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Dynamics in a Confined Polymer Electrolyte: A ^{7}Li and ^{2}H NMR Study

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In this paper, we report the first studies which unambiguously identify both lithium diffusivity and polymer dynamics intercalated in a layered silicate. Conductance (σ) in these two-dimensional systems shows Arrhenius-like activation in the temperature range 250−380 K and, at room temperature, exceeds that of traditional solid polymer electrolytes (SPEs) by 2 orders of magnitude.[1] Hence these materials show promise as alternatives to currently available electrolytes for solid state battery cells.

Traditional SPEs are ionic conductors formed from complexes of alkali metal salts and polar (electron-donating) polymers.[2] EXAFS studies of PEO-based SPEs confirm the solvation of cations by ether oxygens as are found in Li$^+$−crown ether complexes.[3] This points out the dilemma inherent in the design of an efficient ionic salt/polymer electrolyte. On one hand, a polar polymer is necessary to facilitate salt dissociation. On the other hand, the resulting stable cation coordination impedes ion hopping. Hence, significant conductance is measured only in the melt phase of the polymer ($T_m \geq 330$ K). Despite the low mass of Li$^+$, Li$^+$ transference numbers of 0.3−0.5 reflect the greater mobility of the counterions (e.g., BF_4^- or ClO_4^-) due to the relative stability of the cation coordination environment. Chemical and morphological efforts to modify SPEs have not yet overcome this rapid drop in σ below T_m.[4,5]

We focus in this work on a confined polymer electrolyte formed when PEO is intercalated into the layered silicates montmorillonite and fluorohectorite. Mobile cations in the interlayer are present naturally and balance the excess negative charge in the silicate layers. Under ambient conditions, water molecules coordinate to and stabilize the cations. Intercalation of PEO displaces the water of solvation. As the cation and anion are naturally separated, salt dissociation is unnecessary. Moreover, the massive anion is immobile so that the cation transference number is expected to be 1.0.

Our microscopic probe for dynamics in these composite electrolytes is ^{7}Li and ^{2}H variable temperature solid state NMR spectroscopy. Spin-lattice relaxation (T_1) studies suggest that the fluctuating fields responsible for relaxation are the same for both the cation and the polymer, in accord with previous studies on SPEs.[6] We attribute this dynamic process to the polymer. In addition, we have directly analyzed for cation diffusivity by analysis of the temperature dependence of the ^{7}Li line width.

A pellet form of thoroughly mixed PEO (average MW ~ 100 kDa, PolySciences) and Li$^+$-montmorillonite (SWy-1, University of Missouri Clay Source Repository) was heated at 80 °C for 8 h (abbreviated PEO:Li-Mont).[1] Like many naturally occurring silicates, this sample contains paramagnetic impurities (~1 Fe^{3+}/125 Å^2). As unpaired electrons dominate nuclear spin relaxation, T_1 studies were based on a sample of PEO similarly intercalated into a synthetic silicate, Li$^+$-fluorohectorite (PEO:Li-FH). Polymer loading levels were chosen to guarantee uniform environments for all nuclei being studied. At a loading of ≥40 wt %, all lithium cations are surrounded by the polymer matrix. At loading levels ≤20 wt %, all of the polymer is found within the silicate interlayer region. Samples for ^{2}H NMR studies were prepared by adding perdeuterated PEO (>95%) to Li$^+$-fluorohectorite (dPEO:Li-FH).

NMR experiments were carried out in a 7.05 T magnet and a home-built spectrometer. Variable temperature experiments were conducted in a continuous flow cryostat (Oxford Instruments CF-1200), with temperature control of 0.5 °C. Spectra were acquired with appropriate spin- or quadrupolar-echo sequences. The results of inversion−recovery T_1 experiments were similarly detected.

Dynamic processes in solids are most often probed via their impact on spin−lattice relaxation times, T_1. Where Bloembergen, Pound, and Purcell (BPP) theory applies,[7] relaxation rates $1/T_1$ can be related to dynamical correlation times τ_c via

$$\frac{1}{T_1} = K\left(\frac{2\tau_c}{1+\omega_0^2\tau_c^2} + \frac{8\tau_c}{1+4\omega_0^2\tau_c^2}\right) \qquad (1)$$

where ω_0 is the Larmor frequency, and the prefactor K measures the strength of the fluctuating local fields. For ^{2}H and ^{7}Li, K is dominated by the local electric field gradient (EFG). When the temperature dependence of the correlation time is described by the Arrhenius-type law

$$\tau_c = \tau_0 e^{E_a/k_B T} \qquad (2)$$

plots of $\ln(1/T_1)$ vs $1/T$ are linear with slope of magnitude $-E_a/k_B T$ at low temperature, and τ_0 is the correlation time at the infinite temperature limit.

In multilevel spin systems (such as quadrupolar spin species where $I \geq 1$), magnetization recovery curves need not be single-exponential and more complex expressions for the relaxation rates may be required. Nonetheless, for ^{2}H ($I = 1$), a well-characterized T_1 always exists. With the relatively small quadrupolar moment and large dipole−dipole couplings of ^{7}Li, experiments on ^{7}Li almost always yield recovery curves which are sufficiently close to exponential (as in our experiments) that the use of more complicated forms is unjustified.

