Lithium-ion batteries are primary power sources of electrified vehicles because of their high energy density, high power density and long cycle life compared to their closest rivals such as Ni-MH batteries. In the last two decades, numerical simulation has been successfully used as a powerful tool to comprehend the complicated phenomena and processes in lithium-ion batteries, and to optimize the design. The lithium-ion battery model, which is based on the porous electrode theory and concentrated solution theory, is pioneered by Newman group at the University of California, Berkeley. In Newman model, a two-scale modeling approach is adopted. A microscopic particle model describes the diffusion of lithium ions in the spherical active material particle. Then, the microscopic model is embedded into a macroscopic electrode model incorporating the conservation equations for species and charge in the electrolyte phase.

Nowadays, porous electrodes in lithium-ion batteries commonly have a three-scale structure. The first scale is submicron primary particles, the second scale is secondary particles of several microns in radius, and the third scale is the porous electrode with a thickness of about one hundred microns. As shown in Figure 1, the secondary particles are agglomerates composed of primary particles held together by binder. In most of the previous mathematical modeling, electrochemical reactions are assumed to only occur on the surface of the agglomerate.

Recently, morphological studies from Argonne National Laboratory have detected solid electrolyte interphase (SEI) films between the primary particles inside the agglomerate. This finding reveals that electrolyte can soak into the agglomerate and the electrochemical reaction can occur inside the agglomerate. Studies considering such kind of intra-agglomerate electrochemical reactions are relatively rare, except those work from Farrell et al. Dargaville and Farrell, Dees et al., and Huang et al.

Farrell et al. proposed a three-scale model for primary alkaline battery cathode, and then extended it to a LiFePO4 electrode in 2010. In Farrell’s work, (1) reactions only occur on the surface of nonporous crystals at the first scale; (2) the concentrated solution theory and volume averaging method are then applied to describe particles consisting of equally sized crystals at the second scale; (3) the model is finally extended to a porous electrode in the same manner as in step (2). Farrell’s model is solved numerically in time-domain. The structure of the electric double layer and its effects on the electrochemical reactions were not taken into consideration. Besides that, the ionic diffusion across the SEI film was not taken into account.

Similar to Farrell’s work, Dees et al. modeled a single agglomerate considering electrochemical reactions and species transport inside the agglomerate. In Dees model, the nonlinear partial differential equations were solved numerically using the finite element method in both time and frequency domain. The complexity and heavy computational cost of Dees model impedes its application to the whole porous electrode. In addition, the electric double layer and SEI film were also neglected in Dees model.

The characterization and diagnose methods in frequency domain, specifically, the electrochemical impedance spectroscopy (EIS) technique, are preferred in the study of the lithium-ion batteries. The main advantage of EIS is its high resolution to separate multiple processes exhibiting different time constants. However, one of the challenges is how to interpret the EIS data. The interpretation of EIS data relies heavily on the adopted impedance model. In the literature, there are broadly three kinds of impedance model: equivalent electric circuit model, transmission line model, and physical-electrochemical model. The last kind model is the only one that is capable of correlating the structural and material parameters with cell impedance. Therefore, the physical-electrochemical model is powerful and widely employed in the structure-property-performance study in the R&D of lithium-ion batteries, as such in Ref. 16.

The present authors, Huang et al. presented an analytical, physical-electrochemical impedance model for a single agglomerate with the following advantages: (1) the electrochemical reactions and species transport inside the agglomerate are analytically formulated; (2) the electric double layer capacitance is explicitly expressed as a function of physical-electrochemical and structural parameters with considering a refined structure for the electric double layer; (3) the effect of the structure of the electric double layer on the charge transfer reaction rate is evaluated; (4) the diffusion of lithium ions across the SEI film is described.

This study aims to extend our previous agglomerate impedance model to a whole porous positive electrode. To this end, the porous electrode theory and scale-up methods, such as the volume averaging method, are employed. Compared with existing impedance models for a whole porous electrode, the present model inherits the advantages of our previous model as stated above. A three-electrode lithium-ion cell with a Li reference electrode is designed, and the EIS data of the positive electrode of LiNi0.5Mn0.3Co0.2O2 (NMC) are collected for model validation. To achieve a more convincing validation, a separate model was also tested and the results were compared to the present model.
fit case and a simultaneous fit case are conducted. For the former case, the EIS of ten SOCs is fitted one by one, and all the variables except the electrode thickness are set free. For the latter case, the EIS of multiple SOCs is fitted simultaneously. Only five parameters are taken as functions of the SOC, including the ohmic resistance, the exchange current density, the double layer capacitance, the solid phase diffusivity, and the derivative of open circuit potential with respect to the lithium ion concentration. In addition, the identified values of key model parameters are examined against independent data. A parametric study is performed to evaluate the effect of structural and electrochemical parameters on the impedance of the positive electrode. Special attention is paid to the significance of the diffusion of lithium ions in the electrolyte phase.

