is 1:1 (wt) EC:DEC with 1 M LiPF₆ salt. The separator material was a Celgard 2325 PE/PP membrane. Electrodes of 1.6 cm² in area were punched out and used to assemble coin cells. Half-cell and full-cell coin cells were assembled from the graphite and LiNMC punched electrodes. Lithium for the half-cells was obtained from MTI. The lithium metal electrodes were gently brushed before coin cell assembly to remove any unwanted debris.

First, an open-circuit voltage obtained at 25°C temperature for the cell chemistry was measured from the fresh cells. The open-circuit voltage curve vs. state of lithiation (SOL) of the cell was obtained by applying a C/25 discharge current for 1 hour starting at 4.2 V (100% state of charge). The cell potential was allowed to relax to the equilibrium potential for two hours after the constant current discharge. The cell potential was then recorded. The graphite open-circuit potential vs. SOL was assumed from the literature. The LiNMC electrode open-circuit potential vs. SOL curve was obtained from the difference of the two curves. The negative to positive electrode capacity ratio was estimated to be approximately 1.15.

Second, five coin cells were calendar aged. The coin cells were housed in an environmental chamber at 75°C. The cell voltage was held for 3 hours at 50% SOC. Then, the cells were removed from the environmental chamber and soaked at room temperature (ca. 25°C) overnight. Following soaking, the impedance response of the cells was measured.

EIS was performed using a MetroOhm Autolab Potentiostat. A 5 mV_RMS perturbation was applied around the open-circuit voltage over a frequency range of 1 MHz to 5 mHz, for 50 total frequencies logarithmically spaced. Impedance spectra of fresh cells were obtained at the start of the experiment, at 0 hours of calendar aging. Impedance spectra were periodically measured, with a final measurement obtained at 3200 hours of calendar aging.

Following the impedance measurements, the coin cells were disassembled in the glove box and electrodes removed. The electrodes were taken for transmission electron microscopy (TEM). Micrograph of the LiNMC cathode samples were obtained with a Tecnai G2 F30 (FEI, Netherlands) operated at an accelerating voltage of 300 kV. Prior to the imaging, the electrodes were submerged in dimethyl carbonate (DMC) in the glove box. The electrodes were then sonicated to separate NMC particles from the current collector surface. NMC powders, suspended in DMC, were drop cast onto a TEM grid. The samples were exposed to air for a short period of time for transfer to the sample chamber.

**Model Formulation**

Figure 1 is a generic illustration of a full-cell sandwich. The porous electrodes consist of secondary active insertion material particles, binder, and additives to improve electronic conductivity. An electronically inert separator is contained between the two porous electrodes. The secondary particles are composed of smaller primary particles in each electrode. These particles are spherical and can be enveloped in a surface film. Current collectors close the ends of the cell.

Solid phase variables are represented by subscript 1, while electrolyte-phase variables are given as subscript 2. Negative electrode variables are denoted by the subscript – and positive electrode variables by +. The position in the cell is given by the independent variable x. The negative electrode is of thickness L_− and the separator is of thickness L_sp. The positive electrode is of thickness L_+. The total cell thickness is given as L_cell. The current collectors (CC) are represented as ±CC. The radius of the spherical particles in the positive and negative electrodes is given by r_x.

In the next sections, the model is described. First, the governing equations for the cell are given in the time domain. The equations are then transformed into the frequency domain, for which the impedance response is calculated.

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**Time domain representation.**—Intercalation particle equations.—Charge transport across a surface film, double-layer charging, lithium charge-transfer kinetics, and solid phase diffusion of lithium are considered in the single particle equations. At the film-electrolyte interface, the current density leaving the electrolyte, i_{tot,−}, passes into the film

\[
i_{tot,−} = \frac{k_{film,−}}{L_{film,−}} \left( \psi_{film,−} - \psi_{2,±} \right). \tag{1}
\]

In this formulation, \(k_{film}\) is the film conductivity, \(L_{film}\) is the film thickness, \(\psi_{film}\) is the potential at the solid-film interface, \(\psi_{2}\) is the potential at the film-electrolyte interface measured in the electrolyte phase.

The current density that passes through the film resistor reaches the surface of the particle. At this interface, the current can pass across the interface by double-layer charging or an electron-transfer reaction. The current density that crosses is given as

\[
i_{tot,±} = i_{dl,±} + i_{rat,±}, \tag{2}
\]
where \( i_d \) is the current density due to charging the double layer, and \( i_{int} \) is the intercalation current density. The current associated with double-layer charging is given as
\[
i_{dl,\pm} = C_{dl,\pm} \frac{d\left(\psi_{1,\pm} - \psi_{lim,\pm}\right)}{dt}.
\]  
\( C_{dl} \) is the double-layer capacitance of the particle. \( \psi_{1} \) is the solid potential which is set to zero at the graphite current collector. The faradaic reaction rate is governed by the potential drop across the particle-film interface,
\[
i_{int,\pm} = i_{0,\pm} \left( \exp \left[ \frac{\alpha_u F}{R_{tot} T} \left( \psi_{1,\pm} - \psi_{lim,\pm} - U_\pm c_{\pm \mid r=R_e} \right) \right] - \exp \left[ -\frac{\alpha_c F}{R_{tot} T} \left( \psi_{1,\pm} - \psi_{lim,\pm} - U_\pm c_{\pm \mid r=R_e} \right) \right] \right),
\]  
\( i_0 \) is the exchange-current density, \( \alpha_u \) and \( \alpha_c \) are charge-transfer coefficients, \( F \) is Faraday’s constant, \( R \) is 8.314 J·mol\(^{-1}\)·K\(^{-1}\), \( T \) is temperature, and \( U \) is the equilibrium potential. \( c_{\pm \mid r=R_e} \) is the concentration of lithium at the surface of the intercalation particle. The equilibrium potential is a function of the state of lithiation, \( x \), of the respective electrodes
\[
U_+ = 2.494x^4 - 4.2646x^3 + 2.4109x^2 - 1.4027x + 4.3933,
\]  
\[
U_- = -0.039 + 1.41\exp(-3.52x).
\]  
The positive electrode open-circuit potential function is measured in this work.

