

**Reassessing the bulk ionic conductivity of solid state electrolytes**

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Reassessing the bulk ionic conductivity of solid state electrolytes

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The importance of ionic conductivity of the solid-state electrolyte for futuristic battery application is crucial. The ionic conductivity is measured via the bulk resistance of the pellet which not only depends on the materials properties but also on the physical parameters including frequency. It is shown in this study that the later (the high-frequency point) affects the ionic conductivity more than other variables. With a growing number of solid-state battery research, we believe that now it is the time to establish a common standard to measure ionic conductivity for the solid-state electrolyte in Li-ion batteries.

Solid state electrolytes (SSE) are considered to be the most promising solution to the high energy-density requirements for next-generation Li-ion batteries (LIB). Where most SSE have high dimensional and electrochemical stability to provide for the necessary safety and energy-density, their main challenge is the low ionic conductivity^{1,2}. The fast ion conductivity has been the core part of the SSE research for LIB for past few years (Fig. 1). Eventually, there are a few reports of SSE with superionic conductivity, namely the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ ($\sim 10^{-2} \text{ S cm}^{-1}$)³ and the garnet type⁴ $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ($\sim 10^{-3} \text{ S cm}^{-1}$). However, we believe that there are still unanswered questions that need to be addressed before going into the next stage of SSE research. Ionic conductivity of the solid electrolyte depends on the many factors including the materials and physical parameters.¹⁻⁵ Among the materials properties, efforts have been made to improve the ionic conductivity by tuning the lattice parameter, particle size, and relative density. Physical parameters include the temperature, relaxation time, and frequency. In the previous literature, the focus was almost exclusively given on the materials properties. Table S1 provides a list of some such studies that measured the ionic conductivity of SSE. However, looking closely, the range of such measured ionic conductivity is quite large. As established by the previous works, the ionic

conductivity of the SSE, indeed, depends on the lattice parameter, particle size, and relative density. However, the effects of the physical parameters are often ignored. While the structure of the SSE and their basic mechanism of ionic conduction is studied more rigorously in literature⁶⁻¹¹, the effect of different variables such as the temperature, relaxation time, and frequency on the ionic conductivity is often ignored. Here, we want to draw attention to the variations of high-frequency points used in the impedance spectroscopy setup to calculate the ionic conductivity.

Ionic conductivity of solid state electrolytes is usually calculated from the electrochemical impedance spectroscopy by analyzing the Nyquist plot. A typical simple equivalent circuit of $(R_{\text{bulk}})(R_{\text{gb}}Q_{\text{gb}})(Q_{\text{electrode}})$ gives the bulk resistance from the starting point of the semicircle which is the high-frequency point.⁵ From that bulk resistance (R_b), the ionic conductivity (σ) is calculated by using the equation: $\sigma = d / (R_b \times A)$; where d is the thickness, and A is the area of the solid electrolyte pellet. In previous works so far, different high-frequency points (HFP) are adopted in different works (Fig. 1). More importantly, the variation of the ionic conductivity is quite high (sometimes even an order) depending on the high frequency. Even for the same SSE by the same research group, sometimes, a completely different HFP is used. There is no set standard for HFP and other parameters used in the impedance spectroscopy for SSE ionic conductivity measurements. Different researchers have just used different frequencies, without paying attention that the high-frequency point could play a role in the ionic conductivity measurement. More importantly, the HFP that is used to calculate the ionic conductivity in these works is far above than the practical battery testing condition of 1 kHz.

