

Polymer–ceramic composite electrolytes

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Abstract

This paper reviews the state-of-the-art of polymer–ceramic composite electrolytes in view of three main issues, i.e., conductivity, transport number, and electrode–electrolyte interfacial reactions. These issues are believed to be critical to the development and commercialization of solid polymer batteries. The ceramic phase in limited amounts augments conductivity, enhances the cationic transport number, and suppresses electrode–electrolyte interfacial reactions. Scientific explanation for these effects is also discussed.

Keywords: Polymer composite electrolytes; Ceramic

1. Introduction

Solid polymer electrolytes have attracted a great deal of interest. The major motivation for this interest is a technological application – rechargeable and high energy density power sources. The early research results have led to the development of prototype batteries and their extensive evaluation under simulated conditions. The research and development efforts of the last fifteen years have contributed significantly toward the identification and definition of issues for further development of solid polymer electrolytes. Ambient temperature conductivity, the cationic transport number, and electrode–electrolyte interfacial reactions constitute the main issues. These issues need focused attention and satisfactory solutions before solid state polymer batteries become commercially viable.

Polymer–ceramic composite electrolyte is a subset of the general class of solid electrolytes and is continuing to evolve. Only about a dozen papers have been published on this topic. Some of these papers are only exploratory in nature. The purpose of this paper is to review the literature on ceramic–polymer composite electrolytes in the context of the aforementioned issues and then assess the future potential of this new generation of electrolytes.

2. Previous work

Weston and Steele [1] mixed polyethylene oxide (PEO)–LiClO₄ polymer complex with 10 vol.% α -al-

umina powder with the purpose to improve the mechanical stability of the electrolyte. They also investigated the effect of the filler on the ionic conductivity and transport number. Although the effect of α -alumina was negligible on the conductivity and transport number, the mechanical stability over 100 °C exhibited a major improvement. Skaarup et al. [2] investigated mixed phase electrolytes consisting of Li₃N, LiCF₃SO₃ and PEO to take advantage of the desirable attributes of inorganic and polymer components of the mixed phase electrolyte. They reported that at small volume fractions of polymers (0.05–0.10), the room temperature conductivity was larger by about a factor of 1000 than that of the polymer and the activation energy for conduction in the composite electrolyte was comparable to that of the inorganic phase, Li₃N. Plocharski and Wieczork [3] investigated PEO–NaI polymer mixed with Na_{3.2}Zr₂Si_{2.2}P_{0.8}O₁₂ ceramic powder. They reported at least an order of magnitude increase in the conductivity ascribed to the addition of the ceramic powder. They attributed the conductivity enhancement to an increase in the volume fraction of the amorphous polymer phase. Plocharski et al. [4] further investigated the effect of Al₂O₃ and Nasicon powder additions on the properties of PEO–NaI electrolytes. Ionic conductivity exceeding 10⁻⁵ S cm⁻¹ at room temperature was reported. The enhanced conductivity was attributed to the higher volume fraction of the amorphous phase postulated to result from a higher nucleation rate during the solidification process. Skaarup et al. [5] investigated a mixed phase electrolyte containing lithium sulfide glasses

