

Review

Polymer–ceramic composite protonic conductors

Binod Kumar^{a,*}, J.P. Fellner^b

^a *University of Dayton Research Institute, 300 College Park, KL 501, Dayton, OH 45469-0170, USA*

^b *Propulsion Directorate, Air Force Research Laboratory, Wright-Patterson Airforce Base, Dayton, OH 45433-7251, USA*

Received 11 March 2003; accepted 28 March 2003

Abstract

This paper reviews emerging polymer–ceramic composite protonic conductors in the context of their usefulness as membrane material for fuel cells. These composite protonic conductors appear to exhibit a superior propensity to retain water, enhanced conductivity, superior thermal and mechanical robustness, and reduced permeability of molecular species.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Fuel cells; Composite membrane; PEFC

1. Introduction

Composites are an important class of materials. They are comprised of two or more phases mixed in predetermined proportions to obtain superior performance as compared to any of the pure, single-phase, solid components. They have found widespread application as materials of construction in structural components requiring superior mechanical and thermal properties. However, the application of composites as electrical conductors, both electronic and ionic, is in its infancy. It has been shown that the dispersion of fine, electronically conducting particles into an insulator matrix and insulating particles into an ionically conducting matrix leads to enhancements in electrical conductivity by several orders of magnitude. In both cases, a significant concentration (10–30 vol.%) of filler particles is required to achieve the optimum conductivity. To explain the composite effect on electrical conductivity, a unified model has recently been proposed for the two types of composite conductors [1].

The use of solid polymer–ceramic composite materials as protonic conductors has recently attracted significant interest [2–5]. The motivation for the interest is a commercial application as high conductivity and thermally stable membrane material for polymer electrolyte fuel cells (PEFC). Preliminary investigations have shown that these polymer–ceramic composites are associated with attributes, such as enhanced protonic conductivity, improved water retention, increased cell operating temperature, higher carbon

monoxide tolerance threshold, and reduced permeability of molecular species. The improved thermomechanical stability of these membranes in a practical fuel cell is expected to provide them with long-term structural integrity. The polymer–ceramic composite protonic conductors are now a subset of the general class of solid protonic conductors and possess the potential to provide membrane materials for commercial applications.

The history of the composite ionic conductors may be traced to the work of Liang [6]. In a pioneering work, Liang [6] investigated polycrystalline lithium iodide doped with aluminum oxide and reported that lithium iodide doped with 35–45 mol% aluminum oxide exhibited conductivity on the order of 10^{-5} S cm⁻¹ at 25 °C, about three orders of magnitude higher than that of the LiI conductivity. However, no significant amount of aluminum oxide was determined to be soluble in LiI; thus, the conductivity enhancement could not be explained by the classical doping mechanism and creation of Schottky defects such as in the LiI–CaF₂ system. Subsequently, a number of investigations have reported enhanced conductivity of silver in the AgI–Al₂O₃ system [7], copper in the CuCl–Al₂O₃ system [8], fluorine in the PbF₂–SiO₂ and PbF₂–Al₂O₃ systems [9], and lithium in polymer–ceramic composite electrolytes [10]. Two review papers [1,11] also document the developmental history and general characteristics of these fast ionic conductors. Analyses of these reviews point out that a new conduction mechanism evolves which augments the bulk conductivity of single-phase ionic conductors. The new conduction mechanism makes use of interfacial and/or space charge regions between the two primary components.

* Corresponding author. Tel.: +1-937-229-3452; fax: +1-937-229-3433.
E-mail address: kumar@udri.udayton.edu (B. Kumar).

The purpose of this paper is to review the literature on composite protonic conductors in the context of their usefulness as a membrane material, specifically their ability to retain water, enhance conductivity, augment thermal and mechanical robustness, and suppress the permeability of molecular species in a practical, commercially-viable fuel cell.

