STRUCTURE AND DYNAMICS OF LITHIUM POLYMER ELECTROLYTES

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ABSTRACT

The atomic structure and dynamics of PEO-LiClO₄ and PEO-LiTFSI polymer electrolytes have been investigated by neutron scattering experiments and ab initio quantum chemical calculations. The Li⁺ ions are bonded to, on average, five ether-oxygen atoms of the polymer host with an average bond length of 2.1 Å. No cation-anion pairing is observed. On a time scale of 0.01 – 0.1 ns, the segmental motion of the PEO chains is significantly altered by the introduction of the salts compared to pure PEO. The cross-links through the Li-O coordination bonds are believed to be responsible for the change in the dynamics. These results are consistent with a mechanism in which Li⁺ ion transport takes place through the dynamical formation and disruption of Li-O bonds.

INTRODUCTION

Electrolytes made up of polyethylene oxide (PEO) and lithium salts have been developed for use as lightweight electrolytes in secondary lithium batteries aiming at both general consumer and automotive applications (1). These materials also have considerable scientific interest because of the interplay between the mechanical relaxation of the glass-forming liquid and the electrical relaxation resulting from the presence of mobile ions.

At temperatures below their melting points PEO/Li-salt complexes usually exhibit a mixture of supercooled liquid and crystalline regions. It is generally accepted that the ion conduction takes place predominantly in the liquid phases (2). The development of polymer electrolytes with adequate ionic conductivities has been hindered by the limited understanding of their behavior, especially regarding the characteristics of the ion transport mechanisms at a microscopic level. Here we report results of an investigation of the atomic structure and dynamics of polymer electrolytes containing two lithium salts, LiClO₄ and LiTFSI (TFSI = lithium bis (trifluoromethanesulfonyl) imide). The

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techniques used include neutron diffraction with lithium isotope substitution (NDIS), quasielastic neutron scattering (QENS) and \textit{ab initio} quantum chemical calculations.

METHODS

The choice of materials studied here was dictated by the fact that PEO-LiClO\textsubscript{4} is a prototypic polymer electrolyte and PEO-LiTFSI is a promising candidate for technological applications because of its chemical safety and stability and relatively high conductivity (3). The EO:Li ratio of 7.5 was chosen since it corresponds to a composition close to the conductivity maximum and, in the LiTFSI system, is located in a crystallinity gap (3). Polymer electrolytes containing \textsuperscript{6}Li and \textsuperscript{7}Li isotopes were prepared by stepwise drying deuterated acetonitrile solution mixed with PEO and synthesized lithium salt (\textsuperscript{6}LiClO\textsubscript{4}, \textsuperscript{7}LiClO\textsubscript{4}, \textsuperscript{6}LiTFSI, \textsuperscript{7}LiTFSI) in a high vacuum oven (100\textdegree C and ~10\textsuperscript{-6} torr in the final drying stage) for three days. Deuterated (d-) PEO, 1 mm thick, was used for the NDIS measurements and both deuterated (1 mm) and hydrogenated (h-, 0.1 mm) PEO for the QENS measurements. The isotopic enrichment was 96\% for \textsuperscript{6}Li and 98\% for \textsuperscript{7}Li. QENS measurements were also made on pure d- and h-PEO. The materials were loaded into vacuum-tight flat cells with thin vanadium (NDIS) or aluminum (QENS) windows. The NDIS experiments on the PEO-LiClO\textsubscript{4} and PEO-LiTFSI electrolytes were carried out on the D4B diffractometer at ILL and the SANDALS diffractometer at ISIS, respectively, and the QENS experiments on the IRIS back-scattering spectrometer at ISIS.

The \textit{ab initio} quantum chemical calculations were carried out at the HF/6-31G* level of theory (4). These calculations involved the full geometry optimization of the PEO-LiTFSI complex with PEO modeled by diglyme CH\textsubscript{3}O(CH\textsubscript{2}CH\textsubscript{2}O\textsubscript{2})CH\textsubscript{3}. There are numerous possible structures because of the flexibility of the diglyme. In this paper we report results for one structure which has distances that are representative of the other structures that we have located. Previously, we have investigated the lithium ion migration mechanism in Li\textsuperscript{+}-(diglyme), Li\textsuperscript{+}-(diglyme)\textsubscript{2} and LiClO\textsubscript{4}-diglyme complexes with coordination of Li\textsuperscript{+} by 1 to 6 oxygens using \textit{ab initio} molecular orbital theory (5,6).

RESULTS AND DISCUSSION

Experiment

In the NDIS experiments the P(EO)\textsubscript{7.5}LiClO\textsubscript{4} samples were measured at 100\textdegree C and the P(EO)\textsubscript{3}LiTFSI at room temperature, both corresponding to the liquid regions of their respective phase diagrams. The total scattering data from the samples were corrected for instrumental background, container scattering, multiple scattering and absorption, and normalized to scattering from a vanadium plate mounted on the same holder, using standard routines (7). The results were reduced to the neutron-weighted average structure factor \(S(Q)\) and its Fourier transform, the neutron-weighted average pair distribution function \(T(r)\). The local structure around an average Li\textsuperscript{+} ion was determined from the first-order difference.
$$S_{Li}(Q) = \frac{\langle b \rangle_6^2 S_6(Q) - \langle b \rangle_7^2 S_7(Q)}{\langle b \rangle_6^2 - \langle b \rangle_7^2},$$