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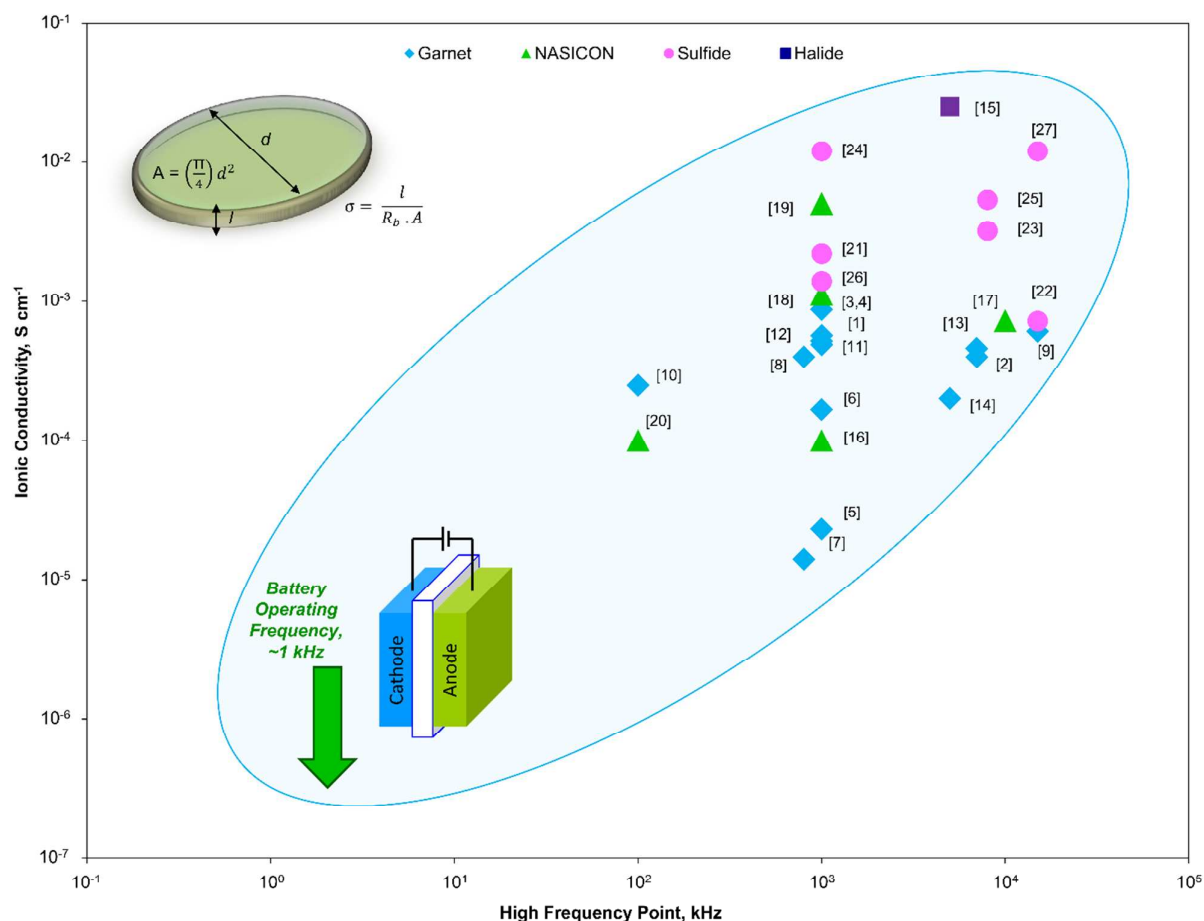


Figure 1. Variation in the high frequency point in impedance spectroscopy measurements by different published works and their corresponding ionic conductivity (the corresponding works are marked with the reference number as shown in Table S1 from Supporting information). All the reported works have used much higher frequency than the practical battery testing frequency of 1 kHz (marked with a down arrow).

The effect of frequency on the ionic conductivity is a common study in solid-state physics research^{12–14}. The ac conductivity of the dielectric matters is primarily a function of frequency. According to the Debye-Falkenhagen theory¹⁵, the conductance is a complex function where each of the terms also depends on the frequency (ω). Further derivation leads to that the conductance dispersion is centered around a critical frequency¹⁶. Thus, the frequency dependent conductivity is, $\sigma'(\omega) = \sigma[1+(\omega/\omega_c)^n]$; where σ is the ionic conductivity, ω is the angular frequency, ω_c is the critical frequency, and the value of n is usually $0 < n < 1$.