($1.2\text{Li}_2\text{S} \cdot 1.6\text{LiI} \cdot \text{B}_2\text{S}_3$) in nonconducting polyethylene. Room temperature ionic conductivities of these electrolytes were about 1000 times higher than those of PEO-based polymer electrolytes. Their results suggested that the polymer phase does not have to be an ionic conducting type polymer and can be chosen to impart superior mechanical, chemical, and thermal properties. Capuano et al. [6] reported that incorporation of $\gamma\text{-Al}_2\text{O}_3$ or LiAlO_2 up to about 10 wt.% in the PEO-based polymer electrolyte increases room temperature conductivity by an order of magnitude. In addition, the composite electrolytes exhibited improved mechanical properties and enhanced interfacial stability. Subsequent work on these electrolytes by Croce et al. [7,8] suggested that the addition of finely dispersed ceramic powders such as $\gamma\text{-LiAlO}_2$ and zeolite effectively controls the morphology and growth of the passivation layer on the lithium electrode. Conductivity enhancement was also reported by Munichandraiah et al. [9] when zeolite up to 30% was introduced in the $(\text{PEO})_8:\text{LiBF}_4$ polymer complex. The enhancement in conductivity was also accompanied by a decrease in heat of fusion and an increase in the glass transition temperature of PEO. Kumar et al. [10] reported no increase in the room temperature conductivity when a lithium borosulfate glass was incorporated in a $\text{PEO}:\text{LiBF}_4$ polymer complex; however, the charge-transfer resistance decreased by a factor of three due to the small addition of the lithium borosulfate glass. Przulski et al. [11] investigated $(\text{PEO}-\text{NaI}):\text{SiO}_2$ composite electrolytes. These electrolytes possessed about an order of magnitude higher conductivity than that of $\text{PEO}-\text{NaI}$ electrolytes at ambient temperature. The conductivity enhancement was attributed to decreased crystallinity which was measured by the X-ray diffraction technique. In addition, they also reported improved mechanical and thermal stabilities of these composite electrolytes. Recently, Kumar and Scanlon [12] investigated $\text{PEO}:\text{LiBF}_4\text{-Li}_3\text{N}$ composite electrolytes containing 5 to 50% Li_3N . An order of magnitude increase in conductivity of the composite electrolytes at ambient temperature was reported. Furthermore, these materials exhibited improved lithium–electrolyte interfacial stability.

The ceramic component of composite electrolytes can be classified into two categories, active and passive. The active components comprise materials such as Li_3N and LiAlO_2 . Due to the presence of lithium ions, these materials do participate in the conduction process. The passive components comprise materials like Al_2O_3 , SiO_2 , etc., which do not participate in the process. The choice between active and passive components has been quite arbitrary up to this point and a preference is beginning to emerge in favor of active components for reasons to be explained later.

It is interesting to note that most of the reported work has primarily focused on conductivity, while paying

little attention to the remaining two issues, i.e., cationic transport number and lithium–electrolyte interface stability. The intent of this paper is to assess these composite electrolytes in view of all three issues.

3. Conductivity

Kumar and Marsh [13] have compared and contrasted ionic conductivity of inorganic solids and polymer electrolytes. The conductivity of most inorganic solids exhibits strong but linear temperature dependence. The temperature dependence can be theoretically predicted on the basis of the vibrational frequency and jump probability of the conducting ions across a potential barrier. However, unlike these inorganic solids, polymer electrolytes display characteristic nonlinear temperature dependence which suggests contributions from more than one mechanism. Kumar and Marsh [13] suggested two concurrent conduction processes, the first resulting from the vibrational frequency (kT/h) and the second from the chain-assisted motion of conducting ions. Based on these analyses, they predicted an enhancement of conductivity if a polymer electrolyte is excited by an external resonant mechanical frequency. The prediction was subsequently verified by experimental results [14]. In contrast to Kumar and co-workers [13,14], Angell [15,16] has explained and assessed conductivity of inorganic glasses and polymers from structural consideration of the liquid state. Angell's primary argument is derived from experimental evidence that electrical and structural relaxation modes in the liquid state are coupled. The coupling of the modes gives rise to the high ($\cong 10^{-1} \text{ S cm}^{-1}$) conductivity of liquid electrolytes. The viscosity of a liquid exemplifies its structural relaxation mode and it is often related to the conductivity. As the temperature is lowered, many liquids transform to glassy solids at the glass transition temperature. The structural mode below the glass transition temperature gets frozen and the electrical relaxation mode thus decouples. Angell [15,16] generalized the concept by proposing a parameter known as the decoupling ratio or constant, R . The decoupling ratio R is defined as:

