The Influence of Anomalous Diffusion on the Impedance Response of LiCoO₂|C Batteries

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Abstract

A process model for impedance analysis was developed in the context of reactions and transport processes that were hypothesized to govern the performance of the Li-ion battery. At the carbon electrode, lithium ions and solvent were considered to react to form a solid-electrolyte interphase (SEI). In addition, lithium ions were assumed to diffuse through the SEI to intercalate into the graphene layers. As these two processes involve an addition of currents, the corresponding impedances were considered to be in parallel. Anomalous diffusion of lithium ions was invoked at the LiCoO₂ electrode to account for the low-frequency line that had a slope steeper than that predicted by ordinary diffusion. This model was fit to all impedance data collected. The model provided a good description for impedance of batteries under normal operating potentials and temperatures. The contribution of anomalous diffusion was diminished at elevated temperatures, suggesting that the free-energy well associated with anomalous or sticky diffusion was shallow.

Keywords: Li-ion batteries, process model, anomalous diffusion, impedance spectroscopy

1. Introduction

Impedance spectroscopy has the potential to provide a powerful insight into the electrochemical performance of Li-ion batteries; however, the models used to interpret the impedance response should account for the chemistry and physics of the electrochemical device. The impedance response of LiCoO₂|C batteries has distinguishing characteristics that should, in principle, be associated with the electrochemical characteristics of the battery. A key feature is the low-frequency impedance that appears in a Nyquist plot as a straight line with an angle with respect to the real axis greater than the 45 degrees expected for a diffusion impedance.

The measurement model analysis presented by Erol et al. [1] provided insight into factors affecting the impedance response of Li-ion batteries, but the measurement model does not give comprehensive mechanistic information. Osaka et al. [2] considered that the low-frequency behavior could be attributed to the parallel contributions associated with diffusion to LiCoO₂ particles of different diameters. They showed that a model of this type could approximate the observed impedance with an angle with respect to the real axis larger than 45 degrees. An alternative approach is presented by Deng et al. [3] who placed a constant-phase element (CPE) in series with circuit elements meant to account for other battery components. This approach has the advantage of providing a good fit to the data, but at the expense of physical interpretation. Li et al. [4] developed an electrochemistry-based impedance model for Li-ion batteries. The resulting model consisted of a porous electrode behavior for the cathode. The model fits well at high frequencies but it deviates at low frequencies. Honda et al. [5] account for the low-frequency behavior with a Warburg element in series with a capacitor, and Gomez et al. [6] use a Randles circuit in series with a capacitor. Neither approach will yield a low-frequency angle with respect to the real axis greater than 45 degrees.

Recent experimental work employing nuclear-magnetic resonance (NMR) to quantify diffusion in solids suggest that, for some systems, the diffusion process has characteristics described by anomalous diffusion

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theories [7, 8, 9, 10]. Rollet et al. [7] showed anomalous diffusion of water in an ionic liquid. They determined the self-diffusion coefficients of cations, anions, and water molecules in their system by pulsed-field gradient NMR. Weber and Kimmich [8] presented anomalous diffusion in polymers using NMR relaxation spectroscopy. The mean-square displacement of their polymer molecules were characterized by a power law which is an indicator of an anomalous diffusion. Cheng et al. [9] observed anomalous diffusion of Xenon in dipeptide nanochannels by NMR spectroscopy. Also, Hayamizu et al. [10] indicated that lithium ions diffuse anomalously in solid polymer electrolytes doped with lithium bis(trifluoromethanesulfonyl)imide ($\text{LiN}(\text{SO}_2\text{CF}_3)_2$) using pulsed-gradient spin-echo (PGSE) NMR measurements. They stated that positive charges located in the polymer chains and the Coulomb repulsive force would prevent free-diffusion of lithium ions.

The object of this work was to employ a mathematical description developed by Bisquert and Compte [11] to develop a mathematical model for the impedance response of $\text{LiCoO}_2|\text{C}$ batteries that accounts for anomalous diffusion. In addition, the model development accounts for the parallel contribution of SEI formation and intercalation reactions at the anode. The model was used to interpret the impedance response of $\text{LiCoO}_2|\text{C}$ batteries at different states-of-charge (SOC) and temperatures.

