Estimation of Diffusion Coefficient of Lithium in Carbon Using AC Impedance Technique

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The validity of estimating the solid phase diffusion coefficient, $D_s$, of a lithium intercalation electrode from impedance measurement by a modified electrochemical impedance spectroscopy (EIS) method is studied. A macroscopic porous electrode model and concentrated electrolyte theory are used to simulate the synthetic impedance data. The modified EIS method is applied for estimating $D_s$. The influence of parameters such as the exchange current density, radius of active material particle, solid phase conductivity, porosity, volume fraction of inert material, and thickness of the porous carbon intercalation electrode, the solution phase diffusion coefficient, and transference number, on the validity of $D_s$ estimation, is evaluated. A simple dimensionless group is developed to correlate all the results. It shows that the accurate estimation of $D_s$ requires large particle size, small electrode thickness, large solution diffusion coefficient, and low active material loading. Finally, a "full model" method is developed for the cases where the modified EIS method does not work well.

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The transport phenomena inside a battery have been attracting a lot of attention. Accurate measurement of parameters such as diffusion coefficients in both the solution phase and the solid phase of a battery can help in understanding what is occurring inside it and ways to improve its performance. The extraction of solid phase diffusion coefficient, $D_s$, of an intercalation electrode in a lithium-ion battery from ac impedance measurement is of great interest to us.1-6

Basically, the impedance data from either the semi-infinite diffusion region or the transition region of the Nyquist plots are used to estimate this parameter.

Among the methods developed to estimate $D_s$ of a lithium-ion electrode, the Yu et al. modified electrochemical impedance spectroscopy (EIS) method6 seems to be very useful. It was an extension of the Haran et al. model1 of a metal hydride electrode for alkaline batteries. Both models are based on the assumption that there is no solution diffusion limitation inside the working porous electrode pellet and each spherical active material particle behaves identically and has the same reaction current density on its surface. One advantage of the Yu et al. model, compared to other approaches such as traditional Warburg approach, potential intermittent titration technique (PITT) and galvanostatic intermittent titration technique (GITT), is that we are not required to know exactly the parameters such as the steady-state lithium-ion concentration, $c_0$, surface concentration, $c_s$, of intercalation species lithium on the solid particle, open-circuit potential (OCP) gradient $dU/dx$ inside the porous electrode, molar volume, $V_m$, of the lithiated material, and effective surface area per unit mass, "A" of the porous electrode.8-11 Another advantage, compared to the traditional Warburg approach, is that the impedance data with even lower frequency, which are supposed to be dominated even more likely by the solid phase diffusion, are used for the estimation of $D_s$. It is easy to realize this by the fact that the traditional Warburg approach uses the impedance data with gradient or slope in the Nyquist plot equal to $-1$ and the modified EIS method uses the data with gradient more negative than $-1.5$, which has even lower frequency.

The Yu et al. model has limitation here. We have no assurance that there is large difference between the values of solution phase diffusion coefficient, $D_s$, and solid phase diffusion coefficient, $D_i$. As a result, the ignorance of solution phase diffusion limitation might be a problem. Furthermore, porous electrodes tend to make the reaction current nonuniformly distributed due to unmatched potential drop in both solution and solid phase caused by their different conductivity. Hence, the validity of the estimation of $D_s$ in the lab by the Yu et al. work is not guaranteed.

Doyle et al.12 investigated the possibility of estimating the parameter $D_s$ from the impedance response of a commercial lithium-polymer cell, which consists of a porous intercalation positive electrode LiTiS$_2$ and a lithium foil negative electrode. They showed that only when the true value of solid phase diffusion coefficient of an intercalation electrode is small enough, i.e., less than $10^{-13}$ cm$^2$/s for the LiTiS$_2$ electrode in their work, they could get a relatively reliable estimation of this parameter from the impedance data of a full commercial cell using the existing methods in the literature. They concluded that the low frequency spectrum needs to be dominated by diffusion impedance in the solid phase if a valid estimation of $D_s$ is desired. The value of $10^{-13}$ cm$^2$/s of $D_s$ of the LiTiS$_2$ electrode seems to be the threshold order of magnitude for such domination in their case. Even though they were estimating $D_s$ from the impedance response of a full cell instead of a working electrode, their result is still persuasive since the contribution to the total impedance from the separator and counter electrode region combined is negligible in the low frequency region, compared to that from the working electrode. This is seen from Fig. 3 of their work. Unfortunately, they did not discuss in their work what we could do in order to get a reliable estimation of $D_s$ assuming the true value of $D_s$ to be around $10^{-10}$ cm$^2$/s or higher, the order of magnitude for lithium intercalation electrode often referred in literature. In this communication, our objective is to find out the experimental conditions under which we can safely estimate the $D_s$ of lithium in a carbon electrode from ac impedance by using the modified EIS model of Yu et al.6 For the case where this method is bad for the estimation, an alternate method is provided and discussed. A Swagelok T-cell structure consisting of porous carbon intercalation working electrode, one lithium foil counter electrode, and one lithium foil reference electrode is considered (Fig. 1). This figure is similar to Fig. 1 in Ref. 6 except that we treat the working electrode as the superposition of two continua, one representing the solution and the other representing the solid matrix, instead of as an assembly of identically behaved spherical particles. The procedure in our study is first, we solve the model equations based on the macroscopic porous electrode theory and concentrated electrolyte theory for the T-cell to generate synthetic impedance data; then, we apply the modified EIS method to extract the value of $D_s$ from these data. And then, we are able to evaluate the accuracy of estimation by comparing the estimated

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value of \( D_s \) with the true parameter value we give as input in our model equations for the impedance simulation. In this work, the effect of some parameters, such as the exchange current density, \( i_0 \), solid phase conductivity, \( \sigma \), thickness \( \delta \), active material particle size, \( R_s \), porosity \( \epsilon \), and volume fraction of inert material, \( f_{\text{inert}} \) (filler plus conducting material) of a porous carbon electrode, solution phase diffusion coefficient, \( D \), and lithium-ion transference number, \( \lambda \), on the reliability of \( D_s \) estimation is studied. The impedance response of the working electrode in reference to a lithium foil adjacent to the interface of the working electrode and separator is used for the extraction of \( D_s \).