**Experimental**

A three-electrode pouch cell was employed for the electrochemical measurements. Lithium nickel-manganese-cobalt dioxide (LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$) and graphite were used as the active materials of the positive electrode and that of the negative electrode, respectively. A polyimide-insulated copper wire, 40 $\mu$m in diameter, with lithium metal coated on one end, was placed between two separators to function as a reference electrode (RE). The electrolyte solution was 1 M LiPF$_6$ in ethylene carbonate (EC)-dimethyl carbonate (DMC)-ethylmethyl carbonate (EMC) mixtures. The cells have a nominal capacity of 5 Ah with the voltage range of 3.0–4.2 V at the rate of 0.3 C. Cell specifications are detailed in Table I.

All of the electrochemical measurements were conducted with a VMP3 multichannel potentiostat from Bio-Logic. The EIS data were acquired in a frequency range from 5 kHz to 20 mHz with an amplitude of 2 A at the open circuit voltage state and 25 $^\circ$C. It is noted that the multichannel capability of the potentiostat enables a simultaneous measurement of the EIS of positive-negative (full cell), positive-reference and negative-reference electrode couples.

**Model Development**

As shown in Figure 2, the three-scale modeling approach consists of two steps: (1) modeling of the impedance of the agglomerates on basis of the impedance expression for primary particles; (2) modeling of the impedance of the porous electrode on basis of the preceding impedance expression for agglomerates.

Model assumptions are listed below:

1. This model is essentially a one-dimensional model. Variations in the electrode plane are not considered, which might be insignificant since only a slight perturbation is applied during EIS test.
2. The primary particles and agglomerates are all in spherical shape and have an equalized size distribution. In addition, the pores in agglomerates are entirely filled with electrolyte.
3. A Gouy-Chapman-Stern model is applied to describe the electric double layer. The faradaic current and double layer charging current are actually decoupled. In addition, an uniform SEI film covers the primary particle, and the ions transportation across the SEI film can be modeled using the concentrated solution theory.
4. At the electrode/electrolyte interface, charge transfer reactions occur at the outer Helmholtz plane, which are formulated in Butler-Volmer equation.

*Scale-up from a primary particle to an agglomerate.—* In terms of scaling up from a primary particle to an agglomerate, we use the impedance model for an agglomerate developed in our previous study. Detailed derivation of the model can be found in Ref. 11. The agglomerate impedance model gives the impedance of an agglomerate as:

$$Z_{ag} = \frac{RT}{F} \frac{\tau}{\varepsilon} \times \frac{v_1 - v_2}{F D_{Li}^{ex} (v_1 (\lambda_1) - v_2 (\lambda_2))} + \frac{\varepsilon}{\varepsilon_0} \frac{\tau}{\varepsilon} \left( v_1 (\lambda_1) - v_2 (\lambda_2) \right)$$

where the meaning of all symbols can be found in the nomenclature in appendix. $\Gamma (\lambda)$ is an introduced function,

$$\Gamma (\lambda) = \sqrt{\lambda} \coth (\sqrt{\lambda}) - 1$$

$\lambda_1$, $\lambda_2$, $v_1$, $v_2$ are introduced parameters formulated as,

$$\lambda_1 = \frac{(\Theta_1 + \Theta_2) + (\Theta_1 - \Theta_2)^2}{2} + 4 \Theta_1 \Theta_3$$

$$\lambda_2 = \frac{(\Theta_1 + \Theta_2) - (\Theta_1 - \Theta_2)^2}{2} + 4 \Theta_2 \Theta_3$$

$$v_1 = \frac{2 \Theta_1}{(\Theta_4 - \Theta_1) + (\Theta_1 - \Theta_2)^2 + 4 \Theta_2 \Theta_3}$$

$$v_2 = \frac{2 \Theta_2}{(\Theta_4 - \Theta_1) + (\Theta_1 - \Theta_2)^2 + 4 \Theta_2 \Theta_3}$$