2. Experimental Method

Electrochemical experiments were performed on commercial $\text{LiCoO}_2|\text{C}$ coin cells. Impedance spectroscopy was used to monitor changes associated with different states-of-charge and temperatures.

2.1. Materials

Commercial secondary LIR2032 button (or coin) cells used for the experiments in which SOC was varied were purchased from AA Portable Power Corp. (Richmond, CA, www.batteryspace.com). The batteries used to explore the influence of temperature were purchased from Battery Junction (Old Saybrook, CT, www.batteryjunction.com). Minor differences between the two batteries were observed. The prefix LIR refers to Lithium-ion rechargeable, and the 2032 specification means that the batteries were 20 mm in diameter and 3.2 mm in height. The cathode was LiCoO_2 , the separator was Celgard with 8 μm thickness, and the anode was carbon.

The normal operating potential range of the cells reported by the suppliers [12, 13] is between 3.0 V (0% state-of-charge) and 4.2 V (100% state-of-charge). The average measured value for the capacity of the LIR2032 battery at a 1C rate was 30 mAh, in agreement with the vendor documentation.[12, 13]. As suggested by Erol et al. [1], a value of 3.2 V was used as a lower limit for the normal potential range. The average measured value for the capacity of the LIR2032 battery, between 3.2 V (0% SOC) and 4.2 V (100% SOC) was 28.8 mAh at a 1C discharge rate and 29.6 mAh at a C/15 discharge rate.

2.2. Instrumentation

Electrochemical impedance measurements were performed using a Gamry PCI4/750 Potentiostat connected to a desktop computer. Gamry’s Virtual Front Panel (VFP600) and Electrochemical Impedance Spectroscopy (EIS300) software packages were used to run the experiments. The primary purpose of the potentiostat in these experiments was to maintain a constant cell potential while measuring the impedance. A Tenney Jr. environmental test chamber was used to control the temperature of a battery and its surroundings.

2.3. Protocol

The protocol followed was described by Erol et al. [1] The impedance response was analyzed throughout the normal potential range under charge and discharge profiles. The $\text{LiCoO}_2|\text{C}$ cells had an open-circuit potential of 3.8 ± 0.2 V, as received. The cells were slowly charged under galvanostatic control at a current of 2 mA (a nominal C/15 rate) to 4.20 V. For impedance measurements in the normal potential range, the cells were held for at least one hour at a constant cell potential of 4.20 V. After the constant-potential rest period,

the impedance was measured **at open-circuit** using a 10 mV perturbation and 100 kHz - 20 mHz frequency range. As suggested by Hirschorn et al. [14], the linear response of low-frequency Lissajous plots was used to ensure linearity during the impedance measurement. Three replicated impedance scans were obtained for each condition tested. Following impedance measurements at a given potential, the cell potential was modified for the discharge profile in 0.20 V increments down to and including 3.2 V. The change in potential was conducted galvanostatically at a 2 mA (**nominal C/15 rate**) current. For each potential step, the battery was allowed to stabilize for a period of one hour, in which the current was reduced to a value that was smaller than 0.02 mA. Impedance measurements were made **at open-circuit** in triplicate following stabilization at the desired potential. The charge profile, following the same procedure, was executed immediately up to and including 4.20 V. These SOC impedance measurements were all executed at 20 °C.

Another set of LiCoO₂|C batteries were analyzed with using impedance spectroscopy and capacity measurements at different surrounding temperature. The temperature was applied between -20 and 60 °C with 10 °C increments with using the environmental temperature chamber. The batteries were held for 30 minutes at each temperature to reach a stable condition. Impedance measurements were performed at 4 V with a 10 mV perturbation and a 100 kHz - 20 mHz frequency range.

Every experiment was repeated 3-4 times with same type of battery to ensure that the results were both consistent and reproducible. The software incorporated in the Gamry system enabled consistent and precise procedures to be performed, which served to reduce errors among the repetitive experiments.

3. Results

The impedance response of the LiCoO₂|C coin cells is presented **as functions of** SOC and temperature.