Although the frequency dependence of the ac conductivity of dielectric materials is an interesting field, its exact mathematical formulation does not pose enough importance for the ionic conductivity measurements of solid-state electrolytes in lithium-ion batteries because of the ion-blocking model of electrochemical impedance spectroscopy (EIS) measurements^{17–19}. For the ionic conductivity measurements in SSE assuming a typical $(R_{\text{bulk}})(R_{\text{gb}}Q_{\text{gb}})(Q_{\text{electrode}})$ equivalent circuit, we only consider the bulk resistance of the pellet which occurs at the starting point

of the semi-circle at the high-frequency zone. Therefore, the HFP in EIS measurements has the most probability to affect the bulk resistance and thereby, the ionic conductivity.

When the frequency is varied from low to high, the actual physical phenomenon in the material that affects the ionic conductivity varies. For dielectric materials, the high frequency possibly causes some effect on the grain boundaries²⁰. When the frequency is high enough it might cause the segregation of some ions in the grain boundary (Fig. 2a), similar to the segregation of Si in Y_2O_3 -stabilized zirconia or the segregation²¹.

In this study, we have varied the HFP in EIS from 1 kHz to 7 MHz keeping the lower side at 10 Hz and recorded corresponding bulk resistance and ionic conductivity of the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ solid electrolyte. We have also studied the effect of relaxation time and temperature on the high-frequency point variations. We have found that the HFP affects the ionic conductivity significantly; the ionic conductivity varies as a function of HFP and the real (true) conductivity at 1 kHz HFP is much lower than typical >1 MHz HFP.

