



Composite Electrolytes for Lithium Rechargeable Batteries

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Abstract. The paper reviews and presents attributes of emerging polymer-ceramic composite electrolytes for lithium rechargeable batteries. The electrochemical data of a diverse range of composite electrolytes reveal that the incorporation of a ceramic component in a polymer matrix leads to enhanced conductivity, increased lithium transport number, and improved electrode-electrolyte interfacial stability. The conductivity enhancement depends upon the weight fraction of the ceramic phase, annealing parameters, nature of polymer-ceramic system, and temperature. The ceramic additive also increases the effective glass transition temperature and thus decouples structural and electrical relaxation modes which in turn increases the lithium transport number. The ceramic additives also provide a range of free energy of reactions with lithium. A few of the ceramic materials (MgO , CaO , Si_3N_4) have positive free energy of reaction and they should not passivate lithium electrodes.

Keywords: composite, electrolyte, polymer-ceramic, lithium, battery

Introduction

Societal needs and concerns call for concerted measures to deal with issues of human transportation, efficient uses of energy, and global warming. In a broader sense, all of these issues are interlinked, and a satisfactory solution will require technological innovations in a number of disciplines. Energy-related issues include efficient generation, storage, and transmission of electricity and its conversion to different forms. The storage aspect of the energy-related issues is addressed by lithium rechargeable batteries. Lithium is the lightest solid element and possesses the highest oxidation potential. These attributes allow lithium batteries to offer higher power and energy densities compared to the standard, state-of-the-art lead acid and nickel metal hydride batteries.

The use of lithium in a battery also brings some interesting challenges. This paper identifies these challenges, reviews literature addressing them, and presents recent experimental results on a new

generation of solid electrolytes – polymer-ceramic composites. A typical lithium rechargeable cell, as depicted in Fig. 1, consists of four primary components: anode, electrolyte, cathode, and current collector. The thickness of these components may vary from a few to several hundred microns, and multilayers of these components may be packaged into a battery of different shapes and sizes.

Typical anodic materials are pure lithium (Li), alloyed lithium (Li-Al), and intercalated graphite (Li_xC_6). Efficient electrode reaction, conductivity (electronic and ionic), and relative potential difference with a suitable cathodic material are some of the primary requirements of the anodic material.

The electrolyte which is the subject matter of this paper resides between the anode and cathode and serves many purposes. First, the electrolyte must allow rapid transport of the lithium ion as the current is discharged into or drawn from the external circuit. To a large extent, the power and energy densities of a battery are determined by the conductivity of the electrolyte. The conductivity is also temperature

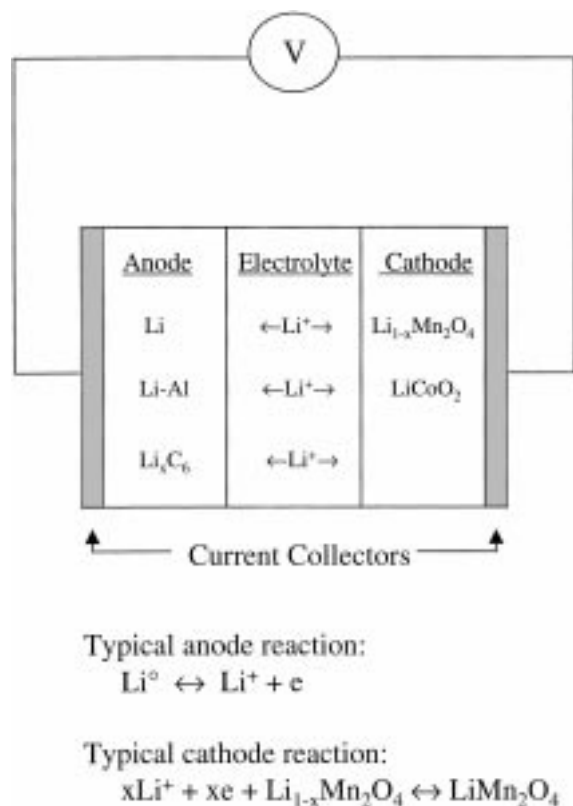


Fig. 1. Schematic illustration of a cell of a solid state lithium rechargeable battery.

dependent, and its large variation in the operational temperature range (-40 to 60°C) is undesirable. The electrolyte must also be thermally stable for a long period of time in the operational temperature range. Transport of charged species other than lithium through the electrolyte is detrimental to the performance of a lithium battery. The transport of other ionic species leads to polarization, which affects cell performance. Electrodes (anode and cathode) will short circuit if the electrolyte has significant electronic conductivity. These considerations require that the transport number of the lithium ion be as high as possible. Within a high voltage electrode couple, the electrolyte is constantly subjected to an electrical potential gradient, and the electrolyte should be able to withstand such a gradient for the entire life of the cell. Furthermore, anode-electrolyte and cathode-electrolyte interfaces are active sites for electrode reactions — ideally these electrode reactions should be reversible. Irreversibility will lead to reduced cycle life and capacity fade.

A typical cathodic material may be comprised of a spinel type inorganic compound of $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ or LiCoO_2 mixed with suitable binders. The cathodic material should be able to accommodate lithium intercalation and de-intercalation without structural and electrochemical failures.

Electronic conductors, such as copper and aluminum, are typical current collectors. Electronic conductivity and cost are prime considerations. Other researchers have attempted to develop and employ polymers as current collectors, because they further improve practical energy density of lithium batteries.

A variety of dielectric materials, such as polymers, glasses, ceramics, and their combination, may be useful as solid electrolytes. Among those materials, polymers have received considerable attention in the last two decades because of their low density, manufacturability, and capacity to accommodate volume changes as compared to a true rigid, inorganic solid electrolyte. The subject of polymer electrolytes has been well covered by review papers and monographs [1,2]. Inorganic solids and glasses as lithium ion conductors have also received significant attention [3,4] but to a lesser degree. In this paper, inorganic solids and glasses are covered under a material popularly known as ceramics.