3.1. State-of-Charge

The impedance response for a commercial LiCoO₂|C coin cells is presented in Figure 1 with cell potential from 4.2 to 3.2 V as a parameter. These results represent the impedance response under normal operating conditions and under the discharge profile. Results obtained under the charge profile were identical to those obtained under the discharge profile. Notably, the impedance, especially at the low frequencies, became larger as the cell potential decreased. **The relationship reported in the legend of Figure 1 between potential and SOC was obtained from a C/15 discharge measurement.**

3.2. Temperature

The impedance response of the LiCoO₂|C coin cell **at a potential of 4 V** is presented in Figure 2 with temperature from 10 to 50 °C as a parameter. The impedance at temperatures of 10 to 30 °C is shown in Figure 2(a), and the results at higher temperatures are shown more clearly in Figure 2(b). **As shown in Figure 2(a), the Nyquist plot at 50 °C consists of two capacitive loops; whereas, the Nyquist plot at 10 °C reveals three capacitive loops. This separation of capacitive loops at low temperature was also reported by Momma et al. [15]**

The lines represent the fit of the model developed in the present paper. Impedance data obtained at 60 °C and at temperatures below 10 °C could not be represented by the model, suggesting a change in the phenomena treated by the model. Distortion of the battery casing was observed at temperatures of 60 °C and -10 °C, indicating that the battery may have suffered damage.

4. Process Model

The impedance data obtained under normal operation conditions, e.g., at 3.6 V, revealed a depressed capacitive loop at high and intermediate frequencies and a straight line at low frequencies with an angle with respect to the real axis greater than 45° as shown in Figure 3. The impedance data could not be described simply by a Randles circuit design because the high-frequency loop is not a perfect semicircle or suppressed semicircle (CPE behavior with one time constant) in a Nyquist plot, and the angle with respect

to the real axis of the low-frequency impedance was near 58° , which is much larger than the 45° associated with the Warburg impedance. An expression for the process model was based on charge-transfer reactions and diffusion proposed to take place at the electrodes occurring in electrodes.

4.1. Anode

The charge-transfer reaction at the carbon electrode is represented by

Given the slow diffusion of the reacting species through the graphite [16] and large particle sizes in the electrode,[17] a Warburg diffusion impedance was assumed for the anode.

The desired electrochemical reaction at anode is the intercalation of lithium, but lithium can also react with components of the electrolyte to form a solid-electrolyte interphase (SEI). The SEI layer is a passivating film that forms at the surface of the active electrode material in the battery, protecting the electrolyte and other battery components (especially graphitic anode) from undesirable reactions. The most common source of capacity fade in Li-ion batteries is the loss of lithium due to the SEI formation and thickening at the negative electrode during charging. A large variety of compounds has been observed in this layer. [18, 19]

Deshpande et al. [20] suggested that the cracks at the graphite particle surface propagate upon electrochemical cycling. For each cycle, the newly cracked surface is exposed to electrolyte and thus results in SEI formation. As a result of diffusion induced stresses, the cracks at the particle surface propagate with cycling, new surface is exposed to electrolyte, and lithium ions are consumed in the formation of new SEI. Aurbach et al. [21] explained that the lithiation of graphite during cycling changes the particle orientation due to cracking. It allows solution species to penetrate between graphite particles, and therefore isolate them electrically from the bulk electrolyte.

As shown in Figure 4, adapted from Pinson and Bazant[18], the processes of lithium intercalation and the SEI formation occur as parallel reactions. Accordingly, the impedances associated with these reactions were considered to be in parallel.

4.2. Electrolyte and Separator

An ohmic resistance (R_e) was used to account for the frequency-independent contribution of the electrolyte and separator. This term could also account for the resistance of electrical contacts to the coin cells.

4.3. Cathode

The charge-transfer reaction at the cathode electrode is represented by

A characteristic feature of the impedance response of the $\text{LiCoO}_2|\text{C}$ battery is the slope of the straight line, seen at low frequencies in the Nyquist plot, that has an angle with respect to the real axis greater than 45 degrees. This behavior is not seen for all lithium battery chemistries. Greenleaf et al. [22] showed that the LiFePO_4 system yields an angle with respect to the real axis of 45 degrees, which is consistent with Fickian diffusion impedance. Osaka et al. [2] suggest that the larger slope can be attributed to diffusion to particles of different sizes. In the present work, an alternative explanation is posed in terms of anomalous diffusion.

