Physical Interpretations of Electrochemical Impedance Spectroscopy of Redox Active Electrodes for Electrical Energy Storage

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ABSTRACT: This study aims to provide physical interpretations of electrochemical impedance spectroscopy (EIS) measurements for redox active electrodes in a three-electrode configuration. To do so, a physicochemical transport model was used accounting for (i) reversible redox reactions at the electrode/electrolyte interface, (ii) charge transport in the electrode, (iii) ion intercalation into the pseudocapacitive electrode, (iv) electric double layer formation, and (v) ion electrodiffusion in binary and symmetric electrolytes. Typical Nyquist plots generated by EIS of redox active electrodes were reproduced numerically for a wide range of electrode electrical conductivity, electrolyte thickness, redox reaction rate constant, and bias potential. The electrode, bulk electrolyte, charge transfer, and mass transfer resistances could be unequivocally identified from the Nyquist plots. The electrode and bulk electrolyte resistances were independent of the bias potential, while the sum of the charge and mass transfer resistances increased with increasing bias potential. Finally, these results and interpretation were confirmed experimentally for LiNi0.6Co0.2Mn0.2O2 and MoS2 electrodes in organic electrolytes.

INTRODUCTION

Electrochemical impedance spectroscopy (EIS) has been used to characterize electrodes for batteries,4−23 electrochemical capacitors,4−23 dye-sensitized solar cells,22,24,25 corrosion tests,26−28 and capacitive deionization.29,30 It consists of imposing a time harmonic oscillating electric potential Ψ(t) around a time-independent "dc" potential at the electrode surfaces and measuring the resulting harmonic current density j(t).31−33 The amplitude of the oscillating potential is typically small and less than 10 mV. Using complex notations, the imposed electric potential Ψ(t) and the resulting current density j(t) can be expressed as

$$Z = \frac{\psi(t) - \psi_{dc}}{\dot{j}(t) - \dot{j}_{dc}} = \frac{\psi_0}{\dot{j}_{dc}} e^{i\phi} = Z_{re} + iZ_{im}$$

where Z_{re} and Z_{im} (expressed in Ω m^2) are the real and imaginary parts of the complex impedance, respectively.

Nyquist plots present the imaginary part Z_{im} as a function of the real part Z_{re} of the complex impedance. They typically consist of one or two semicircles at relatively high frequencies and a nonvertical line with respect to the real axis at low frequencies for electrodes consisting of transition metal oxides or conductive polymers capable of engaging in reversible redox reactions with ions present in the electrolyte. Figure 1 shows a typical Nyquist plot for a redox active electrode. It consists of two semicircles, that is, a semicircle at high frequencies between points A and B and one at intermediate frequencies between points B and C, as well as a nonvertical line at low frequencies beyond point C. Note that the nonvertical line may be absent for some redox active electrodes.1−3,7,8,21−24,28

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Multiple and often contradictory physical interpretations of experimental Nyquist plots have been proposed in the literature. For example, the resistance $R_A$ at point A (Figure 1) has been attributed to (i) the bulk electrolyte resistance or (ii) the sum of the electrolyte resistance, the bulk electrolyte resistance, and the contact resistance between the electrode and the current collector. For Nyquist plots with one semicircle, the diameter of the semicircle has been interpreted as (i) the so-called charge transfer resistance or (ii) the sum of the electrolyte solution and electrode resistances. For Nyquist plots with two semicircles, the diameter of the semicircle at higher frequencies $R_{AB} = R_B - R_A$ (Figure 1) has been assigned to (i) the electrode resistance, (ii) the charge transfer resistance associated with pseudocapacitive charge storage including redox reactions and/or ion intercalation, and (iii) the electrolyte resistance in the porous electrodes. The diameter of the semicircle at lower frequencies $R_{BC} = R_C - R_B$ (Figure 1) has been attributed to (i) the ionic or so-called diffusion resistance of the electrolyte, (ii) the resistance of the solid-electrolyte interphase layer, or (iii) the charge transfer resistance. More conservatively, it has also been pointed out that “definitive assignment of each arc to a particular phenomenon is not possible given the probed data”. Finally, the nonvertical line beyond point C (Figure 1) at low frequencies (if observed) has been assigned to (i) ion transport limitation in the electrolyte in porous electrode structures or (ii) ion transport limitation in the bulk electrolyte.

This study aims to provide a rigorous interpretation of Nyquist plots obtained by EIS for redox active electrodes found in batteries and pseudocapacitors. To do so, EIS measurements of redox active electrodes based on a three-electrode configuration were numerically reproduced for a wide range of electrode conductivity, electrolyte thickness, redox reaction rate constant, and bias potential. Then, the physical interpretation of EIS measurements developed numerically was validated experimentally.

### NUMERICAL ANALYSIS

**Schematic and Assumptions.** Figure 2 shows a one-dimensional (1D) simulated domain consisting of a planar current collector supporting a planar redox active working electrode of thickness $L_p$ and an electrolyte domain of thickness $L$ corresponding to a three-electrode configuration. Note that our model can also be used to simulate porous electrodes through the use of effective electrical conductivity and ion diffusion coefficient. However, finding the best suited effective medium approximation (EMA) to represent actual porous electrodes falls outside the scope of this study. In addition, EMAs are often for two-phase systems while actual electrodes contain multiple constituents of various shapes and sizes including redox active nanoparticles, binder [e.g., polyvinylidene fluoride (PVDF) and carboxymethylcellulose], and electrical conducting materials [e.g., carbon black, graphene, carbon nanotube (CNT)]. To make the problem mathematically tractable, the following assumptions were made: (1) the electrolyte was binary and symmetric, that is, it consisted of two ion species of opposite valency $\pm z$ ($z > 0$). (2) The two solvated ion species were also assumed to have identical effective diameter $a$ and diffusion coefficient $D$, as suggested in the literature. (3) The Stern layer contained no free charge and its thickness $H$ was approximated as the radius of the ions, so that $H = a/2$. (4) The transport properties of the electrolyte and electrolyte were taken as constant. (5) Bulk motion of the electrolyte was negligible. (6) Ion intercalation in the electrolyte was modeled as a diffusion process. (7) Heat generation was ignored and the temperature was uniform and constant in the electrode and electrolyte. (8) The contact resistance between the electrode and the current collector and the resistance of the current collector were negligible. (9) Self-discharge of the electrode was ignored.