Material derived from polymer and ceramic phases can be identified as a polymer-ceramic composite. This composite type of material thus becomes a subset of solid electrolytes and has recently received significant attention. Two review papers [5,6] have been written on the topic. The purpose of this paper is to present the state-of-the-art of the composite electrolytes.

Chemistry, Processing, and Properties

A. Prior Investigations

Because of its popularity, poly(ethylene oxide) has been a polymer of choice for many studies; however, the choice of ceramic phase has been arbitrary and diverse. It may be argued that a suitable matrix should facilitate the transport of lithium ions, which narrows the choice of the polymer component. But, what criteria should be used in selecting a ceramic component? This question was addressed by the authors in an earlier publication [5]. In general, the

ceramic component of composite electrolytes can be classified into two categories: active and passive. The active components are comprised of 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 are comprised of materials such as Al_2O_3 , SiO_2 , etc., which do not participate in the process. The choice between active and passive components has been quite arbitrary.

Weston and Steele [7] mixed a PEO- LiClO_4 polymer complex with a 10 vol% α -alumina powder 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 the α -alumina was negligible on the conductivity and transport number, the mechanical stability over 100°C exhibited a major improvement. Skaarup et al. [8] investigated mixed phase electrolytes consisting of Li_3N , LiCF_3SO_3 , 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 (0.05–0.10), the room temperature conductivity was about a factor of 1,000 larger than that of the polymer, and the activation energy for conduction in the composite electrolyte was comparable to that of the inorganic phase, Li_3N . Plochanski and Wiczork [9] investigated a PEO-NaI polymer mixed with $\text{Na}_{3.2}\text{Zr}_2\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{12}$ ceramic powder. They reported at least an order of magnitude increase in the conductivity which they ascribed to the addition of the ceramic powder. They attributed the conductivity enhancement to an increase in volume fraction of the amorphous polymer phase. Plochanski et al. [10] further investigated the effect of Al_2O_3 and Nasion 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. [11] 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 1,000 times higher than that of PEO-based polymer electrolytes. Their results suggest 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. [12] reported that incorporation of γ - 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 composite electrolytes by Croce et al. [13,14] suggest that the addition of finely-dispersed ceramic powders such as γ - LiAlO_2 and zeolite effectively controls the morphology and growth of the passivation layer on the lithium electrode. A conductivity enhancement was also reported by Munichandraiah et al. [15] when up to 30% zeolite was introduced in the $(\text{PEO})_8 : \text{LiBF}_4$ polymer complex. The conductivity enhancement was also accompanied by a decrease in heat of fusion and an increase in the glass transition temperature of PEO. Kumar et al. [16] reported no increase in room temperature conductivity when a lithium borosulfate glass was incorporated in a PEO: LiBF_4 polymer complex; however, the charge transfer resistance decreased by a factor of three due to a small addition of the lithium borosulfate glass. Kumar and Scanlon [5] investigated PEO: LiBF_4 - Li_3N composite electrolytes containing 5 to 50% Li_3N . An order of magnitude increase in conductivity of the composite electrolytes at the ambient temperature was reported. Furthermore, these materials exhibited improved lithium-electrolyte interfacial stability. Choi and Shin [17] reported properties of $(\text{PEO})_{16} : \text{LiClO}_4$ -SiC/ Si_3N_4 composite electrolytes. They observed a small conductivity enhancement for SiC content less than 15 wt%. Contrary to the general observation, they reported a decrease in T_g and an enhancement in crystalline content as the concentration of SiC increased. Munichandraiah et al. [18] reported no significant increase in conductivity in totally amorphous polymers such as commercial hydrins containing epichlorohydrin repeat units doped with zeolite. A study by Nairn et al. [19] incorporated $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ ceramic into a fully amorphous polyether, an ethylene oxide/propylene oxide copolymer. They reported a conductivity value of $(1.9 \pm 0.2) \times 10^{-4}\text{ S cm}^{-1}$ at 40°C which was approximately an order of magnitude higher than the conductivity of either the polymer or ceramic phase. A polymer-ceramic composite containing a very high concentration of ceramic phase ($0.56\text{Li}_2\text{S} \cdot 0.19\text{B}_2\text{S}_3 \cdot 0.25\text{LiI}$ glass) in a PEO: $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ polymer with an O:Li ratio of 6 was investigated by

Cho and Liu [20]. They reported that the addition of the polymer increased not only the mechanical flexibility but also the ionic conductivity, lithium ion transport number, and stability with respect to Li, Li_xC_6 , and $\text{Li}_2\text{Mn}_2\text{O}_4$ electrode materials. Solid electrolytes have been synthesized by intercalating poly(ethylene oxide) into various layered silicates such as montmorillonite and fluorohectorite [21]. The room temperature lithium ion conductivity was enhanced by two orders of magnitude and conductivity transitions associated with the melting and glass transition temperatures were suppressed.

B. Processing

A number of processing techniques may be used to obtain film and bulk specimens of polymer-ceramic composite electrolytes for laboratory evaluations. The most convenient one is the blend and press technique in which the polymer, lithium salt, and ceramic components are mixed in a predetermined proportion, ground in a mortar and pestle, hot pressed into pellet form, and then rolled into films of desired thickness. The processing parameters such as compacting pressure, temperature, time, and rolling conditions depend upon compositions. A range of materials covering a wide concentration of ceramic phases in a polymer matrix can be obtained by this technique [22]. The second technique involves solvent casting, in which a solid ceramic phase is dispersed in a solution of polymer and lithium salt. The homogenized colloidal solution is then cast into a mold to obtain films of varying thicknesses [23]. These two techniques and their variations can provide films covering a variety of polymers and diverse ceramic components.