Figure 1 shows plots of $\ln(1/T_1)$ vs $1/T$ for the ^{7}Li cations and ^{2}H sites in PEO:Li-FH. Both curves are fitted to BPP expressions satisfying eqs 1 and 2, and the resulting dynamic parameters are summarized in Table 1. Values for E_a and τ_0 from T_1 are sufficiently similar that a single process appears responsible for the fluctuating fields at both nuclei. As the lone-pair electrons from oxygen in the PEO backbone contribute to the EFG at the Li sites, motion of either Li or the polymer will relax the ^{7}Li nuclei equivalently. Polymer motion is required, however, to account for relaxation of the ^{2}H nuclear spins on the polymer backbone, which relax on the same dynamic time scale. This is consistent with most T_1 analyses of SPEs, which find $E_a \approx 22$−27 kJ/mol, and $\tau_0 \approx 10^{-12}$−10^{-13} s at both the

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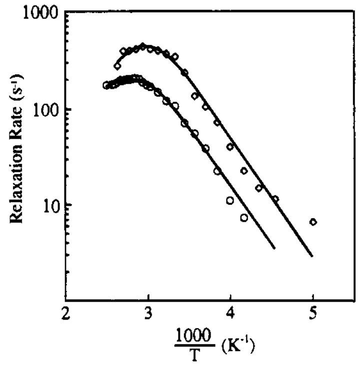

Figure 1. T_1 relaxation rates measured for ^{7}Li (○) and ^{2}H (◇) in PEO-intercalated Li$^+$-fluorohectorite. Fits give comparable activation barriers and correlation times for both nuclei.

Table 1. Dynamic Parameters for T_1 and Line Width Analyses

nuclei	SPEs	E_a (kJ/mol)	τ_0 (10^{-13} s)
		T_1 Analyses	
^{7}Li	PEO:Li-FH	22.1 ± 0.5	5.3 ± 0.9
^{2}H	dPEO:Li-FH	24.2 ± 1.2	3.9 ± 1.7
^{7}Li	PEO:LiClO$_4$	27.7 ± 0.1	1.9 ± 0.1[a]
^{1}H	PEO:LiClO$_4$	22.8 ± 0.2	8.2 ± 0.7[a]
^{7}Li	PPG:LiCF$_3$SO$_3$	24.1 ± 5.8	14.2 ± 1.6[b]
		Line Width Analyses	
^{7}Li	PEO:Li-Mont	26.7 ± 1.8	5700 ± 4600
^{7}Li	PPG:LiCF$_3$SO$_3$	32.8 ± 10.0	8.0 ± 5.0[b]

[a] From ref 6. [b] From ref 8; PPG = poly(propylene glycol).

cation and the polymer.[6,8] As a result, T_1 appears not to usefully measure the cation dynamics associated with conductivity. Moreover, the dynamics probed by T_1 appear similar in these confined polymers and bulk SPEs.

An independent perspective on the cation mobility is available from the temperature dependence of ^{7}Li line width. In inhomogeneous environments as are found in SPEs, only transitions between the spin eigenstates $|^1/_2\rangle$ and $|-^1/_2\rangle$ contribute to the observed spectrum, and its breadth is dominated by couplings to nearby magnetic fields associated with other spins.[9] Line width changes reflect averaging over these local fields due to dynamics. While previous measurements have found that the line width narrowing is associated with the same parameters found by T_1 analyses,[6,8] the interpretation of these results is complicated by the difficulty of disentangling cation, anion, and polymer mobilities, as each may contribute to the dipolar broadening. Similar narrowing is observed in Li$^+$-fluorohectorite.

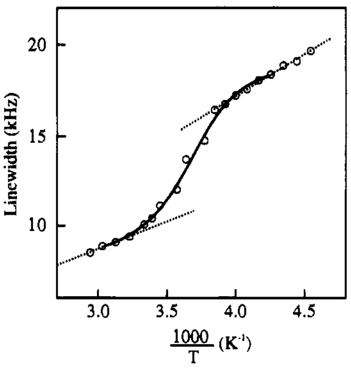

Figure 2. ^{7}Li temperature-dependent line width in PEO-intercalated Li$^+$-montmorillonite at 40 wt % polymer loading. The dotted lines are estimates of the change in electron spin susceptibility at the high- and low-temperature limits.

In montmorillonite, the low-temperature ^{7}Li central transition is broadened to ~20 kHz by Fe^{3+} found in the silicate lattice. Figure 2 represents our data on the ^{7}Li line width vs 1/T. At low and high temperatures, these plots are linear and reflect the decrease in the average electron spin polarization with temperature.[10] At intermediate temperatures, however, the line width changes are much more dramatic and correspond to the onset of cation diffusion. Each ^{7}Li nucleus samples the inhomogeneous distribution of local fields over length scales comparable to the average Fe^{3+} spacing. It is precisely these jumps which are responsible for the observed ionic conductance.

A well-tested phenomenological equation relating the change of line width, $\Delta\nu$, to the correlation time for diffusional dynamics, τ^{diff}, predicts that[7,10,11]

$$\Delta\nu^2 = \left(\frac{2}{\pi}\right)\Delta\nu_u^{\,2} \arctan(\alpha\Delta\nu\tau^{\text{diff}}) \qquad (3)$$

where α is of order 1 and $\Delta\nu_u$ is the low-temperature limiting line width. The varying spin susceptibility accounts for line width changes at high and low temperatures. Where ^{7}Li motion dominates (235−330 K), we ignore this relatively small effect and use eq 3 to reproduce the line width data of Figure 2 with dynamic parameters as found at the bottom of Table 1. We find E_a similar to that found for polymer motion via T_1 analysis. Diffusional motion is sufficient for ^{7}Li$^+$ line narrowing to occur, however, 3 orders of magnitude less often. As the massive anion is immobile, our measurement is the first which unambiguously identifies the cation mobilities. We are exploring the use of these NMR-derived dynamic parameters as input for available theories of bulk conductance in polymer electrolytes.[12]

In summary, we have demonstrated that spin−lattice relaxation studies for the polymer and the cation are similar in this confined ionic electrolyte. T_1 relaxation at the cation reflects the dynamics of the polymer backbone only. Ion transport is accessible only via our line width measurements and occurs substantially more slowly than polymer reorientation.

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