# A Consistent Derivation of the Impedance of a Lithium-Ion Battery Electrode and its Dependency on the State-of-Charge

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ABSTRACT

A derivation of the fundamental impedance of a Lithium-Ion battery electrode is given, exemplarily conducted for a solid thin-film electrode. The focus of this derivation is not on developing a model which is able to reproduce the exact behaviour of a given electrode, but rather on deriving its fundamental characteristics from few and intuitive assumptions in a simple and transparent way. It is thus shown, that the fundamental impedance of a solid thin-film electrode consists of an RC-element for charge-transfer, a Finite-Length Warburg element for diffusion in the electrolyte and a Finite-Space Warburg element for diffusion in the solid-state. The use of a Finite-Length Warburg element with a serially connected capacitor for modelling diffusion in the solid-state is thus indicated to be physically questionable. In addition, the theoretically expected behaviour of charge-transfer and solid-state diffusion on the degree of lithiation (State-of-Charge) is derived and discussed.

## 1. Introduction

The impedance spectrum of a Lithium-intercalation electrode can be considered as the electrode's specific fingerprint: Its different frequency regimes, as exemplarily depicted in Fig. 1, represent its different inherent losses: The finite conductivity of the electrolyte, the electrode and the current collector manifests in the ohmic part of the impedance spectrum. The charge transfer is represented in the high frequency regime of the spectrum. For negative electrodes additional losses caused by the Solid Electrolyte Interphase (SEI) might be visible in the same frequency range.

The low frequent part of the spectrum contains losses from diffusion in the solid-state and in the electrolyte and also carries information about the electrode's differential capacity [1], which represents the local capacitance of the electrode in the operation point, where the spectrum was recorded. The latter is related to the slope of the *OCV* in that operation point and is connected to it by the following relation:

$$C_{\text{diff}} = \left(\frac{\partial U_{\text{OCV}}}{\partial Q}\right)^{-1} \tag{1}$$

In order to quantify the aforementioned contributions, an equivalent circuit model has to be found, which fits the spectrum and, moreover, is physically valid: Only in this case it is allowed to conclude from a good fit to the actual size of physical quantities. For charge transfer, the widely acknowledged impedance model is given by a Randle's circuit [2] or derivatives thereof [3]. For solid-state diffusion however, there is still disagreement: Publication [4] for example suggests modelling diffusion and the differential capacity separately by serially connecting a Finite-Length Warburg Element

$$Z_{\text{FLW}}(\omega) = A \cdot \frac{\tanh\left(\sqrt{\frac{j\omega}{D}} \cdot L\right)}{\sqrt{j\omega D}} \tag{2}$$

for the solid-state diffusion and a capacitor

$$Z_{\text{C}}(\omega) = \frac{1}{j\omega C_{Diff}} \tag{3}$$

for the differential capacity of the electrode. This approach seems intuitive and was thus adapted, among others, by [3], [5] and [6]. On the other hand, publications like [7] and [8] omit a capacitor, but suggest a Finite-Space Warburg element

$$Z_{\text{FSW}}(\omega) = A \cdot \frac{\coth\left(\sqrt{\frac{j\omega}{D}} \cdot L\right)}{\sqrt{j\omega D}} \tag{4}$$
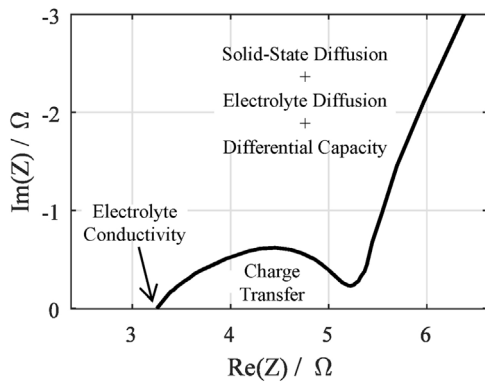
**Fig. 1.** Impedance spectrum of a Nickel-Mangan-Cobalt (NMC) cathode, measured against a reference electrode. The main contributions to the impedance are labelled at the according frequency range.

to model both solid-state diffusion and the differential capacity of the electrode. For a graphical comparison of both approaches see Fig. 2.

Obviously, both approaches yield similar but mathematically not equivalent impedance models and the arising question is: Which is the correct impedance model for solid-state diffusion and how does it relate to the differential capacity of the electrode?

Our approach to solve this problem is to mathematically derive the fundamental impedance model of a solid thin-film Lithium-Ion battery electrode. The derivation starts from the reaction rate of the Lithium intercalation into the electrode. From that, the full impedance model is deduced.

