

Short communication

Heterogeneous electrolytes: Variables for and uncertainty in conductivity measurements

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Abstract

This paper discusses variables and uncertainty associated with the measurement of ionic conductivity of heterogeneous solids. The conductivity data of heterogeneous solids of diverse chemistries have been analyzed. All these solids exhibit space charge and blocking effects. The coexistence of the two effects may lead to significant scatter and uncertainty in the measured values if the variables are not isolated and controlled.
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1. Introduction

Heterogeneous electrolytes have attracted significant interest in recent years [1,2]. The motivation for the interest is a need for high conductivity and stable solid electrolytes for commercial devices such as solid state batteries and fuel cells, electrochemical sensors, and gas separating membranes. The heterogeneous electrolytes offer many advantages over the single phase solid or liquid electrolytes. They can provide higher ionic conductivity, increase mechanical strength, improve thermal stability and safety, and reduce cost. However, these heterogeneous electrolytes must be thoroughly characterized and understood so that they can be reproducibly processed for intended applications. The characterization data will also define engineering design parameters for their real-life applications. One of the issues related to the characterization of heterogeneous electrolytes is a reliable ionic conductivity measurement in the temperature range of interest.

This paper culminated from our prior work on liquid, polymer, polymer–ceramic and ceramic–ceramic composite electrolytes over the last 15 years. Experimental data on these diverse electrolytes have already been published and are

included in this paper to develop a broader understanding. Only the themes relevant to this paper will be presented with appropriate citation. Thus, the objective of this paper is to develop a comprehensive view on variables for and uncertainty in conductivity measurements of heterogeneous solids comprised of an ionic conductor matrix and dispersed dielectric phase.

2. Experimental

Ionic conductivity data of three different types of heterogeneous solid electrolytes: lithium–aluminium–titanium phosphate (LATP) glass–ceramic– Al_2O_3 , polymer (PEO:LiBF₄)–ceramic (TiO₂), and scandia-stabilized zirconia (ScSZ)– Al_2O_3 are covered in this paper. The processing and microstructural characterization data of LATP– Al_2O_3 , PEO:LiBF₄–TiO₂ and ScSZ– Al_2O_3 are reported in respective prior publications [3–5]. The experimental details on processing and microstructural characterization can be found in these publications.

The electrical conductivity of each specimen was measured by the ac impedance technique in the appropriate temperature range. For the ac technique, a Solartron 1260 impedance analyzer with 1287 electrochemical interface in the 0.1–10⁶ Hz frequency range (LATP– Al_2O_3 and ScSZ– Al_2O_3) and an EG&G impedance spectrometer Model 398 in the frequency range of 0.1–100 kHz (PEO:LiBF₄–TiO₂) were used for measurement purposes. The LATP– Al_2O_3 specimens were sputtered

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with 0.5- μm thick gold coating on both sides before loading them into a conductivity cell between stainless steel (SS) electrodes. The ScSZ–Al₂O₃ specimens, after sintering, were coated with platinum paint and fired at 1000 °C for 1 h in an ambient atmosphere furnace and subsequently furnace cooled. The conductivity fixture in this case consisted of machined glass–ceramic (Macor[®]) material of screw and socket design that can be tightened to provide intimate contact between the SS electrodes and the platinum coated specimen. The fixture containing the specimen was inserted into a tube furnace, and the impedance data were collected after stabilizing the specimen for 15 min.

3. Results and discussion

3.1. Nanoscopic view of heterogeneous, solid ionic conductors

Fig. 1 shows a nanoscopic view of a heterogeneous solid ionic conductor. The free ions of the solid are shown by arrows identifying them as vectors. The ions can be truly represented by a vector as they have a magnitude of velocity and direction. Before an electric field is applied, these arrows have localized motion and random direction. The diffusion coefficient is the fundamental parameter that characterizes them. Subsequent to the application of an electric field, these ions participate in the long-range conduction process. Also shown in Fig. 1 are solid circles depicting a dielectric phase that is distributed uniformly in the ionic conducting matrix. The ionic conductor–dielectric interfaces are electrically active regions which may immobilize ions due to an electrical interaction. The immobilization will reduce the number of available conducting ions. The consequence of immobilization is also the creation of a metastable, localized internal electric field that will influence transport of the remaining conducting ions. The metastable electric field is shown by arcs in the vicinity of the immobilized ions in Fig. 1.

