Interplay of Dynamic Constriction and Interface Morphology between Reversible Metal Anode and Solid Electrolyte in Solid State Batteries

Janis K. Eckhardt,* Peter J. Klar, Jürgen Janek, and Christian Heiliger

ABSTRACT: In an all-solid-state battery, the electrical contact between its individual components is of key relevance in addition to the electrochemical stability of its interfaces. Impedance spectroscopy is particularly suited for the non-destructive investigation of interfaces and of their stability under load. Establishing a valid correlation between microscopic processes and the macroscopic impedance signal, however, is challenging and prone to errors. Here, we use a 3D electric network model to systematically investigate the effect of various electrode/sample interface morphologies on the impedance spectrum. It is demonstrated that the interface impedance generally results from a charge transfer step and a geometric constriction contribution. The weights of both signals depend strongly on the material parameters as well as on the interface morphology. Dynamic constriction results from a non-ideal local contact, e.g., from pores or voids, which reduce the electrochemical active surface area only in a certain frequency range. Constriction effects dominate the interface behavior for systems with small charge transfer resistance like garnet-type solid electrolytes in contact with a lithium metal electrode. An in-depth analysis of the origin and the characteristics of the constriction phenomenon and their dependence on the interface morphology is conducted. The discussion of the constriction effect provides further insight into the processes at the microscopic level, which are, e.g., relevant in the case of reversible metal anodes.

KEYWORDS: reversible metal anode, interface morphology, pore formation, constriction effect, impedance modeling, garnet-type solid electrolyte, solid-state battery, electric network model

1. INTRODUCTION

Examining the interfaces of all-solid-state batteries is challenging since they are hardly accessible non-destructively. Impedance spectroscopy (IS) is particularly suitable to systematically investigate changes of the interfaces during operation. Individual impedance contributions, e.g., grain boundary or bulk transport within a ceramic, can be separated from each other, if they differ in their frequency-dependent behavior. However, the correlation between microscopic changes of the interface morphology and the macroscopic impedance signal is nontrivial, making the interpretation of macroscopic impedance data in terms of microscopic processes prone to error.

In all-solid systems, an additional degree of sophistication arises in IS analysis since geometric effects contribute to the measured impedance signal in addition to chemical side reactions.1−3 Thus, the impedance depends not only on the material properties of the solids involved but also on the preparation method of the system. While sputter deposition of the metal electrode typically yields a conformal coating of a sample surface, mechanical interface formation is likely to cause a porous interface accompanied by elastic and plastic deformation. Depending on the preparation conditions, pores of different shapes, sizes, and depths may arise and essentially determine the interface morphology. This also applies when a dynamic change of the system during operation leads to pore formation.4,5

Such a situation is often encountered in the case of reversible metal anodes, when a usually polycrystalline and cation-conducting solid electrolyte (SE) is in contact with an alkali metal electrode. In systems with thermodynamically stable interfaces, such as lithium metal in contact with Li_{x=0.25}Al_{x=0.25}La_{x=1}Zr_{x=12}O_{12} (LLZO),6−9 three different transport processes occur at the microscopic level, i.e., the charge

Received: April 21, 2022
Accepted: July 11, 2022
Published: July 25, 2022
transfer (CT) step at the metal/SE interface and the bulk and grain boundary (GB) transport within the SE (see Figure 1a). It is therefore often mistakenly assumed that the impedance contains only contributions from the transport processes in the SE and the CT. Other origins of impedance signals and effects like the 3D microstructure of the SE (i.e., the geometrical arrangement of the grain boundary network) or the pores at the interface are usually not considered in the interpretation of experimental data, which can easily lead to misinterpretations as will be demonstrated by us. The pores at the interface reduce the electrochemical active surface area. Thus, the ionic current lines in the SE become spatially focused at the contact spots (i.e., form “bottlenecks”). This effect is referred to as current constriction in what follows. This has been well documented in mostly qualitative form in metals and in semiconductors. The effect, however, is often considered to be “static”, i.e., the constriction is assumed to be independent of external influences. It occurs, for example, when the electrode area $A_{\text{lead}}$ is smaller than that of the sample $A_{\text{Int}}$. This means that the sample volume under the non-contacted surface area will also contribute to the transport due to the bended electric equipotential lines within the sample. The effect quantitatively affects all derived transport quantities ($R$, $C$) and depends on the ratio of sample surface area to contact area (see Figure 1b).

Current constriction, however, can also form “dynamically” in a system. This is important, especially when considering pores. At low frequencies, pores are truly locally current-blocking, and at high frequencies, the pores can transfer charge dielectrically (displacement current). Thus, their contribution to the impedance depends on excitation frequency $\nu$ and the constriction effect will disappear, if a certain frequency $\nu_{\text{lim}}$ is exceeded (see Figure 1c). Therefore, both qualitative and quantitative changes of the impedance are to be expected, i.e., the pores at the interface can also cause separate signals in the impedance spectrum (see Figure 1a), which are of purely geometric origin, i.e., due to interface morphology only. This has a major impact on the interpretation of IS results, especially regarding the assignment of the individual signals from the interface, i.e., CT step or constriction effect. Conversely, this means that IS data contain valuable information on the porous 3D microstructure of an electrode interface.