Ordinary diffusion, which obeys Fick's second law, is characterized by the linear time dependence of a mean squared displacement (MSD) expressed as

$$\langle r^2(t) \rangle \sim t \quad (3)$$

where r is the displacement of the diffusion species after the time t . However, if the MSD does not obey equation 3 due to obstacles, time delays, or particle interactions, the diffusion may have a power-law dependence on t given as

$$\langle r^2(t) \rangle \sim t^\gamma \quad (4)$$

where γ is the anomalous diffusion exponent ($\gamma \neq 1$). The processes are termed anomalous diffusion, which no longer follows Fick's second law. When $\gamma < 1$ the process is called sub-diffusive and when $\gamma > 1$ it is super-diffusive.[23, 24] In sub-diffusion case, the constitutive equation differs from ordinary diffusion, being

$$J_i = -D_i \frac{\partial^{1-\gamma}}{\partial^{1-\gamma} t} \frac{\partial c_i}{\partial x} \quad (5)$$

where J_i is the flux of species i , D_i is the diffusion coefficient, and $\partial c_i / \partial x$ is the concentration gradient. This constitutive equation is derived from continuous time random walk in the macroscopic limit. The random walkers wait after each jump for a period of time drawn from a broad power-law distribution. The effect is that some ions remain stuck for a long time and diffusion is slower. The impedance used for this type of anomalous diffusion is associated with systems that show a diffusion hindered by sporadic adsorption of diffusing species to a fixed substrate. The associated impedance response, with a reflecting boundary condition, was derived by Bisquert and Compte [11]. The resulting diffusion impedance is expressed as

$$Z_d(\omega) = \frac{Z_d(0)}{\tau^{\gamma/2}} \coth \left[(j\omega\tau)^{\gamma/2} \right] \quad (6)$$

where $Z_d(0)$ is the zero-frequency asymptote for the real part of the diffusion impedance, and τ is the time constant. In the high-frequency limit, the impedance is proportional to $Z_d(0)/\tau^{\gamma/2}$. [25]

SEI film formation, analogous to that discussed for the anode, has also been reported for the cathode.[26, 27, 28, 29] Regression of the model including an SEI at the cathode was attempted, but the regressed parameters were not statistically significant.

4.4. Mathematical Representation

The equivalent circuit representation of the model developed in the present work for the battery system is shown in Figure 5. The resulting model can be expressed as

$$Z = Z_{a||s} + R_e + Z_c \quad (7)$$

where the impedance is represented by the series contribution of anode and cathode impedances and the ohmic resistance. The anode impedance $Z_{a||s}$, given as

$$Z_{a||s}(\omega) = \frac{(R_{t,a} + Z_{d,a})R_{t,s}}{R_{t,a} + Z_{d,a} + j\omega(R_{t,a} + Z_{d,a})R_{t,s}C_{a||s}} \quad (8)$$

included the parallel contributions of Li^+ intercalation expressed as the sum of the charge-transfer-resistance $R_{t,a}$ and diffusion impedance $Z_{d,a}$; SEI formation expressed as a charge-transfer resistance $R_{t,s}$; and capacitance $C_{a||s}$. The diffusion impedance for the anode, $Z_{d,a}$ was considered to follow a Warburg impedance, i.e.,

$$Z_{d,a} = \frac{A_{W,a}}{\sqrt{j\omega}} \quad (9)$$

where $A_{W,a}$ is the Warburg impedance coefficient. The cathode impedance Z_c was expressed as

$$Z_c(\omega) = \frac{R_{t,c} + Z_{d,c}}{1 + (j\omega)^{\alpha_c}(R_{t,c} + Z_{d,c})Q_c} \quad (10)$$

where the capacitive contribution was expressed as a constant-phase element with parameters α_c and Q_c and the faradaic impedance was expressed as the sum of the charge-transfer resistance $R_{t,c}$ and anomalous-diffusion impedance $Z_{d,c}$. As the measured frequency range did not reveal the sharp increase associated with the reflecting boundary condition, an asymptotic form of the anomalous-diffusion impedance expression was used, i.e.,

$$Z_{d,c}(\omega) = \frac{A_{d,c}}{(j\omega)^{1-\gamma_{d,c}/2}} \quad (11)$$

where $A_{d,c}$ is a lumped parameter

$$A_{d,c} = \frac{Z_{d,c}(0)}{\tau_{d,c}^{\gamma_{d,c}/2}} \quad (12)$$

containing the diffusion time constant, $\tau_{d,c}$

$$\tau_{d,c} = \frac{\delta_{d,c}^2}{D_{d,c}} \quad (13)$$

and the zero-frequency asymptote for the real part of the diffusion impedance, $Z_{d,c}(0)$.

