Mass and Charge Transport in Li$_{1-\delta}$CoO$_2$ Thin Films—A Complete Set of Properties and Its Defect Chemical Interpretation

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ABSTRACT: Lithium insertion materials are an essential class of mixed ionic and electronic conductors, and their electrochemical properties depend on the resistive and capacitive interplay of ions and electrons. However, complete sets of the corresponding elementary material parameters, that is, composition-dependent ionic and electronic conductivity, chemical capacitance, and charge-transfer resistance, are rarely reported for lithium-ion battery electrode materials. Moreover, the interpretation of these properties from a defect chemical point of view is not very common. In this work, the impedance of sputtered Li$_{1-\delta}$CoO$_2$ thin films is analyzed to extract the fundamental electrochemical properties as a function of state-of-charge (SOC). Within the accessible SOC range, the charge transfer resistance and ionic conductivity vary by more than 1 order of magnitude. The chemical capacitance determined from impedance spectra agrees excellently with the differential capacitance from charge/discharge curves, and, in the dilute regime, even matches the absolute values predicted by defect thermodynamics. The evolution of lithium diffusivity along the charge curve is deconvoluted into the separate contributions of ionic conductivity and chemical capacitance. Finally, we apply the principles of defect chemistry to evaluate the observed trends in terms of lithium activity and point defect concentrations and provide a tentative defect model that is consistent with our results. The consistency of impedance measurements, cycling data, and thermodynamic theory highlights the key role of the chemical capacitance as a powerful material descriptor and emphasizes the relevance of defect chemical concepts for all lithium insertion electrode materials.

INTRODUCTION

Cathode materials for rechargeable Li-ion cells continue to be the focus of many research efforts in both academia and industry. With the high demands placed on modern Li-ion batteries with respect to their charging speed and discharge power density, the investigation of Li transport kinetics through the various cell components plays a vital role in optimizing cell performance. However, owing to the morphological and compositional complexities found in porous bulk electrodes, the investigation of their kinetic properties is far from trivial. Measurement approaches range from time-dependent voltage or current measurements, such as the galvanostatic intermittently titration technique, to sophisticated transmission line models, taking account of both electrolyte and electrode. However, as pointed out recently by Chueh, the transport properties, such as Li diffusion coefficients, deduced from different studies often differ by orders of magnitude.

One of the main reasons for this variance is the fact that several time constants are involved in the time- or frequency-dependent responses of highly porous intercalation electrodes. Moreover, even if extracted from geometrically simple samples such as thin films, the chemical diffusion coefficient of Li ($D$) is not the only relevant parameter for the charge and discharge properties of electrode particles. Rather, the kinetics of an individual electrode particle is defined by (i) the interfacial Li exchange reaction with the electrolyte, (ii) the ambipolar conductivity within the mixed conducting electrode material itself, which comprises the ionic and electronic conductivities $\sigma_{\text{ion}}$ and $\sigma_{\text{elec}}$, and (iii) the chemical capacitance $C_{\text{chem}}$, as discussed in more detail below. The chemical diffusivity itself is, however, not an elementary property of the electrode material but a composite parameter of ambipolar conductivity and chemical capacitance. To further complicate things, a battery electrode traverses a broad continuum of operating points or thermodynamic states during every charge/discharge cycle, each being defined by its characteristic Li chemical potential and electrochemical transport parameters. The elucidation of these electrochemical parameters as a function of state-of-charge (SOC) is therefore a notoriously difficult task and has mostly been limited to the evaluation of the chemical diffusion coefficient $D$ from the inverse time constant of the observed diffusion processes, without separate consideration of its resistive and capacitive components.

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It is also frequently overlooked in this context that $C_{\text{chem}}$ which describes the differential variation of Li stoichiometry with the chemical potential, is not only related to the slope of the coulometric titration curve and the energy density but also directly impacts solid-state ambipolar diffusion and hence the power density.\(^\text{(10)}\) Consequently, $C_{\text{chem}}$ can be extracted from AC impedance spectra as well as from DC titration curves, and these values should coincide. However, this connection is rarely made, which is mirrored by the context-dependent labels that are used throughout the battery literature to denote the variation of charge with potential. In order to describe the impedance of mixed conducting electrodes, a one-dimensional transmission-line-equivalent circuit was suggested by Jannik and Maier,\(^\text{(19–23)}\) giving access not only to $C_{\text{chem}}$ but also to the transport properties $\sigma_{\text{ion}}, \sigma_{\text{con}}$ and the interfacial charge-transfer resistance $R_{\text{ct}}$. Applying this model (or simplified versions) to a one-dimensional electrode system, such as a thin-film electrode, should thus enable the analysis of all elementary material parameters and help in understanding the stoichiometry-dependent Li intercalation process into an electrode material. Interestingly, such a transmission-line-based analysis of impedance spectra of mixed conducting thin-film electrodes is quite common in the field of high-temperature solid oxide cells\(^\text{(23–26)}\) but virtually unknown for thin-film electrodes in Li-ion batteries.

In this contribution, we present a comprehensive impedance study of polycrystalline Li$_{1-x}$CoO$_2$ (LCO) thin films on Pt for a wide stoichiometry range (0 $\leq$ $\delta$ $\leq$ 0.4) that also includes the rarely investigated low-potential region up to 3.9 V versus Li$^+$/Li, where the most pronounced changes of the electrochemical properties are observed. Based on these measurements, we discuss three important aspects of Li intercalation into Li$_{1-x}$CoO$_2$. First, we analyze the variation of $\sigma_{\text{ion}}, C_{\text{chem}}, D_j$ and $R_{\text{ct}}$ with the Li chemical potential and discuss their relative contributions to the overall electrode kinetics. Second, the role of $C_{\text{chem}}$ in AC and DC measurements is discussed and experimentally validated, and its overarching significance for ambipolar transport is considered. Third, we provide a defect chemical perspective on the observed trends of stoichiometry, on the rarely investigated SOC region close to full Li-based analysis of impedance spectra of mixed conducting battery electrode materials that are based on an atomistic analysis of the basic relation\(^\text{(19,48)}\)

$$C_{\text{chem}} = q^2 V \left( \frac{\partial \mu_{\text{Li}}}{\partial c_{\text{Li}}} \right)^{-1}$$

which describes the electrochemical Li storage in an electrode with bulk volume $V$ (e.g., a dense thin film with thickness $L_z$ deposited on area $A$) as a function of the equilibrium Li concentration $c_{\text{Li}}$ with the elementary charge $q$. This approach to $C_{\text{chem}}$ is particularly helpful if dilute defect chemical considerations are still valid. The Li chemical potential $\mu_{\text{Li}}$ is related to the Li activity $a_{\text{Li}}$ via

$$\mu_{\text{Li}} = \mu_{\text{Li,metal}} + kT \ln a_{\text{Li}}$$

with $k$ and $T$ denoting Boltzmann’s constant and temperature, respectively, and $\mu_{\text{Li,metal}}$ being the chemical potential of metallic Li. For a given chemical potential difference between Li metal ($a_{\text{Li,metal}} = 1$) and cathode, the cell voltage $E$ can be defined as

$$E = \frac{\mu_{\text{Li,cath}} - \mu_{\text{Li,metal}}}{q} = \frac{kT}{q} \ln a_{\text{Li}}$$

