Ionic Conductivity, Li+ Transference Number, and Diffusion Coefficient of a Solid-State Electrolyte Composite

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Abstract

The design of solid-state electrolyte (SSE) composites involves the fundamental study of transport properties, such as ionic conductivity. This transport property is influenced by the transport mechanisms of the charge species inside the composite, such as diffusion and migration. In this work, we perform the measurement of these three parameters through defined techniques. The resulting parameters were: ionic conductivity, the diffusion coefficient, and the Li+ transference number.

Keywords: SSE composite, ionic conductivity, diffusion coefficient, Li+ transference number .

1 Introduction

Solid-state batteries (SSBs) are a promising energy storage technology for the future energy concerns. Solid-state electrolyte (SSE) composites are the core element SSBs. Different research works on SSEs have demonstrated potential advantages can be obtained from a composite made of polymer (e.g., PEO), ceramics, (e.g., LLZO), salts, (e.g., LiTFSI, $LiNO_3$), and plasticizer (e.g., TEGDME). One of the transport properties a SSE composite must have to be attractive in a SSB is a good ionic conductivity at room temperature.

The ionic conductivity of an SSE composite depends on the concentration of free Li ions and their mobility [1]. Ionic conductivity is the movement of ions by the result of diffusion and migration of the ionic species. The migration describes the effect of the electric field on the transport of the ionic species. The diffusion describes the effect of the non-uniform salt concentration on the transport of the ionic species [2].

The SSE composite contains LiTFSI and $LiNO_3$ as a Li-ion source of this solid electrolyte. The dissociation of this salt forms TFSI-, NO3-, and Li+.

The driving of a good composite is based on the resulting ionic conductivity and transport coefficients because they will impact battery performance. The objective of this work is to estimate the ionic conductivity, Li+ transference number, and diffusion coefficient of an SSE composite which contains a mixed of salts.

2 Materials and Method

2.1 Materials

A stand-alone SSE film was made by infiltrating SSE, a composite solution of PEO, LiTFSI, $LiNO_3$, and TEGDME, into a polymer skeleton of PAN and PMMA. The achieved thickness was 0.0060 cm.

2.2 Methods

The techniques used to estimate the ionic conductivity coefficient, Li+ transference number, and salt diffusion coefficient of the SSE composite film are described as following.

2.2.1 Ionic conductivity

The electrochemical impedance spectroscopy (EIS) along with the blocking electrode technique have been applied in solid-state batteries to measure the charge transport properties such as ionic conductivity and performance of the constituent materials [3].

2.2.2 Li+ transference number

The Evans–Vincent–Bruce method [4] combines alternating current (AC) impedance and direct current (DC) polarization measurement to calculate the Li+ transference number (t_{Li+}).

The direct polarization consists of polarizing the cell at a very low potential value. The current is recorded

during this constant voltage. The current profile has a peak and then it reaches a steady-state where the net velocities of the anions must be zero but the net velocities of the cation is dictated by the imposed current [2].

The t_{Li+} range goes from 0 to 1. t_{Li+} is the fraction of the current carried out by the cation from the total applied current by migration in the absence of concentration gradient [4]. In other words, the conductivity is mainly accomplished by the cation [4].

From a DC polarization test, the initial and steady-state current can be recorded. From AC impedance before and after a direct current voltage polarization is obtained the initial interfacial resistance and the steady-state interfacial resistance.

2.2.3 Salt diffusion coefficient

A method called restricted diffusion is used to estimate the salt diffusion coefficient (D_s) [5, 6]. The D_s indicates how easy the cations move in the electrolyte due to a concentration gradient.

Experimentally, a constant current is applied to the cell for enough time to construct a salt concentration gradient. Then, the current is interrupted, and the potential is monitored while the concentration profiles relax. Then, a natural logarithm of potential versus time is plotted.

3 Results and Discussion

3.1 Ionic conductivity

A symmetric cell with stainless steel (SS) SS|SSE|SS was made of 6.25 cm² and 5.06 cm² SS electrodes, 0.2 mL of 25 mM LiTFSI in TEGDME electrolyte to wet the 6.25 cm² and 60 µm SSE composite layer, and a pouch plastic bag to hold and protect the cell. A weight above the cells was used to make a better contact of the materials. Using a Bio-Logic SP-200 equipment, the EIS was run. The frequency range used was 10 mHz to 3 MHz with a perturbation of 10 mV.