Current constriction is an established concept in the physics of electronic contacts but has not gained great attention in solid-state battery research so far, although it is of great

Figure 1. Overview of different types of current constriction at the electrode/sample interface. (a) Pores at the interface can lead to a separate or overlapping impedance contribution in the spectrum. This is related to the so-called constriction effect, which can be categorized in a “static” (classical) case of an ideal contact (b) and a “dynamic” (frequency-dependent) case of a non-ideal contact (c). In the classical case, the constriction only quantitatively affects the impedance of all transport signals (i.e., scaling), while in the frequency-dependent case, the impedance can be affected quantitatively (black) as well as qualitatively (green) by forming a separate signal that does not correspond to an electric migration process in the system at the microscopic level.
importance, for example, for the potential commercial use of the lithium metal anode. Despite the extensive study of the constriction effect at solid/solid interfaces by Fleig and Maier, it is not fully understood yet. Further research is needed to clarify how the constriction effect can be manipulated or even mitigated.

Using a 3D electric network model, we demonstrate that the interface contribution to the electrode impedance is generally composed of a CT signal and a geometric constriction signal. Both result from the interface but differ in their origins. While the former represents a microscopic electric migration process across the interface, the latter arises from the frequency-dependent change of the electrode area that actively contributes to the transport. The interdependence between the two effects is rather intriguing and needs careful case studies for different realistic situations encountered in experiments. Here, we focus on the specific situation typically observed for a garnet-type SE in all-solid state battery structures that can be well approximated by a homogeneous SE with negligible polarization resistances at the interfaces, i.e., a situation where the CT effect is negligible. This relevant and experimentally accessible situation reveals the pure constriction effect on the impedance data and defines an important starting point for a fundamental study of the interplay between the CT effect and constriction effect.

The systematic analysis presented in this study illustrates the impact of essential parameters such as the electrode geometry and the interface morphology on the dynamic constriction effect. For this purpose, simplified interface morphologies are assumed to highlight major trends and to elucidate fundamental dependencies. Both also qualitatively apply in the case of more realistic interface morphologies but will lose clarity due to disorder effects. The analysis as a whole demonstrates that a careful analysis of impedance data may yield valuable information, for example, on pore formation and dynamics at the metal anode interface.

2. COMPUTATIONAL DETAILS

2.1. Generation of a Three-Dimensional Microstructure. The dynamic constriction effect is studied using a three-
dimensional model system suitable for describing reversible metal anodes. The system under consideration consists of a parent metal electrode (e.g., Li, Na, and Ag), which is in contact with an SE. The complexity of the real system prevents a clear assignment of individual effects on the impedance. Therefore, some simplifications are necessary. We assume a homogeneous SE to better highlight the impact of the interface. The network model used, however, can be easily extended to accounted for typical ceramic SE materials consisting of grains separated by grain boundaries.

Additionally, the number of geometric model parameters describing the interface is reduced by flattening the real interface and considering only pores of the same depth $\delta_{\text{int}}$ in the system (see Figure 2a). The morphology is approximated by one or more square-shaped contact spots in the interface layer whose lateral extension is varied. Such a porous layer describes the averaged geometric properties of the interface.

Four variants of the simplified model system are studied where system parameters are systematically varied. This allows a qualitative investigation of the dynamic constriction effect with respect to its origin, the geometric impact of the electrode size, the effect of the interface morphology, and the impact of the pore characteristics, see Figure 2b–e from left to right, respectively. Despite these simplifications, the conclusions drawn from the computations with respect to the constriction effect are of a general nature and valid for all solid/solid interfaces. In particular, the qualitative results derived also apply to more complex morphologies and microstructures of the SE as observed in the real system.

In this study, we assume that the SE possesses a cubic shape ($L_x = L_y = L_z$) and that one of its surfaces is contacted by the working electrode (WE) forming the porous interface. The depth $\delta_{\text{int}}$ of the pores between the WE and the SE is set to 1/5000 of the geometric extension $L_z$ of the sample perpendicular to the surface, i.e., the nominal transport direction.

### 2.2. Description of Charge Transport through the System

A 3D impedance network is used to describe the transport processes between the electrode and SE across the porous interface of the model system. For this purpose, the entire sample volume (including the pores) is divided into individual voxels of edge length $\delta$. In this process, each voxel is assigned to either a grain within the sample (blue), a pore at the interface (white), or the metal electrode (gray). A single planar layer with voxels of constant thickness $\delta_{\text{int}}$ is inserted between the electrode and the sample to describe the interface morphology and thus the contact between the WE and SE (see Figure 2f).

A nodal network must be set up to determine the impedance on the basis of the discretized model by assigning a node to the center of each voxel. The different transport processes can be distinguished from each other by comparing the structural properties of adjacent voxels. While the dielectric properties of the pores are modeled by a capacitor only, each electric charge transport process is described by an RC-element (see Figure 2g). The microscopic bulk transport within the ceramic is described by two RC-elements connected in series to each other in the branch between two nodes. The charge transport within the electrode (2-Z$\text{Elec}$) and the CT step at the metal/SE interface ($Z_{\text{Elec}} + Z_{\text{CT}} + Z_{\text{Bulk}}$) is described accordingly. In addition, transport between pore voxels and solid voxels, i.e., WE or SE, is described by the series connection of an RC-element with a capacitor ($Z_{\text{Elec}} + Z_{\text{Pore}}$ or $Z_{\text{Bulk}} + Z_{\text{Pore}}$) and the transport between two pore voxels is modeled by two serially connected capacitors ($2-Z_{\text{Pore}}$).