The metastable electric fields of Fig. 1 may disappear if the immobilized ions become free either due to the increased thermal

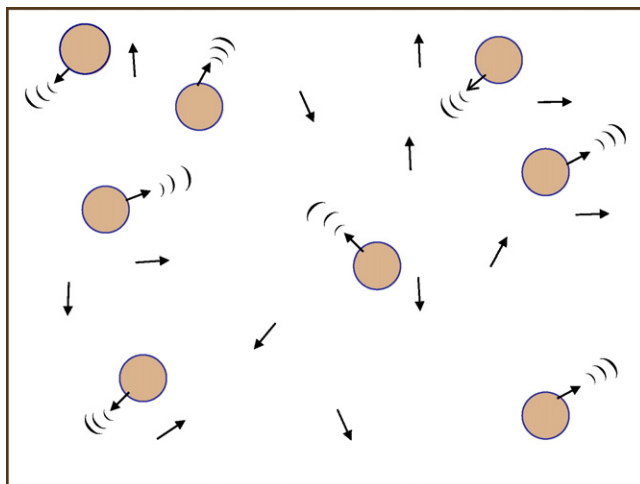


Fig. 1. Schematic presentation of the interaction between conducting ion and dielectric phase in an ionic conducting matrix.

energy or severity of the external field. The existence or non-existence of the metastable electric fields has an effect on the conductivity values. The interaction of the solid ionic conductor dielectric phase interface and ions is thus an important variable during conductivity measurement because it may enhance or suppress ionic conductivity. The variable may also be defined as the space charge effect.

3.2. Blocking and space charge effects

Two physical situations need to be considered and analyzed to explain ionic conductivity of heterogeneous solids. These two situations – blocking and space charge models – have been proposed earlier to explain conductivity of heterogeneous solids [6]. The influence of the blocking entity is perhaps easier to comprehend and is schematically shown in Fig. 2(a). The conducting ions (CI) will move forward in the direction of the applied field, E_a . The blocking entity (dielectric phase) will impede the forward motion of conducting ions and they will be scattered to assume another path in the general direction of the applied field. The blocking effect manifests an increased resistance and hence reduced conductivity.

It is conceivable that the dielectric phase will form an electrically charged interface with the host matrix. The degree of electrical activity of the interface will depend upon the difference of the dielectric constants between the host matrix and the dielectric phase. The electrically active interface now becomes an interaction site for the free conducting ions. If the interaction leads to the immobilization of the conducting ion, then a metastable electric field (E') is established, as shown in Fig. 2(b). The applied external fields, E_a , and the metastable field, E' , collectively yield total field, E_t , acting upon the conducting ions which are present in the vicinity of the metastable field. Such an electric field (E_t) will accelerate transport of conducting ions.

It is apparent that the blocking and space charge effects are antagonistic in nature. One may be more dominant than

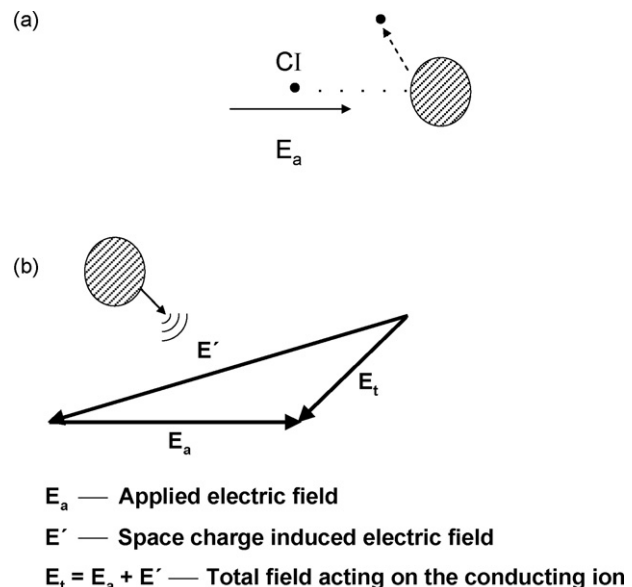


Fig. 2. Schematic presentation of: (a) blocking effect and (b) space charge effect.

the other or both may be of similar magnitude. This illustrates the difficulty in analyzing and interpreting conductivity data of heterogeneous systems. If the two effects are not considered independently, one may arrive at an erroneous conclusion.