**Table I. Specifications of the three-electrode lithium-ion cell.**

| Material          | Cathode: LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ Anode: graphite |
|-------------------|---------------------------------------------------------------|
| Size              | 17 $\times$ 13.5 cm$^2$                                     |
| Number of electrode pairs | 16                                                           |
| Capacity          | 5 Ah (0.3 C, 25 $^\circ$C)                                  |
| Reference electrode | polyimide-insulated copper wire, 40 $\mu$m in diameter, with lithium metal coated onto one end |
| Position of the reference electrode | Between two separators                                      |

Figure 1. SEM image of a NMC agglomerate (left) and the size distribution of the positive electrode (right).
where $\Theta_i$ ($i = 1, 2, 3, 4$) are dimensionless coefficients as functions of physical-electrochemical parameters:

\[
\Theta_1 = - [\xi (1 - t_e) - 1] \frac{\tau_{pp}^2 a_{pp} R_{pp}^2}{\varepsilon_e \varepsilon'_e} \frac{\tau_{pp}^2}{Z_{pp} \sigma_e};
\]
\[
\Theta_2 = j \omega \tau_{pp}^2 F^2 R_{pp}^2 \frac{RT}{\sigma_e} \delta_1; \quad \Theta_3 = \frac{a_{pp} RT R_{pp}^2}{Z_{pp} F^2 \tau_{pp} \delta_1}; \quad \Theta_4 = \frac{Z_{pp}^2}{\sigma_e};
\]

$Z_{pp}$ refers to the impedance expression of primary particles, which has two cases, namely, the SEI film free case, $Z_{pp}^2$, and the SEI film existing case, $Z_{pp}^3$:

\[
Z_{pp}^2 = R_0 + \frac{1}{Z_{pp} + 1 + j \omega C_{sei}};
\]
\[
Z_{pp}^3 = \frac{1}{R_e + \frac{1}{\tau_{pp} \delta_1} + j \omega C_{sei}}; \quad \text{[5]}
\]

\[
Y_s = \frac{R_{pp}}{F D_s \sinh (\sqrt{\tau_{pp}^2 \sigma_e})}; \quad \Omega_s = \frac{\alpha R_{pp}^2}{D_s}; \quad \text{[7]}
\]

$Z_{sei}$ is the SEI film impedance,

\[
Z_{sei} = \frac{\tilde{S}_{sei}}{\sigma_i}; \quad \lambda_3 = \frac{\Omega_s}{\tau_{sei}} \frac{R_{pp}^2 (\Omega_s R_2 + \Omega_s R_1 \cos (\Omega_s a_{sei}) + \sin (\Omega_s a_{sei}))}{\Omega_i} \frac{R_2}{\Omega_i} \frac{(\Omega_s + 1)}{\Omega_i} \sin (\Omega_s a_{sei}) - \Omega_s \cos (\Omega_s a_{sei}) \cos (\Omega_s a_{sei}) \text{[8]}
\]

where, $\Omega_{sei} = \sqrt{-j \omega / D_{sei}}$

Scale-up from an agglomerate to a porous electrode. — In a similar manner as in Ref. 11, the concentrated solution theory is used here to extend the agglomerate impedance model to the porous electrode. The conservation equations for species and charge in the porous electrode are expressed in frequency domain as:

\[
\begin{align*}
\sigma_e & \frac{\partial}{\partial x} (\tilde{e}_x - \tilde{e}_x) - F D_{sei} \frac{\partial^2 \tilde{e}_x}{\partial x^2} = \frac{a_{pp} \tau_{pp}^2}{\varepsilon_e \varepsilon'_e} \frac{\tau_{pp}^2}{Z_{pp}} \\
\frac{j \omega \tau_{pp}^2}{F} \frac{\partial}{\partial x} \tilde{e}_x &= \frac{(1 - t_e) a_{pp} \tau_{pp}^2}{\varepsilon_e \varepsilon'_e} \frac{\tau_{pp}^2}{Z_{pp}} \\
\end{align*}
\]

where $Z_{pp}$ is the impedance of an agglomerate as expressed in Eq. 5-6.