The particles into which lithium intercalates are described as spherical in shape, with a constant diffusivity, \( D \). The governing equation for the spherical particles is given as
\[
\frac{\partial \alpha_u}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right).
\]  
\( c \) is the concentration of lithium in the spherical particles, and \( r \) is the radial coordinate.

**Porous electrode equations.**—Porous electrode transport is described charge conservation equations. Concentration gradients in the electrolyte phase are ignored in this formulation. Conservation of charge for each porous electrode is given as
\[
i_{tot,\pm} = -\frac{1}{a_{u,\pm}} \frac{di_{1,\pm}}{dx}.
\]  
where \( i_2 \) is the current density in the electrolyte phase, and \( a_{u,\pm} \) is the specific interfacial surface area of the electrode assuming a spherical particle packing. Similarly, in the solid phase
\[
i_{int,\pm} = -\frac{1}{a_{c,\pm}} \frac{di_{1,\pm}}{dx}.
\]  
The electrolyte-phase current density is given by Ohm’s Law,
\[
i_2 = -k_2 \frac{k_{2,\pm}}{k_{1,\pm}} \frac{d\psi_{2,\pm}}{dx},
\]  
k\(_2\) is the conductivity of lithium in the electrolyte phase. Electronic current flows in the solid phase and is given by Ohm’s Law,
\[
i_{1,\pm} = -\sigma_{1,\pm} \epsilon_{1,\pm} \frac{d\psi_{1,\pm}}{dx},
\]  
where \( \sigma \) is the electronic conductivity in the solid phase and \( \epsilon \) is the fraction of solid particle. The total current density, \( I \), across the porous electrode is conserved between the solid and electrolyte phases
\[
I = i_1 + i_2.
\]  

**Frequency domain representation.**—The impedance response is obtained by solving the governing system of equations in the time domain for the full cell. The model equations are transformed from the time domain to the frequency domain using the technique described by Meyers et al.\(^\text{6}\) In this formulation, system variables, \( X \), are rewritten as the summation of steady-state variables and perturbed variables
\[
X = \tilde{X} + \text{Re}\left\{\tilde{X}e^{i\omega t}\right\},
\]  
where \( \tilde{X} \) is the steady-state response, \( \tilde{X} \) is a complex phasor, containing both magnitude and phase angle information, \( j \) is the imaginary unit, and \( \omega \) is the angular frequency. Allowing only for small amplitude perturbations, implying a linear response, the function for which a variable is evaluated is expressed as
\[
f(X) = f(X) + \frac{df}{dX} \text{Re}\left\{\tilde{X}e^{i\omega t}\right\},
\]  
where the first derivative is evaluated around the condition of steady state.

**Interparticle particle impedance equations.**—Transformation of the particle Equations 1–4, into the frequency domain gives
\[
\tilde{i}_{tot,\pm} = \frac{k_{lim,\pm}}{L_{lim,\pm}} \left( \tilde{\psi}_{lim,\pm} - \tilde{\psi}_{2,\pm} \right) = \frac{1}{R_{lim,\pm}} \left( \tilde{\psi}_{lim,\pm} - \tilde{\psi}_{2,\pm} \right),
\]  
\[
\tilde{i}_{int,\pm} = \tilde{i}_{dl,\pm} + \tilde{i}_{int,\pm},
\]  
\[
\tilde{i}_{dl,\pm} = j\omega C_{dl,\pm} \left( \tilde{\psi}_{1,\pm} - \tilde{\psi}_{lim,\pm} \right),
\]  
\[
\tilde{i}_{int,\pm} = i_{0,\pm} \left( \alpha_u + \alpha_c \right) F \left( \tilde{\psi}_{1,\pm} - \tilde{\psi}_{lim,\pm} - \left( \frac{dU_\pm}{dc_{1,\pm}} \right) \tilde{c}_{\pm \mid r=R_e} \right).
\]  

**Diffusion into graphite electrode particles.**—The negative electrode particles are treated as single-layered particles. Equation 7 is rewritten for the graphite particles to give
\[
j\omega \tilde{c}_- = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \tilde{c}_-}{\partial r} \right).
\]  
For solid diffusion of spherical particles, the flux across the pore-wall interface is given as
\[
\frac{\tilde{i}_{int,\pm}}{F} = -D_s \frac{\partial \tilde{c}_-}{\partial r} \bigg|_{r=R_e}.
\]  
At the center of the spherical particles, the no flux boundary condition applies
\[
\frac{\partial \tilde{c}_-}{\partial r} \bigg|_{r=0} = 0.
\]  
The analytical solution of the solid phase concentration of lithium in the spherical particles is obtained by solving Equations 19–21 leads to
\[
\tilde{c}_- \bigg|_{r=R_e} = \frac{\tilde{i}_{int,\pm}}{F} \frac{R_e}{D_s} \left( \frac{\sinh \left( \sqrt{\gamma} \right)}{\sinh \left( \sqrt{\gamma} \right) - \left( \sqrt{\gamma} \right) \cosh \left( \sqrt{\gamma} \right)} \right),
\]  
where \( \tilde{c}_- \) is evaluated at the surface of the particle for the graphite electrode and \( \gamma = \frac{\omega \epsilon l_s^3}{D_s} \).