According to Haran et al., the faradaic impedance of an electrode with the intercalation material particle of spherical shape is written as

\[
Z(\omega) = \frac{\partial \eta_{RI}}{\partial I} + \frac{(1-j)\sigma_0}{\sqrt{\omega} \coth(1+j) \sqrt{\frac{\omega R_s^2}{2D_s} - (1-j) \sqrt{\frac{D_s}{2\omega R_s^2}}}}^{1/2}
\]

where \( \eta_{RI} \) is the overpotential at the particle surface (radius \( r = R_s \)), \( I \) is the reaction current on the surface, \( j \) is the imaginary number, \( \sqrt{-1} \), and \( \sigma_0 \) is the modified Warburg prefactor expressed as

\[
\sigma_0 = \frac{\partial J}{\partial \varepsilon} \frac{c_s}{\alpha V (1-\varepsilon)} \frac{m}{\sqrt{2D_s}}
\]

where \( V \) is the volume of the working pellet electrode, \( J \) is the specific current per unit mass of active material, \( m \) is the mass of active material, and \( \alpha \) is the surface area per unit volume of the electrode. After separating the impedance of expression 1 into the real part \( Z_{\text{Re}} \) and the imaginary part \( Z_{\text{Im}} \), one gets the gradient of the impedance curve in the transition region of the Nyquist plot (see Fig. 9 of Ref. 6)

\[
\frac{dZ_{\text{Im}}}{dZ_{\text{Re}}} = \frac{(S_4 S_5 + S_2 S_6 + S_2 S_5) T_4 - 2T_5 (S_2 S_5 + S_2 S_7) T_4 - 2T_5 (S_2 S_5 + S_2 S_7)}{(S_2 S_6 - S_2 S_8 + S_2 S_9 + S_2 S_7) T_4 - 2T_5 (S_2 S_5 + S_2 S_7)}
\]

where

\[
T_3 = (S_4 S_5 - S_2 S_6); \quad T_4 = (S_2^2 + S_2^2); \quad T_5 = (S_4 S_5 + S_2 S_7)
\]

and

\[
S_1 = S_3 S_6
\]

\[
S_2 = 2 \Psi - S_5
\]

\[
S_3 = 2 \coth(\Psi) \cot(\Psi)(1 - \Psi S_6) - 2 \Psi S_5 + S_8
\]

\[
S_4 = 2 \Psi \coth(\Psi) \cot(\Psi) - S_6
\]

\[
S_5 = \coth(\Psi) - \cot(\Psi)
\]

\[
S_6 = \coth(\Psi) + \cot(\Psi)
\]

\[
S_7 = 2 - S_1
\]

\[
S_8 = \cot(\Psi)^2 + \coth(\Psi)
\]

where

\[
\Psi = R_s \sqrt{\frac{\omega}{2D_s}}
\]

In our work, the gradient at each available impedance data point in the transition region is calculated numerically by

\[
\frac{dZ_{\text{Im}}}{dZ_{\text{Re}}} = \frac{Z_{\text{Im}}(\omega + \Delta \omega) - Z_{\text{Im}}(\omega - \Delta \omega)}{Z_{\text{Re}}(\omega + \Delta \omega) - Z_{\text{Re}}(\omega - \Delta \omega)}
\]

This numerical calculation of the gradient works satisfactorily here, since we have as many as 100 points per decade of frequency in our simulation. Next, we can either use a nonlinear parameter estimation technique to get the estimation of \( D_s \) from the calculated impedance gradient data or determine the value of \( \Psi \) at each available data point and then obtain \( D_s \) by substitution into expression 6 of the frequency value at that point and the radius of solid particles. Finally, the validity of the estimation of \( D_s \) is evaluated by the accuracy of estimation

\[
\text{Accuracy} = \frac{\text{estimated value of } D_s}{\text{true value of } D_s} \times 100\%
\]

In this work, a carbon intercalation electrode with 50% state-of-charge is considered.

### Mathematical Model

The model equations used in this pseudo-two-dimensional model for the Swagelok T-cell, one-dimensional with respect to spatial direction \( x \), and pseudo-second dimensional with respect to radial direction inside each spherical particle, are similar to those used by Doyle et al.

Conservation of charge in the porous carbon electrode is given by

\[
aF J_{n,f} = \frac{\partial I_2}{\partial x} - aC_{\|} \frac{\partial (\Phi_1 - \Phi_2)}{\partial t}
\]

with the assumption that the double-layer capacitance \( c_{\|} \) is constant and independent of the solution phase concentration and potential. Equation 10 is used to account for the material balance in the solution phase

\[
\frac{\partial (\rho \varepsilon c)}{\partial x} = \frac{\partial}{\partial x} \left( \varepsilon D_{eff} \frac{\partial c}{\partial x} - \frac{i_2}{F} \frac{\partial I_2}{\partial x} + a_{n,f} (1 - I_2) \right)
\]

\[
+ \frac{aC_{\|}}{F} \frac{\partial (\Phi_1 - \Phi_2)}{\partial t}
\]
where the effective diffusion coefficient, \( D_{\text{eff}} \), is related to the bulk solution diffusion coefficient, \( D \), by expression 11 to account for tortuosity of diffusion path inside the electrode

\[
D_{\text{eff}} = e^{0.5D} \tag{11}
\]

Application of Ohm’s law in the solid phase and solution phase yields

\[
I - i_2 = -\sigma_{\text{eff}} \frac{d\Phi_1}{dx} \tag{12}
\]

\[
i_2 = -\kappa_{\text{eff}} \frac{d\Phi_2}{dx} + \frac{2k_{\text{eff}}RT}{F} \left( 1 + \frac{d\ln f_c}{d\ln c} \right) (1 - \iota_c^0) \frac{d\ln c}{dx} \tag{13}
\]

where the solid phase effective conductivity, \( \sigma_{\text{eff}} \), and the solution phase effective conductivity, \( \kappa_{\text{eff}} \), are related to bulk solid conductivity \( \sigma \) and bulk solution conductivity \( \kappa \) by expressions

\[
\sigma_{\text{eff}} = (1 - \varepsilon)^{1.5} \sigma \tag{14}
\]

\[
\kappa_{\text{eff}} = \varepsilon^{1.5} \kappa \tag{15}
\]

to account for the actual path of the conducting species.\(^{13}\)