$$R = \tau_s / \tau_o$$

where τ_s is the structural relaxation time, and τ_o is the electrical (conductivity) relaxation time. For glassy solids at temperatures below their glass transition temperature (T_g), R can be of the order of 10^{13} , whereas for polymer electrolytes which are useful above T_g , R can approach and even drop below unity. Typically for polymer electrolytes, R is of the order of 10^{-3} , implying the analyses of a structural relaxation time three orders of magnitude lower than the electrical relaxation time. It should also be recognized that morphologies of polymers like PEO are different from those of the inorganic glasses in the

sense that even below the T_g , they are composed of a mixture of amorphous and crystalline phases whose ratio depends upon composition and processing parameters. Although it has been shown that these polymers primarily conduct through the amorphous region, nonetheless interference from the crystalline regions cannot be totally ruled out.

The proposed concepts of the transport process by Kumar and co-workers [13,14] and Angell [15,16] converge and agree, particularly near T_g . Angell's [15,16] analyses originated with a consideration of the structure of liquids while Kumar and co-workers [13,14] first considered ionic conductivity in an inorganic solid where all the lattice sites are rigid and then extended this to explain ionic conductivity in semi-solids such as polymers. The conductivity of polymer–ceramic composite electrolytes can be analyzed using the aforementioned concepts [13–16] of transport mechanisms in a primarily amorphous material such as PEO-based electrolytes near T_g .

Ceramic additives such as Al_2O_3 , $LiAlO_2$, SiO_2 , zeolite and Li_3N in small amounts (<50%) have been shown to increase the ambient temperature conductivity of composite electrolytes. However, there are two reports [1,10] where the addition of α -aluminum oxide and lithium borosulfate glass had shown neither beneficial nor adverse effects on the conductivity. A larger fraction of ceramic additives (>50%) generally has an adverse effect on conductivity. The only exception to this general statement is the composite electrolyte containing Li_3N which can be explained on the basis of its high ionic conductivity. In view of these observations, it may generally be stated that ceramic additives in small amounts have a beneficial effect on conductivity.

The mechanism of conductivity enhancement due to these ceramic additives remains uncertain at the present time. The proposed idea that ceramic additives reduce polymer crystallinity, which in turn enhances conductivity, appears to have a limited appeal in view of a recent report by Munichandraiah et al. [17] in which they observed no significant increase in conductivity in totally amorphous polymers such as commercial hydrins containing epichlorohydrin repeat units doped with zeolite. The ionic conductivity is facilitated in the amorphous phase through the cooperative motion of lithium ions and polymer chains. It is also known that the addition of ceramic particles enhances amorphous phase formation and at the same time raises T_g [9,11]. The increased T_g in turn should reduce the segmental chain motion and thereby reduce the conductivity.

Thus, the effect of ceramic additives in polymers like PEO has two facets, (i) it enhances the volume of the amorphous phase which should help the transport process, and (ii) it also increases the glass transition temperature that suppresses polymer chain motion and thus the transport of lithium ions. Fig. 1 shows ex-

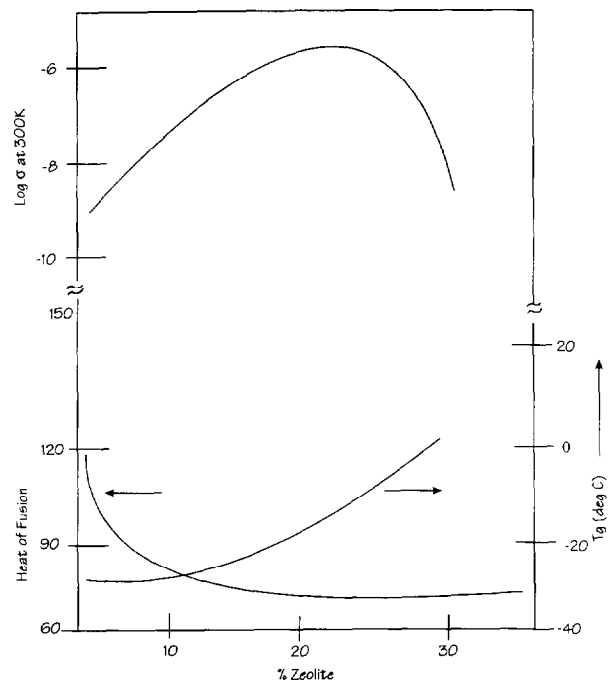


Fig. 1. Effect of zeolite addition on the conductivity, heat of fusion and glass transition temperature (T_g).

