Supporting Information

3D Impedance Modelling of Metal Anodes in Solid-State Batteries – Incompatibility of Pore Formation and Constriction Effect in Physical-Based 1D Circuit Models

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S1. Transformability of Individual Circuit Elements

Circuit models usually consist of different combinations of resistors R, capacitors C, or even inductors L. In electrical engineering, transport processes of charge carriers are usually represented by a parallel connection of a resistor with a capacitor forming a so-called RC-element. For example, in case of spatially inhomogeneous samples such as ceramics consisting of sintered grains, one distinguishes at least two transport processes, i.e., transport in the volume of the grain and across grain boundaries. Such an inhomogeneous sample can then be divided into voxels representing mesoscopic regions, which are either grain-like or grain-boundary like. This discretization of the sample morphology can then be translated into an impedance network of mesoscopic RC-elements which, on the one hand, reflects the materials parameters assigned to the microscopic transport processes and, on the other hand, the morphology of the sample.

Physical-based macroscopic equivalent circuit models for describing experimental impedance spectra usually consist of a few circuit elements connected in series or in parallel. They are one-dimensional (1D) as the macroscopic circuit elements only refer to the microscopic transport processes. Their mostly serial interconnection cannot or only crudely account for the sample morphology and microstructure. Nevertheless, it is argued that information about the microscopic processes may be extracted when fitted to experimental impedance data. In particular, this is assumed for the characteristic time constants of the transport processes. This assumption is motivated by the following consideration. The time dependence of a transport process described by an RC-element in a homogeneous sample of length L and cross section A is solely determined by its microscopic transport parameters, i.e., specific resistivity ρ and relative permittivity ε_r, because $R = \rho \frac{L}{A}$ and $C = \varepsilon_0 \varepsilon_r \frac{A}{L}$ as it holds $\tau = RC = \rho \varepsilon_0 \varepsilon_r$.

However, the question remains to which extend this assumption holds in case of inhomogeneous samples which consist of a network of RC-elements corresponding to different transport processes which are connected in a way fully reflecting the sample's morphology. For example, mesoscopic electrical network models may be three-dimensional (3D) and may consist of several million local equivalent circuit elements. In what follows, we will clarify this point.

An impedance Z_i can generally be expressed as

$$Z(\omega) = |Z| \cdot e^{i\cdot(\varphi+\omega t)}, \tag{S1}$$

where t, ω, φ, and $|Z|$ describe the time, the angular frequency, the phase angle and the absolute value of the impedance, respectively. The impedance for a fixed angular frequency is fully described by its amplitude $|Z|$ acting as a scaling factor and the phase angle between the real (Z') and imaginary (Z'') part. For simplicity and without loss of generality, we will omit the frequency-dependent part $e^{i\omega t}$ in what follows. In a first step, we consider the series and parallel connection of two arbitrary impedances $Z_a = |Z_a| \cdot e^{i\alpha}$ and $Z_b = |Z_b| \cdot e^{i\beta}$, respectively. The total impedance can be described as

$$Z_{\mathrm{tot}}^{\mathrm{serial}} = Z_a + Z_b = \begin{cases} (|Z_a| + |Z_b|) \cdot e^{i\cdot\alpha} & \text{, if } \alpha = \beta \\ |Z_a| \cdot e^{i\cdot\alpha} + |Z_b| \cdot e^{i\cdot\beta} & \text{, else} \end{cases} \tag{S2}$$

$$Z_{\text{tot}}^{\text{parallel}} = (Z_a^{-1} + Z_b^{-1})^{-1} = \begin{cases} \left(\dfrac{|Z_a| \cdot |Z_b|}{|Z_a| + |Z_b|}\right) \cdot e^{i\cdot\alpha} & \text{, if } \alpha = \beta \\ \left(\dfrac{|Z_a|^2 \cdot |Z_b| \cdot e^{i\cdot\beta} + |Z_b|^2 \cdot |Z_a| \cdot e^{i\cdot\alpha}}{|Z_a|^2 + |Z_b|^2 + 2|Z_a||Z_b|\cos(\beta - \alpha)}\right) & \text{, else} \end{cases} \tag{S3}$$

The results indicate that the impedances Z_a and Z_b can be transformed into an equivalent circuit with a single impedance of the form $Z_{tot} = |Z_{tot}|\, e^{i\varphi}$ with $\varphi = \alpha$ only if $\alpha = \beta$. In this case, the phase information is preserved during the transformation step. Interestingly, although the parallel circuit for $\alpha \neq \beta$ can be replaced by a serial circuit, the information about the original phase (α, β) is lost during the transformation step, since the individual prefactors depend on both phases.