For a more detailed analysis of $\mu_{\text{Li}}$ its separation into electronic and ionic contributions is highly useful. Analogously to the defect chemical considerations of mixed conducting oxides in solid oxide fuel cells, Brouwer diagrams thus come into play, where point defect concentrations and their dependence on Li activity are derived from laws of mass action and chemical potentials. However, as emphasized by Maier,\(^\text{(49–53)}\) such concepts have hardly permeated the field of Li electrode materials, despite being very helpful for a more...
Figure 1. (a) General one-dimensional transmission line of a mixed conductor consisting of electronic/ionic resistive elements and chemical capacitors, including terminal R/C elements. (b) Simplified transmission line for a one-dimensional Li storage electrode extended by a serial high-frequency offset resistance. The obtained circuit is fully equivalent to (c) Randles’ circuit. (d) Modified Randles’ circuit with an anomalous diffusion element and nonideal double-layer capacitance. (e) Simulated impedance response of circuits (c,d) for $R_w = 5.66 \, \Omega$, $R_a = 143.6 \, \Omega$, $C_w = 0.12 \, \text{mF}$, $R_{on} = 327 \, \Omega$, and $C_{chem} = 209 \, \text{mF}$. For the modified Randles’ circuit, the interfacial capacitance was modeled as a constant-phase element, with $Q_d = 0.12 \, \text{mF} e^{-0.15}$ and the corresponding constant-phase exponent of 0.85, and the open Warburg element was replaced by an anomalous finite-space diffusion element $W_s^*$ with a nonideality factor of $\alpha = 0.72$ (see eq 19).

Detailed understanding. For this reason, the concept of chemical capacitance and its universal presence in charge/discharge curves, impedance spectra, and ambipolar mass and charge transport has rarely been addressed in Li-ion literature. It is also noted that the interfacial pseudocapacitances of transition-metal oxides include local compositional and oxidation state changes and are thus related to the above definition of chemical capacitances. A detailed discussion of pseudocapacitances can be found, for example, in ref 52.

In this study, we will investigate the electrochemical behavior of Li$_{1-x}$CoO$_2$ in the stoichiometry range $0 \leq \delta \leq 0.4$, where Li is reversibly deintercalated via oxidation of the material, starting at initially full stoichiometry ($\delta \approx 0$). We may consider Li vacancies $V'_i$ and electron holes $h^*$ as the relevant defect species, at least as long as defect chemical concepts are applicable to intercalation processes.\cite{51,53} In order to describe the deintercalation in terms of (initially) dilute point defects, it is convenient to reconsider the chemical potential of atomic Li in Li$_{1-x}$CoO$_2$ (eq 2) in terms of charged species, that is, as $\mu_{Li} = \mu_{Li'} + \mu_{h^*}$. (4) for, defects, transforms into\cite{59}

$$\mu_{Li} = -\mu_{V'_i} + \mu_{h^*}\tag{4}$$

with

$$\mu_{V'_i} = \mu_{V'_i} + kT \ln(a_{V'_i})\tag{5}$$

$$\mu_{h^*} = \mu_{h^*} + kT \ln(a_{h^*})\tag{6}$$

The defect activities $a_i$ are related to the corresponding defect concentrations $c_i$ by the activity coefficients $\gamma_i$ for, for example, Li vacancies by

$$a_{V'_i} = \gamma_{V'_i} c_{V'_i} = \gamma_{V'_i} \delta\tag{7}$$

where $\mu_{h^*}^0$ denotes the standard chemical potential of the respective species, and defect concentrations are referred to the concentration of formula units $\delta^0$. Thus, the nonstoichiometry $\delta$ corresponds to $\delta = c_{V'_i} / c_{h^*}$. Under the assumption of dilute conditions and absence of charge trapping, the defect activity coefficients $\gamma_i \rightarrow 1$ and eq 1 can be evaluated as\cite{54}

$$C_{chem} = \frac{q^2}{kT} \left( \frac{1}{c_{V'_i}} + \frac{1}{c_{h^*}} \right)^{-1}\tag{8}$$

This reflects the behavior of $C_{chem}$ as a serial double capacitor with an effective capacitance that is determined by the concentrations of both ionic and electronic charge carriers. The value of $C_{chem}$ is primarily determined by the minority carrier concentration. In general, the interplay of several defect chemical effects determines the minority species, including intrinsic ionic and electronic disorders, doping, or site changes. Assuming $c_{h^*} \gg c_{V'_i}$, for example, the chemical capacitance becomes

$$C_{chem} = \frac{q^2}{kT} V c_{V'_i}\tag{9}$$

Transmission Line Model, Conductivity, and Chemical Diffusion. In a one-dimensional situation, the electrochemical bulk properties of a mixed ionic electronic conductor at a fixed stoichiometry can be described by a transmission line (Figure 1a) consisting of two resistive rails (ions and electrons) and capacitive connections representing the local chemical charge storage, with $R_i = \sum r_i$ and $C_{chem} = \ldots$
\[ \sum \sigma_{\text{chem}}^{19-23} \] The corresponding bulk properties are thus fully characterized by the three elementary parameters \( \sigma_{\text{eon}}, \sigma_{\text{ion}}, \) and \( C_{\text{chem}}^{19}. \) By definition, the ionic or electronic conductivity of a material is given as

\[ \sigma = \frac{z_q n \mu c_i}{kT} D c_i \]  
with the charge number \( z_q, \) carrier mobility \( \mu, \) carrier diffusion coefficient \( D, \) \( \mu c_i \) and equilibrium concentration \( c_i \) of charge carrier \( i. \) For mixed conduction, the ambipolar conductivity \( \sigma \) can be defined as