4.5. Fitting Procedure

A preliminary data analysis was performed to identify the error structure of the impedance measurements. The data analysis, based on the measurement model described by Agarwal et al., [30, 31, 32] yielded the experimental variance of the spectra which was used to weight the regressions. The measurement model analysis also was used to identify the frequency range that was consistent with the Kramers-Kronig relations. By this procedure, the high-frequency inductive part of the spectrum, such as shown in Figure 3, was identified as an artifact and removed from the data.

Two regression algorithms were used to obtain the fitted values. A preliminary complex nonlinear regression was performed by using a simplex procedure by means of an in-house software developed at the Laboratoire Interfaces et Systèmes Electrochimique (LISE), associated with the University of Paris 6, Paris, France. The model employed for this regression had a more sophisticated description of the anode reactions than that employed in the present work. As the simplex algorithm does not yield confidence intervals for parameter estimates, a Levenberg-Marquardt algorithm was employed using an in-house software coded in Matlab®. The present model yielded parameters values that did not include zero in the 95.4% ($\pm 2\sigma$) confidence interval.

5. Regression Results

The regression results are presented in Figure 6 for the data presented in Figure 1. The results are presented in terms of the modulus and phase angle adjusted for the ohmic resistance. The adjusted modulus is given by

$$|Z|_{\text{adj}} = \sqrt{(Z_r - R_e)^2 + Z_j^2} \quad (14)$$

where the ohmic resistance was obtained by regression of equation 7 to the data. The ohmic-resistance-adjusted phase angle was given by

$$\varphi_{\text{adj}} = \tan^{-1} \left(\frac{Z_j}{Z_r - R_e} \right) \quad (15)$$

The ohmic-resistance-adjusted modulus and phase angle represents the behavior of the battery electrochemistry without the confounding effects of the frequency-independent resistance. The regression results are presented in Figure 7 for the data presented in Figure 2. The quality of the fits presented in Figures 1 and 7 is excellent.

The fitting parameters obtained by using the Levenberg-Marquardt regression analysis corresponding to Figure 6 are shown in Tables 1 and 2, where regressed values of the parameters are provided with their $\pm\sigma$ confidence intervals. The fitting parameters corresponding to Figure 7 are shown in Tables 3 and 4.

All parameter values have confidence intervals that do not include zero and show continuous dependence on cell potential and temperature. The regressed values of the anodic charge-transfer resistance $R_{t,a}$, the SEI charge-transfer resistance $R_{t,s}$, and the cathodic charge-transfer resistance $R_{t,c}$ are presented in Figure 8. The charge-transfer resistance for the SEI formation reaction was an order of magnitude larger than that for the anode intercalation reaction. This result is in agreement with the expectation that the intercalation reaction should dominate. **These measurements were performed after one cycle. It is anticipated that the value of the charge-transfer resistance for the SEI formation reaction should increase after repeated cycling.**

The anodic and SEI formation charge-transfer resistances showed a modest influence of cell potential, but were strongly dependent on temperature. Both $R_{t,a}$ and $R_{t,s}$ decreased with increasing temperature. The lack of dependence of $R_{t,a}$ and $R_{t,s}$ on potential may be attributed to observation that parameters for a more detailed model that accounted for additional mass transfer effects could not be obtained by regression. The charge-transfer resistance may account for coupled phenomena. Similarly, the charge-transfer resistance for the cathode decreased with increasing temperature. In contrast to the anodic and SEI formation charge-transfer resistances, the charge-transfer resistance for the cathodic reaction depended strongly on cell potential. The cathodic charge-transfer resistance decreased at higher potential (larger SOC).

Three capacitive loops are evident in the data at 10 °C shown in Figure 2(a). As shown in Figure 8(b), the charge-transfer resistance for SEI formation $R_{t,s}$ increased dramatically at low temperatures. This result is consistent with the conclusion of Momma et al. [15], who stated that a capacitive loop associated with the SEI was visible only at low temperature.