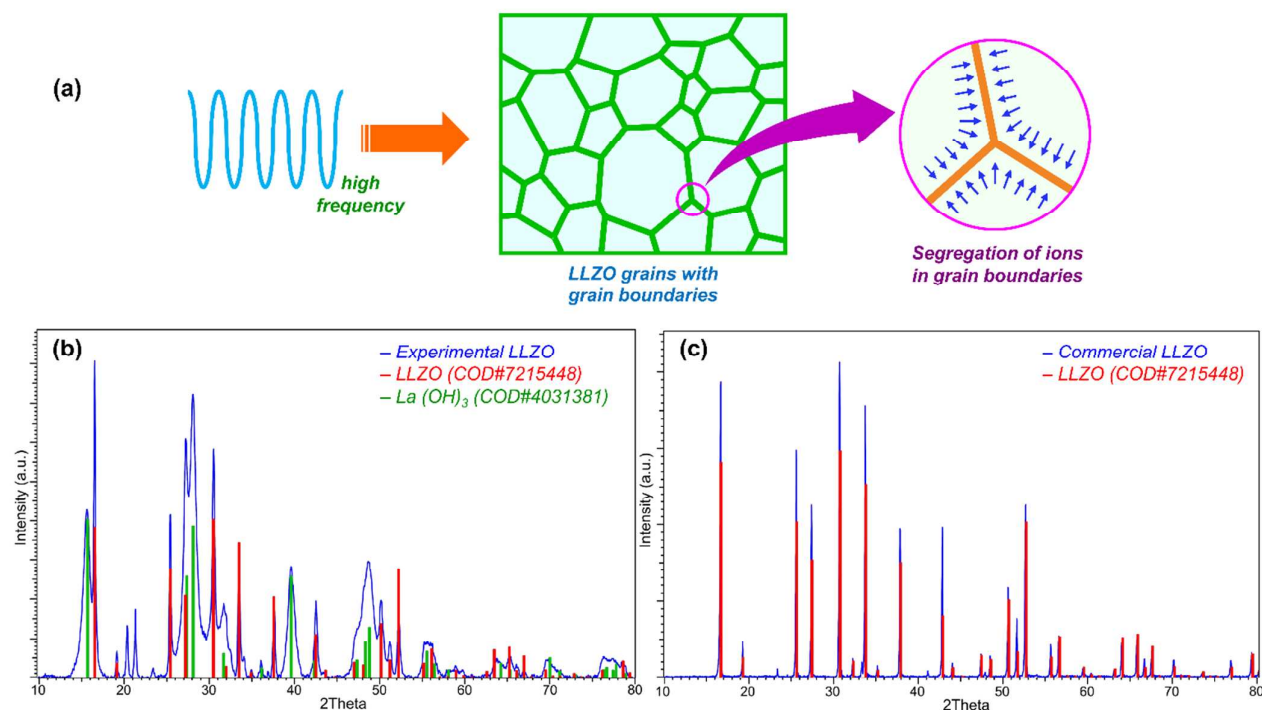


Figure 2 (a) Possible mechanism of segregation of ions in the grain boundaries due to high frequency, (b) X-ray diffraction pattern of the experimental LLZO; (c) X-ray diffraction pattern of the commercial LLZO.

Results and Discussion

To study the effect of the high frequency point on ionic conductivity of the solid electrolyte, we have employed two $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) – one commercial (phase pure, from Toshima, Japan) and one experimentally synthesized by low-temperature single-step calcination after spray drying (details in experimental section). Commercial LLZO XRD pattern (Fig.2c) shows that the material is Garnet cubic phase of LLZO as matched with the crystallographic open database, COD# 7215448. On the other hand, the experimental LLZO is a mixture of two different phases as shown in the XRD pattern (Fig.2b). The XRD result of the as-synthesized Al-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ confirms the cubic phase of LLZO – the Al-doped LLZO (COD# 7215448), along with another phase – $\text{La}(\text{OH})_3$ (COD# 4031381). Previous works have shown that the tetragonal phase of the LLZO usually results in certain splitting of the peaks, especially in the 2θ range of 25° to 60° ^{17,22}. The absence of splitting of the peaks in the experimental pattern confirms that the material is in cubic phase. The existence of cubic phase in lower temperature calcination such as in 900°C is very rare, however, is not uncommon²³. The low-temperature calcination may also be responsible for the other major phase $\text{La}(\text{OH})_3$ found in the structure. There are also a few minor peaks at 19° – 22° that may have been produced by excess lithium content added to remedy the lithium loss during calcination^{10,24}.

The effect of HFP is shown in Fig. 3. For all the measurements, the low-frequency point was kept at 10 Hz. For our

experimental LLZO, for a typical EIS measurement with lithium blocking electrode at the 1MHz-10Hz range, the ionic conductivity was found to be 4.8×10^{-4} S/cm. Yet, as measured at 7MHz-10Hz, the ionic conductivity is increased to 1.2×10^{-3} S/cm; which is our highest ionic conductivity found at room temperature. For a typical battery testing system, the maximum frequency supplied is usually $\sim 1\text{kHz}$. For such case, the measurement (1kHz-10Hz) shows an ionic conductivity of 2.2×10^{-5} S/cm. When we used the non-ion blocking lithium electrode in Argon environment, we have found similar trend (Fig. 3) – the ionic conductivity increases with increasing HFP. The same trend is also seen with the commercial LLZO, with or