perimentally measured data on T_g , heat of fusion (degree of crystallinity), and conductivity of the (PEO)₈: $LiBF_4$ -zeolite composite electrolyte as reported by Munichandraiah et al. [9]. The data are consistent with the preceding analysis and inferences. The two antagonistic effects of amorphous phase formation and T_g on the transport process possibly account for the small increase in conductivity.

The conductivity and T_g in polymer electrolytes are closely linked together. The general observation that polymer solid electrolytes conduct very poorly near or below T_g remains valid even today. But it is interesting to note that in polymer–ceramic composite electrolytes, conductivity increases moderately, in spite of significant increases in T_g [9,11]. Some of this enhancement can be attributed to the increased volume fraction of the amorphous phase; however, a significant fraction could also be associated with the generation of polymer–ceramic grain boundaries. Perhaps the structure and chemistry of ceramic–polymer grain boundaries may have an even more important role than the formation of an amorphous phase in the electrolyte. The grain boundaries are the sites of high defect concentration which may allow faster ionic transport. The chemistry and structure of the grain boundaries will be determined by the chemical compatibility between the polymer and the ceramic component. Reactive ceramics such as Li_3N and $LiAlO_2$ may give rise to more defect-rich grain boundaries than the inert ceramics such as SiO_2 and

Al_2O_3 . It is conceivable that these grain boundaries may serve as channels for the conducting ions and thus the selection of appropriate polymer and ceramic phases become an important consideration in the development of fast ion-conducting composite electrolytes. Solid exhibiting high ionic conductivity such as $\beta\text{-Al}_2\text{O}_3$, RbAg_4I_5 and Li_3N possess conduction channels that allow faster ionic transport ($\cong 10^{-3}\text{--}10^{-4} \text{ S cm}^{-1}$) at ambient temperatures with low activation energy. The high conductivity and low activation energy are complementary to each other and share the same origin. Both properties seems to be optimum in solids with disordered open channels and layered structures in which the number of sites for ion jump outnumber the available ions to occupy them. The polymer–ceramic grain boundaries or interfaces may provide similar structures. The coupling of conductivity and structural modes above T_g is the primary factor for the high conductivity of polymer electrolytes. When a ceramic material in significant amounts is incorporated in a polymer matrix, the coupling induced conductivity is suppressed. A preferred conduction path through grain boundaries in polymer–ceramic composite electrolyte is a reasonable scenario which may account for the moderate increase in conductivity.

If a component such as Li_3N is chosen, its high conductivity should affect the bulk conductivity of composite electrolytes. The rule of mixture may be invoked to make a quantitative prediction on the bulk conductivity. The basic postulate for the proposed rule of the mixture is that if two phases, one with higher conductivity and another with lower conductivity, are mixed together wherein the primary conduction ion is the same in the two phases, the conductivity of the mixed phase will have an intermediate value between the two extreme values of conductivity corresponding to the two phases. Using this postulate and available information in the literature on conductivity of Li_3N and $\text{PEO}:\text{LiBF}_4$ materials, conductivities of the composite electrolytes have been computed and are shown in Fig. 2. It should be noted from Fig. 2 that the conductivity of the composite electrolyte increases for all volume fractions of Li_3N ; however, remarkable increases are achieved only at very high concentrations of Li_3N . In this computation, preferred conduction through the Li_3N –polymer grain boundaries has been ignored.

