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Exceedingly High Lithium Conductivity in Novolac Type Phenolic Resin/PEO Blends

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The rapid chain segmental mobility with high oxygen content makes PEO a favored solid polyelectrolyte.[1,2] In the presence of polar salts such as $LiClO_4$ or $LiCF_3SO_3$, PEO becomes a lithium transport medium used in various apparatus, such as a secondary lithium battery,[3,4] light-emitting chemical cells,[5,6] and a glass tinting layer. High PEO crystallinity, however, has interrupted the lithium transfer pathway and deteriorated the conduction.[7] Furthermore, PEO gives only acceptable conductivity at elevated temperature (around 10^{-3} S/cm at 60 °C),[8] which has severely hampered the utility of PEO at ambient temperature. Many efforts are devoted to creating favorable lithium coordinations of the polyelectrolyte through manipulating the equilibrium of lithium between all substrates. They include incorporation of PEO functional groups to PEO[9] and enhancing miscibility between PEO and electrolytes with modified preparation procedures.[10]

Prior studies suggest that strong intermolecular hydrogen bonding is formed with Novolac type phenolic which reduced PEO crystallinity upon blending.[11] Furthermore, higher chain segmental motion surpassing that of pure PEO is also detected.[12] Excellent lithium conductivity in phenolic/PEO is plausible due to the increase of amorphous components (reduced crystallinity), increase of amorphous phenolic/PEO, and segmental mobility. In this communication, we report the study of lithium conductivity in the novel polyelectrolyte and conclude that reduced PEO crystallinity and lower pseudo activation energy in lithium transfer account for the very high conductivity of the blend.

Novolac type phenolic is prepared as previously described.[13] PEO−$LiClO_4$ salt−phenolic electrolytes are prepared first by mixing completely the desired (5.0, 10.0, and 15.0 wt %) weight percentages of the Li/Li+PEO mixture, followed by blending with different amounts of phenolic resin using a small amount of THF. The residual solvent was removed by heating at 140 °C for 1 day under vacuum. Variable temperature ^7Li solid-state NMR is employed to measure the conformation and lithium motion in a blended system.

The ionic conductivity of the polymer electrolytes was measured by a four-probe method using the complex impedance method using a Keithley 238 at ambient temperature. The results are listed in Table 1 for 5.0, 10.0, and 15.0 wt % $LiClO_4$ series, respectively. The improvements in PEO conductivity through blending is better visualized in the three-dimensional representation in Figure 1, which summarizes the lithium conductivity as a function of both $LiClO_4$ uptake and phenolic content. Except for a narrow window, the conductivity appears in the normal 10^{-6} S/cm region, as most PEO. A continuous analytical surface function is fit to the experimental values to guide the view, which indicated an optimized conductivity of 7.0×10^{-3} S/cm can be reached in the neighborhood of 10.5 wt % $LiClO_4$ and 10.9 wt % phenolic. Four samples are prepared near the optimized conductivity window with the concentration ($LiClO_4$, phenolic) wt % = (9.7, 10.2), (10.0, 11.3), (10.5, 10.9), and (11.0, 11.5), and the measured conductivitys equals 8.0×10^{-4}, 5.6×10^{-3}, 6.5×10^{-3}, and 3.5×10^{-3} S/cm. The conductivity (marked by the star symbols in Figure 1) agrees well with the simulation. The optimum conductivity, 6.5×10^{-3} S/cm, appears near the top of the "cone" and far exceeds that by increasing $LiClO_4$ or by elevating the temperature for PEO. Improvement in conductivity through blending with phenolic is obvious; however, the composition window is narrow.

Table 1. Conductivity and PEO Crystallinity

run no.	phenolic content (wt %)	Li/Li+PEO content (wt %)					
		5		10		15	
		σ (S/cm)	χ (%)	σ (S/cm)	χ (%)	σ (S/cm)	χ (%)
1	0	3.2×10^{-6}	61.4	1.0×10^{-5}	43.1	8.1×10^{-6}	32.9
2	3.5	7.4×10^{-5}	53.2	1.6×10^{-4}	21.6	1.3×10^{-5}	27.3
3	6.25	8.1×10^{-5}	50.2	9.4×10^{-5}	9.3	5.7×10^{-6}	0
4	9	1.1×10^{-4}	44.7	1.2×10^{-3}	0	9.9×10^{-5}	0
5	14.3	9.4×10^{-5}	28.2	6.2×10^{-4}	0	1.1×10^{-4}	0
6	21	1.2×10^{-4}	0	2.2×10^{-4}	0	5.5×10^{-5}	0
7	25	1.3×10^{-4}	0	1.8×10^{-4}	0	4.7×10^{-5}	0