The boundary conditions for the above controlling equations are:

At current collector/electrode interface, $x = 0$:

\[
-zero lithium-ion flux at this interface: \left\{ \begin{array}{l}
\frac{\partial}{\partial x} \tilde{e}_x = 0; \\
\text{all current is conducted in solid phase:} \\
\end{array} \right.
\]

At electrode/separator interface, $x = L$:

\[
\text{assumed constant lithium-ion concentration: } \tilde{e}_x = 0; \quad \text{all current is conducted in electrolyte phase:}
\]

Using the same solution method as in Ref. 11, one can get the expression for the impedance of a porous positive electrode as follows:

\[
Z_{pe} = \frac{\tilde{S}_{sei}}{\sigma_i} \frac{R_{pp}^2 (\Omega_s R_2 + \Omega_s R_1 \cos (\Omega_s a_{sei}) + \sin (\Omega_s a_{sei}))}{\Omega_i} \left\{ \begin{array}{l}
\frac{\partial}{\partial x} \tilde{e}_x - F D_{sei} \frac{\partial^2 \tilde{e}_x}{\partial x^2} = \frac{a_{pp} \tau_{pp}^2}{\varepsilon_e \varepsilon'_e} \frac{\tau_{pp}^2}{Z_{pp}} \\
\frac{j \omega \tau_{pp}^2}{F} \frac{\partial}{\partial x} \tilde{e}_x = \frac{(1 - t_e) a_{pp} \tau_{pp}^2}{\varepsilon_e \varepsilon'_e} \frac{\tau_{pp}^2}{Z_{pp}} \\
\end{array} \right.
\]

where $\gamma = \frac{\sqrt{\lambda_3 \lambda_4}}{\lambda_3 \lambda_4}$, $\lambda_3$, $\lambda_4$, $v_3$, $v_4$ are parameters introduced during solving Eq. 9, which are formulated as,

\[
\lambda_3 = \frac{(\Theta_3 + \Theta_4)}{2}; \quad \lambda_4 = \frac{(\Theta_3 - \Theta_4)}{2}; \quad v_3 = \frac{2}{{\Theta_3}}; \quad v_4 = \frac{2}{{\Theta_3}}
\]

\[
\gamma = \sqrt{\lambda_3 \lambda_4} \text{[13]}
\]
Model Validation Using EIS Data of a Three-electrode Cell

An impedance model must be sufficiently validated before it can be used to elucidate the processes or to identify parameters inside a lithium-ion battery. In principal, a sufficient validation needs to have the same number of degree of freedom (DOF) as that of the model. In this study, two cases of model validation are carried out. For the first case, the EIS of ten SOCs is separately fitted. In addition, all the variables except the electrode thickness are set free. The initial values and constraints are chosen based on literature values and cell specifications. For the second case, the EIS of multiple SOCs are simultaneously fitted. Only five parameters, namely the ohmic resistance $R_o$, exchange current density $i_0$, double layer capacitance $C_{dl}$, solid phase diffusivity $D_s$, and $\frac{\partial U}{\partial c_s}$, are taken as functions of the SOC. Other parameters are constant regardless of varying the SOC.

As noted in the experimental section, the EIS of cathode vs. RE, that of anode vs. RE and that of the full cell were measured simultaneously using a multichannel potentiostat. Figure 3 shows that the sum of cathode impedance and anode impedance agrees well with the measured impedance of the full cell, which confirms the accuracy of the three-electrode lithium-ion cell. The straight line at very high frequencies, which is ascribed to inductive reactance of metallic elements in the cell and connecting wires, is not included in the subsequent fit analysis. Following the inductive line, two semicircles can be found. In general, the first semicircle is associated with the SEI film, and the second semicircle represents the charge transfer process at the electrolyte-electrode interface. In the low frequency range, an oblique line tails up, which is usually ascribed to the diffusion processes in lithium-ion batteries.

To fit the experimental data using the agglomerate model, we adopt the Global Searching algorithm in MATLAB, and the target function is defined as:

$$T = \sum_{i=1}^{N} \left[ \left( Z_{\text{exp}}^{\text{real}}(f_i) - Z_{\text{real}}^{\text{sim}}(f_i) \right)^2 + \psi \left( Z_{\text{exp}}^{\text{imag}}(f_i) - Z_{\text{imag}}^{\text{sim}}(f_i) \right)^2 \right]^{1/2}$$

[15]

$\psi$ is a tuning parameter to determine the weight of the imaginary part of the target function. A value of 10, indicating a dominant imaginary
part since the imaginary part is more sensitive to the frequency change in low frequency range, is adopted for $\psi$ in this study. It should be noted here that the impedance data are defined in area specific impedance, $\Omega^2$, with respect to the surface area of the cell. The Global Searching algorithm was run 50 times for all cases, therefore, through a statistical analysis of all iterations; the error bar plot is given for each identified parameter.

