

# Mixed Solvent and Polymer Coordination in PAN and PMMA Gel Polymer Electrolytes Studied by *Ab Initio* Calculations and Raman Spectroscopy

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The local and mixed solvent and polymer coordination in PAN and PMMA/carbonate (EC/PC) based lithium ion conducting gel polymer electrolytes has been studied by using *ab initio* calculations and Raman spectroscopy. The energies of the coordination complexes were evaluated by density functional theory with a hybrid functional and by performing simple thermodynamic calculations. Observed frequency shifts for EC and PAN due to lithium ion coordination were confirmed by computing the Hessian matrixes for pure and mixed complexes. The lithium ion has been found to prefer to coordinate to EC solvent molecules. In the PAN based gels there was only a slight preference, while for PMMA gels the preference is much larger. The temperature-dependent coordination is found to be directly related to the differences in lithium ion binding energies in the mixed solvent and polymer ligand complexes. The implications for the formation and stability of gels and for the lithium ion transport in different gel systems are discussed.

## Introduction

The state-of-the-art battery technology of today is mainly based on lithium ion conducting gel polymer electrolytes, *i.e.*, Li ion batteries. In such gel electrolytes the macroscopic mechanical stability of a polymer is combined with the liquidlike microscopic dynamics of a low molecular weight solvent. Typical examples are gels made by trapping ethylene carbonate/propylene carbonate (EC/PC) lithium salt solutions in a polymer matrix. Examples of polymers often used are poly(acrylonitrile), PAN, and poly(methyl methacrylate), PMMA. Although the gel electrolyte concept is used commercially there are still fundamental issues to be solved, *e.g.* the ion conduction mechanism and the local coordination in the materials. The conduction mechanism is completely different, at least for polymer dilute materials, from that of polymer electrolytes based on, *e.g.* PEO, where the ionic conductivity of the cation is coupled to the segmental motion of the polymer and the amount of local free volume limits the total ionic conductivity.<sup>1</sup> The polymer matrix does, however, affect the conduction process and thus it is not as simple as for a true liquid electrolyte. Discussions on gel electrolytes are sometimes concerned with whether the polymer matrix significantly interacts with the electrolyte. PAN is suggested to interact more and thus taking an active part in the conduction mechanism, while PMMA is regarded as more passive.

Previously, the dynamics of the materials have been studied by measurements of the relaxation processes present.<sup>2</sup> Recent NMR studies have detected differences with respect to the matrix used.<sup>3,4</sup> However, the underlying local interactions are still not unambiguously revealed; *e.g.* both PAN and PMMA have polar groups present that seemingly would both attract cations. We here present spectroscopic as well as computational data on the local coordination to allow an explanation of the two polymers' different behavior based on the interaction strengths. Focus will be on the cation environment, which is

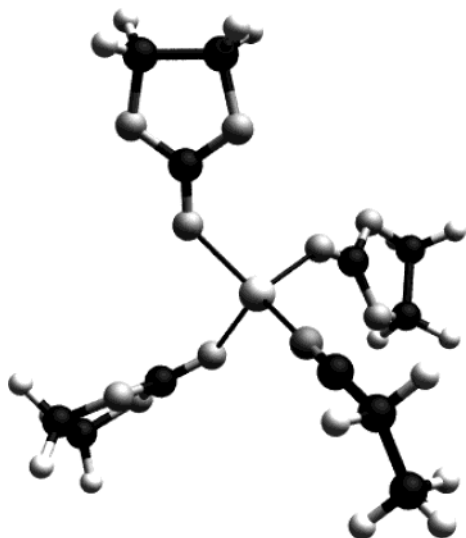
studied spectroscopically by the induced shifts in the molecular vibrations of the counteranion, the solvent, and the polymer host.