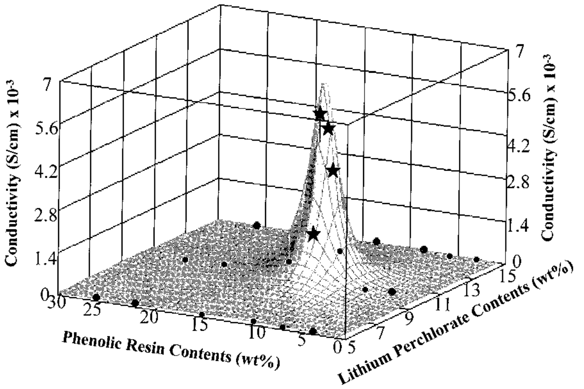

Figure 1. Three-dimensional representation of the effect of $LiClO_4$ and phenolic content to Li conductivity in the phenolic/PEO blend.

Increased density of lithium in conducting pathways and a lowering of the transference activation energy are both responsible for the high flux of lithium and the improvement in lithium ion conductivity. ^7Li solid NMR with sample spinning reveals major lithium species in the polyelectrolyte. A rotation frequency of 2000 Hz is sufficient to remove the small shift anisotropy sidebands without major complications. The quadrupolar coupling constants e^2qQ is estimated to be less than 200 kHz judging from the ($^1/_2$ to $^3/_2$) and ($-^3/_2$ to $-^1/_2$) satellite singularities in the static spectrum. The central transition ($m_s = {}^1/_2$ to $-^1/_2$) of all Li species is thus not affected by the quadrupolar interaction and ensures quantification integrity. Decomposition of the lithium central transition by the least-squares fit between the experimental and the calculated spectra reveals the composition of individual lithium species. Shown in Figure 2a

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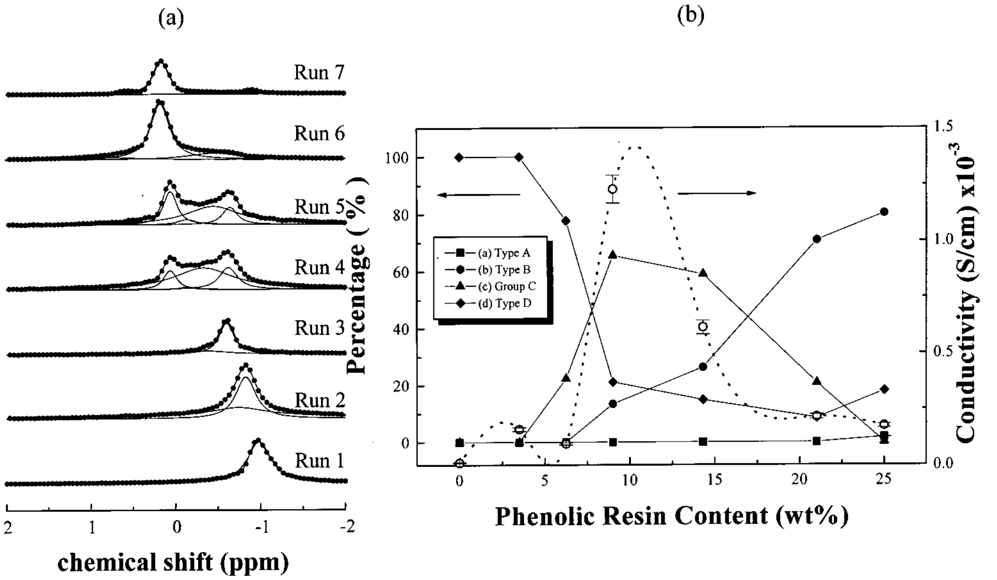

Figure 2. Left: experimental and peak decomposition results of ^{7}Li NMR for blends with 10.0 wt % $LiClO_4$. Right: variations of the four major components with phenolic content.