Introducing a dimensionless impedance \( Z_{one,\pm} \),
\[
Z_{one,\pm} = \frac{FD_s \tilde{c}_- \bigg|_{r=R_e}}{\tilde{i}_{int,\pm} R_e} = \left( \frac{\tanh \left( \sqrt{\gamma} \right)}{\sqrt{\gamma} - \tanh \left( \sqrt{\gamma} \right)} \right),
\]
Two-layer spherical diffusion as with boundary conditions assumed identical, despite the differences in composition of the two open-circuit voltage functions in both the core and shell layer are to aging effects. The core is represented as layer ‘core’ and the shell is on the order of nanometers in thickness. To note, the dimensionless impedance, is the result of manganese dissolution. The core radius is . The two-layer particle illustration is Figure 2. Let and . The diffusivities through the core and shell layer are and respectively.

\[
\hat{\epsilon}_{\text{int}+} = \frac{\hat{\tilde{i}}_{\text{int}+}}{F} = -\frac{\partial \hat{\tilde{c}}_{\text{int}+}}{\partial r} \bigg|_{r=R_+},
\]

Equations 24–25 are solved using the boundary conditions expressed in Equations 26–29 to give the analytical solution for the concentration profile through the shell of the particle

\[
\hat{\epsilon}_{\text{int}+} = \frac{\hat{\tilde{i}}_{\text{int}+} R_+^2}{n F D_{ss}} \left( \frac{K c R_+ \cosh(K c R_+ - K c R_i)}{r(K c R_i, K c R_+, K c R_+ - (1 + A)\sinh(K c R_i - K c R_+))} \right)
\]

Let . The dimensionless impedance, is defined as

In the limiting case that and , Equation 31 reduces to Equation 23.

Combining the linearized Butler-Volmer equation for spherical particles, and the dimensionless impedance Equation 23 gives

\[
\hat{\tilde{i}}_{\text{int}+} (R_{\text{ct}+} + R_{\text{part}+} Z_{\text{one}+}) = (\hat{\psi}_{i,-} - \hat{\psi}_{\text{lim}+}),
\]

The spherical-particle impedance is given as

\[
Z_k = R_{\text{ct}+} + R_{\text{part}+} Z_{\text{one}+},
\]

Combining Equations 16–17, 33 leads to

\[
\hat{\tilde{i}}_{\text{tot}+} = j \omega C_{\text{dl}+} \left( \hat{\psi}_{i,-} - \hat{\psi}_{\text{lim}+} \right) + \left( \frac{\hat{\psi}_{i,-} - \hat{\psi}_{\text{lim}+}}{R_{\text{ct}+} + R_{\text{part}+} Z_{\text{one}+}} \right).
\]

Rearranging Equation 35 leads to

\[
\frac{\hat{\tilde{i}}_{\text{tot}+}}{j \omega C_{\text{dl}+} + (R_{\text{ct}+} + R_{\text{part}+} Z_{\text{one}+})} = \hat{\psi}_{i,-} - \hat{\psi}_{\text{lim}+}.
\]

Equation 29 is used to obtain an estimate of thickness and diffusivity of this layer. Equation 7 is rewritten for two-layer spherical diffusion as

\[
\hat{\tilde{j}}_{\text{tot}+} = j \omega C_{\text{dl}+} \left( \hat{\psi}_{i,-} - \hat{\psi}_{\text{lim}+} \right) + \left( \frac{\hat{\psi}_{i,-} - \hat{\psi}_{\text{lim}+}}{R_{\text{ct}+} + R_{\text{part}+} Z_{\text{one}+}} \right).
\]

Addition of Equation 15 and Equation 36 gives the combined interfacial current density

\[
\hat{\tilde{i}}_{\text{tot}+} = \left( \frac{\hat{\psi}_{i,-} - \hat{\psi}_{\text{lim}+}}{j \omega C_{\text{dl}+} + (R_{\text{ct}+} + R_{\text{part}+} Z_{\text{one}+})} + R_{\text{lim}+} \right).
\]

Finally, the overall particle impedance is given as

\[
Z_{\text{ovr}+} = \left( \frac{1}{j \omega C_{\text{dl}+} + (R_{\text{ct}+} + R_{\text{part}+} Z_{\text{one}+})} + R_{\text{lim}+} \right).
\]