The resistances and capacitances of the local equivalent circuit elements are calculated according to the rules for

---

**Figure 3.** Impact of the contact area at the WE/SE interface on the impedance. (a) The constriction semicircle at low frequencies increases with decreasing contact area. (b) The DRT reveals a shift of the constriction signal toward larger relaxation times. (c–e) These observations are also evident considering the macroscopic transport quantities ($R_i$ and $C_i$). With decreasing contact area, the limiting case of complete contact loss is approached, i.e., $R_{\text{Cstr}} \to \infty$ and $C_{\text{Cstr}} \to C_{\text{Pore}}$. 

https://doi.org/10.1021/acsami.2c07077

ACS Appl. Mater. Interfaces 2022, 14, 35545–35554
3. RESULTS

DRT. regularization term was required in the calculation of each analysis of the impedance spectra, and only a small Thus, the results for all frequencies were considered in the conductors and plate capacitors. The bulk parameters \((\sigma_{\text{bulk}} = 0.46\, \text{mS/cm} \text{ and } \epsilon_{\text{bulk}} = 150 \cdot \epsilon_0)\) are based on the solid electrolyte LLZO, and the permittivity of the pore \(\epsilon_{\text{pore}}\) is in the range of vacuum permittivity \(\epsilon_0^{11,26,27}\). The transport within the electrode and the CT step at the interface is assumed to be resistance-free as proven for garnet-type SEs (\(Z_{\text{elec}} = Z_{\text{CT}} = 0\)). Thus, bulk transport is the only electric migration process considered within the homogeneous SE system. The interplay of the constriction effect with other transport processes like a resistive CT step at the interface or the transport across grain boundaries (see Figure 2a) is beyond the scope of this paper and will be discussed in a subsequent work. Further details about setting up and solving the 3D network model and its solution are given in our previous work.\(^{10}\)

2.3. Technical Details in the Analysis of the Computed Impedance Spectra. The simulation of the impedance spectra based on the simplified 1D fit equivalent circuit and the distribution of relaxation times (DRTs) analyses were performed using the commercial software RelaxIS 3 (version 3.0.18.15, rhd instruments GmbH & Co. KG). The impedance spectra computed by the 3D electric network model are (almost) free of noise signals. The Kramers–Kronig test for these spectra yields residuals in the order of \(10^{-6}\). Thus, the results for all frequencies were considered in the analysis of the impedance spectra, and only a small regularization term was required in the calculation of each DRT.\(^{29}\)

3. RESULTS

3.1. Origin of the Constriction Contribution in the Impedance. To understand the origin of the dynamic constriction effect and its impact on the impedance, we compute a series of impedance spectra of the model system, as depicted in Figure 2b. The electrode and SE surface are of the same size \((A_{\text{electrode}} = A_{\text{SE}})\). The single square-shaped contact spot sandwiched between the square-shaped WE and the square-shaped sample surface is systematically varied in size \((A_{\text{contact}})\). The empty space between the WE and SE surface corresponds to the pore and constitutes a capacitor-like arrangement, i.e., WE→air→SE.

3.1.1. Impedance as Function of the Contact Area between the Electrode and SE. Figure 3a shows the impedance results for five different contact area sizes \(A_{\text{contact}}\) between the WE and SE. Without pores at the interface \((A_{\text{SE}} = A_{\text{electrode}} = A_{\text{contact}})\), the impedance consists of one semicircle only. The reduction of the contact area \((A_{\text{SE}} = A_{\text{electrode}} > A_{\text{contact}})\) however, leads to the formation of a second semicircle at lower frequency without affecting the high-frequency contribution to the impedance. Thus, the latter is independent of the contact area \(A_{\text{contact}}\) between the electrode and the SE and can be assigned to the bulk transport. The semicircle at low frequencies does not correspond to an additional electric microscopic transport process in the system. It solely arises due to the formation of pores at the interface and can be attributed to the resulting dynamic constriction effect.

The described behavior is also reflected in the corresponding DRTs\(^{29,30}\) of the five impedance spectra (see Figure 3b). The DRT consists of a single signal at \(\tau_{\text{bulk}}\) when there is a full contact between the SE and WE. A second signal at a longer relaxation time \(\tau_{\text{str}}\) emerges when the contact area is reduced. The amplitude and the time constant of the second signal increase upon reducing the contact area \(A_{\text{contact}}\).

The computed impedance spectra are fitted with a 1D equivalent circuit model consisting of two RC-elements connected in series to highlight the qualitative changes in the impedance (see Figure 3c). The bulk transport parameters (blue) are independent of the change in contact area \(A_{\text{contact}}\). In contrast, the constriction resistance \(R_{\text{str}}\) (yellow) shows a diverging behavior with decreasing contact area \((R_{\text{str}} \to \infty \text{ for } A_{\text{contact}} \to 0)\). The qualitative behavior is roughly consistent with that of a conductor \((R \sim 1/A_{\text{contact}})\). However, a simple functional relationship between constriction resistance \(R_{\text{str}}\) and contact area \(A_{\text{contact}}\) cannot be observed (c.f. Figure 6).