The electrochemical reaction on the carbon particle surface is given elsewhere\(^6\)

\[
j_{n,f}F = i_0 \left[ \frac{\alpha F}{RT} \left( \Phi_1 - \Phi_2 - U \right) - \exp \left[ -\frac{\alpha F}{RT} (\Phi_1 - \Phi_2 - U) \right] \right] \tag{16}
\]

In Eq. 16, the equilibrium potential, \( U \), is fitted from the experimental data\(^{14}\) by

\[
U = -0.16 + 1.32 \exp \left[ -3.0 \frac{c_s}{c_t} \right] + 10.0 \exp \left[ -2000.0 \frac{c_s}{c_t} \right] \tag{17}
\]

where the surface concentration, \( c_s \), of the active material carbon particle is related to Eq. 18, which describes the solid phase diffusion of Li in the spherical carbon particle, and its boundary conditions 19 and 20

\[
\frac{\partial c_s}{\partial t} = D_s \left( \frac{\partial^2 c_s}{\partial r^2} + \frac{2 \partial c_s}{\partial r} \right) \tag{18}
\]

\[
-D_s \frac{\partial c_s}{\partial r} = 0 \quad \text{at} \quad r = 0 \tag{19}
\]

\[
-D_s \frac{\partial c_s}{\partial r} = j_{n,f} \quad \text{at} \quad r = R \tag{20}
\]

For the separator region, material balance leads to

\[
\frac{\partial (ec)}{\partial t} = \frac{\partial}{\partial x} \left[ \frac{eD_{\text{eff}}}{\partial x} \frac{\partial c}{\partial x} - \frac{i_z \partial i_c^0}{F} \frac{\partial c}{\partial x} \right] \tag{21}
\]

and Ohm’s law leads to the same form of equation as Eq. 13 except that the solution phase current density \( i_2 \) is equal to the total current density \( I \), which does not change with \( x \).

For the counter electrode, a similar form of Butler-Volmer equation to that of Eq. 16 is also assumed. Then, we have Eq. 22 for the counter lithium foil electrode after the consideration of double layer charging and discharging

\[
-I = i_{0,c} \left[ \exp \left[ \frac{\alpha F}{RT} (\Phi_1 - \Phi_2 - U_c) \right] - \exp \left[ -\frac{\alpha F}{RT} (\Phi_1 - \Phi_2 - U_c) \right] \right] + C_{dl,c} \frac{\partial (\Phi_1 - \Phi_2)}{\partial t} \tag{22}
\]

The local equilibrium potential of the counter electrode is zero, independent of the activity of Li or Li\(^+\), in reference to a lithium foil electrode

\[
U_c = 0 \tag{23}
\]

After a similar mathematical treatment of the above equations to that of the Doyle et al. work,\(^{12}\) finally we have the following equations in the frequency domain

\[
e^{\omega \tilde{c}_{l_{\text{im}}}} = e^{D_{\text{eff}} \frac{\partial^2 \tilde{c}_{l_{\text{im}}}}{\partial x^2}} + a \tilde{f}_{n,f,\text{im}} (1 - \iota_c^0) \tag{24}
\]

\[
e^{-\omega \tilde{c}_{l_{\text{im}}}} = e^{D_{\text{eff}} \frac{\partial^2 \tilde{c}_{l_{\text{im}}}}{\partial x^2}} + a \omega \tilde{C}_{dl,\text{im}} \tilde{X}_{1,1,\text{im}} - \tilde{X}_{1,2,\text{im}} \tag{25}
\]

\[
a^{\tilde{f}_{n,f,\text{im}}} = \sigma_{\text{eff}} \frac{\partial^2 \tilde{X}_{1,1,\text{im}}}{\partial x^2} + a \omega \tilde{C}_{dl,\text{im}} \tilde{X}_{1,1,\text{im}} - \tilde{X}_{1,2,\text{im}} \tag{26}
\]

\[
a^{\tilde{f}_{n,f,\text{im}}} = \sigma_{\text{eff}} \frac{\partial^2 \tilde{X}_{1,1,\text{im}}}{\partial x^2} - a \omega \tilde{C}_{dl,\text{im}} \tilde{X}_{1,1,\text{im}} - \tilde{X}_{1,2,\text{im}} \tag{27}
\]

where Eq. 24-29 are used for the porous electrode and Eq. 30-33 for the separator. Note that \( \tilde{f}_{n,f,\text{im}} \) and \( \tilde{f}_{n,f,\text{im}} \) that appeared in Eq. 24-27 are related to \( \tilde{X}_{1,1,\text{im}} \), \( \tilde{X}_{1,2,\text{im}} \), \( \tilde{X}_{2,1,\text{im}} \), and \( \tilde{X}_{2,2,\text{im}} \) by A-1 to A-8.

The boundary conditions for the above Eq. 24-33 are tabulated in Table I.
The real and imaginary parts of impedance of the working electrode are given by

\[ Z_{\text{Re}} = \tilde{\Phi}_{1,\text{Re}}|_{x=0^+} - \tilde{\Phi}_{1,\text{Re}}|_{x=\delta} \]

and

\[ Z_{\text{Im}} = \tilde{\Phi}_{1,\text{Im}}|_{x=0^+} - \tilde{\Phi}_{1,\text{Im}}|_{x=\delta} \] \[34\]

In this work, we treat the total perturbation current, \( I \), as the input perturbation signal with purely real unity value.

### Numerical Solution

We use a numerical algebraic equation package of FORTRAN called General Nonlinear Equation Solver (GNES) to solve the above linear equations Eq. 24-33. This solver has the same calling protocol as that of the differential equation solver called DASSL. As was already demonstrated in Fig. 11-14 of Ref. 14, a sharp profile of concentration and potential exists at the interfaces of the porous electrode and separator, and the separator and lithium foil electrode. In order to resolve the impedance response more appropriately in our work, especially in the high frequency limit, we discretize uniformly the thickness of the porous electrode as well as that of the separator region. In this work, dense node points are applied to the regions adjacent to the interfaces between the porous electrode and separator and between the separator and counter electrode. To transform the differential equations Eq. 24-33 to the algebraic ones, we approximate the derivatives of each dependent variable by using three-point finite difference method. Finally, the solution vector \( \mathbf{Y} \) is found by evaluating the residual vector \( \mathbf{\Delta} \)

\[ \mathbf{\Delta} = \mathbf{G}(\mathbf{X}, \mathbf{Y}) \] \[35\]