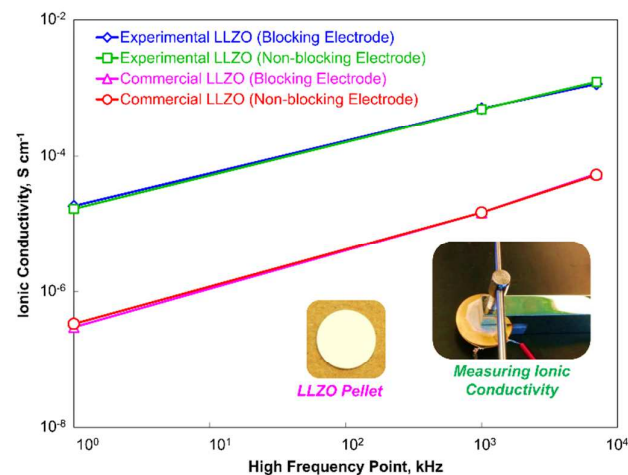


Figure 3 Conductivity dependence on the HFP in EIS measurement

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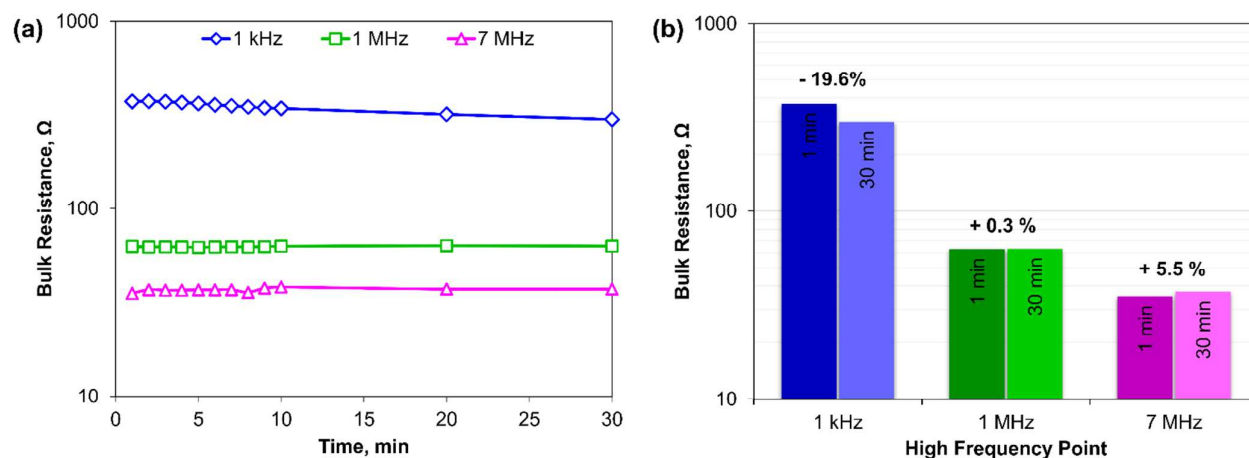


Figure 4 (a) Effect of relaxation time on the conductivity measurement at different HFL, (b) Amount changes of bulk resistance in a bar chart with time at different HFP

without lithium ion-blocking electrode in air and argon environment respectively. The experimental LLZO has shown a higher ionic conductivity compared to the commercial one which is probably because of their nanosized that helped compacting the pellet (Fig S1). Nonetheless, the increase is almost linear in a log-log plot. Probably, if given a chance to increase the high frequency even further, it could lead to a critical highest point of ionic conductivity which is out of the range of our instrument limit. All in all, the ionic conductivity at the practical operating condition of the battery (1 kHz) is quite low. Given that the high ionic conductivity occurs at a higher frequency, as shown in Fig 3 (our work) and Fig 1 (previous works), one might argue to use a higher frequency for battery operation instead. However, that will be realistically impossible because of the technical issues to generate such high frequency (1000 time more) which include excessive noise, probable burn-out of the system, and ultimately high cost. We thus need rather find another way of solving this issue.

Another important parameter for dielectric materials is their relaxation time²⁵. Since the actual variation of relaxation time with frequency is complicated and out of scope in our case, we

have studied the effect by measuring the bulk resistance at a constant interval of time using different HFP. The result is plotted in Fig. 4. Measurements were taken at every 1 min interval till 10 min after which 2 more data points taken were taken at 10 min intervals. Three different HFP were used: 7 MHz, 1 MHz, and 1 kHz and 30 mins of wait time were given in between the measurements at different HFP. Fig. 4a shows that at a lower value of HFP, bulk resistance decreases with time within our observed window of time and Fig 4b shows the percentage change in bulk resistance after 30min. The impedance measurements are more sensitive at a lower value of HFP. Hence, it is important to set a specific time interval in each HFP of EIS measurements if we want the results to be reproducible.