The computed constriction capacitance \(C_{\text{str}}\) (yellow) decreases with decreasing contact area \(A_{\text{contact}}\) (see Figure 3d). Since a decreasing contact area corresponds to an increase in pore volume at the interface, the corresponding geometric

---

**Figure 4.** Frequency-dependent change of the potential distribution in the system. Cross section of a model system, consisting of a metal WE (gray), pore volume (white), and the homogenous SE. Green arrows indicate the current distribution at various frequencies. At high frequencies (left), the pores at the interface are dielectrically shorted and the entire electrode area contributes to the transport. At low frequencies (right), the pores are insulating and the electrode area as well as the SE volume actively contributing to the transport is reduced. The penetration depth increases for lower frequencies leading to the frequency-dependent constriction resistance.
capacitance \( C_{\text{Pore}} \) of the pore volume (black) increases. For small contact areas, the constriction capacitance converges toward this pore capacitance (\( C_{\text{Cap}} \rightarrow C_{\text{Pore}} \) for \( A_{\text{Contact}} \rightarrow 0 \)). Consequently, the constriction capacitance can be used to roughly estimate the (average) depth of the pores.\(^{20-22}\)

The constriction time constant (\( \tau = R \cdot C \)) increases for a decreasing contact area, for instance, for a growing single planar pore \( A_{\text{Pore}} = A_{\text{Electrode}} - A_{\text{Contact}} \) (see Figure 3e). This behavior can be attributed to the larger change in the increasing constriction resistance \( R_{\text{Cap}} \) compared to the decreasing and converging constriction capacitance \( C_{\text{Cap}} \).

### 3.1.2. Understanding the Formation of the Constriction Signal in the Impedance

The formation of the constriction signal in the impedance spectrum for \( A_{\text{SE}} = A_{\text{Electrode}} > A_{\text{Contact}} \) can be understood as follows. An impedance spectrum is measured over an extended frequency range. The conduction response of the individual transport processes in the material (e.g., bulk or GB transport) is frequency-dependent. This also holds for the contribution of the capacitor-like pore at the interface. At high frequencies, the dielectric conduction response starts to dominate, short-circuiting the pores at the interface. As a result, the component of the potential gradient perpendicular to the macroscopic transport direction vanishes. This leads to horizontal equipotential lines perpendicular to the transport direction across the entire sample \( (A_{\text{Electrode, active}} = A_{\text{Electrode}}) \). It corresponds to a quasi-1D transport between the WE and counter electrode (CE) across the electrode area at high frequencies (see arrows in Figure 4 (left)). This situation allows a determination of the bulk transport parameters \( (\sigma_{\text{Bulk}}, \varepsilon_{\text{Bulk}}) \) without pronounced errors based on the cell geometry.\(^{20-25}\)

Upon frequency reduction in the impedance measurement, the conduction response of the individual transport processes changes from dielectric to electric conduction. Since the pores are insulating in this frequency range, the electrode area contributing to transport is reduced to the real contact area between the electrode and the SE \( (A_{\text{Electrode, active}} = A_{\text{Contact}}) \). Similar to the behavior of a conductor \( (R \sim 1/A) \), a smaller active electrode area leads to a larger resistance. Consequently, the frequency-dependent change of the active electrode area \( A_{\text{Electrode, active}} \) leads to the additional constriction contribution in the impedance spectrum.\(^{20-25}\)

The reduction of the active electrode area \( A_{\text{Electrode, active}} \) to the real contact area \( A_{\text{Contact}} \) also affects the potential distribution in the SE and creates a certain SE volume fraction in which lower local current densities are observed (see arrows in Figure 4 (center)). Charge transport near the interface occurs in this case in 3D and not in quasi-1D. An approximate measure of this effect is the penetration depth, which corresponds to the distance from the electrode where the equipotential lines below the electrode within the SE become horizontal again. The corresponding volume ranging from the interface down to the penetration depth is referred to as the constriction region. Since the penetration depth depends on the applied frequency \( \nu \) of the external exciting electric field (see arrows in Figure 4 (right)), the constriction effect is frequency-dependent.

The separation of the impedance into a bulk and a dynamic constriction contribution depends on the frequency, below which the pores at the interface cease to conduct dielectrically (cf. Figure 1c). If the pores are already insulating in the characteristic frequency range of the bulk transport, then both contributions cannot be separated from each other.\(^{22}\) The situation is then comparable to the static constriction effect, in the sense that it leads to a scaling of the individual impedance contributions (cf. Figure 1b). Consequently, the actual specific transport parameters of the bulk process can no longer be determined correctly in this case.

In summary, the frequency-dependent change of the active electrode area \( A_{\text{Electrode, active}} \) and the associated change of the SE volume involved in the transport leads to additional impedance contributions in the spectrum. Thus, a semantic distinction between contact area \( A_{\text{Contact}} \) and electrode area \( A_{\text{Electrode}} \) is necessary to adequately describe the impedance behavior with respect to the dynamic constriction effect. The electrode area \( A_{\text{Electrode}} = E_x E_y \) describes the cross section of...
the electrode to which a potential is applied. The contact area $A_{\text{contact}}$ describes the portion of the electrode area that is in physical contact with the SE. The contact area is often smaller than the electrode area ($A_{\text{contact}} < A_{\text{electrode}}$) due to the mechanic properties of both solids involved, i.e., not the entire solid electrolyte surface is in contact with the metal electrode unlike liquid electrolytes that mostly wet the entire electrode surface.

3.2. Dependence of the Constriction Characteristics on the Interface Morphology. The time constant $\tau_{\text{Cstr}}$ of the constriction contribution has a major influence on the shape of the impedance spectrum (cf. Figure 1c) and, consequently, on the conclusions about the experimentally or theoretically studied system drawn from the impedance analysis. Therefore, further investigations are required considering more realistic systems. In the following, we systematically vary the electrode geometry according to Figure 2c, the interface morphology according to Figure 2d, and the properties of the pores ($\delta_{\text{int}}$) or, more general, insulating inclusions (permittivity $\varepsilon_{\text{int}}$) according to Figure 2e.