\[ \sigma = \frac{\sigma_{\text{eon}} \sigma_{\text{ion}}}{\sigma_{\text{eon}} + \sigma_{\text{ion}}} \]  
and is related to the ambipolar (chemical) diffusion coefficient via\( ^{10} \)

\[ D = \frac{\sigma}{c_{\text{chem}}^V} \]  
where \( C_{\text{chem}}^{V} \) is the volume-specific chemical capacitance, with \( V = AL, A = \) area, and \( L = \) thickness. In the case of high electronic conductivity \( (\sigma_{\text{eon}} \gg \sigma_{\text{ion}}), \) we have \( \sigma \approx \sigma_{\text{eon}} \) and thus

\[ D = \frac{\sigma}{c_{\text{chem}}^V} = \frac{L^2}{R_{\text{eon}} C_{\text{chem}}} \]  
where \( R_{\text{eon}} \) is the total ionic resistance of the thin film in the direction of transport. The ionic conductivity may also be expressed in terms of defects \( (V_{\text{Li}}), \) that is,

\[ \sigma_{\text{ion}} = \frac{q^2}{kT} D_{\text{Li}} c_{V_{\text{Li}}} \]  
and from eqs 9, 10, and 13, we then get \( \tilde{D} = D_{V_{\text{Li}}} \) for \( \sigma_{\text{ion}} \gg \sigma_{\text{eon}}. \)

**Impedance of a Li Intercalation Electrode.** The impedance response of a thin film battery electrode is commonly described by Randles’ circuit, which is shown in Figure 1c.\(^{55,56} \) This intuitively constructed equivalent circuit can also be derived directly from the general transmission line introduced above (Figure 1a) by applying the appropriate boundary conditions and simplifying assumptions.\(^{23} \) First, we assume that \( \sigma_{\text{eon}} \gg \sigma_{\text{ion}} \) and therefore the electrical potential gradients within the material can be neglected. This means that electronic resistances \( \sigma_{\text{eon}} \) in the transmission line can be neglected and the corresponding rail replaced by a short circuit. At the bottom of the thin film, the current collector presents an ion-blocking boundary \( (R_0 \to \infty, C_0 \to 0) \) that is reversibly transmissive for electrons \( (R_0 \to 0, C_0 \to \infty). \) The liquid electrolyte in contact with the thin-film surface is electron-blocking with an interfacial double-layer capacitance \( (R_C \to \infty, C_C \to C_0) \) but allows the reversible transport of Li ions across the corresponding charge-transfer resistance \( (R_0 \to \infty). \) As the interfacial capacitance is assumed to be located on the electronic rail terminal, the remaining capacitance at the ionic terminal is neglected \( (C_0 \to 0). \) Upon adding a serial high-frequency resistance \( R_0 \) to account for an Ohmic offset due to the electrolyte and other cell components, the resulting circuit (Figure 1b) is identical to Randles’ circuit, with the open Warburg element \( W_0 \) being equivalent to the reflective transmission line marked in red. The corresponding expression \( Z_{W_0}(\omega) \) is given by

\[ Z_{W_0}(\omega) = R_0 \coth(\omega R_0)^{1/2} \]  
and describes the impedance of one-dimensional finite-space diffusion, as derived from Fick’s laws.\(^{23} \)

As can be seen from eq 15, the impedance of the Fickian diffusion process is composed of a resistance \( R_{\text{eon}} \) and a time constant \( \tau. \) The chemical diffusion coefficient \( \tilde{D} \) is the inverse time constant normalized by a geometrical factor

\[ \tilde{D} = \frac{L^2}{\tau} \]  
where \( \tau = R_{\text{eon}} C_{\text{chem}}^{19} \)

**EXPERIMENTAL SECTION.**

**Preparation of LiCoO\(_2\) Thin Films.** One-side-polished sapphire (0001) single-crystal substrates with dimensions 10 mm \( \times 10 \) mm \( \times 0.5 \) mm (CrysTec, Germany) were sonicated in ethanol (absolute, VWR, Germany) prior to use. A bilayer of Ti/Pt \( (5/100 \) nm) was deposited on both sides of the substrate as a current collector via DC-sputtering at room temperature, a current density of 5 mA/cm\(^2\), and Ar pressures of 0.7 and 2.0 Pa, respectively. LiCoO\(_2\) thin films were deposited onto the polished side of the substrates via RF magnetron sputtering in a custom-built deposition chamber (Huber Scientific, Austria) at room temperature, a total pressure of 2.5 Pa in an Ar/O\(_2\) mixture \( (25\% \) O\(_2\)), power of 60 W, and a substrate-to-target distance of 8.5 cm. The LiCoO\(_2\) sputter target \( (\text{diameter } 3\)") was obtained from Loyaltargets (China) and abraded with a fine sandpaper before each deposition to eliminate deviations from bulk stoichiometry at the target surface. The thickness of the LiCoO\(_2\) films was approximately 100 nm, as determined by a TEM thickness calibration, and the corresponding deposition rate was 0.5 nm/min. The as-deposited films were annealed in a muffle furnace in air at 700 °C for 5 h at a ramp rate of 10 °C/min. The samples were characterized by grazing-incidence X-ray diffraction (GID, \( \omega = 3° \)), atomic force microscopy (AFM), and elemental analysis via inductively coupled plasma mass spectrometry (ICP-MS).

**Electrochemical Characterization.** After annealing, the thin-film samples were transferred into an argon-filled glovebox (O\(_2\) levels < 0.1 ppm) and assembled into three-electrode test cells (PAT-Cell by EL-Cell, Germany) using a glass fiber separator (260 μm, EL-Cell), 80 μL of a standard organic electrolyte (1 M LiPF\(_6\) in a 1:1 mixture of ethylene carbonate and dimethyl carbonate, Aldrich), and a Li metal anode (0.6 mm, Goodfellow, Germany). All electrochemical measurements were carried out at room temperature on a BioLogic SP200 potentiostat with a built-in impedance analyzer. Directly after assembly, a cyclic voltammogram of the working electrode was recorded at a scan rate of 0.1 mV/s in the potential range of 3.7-4.0 V versus Li\(^+/-\)Li, followed by galvanostatic charge and discharge within the same potential range at a current of 7.16 μA (1 C). Subsequently, a series of potentiostatic impedance spectra (1 MHz to 1 mHz, 6 points per decade, and 10 mV amplitude) was recorded in 10 mV steps, ranging from 3.85 to 4.00 V (charge scan) and back to 3.85 V (discharge scan) versus Li\(^+/-\)Li. Before each measurement, a 15 min constant voltage step was applied to allow the thin film to fully equilibrate at the given potential. To distinguish irreversible degradation from the potential-dependent changes of material parameters, the hysteresis between charge and discharge scans was evaluated. As the hysteresis was substantial for the first set of measurements due to the initial changes of the thin film, the impedance series was repeated, including CV scans before and after, yielding much more stable trends. The spectra obtained after stabilization were then analyzed in detail.
RESULTS AND DISCUSSION