where \( \mathbf{G}(\mathbf{X}, \mathbf{Y}) \) is the governing equation vector in the residual form. \( \mathbf{Y} \) has the structure of

\[
\mathbf{Y} = \begin{bmatrix}
\tilde{c}_{\text{Re}}[1], \tilde{c}_{\text{Im}}[1], \tilde{\Phi}_{1,\text{Re}}[1], \tilde{\Phi}_{1,\text{Im}}[1], \tilde{\Phi}_{2,\text{Re}}[1], \tilde{\Phi}_{2,\text{Im}}[1], \ldots \\
\tilde{c}_{\text{Re}}[i], \tilde{c}_{\text{Im}}[i], \tilde{\Phi}_{1,\text{Re}}[i], \tilde{\Phi}_{1,\text{Im}}[i], \tilde{\Phi}_{2,\text{Re}}[i], \tilde{\Phi}_{2,\text{Im}}[i], \ldots \\
\tilde{c}_{\text{Re}}[N], \tilde{c}_{\text{Im}}[N], \tilde{\Phi}_{1,\text{Re}}[N], \tilde{\Phi}_{1,\text{Im}}[N], \tilde{\Phi}_{2,\text{Re}}[N], \tilde{\Phi}_{2,\text{Im}}[N] \\
\tilde{c}_{\text{Re}}[N+1], \tilde{c}_{\text{Im}}[N+1], \tilde{\Phi}_{2,\text{Re}}[N+1], \tilde{\Phi}_{2,\text{Im}}[N+1], \ldots \\
\tilde{c}_{\text{Re}}[M-1], \tilde{c}_{\text{Im}}[M-1], \tilde{\Phi}_{2,\text{Re}}[M-1], \tilde{\Phi}_{2,\text{Im}}[M-1] \\
\tilde{c}_{\text{Re}}[M], \tilde{c}_{\text{Im}}[M], \tilde{\Phi}_{1,\text{Re}}[M], \tilde{\Phi}_{1,\text{Im}}[M], \tilde{\Phi}_{2,\text{Re}}[M], \tilde{\Phi}_{2,\text{Im}}[M]
\end{bmatrix}
\] \[36\]

The impedance of the whole cell can be obtained by

\[ Z_{\text{Re}} = \tilde{\Phi}_{1,\text{Re}}[1] - \tilde{\Phi}_{1,\text{Re}}[M] \] and \[ Z_{\text{Im}} = \tilde{\Phi}_{1,\text{Im}}[1] - \tilde{\Phi}_{1,\text{Im}}[M] \] \[37\]

and the impedance of the porous electrode in reference to a lithium foil electrode at the interface of the porous electrode and separator is given by
Table II. The values for all the parameters used in this model under base conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Carbon electrode</th>
<th>Separator</th>
<th>Li foil</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_0$ (cm$^2$/s)</td>
<td>$3.9 \times 10^{-10}$</td>
<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>$D$ (cm$^2$/s)</td>
<td>$7.5 \times 10^{-7}$</td>
<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>$i_0$ (mA/cm$^2$)</td>
<td>0.363</td>
<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>$\kappa$ (S/cm)</td>
<td>$2.6 \times 10^{-3}$</td>
<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>$c_t$ (mol/cm$^3$)</td>
<td>0.02639</td>
<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>$c_s$ (mol/cm$^3$)</td>
<td>0.0139867</td>
<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>$e$</td>
<td>0.357</td>
<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>$e_s$</td>
<td>0.724</td>
<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>$e_{av}$</td>
<td>0.172</td>
<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>$C_{dl}$ (F/cm$^2$)</td>
<td>$10^{-5}$</td>
<td></td>
<td>Assumed</td>
<td></td>
</tr>
<tr>
<td>$C_{dl,c}$ (F/cm$^2$)</td>
<td></td>
<td>$10^{-5}$</td>
<td>Assumed</td>
<td></td>
</tr>
<tr>
<td>$i_{th}$ (mA/cm$^2$)</td>
<td>0.11</td>
<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>$i_{th,c}$ (mA/cm$^2$)</td>
<td>1.26</td>
<td></td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>$\sigma$ (S/cm)</td>
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<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>$f^2_{i,0}$</td>
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<td></td>
<td>Assumed</td>
<td></td>
</tr>
<tr>
<td>$c_{i,t}$ (mol/cm$^3$)</td>
<td>0.001</td>
<td></td>
<td>Assumed</td>
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<tr>
<td>$R_t$ (cm)</td>
<td>0.00125</td>
<td></td>
<td></td>
<td>11</td>
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<tr>
<td>$\delta$ (cm)</td>
<td>0.01</td>
<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>$\delta_s$ (cm)</td>
<td>0.0052</td>
<td></td>
<td></td>
<td>11</td>
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<tr>
<td>$T$ (K)</td>
<td>298.15</td>
<td></td>
<td></td>
<td>Assumed</td>
</tr>
</tbody>
</table>

$Z_{re} = \Phi_{1,rel}[N] - \Phi_{2,rel}[N]$ and $Z_{im} = \Phi_{1,im}[N] - \Phi_{2,im}[N]$

Results and Discussion

The base values of all the parameters used for the T-cell system under consideration are tabulated in Table II. A demonstration of the simulated impedance response of the full T-cell, as well as the contribution to the full cell impedance from each region, with base parameter values put in the model equations described above is seen in Fig. 2. The high frequency loop of the full cell impedance curve is overlapped by two semicircles. The appearance of first impedance maximum is caused by the relative domination of the impedance of the counter electrode and separator region. The second maximum is caused by the relative domination of the impedance from the porous carbon electrode. One can realize this by looking at the difference among the high frequency impedance loops simulated by using different parameter values of the exchange current density of both the porous and counter electrodes.

Parameter estimation by the modified EIS method.—Given the values of all the parameters, we are able to generate, by solving the model equations Eq. 24-33, a set of simulated impedance data over a wide range of frequency. The transition region of the Nyquist plot of the simulated impedance data can be used to get $D_s$ back by the modified EIS method. We assume that the synthetic impedance data generated by solving the model equations for the T-cell in this work are “real” enough to represent the actual impedance behavior of such cell in the lab. As a result, the validity of applying the modified EIS method to the estimation of $D_s$ in a carbon electrode can be evaluated after comparing the estimated value with the true value of $D_s$ that we put in our model equations.