3.2.1. Impact of the Electrode Size on the Constriction Effect. First, we will study the impact of the electrode size on the transport behavior of the model system depicted in Figure 2c. Prior to analyzing the data, it should be noted that different electrode sizes $A_{\text{electrode}}$ can lead to different types of constriction effects. A larger surface area of the SE than the electrode area ($A_{\text{SE}} > A_{\text{electrode}} = A_{\text{contact}}$) will always lead to a static constriction since the available pathways through the structure are restricted at the interface. Solely dynamic constriction occurs in the system, when the electrode area is larger than the contact area between the SE and electrode ($A_{A_{\text{SE}} = A_{\text{electrode}} > A_{\text{contact}}}$). In this case, the transport paths are only constrained in a specific frequency range. A superposition of both static and dynamic constriction effects will occur when other relations between the three areas hold, e.g., $A_{\text{SE}} > A_{\text{electrode}} > A_{\text{contact}}$.

As can be seen in Figure 5a, many variations of the superimposed case (left) and the pure static (top right) and dynamic (bottom right) case can be anticipated. Thus, a semantic distinction between absolute contact area $A_{\text{contact}}$ and relative contact area $A_{\text{contact}}/A_{\text{electrode}}$ is beneficial but not mandatory when considering the two pure effects. The change in absolute contact area also results in a change in relative contact area in the case of the dynamic effect, while the relative contact area is always maintained ($= 1$) in the static situation.

Figure 5b shows the impedance results for five different electrode sizes $A_{\text{electrode}}$ at constant relative contact area $A_{\text{contact}}/A_{\text{electrode}}$. Again, all impedance spectra are normalized to the same bulk contribution to not include the quantitative scaling due to the static constriction effect. Also, in this situation, there are significant changes in the dynamic constriction contribution visible in the normalized impedance spectra. The increase in the electrode size $A_{\text{electrode}}$ and the accompanying increase in the absolute contact area $A_{\text{contact}}$ lead to a decrease in the normalized dynamic constriction contribution.

Both series of impedance spectra underline that neither the relative contact area $A_{\text{contact}}/A_{\text{electrode}}$ nor the absolute contact area $A_{\text{contact}}$ alone is sufficient as a descriptor for the constriction effect. Consequently, larger electrodes and also larger absolute contact areas do not necessarily reduce the area-specific constriction resistance. Similarly, equal relative contact areas do not necessarily lead to equal constriction contributions.

3.2.2. Effect of the Distribution of the Contact Area at the Interface. We will now turn to morphology effects, i.e., the effect of the distribution of the contact area at the interface $A_{\text{contact}}$ which is known to have a huge influence on the constriction effect.15 Mapping the real interface morphology in experiments is challenging since it is hardly accessible. The methods commonly used for characterizing interfaces in all-solid-state batteries are transmission electron microscopy or focused ion beam scanning electron microscopy. Both are destructive and cannot be employed in situ on realistic structures. Thus, they usually can only provide static snapshots of a local region of the interface and thus little statistical information.

Obviously, pores are usually distributed over the entire electrode surface and their shapes and sizes can vary locally. Such disorder and inhomogeneities significantly affect the potential distribution within the system and are therefore expected to influence the shape of the impedance contribution due to constriction. To study the influence of individual morphology effects in more detail and to restrict the number of geometric parameters describing the pore distribution, we will analyze two simplified model cases depicted as insets in Figure 6. Instead of one contact spot centered in the interface layer, we will study two effects:
systems. The variations of the depth of the pores and their permittivity result in a change of the constriction capacity that is identical to that of a plate capacitor. 

First, we will solely vary the position of the contact spot sandwiched between the electrode and the SE surface, while the contact area \( A_{\text{contact}} \) is kept constant. Furthermore, we set \( A_{\text{SE}} = A_{\text{electrode}} \) i.e., there is no static constriction effect that affects the computational results. The impedance spectra derived from the 3D electric network model (see Figure 6a) highlight that the larger the distance between the center of the contact spot and the center of the sample, the more pronounced is the dynamic constriction contribution to the impedance. The reason is that moving the single contact spot away from the central position leads to an increased penetration depth and a lower volume involved in the transport. Thus, a larger constriction resistance \( R_{\text{Cstr}} \) arises. The constriction capacitance \( C_{\text{Cstr}} \), however, is almost unaffected. The combined behavior yields a longer time constant \( \tau_{\text{Cstr}} \) when the distance of the contact spot from the sample center increases. When the contact spot is located at the sample center, all distances between the edges of the spot and the edges of the SE are minimized, the size of the constriction region is reduced, and the volume contributing to the transport at low frequencies is maximized. Therefore, the constriction resistance \( R_{\text{Cstr}} \) is minimal in the modeling.

Second, we divide up the contact spot into a number of regularly arranged smaller contacts of the same contact area \( A_{\text{contact}} \). The impedance spectra in Figure 6b show that the dynamic constriction contribution to the impedance decreases with an increasing number of contact spots. The reason is that a finer distribution of the contact area \( A_{\text{contact}} \) increases the contact surface to pore volume ratio at the interface and minimizes the distances between the centers of the contact spots and the centers of the pores. Thus, the penetration depth into the SE decreases leading to an increase in the volume contributing to the transport and a decrease in the constriction resistance \( R_{\text{Cstr}} \). The impact on the constriction capacitance \( C_{\text{Cstr}} \) is small as the capacitor-like pore area \( A_{\text{pore}} = A_{\text{SE}} - A_{\text{contact}} \) is the same in all cases and the pores act, to a first approximation, as capacitors connected in parallel. Due to the reduction of the resistance \( R_{\text{Cstr}} \) with increasing fineness of the pore distribution, the time constant \( \tau_{\text{Cstr}} \) shifts toward smaller relaxation times compared to the single contact case.