3.3. Lithium–aluminium–titanium phosphate (LATP) glass–ceramic–Al₂O₃ electrolyte

The ionic conductivity data of LATP glass–ceramic has been reported by Fu [7] and Thokchom and Kumar [8]. The LATP glass–ceramic primarily consists of highly conductive Li_{1+x}Ti_{2–x}Al_x(PO₄)₃ (*x* ≈ 0.275) phase. The conductive phase is a derivative of LiTi₂(PO₄)₃ which possesses a rhombohedral structure (space group *R* $\bar{3}C$) with an open three-dimensional framework of TiO₆ octahedra sharing all corners with PO₄ tetrahedra. The lithium ion occupies interstitial sites and its conduction takes place along the *c*-axis. This material is a single lithium ion conductor and therefore the material is of special interest for delineating blocking and space charge effects.

Fig. 3 shows the Arrhenius plots of LATP and its composite with 3, 7, and 12 vol.% Al₂O₃. The addition of Al₂O₃ is detrimental to the conductivity across the entire temperature range because it acts as the blocking entity. Nonetheless, the degree of conductivity reduction varies across the temperature range and also from one specimen to another. For example, the 3 vol.% Al₂O₃ specimen shows a major inflection around 27 °C. The inflection transformed into a peak for 7 and 12 vol.% Al₂O₃ specimens. The conductivities for the 12 vol.% Al₂O₃ specimen at –40 and 90 °C were reduced by approximately two and five orders of magnitude.

The peak at around 27 °C in Fig. 3 results from the antagonistic influences of blocking and space charge effects. At low temperatures (<27 °C) the conducting lithium ion interacts with Al₂O₃ forming a charged complex as shown by Eq. (1). The charged complex then becomes a source of localized field which assists in the transport of remaining conducting ions. At temperatures greater than 27 °C, the Al₂O₃:Li⁺ dissociates, leading to

an elimination of the space charge effect and therefore a precipitous drop in conductivity, especially for higher concentrations of Al₂O₃. The difference of the conductivities at –40 and 90 °C in Fig. 3 is approximately three orders of magnitude and is equal to the contribution of the space charge effect below 27 °C.



The formation and dissociation of the charged complex of Eq. (1) can also be characterized as adsorption and desorption processes. The processes can be investigated by measuring the conductivity during heating and cooling cycles. Fig. 4 shows the Arrhenius plots of LATP-3 and 7 vol.% Al₂O₃ specimens during heating and cooling cycles. During the heating cycle, once the lithium ions have been desorbed from the Al₂O₃ surface above 27 °C, the space charge contribution to conductivity is eliminated. Therefore, the specimens exhibit lower conductivity across the entire temperature range during the cooling cycle. It should also be noted that the lithium ion diffusion coefficient at these temperatures (<27 °C) is low but significant, and therefore a re-formation of the space charge if the specimen is kept below 27 °C is a distinct possibility, but it may take a long time (days). In the case of polymer–ceramic composite specimens, it has been shown that the complete recovery of the conductivities at lower temperatures takes from tens to hundreds of hours [9].

The data of Fig. 4 clearly illustrate the variables for and uncertainty in conductivity measurement. The analysis of the blocking effect leads one to conclude that the variables for the effect are concentration and particle size of the dielectric phase [10]. The space charge effect is believed to be determined by variables such as the particle size and the dielectric constant of the dispersed phase. The uncertainty can be reduced by following certain experimental protocols that isolate and control these variables. If the measurements are not conducted with controlled variables, the magnitude of the error could be enormous.

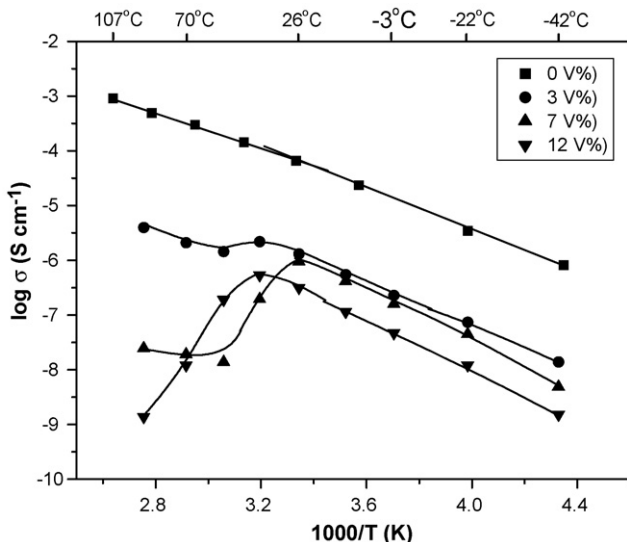


Fig. 3. Arrhenius plots of LATP and its composite with 3, 7 and 12 vol.% Al₂O₃.