To start with, we have to justify which section of the transition region should be used for the estimation of $D_s$ with a desired accuracy. The accuracy of estimation of $D_s$ (for several different true values of $D_s$ while keeping all the other parameters to their base values) from the impedance data in the transition region of Nyquist plot with the gradient ranging from $-1.5$ to $-1.5$ is given in Fig. 3 as a function of gradient. Maple’s fsolve is used here. We observe that the accuracy is better when the gradient is more negative than $-4.0$, compared to the region, from $-1.5$ to $-2.5$, adopted by Yu et al. However, data points with gradient more negative than $-12.0$ are likely to involve large error due to the round-off error caused by small change of the real part of impedance. Therefore, the transition region with gradient ranging from $-4.0$ to $-12.0$ is used in this work for the estimation of $D_s$. We also find that it is feasible to get a reliable estimation of $D_s$ by using the modified EIS method when the true value of this parameter is less than $3.9 \times 10^{-10}$ cm$^2$/s. One needs to know that assigning different base values other parameters, such as kinetics, from the ones in Table II might change the range of validity of $D_s$ estimation. Thus, a thorough investigation of the influence of all the other parameters relevant to the validity of the estimation of $D_s$ is needed. We expect to lead to an instructive
conclusion that helps us get a reliable estimation of \( D_s \) from real impedance data collected in the lab.

A nonlinear parameter estimation technique called Gauss-Newton method\(^{15,16} \) is employed to get \( D_s \) back from the simulated impedance response of the working electrode in the remaining part of this work. The algorithm of this technique for the modified EIS method involves the following steps: First, assume initial guesses for the parameter vector \( \mathbf{b} \), which actually has only one element \( D_s \) in this case. Then, evaluate the Jacobian matrix \( \mathbf{J} \) from Eq. 3, 4, 5, and 6. Next, use Eq. 39 to obtain the correction parameter vector \( \Delta \mathbf{b} \)

\[
\Delta \mathbf{b} = (\mathbf{J}^T \mathbf{J})^{-1} \mathbf{J}^T (\mathbf{Y}^* - \mathbf{Y})
\]  

[39]

where \( \mathbf{Y}^* \) and \( \mathbf{Y} \) are the objective function vector with experimental and estimated values, respectively. After this, a new estimate of the parameter vector is evaluated from Eq. 40

\[
\mathbf{b}^{(m+1)} = \mathbf{b}^{(m)} + \Delta \mathbf{b}^{(m)}
\]  

[40]

where \( m \) is the number of corrections done. The estimation of \( D_s \) converges successfully to a value when the correction vector \( \Delta \mathbf{b} \) becomes very small.

As stated before, for the modified EIS method to work well, the surface of each spherical particle in the porous electrode should have uniform reaction current distribution. Figure 4 demonstrates this, where a nonlinear reaction current inside the porous electrode exists for the true value of \( D_s \), greater than \( 3.9 \times 10^{-10} \) cm\(^2\)/s. The characteristics of a porous electrode tend to make this current non-uniformly distributed. In order to use safely the modified EIS method, we need to make sure that the uniform reaction current distribution on each particle surface is present.

Through a simplified porous electrode model, Newman\(^{17} \) derived two dimensionless groups, the dimensionless current density Eq. 41 and the dimensionless exchange current density Eq. 42, that could be used to judge the uniformity of the reaction current distribution inside the porous electrode.

\[
\Delta = \frac{\alpha F I b}{R T} \left( \frac{1}{\kappa_{\text{eff}}} + \frac{1}{\sigma_{\text{eff}}} \right)
\]  

[41]

\( \gamma^2 = (\alpha + \alpha_s) \frac{F a i_n \delta^2}{R T} \left( \frac{1}{\kappa_{\text{eff}}} + \frac{1}{\sigma_{\text{eff}}} \right)
\]  

[42]

In the above two expressions, \( \Delta \) and \( \gamma^2 \) are ratios of the competing effects of the ohmic potential drop and slow electrode kinetics. For large values of either \( \Delta \) or \( \gamma^2 \), the ohmic effect dominates, and as a result, the reaction distribution is nonuniform. For small values of both \( \Delta \) and \( \gamma^2 \), the reaction distribution is more uniform. In our work, the importance of such parameters as the exchange current density \( i_{\text{ex}} \), thickness \( \delta \) and specific surface area per unit volume \( a \) of the porous electrode to the valid estimation of solid phase diffusion coefficient is investigated. Since Newman’s simple model does not consider solution diffusion limitation, the effect of the solution diffusion coefficient on the validity of estimation of \( D_s \) is also discussed in this paper. The superimposition of both solution phase diffusion and solid phase diffusion is believed to be present in the diffusion region of the impedance plot.\(^{12} \) Besides, the influence of the transference number of lithium ion is also considered. Because the specific surface area \( a \) is related to the radius of the active material particle \( R_s \), the porosity \( \epsilon \), and volume fraction of inert material \( \epsilon_{\text{i}} \), porosity of the porous electrode by expression 43 for the spherical particle geometry, the change of \( a \) can only be made by changing one or some of the three parameters \( R_s \), \( \epsilon \), and \( \epsilon_{\text{i}} \). Separate discussion on each of these parameters is carried out in this work.

\[
a = \frac{3}{R_s} (1 - \epsilon - \epsilon_{\text{i}})
\]  

[43]

Newman also pointed out that the reaction current in a porous electrode is somewhat more uniform as the value of solid phase effective conductivity and solution phase effective conductivity approach each other. By changing the solid phase conductivity, \( \sigma \), and holding the solution phase conductivity, \( \kappa \), constant, we can check the validity of \( D_s \) estimation.

Figure 5 shows that the change of solid phase conductivity has no apparent effect on the estimation accuracy when \( \sigma \geq 0.001 \) S/cm, \( \sigma_{\text{eff}} \geq \kappa_{\text{eff}} \) in this case, by the modified EIS method over the true \( D_s \) range under study here. Thus, the accuracy of

![Figure 4. Comparison of reaction current distributions on the surface of carbon particle for different parameter values of \( D_s \) (all the other unmentioned parameters use their base values).](image1)

![Figure 5. The accuracy of estimation of \( D_s \) with different parameter values of the solid phase conductivity (all the other unmentioned parameters keep their base value).](image2)
estimation by the modified EIS method is insensitive to the relative size of two conductivity parameters of both phases.