C. Recent Development

From Section A (Prior Investigations), it is evident that there is a considerable degree of uncertainty in experiential results reported from various laboratories. The polymer-ceramic composite electrolyte materials cross two established disciplines of science, and at times erroneous interpretations and conflicting results have been reported. But this may be justifiable, as it happens in any evolving field of science. As the field matures, more objective and systematic studies will be reported. We present in this section some of our own recent results highlighting the importance of low temperature annealing and lithium concentration.

1. *Effect of low temperature annealing.* Figure 2 shows the temperature dependence of conductivity of a PEO:LiBF₄-TiO₂ (20 wt %) electrolyte subjected to a wide range of heat treatments. It should be noted that the effect of heat treatment in the 60 to 100°C range on conductivity is pronounced. For example, the room temperature conductivity increases by almost three orders of magnitude between the two extremes of the heat treatment schedule. Furthermore, the conductivity enhancement is also associated with a reduced activation energy for lithium transport.

Figure 3 depicts the conductivity evolution of PEO:LiBF₄-TiO₂ (30%) as a function of heat treatment. As-prepared film exhibits conductivity typical of PEO-based electrolytes. A heat treatment at 87°C for 21 h raises ambient temperature conductivity by four orders of magnitude. However, unlike the PEO:LiBF₄-TiO₂ (20%) specimen shown in Fig. 2, further heat treatments reduce low temperature conductivity.

The conductivity data of Figs. 2 and 3 convincingly demonstrate the importance of heat treatment. Prior investigations have paid little attention to this processing variable and perhaps this may account for the broad range and sometimes even inconsistent results.

2. *Effect of lithium concentration.* Polymer electrolytes in the PEO:LiX system are known to yield optimum conductivity around an oxygen to lithium ratio ([O]:[Li]) of 8. In our earlier work on composite electrolytes involving Li₃N [22] and TiO₂ [24], the [O]:[Li] ratio in the electrolytes was maintained at 8. Figure 4 shows the effect of [O]:[Li] ratio on the conductivity of a PEO:LiBF₄-ZrO₂ (30 wt %) composite electrolyte. The specimens were annealed at 50 and 100°C to stabilize and optimize conductivity. It is interesting to note that even in composite electrolytes, the highest conductivity is obtained when the [O]:[Li] ratio is maintained at 7.73:1. Increasing the lithium concentration ([O]:[Li] = 3.8:1) suppresses high temperature conductivity, reduces the transition effect normally observed around 70°C, and enhances low temperature conductivity. The effect of lithium concentration on conductivity is quite pronounced.

D. Electrochemical Properties

1. *Conductivity.* In a stricter context, a polymer electrolyte refers to a solvent-free material in which

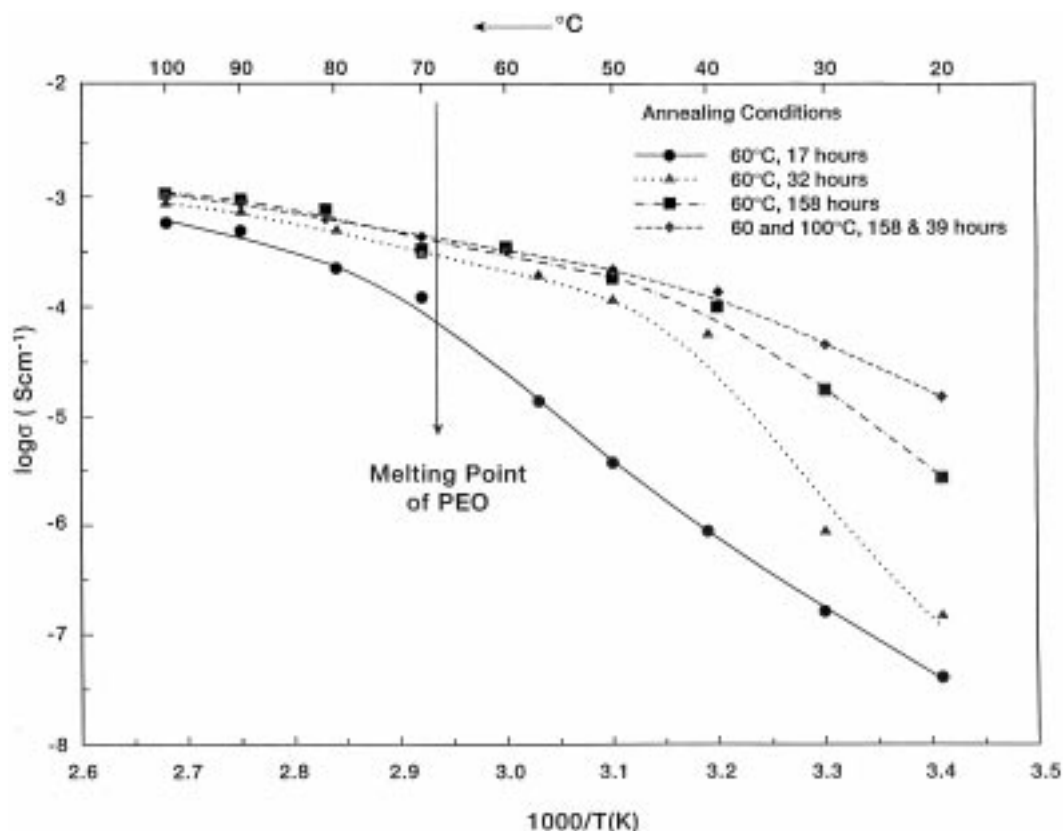


Fig. 2. Log σ versus $1000/T(K)$ of PEO:LiBF₄-TiO₂ (20%) electrolyte annealed under various conditions.