Experimentally measured conductivity for 5, 25, and 40% Li_3N composite electrolytes from the work of Kumar and Schaffer [18] is shown in Fig. 3. It should be noted that conductivity increases not only at ambient temperature but over the entire temperature range as the volume fraction of Li_3N is increased. The conductivity enhancement appears to be consistent with the preceding analysis using the rule of mixture. Unlike the passive ceramic components, these electrolytes do

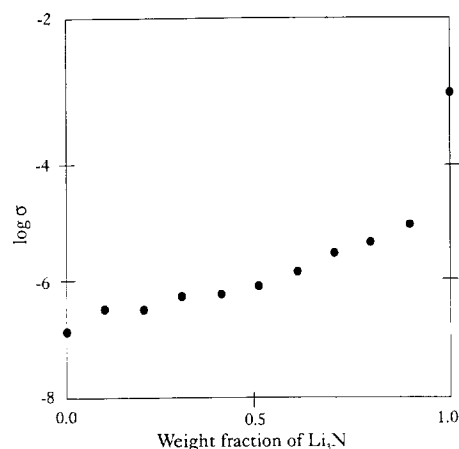


Fig. 2. Conductivity of Li_3N – $(\text{PEO})_8:\text{LiBF}_4$ composite electrolyte vs. volume fraction of Li_3N .

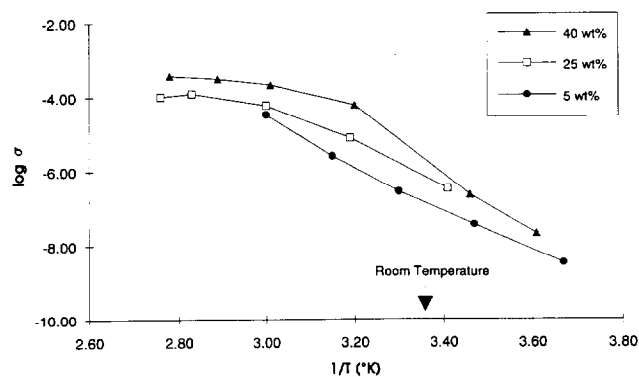


Fig. 3. $\log \sigma$ vs. $1/T$ plots of 5, 25, and 40% Li_3N materials.

not exhibit an optimum concentration of Li_3N above which the conductivity decreases. The a.c. impedance measurements up to 60% of Li_3N reveal continuous increase in conductivity over the 0–100 $^{\circ}\text{C}$ temperature range. It should also be stated here that Li_3N is not electrochemically stable and thus it may have limited applications in lithium batteries.

4. Transport number

The fact that motions of polymer chains contribute to the transport of lithium ions in the polymer electrolytes also has deleterious effects on the transport number. The chain motion also facilitates transport of anionic species and thus the measured conductivity includes contribution from both the species. Although numerous transport number measurements have been reported, a reliable and universally acceptable measurement technique is still lacking as pointed out by Bruce et al. [19]. Nonetheless, some of the polymer electrolytes have cationic transport numbers as small as 0.3 [20]. As a result, when such materials are used

in a battery, extensive concentration gradients are set up during use and they affect its electrical performance.

Why would the large size and heavy mass of the anionic groups compared to lithium have a transport number around 0.7? The literature on polymer electrolytes has not directly addressed this question. In a truly solid electrolyte consisting of similar cationic and anionic species, this behavior is improbable due to the fact that the vibrational frequency and jump probability for cationic species would be much greater than for the anionic species. A possible answer to the question is again related to the coupling phenomenon discussed earlier. It is conceivable that the anionic species is more coupled to the polymeric structure than the cationic species, which may account for its higher transport number. The vibrational frequencies and motion of large anionic species and polymer chains are expected to be more in phase than those of cationic species and polymer chains.