Figure 6 reveals approximately similar phenomena to the above one. The estimation by the modified EIS method is insensitive to the magnitude of exchange current for the case studied here. This information seems to be helpful since knowing the exact kinetics parameter value is not required in order to get a valid estimation of $D_s$.

Figure 7 shows that, except for very small true values of $D_s$, the estimation accuracy tends to decrease as the radius of carbon particle decreases. We can explain this result by noting that the decrease of particle size not only facilitate the diffusion of lithium inside the solid particle (shorter diffusion path) but also increases the surface area of the electrode. All these lead to the increased reaction capability on the particle surface, which has the similar effect to that of having a larger exchange current density $i_0$ in Newman’s dimensionless group 42. On the other hand, bigger particle size favors improved accuracy of the estimation of $D_s$.

The significance of the change of the porous electrode porosity to the validity of $D_s$ estimation is revealed in Fig. 8. For each curve, which corresponds to a fixed true value of $D_s$, the estimation becomes better as the porosity $\varepsilon$ increases. When porosity reaches such a value that the summation of porosity and the volume fraction of inert material $\varepsilon_{\text{inert}}$ approaches unity, the estimation is good even for large true values of $D_s$. The volume fraction of inert material plays a similar role on the validity of $D_s$ estimation, which is demonstrated in Fig. 9. The above two results seem to be encouraging.

---

**Figure 6.** The accuracy of estimation of $D_s$ with different parameter values of the exchange current density (all the other unmentioned parameters keep their base value).

**Figure 7.** The accuracy of estimation of $D_s$ with different carbon particle size (all the other unmentioned parameters keep their base values).

**Figure 8.** The accuracy of estimation of $D_s$ with different parameter values of electrode (all the other unmentioned parameters keep their base values).

**Figure 9.** The accuracy of estimation of $D_s$ with different parameter values of the volume fraction of inert material (all the other parameters keep their base values).
since we might be able to get a good estimation of \( D_s \) if we try to make the summation of \( \varepsilon \) and \( \varepsilon_{\text{inert}} \) approach 1. However, a small amount of loading of active material-carbon particles is required in either case. The mechanical strength of the porous electrode could be a problem if we increase the porosity so much, and the inert material could be not completely inert to lithium intercalation if we increase the volume fraction of this parameter. These things must be taken into account when we prepare electrode for impedance measurement in the lab.

The effect of different electrode thickness on the accuracy of estimation of \( D_s \) is studied by, first, changing the base value of carbon particle radius to 2 \( \mu \)m. Then the validity of estimation of \( D_s \) is investigated for the electrode thickness \( d \) ranging from 10 to 1000 \( \mu \)m. As we can see from Fig. 10, the accuracy of \( D_s \) estimation increases as \( d \) decreases. Since large particle size favors a good estimation of \( D_s \), as is already shown in Fig. 7, a further improvement of estimation might be possible if we hold the particle size to the base value and decrease the electrode thickness to a very small value, such as 50 \( \mu \)m. However, attention must be paid in this case to check if we can use safely the macroscopic model, since the local average quantities might be inappropriate if the electrode thickness is not large compared to the active material particles.

The importance of the solution phase transport of lithium ion to the porous electrode is shown in Fig. 11 and Fig. 12. When the parameter value of solution phase diffusion coefficient is very large, such as \( 7.5 \times 10^{-2} \) cm\(^2\)/s, the accuracy of \( D_s \) estimation is good for all the true values of \( D_s \) ranging from \( 3.9 \times 10^{-2} \) to \( 3.9 \times 10^{-8} \) cm\(^2\)/s. This is demonstrated in Fig. 11. When the value of the solution phase diffusion coefficient decreases, valid estimation of \( D_s \) exists only for very small true value of it. From this result, we may suspect that the limited ability of solution phase transport is responsible for the nonlinear reaction current distribution inside the porous electrode and, as a consequence, the bad estimation of \( D_s \).

Further evidence is given in Fig. 12, where the estimation accuracy for all the true values of \( D_s \) is high when the transference number of lithium ion is close to 1. In this case, the solution phase concentration of lithium ion is actually uniform inside the porous electrode because the solution phase diffusion resistance is absent. Under the condition where there is no solution phase transport limitation, the estimation of \( D_s \) seems to be always good.

To summarize the above results, let us consider a dimensionless group 44, which can be understood as the ratio of two time constants for solid phase diffusion and solution phase diffusion. The accuracy of estimation as a function of this time constant ratio is plotted in Fig. 13. As we can see, when the ratio of two time constants is smaller than 0.001, the estimation is completely bad; when this ratio is larger than 1.0, the estimation is very good. This dimensionless group can help us evaluate the optimal experimental conditions in the lab for a reliable estimation of \( D_s \) from impedance spectrometry

\[
\frac{\tau_s}{\tau_e} = \frac{R_s^2/aD_s}{\delta^2/\varepsilon D_{\text{eff}}} = \frac{D_s R_s^2}{\delta^3} \frac{\varepsilon^{1.5}}{3(1 - \varepsilon - \varepsilon_{\text{inert}})}
\]
Unfortunately, the dimensionless group was seldom made larger than 1.0 in literature. For example, in the work of Yu et al., an estimation of \( D_s \) for graphite was extracted to be \( 1.12 \times 10^{-10} \) and \( 6.51 \times 10^{-11} \) \( \text{cm}^2/\text{s} \) for 0 and 30% state-of-charge (SOC) at 25°C. Since the particle size was quite small, around 1.5 \( \mu \text{m} \) in diam, and the working electrode had the thickness of 95 \( \mu \text{m} \), a rough value of 0.0006-0.001 of the dimensionless time constant ratio is calculated, assuming the solution phase diffusion coefficient to be 7.5 \( \times 10^{-7} \) \( \text{cm}^2/\text{s} \), the porosity to be 0.4 and the volume fraction of inert material to be 0.1. This reminds us that their estimation might involve large error if all the assuming parameter values were appropriate. As another example, consider a \( \text{LiTiS}_2 \) electrode discussed by Doyle et al.\(^6\) When the true value of \( D_s \) is smaller than \( 1 \times 10^{-13} \) \( \text{cm}^2/\text{s} \) in Table II of their work, they had a reasonable estimation with the use of traditional Warburg approach. The dimensionless group for this value equals 1.0, which agrees with our result from the carbon electrode that a valid estimation of \( D_s \) is possible under this condition.