an ionically conducting phase is formed by dissolving lithium salts in a high molecular weight polar polymer matrix. Over the years, this definition has been modified to include gel type electrolytes in which lithium salt is dissolved in a polar liquid and subsequently incorporated in an inert polymer matrix. The transport mechanisms are different for these two types of electrolytes. In the solvent-free, dry electrolytes, the polymer itself is the solvent, and unlike the liquid solvent its mobility is restricted. The first dry polymer electrolytes were based on high molecular weight poly(ethylene oxide), PEO, which remains the mainstay of dry electrolytes as of this writing. The structural unit of PEO is $-(CH_2-CH_2O)-$ which allows a high degree of crystallinity, generally in the range of 70 to 85%. The melting point, T_m , of the crystalline phase of PEO is 65°C and the glass transition temperature, T_g , of the

polymer is -60°C . Berthier et al. [25], using nuclear magnetic correlation function, determined that above the melting temperature of PEO, a fraction of the crystalline phase remained in equilibrium with the liquid phase. As the temperature increased above T_m , the crystalline phase gradually transformed into a liquid structure. During cooling, the liquid structure may transform to an amorphous structure below T_m . The metastable nature of the structure thus must be recognized as these PEO-based electrolytes are subjected to temperature variations. From these experiments, Berthier et al. [25] concluded that the amorphous structure was primarily responsible for lithium ion conductivity. The temperature dependence data of conductivity of these PEO-based electrolytes are even more illustrative. Generally, above the T_m a liquid-like conductivity with low activation energy

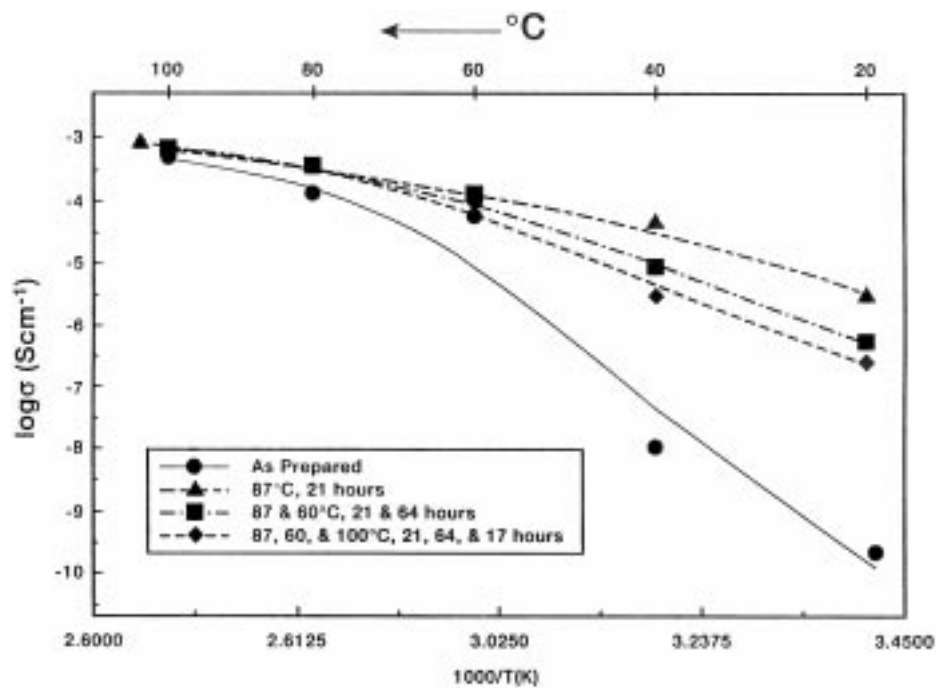


Fig. 3. Log σ versus $1000/T$ (K) of PEO:LiBF₄-TiO₂ (30%) composite electrolyte heat treated under various conditions.

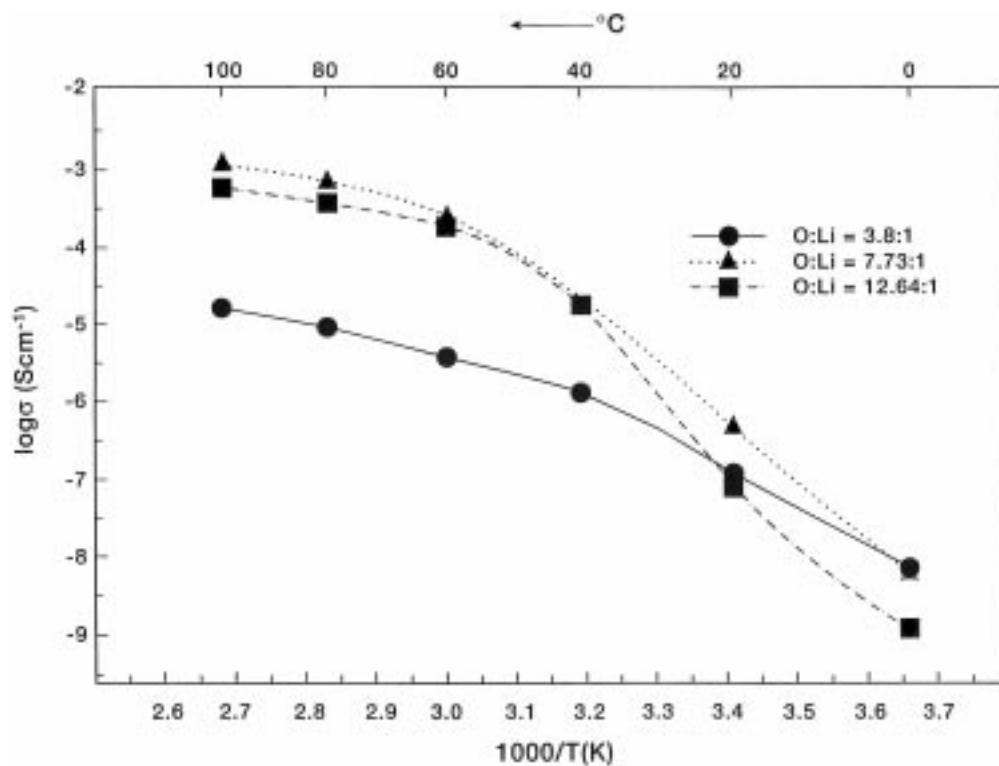


Fig. 4. Conductivity of the PEO:LiBF₄-ZrO₂ (30%) composite electrolyte.