are the experimental Li spectra superimposed with the fitting results for blends containing 10.0 wt % $LiClO_4$. At least four major lithium coordinations from the central transition are apparent. A Lorentzian peak shape yields a better fit than a Gaussian, consistent with previous finding that lithium is in constant motion with short correlation time.[14] Together with the variation of peak intensities with $LiClO_4$ uptake and phenolic content, the peaks are assigned to the four major lithium conformations as the loosely coordinated Li ions near $LiClO_4$ (type A,1.1 to 0.2 ppm), in the form of $ClO_4^{-}Li^{+}ClO_4^{-}$, $Li^{+}Cl^{-}Li$ $^{+}$or species at the surface of the blend; Li ion in phenolic matrix (type B, 0.2 to 0.0 ppm); Li ion resides in the amorphous phenolic/PEO domain (group C, 0.0 to −0.6 ppm); and Li ion resides in the amorphous PEO domain (peak D, −0.6 to −1.1 ppm), respectively. No attempts were made to further differentiate group C species which comprise at least three different fine coordinations having similar environments and was grouped as the intermediate component in the following discussion.

Changes in the composition of the four major Li species with phenolic content for blends containing 10.0 wt % $LiClO_4$ are shown as examples in Figure 2b. Variations in Li coordination are different for the 5.0 and 15.0 wt % $LiClO_4$ samples; however, they can all be explained on the basis of the affinity of lithium salt with phenolic, amorphous PEO, and ClO_4^- anion. The quantitative analysis concludes that lithium favors coordination with phenolic over amorphous PEO at ambient temperature. It is also interesting to note that more Li ion is coordinated with phenolic (type B) with increasing $LiClO_4$ content.

Reduction in PEO crystallinity with increasing phenolic is apparent from DSC measurements (Table 1). A first glance reveals that $LiClO_4$ salt has reduced PEO crystallinity as apparent across the pure PEO samples. PEO becomes completely amorphous with blending of 21.0, 9.0, and 3.5 wt % phenolic for the three series of PEO having different $LiClO_4$ content. This is contrasted with prior results of phenolic/PEO blends where complete amorphous PEO was reached only after 40.0 wt % of phenolic was added.[7,8] Clearly, both the salt and phenolic moieties contribute synergistically to the reduction of PEO crystallinity, thereby facilitating the formation of amorphous PEO.

Useful information about the ^{7}Li dynamics and the kinetics is obtained from temperature-dependent studies of the line widths at 116.9 MHz for the lithium ($-^1/_2$ to $^1/_2$) transition over the temperature range from 295 to 353 K. At high temperatures, the NMR spectra exhibit a single, Lorentzian line shape with no apparent influence of quadrupolar broadening. Motional narrowing begins when the rate of the fluctuations (τ_c^{-1}) of either the local dipolar fields or the electric field gradients (efg) is comparable to their respective rigid lattice line widths (Δ_{RL}) when

$$1/\tau_c \approx \Delta_{RL} \qquad (1)$$

with τ_c being the motional correlation time. That is, the narrow component due to the dipolar interaction undergos motional narrowing before the broad component. The NMR line shape was motionally narrowed with increasing temperature and could be accurately fit with a Lorentzian line shape where the fwhm (Δ_{LW}) is a well-defined parameter in terms of spin−spin relaxation time (T_2), i.e.,

$$\Delta_{LW} = 1/(\pi T_2) \qquad (2)$$

The smoothed fitting value for T_2 with increasing temperature is shown in Figure 3 where the two most prominent Li coordinations, group C and type D, are presented for the10.0% phenolic sample series. The results are found to be sensitive to the concentrations of Li/Li+PEO and the temperature. Aggregates have effected to slightly immobilize the Li^+ cation, resulting in broadening of line shapes. This is not entirely surprising because increased ion pairing and ion aggregation are known to occur at high temperature.[15] Other pieces of evidence for ion pairing as temperature increases are observed for resonance at $\delta = 0.2{-}1.1$ ppm (type A). Other sample series having different salt concentration shows T_2 maximum occurs at different temperatures, demonstrating the difference in Li correlation time with salt content. The changes in relaxation time indicate that all samples are governed by a

