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Ion transport limitations in all-solid-state lithium battery electrodes containing a sulfide-based electrolyte

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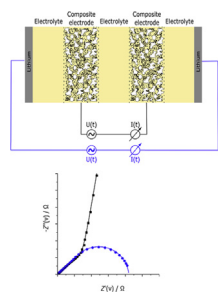
HIGHLIGHTS

- Ion transport limitations in composite electrodes for all-solid-state batteries is studied.
- Tortuosities are determined by means of impedance spectroscopy.
- Resistances are calculated based on a transmission-line model or from Li + ion current.
- Power density of solid-state should at least equal that of liquid-based batteries.

GRAPHICAL ABSTRACT



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ABSTRACT

We study ion transport limitations in composite electrodes for all-solid-state lithium batteries. These electrodes are composed of variable volume fractions of active material particles ($Li_4Ti_5O_{12}$) and of a sulfide-based solid electrolyte, while the volume fraction of carbon black acting as conductive additive is held constant. The ion transport limitations are characterized by impedance spectroscopic measurements on different types of symmetrical solid-state cells. Ion transport resistances are calculated either based on a transmission line model or from the Li^+ ion current under electron-blocking conditions. In addition, we demonstrate a cell setup, for which both types of measurements can be carried out on the same composite electrodes. Effective ion transport tortuosities τ_{eff} are then derived from the resistance values and analyzed in dependence on the volume fraction of the solid electrolyte in the composite electrodes, ε . We show that for $\varepsilon \geq 0.4$, both methods yield very similar tortuosity values, while discrepancies between the results obtained from the two methods are found for $\varepsilon < 0.4$. Our results give strong indication that the power density of solid-state batteries with volume fractions ε around 0.4 of the best solid Li^+ electrolytes should be at least equal that of commercial liquid electrolyte-based Li-ion batteries.

1. Introduction

All-solid-state Li batteries (ASSLBs) are promising candidates as next-generation energy source in electric vehicles (EVs). In comparison to conventional Li-ion batteries containing liquid electrolytes, ASSLBs exhibit potentially higher energy and power densities [1–3]. The electrodes in high-energy ASSLBs are typically composites, consisting of mixtures of a Li storage material (active material), a solid electrolyte and a conductive additive, like carbon black. A prerequisite for a high power density is a fast transport of ions and electrons inside the composite [4]. While electronic transport is typically not an issue, when the composite electrode contains a conductive additive, the ionic transport

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is indeed a critical factor for the battery performance. The ion transport resistance depends on the ionic conductivity of the solid electrolyte as well as on the morphology of the composite electrode, which determines the structure of the ion transport pathways. A quantity describing the effectiveness of the ion transport is the effective tortuosity τ_{eff}. In an ideal composite electrode structure, where the ions migrate across straight pathways with uniform diameter, the effective tortuosity τ_{eff} is unity. However, in a real electrode, the ion transport pathways are longer than in the ideal case, and bottlenecks (constrictivities) exist along the pathways. This leads to effective tortuosities > 1.

In general, the tortuosity increases strongly with decreasing volume fraction of the conducting phase, ε [4–9]. Therefore, it is expected that a low volume fraction of the solid electrolyte in a composite electrode leads to slow ion transport and to a high effective tortuosity. On the other hand, a low volume fraction of the solid electrolyte and a high volume fraction of the active materials is advantageous for the energy density. Therefore, it is important to find an optimal composition of the electrode, which gives the best compromise between fast ion transport and high energy density. To this end, ion transport tortuosities of real electrodes in dependence on the volume fraction of the electrolyte, ε , have to be determined.

This was done for a wide range of lithium-ion battery electrodes filled with liquid electrolytes: Thorat et al. used stationary Li^+ current measurements to determine the effective tortuosities of laboratory-made $LiFePO_4$ and $LiCoO_2$ electrodes. Their effective tortuosities ranged from 2.5 to 3.5 for volume fractions ε ranging from 0.57 to 0.30 [10]. Landesfeind et al. conducted transmission line-type impedance measurements in order to determine the effective tortuosities of various laboratory-made electrodes with $LiFePO_4$, graphite, $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ as active materials. They obtained effective tortuosities between 3 and 7 for ε ranging from 0.7 to 0.3 [9]. Inoue and Kawase evaluated the ion transport in a $LiCoO_2$ composite electrode with $\varepsilon = 0.28$ employing transmission line-type impedance measurements as well as random walk simulations on a reconstructed subvolume of the electrode. The obtained effective tortuosities were 3.1 from the impedance measurements and 4.7 from the simulations, respectively [11]. Ender et al. analyzed a commercial $LiFePO_4$ high-power cathode with $\varepsilon = 0.38$ b y means of focused ion beam combined with scanning electron microscopy (FIB-SEM). Ion transport simulations in the reconstructed volume of the electrode yielded an effective tortuosity value of 2.1, which is sufficient for power density requirements of commercial batteries [12].