Simulations reported in this study for redox active electrodes were based on the modified Poisson–Nernst–Planck (MPNP) model for binary and symmetric electrolyte along with the Frumkin–Butler–Volmer equation for redox reactions. The governing equations, initial and boundary conditions, and method of solution were described in detail in refs 59 and 60 and need not be repeated. They are reproduced in Supporting Information for the sake of completeness. The MPNP model governed the spatiotemporal evolution of the potential $\psi(x,t)$ in the electrode and electrolyte as well as the concentrations $c_i(x,t)$ of cations and $c_{ai}(x,t)$ of anions in the electrolyte. In addition, the concentration $c_{i,p}(x,t)$ of ions intercalated in the electrode was governed by the diffusion equation. Moreover, the potential $\psi(x,t)$ at the
current collector/electrode interface was imposed as (i) a harmonic function of time $t$ for EIS simulations [eq S7] and (ii) a triangular function of time $t$ for cyclic voltammetry [eq S8]. The potential and the ion concentrations remained as their initial values at the centerline (Figure 2).

**Constitutive Relationships.** In order to solve the coupled transient 1D equations as well as the initial and boundary conditions, a total of 21 parameters were necessary including (i) the electrode properties $\sigma_{\circ}$, $k_D$, $\Delta \psi_{eq}$, $c_{i,P,max}$, $c_{i,P,0}$, $\alpha$, and $D_{i,P}$, (ii) the electrolyte properties $\epsilon_r$, $\epsilon$, $\mu$, $\sigma$, and $D$, (iii) the dimensions of the simulated electrode and electrolyte domains $L_p$ and $L$, along with (iv) the operating conditions $\psi_{dc}$, $\psi_{max}$, and $\nu$ for cyclic voltammetry, and (v) temperature $T$ (in K).

The electrical conductivity $\sigma_{\circ}$ of the electrode, the length of the electrolyte domain $L$, the redox reaction rate constant $k_D$, and the bias potential $\psi_{dc}$ were treated as variables to achieve various resistances. Most parameters were set as taken from the literature. For electrodes consisting of transition metal oxides, the equilibrium potential difference $\Delta \psi_{eq}$ can be modeled as a linear function of the state-of-charge (SOC) defined as $c_{i,P}/c_{i,P,max}$ where $c_{i,P,max}$ is the maximum intercalated lithium concentration in the pseudocapacitive electrode.\(^{61\text{-}65}\) Note that for 100 $\mu$m thick MnO$_2$ dense films, $\Delta \psi_{eq}(t)$ (in V) was measured as\(^{64}\)

$$\Delta \psi_{eq}(t) = 10.5(4 - c_{i,P}(t)/c_{i,P,max}) - 39.9 \tag{3}$$

Here, $c_{i,P,max}$ was taken as $c_{i,P,max} \approx 31.9 \text{ mol/L}$ corresponding to fully lithiated manganese dioxide LiMnO$_2$.\(^{65,66}\) The initial concentration of Li$^+$ in the electrode $c_{i,P,0}$ was chosen as the equilibrium concentration solution for electrode potential equal to $\psi_{dc}$. The transfer coefficient $\alpha$ was assumed to be 0.5. This choice was made to reduce the parameter space of the problem and to consider the ideal case of identical energy differences with no kinetic limitations.\(^{62}\) The diffusion coefficient $D_{i,P}$ of the intercalated Li$^+$ in the transition metal oxides typically ranges from $10^{-16}$ to $10^{-10}$ $\text{m}^2/\text{s}$.\(^{67}\) Here, $D_{i,P}$ was chosen as $10^{-14}$ $\text{m}^2/\text{s}$.

As for the electrolyte, we considered 1 M LiClO$_4$ salt in propylene carbonate (PC) solvent such that the bulk ion concentration $c_\circ = 1 \text{ mol/L}$ and valency $z = 1$. The dielectric constant was taken as that of PC, that is, $\epsilon_r = 64.4$.\(^{68}\) The effective solvated ion diameter and diffusion coefficient $D$ were taken as those of solvated Li$^+$ ions in PC such that $a = 0.67 \text{ nm}$ and $D = 2 \times 10^{-11}$ $\text{m}^2/\text{s}$.\(^{69}\)

Finally, for EIS simulations, the oscillating potential amplitude was set as $\psi_{max} = 5 \text{ mV}$ and the frequency $f$ varied between 0.1 and 8 $\times 10^4$ Hz. For cyclic voltammetry, the potential window was $\psi_{min} = 0 \text{ V}$ and $\psi_{max} = 0.5 \text{ V}$ and the scan rate $\nu$ was very low, that is, $\nu = 0.001 \text{ mV/s}$ to reproduce conditions with no kinetic limitations. The temperature $T$ was set as $T = 298 \text{ K}$. Table 1 summarizes the values or ranges of these different input parameters.