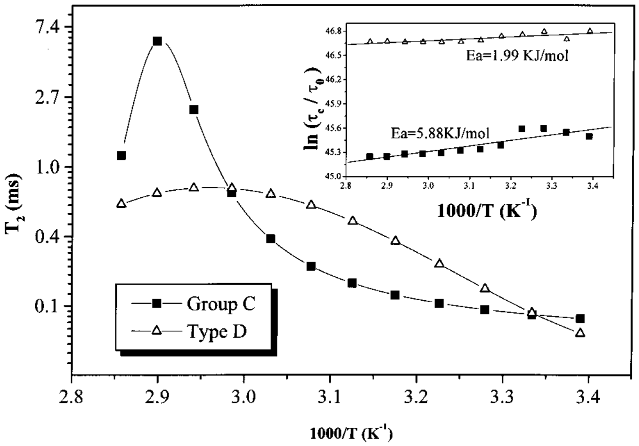

Figure 3. Li T_2 as a function of inverse temperature for group C and peak D in the PEO blend containing 10.0 wt % $LiClO_4$ and 10.0 wt % phenolic. The inset shows the correlation between $\ln(\tau_c/\tau_0)$ and inverse temperature.

Table 2. Pseudo Activation Energy of Li Conduction in Phenolic/PEO Blend (10 wt % Phenolic)

		$LiClO_4$ (wt %)		
		5	10	15
group C	τ_0 (s)	6.3×10^{-22}	6.0×10^{-22}	6.4×10^{-20}
	E_a (kJ/mol)	6.29	5.88	4.18
type D	τ_0 (s)	7.1×10^{-22}	3.2×10^{-22}	6.0×10^{-20}
	E_a (kJ/mol)	3.58	1.99	0.18

common diffusion mechanism. The pseudo activation energy (E_a) of lithium transference in each Li coordination is expected to be different; however, it is difficult to deduce activation energy directly from narrowing of the line width because the lifetime broadening of the spin states must be taken into consideration. However, estimates may be obtained from the narrowing of the line width, which can be described in its most simple form by Abragam[16]

$$\tau_c = (\alpha/\Delta_{LW}) \tan[(\pi/2)(\Delta_{LW}/\Delta_{RL})^2] \tag{3}$$

where α is a parameter with order of unity. Assuming τ_c to be thermally activated,

$$\tau_c = \tau_0 \exp(E_a/RT) \tag{4}$$

where τ_0 is the dwell time. The lithium transference pseudo activation energy is estimated from the slope of the motional correlation time $\ln(\tau_c/\tau_0)$ as a function of inverse temperature depicted in the inset of Figure 3. The results are summarized in Table 2 for group C and D lithium of the 10.0 wt % phenolic sample. In general, type D coordination exhibits lower E_a than that in group C environment. Because Li^+ cation transfer is favored in environments of low activation energy, type D offers more favorable conduction than that of group C. Although the activation energy of 15.0 wt % $LiClO_4$ is lower than that of 10.0 and 5.0 wt %, ion pairing and ion aggregation are so severe in these concentrations that much less Li exists in the conduction pathway. For 5.0 and 10.0 wt % lithium salt, the higher activation energy suggested 5.0 wt % sample is less favorable than 10.0 wt % for lithium conduction, possibly related to slower PEO segmental motion due to higher PEO crystallinity. The E_a value for group C lithium lies in the range 4−7 kJ/mol, which is $^1/_4$ to $^1/_3$ of that reported in prior studies for lithium transference in pure PEO.[17] As conductivity is logarithmically related to E_a, current results are in full agreement with the 2−3 order of increase in conductivity observed for the phenolic/PEO blend.

The study concludes that crystalline PEO and ions pairing of $LiClO_4$ are obstructing lithium transfer. The general Li conduction is low for the 15.0 wt % $LiClO_4$ series, since the majority of Li is coordinated either with phenolic units or showing ion aggregation. The conduction is also low for the 5.0 wt % $LiClO_4$ series because the PEO crystallinity and the transfer activation energy are both high while the lithium content is low. Blending with phenolics alters the partition of amorphous PEO, phenolic/PEO, and crystalline PEO in the material, leading to changes in Li coordination and lithium conductivity. Although excess phenolic appears to trap lithium, rendering it less conductive, small amounts of Novolac type phenolic provide more lithium transfer channels and improve the overall conductivity. The best composition of lithium salt and phenolic with optimized conductivity near 10^{-2} S/cm appears within a small window in the neighborhood of 10.5 wt % $LiClO_4$ and 10.9 wt % phenolic. The novel polyelectrolyte exhibits outstanding conducting currents at ambient temperature, far exceeding that observed in conventional PEO and other polyelectrolytes.

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