2. Prior work: chemistry, processing, and properties

Since Nafion[®] has been the mainstay of protonic conductors, a number of studies on composite protonic conductors have been conducted using it as a matrix for reinforcing ceramic particles. Mauritz et al. [12] reported a processing method for producing nanocomposites of Nafion[®] and silica using the sol–gel reactions. They observed that the polar/nonpolar nanophase-separated morphological template exists despite incorporation of silicon oxide phase in the composite. The highest silicon oxide concentration was observed near the surface and decreased to a minimum in the center of the specimen. Watanabe et al. [2] extended the work of Mauritz et al. [12] towards the applicability of the nanocomposite for a fuel cell membrane. Watanabe et al. [2] characterized these nanocomposites as ‘self-humidifying,’ as colloidal silica (silica gel) possesses an inherent capacity to absorb and retain water. They also reported that in addition to water retention capability, silica particles also suppressed H₂ and O₂ crossover through the membrane. The use of the nanocomposite membrane also facilitated cold starts of the cell. Antonucci et al. [3] reported the use of Nafion[®] and silica nanocomposite in direct methanol fuel cells (DMFC) at 145 °C. The favorable humidification conditions in the nanocomposite allowed high operating temperatures and enhancement of methanol oxidation kinetics. A peak power density of 240 mW cm² for the oxygen-fed fuel cell was obtained. Park and Nagai [13] fabricated fast protonic organic–inorganic hybrid nanocomposites from the hydrolysis and condensation reaction of 3-glycidoxypropyltrimethoxy silane and tetraethylethoxysilicate. The protonic conductivity of the composite increased up to 1.0×10^{-1} S cm⁻¹ by the addition of silicotungstic acid. The sol–gel derived Nafion[®]/silica composite membrane was also investigated by Miyake et al. [4] as a membrane material for fuel cells. These membranes exhibited higher water contents at 25 and 120 °C but not at 150 and 170 °C. Despite the higher water content, the protonic conductivity of the membranes were lower or equal to unmodified Nafion[®] membranes. Miyake et al. [14] also investigated uptake and permeability of methanol in liquid and vapor phases as a function of temperature. They concluded that the Nafion[®]/silica hybrid membranes with high silica content ($\cong 20$ wt.%) are potentially useful as membranes for direct methanol fuel cells using either liquid or vapor-feed fuels. Adjemian et al. [5] also investigated silicon oxide/Nafion[®] composite membranes in hydrogen/oxygen proton-exchange membrane fuel cells

from 80 to 140 °C. All composite membranes had a silicon oxide content of less than or equal to 10 wt.%. The silicon oxide enhanced the water retention of the composite membranes and contrary to the report of Miyake et al. [4] these membranes exhibited increased protonic conductivity at elevated temperatures. They also exhibited impressive current densities—four times greater than unmodified Nafion[®] at 130 °C and a pressure of 3 atm. Furthermore, these membranes were structurally and mechanically robust in comparison to unmodified Nafion[®], which degraded after a higher operating temperature and thermal cycling. Uchida et al. [15] reported attributes of titanium dioxide/Nafion[®] composites prepared by the sol–gel reactions. They reported increased water absorbability and self-humidifying characteristics by dispersing only 2 wt.% TiO₂.

Analyses of the aforementioned investigations appear to suggest that the incorporation of a ceramic phase in the polymer matrix provides some benefits such as superior water retention, higher operating temperature, and enhanced thermal stability. However, a scientific and quantitative basis for the formulation and optimization of the composites is lacking. The qualitative approach of composite formulation and nonstandard processing techniques may also account for the deviations in properties from the aforementioned general observations.

3. Discussion

3.1. Water retention

Silicates and aluminosilicates are known to be associated with various concentrations of water. Silica gel, for example, is a prominent desiccant. It can adsorb water and also react to form silicic acid. The substitution of silicon by aluminum in the silica network leads to the formation of a variety of aluminosilicate minerals (felspar, clay, zeolites, and mica) in nature [16]. These minerals can be associated with various concentrations of water. For example, clay (Al₂O₃·2SiO₂·2H₂O) is a layered silicate and the chemically-held water is retained up to 560 °C. Similarly, a cage-type structure of zeolites can physically hold significant concentrations of water.

A composite membrane also possesses a very high concentration of polymer–ceramic interfaces. These interfaces possess a defect structure and free volume which can accommodate significant concentration of water. The interfaces can serve as a water reservoir, and it is likely that non-silicates and non-aluminosilicates can also improve water retention.