### Table 1. Value or Range of Electrode and Electrolyte Properties and Dimensions Used in the Simulations Reported in This Study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode conductivity</td>
<td>$\sigma_{\circ}$</td>
<td>$10^{-1} \text{ to } 10^{0}$</td>
<td>S/m</td>
</tr>
<tr>
<td>Maximum ion concentration in the electrode</td>
<td>$c_{i,P,max}$</td>
<td>31.9</td>
<td>mol/L</td>
</tr>
<tr>
<td>Initial ion concentration in the electrode</td>
<td>$c_{i,P,0}$</td>
<td>6.38 - 6.58</td>
<td>mol/L</td>
</tr>
<tr>
<td>Reaction rate constant</td>
<td>$k_0$</td>
<td>$10^{-8} \text{ to } 10^{-6}$</td>
<td>$\text{mol}^{-1} \text{cm}^{2} \text{s}^{-1}$</td>
</tr>
<tr>
<td>Transfer coefficient</td>
<td>$\alpha$</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Diffusion coefficient in the electrode</td>
<td>$D_{i,P}$</td>
<td>$10^{-14}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>Bulk ion concentration</td>
<td>$c_\circ$</td>
<td>1</td>
<td>mol/L</td>
</tr>
<tr>
<td>Valency</td>
<td>$z$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>$\epsilon_r$</td>
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<td></td>
</tr>
<tr>
<td>Ion diameter</td>
<td>$a$</td>
<td>0.67</td>
<td>nm</td>
</tr>
<tr>
<td>Diffusion coefficient in the electrolyte</td>
<td>$D$</td>
<td>$2 \times 10^{-11}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>Electrode thickness</td>
<td>$L_p$</td>
<td>100</td>
<td>nm</td>
</tr>
<tr>
<td>Electrolyte thickness</td>
<td>$L$</td>
<td>16 - 64</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>Bias potential</td>
<td>$\psi_{dc}$</td>
<td>0.1 - 0.6</td>
<td>V</td>
</tr>
<tr>
<td>Amplitude of oscillating potential</td>
<td>$\psi_{max}$</td>
<td>5</td>
<td>mV</td>
</tr>
<tr>
<td>Frequency</td>
<td>$f$</td>
<td>0.1 to $5 \times 10^4$</td>
<td>Hz</td>
</tr>
<tr>
<td>Potential window</td>
<td>$\psi_{min}$</td>
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<td>V</td>
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<td>$\psi_{max}$</td>
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<td>V</td>
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<tr>
<td>Scan rate</td>
<td>$\nu$</td>
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<td>mV/s</td>
</tr>
<tr>
<td>Temperature</td>
<td>$T$</td>
<td>298</td>
<td>K</td>
</tr>
</tbody>
</table>

\[ j_{eq}(L_p, t) = -\frac{\partial \psi}{\partial x} \Delta \psi_{eq}(L_p, t) \tag{4} \]

where $\epsilon_0 = 8.854 \times 10^{-12} \text{ F/m}$ is the vacuum permittivity. The Faradaic current density $j_p(LP,t)$ can be defined by the generalized Frumkin–Butler–Volmer model evaluated at the electrode/electrolyte interface and expressed as\(^{34}\)

$$j_p(L_p, t) = j_{eq}(L_p, t) \left[ \exp \left( \frac{1 - \alpha}{RT} \right) \left( \frac{-\alpha z F \psi_{eq}(L_p, t) \psi_{eq}(L_p, t)}{R T \nu} \right) - \exp \left( \frac{-\alpha z F \psi_{eq}(L_p, t)}{R T \nu} \right) \right] \tag{5}$$

where $j_{eq}(L_p, t)$ is the so-called exchange current density, $F = c N_A = 6.023 \times 10^{23} \text{ mol/mol}$ is the Faraday’s constant, and $R_0 = 8.314 \text{ J mol}^{-1} \text{K}^{-1}$ is the universal gas constant. The exchange current density $j_{eq}(L_p, t)$ can be written as\(^{71,72}\)

$$j_{eq}(L_p, t) = z F k_0 c_{i,P}(L_p, t)^{1 - \alpha} [c_{i,P,max} - c_{i,P}(L_p, t)]^{\alpha} \left[ c_{i,P}(L_p, t) \right]^\beta \tag{6}$$

In addition, the surface overpotential $\eta(L_p, t)$ necessary to drive the redox reactions at the electrode/electrolyte interface can be expressed as\(^{34}\)

$$\eta(L_p, t) = \Delta \psi_{eq}(t) - \Delta \psi_{dc}(t) \tag{7}$$

where $\Delta \psi_{dc}$ is the potential drop across the Stern layer of thickness $H = a/2$ and located between $x = L_p$ and $x = L_p + H$ (Figure 2).

**Electrical Resistances.** The electrical resistance $R_p$ (in $\Omega \text{ m}^2$) per unit surface area of the planar electrode and the bulk...
electrolyte resistance $R_{\infty}$ (in $\Omega$ m$^2$) depend on the thicknesses \( L_p \) and \( L \) and the electrical conductivities \( \sigma_p \) and \( \sigma_\infty \) of the electrode and electrolyte according to\(^{34}\)

$$ R_p \equiv L_p / \sigma_p \tag{8} $$

and

$$ R_{\infty} \approx L / \sigma_\infty \quad \text{with} \quad \sigma_\infty = (2z^2 F^2 D_{\text{eq}})/(R_a T) \tag{9} $$

Moreover, the so-called charge-transfer resistance $R_{\text{ct}}$ (in $\Omega$ m$^2$) under EIS simulations can be expressed as\(^{34}\)

$$ R_{\text{ct}} = \frac{\eta - \eta_{\text{dc}}}{j_{F} - j_{F,\text{dc}}} \tag{10} $$

where \( \eta \) (in V) is the surface overpotential [eq 7], \( \eta_{\text{dc}} \) is the time-independent dc overpotential, \( j_F \) (in A/m$^2$) is the resulting Faradaic current density, and \( j_{F,\text{dc}} \) is the time-independent dc Faradaic current density. Here, \( \eta \) and \( j_F \) can also be expressed in complex notation as

$$ \eta(t) = \eta_{\text{dc}} + \eta_0 e^{i(2\pi t - \phi_{\eta}(f))} $$

and

$$ j_F(t) = j_{F,\text{dc}} + j_{F,0} e^{i(2\pi t - \phi_{j_F}(f))} \tag{11} $$

where \( \eta_0 \) is the amplitude of the oscillating overpotential, \( \phi_{\eta}(f) \) is the frequency-dependent phase angle between the imposed potential \( \psi_F(t) \) and the overpotential \( \eta(t) \), \( j_{F,0} \) is the amplitude of the oscillating Faradaic current density, and \( \phi_{j_F}(f) \) is the frequency-dependent phase angle between the imposed potential \( \psi_F(t) \) and the Faradaic current density \( j_F(t) \).