The ohmic resistance (shown in Tables 1-4) was roughly independent of temperature between 20 °C to 50 °C. The regressed values of the cathodic CPE exponent (α_c) and the cathodic anomalous diffusion exponent ($\gamma_{d,c}$) are shown in Figure 9 as functions of cell potential and temperature. The cathodic CPE exponent α_c tended toward unity at higher potential (larger SOC) and at high temperature. The potential and temperature dependence of the cathodic CPE exponent indicates that lithium ion diffusion was stickier at lower potentials (lower SOC) and at low temperature. In other words, the diffusion became more Fickian at higher temperature and potentials.

6. Discussion

This work provides an alternative explanation for the slope of the low-frequency impedance response for LiCoO₂ cathodes that is steeper than that associated with Fickian diffusion impedance. This effect is clearly associated with the unique properties of the LiCoO₂ cathode as the low-frequency impedance response of other Li-ion battery cathodes, e.g., LiFePO₄ and LiMn₂O₄, show different behaviors.[22] The group of Osaka [2] have attributed this behavior to the different time constants for diffusion to particles of different sizes. The present work shows that anomalous diffusion may provide an alternative explanation that is specific to the properties of LiCoO₂.

The present data and that published in the literature suggest that LiCoO₂ possesses a property that causes a diffusion impedance that differs from that of other cathode materials. In situ nuclear magnetic resonance (NMR) might be used in order to detect the anomalous lithium ion diffusion inside the cathode. NMR can be a supportive spectroscopic method to show that the anomalous diffusion occurs in LiCoO₂ electrodes. The contribution of anomalous diffusion was diminished at elevated temperatures, suggesting that the free-energy well associated with anomalous or sticky diffusion was shallow.

7. Conclusions

A process model for impedance analysis was developed in the context of reactions and transport processes that were hypothesized to govern the performance of commercial LiCoO₂|C batteries. At the carbon electrode, lithium ions and solvent were considered to react to form a solid-electrolyte interphase (SEI). In addition, lithium ions were assumed to diffuse through the SEI to intercalate into the graphene layers. As these two processes involve an addition of currents, the corresponding impedances were considered to be in parallel. Anomalous diffusion of lithium ions was invoked at the LiCoO₂ electrode to account for the low-frequency line that was steeper than the 45 degrees predicted by ordinary diffusion. This model was fit to all impedance data collected and provided a good description for impedance of batteries under normal operating potentials and temperatures.

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Table 1: Regression results and $\pm\sigma$ confidence intervals of a fit of equation 7 to the data for cell potential ranging from 4.2 to 3.8 V at a temperature of 20 °C. The potential range of 3.6-3.2 V is shown in Figure 2.

Parameter	4.2 V	4 V	3.8 V
$C_{a S} / \mu\text{F cm}^{-2}$	39 $\pm$ 2.8	41 $\pm$ 2.5	44 $\pm$ 4.4
$A_{W,a} / \Omega \text{ cm}^2 \text{ s}^{-0.5}$	53 $\pm$ 1.4	51 $\pm$ 1.1	47 $\pm$ 1.5
$R_{t,a} / \Omega \text{ cm}^2$	0.173 $\pm$ 0.0084	0.180 $\pm$ 0.0069	0.180 $\pm$ 0.010
$R_{t,S} / \Omega \text{ cm}^2$	1.10 $\pm$ 0.019	1.19 $\pm$ 0.018	1.17 $\pm$ 0.022
$R_e / \Omega \text{ cm}^2$	0.874 $\pm$ 0.0053	0.894 $\pm$ 0.0048	0.893 $\pm$ 0.0077
$R_{t,c} / \Omega \text{ cm}^2$	0.36 $\pm$ 0.021	0.39 $\pm$ 0.019	0.40 $\pm$ 0.023
α_c	0.91 $\pm$ 0.015	0.92 $\pm$ 0.014	0.96 $\pm$ 0.018
$Q_c / \text{F cm}^{-2} \text{ s}^{\alpha_c-1}$	0.0335 $\pm$ 0.00066	0.0333 $\pm$ 0.00061	0.0375 $\pm$ 0.0011
$\gamma_{d,c}$	0.644 $\pm$ 0.0054	0.617 $\pm$ 0.0043	0.551 $\pm$ 0.0099
$A_{d,c} / \Omega \text{ cm}^2 \text{ s}^{-\gamma_{d,c}/2}$	0.1382 $\pm$ 0.00093	0.1821 $\pm$ 0.00098	0.112 $\pm$ 0.0013