for lithium transport is noted. As the temperature is lowered below T_m , a rapid drop in conductivity is observed. As stated earlier, even below the T_m of PEO there is a considerable volume fraction of amorphous phase, approximately 30%, yet the conductivity drops precipitously.

Kumar and Marsh [26] have compared and contrasted the ionic conductivity of inorganic solids and polymer electrolytes. The conductivity of most inorganic solids exhibits strong and linear temperature dependence. However, unlike these inorganic solids, polymer electrolytes display characteristic nonlinear temperature dependence which implies that one needs to consider contributions from more than one mechanism. Kumar and Marsh [26] 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 and determined [27] an enhancement of conductivity if a polymer electrolyte is excited by an external resonant mechanical frequency. In contrast to the analysis of Kumar and Marsh [26] and Kumar et al. [27], Angell [4,28] has explained the conductivity of inorganic glasses and polymers from structural attributes 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 gives rise to high ($\cong 10^{-1} \text{ S cm}^{-1}$) conductivity of liquid electrolytes. The viscosity of a liquid exemplifies its structural relaxation mode and is often related to the conductivity. As the temperature is lowered, many supercooled liquids transform to amorphous (glassy) solids at the glass transition temperature. The structural mode below the glass transition temperature freezes and the electrical relaxation mode thus decouples. Angell [4,28] generalized the observations by using a concept of decoupling ratio which is defined as $R = \tau_s/\tau_\sigma$, where τ_s is the structural relaxation time and τ_σ is the electrical (conductivity) relaxation time. For glassy solids at temperatures below their 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 three orders of magnitude lower structural relaxation time than the electrical relaxation time.

The structural unit of PEO adopts a helical conformation as shown in Fig. 5. For quite some time, it was believed that the lithium ion moved along a helical structure, now proven to be incorrect. Segmental chain motions are now believed to be a predominant mechanism in the conduction process that may also account for the rather large contribution to the conductivity from the transport of anions. Because of the proximity of sizes in large anion and polymer chains, their motions are believed to be synchronized, which in turn enhances the mobility of large anions. The lithium ion in PEO electrolytes is coordinated with five oxygen atoms and the probability of assuming a similar coordination as it moves in the structure is low. These arguments account for the low lithium ion transport number.

The transport mechanisms for lithium ion conduction become more complicated as the polymer and ceramic phases are mixed together in a composite electrolyte. Not only does one need to be concerned about the transport mechanisms in pure polymer and ceramic components, but also the chemical and physical interaction between the phases and the resulting structure, such as morphology and phase boundaries. The complexity explains the existence of diverse and conflicting views on the lithium transport mechanism in polymer-ceramic composite electrolytes, but experimental results reported from various laboratories show that ceramic additives such as Li_3N , Al_2O_3 , LiAlO_3 , SiO_2 , SiC , $\text{Ti}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$, TiO_2 , ZrO_2 , and zeolite in small amounts ($\leq 30 \text{ wt } \%$) increase ambient temperature conductivity. A larger volume fraction of inert ceramic additives such as Al_2O_3 , SiC ($> 50 \text{ wt } \%$) generally has an adverse effect.

An expression for conductivity, σ , in a true solid as derived from basic principles is given by Eq. (1). The equation has adequately quantified ionic conductivity of solids [29].

$$\sigma = \left[\frac{n\alpha z^2 e^2 b^2}{2h} \right] \exp\left(-\frac{\Delta H}{RT}\right) \quad (1)$$

where

- n = number of ions per cubic centimeter,
- α = accommodation coefficient,
- z = valence on ion,