**Separate fit case.**—Figure 4 shows a comparison between experimental and simulated EIS at ten SOCs for the first case. An excellent agreement can be found at all evaluated frequency points and SOC points. Even though the validation is done in a wide SOC range, agreement can be found at all evaluated frequency points and SOC.

Figure 5 presents the radius of primary particles and that of agglomerates in the first fit case.

![Figure 4](image) A comparison between experimental EIS data (markers) and simulation results (solid lines) at different SOCs in the separate fit case.

![Figure 5](image) Error bar plots for the radius of primary particles and agglomerates in the first fit case.
has a conductivity around 0.01 S/m, of which the magnitude is in good consistency with widely accepted literature values (or example in Ref. 19). However, the present model reveals that the electrolyte conductivity is a function of SOC with noticeable fluctuations while most of the literatures assumed a constant value determined by electrolyte concentration.19 Thereby, the electrolyte properties including the diffusivity and conductivity are set as constant values at all evaluated SOCs in the simultaneous fit case. In addition, the conductivity of the SEI film is two orders smaller than the electrolyte conductivity, which is consistent with common knowledge.

Figure 6d compares the diffusivity of Lithium ions in the solid phase, electrolyte phase, and SEI film. It is found that: (1) the electrolyte phase diffusivity is between $10^{-10}$ and $10^{-8}$ m² s⁻¹; (2) the diffusivity in solid phase is about four to five orders smaller than that in the electrolyte phase; (3) the SEI film diffusivity is comparable with the solid phase diffusivity. The order of difference between the diffusivity in the electrolyte phase and that in active particles is consistent with literature values (for example in Ref. 21).

Simultaneous fit case.— As mentioned above, the structural parameters such as the radius and the porosity, and electrochemical parameters such as the electrolyte diffusivity are always considered as constants with varying the SOC. To this end, a simultaneous fit of five SOCs is carried out in the second fit case. It is noted that only five parameters are considered as functions of the SOC. Figure 7 shows a comparison between experimental and simulated EIS at five SOCs for the second fit case. A good agreement can be found at all evaluated frequency points and SOC points, which further enhances the credibility of the model predictions. In addition, the obtained exchange current density, which is considered as a function of SOC, is in good consistency with the value calculated from Eq. 16 ($k = 2.3 \times 10^{-5}$, $x_{\text{eq}} = 1, x_{\text{eq}} = 0.4, c_e = 1200, c_s_{\text{max}} = 16.1 \times 10^3$).

Discussion on model fit.—We attempted to validate our model by conducting a two-level of fit and by examining key parameters against

Figure 6. Variation of key electrochemical parameters with respect to the SOC for the separate fit case.

Figure 7. Examination of the second fit case: (a) a comparison between measured and simulated EIS data; (b) a comparison between calculated and simulated exchange current density.
Table II. Benchmark parameters used in impedance simulation.

| L/m | Rsp/m | Rp/m | δpp/m | εfpp | εf | τpe | τsp | \(D_e/m^2s^{-1}\) | \(D_s/m^2s^{-1}\) |
|-----|-------|------|--------|------|----|-----|-----|----------------|----------------|
| 9.1E-05 | 5.0E-06 | 5.0E-07 | 2.0E-08 | 0.4 | 0.4 | 2 | 2 | 4E-14 | 2E-08 |
| 1E-13 | 7E-03 | 2E-04 | 5E-05 | 5 | 3 | 1 | 0.2 | 2E-04 | -4E-05 |

Effect of structural parameters.—The frequency range is from 10 kHz to 10 mHz.

Figure 8. Effect of structural parameters on the impedance of positive electrode. The frequency range is from 10 kHz to 10 mHz.

- **(a)** Radius of primary particle
- **(b)** Radius of agglomerate
- **(c)** Volume fraction of active material in agglomerate
- **(d)** Volume fraction of active material in positive electrode

- **(e)** Zimag / \(\Omega m^2\)
- **(f)** Zreal / \(\Omega m^2\)

Parametric Study Based on the Agglomerate Model for the Electrode

Using the validated model, we conduct parameters analysis in this section, focusing on the structural parameters, the properties of the SEI film, and transport coefficients. Benchmark parameters used in impedance simulation are listed in Table II.