**Computational.** The present paper is, to the best of our knowledge, the first that applies *ab initio* Hartree–Fock (HF) type calculations to these kinds of gel systems. However, some related studies exist. The interactions within a liquid EC electrolyte (EC<sub>x</sub>:Li) were first modeled by Blint in 1995,<sup>5</sup> later by Klassen *et al.*,<sup>6</sup> and by Wang *et al.*<sup>7</sup> The most rigorous study is the latter. Also molecular dynamics simulations have been undertaken to study lithium salt EC/PC/DMC solutions at different temperatures.<sup>8,9</sup>

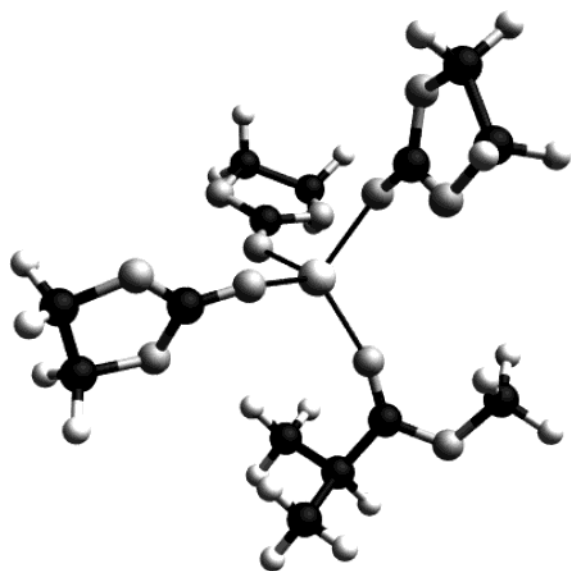
Here all molecular models were based on a central lithium ion with different ligands present to model the possibilities of mixed coordination of solvent (EC) and polymer (PAN or PMMA) using a metal–core complex model: [Li(EC)<sub>x</sub>(polymer)<sub>y</sub>]<sup>+</sup> ( $x = 0–4$ ,  $y = 0–4$ , and  $\Sigma(x+y) = 0–5$ ). Two examples are given in Figures 1 and 2.  $y$  denotes a stepwise increase in oligomer length: monomer to tetramer. This way coordination by sequential coordinating groups from the same polymer chain was simulated. The monomeric units used were CH<sub>3</sub>CH<sub>2</sub>CN (PAN) and CH<sub>3</sub>CH(COOCH<sub>3</sub>)CH<sub>3</sub> (PMMA). Only the first solvation shell of the cation has been considered. No PC molecules were used as model compounds for the liquid solvent, as the differences in coordination properties as compared to EC are negligible.<sup>9</sup> A total of 22 different complexes was obtained.

All complexes were manufactured “by hand” and initial calculations, preoptimizations, were for most systems made with the semiempirical PM3 method followed by optimizations using HF/3-21G\*. Subsequent final geometry optimizations at the HF level used the standard 6-31G\* basis set. Vibrational frequency calculations were performed at this level of theory to confirm that the structures obtained were true minima and not related to transition states. All obtained frequencies were scaled by a factor 0.9 in order to correct for systematic errors.<sup>10</sup> Selected complexes were subject to final single-point calculations using a larger basis set (6-311++G\*\*) and a gradient-corrected hybrid

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**Figure 1.** Structure of  $[\text{Li}(\text{EC})_3(\text{PAN})]_1^+$ . (Black = C, darkgray = N, gray = O, lightgray = Li, and white = H.)



**Figure 2.** Structure of  $[\text{Li}(\text{EC})_3(\text{PMMA})]_1^+$ . (Black = C, gray = O, light gray = Li, and white = H.)

DFT method, Becke3-Lee-Yang-Parr (B3LYP/6-311++G\*\*//HF/6-31G\*).<sup>11,12</sup>

The binding energies are defined as  $\Delta E_{\text{bind}} = E(\text{Li}^+ \text{ complex}) - \Sigma(E(\text{Li}^+) + E(\text{complex w/o Li}^+))$ . Stepwise binding energies,  $\Delta\Delta E_{\text{bind}}$ , were also calculated. No basis set superposition error (BSSE) corrections have been applied. To get a rough estimate of the temperature sensitivity of the complex equilibria present in the materials, simple entropy calculations were performed using the results from the highest level calculations and the approximations  $\Delta E = \Delta U_{0\text{K}}$  and  $K_T = e(-\Delta U_{0\text{K}}/RT)$ . The equilibrium constants  $K_T$  were then computed for  $T = 296$  and  $373$  K.

