Conductivity Anisotropy of Polyphosphazene−Montmorillonite Composite Electrolytes

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Solvent-free electrolytes are of great interest because of fundamental questions of their charge-transport mechanisms and their possible applications in electrochemical devices.[1−3] Clay minerals such as sodium−montmorillonite (NaMont) have appreciable ionic conductivities when swollen by water,[4−6] and recent work has shown that polar polymers also mobilize Na^+ in NaMont.[7−15] NaMont, a naturally occurring mineral from the clay group *smectites*, has a structure consisting of extended anionic layers balanced by mobile interlayer cations and a unit formula of $Na_{0.6}[(Mg_{0.6}Al_{3.4})Si_8O_{20}(OH)_4]$. Smectites are interesting subjects for studies of cation mobility for a number of reasons, most notably because they are polyelectrolytes with fixed anions. The identity of current carriers is less ambiguous in this type of electrolyte than in salt solutions where both anions and cations are mobile. The mobility of a single type of ion also can be advantageous in electrochemical devices. Additionally, the charged sites in montmorillonite are well separated, so ion pairing with the mobile cation is attenuated. To further reduce attractive forces between the cation and the aluminosilicate sheets, a variety of solvating species have been intercalated into clays such as poly(ethylene oxide) (PEO),[8−14] poly[bis(methoxyethoxy)ethoxyphosphazene] (MEEP),[7] poly(oxymethylene oligo(ethylene oxide)),[10] cryptands,[7,15] and crown ethers.[15] The cation mobility of these composite electrolytes is highly anisotropic,[13] and it is greatly enhanced in comparison with the parent clay. The role of the intercalated polymer and the mechanism of ion conductivity is difficult to fully characterize experimentally. For PEO·montmorillonite composites, Ruiz-Hitzky and co-workers have ascribed the conductivity enhancement to increased layer separation and factors associated with relaxations of the polymer chain.[11,12]

Lerner and co-workers suggest that the polymer decreases interactions between the cation and the negatively charged clay surface and thereby increases conductivity.[10] Giannelis, Zax and co-workers have probed polymer dynamics and lithium ion transport in PEO·lithium−montmorillonite composites with a variety of solid-state NMR techniques.[16] In the present paper on a MEEP·NaMont composite, we examine the role of the intercalated polymer in long-range ion transport by an analysis of the temperature-dependent conductivity, and we describe the methodology and results of conductivity anisotropy measurements.

To minimize proton conduction by adventitious H_2O, the materials were thoroughly dried on a high-vacuum line (ca. 3×10^{-5} Torr at 110 °C) and handled under a dry, inert atmosphere. Samples and starting materials were checked by FTIR spectroscopy in the region of $3000−4000$ cm^{-1} to verify dryness. NaMont was prepared by Na^+ exchanging montmorillonite (SWy-2) from the Source Clays Repository. The MEEP·NaMont composite was prepared in a composition of 1 MEEP repeat unit ($PN(CH_3OC_2H_4OC_2H_4O)_2$) to 2 clay Si_8O_{20} units (MEEP·NaMont) by adding $1/2$ equiv of MEEP[18] (molecular weight = 10 300 by gel-phase chromatography) dissolved in CH_3CN (distilled from CaH_2) to a slurry of NaMont. The progress of the intercalation was followed by monitoring the *d* spacing of solvent-free samples with powder XRD. When there was no evidence of unintercalated NaMont by powder XRD, the reaction was considered complete, and the homogeneous light-brown slurry was slowly filtered through a medium glass frit (nominal pore size $10−20$ μm). The filtrate showed no signs of MEEP as judged by ^1H, ^{31}P, and ^{13}C NMR. The composite was dried slowly on the frit to prevent cracking of the resulting pellet (thickness ca. 2 mm). This product exhibits an XRD powder pattern with one low-angle peak corresponding to a *d* spacing of 19 Å. An X-ray pole analysis of the sample indicates strong preferential orientation of the clay layers parallel to the pellet faces.

Impedance measurements perpendicular to the smectite layers were made directly on pressed pellets of the composite (Figure 1a). The exceptional thickness of the composite pellets allowed us to prepare samples with cross sections large enough for impedance measurements parallel to the smectite layers. The composite pellet was cut under an inert atmosphere with a wire saw (Figure 1b) and the faces normal to the measurement plane were sputtered with gold to ensure good electrical contact with the electrode. This sample was placed inside an O-ring-sealed impedance cell with symmetric stainless steel electrodes normal to the measurement plane. Measurements were performed over a temperature range of $273−373$ K. The variable-frequency impedance response was fit by a nonlinear least-squares routine,[19] to an equivalent circuit consisting of a parallel resistor-constant phase element (C.P.E.)
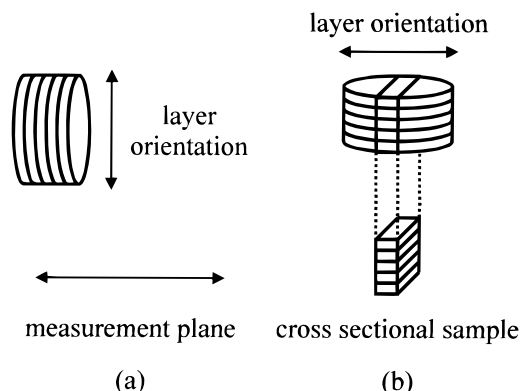
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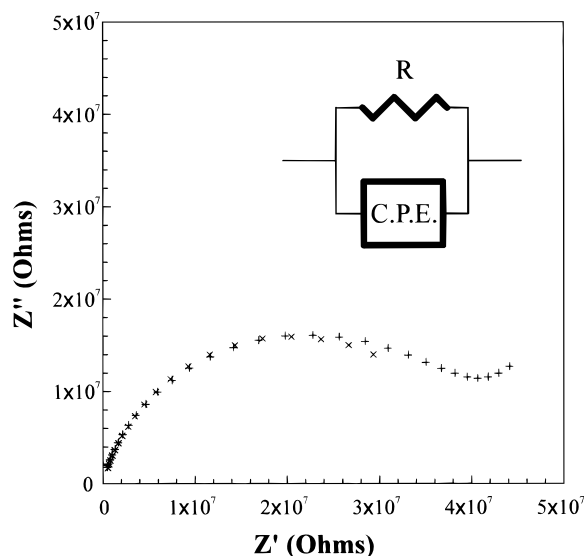(16) Wong, S.; Vasudevan, S.; Vaia, R.; Giannelis, E.; Zax, D. *J. Am. Chem. Soc.* **1995**, *117*, 7568−7569.
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Figure 1. Relative orientation of composite layers for measurements (a) perpendicular to the measurement plane, σ_{perp}, and (b) parallel to the measurement plane, σ_{para}.