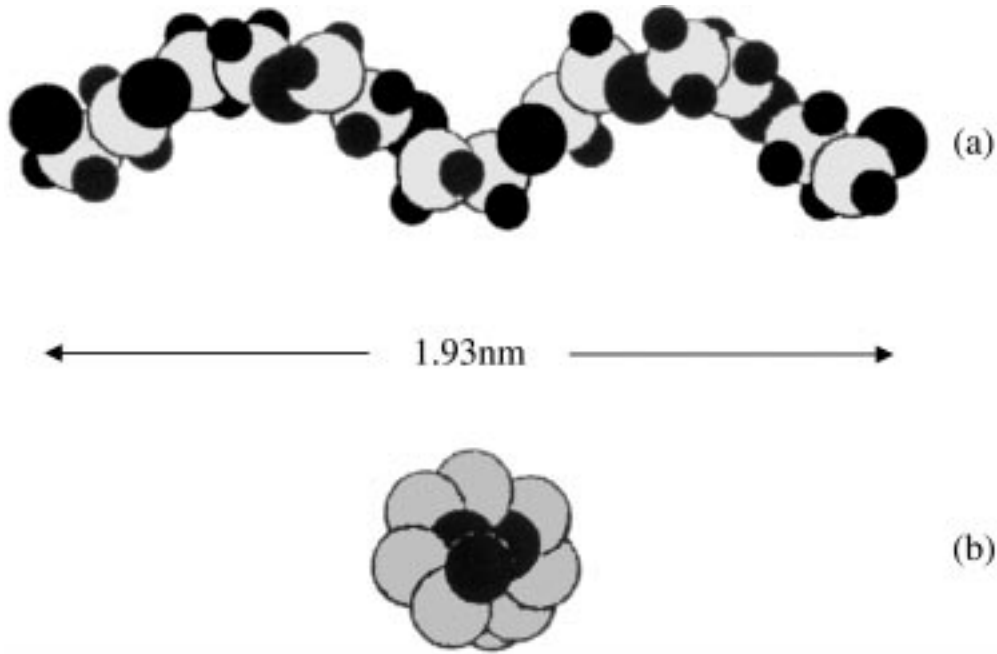


Fig. 5. Poly(ethylene oxide), PEO, structure viewed (a) parallel and (b) normal to the axis of the helix. The black and white circles represent oxygen and carbon atoms, respectively. Hydrogen and lithium atoms are not shown.

e = electronic charge,
 b = distance between potential wells,
 h = Planck's constant,
 ΔH = activation energy,
 R = gas constant and
 T = temperature.

In the PEO:LiBF₄-TiO₂ system subjected to varying annealing schedules, n remains constant, yet three to four orders of magnitude enhancement in conductivity is observed when the specimens are optimally annealed. The enhancement in conductivity, σ , is accompanied by a decrease in the activation energy, ΔH . Nonetheless, σ cannot be entirely correlated with ΔH . The experimental value of ΔH can be substituted in Eq. (1) and the maximum conductivity enhancement achievable is by a factor of 3 to 7. Thus, it is justifiable to look for other mechanisms to account for the observed enhancement in conductivity. The obvious choice is to consider the remaining two variables: accommodation coefficient (α) and distance between potential wells (b). Generally, b is of the order of atomic size and bond

lengths. Orders of magnitude increases in the parameter b is physically unrealistic. It is conceivable that the annealing creates a large number of thermally-induced defects at the polymer ceramic interfaces. These defects accommodate and facilitate movement of lithium ions and impart orders of magnitude increases in conductivity.

Another quantitative description of conductivity is expressed by Eq. (2).

$$\sigma_i = \mu_i(n_i z_i e) \quad (2)$$

The term μ_i refers to the mobility of the i th specie and other terms have the same definitions as in Eq. (1). It is imperative from Eq. (2) that conductivity is directly related to the mobility and concentration of the lithium ion. If the concentration is kept constant, the mobility must increase to account for conductivity enhancement. The mobility in the polymer-ceramic composite electrolytes is increased through the annealing process by creating a large number of defects at the polymer-ceramic interfaces. Such a transport mechanism scenario also implies that the hopping mechanism of the lithium ion motion is operative.

2. *Transport number.* The fact that motions of polymer chains contribute to the transport of the lithium ion in polymer electrolytes also has deleterious effects on the transport number. The chain motion also facilitates transport of larger anionic species and thus measured conductivity includes contribution from both species. Lithium is coordinated with five oxygen atoms, and the probability of finding a similar site for lithium transport is low. The polymer electrolytes have a lithium ion transport number which may be as small as 0.3. As a result, when such materials are used in a lithium cell, extensive concentration gradients are set up during use and affect their performance.

The cationic transport number in amorphous inorganic and polymeric electrolytes can be approximated through the use of the decoupling constant, $R(\tau_s/\tau_\sigma)$. The larger the value of R , the greater is the structural relaxation time and less is the transport of anions and cations mediated by the structure. In the polymer-ceramic composite electrolytes, the glass transition temperature increases in proportion to the volume fraction of the ceramic phase. Przulski et al. [30] reported an increase of 50°C in T_g when 20 wt % hydrophobic SiO_2 was introduced to a $\text{PEO}_{10}\text{NaI}$ polymer. Munichandraiah et al. [15] reported an increase of 25°C in the transition temperature when 29% of the zeolite was introduced in a $\text{PEO}:\text{LiBF}_4$ electrolyte. Angell [4] 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 transport number to around 0.9.

The conductivity of polymer electrolytes originates from two distinct processes: ion hopping and ion transport assisted by polymer chain motion. The addition of a ceramic phase suppresses the chain motion-mediated contribution and thus 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 cationic species because of its small size and mass than that of the anionic species. This scenario, as shown in Fig. 6, suggests an enhanced cationic transport number as the volume fraction of 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. [31] and

Peled et al. [32]. They calculated conductivity from bulk resistance, R_b measured at high frequency and transport number, t^+ using Eq. (3)

$$t^+ = \frac{R_b}{R_b + Z_d} \quad (3)$$

where Z_d is diffusional impedance as measured from the Nyquist plot. For the composite electrolyte film containing 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. Cho et al. [20] report a transport number of 0.98 for a glass-polymer composite electrolyte containing 13 vol % $\text{PEO}:\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and 87% $0.56\text{Li}_2\text{S} \cdot 0.19\text{B}_2\text{S}_3 \cdot 0.25\text{LiI}$. More recently, Croce et al. [33] reported a transport number of 0.6 in a $\text{PEO}:\text{LiCO}_4\text{-TiO}_2$ (10 wt %) composite electrolyte in the 45 to 90°C temperature range.

3. *Interfacial stability.* In a lithium rechargeable battery, the lithium metal and electrolyte interface is of critical importance. Due to the extreme reactivity of the lithium metal, most of the polymer electrolytes passivate lithium. In particular, impurities such as oxygen and water tend to accelerate the passivation mechanism and eventually consume the lithium electrode. Emerging solid electrolytes must perform better to have a significant commercial impact. What advantages do these polymer-ceramic composite electrolytes provide? Perhaps the question can be answered by examining lithium reactivity with a few common ceramics. These reactions with their standard free energies of reaction [34] are presented in Table 1.