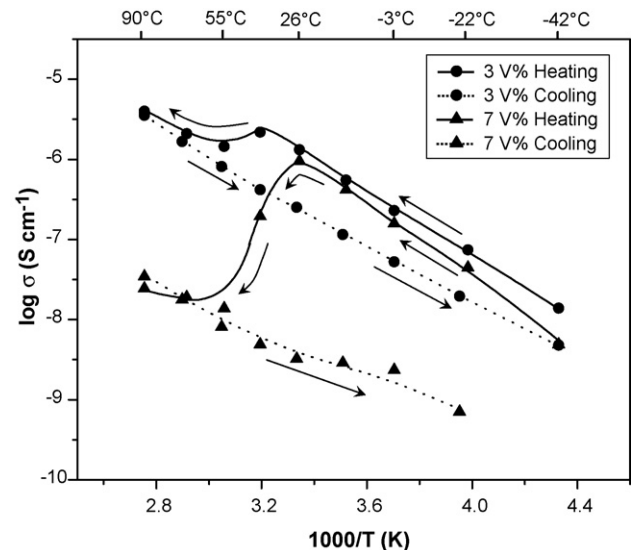


Fig. 4. Arrhenius plots of the conductivity of LATP-3 and 7 vol.% Al₂O₃ during heating and cooling cycles.

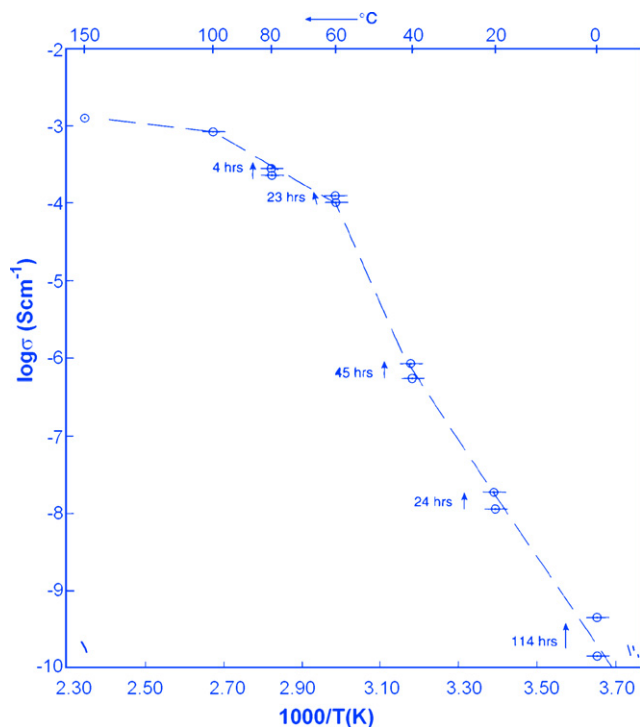


Fig. 5. Conductivity of PEO:LiBF₄–TiO₂ (20 wt%) composite electrolyte during heat-up. The specimen was heat treated at 150 °C for 30 min and then quenched to 0 °C before the conductivity measurement.

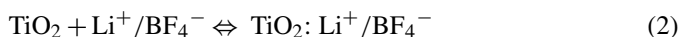
3.4. Polymer–ceramic composite electrolyte

An electrolyte derived from polymer and ceramic phases is identified as a polymer–ceramic composite. An analysis of a broader range of polymer–ceramic composite electrolytes has shown that the incorporation of ceramic components in a polymer matrix leads to enhanced ionic conductivity, cationic transport number and electrode–electrolyte interfacial stability [11].