**LiCoO$_2$ Thin Films.** The GID pattern of a typical LiCoO$_2$ thin-film sample and its corresponding AFM image are displayed in Figure 2. The diffraction pattern shows the most characteristic LiCoO$_2$ reflexes around 18.9° (003), 37.5° (101), and 45.3° (104). In addition, signals stemming from the Pt current collector can be clearly identified, as well as some impurity signals, most likely due to small amounts of Co$_3$O$_4$ in the sample. The AFM image reveals a reasonably homogeneous and polycrystalline morphology of the thin film, with an RMS roughness of approximately 10 nm. ICP-MS analysis of a thin film dissolved in concentrated hydrochloric acid yielded a Li/Co ratio of 0.95, indicating that the deposition of LiCoO$_2$ was almost stoichiometric.

**DC Cycling.** Figure 3a shows the initial CV curve of the pristine sample (first charge/discharge) and CV curves after some initial changes and stabilization. More specifically, the latter correspond to the stabilized curves measured before and after the relevant series of impedance measurements discussed in this study. The film shows good electrochemical reversibility, with the initial discharge capacity of 116 mAh/g being in good agreement with the common literature values at this cutoff voltage. To evaluate the thin-film potential as a function of charge and Li stoichiometry, the CV curves are converted into the coulometric titration curves shown in Figure 3b. As is characteristic for LCO, the curves exhibit a plateau around 3.9 V, followed by a moderate and roughly constant slope up to 4.0 V. Nominal nonstoichiometry values $\delta$ are also shown in Figure 3b, which are deduced by assuming $\delta = 0.4$ at 4.0 V for the CV scan before EIS. Charge values are normalized to the pristine thin-film mass.

Some degradation of the film capacity occurs between the initial cycle and the start of the impedance measurements, with a significant broadening of the CV current peak and the charge curve plateau becoming increasingly inclined. In terms of discharge capacity, the electrode drops to 89 mA h/g or 77% of its initial capacity. A similar broadening of the CV current (or differential capacity) peak accompanying this capacity loss has also been reported for porous bulk electrodes, and the frequently observed irreversible capacity losses of layered oxide cathodes are attributed to, among other factors, oxygen release and structural degradation toward denser spinel and rock salt phases, especially in the near-surface region, due to the thermodynamic instability of partially delithiated LCO. More importantly, however, there is only minor further degradation throughout the impedance measurements, meaning that the electrochemical properties extracted from the collected impedance spectra can be assumed to vary reversibly with the electrode potential.
The DC data can now be used to determine the chemical capacitance (differential capacity) as a function of electrode potential. In the context of porous bulk electrodes, differential capacity curves are typically obtained via differentiation of galvanostatic charge curves from long cycling experiments, which require galvanostatic conditions to simulate a constant load. However, we perceive CV curves as a more suitable starting point when galvanostatic conditions are not required, as is the case for thin-film studies. This is because the differentiation of galvanostatic data often yields discontinuous and noisy capacitance curves due to the slight potential fluctuations in the original data. As a result, these data require smoothening prior to their conversion into differential capacity values. For CV curves, on the other hand, at a given scan rate \( v \) and film thickness \( L \), the measured current density \( i \) is directly related to the chemical capacitance via

\[
C_{\text{chem}} = \frac{i}{vL} \tag{18}
\]

assuming the scan rate is slow enough for the electrode to remain in equilibrium, that is, spatially homogeneous. For \( v = 0.1 \text{ mV/s} \) and \( L = 100 \text{ nm} \), the current density in \( \mu\text{A/cm}^2 \) is equivalent to the chemical capacitance in \( \text{kF/cm}^3 \). Values of 4 to 29 \( \text{kF/cm}^3 \) result for our films, and these values can then be directly compared to \( C_{\text{chem}} \) values from impedance fits, as shown in Figure 4 and discussed in the following sections.

**Impedance Spectra and Their Analysis.** Figure 5a,b shows the impedance spectra of the LiCoO\(_2\) thin film in the potential range of 3.85 to 4.00 V versus Li\(^+\)/Li. The sharp increase and subsequent gradual decrease in chemical capacitance toward higher potentials are indicated by the height of the low-frequency tail. Insets show (i) Warburg-like high-frequency tail of the charge-transfer arc and (ii) inverse variation of the charge-transfer resistance with potential. (b) Exemplary least-squares fit of an impedance spectrum, acquired at an equilibrium electrode potential of 3.91 V vs Li\(^+\)/Li, using a modified Randles’ circuit (Figure 1d). The resulting fit corresponds to the simulated spectrum in Figure 1e. Insets show magnifications of (i) high-frequency region with the onset of the charge-transfer arc and (ii) mid-frequency region with the transition from charge transfer to the solid-state diffusion regime. Measurement points at or above 389 Hz were excluded from the fit and treated as a high-frequency offset.

Figure 5. Impedance spectra of the Li\(_{1-\delta}\)CoO\(_2\) thin film at various electrode potentials. (a) Full spectra with decreasing real impedance in the low-frequency region. The sharp increase and subsequent gradual decrease in chemical capacitance toward higher potentials are indicated by the height of the low-frequency tail. Insets show (i) Warburg-like high-frequency tail of the charge-transfer arc and (ii) inverse variation of the charge-transfer resistance with potential. (b) Exemplary least-squares fit of an impedance spectrum, acquired at an equilibrium electrode potential of 3.91 V vs Li\(^+\)/Li, using a modified Randles’ circuit (Figure 1d). The resulting fit corresponds to the simulated spectrum in Figure 1e. Insets show magnifications of (i) high-frequency region with the onset of the charge-transfer arc and (ii) mid-frequency region with the transition from charge transfer to the solid-state diffusion regime. Measurement points at or above 389 Hz were excluded from the fit and treated as a high-frequency offset.