Angell [15,16] has assessed the transport number of amorphous polymer electrolytes and glassy inorganic solids in terms of the decoupling constant, R . For glassy inorganic solids, at temperatures below their T_g , R can be of the order of 10^{13} , whereas R approaches and even drops below unity for polymer electrolytes near the ambient temperature. Typically for polymer solid electrolytes, R is of the order of 10^{-3} , implying structural relaxation time three orders of magnitude lower than the electrical relaxation time.

In general, the decoupling index R is an indicator of the transport number. The larger the value of R , the greater is the cationic transport number at a given temperature. In the polymer–ceramic composite electrolytes, T_g increases in proportion to the volume fraction of the ceramic phase. Przulski et al. [11] reported an increase of 50 °C in T_g when 20 wt.% hydrophobic SiO_2 was introduced into a $(\text{PEO})_{10}\text{-NaI}$ polymer. Munichandraiah et al. [9] reported an increase of 25 °C in the transition temperature when 29% of the zeolite was introduced into a $\text{PEO}:\text{LiBF}_4$ electrolyte. Angell [15] has shown that at $T/T_g = 1.2$, the R value could be $\sim 10^2$ and the transport number could be over 0.9. An increase of 50 °C in the T_g in most polymer electrolytes will bring the T/T_g ratio to 1.2 and the transport number to around 0.9.

The conductivity of polymer electrolytes originates from two distinct processes, i.e., ion hopping and ion transport assisted by polymer chain motion. The measured conductivity is thus comprised of contributions from these two processes. The addition of a ceramic phase suppresses the chain motion mediated contribution and thus it must increase the contribution associated with ion hopping such that the conductivity remains the same (the worst case-scenario). The ion-hopping process is more favorable for the cationic species because of its small size and mass than for the

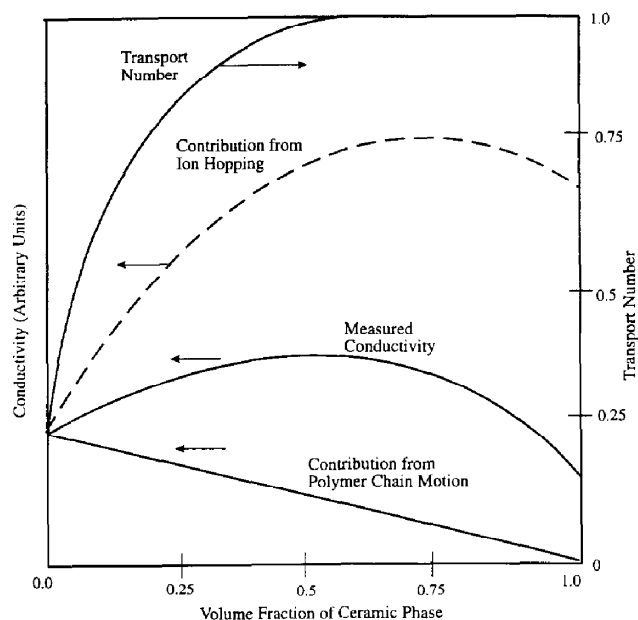


Fig. 4. Schematic representation of conductivity at ambient temperature; contributions from ion hopping and polymer chain motion, and transport number.

anionic species. This scenario as shown in Fig. 4 suggests an enhanced cationic transport number as the volume fraction of the ceramic phase increases.

The conductivity and transport number of polymer–ceramic composite electrolytes comprising LiI , PEO , SiO_2 , MgO , and Al_2O_3 have been measured and reported by Nagasubramanian et al. [21] and Peled et al. [22]. They calculated conductivity from bulk resistance and R_b measured at high frequency and transport number, t^+ using the equation:

$$t^+ = \frac{R_b}{R_b + Z_d}$$

where Z_d is diffusional impedance as measured from Nyquist or Bode plots. For the composite electrolyte film with 0.05 μm alumina the bulk conductivity is around $10^{-4} \text{ S cm}^{-1}$ and the lithium ion transport number is close to unity at 104 °C. This experimental evidence adds further credence to our proposed effect of ceramic additives on the transport number.