A PEO:LiBF₄–TiO₂ (20 wt%) film specimen sandwiched between SS blocking electrodes was heated to 150 °C, held at this temperature for 30 min, and then rapidly cooled to 0 °C. The conductivity of this specimen was measured as a function of temperature and time while the temperature was raised from 0 to 150 °C. The conductivity data are presented in Fig. 5. At each temperature there are two data points, an arrow, and number of hours. The data points represent the range of conductivity values, the arrow pointing upward indicates conductivity enhancement, and the number of hours is the time interval between the two measured values of conductivity. For example, at 0 °C, after the specimen was cooled from 150 °C, the log σ (σ = conductivity) was –9.85. The log σ increased to –9.37 after it was held for 114 h. This type of conductivity enhancement appears at all temperatures; however, the degree of enhancement, as measured by the absolute difference between the two data points and normalized to the hold time, diminished as the temperature was raised from 0 to 150 °C.

The PEO:LiBF₄–TiO₂ (20 wt%) electrolyte is complex in the sense that it contains two mobile species, Li⁺ and BF₄[–]. Both of these are expected to interact with the dielectric phase

TiO₂. Therefore, the precise nature of the space charge formation due to the interaction of mobile species and TiO₂ is not clear. However, the conductivity data of Fig. 5 shows that at a given temperature, certain ions are being immobilized that in turn is enhancing conductivity. Eq. (2) depicts a general feature of the immobilization mechanism. It is also observed that at a lower temperature, the mechanism is more favorable as compared to the higher temperature. This observation suggests that the TiO₂:Li⁺/BF₄[–] complex is more stable at lower temperatures and also justifies the reversible nature of Eq. (2).



The specimen whose thermal history and conductivity data are shown in Fig. 5 was equilibrated for 30 min after it reached 150 °C and then cooled down gradually and slowly to 100, 80, 60, 40, 20, and 0 °C for conductivity measurement. The conductivity values and hold time at each of the temperatures, shown in Fig. 6, are similar to the one shown in Fig. 5. In this case, the conductivity decreased as the hold time increased at the given temperature. The conductivity decreases as a function of hold time at all temperatures above 20 °C were small but measurable and significant. This phenomenon is attributed to the reaction (2) progressing in the reverse direction. The conductivity data of the PEO:LiBF₄–TiO₂ (20 wt%) in the 20–150 °C can vary by over two orders of magnitude depending on whether the conductivity was measured during the heating or cooling cycle and also on equilibration time at a given temperature.

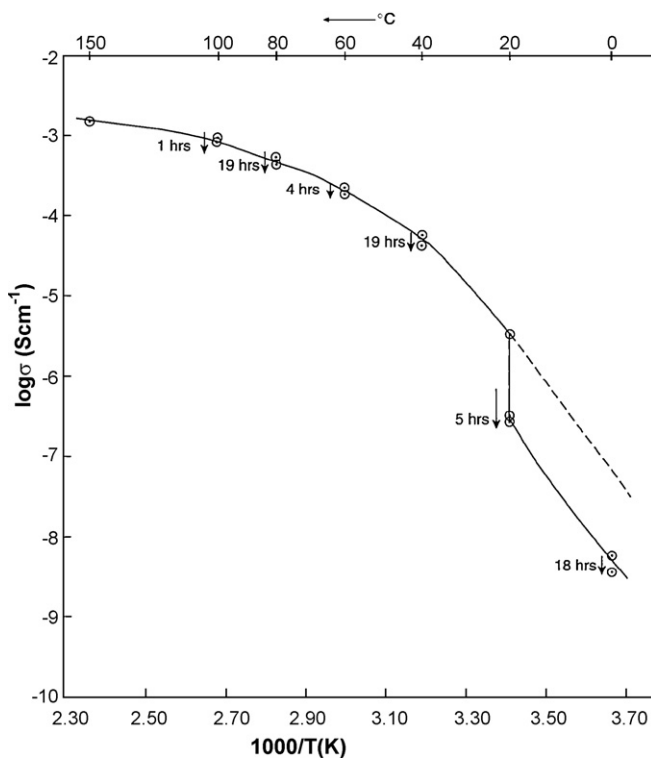


Fig. 6. Conductivity of PEO:LiBF₄–TiO₂ (20 wt%) composite electrolyte heat treated at 150 °C for 30 min. The conductivity was measured while the specimen was slowly cooled from 150 °C and stabilized at the temperature of measurement.