Finally, to see the effect of temperature, measurements were taken at different temperature and different HFP. The ionic conductivity of the commercial LLZO pellet at different temperature was measured with each HFP and was plotted in an Arrhenius plot (Fig. 5a). The activation energy (E_a) of conductivity can be calculated from the Arrhenius equation, $\sigma = T \cdot A \exp(-E_a/kT)$, where σ is the conductivity at temperature T , A is a given constant, E_a is the activation energy, and k is the

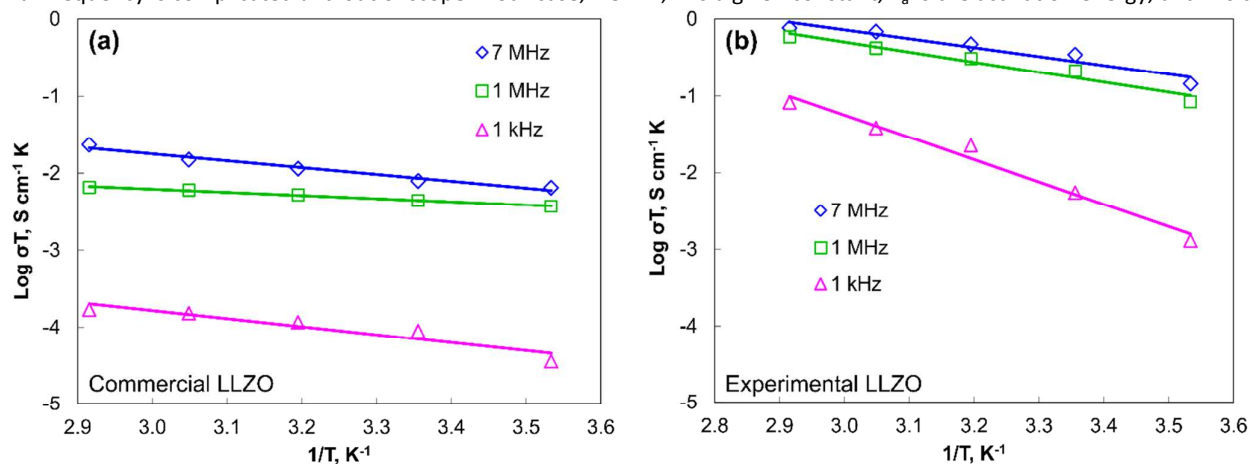


Figure 5 Arrhenius plots of (a) commercial LLZO and (b) experimental LLZO at different HFL; the activation energy is highest for a practical battery operation frequency of ~1kHz.

Boltzmann constant. Fig. 5b shows the Arrhenius plot of our experimental LLZO with same HFPs. Overall, Fig. 5 shows that the activation energy is lower at a higher value of HFP. With lower value of HFP, the ionic conductivity decreases.

The reduced value of activation energy and high ionic conductivity of the LLZO pellet at higher HFP suggests that the physical phenomenon occurring inside the LLZO due to high frequency helps the ion-conduction (Fig 2a). The exact nature of such physical phenomenon required further studies. However, as a possible hypothesis, the high frequency might help inducing segregation of some entity in grain boundaries similar to the Si segregation in Y_2O_3 that could have helped to increase the ion mobility and thus the ion-conduction^{5,26}.

Conclusions

Ionic conductivity and the bulk resistance of the LLZO solid electrolytes have shown strong dependency upon the high frequency point, relaxation time, and temperature. Within the reported range, the ionic conductivity increases as the high frequency point increases. Moreover, the effect is quite large compared the effect of other material properties such lattice parameters, particle size, density, etc. This effect is found to be independent of the crystallinity or the purity of the LLZO solid electrolyte as well as independent of the blocking or non-blocking electrode and the environment used. This helps understand why the reported ionic conductivities in different previous research works are not comparable to each other. At practical frequency (~1kHz) of the real battery system, the ionic conductivity is quite low. Thus, the current scenario of ionic conductivity measurement is very unclear; we need to go back and rethink about the effect of high frequency point on the ionic conductivity of the real battery operation. With a growing number of SSE research, now it is the time to find a common standard to measure the ionic conductivity of solid-state electrolytes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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Table of Content Entry

Urgent necessity to establish a standard for bulk resistance quantification is identified via ionic conductivity dependence on high frequency point.