In and around a fuel cell membrane, water formation, retention, and movement at elevated temperatures must be regulated in a precise manner. The incorporation of a ceramic component is expected to facilitate the water management issue. However, water that is physically held in voids and interfaces may be lost around its boiling point. The structural

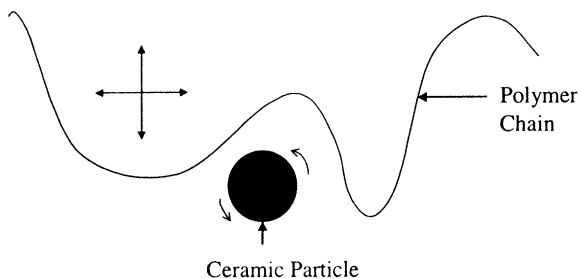


Fig. 1. Schematic representation of a polymer chain segment and ceramic particle interaction.

or chemically-held water may be useful for protonic conductivity up to its decomposition temperature.

3.2. Polymer–ceramic particle interaction and microstructure

An interaction between a polymer chain and a ceramic particle is schematically illustrated in Fig. 1. The length of the polymer chain will depend upon its molecular weight. The size of the ceramic particle may vary from a few nanometers to several micrometers. The shape of the ceramic particle may also vary. The extent of the polymer chain–ceramic particle interaction will depend upon the polymer chain length and the ceramic particle size. For example, if the polymer chain length (generally of the order of microns) and weight percent of ceramic particles are maintained constant and the particle size of the ceramic phase is reduced from $10\ \mu\text{m}$ to $10\ \text{nm}$, the number of polymer–ceramic interaction sites is increased by a factor of 10^9 and the distance between the ceramic particles is reduced from $4.12\ \mu\text{m}$ to $4.12\ \text{nm}$. These approximations are based on the assumptions that the agglomeration of ceramic particles is absent and particles are uniformly distributed.

A difference in the dielectric constants of the polymer and ceramic phases may lead to a chemical interaction between them resulting in the formation of chemical bonds. In fact, the formation of chemical bonds in PEO:LiBF₄–MgO, a lithium ion composite material, has been demonstrated [17].

It has been shown that in the PEO:LiBF₄–MgO system, lithium ion conductivity is enhanced initially by reducing the degree of polymer crystallinity and subsequently by facilitating the polymer chain–ceramic particle interaction. The interaction is further enhanced by reducing the particle size and mass of the ceramic particle [10]. A similar interaction and microstructure are expected in composite protonic conductors, which may facilitate the protonic conduction.

There is a similarity in the microstructure of polymer–ceramic composites and Nafion[®]—the mainstay of solid polymer protonic conductors. Nafion[®] is produced by attaching a side chain to polytetrafluoroethylene (PTFE). The end of the side chain is sulfonated, which is highly hydrophilic. The side chain molecules of Nafion[®] tend to cluster, thus creating hydrophilic regions within a gener-

ally hydrophobic material, PTFE. The hydrophilic regions allow for the absorption of large quantities of water—up to 50 wt.% of dry Nafion[®]. The inhomogeneous nature of the microstructure and regions for storage of water resemble characteristics of the two classes of materials.

3.3. Transport of charged species in a composite material

A composite material in which metallic particles are dispersed in an insulating matrix displays the electronic conductivity enhancement as a function of weight fraction of the metallic filler particle as depicted in Fig. 2a. Initially, there is little influence on conductivity as the metallic particles are introduced, but around 20 wt.% of the metallic component, there is a sharp jump—about 10 orders of magnitude—in conductivity. At this concentration level of the metal phase, the microstructure allows steady-state percolation of electrons and thus it is defined as the percolation threshold. The percolation threshold varies (shown by arrows in Fig. 2a) depending upon the nature of the metal and insulating phases.