Table 2: Regression results and $\pm\sigma$ confidence intervals of a fit of equation 7 to the data for cell potential ranging from 3.6 to 3.2 V at a temperature of 20 °C. The potential range of 4.2-3.8 V is shown in Figure 1.

Parameter	3.6 V	3.4 V	3.2 V
$C_{a S} / \mu\text{F cm}^{-2}$	63 $\pm$ 2.4	68 $\pm$ 2.4	64 $\pm$ 5.1
$A_{W,a} / \Omega \text{ cm}^2 \text{ s}^{-0.5}$	35.9 $\pm$ 0.57	34.0 $\pm$ 0.57	37.1 $\pm$ 1.3
$R_{t,a} / \Omega \text{ cm}^2$	0.197 $\pm$ 0.0044	0.198 $\pm$ 0.0043	0.177 $\pm$ 0.0097
$R_{t,S} / \Omega \text{ cm}^2$	1.15 $\pm$ 0.012	1.12 $\pm$ 0.015	0.94 $\pm$ 0.025
$R_e / \Omega \text{ cm}^2$	0.940 $\pm$ 0.0030	0.945 $\pm$ 0.0027	0.949 $\pm$ 0.0056
$R_{t,c} / \Omega \text{ cm}^2$	0.61 $\pm$ 0.012	0.77 $\pm$ 0.016	1.21 $\pm$ 0.029
α_c	0.930 $\pm$ 0.0067	0.869 $\pm$ 0.0062	0.755 $\pm$ 0.0076
$Q_c / \text{F cm}^{-2} \text{ s}^{\alpha_c-1}$	0.0527 $\pm$ 0.00058	0.0560 $\pm$ 0.00061	0.0556 $\pm$ 0.00092
$\gamma_{d,c}$	0.379 $\pm$ 0.0045	0.311 $\pm$ 0.0032	0.247 $\pm$ 0.0039
$A_{d,c} / \Omega \text{ cm}^2 \text{ s}^{-\gamma_{d,c}/2}$	0.1374 $\pm$ 0.00068	0.2060 $\pm$ 0.00069	0.407 $\pm$ 0.0014

Table 3: Regression results and $\pm\sigma$ confidence intervals of a fit of equation 7 to the data for cell temperature ranging from 10 to 20 °C at a potential of 4 V. The temperature range of 30-50 °C is shown in Table 4.

Parameter	10 °C	20 °C
$C_{a S} / \mu\text{F cm}^{-2}$	28 $\pm$ 1.8	28.8 $\pm$ 0.84
$A_{W,a} / \Omega \text{ cm}^2 \text{ s}^{-0.5}$	58.8 $\pm$ 0.87	52.5 $\pm$ 0.51
$R_{t,a} / \Omega \text{ cm}^2$	0.256 $\pm$ 0.0066	0.195 $\pm$ 0.0045
$R_{t,S} / \Omega \text{ cm}^2$	1.93 $\pm$ 0.013	1.383 $\pm$ 0.0073
$R_e / \Omega \text{ cm}^2$	1.357 $\pm$ 0.0074	0.845 $\pm$ 0.0022
$R_{t,c} / \Omega \text{ cm}^2$	1.19 $\pm$ 0.018	0.954 $\pm$ 0.0094
α_c	0.912 $\pm$ 0.0074	0.938 $\pm$ 0.0052
$Q_c / \text{F cm}^{-2} \text{ s}^{\alpha_c-1}$	0.0662 $\pm$ 0.00088	0.0608 $\pm$ 0.00065
$\gamma_{d,c}$	0.72 $\pm$ 0.015	0.785 $\pm$ 0.0087
$A_{d,c} / \Omega \text{ cm}^2 \text{ s}^{-\gamma_{d,c}/2}$	0.254 $\pm$ 0.0042	0.203 $\pm$ 0.0023

Table 4: Regression results and $\pm\sigma$ confidence intervals of a fit of equation 7 to the data for cell temperature ranging from 30 to 50 °C at a potential of 4 V. The temperature range of 10-20 °C is shown in Table 3.