Similarly, the mass-transfer resistance $R_{\text{mt}}$ (in $\Omega$ m$^2$) caused by ion transport in the diffuse layer can be expressed as\(^{34}\)

$$ R_{\text{mt}} = \frac{\Delta \psi_D - \Delta \psi_{D,dc}}{j_F - j_{F,\text{dc}}} \tag{12} $$

where \( \Delta \psi_D \) (in V) is the potential drop across the diffuse layer of thickness \( L_D \) and located between \( x = L_p + H \) and \( x = L_p + H + L_D \) (Figure 2), while \( \Delta \psi_{D,dc} \) is the time-independent dc potential drop across the diffuse layer. Similarly, using complex notations, \( \Delta \psi_D \) can be expressed as

$$ \Delta \psi_D = \Delta \psi_{D,dc} + \Delta \psi_{D,0} e^{i(2\pi t - \phi_{\psi_D}(f))} \tag{13} $$

where \( \Delta \psi_{D,0} \) is the amplitude of the oscillating potential drop across the diffuse layer and \( \phi_{\psi_D}(f) \) is the frequency-dependent phase angle between the imposed potential \( \psi_D(t) \) and the potential drop across the diffuse layer \( \Delta \psi_D(t) \).

### EXPERIMENTAL METHODS

In order to validate experimentally the physical interpretation of EIS obtained numerically, a redox active MoS$_2$ electrode was synthesized. First, a slurry was prepared by mixing 70 wt % MoS$_2$ nanoparticles, 10 wt % Super P (Alfa Aesar), 10 wt % multwall CNTs (mwCNT, Sigma-Aldrich), and 10 wt % PVDF (Kynar) in N-methyl-2-pyrrolidinone (Sigma-Aldrich). The MoS$_2$ nanoparticles were synthesized through the sulfuration of MoO$_2$ nanoparticles according to a previously reported procedure. Then, the slurry was drop-cast onto a 1 cm$^2$ carbon-coated aluminum current collector (MTI) with a weight loading of 0.4 mg MoS$_2$ nanoparticles. The electrode was dried in air overnight and under vacuum at 120 $^\circ$C for at least 2 h. Finally, the electrode was placed in a three-half-cell with activated carbon counter and (i) Li/Li$^+$ or (ii) Na/Na$^+$ reference electrodes, where each electrode was clipped to and immersed in (i) 1 M LiClO$_4$ (Sigma-Aldrich) in ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 by volume) or (ii) 1 M NaClO$_4$ (Alfa Aesar) in EC/DMC (1:1 by volume) electrolyte. MoS$_2$ electrodes were conditioned prior to EIS experiments using a 70 $\mu$A current (1C based on the 167 mAh/g theoretical capacity of MoS$_2$) from 0.8 to 2.5 V vs Li/Li$^+$ and 0.6 to 2.5 V vs Na/Na$^+$ for 10 cycles to ensure conversion of the MoS$_2$ from the semiconducting 2H to the semi-metallic 1T phase. EIS measurements were performed on the MoS$_2$ electrode with a potential amplitude \( \psi_0 \) of 10 mV$_F$ bias potential \( \psi_{\text{dc}} \) versus reference electrodes ranging between 1.8 and 2.2 V and frequency $f$ ranging between 0.1 and 2 $\times$ $10^5$ Hz. Note that the electrodes were charged/discharged to each bias potential using a low constant current of about 70 $\mu$A.  

### RESULTS AND DISCUSSION

Table 2 summarizes the eight different cases considered to identify the electrode $R_{\text{sp}}$, electrolyte $R_{\text{eq}}$, and charge transfer $R_{\text{ct}}$.
and mass transfer $R_{mt}$ resistances from the Nyquist plots of redox active electrodes in a three-electrode configuration.

**Current Densities and Overpotentials.** Figure 3a−c shows the (i) Faradaic current density $j_F(t)$, (ii) capacitive current density $j_C(t)$, and (iii) total current density $j_s(t) = j_F(t) + j_C(t)$ as functions of the dimensionless time $ft$ during one EIS cycle for case 1 (Table 2) at frequency $f$ equal to (a) 2, (b) 20, and (c) 2000 Hz. A phase shift between capacitive and Faradaic current densities was observed at all frequencies. In addition, the Faradaic current density $j_F(t)$ always dominated over the capacitive current density $j_C(t)$ (i.e., $j_{F,dc} > j_{C,dc}$) and their amplitudes were dependent on frequency. Figure 3d shows the amplitudes of oscillations of (i) the Faradaic current density $j_{F,0}$, (ii) the capacitive current density $j_{C,0}$, and (iii) the total current density $j_{s,0}$ as functions of frequency $f$. It indicates that the amplitude of the Faradaic current density $j_{F,0}$ was the largest at low frequencies while that of the capacitive current density $j_{C,0}$ was the largest at high frequencies. In other words, the major contribution to the impedance $Z$ was the Faradaic reactions at low frequencies and the EDL formation at high frequencies.