\( W_\infty \) is that the transition between the semi-infinite and finite-space regimes appears continuous, rather than confined to a specific knee frequency. The charge-transfer resistance and the ionic resistance (as visually estimated by the extrapolated real axis intercept of the diffusional tail) decrease significantly toward higher electrode potentials. A more detailed and quantitative analysis of this part of the spectra is presented below.
At the high-frequency end of the spectrum, a small Warburg-like feature with a real impedance of about $6 \, \Omega$ is observed that appears independent of the electrode’s SOC. Although we cannot unambiguously assign this feature, it could possibly originate from the substantial surface roughness of the films and some residual porosity or cracks in the thin film. Due to its invariance, small magnitude, and confinement to the high-frequency region, the corresponding frequency points are excluded from the fit, and thus the feature is simply treated as a real axis offset in the following analysis; cf. inset (i) in Figure 5b.

As pointed out in the original literature on finite-space Warburg impedance,$^{12,13,14,42}$ the purely capacitive low-frequency region allows the simultaneous extraction of $R_{\text{ion}}$ and $C_{\text{chem}}$ from the impedance spectrum, as the two parameters are completely separated into the real and imaginary parts of the overall impedance. Another direct consequence of this separation is that for a series of impedance spectra over the same frequency range, the height of the capacitive tail in a Nyquist plot directly indicates the capacitance and thus the steepness of the equilibrium charge/discharge curve at the given electrode potential. Indeed, the height of the diffusional tails in Figure 5a,b clearly reflects the shape of the charge given electrode potential. Indeed, the height of the diffusion element reported by Bisquert,$^{13,14,15,42}$ then used it as a fixed parameter for the impedance fits to electrode, for example, in refs 44,45, and 71. $R_{\text{ion}}$ and $C_{\text{chem}}$ via CNLS fits of Randles’ circuit can be rather tricky, as the suggested ideal capacitive behavior at low frequencies does not consider nonidealities such as polycrystallinity of the LCO films on Pt, anisotropy of ion conduction in LCO, surface roughness of the films, cracks or residual porosity of the film, and any type of side reactions. Moreover, the frequency range of the measurement is limited by the rapidly increasing measurement times in the low-frequency region. Deviations from ideality can lead to a flattening of the capacitive line below $90^\circ$ and a smearing out of the transition between $45^\circ$ and $90^\circ$, making it increasingly difficult to achieve reliable fit results. Presumably, due to this reason, previous thin-film studies mostly derived $C_{\text{chem}}$ or rather $\frac{\partial E}{\partial x}$, from coulometric titration curves and then used it as a fixed parameter for the impedance fits to extract $R_{\text{ion}}$ or $D$. $C_{\text{chem}}$ and information about the equilibrium charge curve (or differential capacity curve), was directly extracted from the impedance spectra of a Li-ion electrode, for example, in refs 44,45, and 71.

In our case, we found that reliable fit results can be obtained by using an anomalous finite-space diffusion element $W_{\text{a}}$ implemented in the impedance-analyzing software EC-Lab (BioLogic, France) that is similar to the anomalous finite-space diffusion element reported by Bisquert,$^{47}$ yielding the impedance expression

$$Z_{W_{\text{a}}} = R_{\text{ion}} \frac{\coth(i\omega \tau)^{n/2}}{(i\omega \tau)^{1-n/2}} \quad (19)$$

which allows for a more general power law dependence on time of the mean-squared displacement $\langle r^2 \rangle \propto \tau^p$ rather than the standard linear behavior. More specifically, eq 19 leads to a phase shift $\geq 45^\circ$ in the semi-infinite and $\leq 90^\circ$ in the finite-space regime, which correctly describes the practical impedance behavior of virtually all thin-film battery electrodes (see Figure 5a).$^{12,44,45,42}$ In our case, the nonideality parameter $0 \leq \alpha \leq 1$ turned out to be in the range of 0.6–0.7.

As already discussed above, this also means that any conductivity or diffusion coefficient measured in such films must be viewed as an effective rather than a strictly material-intrinsic parameter. Also, normalization of $R_{\text{ct}}$ to the nominal surface area $A$, that is, without considering the surface roughness or cracks/pores, may somewhat underestimate the true area-specific resistance. Nonetheless, it is fair to assume that the observed general trends, that is, the essential dependences on the electrode potential, remain valid regardless of the film morphology or grain shape and grain size distribution. The impedance expression, as given by eq 19, is substituted for the classical $W_{\text{a}}$ element into Randles’ circuit. Similarly, the interfacial double-layer capacitance is fitted as a constant-phase element $Q_{\text{dl}}$ to account for the nonideal capacitive behavior. The modified equivalent circuit used for fitting and its simulated impedance response are shown in Figure 1d,e.

**Fit Results of Elementary Material Parameters.** As shown by the exemplary least-squares fit in Figure 5b, the equivalent circuit in Figure 1d adequately describes the recorded impedance spectra and therefore allows the extraction of electrochemical properties as a function of electrode potential. The values of $1/R_{\text{ct}}$ and $\sigma_{\text{ion}}$ shown in Figure 6a,b, respectively, are directly obtained from the fit and subsequent normalization by sample geometry ($A$ and $L$). $C_{\text{chem}}$ results directly from $\tau$ and $R_{\text{ion}}$ according to eq 17 and is plotted in Figure 4. Finally, $D$ either results directly from $\tau$ in

**Figure 6.** Logarithmic plot of (a) inverse charge-transfer resistance $1/R_{\text{ct}}$ and (b) ionic conductivity $\sigma_{\text{ion}}$ vs electrode potential and log $\alpha_{\text{Li}}$. The dilute (activity coefficient $\gamma = 1$) to nondilute transition region $3.89–3.92$ V is marked in dark around a central line at $3.905$ V. Linear fits for the dilute region are shown as dotted lines.
eq 16 or from $C_{\text{chem}}$ and $R_{\text{ion}}$ in eq 13, as shown in Figure 7. The parameter values vary by more than 1 order of magnitude and are plotted logarithmically versus the electrode potential and $\log a_{\text{Li}}$ to facilitate their interpretation. The entire dataset shows a minor hysteresis with respect to the scan direction. In the discharge scan starting at 4.0 V, resistances are slightly higher, and chemical capacitances are lower compared to the charge scan. However, these differences are negligible for the overall trends.

The charge-transfer resistance is the highest (about 1000 $\Omega$ $\text{cm}^2$) in the low-potential region and then strongly decreases down to about 100 $\Omega$ $\text{cm}^2$ at 3.99 V, in good agreement with the literature,\textsuperscript{12,14,15,42} At lower potentials, up to ca. 3.9 V, a constant slope of about 0.8 results from the log−log plot of $1/R_{\text{ct}}$ versus $a_{\text{Li}}$. Above a threshold potential of around 3.89−3.92 V, the log−log behavior flattens out. Judging by the values of $\delta$ in Figure 3, the corresponding stoichiometry of this transition is approximately $\text{Li}_{0.78−0.92} \text{CoO}_2$, although this can only be taken as a rough estimate due to the strong variation of stoichiometry in this potential region. In the following, the low- and high-potential regions separated by this transition will be referred to as dilute and nondilute regimes, respectively.