Overall cell impedance equations.—The impedance of the porous electrode is obtained by combining the particle impedance with the equations that govern transport in the porous electrode. Equations 8–12 can be rewritten in the frequency domains as

\[
\hat{\tilde{i}}_{\text{tot}+} = - \frac{1}{a_{\alpha,\pm} + \frac{1}{dx}} d\hat{\tilde{i}}_{\text{ct}+},
\]

\[
\hat{\tilde{i}}_{\text{tot},\pm} = \frac{1}{a_{\alpha,\pm} + \frac{1}{dx}} d\hat{\tilde{i}}_{\text{ct},\pm}.
\]

\[
\hat{\tilde{i}}_{\text{tot},\pm} = -k_{\alpha,\pm} \frac{1}{dx} \frac{d\hat{\tilde{i}}_{\text{ct},\pm}}{\partial x}.
\]
Similarly, the impedance of the positive electrode, a differential equation expressing the potential differences across the electrodes and separator is required. First, an equation for the potential difference at any position in the electrodes is obtained. Subtracting Equation 41 from Equation 42 and then substituting Equations 39, 40, 43 gives

\[
\frac{d^2 (\tilde{\psi}_{1,\pm} - \tilde{\psi}_{2,\pm})}{dx^2} = \left( \frac{1}{\sigma_{1,\pm} x_{1,\pm}} + \frac{1}{k_{2,\pm} x_{2,\pm}} \right) a_{a,\pm} \tilde{I}_{\text{tot},\pm}.
\]

\[\tilde{I} = \tilde{i}_{1,\pm} + \tilde{i}_{2,\pm}.
\]

To obtain an analytical solution for the impedance response across the porous electrode, a differential equation expressing the potential differences across the electrodes and separator is required. First, an equation for the potential difference at any position in the electrodes is obtained. Subtracting Equation 41 from Equation 42 and then substituting Equations 39, 40, 43 gives

\[
\frac{d^2 (\tilde{\psi}_{1,\pm} - \tilde{\psi}_{2,\pm})}{dx^2} = \left( \frac{1}{\sigma_{1,\pm} x_{1,\pm}} + \frac{1}{k_{2,\pm} x_{2,\pm}} \right) a_{a,\pm} \tilde{I}_{\text{tot},\pm}.
\]

\[\tilde{I}_{\text{tot},\pm} \text{ is obtained from Equation 37.}
\]

For each electrode, boundary conditions are required to solve Equation 44. At the current collectors of the cell, the current density flows through the solid matrix,

\[\tilde{i}_{1,-}|_{x=0} = 0, \quad \tilde{i}_{2,+}|_{x=L_{\text{cell}}} = 0.
\]

At separator-electrode interfaces, the current flows in the electrolyte phase,

\[\tilde{i}_{1,-}|_{x=L_{-}} = 0, \quad \tilde{i}_{1,+}|_{x=L_{-} + L_{\text{sep}}} = 0.
\]

For the negative electrode, solving Equation 44 using the boundary conditions of Equations 45, 46 gives

\[
\tilde{\psi}_{1,-} - \tilde{\psi}_{2,-} = \frac{\tilde{I}}{k_{2,-} x_{2,-} \sigma_{1,-} \beta_-} \times \left( \sigma_{1,-} \cosh (\beta_- x) + k_{2,-} x_{2,-} \cosh (\beta_- (x - L_-)) \right).
\]

where

\[\beta_- = \sqrt{\left( \frac{1}{\sigma_{1,-}} + \frac{1}{k_{2,-} \sigma_{2,-}} \right)} \left( a_{a,-} Z_{\text{over,-}} \right)^{-1}.
\]

Evaluation of Equation 47 at the negative electrode current collector defines the potential difference between the solid and electrolyte phases, \(\tilde{\psi}_{1,-}|_{x=0} - \tilde{\psi}_{2,-}|_{x=0}\).

Second, the electrolyte potential is obtained by solving the differential equation obtained combining Equations 39, 41, 43. This equation can then be evaluated at the current collector and electrode-separator interfaces and subtracted from Equation 47. The potential difference across the electrode is then

\[
\tilde{\psi}_{1,-}|_{x=0} - \tilde{\psi}_{2,-}|_{x=L_{-}} = \frac{\tilde{I}}{k_{2,-} x_{2,-} \sigma_{1,-} \beta_-} \times \left( \left( k_{2,-} x_{2,-} \beta_- \right)^2 + \sigma_{1,-}^2 \right) \cosh (\beta_- L_-) + 2k_{2,-} x_{2,-} \sigma_{1,-} + \beta_- k_{2,-} x_{2,-} \sigma_{1,-} L_- \sinh (\beta_- L_-)) \sinh (\beta_- L_-) \beta_- k_{2,-} x_{2,-} \sigma_{1,-} + \left( k_{2,-} x_{2,-} + \sigma_{1,-} \right).
\]

Rearranging Equation 49 gives the impedance of the negative electrode, \(Z_{p,-}\), as,

\[
Z_{p,-} = \frac{\tilde{\psi}_{1,-}|_{x=0} - \tilde{\psi}_{2,-}|_{x=L_{-}}}{\tilde{I}} = \frac{\left( k_{2,-} x_{2,-} \beta_- \right)^2 + \sigma_{1,-}^2}{\sinh (\beta_- L_-) \beta_- k_{2,-} x_{2,-} \sigma_{1,-} + \left( k_{2,-} x_{2,-} + \sigma_{1,-} \right)} \sinh (\beta_- L_-) \beta_- k_{2,-} x_{2,-} \sigma_{1,-} + \left( k_{2,-} x_{2,-} + \sigma_{1,-} \right).
\]