Since the modified EIS method cannot give us a reliable estimation if the dimensionless group is much less than 1.0, a “full model” method is developed as a strategy to address such situation.

**Numerical parameter estimation by a full model.**—By full model we mean we apply the same form of model equations Eq. 24-33, as are also used for the generation of simulated impedance data, for the estimation of \( D_s \). This method is expected to work very well when we know the values for all the other parameters exactly. However, some parameters are very hard to be known with high accuracy, such as the exchange current density. Therefore, it is desired that we are still able to get a good estimation of \( D_s \) when the values of some other parameters are not assigned correctly. As an analogy to the modified EIS method, the gradient in the transition region is chosen to be the objective function here. We can write the gradient of Nyquist plot as an implicit function 45 of frequency and all the parameters

\[
\frac{dZ_{\text{Im}}}{dZ_{\text{Re}}} = f(\omega, D_s, D_i, i_0, f', \delta, \ldots)
\]  

Basically, a similar nonlinear parameter estimation technique to the one discussed above is also used here to get \( D_s \) back except that we have to resort to the numerical calculation for each element of the Jacobian matrix Eq. 46

\[
J_{ij} = \frac{(dZ_{\text{Im}}/dZ_{\text{Re}})_{i+j+\Delta P_i} - (dZ_{\text{Im}}/dZ_{\text{Re}})_{i+j-\Delta P_i}}{2\Delta P_i} \quad [46]
\]

where \( J_{ij} \) refers to the \( i \)th element of the one-dimensional matrix.

As is the case for the modified EIS method, we expect that some of the parameters in the full model might not be important and would not require the exact knowledge of their values. Thus, it is important to determine the sensitivity of the model predictions to changes in the model parameters. If the model predictions are relatively insensitive to one or more of the parameters, then a fairly wide range of values for these insensitive parameters could be used without significantly affecting the predictions of the model. The sensitivity of the model predictions to changes in parameters is determined here by monitoring the change in the gradient of the Nyquist impedance curve. While holding all the other parameters constant, the parameter of interest is perturbed slightly and the resulting change in impedance gradient ranging from \(-4.0\) to \(-12.0\) is noted. We can find the sensitivity coefficient, \( SC_i \), of that parameter by Eq. 47, following the same formula adopted by Evans and White\(^15\)

\[
SC_i = \frac{\sum_{j=1}^{n} \Delta \left( \frac{dZ_{\text{Im}}}{dZ_{\text{Re}}}_j \right)}{n|\Delta P_i|} \quad [47]
\]

where

\[
\Delta \left( \frac{dZ_{\text{Im}}}{dZ_{\text{Re}}} \right)_j = \left( \frac{dZ_{\text{Im}}}{dZ_{\text{Re}}} \right)_j - \left( \frac{dZ_{\text{Im}}}{dZ_{\text{Re}}} \right)_j^* \quad [48]
\]

and

\[
\Delta P_i = \frac{P_i - P_i^*}{P_i^*} \quad [49]
\]
where $P_i$ and $P_i^\#$ are the perturbed value and the reference value of parameter $i$, respectively. $(dZ_{lm}/dZ_{Re})_i$ is the value of the impedance gradient when using $P_i$, and $(dZ_{lm}/dZ_{Re})_i^\#$ is the value when using $P_i^\#$. Finally, $n$ is the number of data points over which the gradients are compared.

Figure 14 gives the sensitivity of the impedance gradient to all the parameters that are important to the estimation of $D_i$ over a range of true values of $D_i$. In this figure, all the other parameters except $D_i$ and the parameter of interest are held at their base values. As is shown, when the true value of $D_i$ is very small, i.e., less than $3.9 \times 10^{-10}$ cm$^2$/s, only the particle size $R_i$ and $D_i$ are important. This agrees with the modified EIS method that has no requirement of knowing all the other parameter values except $R_i$ and $D_i$. However, when the true value of $D_i$ is larger than $3.9 \times 10^{-10}$ cm$^2$/s, all the other parameters such as the exchange current density $i_0$, solid phase conductivity $\sigma$, porosity $\epsilon$, volume fraction of inert material $e_{\text{inert}}$, active material particle size $R_{\text{p}}$, thickness $\delta$ and solution phase diffusion coefficient $D$ are also important and affect the impedance response. The impedance gradient becomes more insensitive to the change of solid phase diffusion coefficient $D_i$ as the true value of this becomes bigger. This warns us that an exact knowledge of the values for all the possible parameters is needed for the estimation of $D_i$ for high true values of $D_i$. It can also be seen from Fig. 14 that the solid phase conductivity always plays an insignificant role.

The impedance data we collect in the lab usually involve error or noise, the origin of which might not be clear. In this work, we also include some random noise to the synthetic impedance gradient data calculated from the simulation. A random error generator by Maple VI was used to produce a group of normally distributed error, $\phi$, with mean zero and variance one [i.e., $\sim N(0, 1)$]. This error is added to the synthetic gradient data ranging from $-4.0$ to $-12.0$ by

$$
\frac{(dZ_{lm})}{dZ_{Re}} = \frac{(dZ_{lm})}{dZ_{Re}} + 0.05\phi
$$

As was stated by Evans and White, an estimate of a parameter has little meaning unless it is accompanied by some approximation of the possible error it possesses. Therefore, a confidence interval is needed to obtain together with the estimation. It can be calculated by the following expression

$$P_i = \tilde{P}_i + t_{1-\gamma/2}(n-m)S_{P_i}$$

where $\tilde{P}_i$ is the estimate of parameter $P_i$, $t_{1-\gamma/2}(n-m)$ is the student $t$-distribution at $(1 - \gamma/2) \times 100\%$ confidence level, $n$ is the number of observations, $m$ is the number of parameters, $n - m$ is the degree of freedom, and $S_{P_i}$ is the estimate of the variance for $P_i$, which is calculated from mean square error, $S_E^2$, by

$$S_{P_i} = \sqrt{(J^TJ)^{-1}S_E^2}$$

where $J$ is the Jacobian matrix (see Eq. 46) and $S_E^2$ is calculated by

$$S_E^2 = \frac{\sum_{j=1}^{n} \left( \frac{(dZ_{lm})}{dZ_{Re}} - \frac{(dZ_{lm})}{dZ_{Re}} \right)^2}{n - m}$$