On the other hand, there is only very limited data available for composite electrodes containing solid electrolytes. Siroma et al. determined the ionic and electronic resistance of composite electrodes consisting of an amorphous Li_2S-P_2S_5 solid electrolyte (SE) and either of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ particles or of graphite particles as active material. When the volume fraction of the solid electrolyte, ε, was reduced from 0.5 to 0.3, the effective tortuosity of the ion transport increased from about 3 to about 10. However, unknown high-frequency processes complicated the analysis of the impedance spectra [13], leading to relative large uncertainties of the ion transport resistance at low volume fractions of the SE. Zhang et al. built composite $LiCoO_2/Li_7La_3Zr_2O_{12}$ electrodes with an electrolyte weight ratio of 0.25–0.75. The ionic conductivity was evaluated by DC polarization measurements and was found to be below $10^{-10}\ S{\cdot}cm^{-1}$. Thus, the resulting effective tortuosity was very large ($> 10^6$) [14]. Due to the limited amount of data, it is not yet clear at present, what values for the effective ion transport tortuosities are achievable for ε values around 0.3–0.4, which are desirable for high-energy ASSLBs.

In this paper, we study the relation between effective tortuosity and volume fraction of the solid electrolyte for a typical composite electrode system. The composite electrodes consist of the active material $Li_4T_5O_{12}$, of the solid electrolyte $Li_7P_2S_8I$, and of carbon black as conductive additive. The preparation is based on ball milling of the materials and subsequent compression under high pressure. The volume fraction of the solid electrolyte, ε, is varied between 0.3 and 0.66. In order to determine the effective ion transport tortuosity τ_{eff}, we measure the impedance spectra of three different symmetrical cells: (i) Composite electrode | solid electrolyte | composite electrode. In this setup, a transmission line model (TLM) is used for the analysis of the impedance spectra. (ii) Li metal | solid electrolyte | composite electrode | solid electrolyte | Li metal. In this setup, the Li ion transport resistance of the composite under electron-blocking conditions is measured and used for calculating τ_{eff}. (iii) The third cell lithium metal | electrolyte | composite electrode | electrolyte | composite electrode |electrolyte | lithium metal is used for carrying out both types of measurements on the *same* composite electrodes. We find that for volume fractions $\varepsilon \geq 0.4$, the results obtained for τ_{eff} in the two setups are very similar, while there are discrepancies at $\varepsilon < 0.4$. We discuss the dependence of the effective ionic conductivity of the composite electrodes on the volume fraction of the SE and compare the results to electrodes for conventional Li-ion batteries filled with liquid electrolyte.

2. Theory

2.1. Effective ion transport tortuosity and Bruggeman relation

The effective ionic conductivity of a composite electrode, $\sigma_{ion,eff}$ is given by:

$$\sigma_{ion,eff} = \frac{d_{composite}}{R_{ion}{\cdot}A_{composite}} \tag{1}$$

Here, R_{ion} denotes the ion transport resistance of the composite electrode, while $d_{composite}$ and $A_{composite}$ are the thickness and the area of the composite, respectively. is related to the ionic conductivity of the pure solid electrolyte, $\sigma_{ion,electrolyte}$, via:

$$\sigma_{ion,eff} = \sigma_{ion,electrolyte}\frac{\varepsilon}{\tau_{eff}} \tag{2}$$

with ε and τ_{eff} denoting the volume fraction of the solid electrolyte and the effective ion transport tortuosity, respectively. The relation between the volume fraction and the effective tortuosity is often described by the empirical Bruggeman relation:

$$\tau_{eff} = \varepsilon^{-\alpha} \tag{3}$$

with the Bruggeman exponent α. For high volume fractions of a homogeneous electrolyte filling the pore space between spherical particles, the exponent is $\alpha = 0.5$ [5,8,9].

2.2. Determining the ion transport resistance based on the transmission line model

One method for determining the ion transport tortuosity of a composite electrode is based on the transmission line model (TLM) without Faradaic reactions [9,15,16]. In this case, the state of charge of the active material is chosen such that the charge transfer resistance at the interface between solid electrolyte and active material is very high. If, in addition, the electronic resistance of the composite electrode is negligible, the resulting TLM equivalent circuit is illustrated in Fig. 1 [16]. The total ion transport resistance is given by $R_{ion} = d_{composite}{\cdot}r_{ion}{\cdot}\pi{\cdot}r^2 \div (A_{composite}{\cdot}\varepsilon)$. Here r_{ion} denotes the electrolyte resistance per unit length and r is the radius of the pore. The interface between active material and electrolyte is described by the total double layer capacitance $C_{dl} = c_{dl}{\cdot}2{\cdot}d_{composite}{\cdot}A_{composite}{\cdot}\varepsilon \div r$. In this case, the impedance of the composite electrode, $Z_{composite}$, is given by:

$$Z_{composite} = \sqrt{\frac{R_{ion}}{i\omega C_{dl}}}\coth\sqrt{R_{ion}i\omega C_{dl}} \tag{4}$$

Here, i and ω are the imaginary unit number and the angular frequency, respectively. Non-idealities in the double layer formation can be taken into account by replacing the capacitors in Fig. 1 by constant phase

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