The decline in conductivity at 20 °C in Fig. 6 is pronounced. The conductivity decreased more than an order of magnitude in the first 2–3 h. The rapid decline in conductivity was attributed to the crystallization of the polymer matrix (PEO:LiBF₄) [4]. The TiO₂ phase is expected to suppress or even eliminate crystallization of the polymer matrix, but the experimental data show otherwise.

The conductivity data of Figs. 5 and 6 clearly illustrate the variables and associated uncertainty in conductivity measurement in heterogeneous systems of polymer–ceramic type. The statistical nature of conductivity data must also be accounted for while designing devices based on these heterogeneous systems.

3.5. ScSZ–Al₂O₃ electrolytes

The ScSZ electrolytes are known to exhibit higher oxygen ion conductivity as compared to the state-of-the-art yttria-stabilized zirconia (YSZ) materials. The conductivity enhancement in the ScSZ material is attributed to a minimal difference in ionic radii of the host Zr and Sc dopant [12]. The conductivity of ScSZ materials can be further enhanced by the use of a heterogeneous dopant such as Al₂O₃ [5]. However, these heterogeneously doped ScSZ materials have a tendency to show significant scatter in conductivity data [5], similar to other solid heterogeneous electrolytes covered in this paper.

The conductivities of ScSZ–Al₂O₃ (0, 10, 20, and 30 wt%) specimens are shown in Fig. 7. Three specimens corresponding to each Al₂O₃ concentration were characterized at 800, 850, 900, and 950 °C. The conductivity values, their mean and a solid line obtained by the regression analysis are shown in

Fig. 7. It is noted that at all temperatures ranging from 800 to 950 °C the conductivity is enhanced by the addition of Al₂O₃. However, the spread in the measured conductivity values intensifies with increasing concentration of Al₂O₃. Furthermore, the spread masks the effect of Al₂O₃ addition on conductivity. The spread is explained on the basis of interaction between Al₂O₃ and oxygen vacancies (V_o^{••}) which is illustrated by Eq. (3). A complex, Al₂O₃:V_o^{••} is formed due to the interaction of Al₂O₃ and V_o^{••} which becomes a source of internal electric field that in turn influences transport of the remaining conducting ions. The concentration of the complex is directly related to the weight percent of Al₂O₃. The equilibrium constant of reaction (3) as shown by Eq. (4), is temperature dependent. Eq. (3) also explains the statistical distribution in the measured conductivity values, Fig. 7.



$$K = \frac{[\text{Al}_2\text{O}_3 : \text{V}_o^{\bullet\bullet}]}{[\text{Al}_2\text{O}_3][\text{V}_o^{\bullet\bullet}]} \quad (4)$$

The Al₂O₃:V_o^{••} complex is relatively stable. It may become unstable if enough thermal energy becomes available to dissociate the complex; however, in the temperature range (800–950 °C) of investigation, such a phenomenon has not been observed.

In a recent publication [13] it has been reported that the number of oxygen vacancies (V_o^{••}) is reduced and the mobility (μ , cm² s⁻¹ V⁻¹) is increased after interaction of the V_o^{••} with Al₂O₃. The experimental observation of the publication [13] was explained by employing Fig. 1.