Effect of structural parameters.—As shown in Figure 8a–8b, reducing the radius of the primary particle and that of the agglomerate reduce the overall impedance of the positive electrode. This can be easily understood based on the relationship between the active area and the particle size. Smaller size of particles will enlarge the active surface area of the electrode, therefore, leading to lower electrode impedance. However, qualitatively speaking, downsizing the particle size will also increase the tortuosity in the agglomerate and that in the electrode, on the contrary, which results in an increase in electrode impedance. As a consequence, there should exist an optimal value for the size of primary particles and agglomerates. Nevertheless, determination of such an optimal value needs an explicit relationship between the particle size and the tortuosity, which is absent in the literature.

If one want to analyze the effect of the volume fraction of active material on the electrode impedance, it should be noted that there exists a correlation between the porosity and the tortuosity. In this study, we adopt the relation introduced in Ref. 23 for porous media, as follows:

\[
\tau = 1 + 1.6 \ln \left(\frac{\varepsilon_s}{\varepsilon_f}\right)
\]

where \(\varepsilon_s = 1 - \varepsilon_f - \varepsilon_a\), \(\varepsilon_s\), \(\varepsilon_f\), and \(\varepsilon_a\) are the volume fraction of the active materials and that of the filler, respectively. Here, we set \(\varepsilon_f = 0.18\).
As shown in Figure 8c–8d, there exists an optimal value of the volume fraction of active material in the agglomerate and that in a positive electrode, respectively. For the case of parameters used in this study, these two optimal values are $\varepsilon_{sp}^0 = 0.72$, $\varepsilon_{pe}^0 = 0.56$.

Effect of SEI film parameters.— SEI film growth has been widely accepted as the primary cause of capacity fade in lithium-ion batteries. Such effect is recently modeled in Ref. 24. Figure 9 shows the effect of the SEI film parameters on the positive electrode impedance. Increasing the thickness of the SEI film and lowering its conductivity also have an effect on the second semicircle which is associated with the SEI film growth has been widely accepted as the primary cause of capacity fade in lithium-ion batteries.

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Effect of diffusivities.— EIS is one of the widely used methods to calculate the diffusion coefficients in lithium-ion batteries. Usually, the electrolyte diffusion is neglected because the electrolyte diffusivity is four orders smaller than the solid phase diffusivity. However, we will show that this assumption is not always correct in lithium-ion battery electrode.

The characteristic frequency of the diffusion process is expressed as:

$$f_s = \frac{D}{L_{c}^2}$$  \[18\]

Where $D$ is the diffusion coefficient, $L_c$ the characteristic diffusion length, $f_s$ the characteristic diffusion frequency.

The lithium-ion diffusion in active material occurs in primary particles, therefore, its characteristic diffusion length is the primary particle radius, $L_e = R_{pp}$. Regarding the electrolyte phase diffusion, three are two different scales. One is the electrode scale, which corresponds to the electrolyte phase diffusion of lithium-ions across the electrode. The other is the agglomerate scale, which represents the electrolyte phase diffusion of lithium-ions inside the agglomerate.

For the case of electrolyte phase diffusion in agglomerate scale, $L_e = R_{yp}$. An order of magnitude analysis gives, $D_e \sim 10^{-4} D_i$, $L_e^r \sim (10^{-1} - 10^{-2}) L_e$. Consequently, one gets,

$$f_s^e = \frac{D_e}{L_e^{r2}} \approx \frac{10^{-4} D_e}{(10^{-1} - 10^{-2}) L_e^{r2}} = (0.01 - 1) f_s^i \quad [19]$$

where, $f_s^i$, $f_s^e$ refer to the characteristic frequency of electrolyte phase diffusion and that of solid phase diffusion, respectively. For the case of electrolyte phase diffusion across the electrode, the characteristic diffusion length can be the electrode thickness, $L_e^r = L_e$. An order of magnitude analysis gives, $D_e \sim 10^{-4} D_i$, $L_e^r \sim (10^{-2} - 10^{-3}) L_e$. Consequently, one gets,

$$f_s^i = \frac{D_i}{L_e^r} \approx \frac{10^{-4} D_i}{(10^{-2} - 10^{-3}) L_e^r} = (1 - 100) f_s^e \quad [20]$$

Eq. 19–20 says that the electrolyte phase diffusion can have a comparable or even lower characteristic frequency compared with the solid phase diffusion, even though the electrolyte diffusivity is much smaller than solid phase diffusivity. In this regard, the electrolyte diffusion cannot be neglected in low frequency range. However, a quantitatively separation between the solid phase diffusion and the electrolyte phase diffusion remains difficult, due to the multiscale property of the electrolyte phase diffusion.