All computations were performed with the TITAN and GAUSSIAN98 program packages.<sup>13,14</sup>

## Experimental Section

All gel electrolytes were prepared similarly by first preparing a solution of  $\text{LiClO}_4$  in EC/PC. EC (Aldrich, reagent grade) was melted on a hotplate ( $\sim 80$  °C) and then mixed with PC (Aldrich, reagent grade, 99.7% anhydrous) in a 2.45:1 molar

ratio. A lithium salt solution was made by dissolving  $\text{LiClO}_4$  (Fluka, reagent grade, 99.7% anhydrous) by thorough mixing using a magnetic stirrer. Appropriate amounts of the salt solution and polymer powder (PAN, Aldrich, reagent grade,  $M_w$  not supported, or PMMA, Aldrich, reagent grade,  $M_w = 996\,000$  g  $\text{mol}^{-1}$ ) were mixed for 2–6 h. The samples were then subject to heating to  $\sim 120$  °C and after 2–4 min the milky solutions were transformed into transparent and rubbery gels. The molar ratios  $\text{LiClO}_4$ :EC:PC:polymer in the samples were 8:45:18:29, with respect to the monomer units of PAN and PMMA. The electrolyte solution was 1.66 M. This salt concentration allowed detection of changes in the ionic equilibrium and the Raman spectra.

All components were dried under vacuum before usage and all preparation and subsequent handling was made under argon atmosphere in a glovebox. All gels were made in small tubes (diameter = 10 mm) and for the Raman measurements a small amount ( $< 0.03$  g) of the gel was placed between two thin glass sheets sealed with adhesives. The samples were placed in an oven (Linkam THMS 600 with a Linkam 93 controlling device) and the oven was flushed with nitrogen gas. The oven was set up at a Dilor-Labram Raman spectrometer equipped with a confocal microscope, Olympus BX40, and a He–Ne laser (632.8 nm, 7 mW) as excitation source. All Raman spectra were recorded in vertical–vertical polarization and the resolution was set to  $\sim 2$   $\text{cm}^{-1}$ . Measurements were made at 23, 40, 60, 80, and 100 °C with time given ( $\sim 15$  min) between temperature steps to allow equilibration of the samples. Additional Raman measurements on salt-free EC/PC/polymer systems for comparison purposes were made along the same route.

## Results

The calculations were mainly performed to obtain properties directly comparable to experiments. Thus additional information such as resulting geometries, charge transfer effects, and spectral properties other than obtained shifts will be only briefly described below. We first present the energy-based results, then the computed spectroscopic data, and finally the experimental observations.

**Binding Energies.** To model the pure liquid electrolyte ( $\text{LiClO}_4/\text{EC}/\text{PC}$ ), properties of complexes of  $\text{Li}^+$  with up to four EC ligands were calculated. Binding energy data for all  $\text{LiEC}_x$  ( $x = 1-4$ ) complexes are found in Table 1. Blint extrapolated from his calculations on  $\text{Li}^+$  with up to three EC ligands and similar computations on acetaldehyde that a four-coordinated complex would be dominant also for EC ligands.<sup>5</sup> Later, Klassen *et al.* computed  $\Delta H$  for complexes with up to six EC ligands and found endothermal heats of formation for larger complexes than  $\text{Li}(\text{EC})_4^+$ .<sup>6</sup> Those latter findings are in contradiction with recent higher levels of calculations by Wang *et al.*, observing exothermal formation reactions also for  $\text{Li}(\text{EC})_5^+$ .<sup>7</sup> However, the study by Wang *et al.* also found that the Gibbs free energy supported the four coordinate complex to be the prevailing component. This is in excellent agreement with spectroscopic data as well as with data from classical MD simulations.<sup>8,9,15-17</sup> Thus Blint was essentially correct in his extrapolation. In Table 2 the stepwise energies are summarized, together with literature data. Even if the present binding energies are higher (due to computational restrictions), they show a consistent trend. The additional single-point calculations improve the present values (Table 1).