Similarly, the impedance of the positive electrode, \(Z_{p,+}\), is

\[
Z_{p,+} = \frac{\tilde{\psi}_{1,+}|_{x=L_{\text{cell}}} - \tilde{\psi}_{2,+}|_{x=L_{-} + L_{\text{sep}}}}{\tilde{I}} = \frac{\left( k_{2,+} x_{2,+} \beta_+ \right)^2 + \sigma_{1,+}^2}{\sinh (\beta_+ L_+) \beta_+ k_{2,+} x_{2,+} \sigma_{1,+} + \left( k_{2,+} x_{2,+} + \sigma_{1,+} \right)} \sinh (\beta_+ L_+) \beta_+ k_{2,+} x_{2,+} \sigma_{1,+} + \left( k_{2,+} x_{2,+} + \sigma_{1,+} \right).
\]

where \(L_+ = L_{\text{cell}} - L_- - L_{\text{sep}}\).
Parameter fitting.—Model equations are solved in MATLAB. Parameter estimation is done by minimizing the difference between the experimental and simulated impedance spectra using the finsearch algorithm in MATLAB. The total error between the two measurements is given as

$$\text{Err} = \sum_i \left( (Z_{i,\text{sim}} - Z_{i,\text{exp}})^2 + (Z_{i,\text{sim}} - Z_{i,\text{exp}})^2 \right).$$  \[59\]

Err is the summed difference between the experimental and simulated impedance responses. The counter $i$ is used to denote the frequency of measurement. The subscripts sim, exp, Re, and Im are representative of the simulated impedance response, the experimental impedance response, the real component of the impedance, and the imaginary component of the impedance, respectively.

Results and Discussion

There are several methods that can be used to determine electrode-electrolyte parameters and perform model validation. The approach taken in this work was to use fresh and degraded half-cell and full-cell EIS measurements for model validation. As a supporting measurement, TEM micrographs were used to estimate the positive electrode particle core-shell structure for the positive electrode particles. In Table I, TEM micrographs were used to estimate the positive electrode core-shell structure for the positive electrode particles. The particle surface appears to have formed a film-like structure (boxed in red) due to the high-temperature calendar aging process (Reproduced from Reference 20).

Figure 3. TEM micrographs of the cathode particles before and after degradation. (a) Fresh electrode particles and (b) degraded electrode particles. The particle surface appears to have formed a film-like structure (boxed in red) due to the high-temperature calendar aging process (Reproduced from Reference 20).

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$$\text{Err} = \sum_i \left( (Z_{i,\text{sim}} - Z_{i,\text{exp}})^2 + (Z_{i,\text{sim}} - Z_{i,\text{exp}})^2 \right).$$  \[59\]

Err is the summed difference between the experimental and simulated impedance responses. The counter $i$ is used to denote the frequency of measurement. The subscripts sim, exp, Re, and Im are representative of the simulated impedance response, the experimental impedance response, the real component of the impedance, and the imaginary component of the impedance, respectively.

Results and Discussion

There are several methods that can be used to determine electrode-electrolyte parameters and perform model validation. The approach taken in this work was to use fresh and degraded half-cell and full-cell EIS measurements for model validation. As a supporting measurement, TEM micrographs were used to estimate the positive electrode core-shell structure for the positive electrode particles. In Table I, TEM micrographs were used to estimate the positive electrode core-shell structure for the positive electrode particles. The particle surface appears to have formed a film-like structure (boxed in red) due to the high-temperature calendar aging process (Reproduced from Reference 20).

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resistance double-layer charging across the electrode current collectors, electrolyte interface.

Both the graphite and LiNMC kinetic responses are visible in the mid-frequency range (10 Hz–1 kHz). The kinetic arcs are the result of the lithium redox reaction occurring at the surfaces of each electrode. Both responses have similar characteristic frequencies, which can cause the appearance of one large, overlapping peak in the full cell spectrum. A comparison of Figure 4a and Figure 4b in the mid-frequency range illustrates that the graphite and LiNMC electrode responses have unique characteristic frequencies. The LiNMC kinetic response is visible at slightly higher frequencies and is smaller in arc width than the graphite electrode kinetic response.

In the lower frequency range of the response (<10 Hz), electrolyte-phase and solid-phase transport dominate the spectra. Inflection points between 0.1 Hz–3 Hz imply the separation of the kinetic and mass-transport processes in the system. Additionally, the degraded Li/LiNMC includes a new arc at approximately 5.6 Hz. The new arc is partially produced in the model by defining an additional mass-transport regime across multilayer, positive electrode particles.

In Figure 5, impedance spectra of fresh cells at 50% SOC are given with simulation results overlaid on the experimental measurements. The impedances of the cells are repeatable with an identical feature set and similar magnitudes. A clear separation of characteristic frequencies for the kinetic and mass-transport processes is visible for the cell between approximately 10 Hz and 1 Hz. The kinetic arc is depressed compared to an ideal RC process and includes a high frequency shoulder (ca. 10 kHz). The mass transport tail has an inflection point (ca. 10 mHz), which suggests two partially overlapping processes. The model includes processes that match each feature of the impedance spectra and can produce a very close fit. Using this physics-based impedance model, each feature of the impedance spectra can be interpreted.

The high frequency response capacitive loop is visible due to the current-collector double-layer charging and contact resistance. In Equation 53, \( R_{cc} \) and \( Q_{cc} \) are lumped values that account for the resistance and modified capacitance of the current collectors. The magnitudes of the extra resistor and modified capacitor are constrained so that their characteristic frequencies are greater than 10 kHz. The arc is slightly flattened in some cases. The magnitude of \( R_{cc} \) adjusts the flatness of the arc that is formed from this process.

The mid-frequency arc is a result of the charge-transfer reactions at both electrodes. The sum of both electrode responses is captured in the single arc. The magnitude of the exchange-current densities, double-layer capacitances, and Bruggeman exponent alter the height and width of the kinetic arc. The exchange current densities and capacitances are fitted based on the observed order of imaginary impedance responses measured of the half-cells in Figure 4. A common value assigned to the Bruggeman exponent is 1.5. In this work, the Bruggeman exponent is a fitted parameter with magnitude greater or equal to 1.5. Setting the exponent as a fitted parameter improves the fit significantly.