A comparison of the estimation results, between the full model method and the modified EIS method, from the same synthetic impedance data with noise is tabulated in Table III. All the other parameters except $D_i$ are assumed to be known exactly to us before we apply the full model method to the estimation. As we can see, the full model does give reasonable estimations of $D_i$ for all the true

<table>
<thead>
<tr>
<th>True value of $D_i$ (cm$^2$/s) used in the impedance simulation</th>
<th>Estimation of $D_i$ (cm$^2$/s) if $\sigma = 0.001$ S/cm</th>
<th>Estimation of $D_i$ (cm$^2$/s) if $\sigma = 0.01$ S/cm</th>
<th>Estimation of $D_i$ (cm$^2$/s) if $i_0 = 1.1 \times 10^{-2}$ A/cm$^2$</th>
<th>Estimation of $D_i$ (cm$^2$/s) if $i_0 = 1.1 \times 10^{-6}$ A/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3.9 \times 10^{-10}$</td>
<td>$(2.71 \pm 0.46) \times 10^{-10}$</td>
<td>$(4.54 \pm 1.21) \times 10^{-10}$</td>
<td>Not Converge</td>
<td>$(3.90 \pm 0.01) \times 10^{-10}$</td>
</tr>
<tr>
<td>$3.9 \times 10^{-9}$</td>
<td>$(9.00 \pm 0.04) \times 10^{-10}$</td>
<td>$(9.00 \pm 0.04) \times 10^{-10}$</td>
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</tr>
<tr>
<td>$3.9 \times 10^{-10}$</td>
<td>$(3.42 \pm 0.21) \times 10^{-10}$</td>
<td>$(2.23 \pm 0.22) \times 10^{-10}$</td>
<td>Not Converge</td>
<td>$(1.03 \pm 0.32) \times 10^{-10}$</td>
</tr>
<tr>
<td>$3.9 \times 10^{-10}$</td>
<td>$(9.02 \pm 0.03) \times 10^{-10}$</td>
<td>$(9.02 \pm 0.03) \times 10^{-10}$</td>
<td>$(9.02 \pm 0.03) \times 10^{-10}$</td>
<td>$(9.02 \pm 0.03) \times 10^{-10}$</td>
</tr>
<tr>
<td>$3.9 \times 10^{-10}$</td>
<td>$(3.80 \pm 0.12) \times 10^{-10}$</td>
<td>$(3.88 \pm 0.09) \times 10^{-10}$</td>
<td>Not Converge</td>
<td>$(3.80 \pm 0.01) \times 10^{-10}$</td>
</tr>
<tr>
<td>$3.9 \times 10^{-11}$</td>
<td>$(3.61 \pm 0.01) \times 10^{-10}$</td>
<td>$(3.61 \pm 0.01) \times 10^{-10}$</td>
<td>$(3.61 \pm 0.01) \times 10^{-10}$</td>
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</tr>
<tr>
<td>$3.9 \times 10^{-11}$</td>
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</tr>
<tr>
<td>$3.9 \times 10^{-12}$</td>
<td>$(3.90 \pm 0.01) \times 10^{-12}$</td>
<td>$(3.90 \pm 0.01) \times 10^{-12}$</td>
<td>$(3.90 \pm 0.01) \times 10^{-12}$</td>
<td>$(3.90 \pm 0.01) \times 10^{-12}$</td>
</tr>
</tbody>
</table>

| a | Estimation by the full model method. | b | Estimation by the modified EIS method. |
values of this parameter, with the expected true value lying between the confidence intervals. However, one should also notice that the confidence intervals for larger true values of $D$ are large compared to those for smaller true values. This can be explained by that the impedance gradient is not sensitive to the change of solid phase diffusion coefficient at higher true values of them, compared with other parameters, if we look at Fig. 14. A small noise might produce much deviation from the expected estimation. When the true value of $D_s$ is smaller than $3.9 \times 10^{-10}$ cm$^2$/s, both methods are equally accurate because the impedance gradient is very sensitive to the change of solid phase diffusion coefficient.

As explained before, we might expect that the full model method does not require knowing exactly some of the parameters, such as solid phase conductivity, exchange current density, etc. To check this, we use the same synthetic impedance data as those used for the case in Table III. Then we assume that one of the parameters, such as the exchange current density and solid phase conductivity, is not known correctly. After this, we find the estimation of $D_s$ by assigning different values of this parameter. The results are shown in Table IV. We observe that the two methods agree with each other when the expected true value of $D_s$ is small, i.e., less than $3.9 \times 10^{-10}$ cm$^2$/s in this case. We also observe that inaccurate knowledge of the values for such parameters as the exchange current density and solid phase conductivity leads to large estimation error if the true value of $D_s$ is large, where the solid phase diffusion is not the dominant process. We can suspect from this that exactly knowing the values for all the parameters discussed in this work is required if we want to use the full model to get a reliable estimation of $D_s$ from the impedance response where the modified EIS method becomes bad.

Conclusion

We conclude from above discussion that the validity of estimating $D_s$ from the impedance response of a porous intercalation electrode by the modified EIS method is not assured if we have limited capability of transport of lithium ion of the solution phase in the porous intercalation electrode. A dimensionless group, the ratio of time constant of solid phase diffusion $\tau_s$ and that of solution phase diffusion $\tau_i$, is useful to evaluate the experimental conditions by using this method for a reliable estimation of $D_s$ from a porous electrode. Big particle radius, small electrode thickness, large difference of the true parameter value of $D$ and $D_s$, and small active material loading are conducive to a valid estimation of solid phase diffusion coefficient.

For the case where the modified EIS method works poorly, a full model method is provided here. However, exactly knowing the values of all the other parameters is required in order to get a valid estimation.

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\( \Phi_{2R} \), real part of the deviation of solution phase potential in Laplace domain, V

\( \Phi_{2\text{Im}} \), imaginary part of the deviation of solution phase potential in Laplace domain, V

\( \omega \), angular frequency, rad/s

Subscripts

+ to the right of an interface

− to the left of an interface

Superscripts

T transpose of a matrix

−1 the inverse of a matrix

References