The algebraic sign and magnitude of the free energy of a reaction determine whether lithium will be passivated or not. The positive sign of the free energy for the reactions suggests that lithium passivation is unlikely to occur when it is kept in contact with CaO , MgO , and Si_3N_4 . The passivation is feasible with other ceramics because the reactions have negative free energies.

The passivation of lithium electrode in nonaqueous organic electrolyte is an investigated and better understood phenomenon [35]; however, lithium-solid polymer electrolyte interfacial study is still in its infancy. Croce et al. [13,14] have investigated $\text{Li}/(\text{PEO})_8:\text{LiClO}_4$, $\text{Li}/(\text{PEO})_8:\text{LiClO}_4\text{-}\gamma\text{LiAlO}_2$, and $\text{Li}/\text{PAN-EC-PC}:\text{LiClO}_4$ interfaces using ac impe-

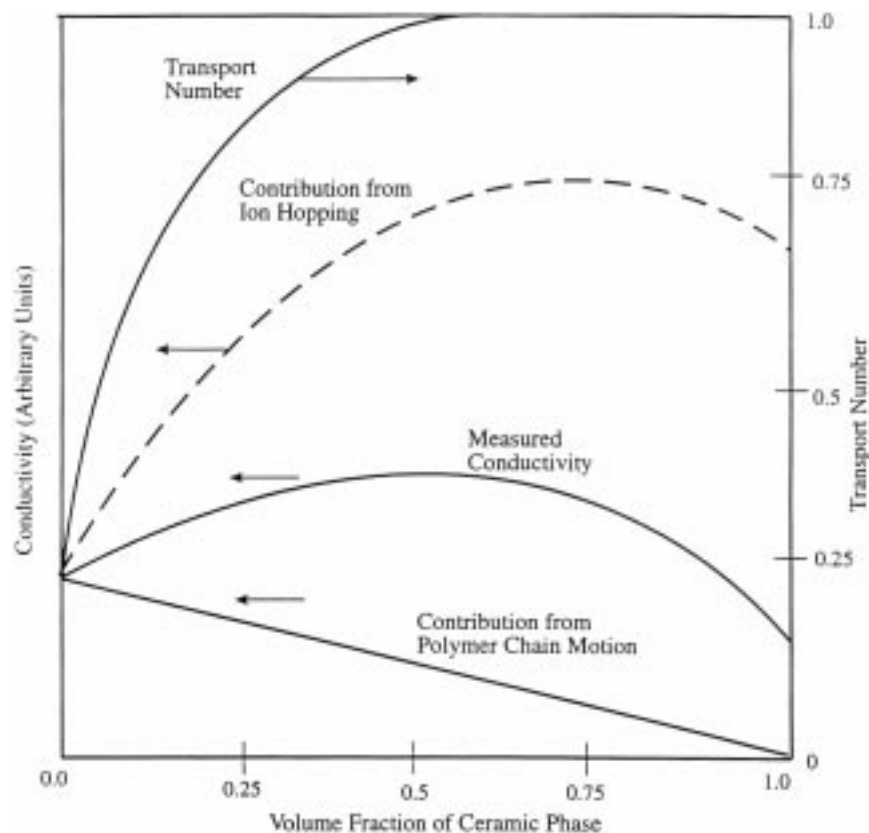


Fig. 6. Schematic representation of conductivity at ambient temperature; contributions from ion hopping and polymer chain motion and transport number.

dance spectroscopy. Among the three interfaces, the $\text{Li}/(\text{PEO})_8 : \text{LiClO}_4\text{-}\gamma\text{LiAlO}_2$ interface exhibited the most stable behavior. Croce et al. [13,14] speculated that the interfacial stability resulted from the scavenging ability of the ceramic powder, γLiAlO_2 , in the electrolyte. Kumar et al. [16] reported suppression of the charge transfer resistance of a

$\text{Li}/\text{PEO}:\text{LiBF}_4$ interface by a factor of three when a glass powder of the $0.4\text{B}_2\text{S}_3 \cdot 0.4\text{Li}_2\text{O} \cdot 0.2\text{LiSO}_4$ composition was introduced in the polymer electrolyte. The charge transfer resistance is an indirect indicator of the passivation phenomenon and interfacial stability. Munichandraiah et al. [18] reported that at low temperatures and low concentrations of

Table 1. Free energies of reaction of some common ceramics with lithium

Reaction	ΔG° (k Cal mol ⁻¹)
$2\text{Li} + \text{CaO} \rightarrow \text{Li}_2\text{O} + \text{Ca}$	+7
$2\text{Li} + \text{MgO} \rightarrow \text{Li}_2\text{O} + \text{Mg}$	+4
$6\text{Li} + 1/2\text{Si}_3\text{N}_4 \rightarrow 2\text{Li}_3\text{N} + 3/2\text{Si}$	+3
$3\text{Li} + \text{BN} \rightarrow \text{Li}_3\text{N} + \text{B}$	-8
$4\text{Li} + 2/3\text{Al}_2\text{O}_3 \rightarrow 2\text{Li}_2\text{O} + 4/3\text{Al}$	-18
$4\text{Li} + \text{ZrO}_2 \rightarrow 2\text{Li}_2\text{O} + \text{Zr}$	-25
$2\text{Li} + \text{ZnO} \rightarrow \text{Li}_2\text{O} + \text{Zn}$	-58
$4\text{Li} + \text{TiO}_2 \rightarrow 2\text{Li}_2\text{O} + \text{Ti}$	-66
$4\text{Li} + \text{SiO}_2 \rightarrow 2\text{Li}_2\text{O} + \text{Si}$	-73

zeolite, the exchange current density for Li/Li^+ reaction in a $\text{Li}/\text{composite electrolyte}/\text{Li}$ cell increases. The composite electrolyte consisted of hydrix elastomer doped with LiBF_4 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 et al. [36–38]. The ceramic electrolyte consisted of a thin film of lithium phosphorus oxynitride which was prepared by sputtering Li_3PO_4 in a pure nitrogen atmosphere. A typical composition of the electrolyte was $\text{Li}_{2.9}\text{PO}_{3.3}\text{N}_{0.46}$. The electrolyte exhibited excellent long-term stability in contact with lithium. Although it is recognized that these ceramic electrolytes are altogether different from polymer-ceramic composite electrolytes, the important point to note is that the lithium-ceramic interfaces do exhibit stable behavior.