The ionic conductivity was calculated according to Eq. (1). This equation [7] relates the surface area A in cm², the bulk resistance of the electrolyte R_b in Ω, the

thickness of the composite in cm, and the conductivity k in S/cm.

$$k = \frac{L}{A * R_b} \qquad (1)$$

A higher conductivity of 10^{-3} S/cm at room temperature is desirable to the charging/discharging steps of a battery [8].

The Nyquist plot obtained from the EIS method in the SS|SSE|SS symmetric cell is shown in Figure 1. The impedance observed in the Nyquist plot indicates that the corresponding equivalent circuit is the Randles circuit modified with a constant phase element. It is observed the electrolyte resistance (R_b), the charge transfer resistance (R_{ct}), the constant phase element (CPE), and the Warburg (W) elements.

With the software in the BioLogic equipment, a semi-circle fit was made to estimate the Rb accurately presented as the low-x intersect. The resulting ionic conductivity was 0.13 mS/cm using the Eq. (1) considering L= 0.0060 cm, A= 5.06 cm², and R_b = 9.14 Ω was mS/cm.
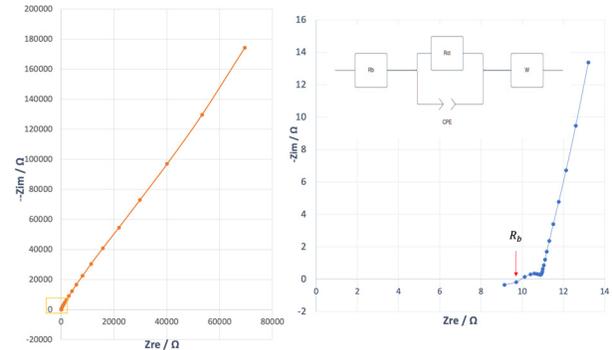

Figure 1: All frequency range impedance diagram of SS|SSE|SS symmetric cell and zoom of the impedance diagram (the inset) and its equivalent circuit (the inset) at room temperature.

It can be observed in the graph there is not a perfect fit of the semicircle at high frequencies. One of the main reasons is the contact between the SSE and the stainless steel which is called contact resistance. This contact was reduced by adding salt and TEGDME to wet the SSE. The bulk resistance is the resistance we tried to find to later calculate the conductivity. The resulting conductivity is 0.13 mS/cm which is comparable to other functional SSE composites reported in literature [9, 10]. However, still some

efforts need to be done to increase that ionic conductivity. Some of those efforts are to further reduce even more the contact resistance and to increase the amount of conductive particles in the SSE composite.

3.2 Li$^+$ transference number

A Li|SSE|Li pouch cell was made of 6 cm² of SSE composite film, Cu electrodes of 6.1 cm² and 5.6 cm² to be used as current collectors for Li foils, a plastic pouch, and electrolyte of 1M LiTFSI in a 1:9 mixture of FEC and DMC:EC (50/50) v/v. This cell was polarized at a constant 0.01 V for 60 min using the equipment MACCOR 4300. After polarizing, the impedance was measured with the EIS technique under the same conditions used in the ionic conductivity test.

Eq. (2) [11] presents how to estimate the Li$^+$ transference number (t_{Li^+}). R_0 is the initial interfacial resistance and R_{SS} the steady-state interfacial resistance in Ω. I_0 is the initial current and I_{SS} is the steady-state current in A.

$$t_{Li^+} = \frac{I_{SS}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss}R_{ss})} \qquad (2)$$

A high t_{Li^+} can reduce the changes of electrolyte [12] concentration in a battery [8]. In literature for SSE composites the t_{Li^+} range goes from 0.46 to 0.86 [13, 14].

The calculated cation transference number was t_{Li^+} = 0.52 using the Eq. (2) and the date presented in Figure 2 where R_0=74 Ω, R_{SS}=74 Ω. I_0= 0.091 A was the initial current and I_{SS}=0.000047 A was the steady-state current.

The resistances R_0 and R_{SS} are calculated by: $R_{SS} = R_0 = R_{ct} = R_i - R_b$. Since it was proved that the impedance stays constant before and after polarizing [9] with the small voltage after polarization, the same impedance data can be used.