Moreover, Figure 3e shows the overpotential $\eta(t)$ and the Faradaic current density $j_F(t)$ as functions of the dimensionless time $ft$ for case 1 (Table 2) at frequency $f$ equal to 2, 20, and 2000 Hz. It indicates that $\eta$ and $j_F$ were in phase at all frequencies, that is, $\phi_\eta(f) = \phi_F(f)$ [eq 11]. Figure 3f shows $j_F$ as a function of $\eta$ for EIS simulations for case 1. It established a linear relationship between $j_F$ and $\eta$ for all frequencies considered. In addition, the amplitude $\eta_0$ of the overpotential oscillations were very small. Note that similar conclusions can be drawn from the plot of $j_F$ as a function of $\Delta\psi_D$ (Figure S1 in Supporting Information). Thus, the charge transfer resistance and mass transfer resistance, given by eqs 10 and 12, can be estimated as

$$\frac{1}{R_{ct}} = \frac{j_F(t) - j_{F,dc}}{\eta(t) - \eta_{dc}} \approx \frac{\partial j_F}{\partial \eta} \bigg|_{\eta = \eta_{dc}}$$

(14)

$$\frac{1}{R_{mt}} = \frac{j_F(t) - j_{F,dc}}{\Delta\psi_D(t) - \Delta\psi_{D,dc}} \approx \frac{\partial j_F}{\partial \Delta\psi_D} \bigg|_{\Delta\psi_D = \Delta\psi_{D,dc}}$$

(15)
In other words, $1/R_{ct}$ and $1/R_{mt}$ correspond, respectively, to the slope of $j_0$ versus $\eta$ and $j_0$ versus $\Delta \psi_D$ near the dc operating points. Figure 3f also indicates that $R_{ct}$ was independent of frequency. Similar observations can be made for the mass transfer resistance $R_{mt}$ [Figure 5b in Supporting Information].

**Interpretation of Nyquist Plots. Electrode Resistance $R_P$.** Figure 4 shows the Nyquist plots for the electrodes of cases 1–3 featuring electrode resistance $R_P$ equal to (a) 10, (b) 20, and (c) 100 $\Omega$ cm$^2$.

![Figure 4](image)

Figure 4. Nyquist plots for redox active electrodes for cases 1–3 featuring electrode resistance $R_P$ equals to (a) 10, (b) 20, and (c) 100 $\Omega$ cm$^2$.

1–3 featuring electrode electrical conductivity $\sigma_P$ equal to (a) $1 \times 10^{-4}$, (b) $5 \times 10^{-5}$, and (c) $1 \times 10^{-5}$ S/m, corresponding to electrode resistance $R_P$ [eq 8] equal to (a) 10, (b) 20, and (c) 100 $\Omega$ cm$^2$, respectively. All other parameters remained the same in these three cases (Table 2). Note that all values of $-Z_{im}$ simulated were positive for all frequencies. Figure 4 indicates that the high-frequency intersection of the Nyquist plot with the $Z_{re}$-axis (corresponding to $R_A$ in Figure 1) increased with decreasing conductivity $\sigma_P$ and was systematically equal to the electrode resistance $R_P$. Note that the contact resistance was neglected in the current simulations. However, it can be modeled as a resistor in series with the electrode resistance $R_P$. Its sole effect would be a horizontal shift of the Nyquist plot along the $Z_{re}$-axis. The same observations have already been made for simulations of electrochemical double layer capacitor (EDLC) electrodes.73

Moreover, the diameter of the semicircle at high frequencies (corresponding to $R_{AB} = R_B - R_A$ in Figure 1) was not affected by the electrode conductivity and was equal to 4.2 $\Omega$ cm$^2$ in all cases. By contrast, the diameter of the semicircle at lower frequencies (corresponding to $R_{BC} = R_C - R_B$ in Figure 1) decreased with decreasing electrode conductivity $\sigma_P$.

**Bulk Electrolyte Resistance $R_\infty$.** Figure 5 shows the Nyquist plots for electrodes of cases 2, 4, and 5 featuring electrolyte resistance $R_\infty$ equal to (a) 4.2, (b) 2.1, and (c) 1.05 $\Omega$ cm$^2$.

![Figure 5](image)

Figure 5. Nyquist plots for redox active electrodes for cases 2, 4, and 5 featuring bulk electrolyte resistance $R_\infty$ equals to (a) 4.2, (b) 2.1, and (c) 1.05 $\Omega$ cm$^2$. 

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thickness \( L \) equal to (a) 64, (b) 32, and (c) 16 \( \mu \)m, corresponding to bulk electrolyte resistance \( R_\infty \) [eq 9] equal to (a) 4.2, (b) 2.1, and (c) 1.05 \( \Omega \) cm\(^2\), respectively. All other parameters remained the same in these three cases. Here, the electrode resistance \( R_\varepsilon \) was constant and equal to 20 \( \Omega \) cm\(^2\) for all three cases. A previous conclusion identifying \( R_A = R_P \) was also valid for these cases. In addition, Figure 5 establishes that the diameter of the semicircle at high frequencies (corresponding to \( R_{AB} = R_A - R_{\infty} \) in Figure 1) was equal to the bulk electrolyte resistance, that is, \( R_{AB} = R_{\infty} \). In fact, the same observations were made for EDLC electrodes. However, increasing the electrolyte thickness \( L \) reduced the diameter of the semicircle at lower frequencies, corresponding to \( R_{BC} = R_C - R_{\infty} \) (Figure 1).