Schematic diagrams of the lithium-composite electrolyte interfaces are shown in Fig. 7(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 improved performance compared to larger size particles because they cover more surface area. The formation of an insulating layer of ceramic particles at the electrode surface is probable at higher volume fraction of a passive ceramic phase.

The experimental evidence is numerous and consistently show that the lithium-composite electrolyte interfaces are more stable and efficient than lithium-polymer electrolyte interfaces.

4. *Electrochemical stability.* Electrolytes after being assembled into a cell are constantly subjected to a dc bias equal to the cell voltage. High voltage cathode materials such as LiMn_2O_4 and LiCoO_2 require that useful solid electrolytes possess a voltage window of about 5 V. The ability of the electrolytes to withstand the dc electrical potential is often termed in

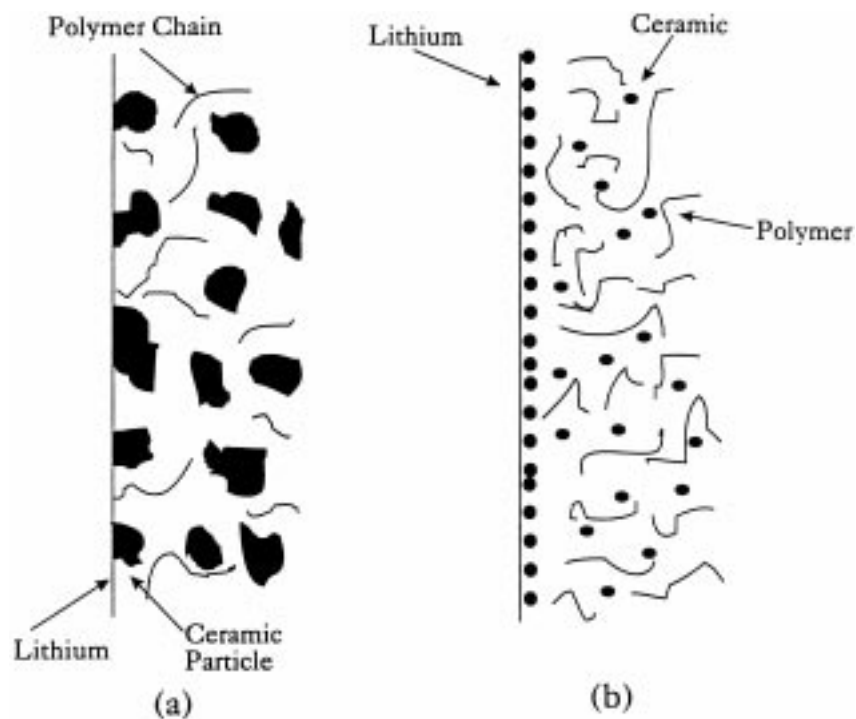


Fig. 7. Schematic diagram of lithium-composite electrolytes (a) larger size particles, and (b) smaller size particles.

the literature as “electrochemical stability,” “electrochemical decomposition potential,” and “voltage window.” These terms are used arbitrarily and interchangeably. Although polymer-ceramic composite electrolytes have not been carefully investigated for their electrochemical stability, Kumar et al. [39] have assessed electrochemical stability of ceramic-ceramic composite electrolytes using cyclic voltammetry and linear sweep techniques. The electrochemical stability is comprised of two parts: (1) dielectric response and breakdown of electrolyte under an applied electric field, and (2) electrochemical response of the electrode-electrolyte interfaces. In ceramic-ceramic composite electrolytes, the decomposition potential, V_d , was determined to be greater as compared to the component members of the electrolyte due to increased dissipation of energy. The same logic if applied to polymer-ceramic composite electrolytes suggest that they should have improved electrochemical stability as compared to polymer electrolytes.

Summary and Conclusions

A review of the emerging polymer-ceramic composite electrolytes for the lithium rechargeable battery has been presented and discussed. An analysis of a broader range of the composite electrolytes reveals that the incorporation of ceramic components in a polymer matrix leads to enhanced conductivity, cationic transport number, and electrode electrolyte interfacial stability.

The conductivity enhancement varies depending upon the fraction of ceramic phase, annealing parameters, polymer-ceramic systems, and temperature. In some polymer-ceramic systems approximately four orders of magnitude increase in conductivity around and below ambient temperature has been achieved. The enhancement is accompanied by a reduction in temperature dependence of conductivity. Analyses of experimental data using fundamental equations for conductivity and activation energy for ionic transport strongly suggest that a new transport mechanism through polymer-ceramic interfacial regions evolves.

The fact that polymer chain motion contributes to the transport of lithium ions in the polymer

electrolytes also has deleterious effect on the lithium transport number. The chain motion also facilitates transport of anionic species and thus measured conductivity includes contributions from both species. Some of the polymer electrolytes have a lithium transport number as small as 0.3. 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 because 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 related to the coupling phenomenon. 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. Ceramic additives decouple structural and electrical relaxations by increasing T_g . A number of experimental results on lithium ion transport number support this hypothesis.

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. A few of the ceramic materials (MgO , CaO , Si_3N_4) have positive free energy of reaction and should not passivate lithium when used with a polymer.

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