The discussion of the interface morphology highlights that a sole rearrangement of the contact spot(s) for a given contact area \( A_{\text{contact}} \) will already yield a different dynamic constriction behavior. Therefore, it is challenging to derive any (simple) functional relationship between the constriction parameters \((R_{\text{Cstr}} \text{ and } C_{\text{Cstr}}) \) and the contact area \( A_{\text{contact}} \).

3.2.3. Effect of the Pore Characteristics at the Interface. Finally, we address the impact of the pore properties or, more general, of insulating inclusions. The constriction effect in the case of lithium metal in contact with LLZO is caused by the formation of pores at the interface. Pores, however, are not necessarily required to cause dynamic current constriction. The continuous formation of a spatially heterogeneous insulating layer such as a highly resistive SEI at the interface can also lead to current constriction. The same holds true for the time-dependent depletion of charge carriers at the interface due to the finite diffusion coefficient of the electrode material. Hence, it is worth knowing how different (pore) permittivities \( \varepsilon_{\text{int}} \) and pore depths \( \delta_{\text{int}} \) may affect the dynamic constriction phenomenon.

Both parameters do not influence the constriction resistance \( R_{\text{Cstr}} \), but the constriction capacitance is proportional to the permittivity of the pores or inclusions \((C_{\text{Cstr}} \sim \varepsilon_{\text{int}}) \) and inversely proportional to the pore depths \((C_{\text{Cstr}} \sim 1/\delta_{\text{int}}) \). It should be emphasized that the qualitative changes are the same as those of a plate capacitor (see Figure 7). The time constant \( \tau_{\text{Cstr}} \) shifts toward larger relaxation times for larger permittivity and toward smaller relaxation times for larger pore depth. It suggests that a local variation of the pore depth at the interface results in a distribution of time constants. Thus, a distortion of the low-frequency contribution of the impedance in the Nyquist representation is expected. As a consequence, the shape of the impedance spectrum provides first indications about the homogeneity of the interface.

The discussed dependence of the constriction impedance on the pulse characteristics shows that certain pore depths cannot be resolved experimentally with IS. Deep pores have a small time constant, which may well be in the range of bulk transport, leading to a transport behavior comparable to static constriction and a quantitative scaling of individual impedance signals. Thus, the impact of constriction is not separable from the individual impedance contributions of the transport signals. In contrast, shallow pores show large relaxation times, which may correspond to characteristic frequencies outside the typical frequency range of IS, i.e., these pores remain dielectrically conductive in the measurement range between MHz and several Hz. Therefore, it is possible that the IS data will not significantly differ from an ideal contact, if the
constriction impedance is not within the chosen frequency interval. Unfortunately, it is not possible to give a universal value for the lower detection limit of pores since constriction as a geometric phenomenon also depends on various other parameters such as the interface morphology or the sample dimensions.

4. SUMMARY AND CONCLUSIONS

The following recommendations for the analysis of experimental impedance results can be derived from the 3D modeling of metal anodes with constriction effect:

- The interface contribution to the impedance is, in general, composed of a (true) charge transfer and a dynamic constriction contribution. Current constriction is not a self-contained type of migration process in the strict sense, i.e., it is not comparable to electric grain boundary or bulk transport. Rather, the dynamic constriction contribution in the impedance is related to the frequency-dependent change of the electrode area actively contributing to the transport (electrode area ↔ contact area), representing the frequency-dependent role of dielectric charge transfer across purely capacitive regions (e.g., pores or insulating interlayer patches) at the interface. It is a geometric effect that must be expected at different length scales.

- The constriction phenomenon is mainly affected by the SE volume near the interface (constriction region). The distance from the interface to the compensation of the constriction (penetration depth) is, in general, a function of the frequency.

- The spatial distribution of the contact area at the interface has a significant impact on the penetration depth into the SE. This is accompanied by a change in the fraction of the SE volume that contributes to the transport at low frequencies. A larger SE volume contributing leads to a lower constriction resistance $R_{\text{constr}}$. Consequently, it is challenging to derive a simple relationship between constriction resistance and contact area.

- The constriction capacity is influenced by the morphology of the interface, e.g., the shape of the pores and the distribution of the contact area. Its behavior is identical to that of a plate capacitor ($C_{\text{constr}} \sim \varepsilon_{\text{tot}}/d_{\text{tot}}$) when the depth of the pore(s) and its permittivity change. The constriction capacitance converges against the geometric capacitance of the macroscopic pore at the interface when the contact area $A_{\text{contact}}$ goes to zero.

The 3D electric network model presented allows the systematic study of morphology changes at the electrode/sample interface and their influence on the impedance response of the system. The constriction contribution in the impedance results from, e.g., pores or inclusions at the interface, whose conductive behavior changes from dielectrically conductive to insulating with decreasing frequency of the external electric field. The dynamic constriction phenomenon is solely a geometric effect, and its impact (e.g., size of the constriction region or even the effective contact area) is not constant but depends on the excitation frequency. The phenomenon may have its origin on various length scales of the system ranging from mesoscopic to macroscopic. Thus, the “interface impedance” in the case of many solid/solid interfaces is more than a pure charge transfer step as it is often assumed in the literature. Therefore, the term interface impedance should be avoided; instead, it is better to classify the interface contribution to the impedance spectrum according to its origin as charge transfer contribution or constriction contribution.