Effective ionic conductivities strongly increase with the electrode potential, ranging from about $10^{-8.7}$ S/cm at 3.85 V up to $10^{-7.4}$ S/cm at 3.99 V. Literature reports of ionic conductivity as a function of stoichiometry are scarce—the only reported values we could find are around $10^{-7.3}$ to $10^{-6.3}$

**Figure 7.** Chemical diffusion coefficient compared to its constituent parameters. The absolute value of $D$ is given on the left. Values of $D$, $C_{\text{chem}}$, and $\sigma_{\text{ion}}$ on the right axis were normalized to their average value at 3.85 V to emphasize their relative trends. The dilute (gray) to nondilute (red) transition region 3.89−3.92 V is marked in dark around a central line at 3.905 V.

**Figure 8.** Electrochemical transport parameters of the Li$_{1-\delta}$CoO$_2$ thin film extracted from impedance spectra shown as log−log plots vs $\delta$ (a,c,d) or $\delta(1-\delta)$ (b). Values of $\delta$ were obtained from Figure 3b by taking the average of all four coulometric titration curves. (a) Inverse charge-transfer resistance, (b) ionic conductivity, and (c) chemical capacitance from impedance fits. The solid blue line indicates the theoretical values predicted by eq 9. (d) Chemical diffusion coefficient compared to its constituent parameters. The absolute value of $D$ is given on the left. Values of $D$, $C_{\text{chem}}$, and $\sigma_{\text{ion}}$ on the right axis were normalized to their average value at 3.85 V to emphasize their relative trends. The dilute to nondilute transition region 3.89−3.92 V is marked in dark around a central line at 3.905 V. Linear fits for the dilute region are shown as a dotted line.
S/cm up to $\delta = 0.5$, although the corresponding dataset does not show the expected decrease of conductivity for low $\delta$.\textsuperscript{42} In the dilute regime, a slope of 1.2 is observed in the log–log plot of $\sigma_{\text{ion}}$ versus $a_{\text{Li}}$ up to the threshold potential region around 3.89–3.92 V, above which the slope starts to decrease as already seen for $1/R_c$.\textsuperscript{6}

The values of $C_{\text{chem}}$ obtained from the impedance fits are plotted in Figure 4, together with the CV data. Both sets of data are in very good qualitative and quantitative agreement, starting at very small values at low potentials, sharply increasing toward a marked peak of roughly 30 kF/cm² around 3.9 V, and then decreasing to moderately values. The peak absolute values are in excellent agreement with the typical differential capacities found in the literature,\textsuperscript{13,14,17,76} all of the cited values being in the range of 30–40 kF/cm² when normalized by sample geometry. The close match of values from AC and DC data demonstrates the often-overlooked fact, that the properties of a Li electrode’s equilibrium charge curve are fully contained within its potential-dependent impedance response, because both $E$ and $C_{\text{chem}}$ relate back to the fundamental thermodynamic relationship between $\mu_{\text{Li}}$ and $a_{\text{Li}}$ in eq 2. Again, a power law dependence between $C_{\text{chem}}$ and $a_{\text{Li}}$ can be observed in the dilute regime, this time with a slope of 1.0. A more detailed interpretation of the slope of 1 in terms of defect chemistry is given in the next section.

Finally, the chemical diffusion coefficient, as calculated from eq 16, is shown in Figure 7. As $\sigma_{\text{ion}}$ and $C_{\text{chem}}$, both of which increase exponentially with $E$, show a similar increase up to 3.9 V, $D$ remains nearly constant around $10^{-12}$ cm²/s in the dilute regime. Above 3.9 V, $D$ increases up to almost $10^{-11}$ cm²/s, driven by both an increasing $\sigma_{\text{ion}}$ and a decreasing $C_{\text{chem}}$. Values below 3.9 V are rarely reported, but the diffusivities at higher potentials are in good agreement with other studies of LCO thin films.\textsuperscript{12–15,18,72}

As both the DC data and $C_{\text{chem}}$ from impedance fits clearly show that the dependence of $\delta$ on $E$ deviates from a purely exponential behavior in the nondilute regime (i.e., $E \neq \kappa E + kT \ln \delta$, $\alpha = \text{const}$), it is hardly surprising that the corresponding electrochemical properties show a similar deviation. To isolate the concentration dependences from other factors that influence $E$, it is therefore useful to plot all parameters also in dependence of $\delta$. As shown in Figure 8a, the trend of $1/R_c$ straightens, and we get an almost constant slope in the entire range when plotting as a function of nonstoichiometry. In Figure 8b, the ionic conductivity is plotted as a function of $\delta(1 - \delta)$ rather than $\delta$ to account for the limited number of available lattice sites. This also leads to a straightening of the trend, as compared to Figure 6b, with $\sigma_{\text{ion}}$ increasing even toward the highest values of $\delta(1 - \delta)$, albeit with a smaller slope.

Given the nonidealities of the used impedance model and thus unavoidable uncertainties of the extracted parameters, we consider the slope of $\sigma_{\text{ion}}$ in the dilute regime as close to unity. This suggests that for the dilute regime, ion conduction in LCO can be well described by a vacancy-mediated process with almost constant vacancy mobility. At higher vacancy concentrations (nondilute regime), the slope of $\sigma_{\text{ion}}$ decreases, meaning that the ionic mobility decreases, probably due to some defect interaction. However, still the total conductivity increases with increasing $\delta$, even for very high vacancy concentrations. This is very different from the often-observed conductivity decrease of oxide ion conductors with increasing doping and thus oxygen vacancy concentration (e.g. yttria-stabilized zirconia,\textsuperscript{73} or doped ceria,\textsuperscript{74–76}). Since it is mainly the high concentration of the dopants themselves that reduces the defect mobility in those oxide ion conductors, the reason for the different behavior of our LCO thin films might be the absence of a varying dopant concentration.

The observed log–log dependence of $R_c$ on $\delta$ (slope 0.8) is in line with a defect chemical picture, where a Li' ion from the electrolyte needs a Li vacancy at the LCO surface for a charge transfer into the electrode. The exact dependence of this charge-transfer reaction on the specific defect concentrations, however, also varies with the concentration dependence of the corresponding Galvani potential step,\textsuperscript{7} and a more detailed discussion is beyond the scope of this paper.