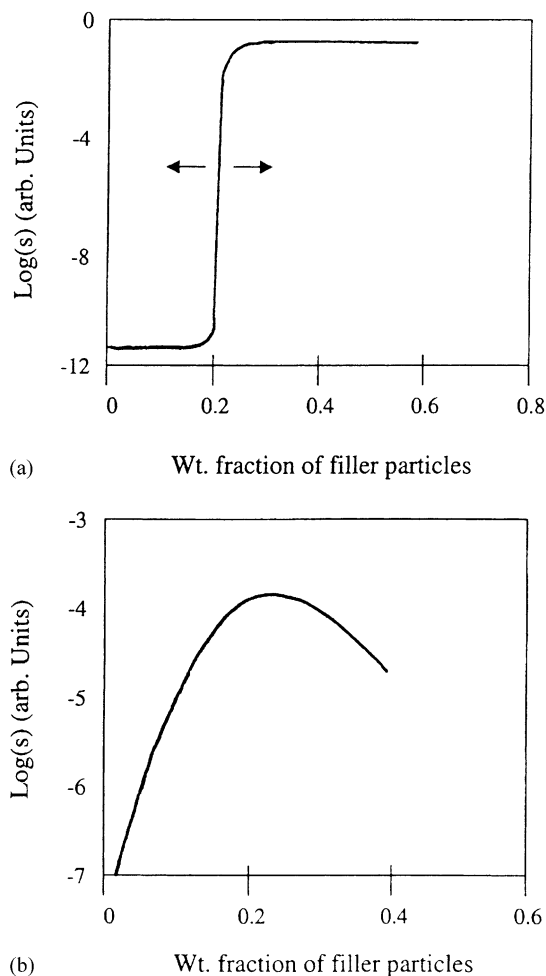


Fig. 2. Schematic representation of the effect of reinforcement on conductivity. (a) Electronic conductivity of insulating matrix reinforced with metallic particles; (b) ionic conductivity of ionically conducting matrix reinforced with insulating particles.

The steady-state conductivity of the composite beyond the percolation threshold is comparable to the conductivity of the metal phase.

Fig. 2b schematically shows the effect of insulating particle reinforcement on the conductivity of the ionically conducting matrix. Unlike Fig. 2a, the ionic conductivity of the composite in this case gradually increases and reaches a peak at around 20 wt.% of the insulating doping phase. Further increases of the dopant decreases the conductivity as it impedes the transport of charged species. Again in this case, steady-state percolation occurs around 20 wt.% of the insulating dopant phase. The percolation threshold may vary depending upon the matrix and dopant chemistries, particle sizes, and processing parameters. This composite effect has been demonstrated in a number of diverse ionic conductors [6–11].

The schematic data shown in Fig. 2a and b are based on a number of theoretical and experimental investigations. A review of these investigations can be found in [1,11]. The intent of presenting the electronic and ionic conductivity of composite materials in Fig. 2a and b is to impress upon readers the role of microstructures on the transport of charged species. In a fuel cell membrane, the lowest electronic conductivity (preferably zero) is desired. However, for electrode materials, mixed (electronic and ionic) conductivity is required. It is anticipated that the transport of protons should also be facilitated in the composite microstructure. However, authentic experimental evidence correlating the protonic conductivity and composite microstructure is lacking.

In the fuel cell literature, one of the widely accepted protocols for evaluating a membrane material is to obtain polarization curves (V - j plots) as schematically shown in Fig. 3. The figure illustrates regions in which various types of voltage losses occur. From Fig. 3 it can be seen that at low current densities, the major contribution to the losses originate from activation polarization, which is characterized by a sharp drop in voltage with increasing current. As the current increases, ohmic loss emerges, as exhibited by linearity in the central region of Fig. 3. At high currents,

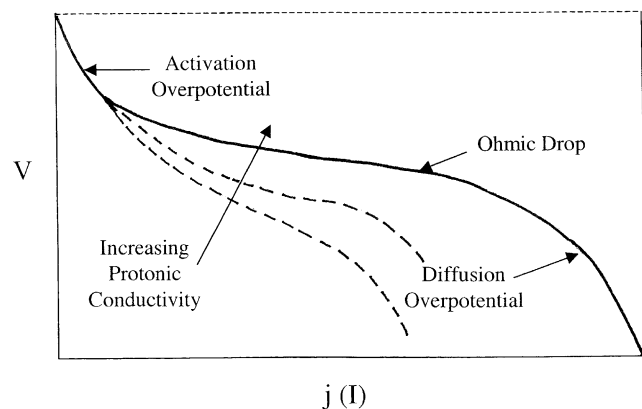


Fig. 3. Schematic of cell voltage, V vs. current density, j of a typical cell.

the cell resistance is controlled by mass transport limitation (diffusion overpotential), resulting in a rapid decline in voltage.