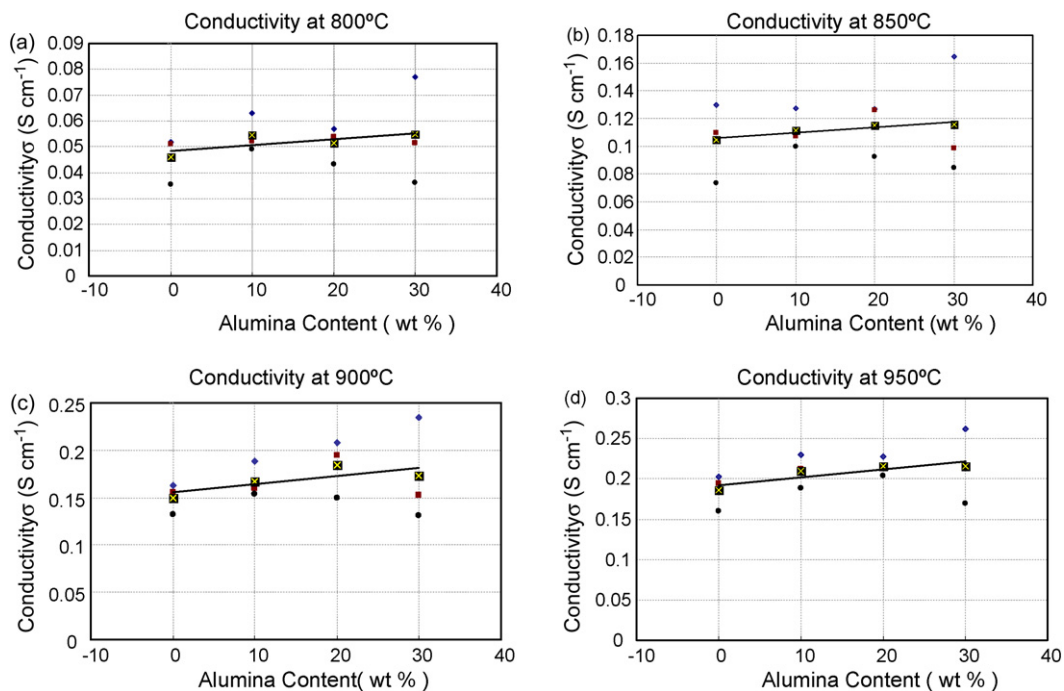


Fig. 7. The mean conductivity (as designated by the symbol ×) of the samples measured at various temperatures (a) 800 °C, (b) 850 °C, (c) 900 °C, and (d) 950 °C without correcting for the nonconducting Al₂O₃ phase.

4. Summary and conclusions

This paper presented and discussed variables for and associated uncertainty in the conductivity measurements of heterogeneous electrolytes. The conductivity data of three different types of heterogeneous solids: LATP–Al₂O₃, PEO:LiBF₄–TiO₂, and ScSZ–Al₂O₃ were analyzed. The LATP–Al₂O₃ system is a single, lithium ion conductor and clearly exhibited the existence of blocking and space charge effects. The LiBF₄–TiO₂ system is associated with two conducting ions; i.e., Li⁺ and BF₄[−], and even this system exhibits the presence of the space charge effect, especially at lower temperatures. The ScSZ–Al₂O₃ material is an oxygen ion conductor and exhibits significant scatter in conductivity data which is believed to be associated with the space charge effect involving the Al₂O₃:V₆^{••} complex.

The conductivity data of all three heterogeneous solids can be explained on the basis of an interaction between the conducting ion and the dielectric phase. The variables that influence the interaction are concentration, dielectric constant, and particle size of the dielectric phase, temperature, and thermal stability of the dielectric ionic complex. All these variables collectively contribute to the uncertainty in the conductivity measurement.

The blocking and space charge effects coexist in heterogeneous solids and their magnitude differs from one system to another.

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References

- [1] B. Kumar, *J. Power Sources* 135 (2004) 215–231.
- [2] B. Kumar, C. Chen, C. Varanasi, J.P. Fellner, *J. Power Sources* 140 (1) (2005) 12–20.
- [3] J.S. Thokchom, B. Kumar, *J. Electrochem. Soc.* 154 (4) (2007) A331–A336.
- [4] B. Kumar, L.G. Scanlon, R.J. Spry, *J. Power Sources* 96 (2001) 337–342.
- [5] C. Varanasi, J. Juneja, C. Chen, B. Kumar, *J. Power Sources* 147 (1–2) (2005) 128–135.
- [6] B. Kumar, S. Nellutla, J.S. Thokchom, C. Chen, *J. Power Sources* 160 (2006) 1329–1335.
- [7] J. Fu, *Solid State Ionics* 96 (3–4) (1997) 195–200.
- [8] J.S. Thokchom, B. Kumar, *Solid State Ionics* 177 (7–8) (2006) 727–732.
- [9] B. Kumar, L.G. Scanlon, *Solid State Ionics* 124 (3–4) (1999) 239–254.
- [10] B. Kumar, S.J. Rodrigues, L.G. Scanlon, *J. Electrochem. Soc.* 148 (10) (2001) A1191–A1195.
- [11] B. Kumar, L.G. Scanlon, *J. Electroceram.* 5 (2) (2000) 127–139.
- [12] O. Yamamoto, Y. Arati, Y. Takeda, N. Imanishi, Y. Mizutanj, M. Kawai, Y. Nakamura, *Solid State Ionics* 79 (1995) 137.
- [13] B. Kumar, J.S. Thokchom, *J. Am. Ceram. Soc.*, doi:10.1111/j.1551-2916.2008.02257.x.