Secondly, we increase the complexity of the system by considering the parallel connection of two different transport paths typically observed in experiments. We assume that each serial path is described by two impedances that differ in amplitude and phase angle, but we assume that the same phase angles α and β are involved in both serial paths. The total impedance can be expressed as

$$Z_{\text{tot}} = \left(\frac{1}{Z_{\text{a1}} + Z_{\text{b1}}} + \frac{1}{Z_{\text{a2}} + Z_{\text{b2}}}\right)^{-1} = \frac{\left(|Z_{\text{a1}}| \cdot e^{i\cdot\alpha} + |Z_{\text{b1}}| \cdot e^{i\cdot\beta}\right) \cdot \left(|Z_{\text{a2}}| \cdot e^{i\cdot\alpha} + |Z_{\text{b2}}| \cdot e^{i\cdot\beta}\right)}{(|Z_{\text{a1}}| + |Z_{\text{a2}}|) \cdot e^{i\cdot\alpha} + (|Z_{\text{b1}}| + |Z_{\text{b2}}|) \cdot e^{i\cdot\beta}} \tag{S4}$$

It is of particular interest to investigate whether the superposition of the individual impedances contains parts showing the pure phase angles α and β. For this purpose, we rearrange equation (S4) and indeed identify parts that contain exclusively the phase information either of α or β:

$$\begin{aligned} Z_{\text{tot}} = {} & \frac{|Z_{\text{a1}}| \cdot |Z_{\text{a2}}|}{|Z_{\text{a1}}| + |Z_{\text{a2}}|} \cdot e^{i\cdot\alpha} + \frac{|Z_{\text{b1}}| \cdot |Z_{\text{b2}}|}{|Z_{\text{b1}}| + |Z_{\text{b2}}|} \cdot e^{i\cdot\beta} \\ & + \frac{(|Z_{\text{a1}}| \cdot |Z_{\text{b2}}| - |Z_{\text{a2}}| \cdot |Z_{\text{b1}}|)^2 \cdot e^{i\cdot(\alpha+\beta)}}{(|Z_{\text{a1}}| + |Z_{\text{a2}}|) \cdot (|Z_{\text{b1}}| + |Z_{\text{b2}}|) \cdot ((|Z_{\text{a1}}| + |Z_{\text{a2}}|) \cdot e^{i\cdot\alpha} + (|Z_{\text{b1}}| + |Z_{\text{b2}}|) \cdot e^{i\cdot\beta})} \end{aligned} \tag{S5}$$

The expression consists now of three terms, one with the phase information α, one with the phase information β, and one mixed contribution. The effective amplitudes of both "pure" terms result from a parallel connection of the absolute impedances $|Z_i|$ with identical phases. The third (mixed) term can be rearranged similar to equation (S3) in order to obtain a real prefactor:

$$Z_{\text{mix}} = \frac{(|Z_{\text{a1}}| \cdot |Z_{\text{b2}}| - |Z_{\text{a2}}| \cdot |Z_{\text{b1}}|)^2 \cdot e^{i\cdot(\alpha+\beta)}}{(|Z_{\text{a1}}| + |Z_{\text{a2}}|) \cdot (|Z_{\text{b1}}| + |Z_{\text{b2}}|) \cdot ((|Z_{\text{a1}}| + |Z_{\text{a2}}|) \cdot e^{i\cdot\alpha} + (|Z_{\text{b1}}| + |Z_{\text{b2}}|) \cdot e^{i\cdot\beta})} \tag{S6}$$

with $\xi = |Z_{\text{a1}}| \cdot |Z_{\text{b2}}|;\ \mu = |Z_{\text{a2}}| \cdot |Z_{\text{b1}}|;\ \delta = (|Z_{\text{a1}}| + |Z_{\text{a2}}|);\ \gamma = (|Z_{\text{b1}}| + |Z_{\text{b2}}|)$

$$= \frac{(\xi - \mu)^2 \cdot e^{i\cdot(\alpha+\beta)}}{\delta\gamma \cdot (\delta \cdot e^{i\cdot\alpha} + \gamma \cdot e^{i\cdot\beta})} = \frac{(\xi - \mu)^2 \cdot (\gamma e^{i\cdot\alpha} + \delta e^{i\cdot\beta})}{\delta^3\gamma + \delta\gamma^3 + 2 \cdot \delta^2\gamma^2 \cdot \cos(\beta - \alpha)} \tag{S7}$$

The structure of this expression and thus the conclusions derived from it are comparable to the "asymmetric" (with respect to the phases involved) parallel circuit of two *RC*-elements in the lower expression of equation (S3).

Overall, this example illustrates that the phase information of the constituents of the serial circuits is always part of the superimposed (phase of the) total impedance if the transport process *a* and *b* occur in both serial paths. If this is not the case, e.g., $|Z_{a1}| = 0$, the pure phase information α is lost, since the corresponding prefactor in equation (S5) becomes zero.