where the subscripts 6 and 7 refer to the $^6$Li and $^7$Li samples, respectively, and $\langle b \rangle$ denotes the mean neutron scattering length for the sample, and from its corresponding pair distribution function $T_{Li}(r)$. As an example, $T_{Li}(r)$ for P(EO)$_{7.5}$LiTFSI is shown in Fig. 1 together with Gaussian functions fitted to the principal peaks. Based on information from analogous crystal structures (8-10) and the ab initio calculations discussed below, we can associate the peak at 2.1 Å with Li-O correlations. Integration over the peak, taking account of the appropriate weighting factors, gives a coordination of 4.9 oxygen atoms about each Li$^+$ ion. The peak at 3.05 Å is assigned to Li-C with some Li-H correlations, and that at 3.8 Å to Li-H with some second-neighbor Li-O correlations. Taking the intensities of these peaks into account, together with the ab initio results and information from the crystallographic studies (8-10), we conclude that the five oxygens around each lithium ion are ether oxygens from the polymer. There is no cation-anion pairing at distances less than 4.8 Å, where the fourth peak in Figure 1 may result from correlations between the lithium ions and oxygens on the anions.

![Figure 1. Lithium-difference pair-distribution function for liquid P(EO)$_{7.5}$LiTFSI at room temperature. The dashed lines represent Gaussian functions fitted to the first three peaks and the solid line the total fit.](image)

In lithium polymer electrolytes, the Li$^+$ ion transport is believed to be coordinated with ether-oxygen atoms of the neighboring polymer chains (11,12). The formation and disruption of the Li-O coordination must be accompanied by strong relaxation of the...
local chain structure in order to reduce the total free energy. An experimental investigation of the dynamics of Li\(^+\) ion diffusion and the associated motions of the chain segments requires a probe with a dynamic range in the nanosecond time scale. QENS provides an especially powerful tool on this time scale, with a considerable dynamic range in both frequency and scattering vector. Figure 2 shows results from the QENS measurements in terms of the intermediate scattering function \(I(Q,t)\) at a typical value of the scattering vector \(Q\). A dramatic effect on the dynamics of the d- and h-PEO occurs with addition of the LiClO\(_4\). Two kinds of time-dependent functions are observed: while pure PEO sample obeys a stretched exponential (Kohlrausch-Williams-Watts) behavior,

\[
I(Q,t) = I(Q,0)\exp\left(-\left(t/\tau_k\right)^\beta\right),
\]

PEO/Li-salt samples exhibit a pure exponential behavior (Debye) fast relaxation,

\[
I(Q,t) = I(Q,0)\exp\left(-t/\tau\right)
\]

together with a slow relaxation that appears to be independent of time in these measurements. This dramatic change of dynamical behavior of polymer chains is believed to arise from motion of short PEO segments linked through Li-O bonds. The fast relaxation corresponds to rapid conformational fluctuations of these segments, while the slow processes reflect the slowing down of the translational motions observed in the pure PEO to a time scale that appears static on the spectrometer used.

![Figure 2](image_url)

Figure 2. Time dependence of the relaxation in pure PEO polymer and P(EO)\(_{7.5}\)LiClO\(_4\) polymer electrolyte for a typical scattering vector \(Q\), measured by QENS on a neutron back-scattering spectrometer at 75°C. The labels H and D refer to hydrogenated and deuterated material, respectively. The relaxation in the polymer electrolyte continues for at least another decade in time, determined in subsequent measurements on a neutron spin-echo spectrometer.
**Ab Initio Quantum Chemical Calculations**

The HF/6-31G* optimized structure of a LiTFSI-diglyme complex with five coordination is shown in Figure 3. This complex corresponds to one LiTFSI per three ethylene oxides. The lithium cation is coordinated to two oxygens from the TFSI anion and three oxygens from the diglyme. The Li-O distances range from 1.97 to 2.13 Å. This is similar to the Li-O distances found in our previous ab initio calculations on Li⁺-(diglyme)$_2$ and LiClO$_4$-diglyme complexes (6). Hence, the Li-O distances are similar with and without the presence of the anion. However, from the intensities of the NDIS peaks it is clear that in the LiTFSI-PEO material the oxygens come from the polymer only (see above). The Li-C distances from the diglyme range from 2.91 to 3.14 Å while the Li-C distances from the TFSI anion are 4.23 and 4.48 Å.

In our previous work (6) the barrier heights for $n+1 \rightarrow n$ coordination of the lithium cation by oxygen decrease with increasing coordination number $n$, with the smallest Li$^+$ migration barriers (7–11 kcal/mol) occurring for complexes with the highest coordination numbers. The reaction coordinate for lithium ion migration between coordination sites is the torsional motion of the diglyme backbone and involves making and breaking of the Li-O bonds. These ab initio calculations of the pathway for Li cation migration are consistent with the QENS results reported in this study that indicate a dramatic change of dynamical behavior of polymer chains when the salt is introduced due to motion of short PEO segments linked through Li-O bonds.

![Figure 3. HF/6-31G* optimized structure of LiTFSI-diglyme](image-url)
SUMMARY

The atomic structure and dynamics of PEO-LiClO₄ and PEO-LiTFSI polymer electrolytes have been investigated by neutron scattering experiments and ab initio quantum chemical calculations. The Li⁺ ions are bonded to, on average, five ether-oxygen atoms of the polymer host with an average bond length of 2.1 Å and no cation-anion pairing is observed. On a time scale of 0.01 – 0.1 ns, the segmental motion of the PEO chains is significantly altered by the introduction of the salts. The cross-links through the Li-O coordination bonds are believed to be responsible for the change in the dynamics. These results are consistent with a mechanism in which Li⁺ ion transport takes place through the dynamical formation and disruption of Li-O bonds.

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