Parameter	30 °C	40 °C	50 °C
$C_{a S} / \mu\text{F cm}^{-2}$	43±1.8	56±2.1	84±2.7
$A_{W,a} / \Omega \text{ cm}^2 \text{ s}^{-0.5}$	34.2±0.77	25.9±0.82	13.1±0.15
$R_{t,a} / \Omega \text{ cm}^2$	0.138±0.0048	0.103±0.0035	0.097±0.0018
$R_{t,S} / \Omega \text{ cm}^2$	0.73± 0.010	0.46±0.011	0.42±0.016
$R_e / \Omega \text{ cm}^2$	0.809±0.0020	0.767±0.0013	0.792±0.0011
$R_{t,c} / \Omega \text{ cm}^2$	0.30±0.011	0.12±0.011	0.039±0.0017
α_c	0.98±0.016	0.99±0.020	1.00±0.01
$Q_c / \text{F cm}^{-2} \text{ s}^{\alpha_c-1}$	0.054±0.0019	0.049±0.0035	0.013±0.0033
$\gamma_{d,c}$	0.886±0.0063	0.925±0.0039	0.944±0.0057
$A_{d,c} / \Omega \text{ cm}^2 \text{ s}^{-\gamma_{d,c}/2}$	0.209±0.0017	0.198±0.0010	0.172±0.0012

Figure 1: Impedance response in Nyquist format for a LiCoO₂|C coin cell under normal operating conditions with cell potential as a parameter, ranging from 4.2 V to 3.2 V. The impedance was measured under the discharge profile. The lines represent a fit of equation 7 to the data. The estimate for relationship between potential and SOC was obtained from a C/15 discharge measurement.

(a)

(b)

Figure 2: Impedance response in Nyquist format for a LiCoO_2/C coin cell at a 4 V cell potential with temperature, ranging from 10 to 50 °C, as a parameter: a) complete spectra and b) low impedance values corresponding to the box in (a). The lines represent a fit of equation 7 to the data.

Figure 3: Typical impedance response of a LiCoO_2/C coin cell at a potential of 3.6 V, obtained from the present work.

Figure 4: Schematic representation of a graphite anode for which the process of SEI formation occurs in parallel with intercalation of lithium ions. Adapted from Pinson and Bazant[18].

Figure 5: Equivalent circuit representation of the model developed in the present work for the complete Li-ion battery system.

Figure 6: Impedance response for a LiCoO₂/C coin cell with cell potential (SOC) as a parameter: a) ohmic-resistance-corrected modulus $|Z|_{adj}$ as a function of frequency; b) ohmic-resistance-corrected phase angle φ_{adj} as a function of frequency. These results provide a different representation of the data presented in Figure 1. The lines represent fits of equation 7 to the data. The estimate for relationship between potential and SOC was obtained from a C/15 discharge measurement.

Figure 7: Impedance response for a LiCoO_2/C coin cell with temperature as a parameter: a) ohmic-resistance-corrected modulus $|Z|_{\text{adj}}$ as a function of frequency; b) ohmic-resistance-corrected phase angle φ_{adj} as a function of frequency. These results provide a different representation of the data presented in Figure 2. The lines represent fits of equation 7 to the data.

Figure 8: Regressed values for the anodic, SEI formation, and cathodic charge-transfer resistances: a) as a function of **state of charge as obtained from a C/15 discharge measurement** at a temperature of 20 °C; b) as a function of temperature at a potential of 4 V. The line is a spline fit used to guide the eye. Error bars represent the $\pm\sigma$ confidence intervals obtained from the regression.

(a)

(b)

Figure 9: Regressed values for the cathodic CPE exponent and the cathodic anomalous diffusion exponent: a) as a function of **state of charge as obtained from a C/15 discharge measurement** at a temperature of 20 °C; b) as a function of temperature at a potential of 4 V. The line is a spline fit used to guide the eye. Error bars represent the $\pm\sigma$ confidence intervals obtained from the regression.

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