The chemical capacitance in Figure 8c, however, retains its peak in the transition region of the log $C_{\text{chem}}$ versus log $\delta$ plot and strongly decreases in the nondilute regime. In the dilute regime, $C_{\text{chem}}$ is also proportional to $\delta$ and thus to the vacancy concentration. This is in accordance with the expected defect dependence of eq 9, that is, for $c_{\text{Li}} \gg c_{\text{V}_\text{Li}}$. As indicated by the blue solid line in Figure 8c, the values of $C_{\text{chem}}$ predicted by eq 9 are even in excellent quantitative agreement with the experimental data, strongly suggesting that the therein contained assumption $c_{\text{Li}} \gg c_{\text{V}_\text{Li}}$ is in fact valid for low vacancy concentrations, as will be discussed in the next section. Furthermore, this striking agreement of theory and experiment demonstrates that the thermodynamic description based on dilute point defects can offer valuable hints at the underlying defect chemistry of Li-ion battery electrode materials and once more highlights the central importance of the chemical capacitance as a powerful, readily accessible material descriptor.

**Defect Chemical Perspective.** From all the data presented in Figures 4–8, we conclude that (i) in the dilute regime, log $\delta$ is proportional to $-\log a_{\text{Li}}$ with a slope close to unity, and (ii) upon transition to the nondilute regime, the electrochemical properties of LCO collectively change in their dependence on Li activity and electrode potential. This dilute to nondilute transition occurs precisely in the region of the highest chemical capacitance—the plateau of the charge curve—where the stoichiometry strongly varies with the electrode potential and particularly affects properties, which themselves include a dependence on the Li activity ($C_{\text{chem}}$, $D$). Charge transport and transfer ($\sigma_{\text{ion}}$ and $R_c$), on the other hand, which primarily depend on the Li vacancy concentration, remain unaffected when plotted versus $\delta$ rather than Li activity. We first consider the dilute regime and discuss the possible defect chemical reasons behind the slopes of $C_{\text{chem}}$ and $\sigma_{\text{ion}}$ in their respective log–log plots versus $a_{\text{Li}}$, both being reasonably close to 1. We combine eqs 4–6 and, under dilute assumptions, arrive at

$$\mu_{\text{Li, cath}} = -\mu_{\text{V}_\text{Li}}^0 - \mu_{\text{Li}}^0 - kT \ln \delta - kT \ln \frac{c_{\text{Li}}}{c_{\text{Li}}^0}$$

(20)

and thus

$$E = E^0 + \frac{kT}{q} \ln \delta + \ln \frac{c_{\text{Li}}}{c_{\text{Li}}^0}$$

(21)

with

$$E^0 = \frac{\mu_{\text{Li, metal}} + \mu_{\text{V}_\text{Li}}^0 + \mu_{\text{Li}}^0}{q}$$

(22)
In accordance with eq 2, we may also write
\[
a_{\text{Li}} = \frac{(c_0^0)^{-2qE/kT}}{c_{V_L}^e}\frac{1}{e}
\]  
(23)

Assuming negligible defect concentrations due to intrinsic ionic or electronic disorder and the absence of any dopant charge, charge neutrality requires \(c_{V_L}^e = c_0^E = \delta e^0\), and eq 21 reduces to
\[
E = E^0 + \frac{2kT}{q} \ln \delta
\]  
(24)

Similarly, eq 23 leads to
\[
-E = \frac{qE^0}{kT} \ln \delta + \frac{qE^0}{kT} \ln a_{\text{Li}}
\]  
(25)

Equation 25 predicts a slope of 1/2 in a plot of log \(\delta\) versus \(-\log a_{\text{Li}}\) that is, in a Brouwer diagram.

Alternatively, and perhaps more intuitively, the power law dependences of point defect concentrations on activity can also be derived from equilibrium mass action laws.\(^{29}\) For the case of Li intercalation into a cathode material, the equilibrium reaction and its corresponding mass action law can be formulated as
\[
\text{Li} + h^* + V_L^e \rightleftharpoons \text{Li}_0^e
\]  
(26)

\[
K = (a_{\text{Li}}c_{V_L}^{-e})^{-1}
\]  
(27)

where \(K\) is the equilibrium constant of the intercalation reaction. In accordance with eq 25, eq 27 predicts \(a_{\text{Li}}\propto (c_{V_L}^e)^{-1}\) and therefore a slope of 1/2 in a plot of log \(\delta\) versus \(-\log a_{\text{Li}}\) again assuming \(c_{V_L}^e = c_0^E\) due to charge neutrality.

Instead, we find for \(\sigma_{\text{ion}}\) a slope of roughly 1 in the log \(\sigma_{\text{ion}}\) versus log \(a_{\text{Li}}\) plot. This somewhat surprising result is very consistent with the potential dependence of \(C_{\text{chem}}\) (i.e., Li deintercalation, \(c_{V_L}^e = c_0^E = \delta e^0\)) and the expectation of a slope of 1/2 according to eqs 8, 25, and 27. However, the measured slope for \(C_{\text{chem}}\) is also close to 1. Within the thermodynamic description of \(C_{\text{chem}}\) presented above, a slope of 1 could be explained if \(c_{V_L}^e \gg c_0^E\) or \(c_0^E \gg c_{V_L}^e\) and assuming the majority carrier concentration as relatively constant on a logarithmic scale. Given the strong variation of \(R_0\) and \(\sigma_{\text{ion}}\), Li vacancies can be assumed to be the minority carriers, and \(c_0^E\) has to be pinned significantly above \(c_{V_L}^e\) to explain the observed slopes. The excellent quantitative agreement of the experimental values of \(C_{\text{chem}}\) with eq 9 also supports this assumption. If the concentrations of both vacancies and holes were relevant, eq 8 would predict \(C_{\text{chem}}\) values to be lower by a factor 2 compared to those found experimentally.

From a defect chemical perspective, pinning of \(c_0^E\) might occur if the hole concentration introduced through nonstoichiometry is negligible compared to the levels of either (i) intrinsic electronic disorder or (ii) extrinsic acceptor doping. The evaluation of the former is far from trivial, as \(\text{Li}_{1-d}\text{CoO}_2\) is known to undergo a semiconductor–metal transition upon delithiation, accompanied by a significant increase in electronic conductivity and hole mobility as the conduction mechanism transitions from localized polaron hopping toward delocalized metallic conductivity.\(^{60,63,78}\) Owing to the close entanglement of mobility and conductivity, it is not entirely clear how \(c_0^E\) behaves in this stoichiometry range. Furthermore, the defect chemical description of electronic charge carriers relies on the semiconductor-type behavior with thermally activated, localized polarons and therefore fails to describe metallic conductivity.