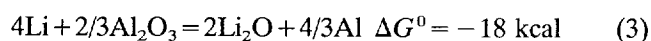
5. Interfacial stability

In a lithium rechargeable battery, the lithium electrolyte interface is of critical importance. Due to the extreme reactivity of the lithium metal, most of the developed polymer electrolytes passivate lithium. In particular, impurities such as oxygen and water tend to accelerate the passivation mechanism and eventually consume the lithium electrode.

Passivation of the lithium electrode in a non-aqueous organic electrolyte is a well recognized and thoroughly investigated phenomenon [23], however, lithium–solid polymer electrolyte interfacial study is still in its infancy. Croce and co-workers [7,8] have investigated Li/(PEO)₈:LiClO₄, Li/(PEO)₈:LiClO₄- γ -LiAlO₂, and Li/PAN-EC-PC:LiClO₄ interfaces using a.c. impedance spectroscopy (PAN=polyacrylonitrile, EC=ethylene carbonate, PC=propylene carbonate). Among the three interfaces, the Li/(PEO)₈:LiClO₄- γ -LiAlO₂ interface exhibited the most stable behavior. Croce and co-workers [7,8] speculated that the interfacial stability resulted from the scavenging ability of the ceramic powder, γ -LiAlO₂, in the electrolyte. Kumar et al. [10] reported suppression of the charge-transfer resistance in a Li/PEO:LiBF₄/Li cell by a factor of three when a glass powder of the 0.4B₂O₃·0.4Li₂O·0.2Li₂SO₄ composition was introduced into the polymer electrolyte. The charge-transfer resistance is an indirect indicator of the passivation phenomenon and interfacial stability. A few of these symmetric Li/electrolyte/Li cells employing composite electrolytes were cycled for over 1500 cycles at ambient temperature with no obvious problems. Munichandraiah et al. [17] reported that at low temperatures and low concentrations of zeolite the exchange current density for the Li/Li⁺ reaction in a Li/composite electrolyte/Li cell increases. The composite electrolyte consisted of hydrin elastomer doped with LiBF₄ and zeolite. The enhanced exchange current density was attributed to the presence of zeolite.

Thin rechargeable lithium batteries with ceramic electrolytes have been investigated by Bates and co-workers [24–26]. The ceramic electrolyte consisted of a thin film of lithium phosphorus oxynitride which was prepared by sputtering Li₃PO₄ in a pure nitrogen atmosphere. A typical composition of the electrolyte was Li_{2.9}PO_{3.3}N_{0.46}. The electrolyte exhibited excellent long-term stability in contact with lithium. Although it is recognized that these ceramic electrolytes are altogether different to the polymer–ceramic composite electrolytes, the important point to note is that the lithium–ceramic interfaces do exhibit stable behavior.

Why would a lithium–ceramic interface be more stable than that of a lithium–polymer interface? Perhaps the question can be answered by examining lithium reactivity with typical ceramics such as CaO, MgO, Al₂O₃ and SiO₂. These reactions along with their standard free energies of reaction [27] are presented in Eqs. (1)–(3):



The algebraic sign and magnitude of the free energy of reactions determine whether lithium will be passivated or not and if passivated what the degree of passivation will be. The positive sign of the free energy for reactions (1) and (2) suggests that lithium passivation is unlikely to occur when it is kept in contact with either CaO or MgO. The passivation is predictable with Al₂O₃ and SiO₂ due to the fact that reactions (3) and (4) have negative free energies. In addition, the more negative is the free energy, the more stable the passivated film (Li₂O) will be. In other words, the stability of Li₂O at the Li–SiO₂ interface is favored as compared to the Li–Al₂O₃ interface. Even the stability of the Li–Al₂O₃ interface is questionable in view of the experimental data on Li and (Li) β -Al₂O₃ interfaces investigated and reported by Farrington and Roth [28].