Overall, the network model used is a powerful tool to gain a better understanding of experimental impedance data. It may provide valuable insight into the microscopic processes occurring within the considered electrochemical cell, e.g., at the WE/SE interface. Making full use of the strength of the modeling requires reliable structural information of the interfaces and layers comprising the sample. Thus, a careful structural analysis of the specimens studied is essential and must accompany the theoretical analysis of the impedance data. Theory alone can only point out qualitative trends arising from changes of material parameters or specific morphological changes, whereas the combined analysis will yield more valuable information, e.g., on the correlation between pore formation and dynamics at the metal anode interface of all-solid-state batteries. Such an approach may have the potential for the targeted monitoring of hidden morphological changes at the metal/SE interface at the mesoscopic level and, thus, for a kind of “state-of-health” control system in applications. However, this vision requires more systematic combined experimental and theoretical studies on model systems with a high degree of control over the interfacial morphology.

# AUTHOR INFORMATION

Corresponding Author

Janis K. Eckhardt — Institute for Theoretical Physics and Center for Materials Research (ZfM), Justus Liebig University, D-35392 Giessen, Germany; @ orcid.org/0000-0002-2799-0599; Email: janis.k.eckhardt@theo.physik.uni-giessen.de

Authors

Peter J. Klar — Center for Materials Research (ZfM) and Institute of Experimental Physics I, Justus Liebig University, D-35392 Giessen, Germany; @ orcid.org/0000-0002-4513-0330

Jürgen Janek — Center for Materials Research (ZfM), Justus Liebig University, D-35392 Giessen, Germany; Institute of Physical Chemistry, Justus Liebig University, D-35392 Giessen, Germany; @ orcid.org/0000-0002-9221-4756

Christian Heiliger — Institute for Theoretical Physics and Center for Materials Research (ZfM), Justus Liebig University, D-35392 Giessen, Germany

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.2c07077

Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

We greatly appreciate helpful discussions with Till Fuchs and Simon Burkhard. We acknowledge computational resources provided by the HPC Core Facility and the HRZ of the Justus-Liebig-University Giessen. We would like to thank MSc. Philipp Ristus and Dr. Marcel Giar of HPC-Hessen, funded by the State Ministry of Higher Education, Research, and the Arts (HMWK), for programming advice. Financial support is provided by the DFG via the GRK (Research Training...
Group) 2204 “Substitute Materials for Sustainable Energy Technologies”.

REFERENCES

(1) Takeda, Y.; Yamamoto, O.; Imanishi, N. Lithium Dendrite Formation on a Lithium Metal Anode from Liquid, Polymer and Solid Electrolytes. *Electrochemistry* 2016, 84, 210–218.

(2) Tarascon, J. M.; Armand, M., Issues and challenges facing rechargeable lithium batteries. In *Materials for Sustainable Energy*; Co-Published with Macmillan Publishers Ltd: UK: 2010; pp. 171–179.

(3) Xu, K. Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. *Chem. Rev.* 2004, 104, 4303–4418.

(4) Janek, J.; Majoni, S. Investigation of Charge Transport Across the Ag/AgI-interface: (1) Occurrence of Periodic Phenomena During Anodic Dissolution of Silver. *Ber. Bunsenges. Phys. Chem.* 1995, 99, 14–20.

(5) Schmalzried, H.; Janek, J. Chemical kinetics of phase boundaries in solids. *Ber. Bunsenges. Phys. Chem.* 1998, 102, 127–143.

(6) Murugan, R.; Thangadurai, V.; Weppner, W. Fast Lithium Ion Conduction in Garnet-Type Li$_2$La$_2$Zr$_2$O$_12$: *Angew. Chem., Int. Ed.* 2007, 46, 7778–7781.

(7) Zhu, Y.; Connell, J. G.; Tepavcevic, S.; Zapol, P.; Garcia-Mendez, R.; Taylor, N. J.; Sakamoto, J.; Ingram, B. J.; Curtiss, L. A.; Freeland, J. W.; Fong, D. D.; Markovic, N. M. Dopant-Dependent Stability of Garnet Solid Electrolyte Interfaces with Lithium Metal. *Adv. Energy Mater.* 2019, 9, 1803440.

(8) Connell, J. G.; Fuchs, T.; Hartmann, H.; Krauskopf, T.; Zhu, Y.; Sann, J.; Garcia-Mendez, R.; Sakamoto, J.; Tepavcevic, S.; Janek, J. Kinetic versus Thermodynamic Stability of LLZO in Contact with Lithium Metal. *Chem. Mater.* 2020, 32, 10207–10215.

(9) Zhu, Y.; He, X.; Mo, Y. Origin of Outstanding Stability in the Lithium Solid Electrolyte Materials: Insights from Thermodynamic Analysis Based on First-Principles Calculations. *ACS Appl. Mater. Interfaces* 2015, 7, 23685–23693.

(10) Eckhardt, J. K.; Burkhardt, S.; Zahnow, J.; Elm, M. T.; Janek, J.; Klar, P. J.; Heiliger, C. Understanding the Impact of Microstructure on Charge Transport in Polycrystalline Materials Through Impedance Modelling. *J. Electrochem. Soc.* 2021, 168, No. 090516.

(11) Krauskopf, T.; Hartmann, H.; Zeier, W. G.; Janek, J. Toward a Fundamental Understanding of the Lithium Metal Anode in Solid-State Batteries—An Electrochemo-Mechanical Study on the Garnet-Type Solid Electrolyte Li$_{25}$Al$_{63}$La$_2$Zr$_2$O$_{12}$. *ACS Appl. Mater. Interfaces* 2019, 11, 14463–14477.