To achieve a clear and qualitative understanding, we explore the variations in the electrode impedance when changing the solid phase and electrolyte phase diffusivities. Figure 10 shows the effect of transport coefficients on the positive electrode impedance. For the case of
Figure 10, the electrode thickness \( L = 100 \, \mu m \) is three orders larger than the radius of the primary particle \( R_{pp} = 0.1 \, \mu m \). Three cases are included:

1. For case 1 (base case), \( D_s = 10^{-4} D_e \), so \( f_c^e = 0.1 \, Hz \). \( f_c^s = 10 \, Hz \). As a result, the oblique line in low frequency range \( (10^{-1}–10^{-3} \, Hz) \) can be considered as the signature of electrolyte phase diffusion.

2. For case 2, only the solid phase diffusivity is reduced by two orders, that is, \( D_s = 10^{-6} D_e \), so \( f_c^e = 0.1 \, Hz \). \( f_c^s = 10 \, Hz \). Compared with case 1, the impedance at the end frequency (1 mHz) is almost the same, the change only occurs in the moderate-to-low frequency range \( (100–10^{-2} \, Hz) \). Specifically, a 45-degree oblique line occurs, which is believed to represent the solid phase diffusion in primary particles. As a result, it is concluded that the solid phase diffusion controls the moderate-to-low frequency range \( (10^0–10^{-2} \, Hz) \).

3. For case 3, only the electrolyte phase diffusivity is reduced by two orders, that is, \( D_e = 10^{-2} D_e \), so \( f_c^e = 0.001 \, Hz \). \( f_c^s = 10 \, Hz \). Compared with case 1, the impedance in moderate-to-low frequency range \( (10^0–10^{-2} \, Hz) \) almost keeps the same. However, the oblique line in very low frequency \( (10^{-2}–10^{-3} \, Hz) \) is extended significantly. Consequently, electrolyte phase diffusion controls the very low frequency range \( (10^{-2}–10^{-3} \, Hz) \).

The above analysis indicates that the electrolyte phase diffusion can have a comparable or even lower characteristic frequency compared with the solid phase diffusion in primary particles, and therefore cannot be neglected in low frequency range. In other words, models, such as the present model, that are capable of distinguishing between the solid phase diffusion and the electrolyte phase diffusion should be used to calculate the diffusivity in active materials from EIS data. Otherwise, significant errors would occur in the obtained values.

Conclusions

In this study, a three scale impedance model with analytical expressions has been developed for porous electrodes in lithium-ion batteries. Compared with existing two-scale impedance models, this model is featured with the modeling of electrochemical reactions and species transport inside the agglomerates, a detailed description for the electrode/electrolyte interface and the analytical nature. The present model was validated using EIS data at ten SOCs of an NMC positive electrode in a three-electrode lithium-ion cell. A good agreement was
obtained between model predictions and experimental data in both separate and simultaneous fit cases. In addition, the identified values of key parameters are also compared with results obtained using complementary methods or from the literature. The parameters analysis indicates that: (1) there exist optimal values for the volume faction of active material in an agglomerate and that in a positive electrode. For the case of parameters used in this study, these two optimal values are \( \varepsilon_{sp} = 0.72, \varepsilon_{pe} = 0.54 \); (2) SEI film parameters have a noticeable effect in the electrode impedance. A decrease in its conductivity and an increase in its thickness give a rise to the cell impedance; (3) the characteristic frequency of electrolyte phase diffusion can be comparable or even smaller than that of solid phase diffusion. As a result, models that can distinguish between the solid phase diffusion and the liquid phase diffusion should be used if one want to extract the diffusivity in active materials from EIS data.