Increasing the magnitude of the Bruggeman exponent flattens and widens the kinetic arcs of both electrodes. Effectively, the current perturbation traverses across the thickness of the electrode as frequency decreases. Along the current path, the perturbation signal encounters more and more electrolyte resistance and double-layer capacitance. The additional electrolyte resistance and capacitance is analogous to a transmission line, causing the appearance of a \( 45^\circ \) sloped imaginary vs. real in the high-frequency portion of the response. The electrolyte conductivity, the porosity, and Bruggeman exponent are the parameters that determine the magnitude of the electrolyte resistance. A larger Bruggeman exponent means that more electrolyte resistance is encountered, leading to more flattening of the kinetic arc.

The low frequency response is the sum of processes that occur on long time scales. These processes include, but are not limited to, contributions from concentration impedances in the electrolyte and solid-phase mass-transport processes. In this work, we ignore electrolyte concentration gradients in our mathematical representation. Therefore, the model presented in this work only reproduces solid-phase mass-transport impedances. Particle size distributions are known to occur in lithium-ion battery porous electrodes. The fittings shown are with two particle sizes. The small-sized particles have short diffusional tails, and primarily behave as capacitors at low frequencies. The sum of these low-frequency capacitive small particles and large particles increase the slope of the low frequency response to improve agreement.

In Figure 5c, simulated fresh graphite and LiNMC individual electrode responses for cell 5 are given. The ratio of the two electrode impedance responses is comparable to the half-cell measurements in Figure 4a. The characteristic frequency for LiNMC electrode is greater than the graphite electrode. Additionally, the LiNMC arc width is less than the graphite arc width, which is consistent with the measurements. From the fresh cell simulations, we conclude that the model accurately reproduces the frequency of measurement of the kinetic responses.

In Figure 6, impedance spectra of degraded cells at 50% SOC are given with simulation results overlaid on the experimental measurements. The simulated impedance response reproduces the prominent features of the measured response. As with the fresh cell responses, the current-collector charging process is used to fit the high frequency arc formed. There is a slight increase in the high frequency real impedance of the data but is hardly noticeable when comparing Figure 6b to Figure 5b. The increase is consistent with film formation in the negative and positive electrodes, assumed ohmic resistors. However, the small increase indicates that the contribution to the high frequency impedance from the film is not significant. The kinetic arc is now
Figure 5. The impedance response at 50% SOC for fresh, graphite|LiNMC full cells. Simulation results are overlaid on the experimental measurements. In (a), imaginary vs. real component of the response and (b) expanded axes of (a). In (c), the simulated individual electrode responses corresponding to graphite|LiNMC 5.

Figure 6. The impedance response at 50% SOC for aged, graphite|LiNMC full cells. Simulation results are overlaid on the experimental measurements. In (a), imaginary vs. real component of the response and (b) expanded axes of (a). In (c), the simulated individual electrode responses corresponding to graphite|LiNMC 5. The simulated LiNMC response contains a third arc at approximately 6 Hz, which is a result of the core-shell model in the electrode.
expanding in width (ca. a factor of 2), comparing Figure 6b to Figure 5b. This arc appears at a slightly lower frequency in the aged vs. fresh full-cell response, which is consistent with a higher kinetic resistance. As in the case of the fresh cell response, the Bruggeman relation is critical to fitting the data in the aged cell response.

An additional time constant appears after degradation in the mid-frequency region of the response (1–15 Hz), similar to the half-cell positive electrode response. The core-shell spherical particle model allows capturing part of this portion of the response. The shell portion of the response is located close to 1 Hz and creates an open-boundary finite Warburg element, due to the fixed boundary conditions that are applied. The core portion of the response is a reflective boundary, finite Warburg element. The remaining portion of the third arc is a sum of the contributions of the second particles in each electrode.

At the low frequency end of the spectrum (<1 Hz), the sum of the impedances from the solid-phase diffusion processes in both electrodes dominates the response. The shape of the aged-cell response is similar to the fresh-cell data provided in Figure 5c. The length of the tails are slightly different. The difference can be a result of a slight change in the SOL of each electrode, which would alter the magnitude of the open-circuit potential of each electrode. Such a change is possible due to a self-discharge current developing in the cell during the calendar aging period. Another cause of the lengthening of the low frequency tail is from increased concentration impedances in the electrolyte due to the degradation. Any changes in the length of the low frequency diffusional impedance in this model are due to the inclusion of the core-shell cathode particle and ratio of large to small particles in the electrodes.

In Figure 6c, simulated degraded graphite and LiNMC individual electrode responses for cell 5 are given. Similar to the fresh electrode responses, the ratio of the two electrode impedance responses is comparable to Figure 4b. The characteristic frequency for kinetic LiNMC electrode is greater than the graphite electrode. The LiNMC arc width is less than the graphite arc width, which is also consistent with the half-cell measurements. Additionally, the third new arc that appears in the LiNMC degraded half-cell spectra is reproduced in the simulation with the inclusion of the core-shell particle diffusion representation.