(12) Sharati, A.; Kaziyak, E.; Davis, A. L.; Yu, S.; Thompson, T.; Siegel, D. J.; Dasgupta, N. P.; Sakamoto, J. Surface Chemistry Mechanism of Ultrafast Interfacial Resistance in the Solid-State Electrolyte Li-La$_2$Zr$_2$O$_{12}$. *Chem. Mater.* 2017, 29, 7961–7968.

(13) Gao, J.; Guo, X.; Li, Y.; Ma, Z.; Guo, X.; Li, H.; Zhu, Y.; Zhou, W. The Ab Initio Calculations on the Areal Specific Resistance of Li-Metal/Li$_2$La$_2$Zr$_2$O$_{12}$ Interface. *Adv. Theory Simul.* 2019, 12, 1900028.

(14) Holm, R., *Electric Contacts: Theory and Application*; Springer Verlag: 1967; p 484, DOI: 10.1007/978-3-662-06688-1_88.

(15) Slade, P. G., *Electrical contacts: principles and applications*; CRC press: 2017; p 1311, DOI: 10.1201/b15640.

(16) Denhoff, M. W. An accurate calculation of spreading resistance. *J. Phys. D: Appl. Phys.* 2006, 39, 1761–1765.

(17) Kennedy, D. P. Spreading Resistance in Cylindrical Semiconductor Devices. *J. Appl. Phys.* 1960, 31, 1490–1497.

(18) Mazur, R. G.; Dickey, D. H. A Spreading Resistance Technique for Resistivity Measurements on Silicon. *J. Electrochem. Soc.* 1966, 113, 255.

(19) Zhang, P.; Lau, Y. Y.; Timsit, R. S. On the Spreading Resistance of Thin-Film Contacts. *IEEE Trans. Electron Devices* 2012, 59, 1936–1940.

(20) Fleig, J.; Maier, J. Finite element calculations of impedance effects at point contacts. *Electrochem. Acta* 1996, 41, 1003–1009.

(21) Fleig, J.; Maier, J. Point contacts in solid state ionics: finite element calculations and local conductivity measurements. *Solid State Ionics* 1996, 86–88, 1351–1356.

(22) Fleig, J.; Maier, J. The Influence of Laterally Inhomogeneous Contacts on the Impedance of Solid Materials: A Three-Dimensional Finite-Element Study. *J. Electrochem. Soc.* 1997, 1, 73–89.

(23) Fleig, J.; Maier, J. Rough electrodes in solid and liquid electrochemistry: impact of morphology on the impedance. *Solid State Ionics* 1997, 94, 199–207.

(24) Fleig, J.; Maier, J. The Influence of Current Constriction on the Impedance of Polarizable Electrodes: Application to Fuel Cell Electrodes. *J. Electrochem. Soc.* 1997, 144, L302–L305.

(25) Fleig, J.; Maier, J. Finite-Element Calculations on the Impedance of Electroceramics with Highly Resistive Grain Boundaries: I, Laterally Inhomogeneous Grain Boundaries. *J. Am. Ceram. Soc.* 1999, 82, 3485–3493.

(26) Rettenwander, D.; Welzl, A.; Cheng, L.; Fleig, J.; Musso, M.; Suard, E.; Doeff, M. M.; Redhammer, G. J.; Amthauer, G. Synthesis, Crystal Chemistry, and Electrochemical Properties of Li$_{25}$La$_2$Zr$_2$Mo$_{12+}$ (x = 0.1–0.4): Stabilization of the Cubic Garnet Polymorph via Substitution of Zr$^{4+}$ by Mo$^{6+}$. *Inorg. Chem.* 2015, 54, 10440–10449.

(27) Loho, C.; Djenadic, R.; Bruns, M.; Clemens, O.; Hahn, H. Garnet-Type Li-La$_2$Zr$_2$O$_{12}$ Solid Electrolyte Thin Films Grown by CO$_2$-Laser Assisted CVD for All-Solid-State Batteries. *J. Electrochem. Soc.* 2017, 164, A6131.

(28) Boukamp, B. Electrochemical impedance spectroscopy in solid state ionics: recent advances. *Solid State Ionics* 2004, 169, 65–73.

(29) Wan, T. H.; Saccoccio, M.; Chen, C.; Ciucci, F. Influence of the Discretization Methods on the Distribution of Relaxation Times Deconvolution: Implementing Radial Basis Functions with DRTools. *Electrochim. Acta* 2015, 184, 483–499.

(30) Ivers-Tiffée, E.; Weber, A. Evaluation of electrochemical impedance spectra by the distribution of relaxation times. *J. Ceram. Soc. Jpn.* 2017, 125, 193–201.

(31) Otto, S.-K.; Fuchs, T.; Moryson, Y.; Lerch, C.; Mogwitz, B.; Sann, J.; Janek, J.; Henss, A. Storage of Lithium Metal: The Role of the Native Passivation Layer for the Anode Interface Resistance in Solid State Batteries. *ACS Appl. Energy Mater.* 2021, 4, 12798–12807.

(32) Krauskopf, T.; Mogwitz, B.; Rosenbach, C.; Zeier, W. G.; Janek, J. Diffusion Limitation of Lithium Metal and Li–Mg Alloy Anodes on LLZO Type Solid Electrolytes as a Function of Temperature and Pressure. *Adv. Energy Mater.* 2019, 9, 1902568.

(33) Krauskopf, T.; Richter, F. H.; Zeier, W. G.; Janek, J. Physicochemical Concepts of the Lithium Metal Anode in Solid-State Batteries. *Chem. Rev.* 2020, 120, 7745–7794.