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List of Symbols

\( a_{sp} \) volumetric electrolyte/electrode interface area in agglomerate, \( \text{m}^{-1} \)

\( a_{pe} \) volumetric electrolyte/electrode interface area in positive electrode, \( \text{m}^{-1} \)

\( c_e \) Lithium-ion concentration in electrolyte phase, \( \text{mol m}^{-3} \)

\( c_{ref} \) reference concentration, \( \text{mol m}^{-3} \)

\( c_l \) Lithium-ion concentration in solid phase, \( \text{mol m}^{-3} \)

\( c_{l,max} \) maximum lithium-ion concentration in solid phase, \( \text{mol m}^{-3} \)

\( C_{dl} \) double layer capacitance, \( \text{F/m}^2 \)

\( C_{sei} \) SEI film capacitance, \( \text{F/m}^2 \)

\( D_e \) diffusion coefficient in electrolyte phase, \( \text{m}^2 \text{s}^{-1} \)

\( D_s \) diffusion coefficient in solid active material phase, \( \text{m}^2 \text{s}^{-1} \)

\( D_{sei} \) diffusion coefficient in SEI film, \( \text{m}^2 \text{s}^{-1} \)

\( D_{e,c} \) \( D_{c,e} \) (see Eq. (A 2.3) in Ref. 9), \( \text{m}^2 \text{s}^{-1} \)

\( f \) frequency, Hz

\( F \) faradaic constant, \( \text{C mol}^{-1} \)

\( i_0 \) exchange current density, \( \text{A m}^{-2} \)

\( I_{app} \) applied current density, \( \text{A/m}^2 \)

\( j \) imaginary unit

\( k \) reaction kinetic constant, \( \text{A m}^{2.5} \text{mol}^{-1.5} \)

\( L \) positive electrode thickness, m

\( N \) number of measured frequency points

\( R_{pp} \) primary particle radius, m

\( R_{sp} \) agglomerate radius, m

\( R_2 \) \( R_{pp} + \delta \) \( \text{m} \)

\( R_3 \) \( R_{pp} + \delta_l \) \( \text{m} \)

\( R \) universal gas constant, \( \text{J mol}^{-1} \text{K}^{-1} \)

\( R_0 \) Ohmic resistance, \( \Omega \text{m}^2 \)

\( R_t \) charge transfer resistance, \( \Omega \text{m}^2 \)

\( \tau_{se} \) transference number

\( T \) temperature, K, or target function in global search algorithm

\( U \) equilibrium potential, V

\( v_i \) dimensionless variables

\( x \) variable or spatial dimension

\( x_{0.06} \) stoichiometry at 0% SOC

\( x_{100} \) stoichiometry at 100% SOC

\( Y_1 \) transfer function defined in

\( Z \) impedance, \( \Omega \text{m}^2 \)

\( Z_{sei} \) impedance of primary particle without SEI film, \( \Omega \text{m}^2 \)

\( Z_{sp} \) impedance of agglomerate, \( \Omega \text{m}^2 \)

\( Z_{pe} \) impedance of positive electrode, \( \Omega \text{m}^2 \)

Greek Symbols

\( b_{OHP} \) thickness of the outer Helmholtz plane (OHP), m

\( b_{sei} \) thickness of the SEI film, m

\( \eta \) overpotential, V

\( \kappa \) dimensionless variable

\( \sigma_s, \sigma_e \) conductivity, \( \text{S m}^{-1} \)

\( \nu_s, \nu_e \) volume fraction of electrolyte phase in agglomerate

\( \nu_{pe} \) volume fraction of electrolyte phase in positive electrode

\( \Phi \) potential, V

\( \Theta_s \) Debye length, m, or eigenvalues

\( \gamma \) tuning parameter to determine the weight of the imaginary part in the target function

\( \varsigma \) dimensionless variable,

\( \tau_{sp} \) tortuosity in agglomerate

\( \tau_{pe} \) tortuosity in positive electrode

\( \Omega \) frequency

\( \Omega_{se} \) \( \Omega_{sei} = \sqrt{\frac{\omega}{j \omega / D_{sei}}} \)

Subscripts

\( ct \) charge transfer reaction

\( dl \) electric double layer

\( f \) filler

\( OHP \) outer Helmholtz plane

\( IHP \) inner Helmholtz plane

\( pp \) primary particle

\( pe \) positive electrode

\( real \) real part of complex number

\( imag \) imaginary part of complex number

\( sp \) secondary particle

\( sei \) solid electrolyte/electrode interphase

\( ref \) reference

\( e \) electrolyte phase

\( s \) electrode phase

\( - \) anions

\( + \) cations

Superscripts

\( \exp \) experimental

\( \text{over-bar} \) dimensionless variable or constant value of variables

\( \text{over-tilde} \) variables in frequency domain or the perturbation of variables

\( sim \) simulation

\( suf \) surface

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