Identification of degradation modes.—There are several degradation modes that manifest themselves in the impedance spectra. Estimates of the contribution of each of these modes is obtained following the fitting of the impedance spectra. Each of the two particles in each of the two electrodes (4 particles in total) is allowed to exhibit a unique fitting of the impedance spectra. Each of the two particles in each of the two electrodes (4 particles in total) is allowed to exhibit a unique fitting of the impedance spectra. Each of the two particles in each of the two electrodes (4 particles in total) is allowed to exhibit a unique fitting of the impedance spectra.

Electrode kinetics and Bruggeman exponent.—The characteristic frequencies of the kinetic arcs are defined by the large and small particle double-layer CPEs and exchange-current densities. The arc widths are determined by the magnitude of the exchange-current densities and Bruggeman exponents. The exchange-current densities decrease as the electrode decomposes due to the prolonged high-temperature exposure. Aging increases the Bruggeman exponent values for both electrodes. The increase in the exponent is consistent with film formation in both the negative and positive electrodes due to electrolyte decomposition. The films in both electrodes fill the pores of the active material, decreasing the effective conductivity of the electrolyte across the electrode. The positive electrode film is measured only a few nanometers in thickness but is able to clog the electrolyte-containing pores. A potential consequence of pore clogging is loss of intercalation surface area and cell capacity.

The magnitude of the Bruggeman exponents for the negative and positive electrodes are particularly large compared to the most frequently assumed value of 1.5. The large values of the exponents result from the model reproducing the flattened kinetic arcs for both electrodes and ignoring of concentration gradients in the electrodes and separator. Effectively, the kinetic arc width increases with increasing values of the Bruggeman exponent. The increase in arc width is directly attributable to an exaggerated porous electrode effect, which is contained within the high-frequency portion of the kinetic arc. With the larger magnitude Bruggeman exponents, the perturbation signal encounters more transport resistance due to a higher resistive path. The response is a 45° straight line at high frequencies. The length of the straight line increases with increasing magnitude of Bruggeman exponent. The line begins to curve over after the perturbation signal reaches the back of the electrode, at which point the electron transfer process dominates the response. The combination of the electron transfer process and porous electrode effect produces a slightly flattened arc that can be used to better represent the experimental impedance responses. To note, the negative electrode exponent is significantly larger than that of the positive electrode.

Small particle fraction.—The small negative and positive electrode particles are set to average to approximately 70 nm and 60 nm, respectively. The surface area of each electrode is a sum of the surface areas of large and small particles. The particles are assumed spherical with idealized packing density. The small particle surface areas decrease in each electrode after degradation, consistent with loss of active surface area from pore blocking or current collector delamination.

Shell thickness and diffusivity.—In Figure 7, the diffusivity of lithium through the shell of the positive electrode particles is shown for each cell. The shell thickness is set at 3 nm, which is assigned based on the TEM images provided. The diffusivity of lithium through the shell is calculated to be approximately two orders of magnitude less than that of the core. The shell arc width and characteristic frequency are two independent physical properties that fit to the two parameters. The diffusivity is consistent with slow diffusion through the shell of the particle, followed by faster diffusion through the core of the particle. The core-shell is consistent with structural degradation of the solid particles. Dissolution of metal cations from the host structure is assumed to be the predominant cause of such a structure. A cation dissolution mechanism would create a shell with different physical characteristics than the core of the particle.

In Figure 8, the role of the shell thickness and negative electrode small particle fraction is explored. The parameter set used has been chosen to exaggerate the interesting portions of the impedance response. In Figure 8a, the shell thicknesses of the positive electrode

| Parameter | Units | Fresh | Degraded |
|-----------|-------|-------|----------|
| Q_{large,dl} | F/m² | 0.08 | 0.17 |
| R_{cPE,large,dl} | Ω/m² | 0.96 | 0.95 |
| Q_{large,dl} | F/m² | 0.06 | 0.12 |
| R_{cPE,large,dl} | Ω/m² | 0.99 | 0.95 |
| Q_{small,dl} | F/m² | 0.06 | 0.33 |
| R_{cPE,small,dl} | Ω/m² | 0.94 | 0.87 |
| Q_{small,dl} | F/m² | 0.04 | 0.01 |
| R_{cPE,small,dl} | Ω/m² | 0.99 | 0.95 |
| i₀,large,− | A/m² | 5.56 | 3.95 |
| i₀,large,− | A/m² | 3.16 | 3.16 |
| i₀,small,− | A/m² | 0.53 | 0.35 |
| i₀,small,− | A/m² | 1.75 | 0.69 |
| b− | N/A | 6.00 | 7.26 |
| b− | N/A | 4.51 | 5.36 |
| f_{large,−} | N/A | 2.74 | 2.74 |
| f_{small,−} | N/A | 0.26 | 0.21 |
| f_{small,−} | N/A | 0.08 | 0.05 |
| κ_{large,−} | S/m | N/A | 1.36 × 10⁻⁴ |
| L_{large,−} | m | N/A | 5 × 10⁻⁹ |
| Q_{cc} | F/m² | 0.25 | 0.05 |
| R_{cc} | Ω/m² | 8.33 × 10⁻⁵ | 1.25 × 10⁻⁴ |
| R_{cPE,cc} | Ω/m² | 0.92 | 0.92 |
| D_{large,−} | m²/s | N/A | 1.81 × 10⁻¹⁶ |
| R_{large,−} | m | N/A | 3.0 × 10⁻²⁹ |
Figure 7. Diffusivity of lithium through the shell of the particle for the degraded cells.