A more accessible explanation lies in the presence of an extrinsic acceptor dopant in the material. As reported in the literature, the formation energies of antisite defects such as \(\text{Li}_{\text{Co}}\) are relatively low, and the defect chemical composition of nominal \(\text{LiCoO}_2\) thin films is highly sensitive to synthesis conditions.\(^{53,79–81}\) It would therefore come as no surprise if the sputter-deposited and post-annealed thin films examined in this work contained a significant amount of \(\text{Li}_{\text{Co}}\) defects that act as acceptor dopants in the material, although further experimental investigation would be required to corroborate this hypothesis.

Based on the assumed presence of an acceptor dopant such as \(\text{Li}_{\text{Co}}\), we can also propose a Brouwer diagram. The dopant requires compensation by a formally positively charged defect species to preserve charge neutrality. For high \(a_{\text{Li}}\) and thus low \(c_{V_L}^e\) (see eq 27), the dopant causes a fixed hole concentration to satisfy the electroneutrality condition \(c_0^E = 2c_{V_L}^e\). As long as the additional hole concentration introduced through the charging of the electrode is comparatively small, the overall hole concentration will therefore remain near-constant on a logarithmic scale. If \(c_0^E\) is constant, eq 27 requires \(c_{V_L}^e \propto a_{\text{Li}}^{-1}\). This situation, labeled as A (acceptor) regime, is shown on the left side of Figure 9 at high lithium activities. Once the initially fixed hole concentration is surpassed by the additional concentrations introduced through nonstoichiometry, the activity dependences of \(c_0^E\) and \(c_{V_L}^e\) behave according to eqs 24 and 25. The proposed defect model would therefore not only explain the slope of about 1 for \(\sigma_{\text{ion}}\) at low \(\delta\) but would even predict a change of slope toward 1/2 at high \(\delta\), where
A full set of electrochemical parameters describing the mass and charge transport properties of Li$_{1-x}$CoO$_2$ thin films could be simultaneously extracted from impedance spectra measured in dependence of the SOC. The relevant elementary material parameters are the ionic conductivity $\sigma_{\text{ion}}$, charge-transfer resistance $R_{\text{ct}}$, and chemical capacitance $C_{\text{chem}}$. It is shown that the chemical capacitance can be deduced alternatively from DC data (coulometric titration curve or CV), and both approaches lead to very consistent results. For a dilute regime ($\delta < 0.1$), the chemical capacitance is even in excellent quantitative agreement with defect chemical predictions. This demonstrates the central importance of the chemical capacitance as a powerful, readily accessible material descriptor. The Li chemical diffusion coefficient, on the other hand, is a composite property, and its dependence on the SOC can only be understood from the underlying ionic conductivity and chemical capacitance. By evaluating the dependence of all elementary material parameters on Li activity and stoichiometry, it was shown that at low potentials, that is, low vacancy concentrations, the transport properties of the investigated Li$_{1-x}$CoO$_2$ thin films are consistently described by a dilute defect chemical model. However, the analysis of slopes in the log–log plots of $\sigma_{\text{ion}}$ and $C_{\text{chem}}$ versus Li activity, as well as the absolute values of $C_{\text{chem}}$, strongly suggests the presence of an acceptor dopant. Li$_{x}$Sn$_{1-x}$ antisite defects, inadvertently introduced during sputter deposition, are proposed as the plausible acceptor species.

As a result, both $C_{\text{chem}}$ and $\sigma_{\text{ion}}$ increase exponentially with the electrode potential (up to $\delta \approx 0.1$), and $D$ remains nearly constant. At high potentials, that is, high vacancy concentrations, the dilute model fails as activity coefficients start to become relevant and $C_{\text{chem}}$ begins to decrease. The measured increase of $D$ for $\delta > 0.1$ can therefore serve as an indicator of the material moving beyond the ideal dilute behavior. The ionic conductivity, however, increases almost linearly in the corresponding log–log plot versus $\delta (1 - \delta)$ for the entire stoichiometric range, which indicates little concentration dependence of the vacancy mobility.

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CONCLUSIONS

A full set of electrochemical parameters describing the mass and charge transport properties of Li$_{1-x}$CoO$_2$ thin films could be simultaneously extracted from impedance spectra measured in dependence of the SOC. The relevant elementary material parameters are the ionic conductivity $\sigma_{\text{ion}}$, charge-transfer resistance $R_{\text{ct}}$, and chemical capacitance $C_{\text{chem}}$. It is shown that the chemical capacitance can be deduced alternatively from DC data (coulometric titration curve or CV), and both approaches lead to very consistent results. For a dilute regime ($\delta < 0.1$), the chemical capacitance is even in excellent quantitative agreement with defect chemical predictions. This demonstrates the central importance of the chemical capacitance as a powerful, readily accessible material descriptor. The Li chemical diffusion coefficient, on the other hand, is a composite property, and its dependence on the SOC can only be understood from the underlying ionic conductivity and chemical capacitance. By evaluating the dependence of all elementary material parameters on Li activity and nonstoichiometry, it was shown that at low potentials, that is, low vacancy concentrations, the transport properties of the investigated Li$_{1-x}$CoO$_2$ thin films are consistently described by a dilute defect chemical model. However, the analysis of slopes in the log–log plots of $\sigma_{\text{ion}}$ and $C_{\text{chem}}$ versus Li activity, as well as the absolute values of $C_{\text{chem}}$, strongly suggests the presence of an acceptor dopant. Li$_{x}$Sn$_{1-x}$ antisite defects, inadvertently introduced during sputter deposition, are proposed as the plausible acceptor species. As a result, both $C_{\text{chem}}$ and $\sigma_{\text{ion}}$ increase exponentially with the electrode potential (up to $\delta \approx 0.1$), and $D$ remains nearly constant. At high potentials, that is, high vacancy concentrations, the dilute model fails as activity coefficients start to become relevant and $C_{\text{chem}}$ begins to decrease. The measured increase of $D$ for $\delta > 0.1$ can therefore serve as an indicator of the material moving beyond the ideal dilute behavior. The ionic conductivity, however, increases almost linearly in the corresponding log–log plot versus $\delta (1 - \delta)$ for the entire stoichiometric range, which indicates little concentration dependence of the vacancy mobility.
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