Figure 2 shows that the current was not stable in the steady-state part but tended toward steady-state. Many factors could have been contributed to this instability. Some of them are the homogeneity of the constituent materials in the SSE. The other factors are the connection of the leads to the pouch cell and the accuracy of the equipment. To estimate the steady-state current, an average of the values was made. In the inset graph, the Nyquist plot shows a different behavior in comparison to the impedance plot in Figure 1. The main difference is the configuration of the cell. The cell used for this experiment is a symmetric cell of lithium foils where we have a greater diffusion and kinetics control in contrast to the blocking-electrode method.
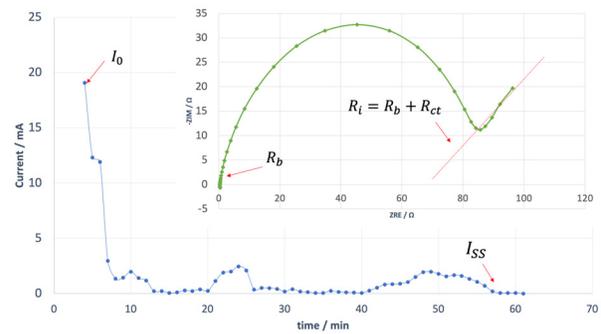

Figure 2: Polarization curve and initial and steady-state impedance diagram (the inset) of Li|SSE film|Li at room temperature.

The result t_{Li^+} = 0.52 is comparable to other reported values which are in a range of 0.46 to 0.81 [13, 14]. This value let us know that the Li$^+$ carry 52 % of the charge by the migration mechanism when current is applied. In other words, it tells us how much of the current is carried by the Li$^+$ in the absence of a concentration gradient.

3.3 Salt diffusion coefficient

The same cell described in the cation transference number test was used (i.e., Li|SSE|Li). The same procedure was followed, as described elsewhere [15]. First, the cell was cycled to form a solid electrolyte interface (SEI) in the Li metal. Then, the cell was polarized using the MACCOR 4300 by passing a fixed voltage 0.01 V through the cell for 3 minutes to set up a salt concentration gradient. The voltage was turned off or interrupted. After interruption of the current, the system was then allowed to equilibrate or relax for 30 min. We can also obtain the diffusion coefficient by using the Warburg impedance [1].

Eq. (3) was used to obtain the D_s in cm²/s. L was the thickness of the SSE composite film in cm. The slope was the plot of the time in min vs. -ln(potential) in V during the relaxation profiles.

$$\text{slope} = -\frac{\pi^2 D_s}{L^2} \qquad (3)$$

The D_s values reported for SSE composites are in a range from 10^{-9} to 10^{-11} cm²/s. [1, 6]

Figure 3 is a representation of how the voltage behaves after the voltage supply is turned off. It decreases over a few seconds. In Figure 3, y_2 = 5.8, y_1 = 4.82, x_2 = 2, and x_1 = 10 was used for estimating the slope of -ln(potential) vs. time (t). L = 0.0060 cm as the thickness of the film. A result, D_s = 4.7 × 10^{-7} cm²/s was obtained., which is competitive other values reported in literature about SSE composites [1, 6].
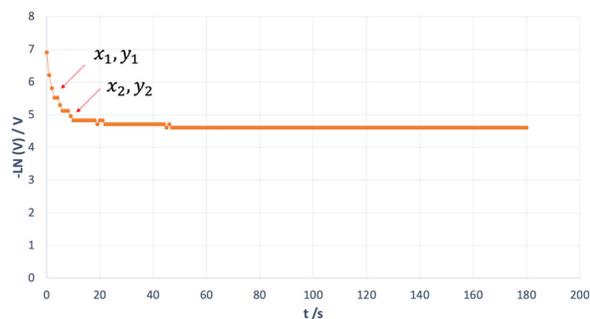

Figure 3: Relaxation profile of Li|SSE|Li at room temperature.

4   Conclusions

The transport properties such as ionic conductivity and parameters that affect the ionic conductivity such as Li+ transference number and diffusion coefficient are relevant to understand the transport mechanism inside an SSE composite. The study of an SSE intended to substitute the liquid electrolyte must be adequate and rigorous in electrochemical and transport topics to predict the behavior of the composite in a real battery system.

5   Acknowledgements

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