Figure 2. Superposition of a typical impedance spectrum (10−10 000 Hz) of Meep·NaMont measured parallel to the clay layers at 67 °C (+), and a nonlinear least-squares fit of the high-frequency region (×). The equivalent circuit is represented above.

equivalent circuit (Figure 2). The conductivity of the MEEP·NaMont is substantially enhanced over pristine NaMont, with a $\sigma_{para}/\sigma_{perp}$ ratio of about 100 (Figure 3). Both the parallel and perpendicular conductivities of the MEEP·NaMont were fit to the Vogel−Tammann−Fulcher (VTF) equation[20] which is commonly used to fit the conductivities of polymer electrolytes:[1,21−27]

$$\sigma = \sigma_0 e^{-\beta/R(T-T_0)}$$

The VTF dependence is strongly suggestive of coupling

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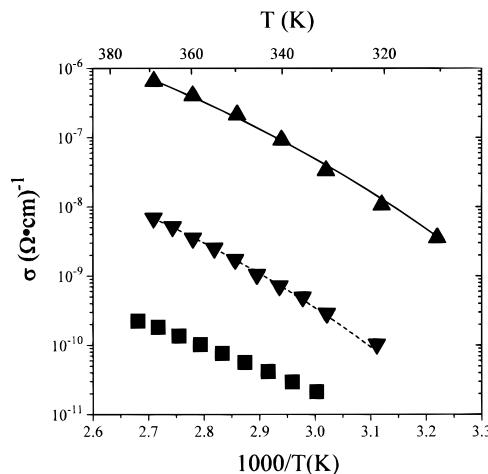(23) Killis, A.; LeNest, J. F.; Gandini, A.; Cheradame, H. J. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1073.
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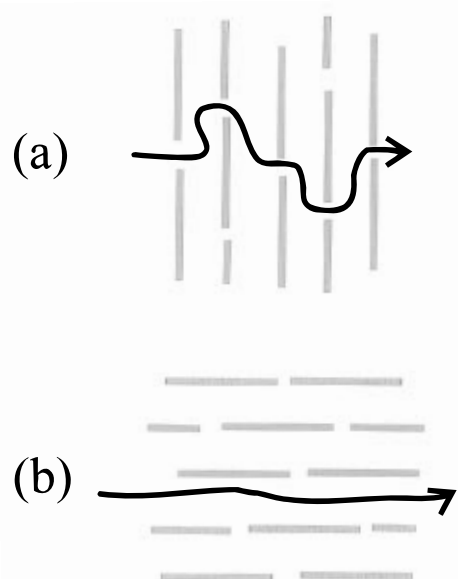(25) Druger, S. D.; Ratner, M. A.; Nitzan, A. *Phys Rev. B* **1985**, *31*, 3939.
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Figure 3. Temperature-dependent conductivities (σ) of MEEP·NaMont parallel to the composite layers, (▲) VTF fit; (−) MEEP·NaMont perpendicular to the composite layers, (▼) VTF fit (− − −); Pristine NaMont (■) measured perpendicular to the layers.

Figure 4. Schematic of the Na$^+$ diffusion path in a MEEP·NaMont composite (a) perpendicular and (b) parallel to the composite layers.

Table 1. VTF Parameters for MEEP·NaMont

sample	σ_0 (Ω^{-1} cm^{-1} K$^{1/2}$)	β (J)	T_0 (K)
σ_{perp}	2.2×10^{-3}	1.2×10^4	218
σ_{para}	2.1×10^{-1}	1.3×10^4	204

between polymer high-amplitude segmental motion and long-range cation transport in these composites. From the similar temperature dependencies of σ_{para} and σ_{perp} in the MEEP·NaMont composite (Table 1) it appears that the coupling between Na$^+$ transport and polymer motion is similar perpendicular and parallel to the composite layers. The conductivity anisotropy arises from the variation in the σ_0 term, and we attribute the low σ_0 term to greater tortuosity of the perpendicular diffusion path which is indicated by the preferential orientation of the specific layers (Figure 4).