**Charge Transfer Resistance \( R_\varepsilon \) and Mass Transfer Resistance \( R_{mt} \).** To further explain the diameter of the semicircle at intermediate frequencies (\( R_{BC} \) in Figure 1), charge transfer resistance \( R_\varepsilon \) and mass transfer resistance \( R_{mt} \) were varied by changing the reaction rate constant \( k_0 \). Figure 6 shows the Nyquist plots for electrodes for cases 4, 6, and 7 featuring redox reaction rate constant \( k_0 \) equal to (a) \( 10^{-9} \), (b) \( 5 \times 10^{-9} \), and (c) \( 10^{-9} \) m\(^5\) mol\(^{-1}\) s\(^{-1}\). These cases corresponded to charge transfer \( R_{ct} \) [eq 10] and mass transfer \( R_{mt} \) [eq 12] resistances equal to (a) 24.3 and 20.2 \( \Omega \) cm\(^2\), (b) 13.5 and 11.7 \( \Omega \) cm\(^2\), and (c) 7.6 and 6.6 \( \Omega \) cm\(^2\), respectively. All other parameters remained the same in these three cases. In particular, \( R_\varepsilon \) and \( R_{mt} \) were equal to 20 and 2.1 \( \Omega \) cm\(^2\), respectively. Here also, previous identifications of \( R_A = R_P \) were valid in these cases. Figure 6 establishes that the diameter of the semicircle at lower frequencies \( R_{BC} \) (Figure 1) was systematically equal to the sum of charge transfer resistance \( R_\varepsilon \) and mass transfer resistance \( R_{mt} \) estimated using eqs 14 and 15, that is, \( R_{BC} = R_\varepsilon + R_{mt} \).

In addition, Figures 4 and 5 indicate that \( R_\varepsilon \) and/or \( R_{mt} \) decreased with (i) decreasing electrode conductivity \( \sigma_\varepsilon \) and (ii) increasing electrolyte thickness \( L \). To explain the trend in \( R_{BC} \), Figure 7a,b shows (i) \( j_F \) versus \( \eta \) and \( j_F \) versus \( \Delta \psi_F \) under cyclic voltammetry at very low scan rate (\( v = 0.001 \) mV/s), where there are no kinetic limitations and (ii) the points \( (\eta_{\varepsilon,ct}, j_F), (\Delta \psi_{F,D,ct}, j_F), \) and \( (\Delta \psi_{F,eq,ct}, j_F) \) obtained from EIS simulations and averaged from all frequencies considered for different values of (a) \( \sigma_\varepsilon \) in cases 1–3 and (b) \( L \) in cases 2, 4, and 5. The figures indicate that the \( j_F \)–\( \eta \) curve remained nearly the same for different values of \( \sigma_\varepsilon \) and \( L \). In addition, the slope of the \( j_F \)–\( \eta \) curve at \( (\eta_{\varepsilon,ct}, j_F) \), corresponding to 1/\( R_\varepsilon \) [eq 14], decreased with increasing dc overpotential \( \eta_{\varepsilon,ct} \) which increased with increasing \( \sigma_\varepsilon \) and decreasing \( L \). Similar observations were made for \( j_F \)–\( \Delta \psi_F \) curve and 1/\( R_{mt} \).

To further explain the trend in the overpotential \( \eta_{\varepsilon,ct} = \Delta \psi_\varepsilon - \Delta \psi_{eq,ct} \) and potential drop across the diffuse layer \( \Delta \psi_{D,ct} \) Figure 7c,d shows the dc potential drops across (i) the electrode \( \Delta \psi_{F,\varepsilon,ct} \) (ii) the Stern layer \( \Delta \psi_{\varepsilon,ct} \), (iii) the diffuse layer \( \Delta \psi_{D,ct} \), and (iv) the bulk electrolyte \( \Delta \psi_{\varepsilon,eq} \) for different values of (a) \( \sigma_\varepsilon \) in cases 1–3 and (d) \( L \) in cases 2, 4, and 5. Note that the imposed dc potential \( \psi_{\varepsilon,ct} \) at the current collector is such that

\[
\psi_{\varepsilon,ct} = \Delta \psi_{F,\varepsilon,ct} + \Delta \psi_{\varepsilon,ct} + \Delta \psi_{D,\varepsilon,ct} + \Delta \psi_{\varepsilon,eq,ct} \quad (16)
\]

Figure 7c indicates that the potential drops \( \Delta \psi_{F,\varepsilon,ct}, \Delta \psi_{\varepsilon,ct}, \Delta \psi_{D,\varepsilon,ct}, \) and \( \Delta \psi_{\varepsilon,eq,ct} \) increased with increasing \( \sigma_\varepsilon \) to compensate for the decrease in the potential drop across the electrolyte \( \Delta \psi_{\varepsilon,eq,ct} \) so as to maintain the imposed \( \psi_{\varepsilon,ct} \). Similarly, Figure 7d establishes that the potential drops \( \Delta \psi_{F,\varepsilon,ct}, \Delta \psi_{\varepsilon,ct}, \Delta \psi_{D,\varepsilon,ct} \), and \( \Delta \psi_{\varepsilon,eq,ct} \) decreased with increasing electrolyte thickness \( L \) to compensate for the increase in the potential drop across the bulk electrolyte \( \Delta \psi_{\varepsilon,eq,ct} \) while \( \psi_{\varepsilon,ct} \) remained constant. In other words, both potential drops \( \Delta \psi_{F,\varepsilon,ct} \) and \( \Delta \psi_{\varepsilon,ct} \) increased with increasing \( \sigma_\varepsilon \) and decreasing \( L \). In addition, under EIS simulations, the variation of SOC of the electrode was negligible, resulting in nearly constant \( \Delta \psi_{\varepsilon,eq,ct} \). Thus, the dc overpotential \( \eta_{\varepsilon,ct} = \Delta \psi_{\varepsilon,ct} - \Delta \psi_{eq,ct} \) and the charge transfer resistance \( R_\varepsilon \) varied like \( \Delta \psi_{\varepsilon,ct} \) that is, they increased with increasing electrical conductivity and decreasing electrolyte thickness \( L \). Note that the potential drop across the diffuse layer \( \Delta \psi_{\varepsilon,ct} \) and the potential drop across the stern layer \( \Delta \psi_{\varepsilon,ct} \) were related [see detailed derivation in Supporting Information] Therefore, the charge transfer resistance \( R_\varepsilon \) [eq 10] and the mass transfer resistance \( R_{mt} \) [eq 12] were coupled and could not be separated in the Nyquist plot.
Effect of Bias Potential $\psi_{dc}$. Figure 8a shows the Nyquist plot for cases 8 and 9 with bias potential $\psi_{dc}$ ranging from 0.1 to 0.6 V. All parameters were identical in cases 8 and 9 except for $k_0$ equals to $k_0 = 10^{-8}$ m$^{-2.5}$ mol$^{-0.5}$ s$^{-1}$ in case 8 (redox active) and $k_0 = 0$ in case 9 (EDLC) (Table 2). Two semicircles were observed for case 8, whereas only one semicircle and a nearly vertical line were observed for case 9. It is important to note that the high frequency semicircle AB for cases 8 and 9 overlapped. In addition, the intercept of the Nyquist plot with the $Z_{re}$ axis (point A) and the semicircle AB at high frequency were independent of $\psi_{dc}$. Indeed, the resistances of the electrode $R_P$ and bulk electrolyte $R_\infty$ are properties of the electrode and electrolyte. They were both independent of redox reactions and of $\psi_{dc}$ as indicated in eqs 8 and 9. Moreover, the nearly vertical lines (diffusion tail) observed for case 8 were also nearly independent of dc potential $\psi_{dc}$ as previously observed for EDLC electrodes. The slope of the line indicated whether the charging process was controlled by EDL formation (large slope) or limited by ion diffusion in the electrolyte (small slope). Here, the slope of the nonvertical line was very steep, indicating that the charging process was controlled by EDL formation in absence of Faradaic reactions.