An increase in the protonic conductivity of the membrane is reflected by a change in the slope of the linear ohmic region. The composite protonic conductors are expected to have lower slope in the ohmic region. In fact, there is evidence of this kind of behavior in Nafion 115 and 6% SiO_2 composite membranes investigated by Adjemian et al. [5].

4. Thermal and mechanical robustness

Improvements in the thermal and mechanical robustness of commercial polymers have been a topic of considerable interest. A number of different types of fillers such as clay, carbon, and mica have been incorporated in polymer matrices to improve wear resistance, retard flammability, and enhance the heat distortion temperature of industrial polymeric products. In recent times, the heat resistance of a commercial Nylon 6 has been improved by incorporating clay [18–20]. The Nylon 6 begins to soften at 60°C ; however, the addition of 3–5 wt.% of clay raises the softening temperature to 140°C . Furthermore, the clay additive improved dimensional stability, enhanced barrier properties, and retarded flammability. In general, the addition of a ceramic phase to a polymer matrix raises the glass transition temperature, T_g [21]. The modulus of elasticity also increases with the incorporation of a ceramic phase in polymers [22].

It is evident that ceramic additives impart large positive influences on the mechanical and thermal properties of polymers. These benefits are of enormous interest in developing robust, durable, and high performance membrane materials for fuel cells.

5. Permeability of molecular species

The permeation of molecular species, either from anode or cathode side through the electrolyte, is detrimental to the electrochemical performance of a fuel cell. The permeability of the species through the membrane must be reduced to a minimum, preferably zero. The ceramic additives in a polymer matrix have been found to be effective in reducing permeability of molecular species. Miyake et al. [14] reported that a hybrid membrane containing 20 wt.% silica in a Nafion[®] matrix exhibited significantly lower methanol permeation rates.

The mechanism for reducing the permeability of gases through the membrane is believed to originate from rigid scattering sites and tortuous pathways that a permeant must encounter to transverse the composite material. Fig. 4a schematically illustrates backscattering of the molecular species by rigid spherical ceramic particles in a polymer matrix, whereas Fig. 4b depicts a tortuous pathway, as

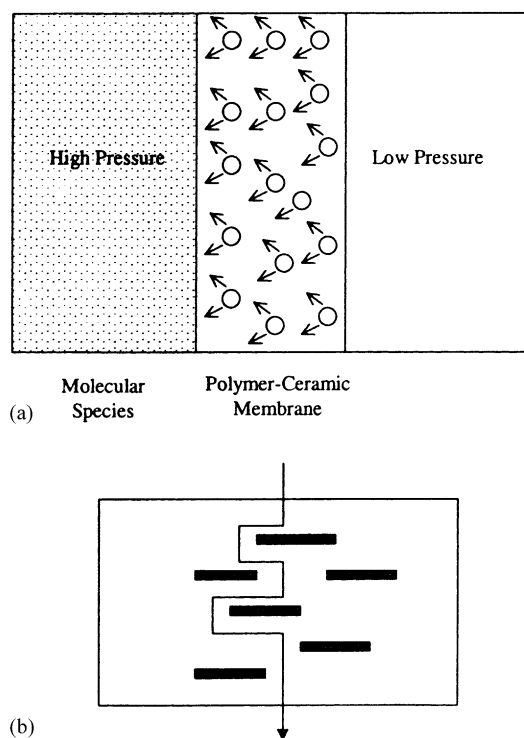


Fig. 4. A schematic of a polymer–ceramic membrane showing (a) backscattering, and (b) tortuous pathway of molecular species.

proposed earlier by Yano et al. [23] in a composite membrane containing a platelet type ceramic phase, for example, clay in a polymer.

6. Summary and conclusions

A review of the state-of-the-art polymer–ceramic protonic conductors for application as membranes in fuel cells have been presented and discussed. The discussion focused on the key attributes of the membrane such as water retention, polymer–ceramic particle interaction, transport of charged species through a composite structure, thermal and mechanical properties, and permeability of molecular species. An analysis of a broader range of ceramic fillers reveals that while silicates and aluminosilicates have an inherent capacity to retain water, non-silicates and non-aluminosilicates can enhance water retention by providing polymer–ceramic interfacial regions as water storage channels. The polymer and ceramic phases can also chemically interact, leading to nanostructures and microstructures beneficial for protonic conductivity and mechanical and thermal properties. The microstructure of solid composites facilitates transport of charged species provided that there is a large difference in the electronic properties and structure of the components of the composite. The observation is valid for an electron and also for a number of ionic species. Thus, it is expected

that the structure of polymer–ceramic composites should enhance protonic conductivity; however, definitive experimental evidence is yet to emerge. A number of reports in the literature support the claim that a ceramic phase in the composite enhances mechanical and thermal properties. It has also been suggested that the polymer–ceramic composites should exhibit suppressed permeability of molecular species.