Ceramic additives such as nitrides (AlN, BN, etc.) may perform better than SiO₂ or Al₂O₃ because passivation of lithium metal will result in the formation of Li₃N which has a higher ionic conductivity and may even facilitate transport of lithium through the passivated layer.

Thermodynamic data on the interfacial reactions of lithium–polymer electrolytes are not available which severely limits our ability to make quantitative predictions with respect to improvements realizable by the use of a specific ceramic additive in a given polymer electrolyte.

Schematic diagrams of the lithium–composite electrolyte interfaces are shown in Fig. 5(a) and (b). The ceramic particles, depending upon the volume fraction, would tend to minimize the area of lithium electrode exposed to polymers containing O, OH⁻ species and thus reduce the passivation process. It is also foreseeable that smaller size particles for a similar volume fraction of the ceramic phase would impart an improved performance as compared to larger size particles because they will cover more surface area. The formation of an insulated layer of ceramic particles at the electrode surface is probable at higher volume fraction of a

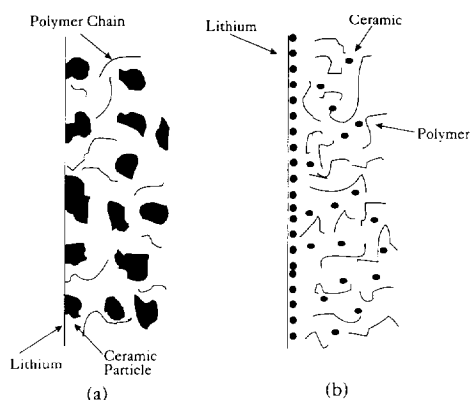


Fig. 5. Schematic diagram of lithium–composite electrolytes: (a) larger size particles, and (b) smaller size particles.

passive ceramic phase. The insulating layer will impede electrode reactions. This may very well have happened when excessive amounts of the passive ceramic phase were introduced into the polymer matrix [7,9].

The experimental evidences are numerous and consistently show that the lithium–composite electrolyte interfaces are more stable and efficient than Li–polymer electrolyte interfaces. The mechanism for the improved stability and efficiency is not well understood. However, some proposals do exist in the literature and these include scavenging effects of the ceramic phase and screening of lithium electrodes with an inert ceramic solid. It will take careful and sustained experimental studies to unfold the underlying mechanisms for improved interfacial stability.

6. Summary and conclusions

A review of the state-of-the-art of polymer–ceramic composite electrolytes along with some experimental data obtained in the authors' laboratory on $\text{Li}_3\text{N}:\text{PEO}:\text{LiBF}_4$ electrolytes have been presented and discussed. An analysis of a broader range of composite electrolytes with respect to their conductivity reveals that the incorporation of a ceramic phase in a polymer matrix leads to two effects. The first is the enhancement of the amorphous phase which should theoretically enhance conductivity. The second effect is an increase of T_g with increasing volume fraction of the ceramic phase which should reduce conductivity due to the fact that the polymer chain assisted motion of the conducting ion is suppressed. These two effects are antagonistic in nature and perhaps account for the relatively small reported increase in conductivity in polymer–ceramic composite electrolytes. A possibility of developing conduction channels through the grain boundary has been discussed. A proper selection of polymer and ceramic components may lead to a polymer–ceramic interfacial structure conducive to enhance the transport process. This is a potentially important avenue to accomplish further increases in conductivity.

Although at the present time the benefit from the conductivity point of view is small, all the available information suggests that these composite electrolytes should have a high cationic transport number due to decoupling of structural and electrical relaxations which occurs by the enhancement of T_g when a ceramic phase is introduced into a polymer matrix. Perhaps the possibility of cationic transport number augmentation is the most important feature of these composite electrolytes.

The experimental data and theoretical considerations on lithium–composite electrolyte interfaces reveal promising features. These interfaces are extremely stable and efficient.

It should be stated here that electrochemical data on the composite electrolytes are still scarce; nonetheless, they appear to possess many beneficial properties that may lead to their use in commercial rechargeable lithium batteries.

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