Furthermore, for case 8, the diameter of the semicircle BC at lower frequency, that is, the charge and/or mass transfer resistances $R_A$ and $R_{mt}$ increased with increasing $\psi_{dc}$. Indeed, Figure 8b plots the Faradaic current density $j_F$ versus overpotential $\eta$ and $j_F$ versus potential drop across the diffuse layer $\Delta \psi_D$ under cyclic voltammetry at very low scan rate ($v = 0.001$ mV/s), that is, without kinetic limitations. It also plots the corresponding points ($\eta_{dc}$, $j_F$, $\psi_{dc}$) and ($\Delta \psi_D$, $j_F$, $\psi_{dc}$) (averaged from all frequencies considered) from EIS simulations and (c,d) $\psi_{dc}$ potential drops from EIS simulations for different values of (a,c) $\sigma_p$ in cases 1–3 and (b,d) L in cases 2, 4, and 5.

Comparison with Experimental Data. Figure 9a shows the Nyquist plots reported in the literature and obtained experimentally for the LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ electrode in 1 M LiPF$_6$ in EC and ethyl–methyl carbonate (EC/EMC, 3:7) electrolyte for a bias potential $\psi_{dc}$ of 3.7–4.2 V. The experiment was performed in coin-type cells with lithium foil as the counter and reference electrode. Here, the lithium foil electrode was not expected to contribute to the semicircles of the Nyquist plot due to strong redox activity, while the Ohmic resistance of the Li electrode could cause a horizontal shift of the Nyquist plot along the $Z_{re}$-axis. The Nyquist plots featured two semicircles and closely resembled numerically generated Nyquist plots illustrated in Figure 8a. Note that similar trends were observed in the Nyquist plots obtained for other material systems including corrosion test of SiC composite in sodium hydroxide solution and dye sensitized solar cells. In addition, neither the high-frequency intersection of the Nyquist plot with the $Z_{re}$-axis $R_A$ nor the diameter of the high frequency semicircle $R_{AB}$ was affected by $\psi_{dc}$. Similarly, the resistance $R_{BC}$, interpreted as the charge $R_c$ and/or mass.
The high frequency arc AB were not a transport in the electrolyte (corresponding to semicircles overlapped could be attributed to the fact that ion nonvertical line at low frequencies. The fact that the two measured Nyquist plots feature two partially overlapping (or between 1.8 and 2.2 V. For both systems, the experimentally observed in the simulations.

Figure 8. (a) Nyquist plot for cases 8 (redox reactions) and 9 (no redox reactions) with bias potential $\psi_{dc}$ of 0.1–0.6 V. (b) Corresponding Faradaic current density $j_f$ as a function of overpotential $\eta$ and of potential drop across the diffuse layer $\Delta \psi_D$ under cyclic voltammetry at very low scan rate ($v = 0.001$ mV/s) as well as $(\psi_{dc}, j_f, \Delta \psi_D)$ (averaged from all frequencies considered) from EIS simulations for case 8.

Figure 9b,c shows the Nyquist plots obtained experimentally for MoS$_2$ mesoporous electrodes in a three-electrode configuration in (b) 1 M NaClO$_4$ (EC/DMC) and (c) 1 M LiClO$_4$ (EC/DMC) electrolytes for bias potential $\psi_{dc}$ ranging between 1.8 and 2.2 V. For both systems, the experimentally measured Nyquist plots feature two partially overlapping (or depressed) semicircles at high frequencies as well as a nonvertical line at low frequencies. The fact that the two semicircles overlapped could be attributed to the fact that ion transport in the electrolyte (corresponding to $R_w$ and ion intercalation into the MoS$_2$ electrode (related to $R_a$ and/or $R_{in}$) took place simultaneously throughout the porous electrode. In addition, for both systems, the high-frequency intersection of the Nyquist plot with the $Z_w$-axis (point A) and the high frequency arc AB were not affected by $\psi_{ac}$. These experimental observations agreed with numerical simulations presented earlier. Moreover, the resistance $R_a$ was identical in both experimental systems. This was consistent with the interpretation that $R_a$ corresponded to the electrode resistance and the fact that both electrodes were nearly identical. In fact, the electrode resistance was equal to 10 $\Omega$ and similar to that of activated carbon electrodes (5–10 $\Omega$) of similar dimensions reported in our previous study. On the other hand, the resistance $R_{AB}$ for the system with NaClO$_4$ electrolyte [Figure 9b] was larger than that for LiClO$_4$ electrolyte [Figure 9c]. This was in line with the fact that $R_{AB}$ corresponded to the bulk electrolyte resistance and that NaClO$_4$ in EC/DMC feature lower ionic conductivity ($\sim$5 mS/cm) than LiClO$_4$ in EC/DMC ($\sim$8.4 mS/cm) at room temperature.