Modelling a solid thin-film electrode and thus neglecting the important effect of porosity or inhomogeneity of realistic electrodes [9–11] was purposely decided for the sake of simplicity. Also, it is purposely refrained from discussing the differences arising from different diffusion geometries [12]. The goal of this publication is instead, to present a consistent mathematical framework in which the impedance of an electrode is derived from few and very general assumptions. Due to its consistency, all fundamental impedance contributions are covered and the physical dependencies of all impedance elements on the degree of lithiation (State-of-Charge) are obtained. Thereby, the results add to the results given in [10], as the effect of diffusion of Lithium-Ions in the electrolyte is now additionally covered. Moreover, while in [10] the dependency of

the charge-transfer resistance with respect to the degree of lithiation (State-of-Charge) is not explicitly derived, in this work an analytical dependency is obtained. The latter is in accordance with experimental results [13]. In addition, the course of the charge-transfer resistance over the degree of lithiation (State-of-Charge) is shown to be a function of the transfer coefficient of the Butler-Volmer equation. These results open up new possibilities to understand the course of impedance spectra of battery electrodes over the degree of lithiation and possibly to even determine the transfer coefficient from a number of impedance measurements with varying degree of lithiation.

The derived results are extendable to the case of porous electrodes by inserting the derived model into a transmission line framework [14–16] or by combining our results with approaches shown in [9–11].

## 2. Theory

### 2.1. Derivation of the Impedance of a Lithium-Ion Battery Electrode

The starting point of the derivation of the impedance of a solid thin-film Lithium-Ion battery electrode is the intercalation reaction of Lithium:

$$Li^+ + e^- + V_{Li} \rightleftharpoons Li^I \qquad (5)$$

There, $Li^+$ denotes a Lithium-Ion in the electrolyte, $e^-$ an electron, $V_{Li}$ a Lithium vacancy in the host lattice of the electrode and $Li^I$ intercalated Lithium. According to [17] the reaction rates of the intercalation and extraction reaction are given by

$$v_{in} = k_{in} \cdot c_{Li^+} \cdot c_{e^-} \cdot c_{V_{Li}} \cdot e^{-\frac{E_{in}}{RT}} \qquad (6)$$

and

$$v_{ex} = k_{ex} \cdot c_{Li^I} \cdot e^{-\frac{E_{ex}}{RT}} \qquad (7)$$

where $c_x$ denotes the concentration of species $x$, $k_{in}$ and $k_{ex}$ the rate constant and $E_{in}$ and $E_{ex}$ the activation energies of the intercalation and extraction reaction. Both equations are intuitively accessible: The larger the concentration of Lithium-Ions in the electrolyte and the larger the concentration of Lithium-vacancies in the host lattice, the more ions and vacancies are available for an intercalation reaction. The lower the activation energy for intercalation, the more likely a potentially intercalating ion will
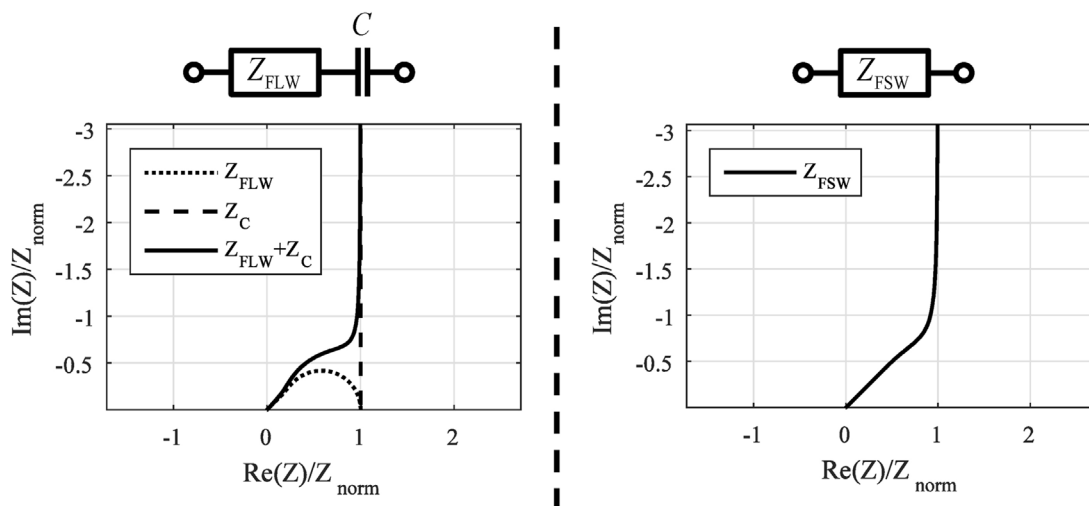


**Fig. 2.** In literature two approaches for modelling the low-frequent regime of the impedance spectrum of a Lithium-Ion battery electrode coexist: (left) Serial connection of a Finite-Length Warburg element described by Eq. (2) and a capacitor described by Eq. (3). (right) A Finite-Space Warburg element, described by Eq. (4). Both impedances are normalized by their maximum real part.