Figure 8. Parameter variation on the impedance response. Full-cell impedance responses are given for (a) a varying shell thickness for the two-layer positive electrode particles; (b) The negative electrode response to illustrate the effect of the small particle fraction on the arc width and low-frequency mass-transport slope.

particles are doubled from 3 nm and 6 nm. Doubling the thickness doubles the width of the low-frequency arc. The thicker shell response is found at a slightly lower frequency. As mentioned previously, the core-shell structure of the positive electrode particles reproduces a finite-Warburg element in series with a closed Warburg element. The finite-Warburg element has an initial slope of one on the higher-frequency end of the response and eventually curves toward the real axis. Using the finite Warburg for the shell structure is an effective method to introduce another arc in the spectra.

In Figure 8b, the negative electrode impedance response is simulated for two values of \( \epsilon_{\text{small},-} \). The second condition, \( \epsilon_{\text{small},-} = 0.15 \), is half of the initial condition. The decrease in the fraction of small particles alters the mid- and low-frequency portions of the impedance spectrum. The mid-frequency arc width is increases because the surface area for intercalation decreases. At low frequencies, the slope of the Warburg tail decreases. This behavior is because the small particles behave primarily as capacitors at low frequencies. Capacitors are vertical lines on a Nyquist plot. Hence, less curvature is observed in the low-frequency response for the negative electrode with more small particles (\( \epsilon_{\text{small},-} = 0.30 \) at 1.6 mHz). In this work, two particles are included in each electrode which represent the average of all of the intercalation particles in the electrode. An alternative method to model the low-frequency response is to include a complete distribution of particle sizes. Again, the smaller particles in such a distribution would have shorter finite diffusional lengths than the larger particles.

Conclusions

Degradation modes of a graphite|LiNMC cells are investigated for 3200 hours of 75 °C calendar aging using EIS. Physical parameters are estimated through model-based fitting and are used to identify the potential causes of the changes in the impedance response. The model is validated using experimental impedance response measurements, both half- and full-cell data. TEM micrographs are used to obtain estimates on positive-electrode surface characteristics.

Experimental fresh electrode, half-cell impedance testing indicates that the cathode kinetic response is at higher frequencies than the anode response. Micrographs of the positive electrode indicates significant surface structural changes on the particles post aging. The structural changes are difficult to distinguish but appear to be a combination of a surface film and a shell on the positive electrode particles. High-temperature calendar aging causes an increase in the measured full-cell impedance. Despite film formation in both electrodes, the high-frequency intercept does not appreciably change after aging. The shift is consistent with thicker and less conductive surface films, potentially in both electrodes. The graphite and LiNMC kinetic rate constants decrease following aging. The kinetic arc widths are also dependent on the Bruggeman exponents in both electrodes. The exponent, which describe transport in each electrode, increases after aging. The change in the exponent is consistent with the observed film formation in the electrodes. The magnitude of the Bruggeman exponent is greater in the graphite electrode than the LiNMC electrode. The magnitude of the exponents are greater than typically reported (i.e. approximately 3 to 8).

The positive electrode impedance response includes a new low-frequency arc following aging. The new arc is reproduced using a core-shell model the spherical LiNMC electrode particles, which is consistent with TEM observations. The core-shell structure is attributable to a manganese dissolution process that is known to plague NCM electrodes. The shell thickness has slower diffusivity than the core of the particle. The result indicates that manganese dissolution is potentially diagnosed by impedance spectroscopy. The addition of a small particle improves simulation and experimental agreement, primarily in the low-frequency portion of the response.

Acknowledgments

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List of Symbols

A
a
b
+c
c
CC
C \text{dl}
D
Err
F
I
j
+i0
K
LiNCA
LiNMC
L
n_{\text{pe}}
Q'
R_{\text{gas}}
r
R_{\text{ct}}
R_{\text{out}}
+
S
SEI
SOL
T
t
U
x
X
Z

Greek

\alpha
\epsilon
\varepsilon
k
\Phi
\sigma_1
\omega

Subscripts

a
cpe
c
c\text{t}
dl
dep
exp

far
film
int
large
max
one
overbar
sim
small
solid
tilde
tot
+\text{solid}
+1
+2
1
2

dimensionless diffusional impedance parameter
interfacial surface area [1/m]
Bruggeman exponent
positive electrode particle core
concentration [mol/m³]
Current collector
double-layer capacitance [F/m²]
Diffusivity [m²/s]
error between simulation and experiment
total current density across the electrode [A/m²]
exchange-current density [A/m²]
imaginary unit
equilibrium potential [V]
 fraction of lithium at the solid surface
fraction of lithium at the solid surface
general transformation variable
Faradeic
solid-film interface
intercalation
large particle
maximum
dimensionless impedance parameter
overbar
simulation
small particle
solid portion of the particular electrode
tilde
total
LiNMC electrode
graphite electrode
core of particle
shell of particle
solid phase
electrolyte phase
solid phase
+1 solid phase
+2 shell of particle

dimensionless diffusional impedance parameter
modified double-layer capacitance [F/m²/s^{1-n}]
radial coordinate [m]
charge-transfer resistance [Ω·m²]
particle resistance [Ω·m²]
positive electrode particle shell
solid electrolyte interphase
state of lithiation
cell temperature [K]
time [s]
equilibrium potential [V]
fraction of lithium at the solid surface
general transformation variable
impedance [Ω·m²]

kinetic parameter
fraction of void space
solid volume size fraction
conductivity [S/m]
potential [V]
conductivity of the solid phase [S/m]
angular frequency [rad/s]

anodic
constant phase element
cathodic
charge transfer
double layer
experimental


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