Furthermore, for both systems, the diameter of the second arc BC, that is, the resistance $R_{BC}$, increased with increasing $\psi_{dc}$. This was consistent with numerical simulations in the presence of redox reactions (case 8, Figure 8). In addition, for any given bias potential, the resistance $R_{BC}$ for NaClO$_4$ electrolyte was larger than that for LiClO$_4$ electrolyte. Note also that the pseudocapacitive charge storage mechanism for MoS$_2$ electrode was mainly due to ion intercalation. However, the kinetics of Na$^+$ intercalation into the MoS$_2$ electrode was slower than that of Li$^+$ because of the larger radius and heavier mass of Na$^+$ compared with Li$^+$. This resulted in larger charge and mass transfer resistances in the NaClO$_4$ than in the LiClO$_4$ electrolyte.

Moreover, the nonvertical line beyond point C could be assigned to ion transport limitation in the electrolyte in the porous electrodes or in the diffuse layer of the EDL. This feature was not observed (i) in numerical simulations for planar redox active electrodes [case 8, Figure 8a] or (ii) in experiments for electrodes made of battery-type Li-Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ material shown in Figure 9a. The latter can be attributed to the dominance of Faradaic reactions at low frequencies (beyond point C). However, a similar nonvertical line was observed in numerically generated Nyquist plots for EDLC electrodes [case 9, Figure 8a], as previously discussed. In fact, by contrast with planar pseudocapacitive electrodes or battery electrodes, the current contribution from EDL formation was likely large in the highly porous MoS$_2$ electrodes due to the large surface area offered by other constituents of the electrodes (e.g., mwCNT’s).

Finally, Figure 9d shows the internal resistance $R_{GC}$ retrieved from the “IR drop” in galvanostatic cycling (see Supporting Information) as a function of the imposed current $i_{dc}$ (1–8 mA) as well as $R_{B} = R_{B} + R_{AB}$ retrieved from the Nyquist plots for the two systems considered in Figure 9b,c. It indicates that $R_{GC}$ was nearly independent of the imposed current $i_{dc}$ and was approximately equal to $R_B$. Note that $R_{GC}$ has been attributed to the Ohmic resistance of the system and is equal to the sum of the electrical resistance of the electrode $R_E$ and the ionic resistance of the electrolyte $R_w$.

This result confirms the physical interpretation developed from the numerical simulations establishing that $R_B = R_E + R_w$.

### CONCLUSIONS

This study presented physical interpretations of EIS results for redox active electrodes. The Nyquist plots presenting the imaginary and real parts of the complex impedance of individual electrodes were numerically reproduced based on the MPNP model along with the generalized Frumkin–Butler–Volmer equation for redox reactions and closely resembled experimental measurements. This study established that intercepts with the real axis, $R_A, R_{AB}$ and $R_{BC}$ (shown in Figure 1) can be interpreted as the electrode resistance, the electrolyte resistance, and the sum of charge and mass transfer resistances, respectively. Furthermore, the electrode and bulk electrolyte resistances were independent of the bias potential, while the sum of the charge and mass transfer resistances increased with increasing bias potential. Finally, these results and interpretations were confirmed experimentally for
LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 and MoS_2 electrodes in organic electrolytes.

■ ASSOCIATED CONTENT

* Supporting Information

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Governing equations; initial and boundary conditions of the model; results including current oscillations, potential drops across stern and diffuse layers; and experimental potential evolution under galvanostatic cycling (PDF)

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■ NOMENCLATURE

\( a \) effective ion diameter (nm)
\( c \) ion concentration (mol/L)
\( c_{1,P} \) concentration of intercalated ion in the pseudocapacitive layer (mol/L)
\( c_{1,P,0} \) initial concentration of intercalated ion in the pseudocapacitive layer (mol/L)
\( c_{1,P,max} \) maximum concentration of intercalated ion, \( c_{1,P,max} = \frac{mp}{M} \) (mol/L)
\( D \) diffusion coefficient of ions in electrolyte (m^2/s)
\( D_{1,P} \) diffusion coefficient of intercalated ion in the pseudocapacitive electrode (m^2/s)
\( e \) elementary charge, \( e = 1.602 \times 10^{-19} \) C
\( f \) frequency (Hz)
\( F \) Faraday’s constant, \( F = cN_A = 9.648 \times 10^4 \) C mol\(^{-1}\)
\( H \) stern layer thickness (nm)
\( i \) imaginary unit, \( i^2 = -1 \)

Figure 9. Nyquist plot obtained experimentally for porous electrodes made of (a) LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 in 1 M LiPF_6 in EC/EMC(3:7) for bias potential \( \psi_{dc} \) of 3.7–4.2 V, (b,c) for MoS_2 mesoporous electrodes in (b) 1 M NaClO_4 in EC/DMC and (c) 1 M LiClO_4 in EC/DMC for bias potential \( \psi_{dc} \) of 1.8–2.2 V. (d) Internal resistance \( R_{GC} \) obtained experimentally from galvanostatic cycling as a function of current \( i_{GC} \) and \( R_B \) obtained from EIS measurement shown in (b,c) for MoS_2 electrodes.