Acknowledgements

One of the authors (B. Kumar) gratefully acknowledges the financial support provided by the Propulsion Directorate, Air Force Research Laboratory, under Contract no. F33615-98-D-2891, DO 18. The authors also express their gratitude to Dr. S.J. Rodrigues for reading the manuscript.

References

- [1] A. Mikrajuddin, G. Shi, K. Okuyama, *J. Electrochem. Soc.* 147 (8) (2000) 3157–3165.
- [2] M. Watanabe, H. Uchida, Y. Seki, M. Emori, *J. Electrochem. Soc.* 143 (12) (1996) 3847–3852.
- [3] P.L. Antonucci, A.S. Arico, P. Creti, E. Ramunni, V. Antonucci, *Solid State Ionics* 125 (1999) 431–437.
- [4] N. Miyake, J.S. Wainright, R.F. Savinell, *J. Electrochem. Soc.* 148 (8) (2001) A898–A904.
- [5] K.T. Adjemian, S.J. Lee, S. Srinivasan, J. Benziger, A.B. Bocarsly, *J. Electrochem. Soc.* 149 (3) (2002) A256–A261.
- [6] C.C. Liang, *J. Electrochem. Soc.* 120 (1973) 1289.
- [7] K. Shahi, J.B. Wagner, *Solid State Ionics* 3–4 (1981) 295.
- [8] T. Jow, J.B. Wagner, *J. Electrochem. Soc.* 126 (1979) 1963.
- [9] K. Hariharan, J. Maier, *J. Electrochem. Soc.* 142 (10) (1995) 3469.
- [10] B. Kumar, S.J. Rodrigues, L.G. Scanlon, *J. Electrochem. Soc.* 148 (10) (2001) A1191.
- [11] P. Knauth, *J. Electroceram.* 5 (2) (2000) 111–125.
- [12] K.A. Mauritz, I.D. Stefanithis, S.V. Davis, R.W. Scheetz, R.K. Rope, G.L. Wilkes, H. Huang, *J. Appl. Polym. Sci.* 55 (1995) 181–190.
- [13] Y. Park, M. Nagai, *J. Electrochem. Soc.* 148 (6) (2001) A616–A623.
- [14] N. Miyake, J.S. Wainright, R.F. Savinell, *J. Electrochem. Soc.* 148 (8) (2001) A905–A909.
- [15] H. Uchida, Y. Ueno, H. Hagihara, M. Wantanabe, *J. Electrochem. Soc.* 150 (1) (2003) A57–A62.
- [16] W.D. Kingery, H.K. Bowen, D.R. Uhlmann, *Introduction to Ceramics*, Wiley, New York, 1976, pp. 77–80.
- [17] B. Kumar, S.J. Rodrigues, R.J. Spry, *Electrochim. Acta* 47 (2002) 1275–1281.
- [18] Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kuranchi, O. Kamigaito, *J. Mater. Res.* 8 (1993) 1185–1189.
- [19] Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, T. Kuranchi, O. Kamigaito, *J. Appl. Polym. Sci.* 49 (1993) 1259–1264.
- [20] Y. Kojima, K. Fukumori, A. Usuki, A. Okada, T. Kuranchi, *J. Mater. Sci. Lett.* 12 (1993) 889–890.
- [21] B. Kumar, L.G. Scanlon, *J. Power Sources* 52 (1994) 261–268.
- [22] F. Rodriguez, *Principles of Polymer Systems*, Hemisphere Publishing Corporation, New York, 1989, p. 254.
- [23] K. Yano, A. Usuki, A. Okada, T. Kuranchi, O. Kamigaito, *J. Polym. Sci., Part A: Polym. Chem.* 31 (1993) 2493–2498.