The  $\text{ClO}_4^-$  anion, highly dissociative, was not regarded in the present computational study. Each EC ligand started in  $C_2$  symmetry, a slightly skewed ring, but no symmetry was imposed

**TABLE 1: Lithium Ion Binding Energies,  $\Delta E_{\text{bind}}$ , at HF/6-31G\* (B3LYP/6-311++G\*\*//HF/6-31G\*)**

polymer	polymer coord (y)	EC coord (x)				
		0	1	2	3	4
PAN	0		−242 (−231)	−440	−580	−681 (−625)
	1	−194 (−197)	−405	−554	−662 (−619)	
	2	−285	−468	−595 (−559)		
	3	−354	−516 (−491)			
PMMA	1	−222 (−214)	−422	−562	−660 (−608)	
	2	−387	−542	−644 (−592)		
	3	−467	−596 (−547)			

**TABLE 2: Stepwise Formation Energies for  $[\text{Li}(\text{EC})_x]^+$  [kJ mol<sup>−1</sup>]**

reaction	$\Delta \Delta E_{\text{bind}}$	$\Delta \Delta E[7]$	$\Delta G[7]$	$\Delta H[6]$	$\Delta \Delta E[5]$
$\text{Li}^+ + \text{EC} \rightarrow [\text{Li}(\text{EC})_1]^+$	−242	−206	−188	−248	−218
$[\text{Li}(\text{EC})_1]^+ + \text{EC} \rightarrow [\text{Li}(\text{EC})_2]^+$	−198	−158	−129	−190	−172
$[\text{Li}(\text{EC})_2]^+ + \text{EC} \rightarrow [\text{Li}(\text{EC})_3]^+$	−140	−99	−53	−112	−97
$[\text{Li}(\text{EC})_3]^+ + \text{EC} \rightarrow [\text{Li}(\text{EC})_4]^+$	−101	−55	−25	−62	
$[\text{Li}(\text{EC})_4]^+ + \text{EC} \rightarrow [\text{Li}(\text{EC})_5]^+$		−43	+38	+8	

in the geometry optimizations of the complexes. The largest obtained complex is approximately a tetrahedron ( $\sim S_4$  symmetry) with the lithium ion at the center. For  $x = 1$  the lithium ion has a significant effect on the charge distribution and intramolecular distances within the EC ligand, but as the coordination number (CN) for  $\text{Li}^+$  increases, these effects become less pronounced and almost converge back toward the values for pure EC (for CN = 4). The  $\text{Li}^+$  to carbonyl oxygen atom average distance increases from 1.76 to 1.96 Å. The structures agree well with those reported in earlier studies.<sup>5–9</sup>

For the PAN complexes, pure and mixed with EC, the binding energy values are given in Table 1. The nitrile group has different characteristics than the carbonyl group and thus the binding to  $\text{Li}^+$  is also different. The  $x = 0$ ;  $y = 1$  complex has the shortest Li–N distance: 1.93 Å. Oligomers up to trimers could successfully be fitted around the lithium ion; however, attempts to use tetramers, or even longer oligomers, resulted in detachment of coordination sites. The highest CN possible was four using this approach. The most stable complex obtained was  $[\text{Li}(\text{EC})_3(\text{PAN})_1]^+$  (Figure 1); however, it is less stable than  $[\text{Li}(\text{EC})_4]^+$ .

The PMMA ligands, finally, do each have two possibilities of lithium ion coordination: either by the carbonyl group or by the ether oxygen atom. A control calculation showed the large preference for the carbonyl site (−222 vs −147 kJ mol<sup>−1</sup> (HF/6-31G\*)), and thus all complexes were made with the carbonyl group as the preferred lithium ion coordination site. The EC and PMMA coordinating groups show essentially the same distances (Li–O<sub>carb</sub>) for the monoligand complexes, but EC is coordinated somewhat more strongly. Similar to PAN, no complexes with longer oligomers than trimers were obtained and the highest CN was four. All binding energies are given in Table 1, and the most stable complex was  $[\text{Li}(\text{EC})_3(\text{PMMA})_1]^+$  (Figure 2); however, it is less stable than both the corresponding PAN complex and the  $[\text{Li}(\text{EC})_4]^+$  complex.

**Computed Vibrational Frequencies.** In the gel systems the EC (and PC) solvent is the major lithium ion coordinating component and thus we expect the shifts computed for a  $[\text{Li}(\text{EC})_4]^+$  complex, compared to the frequencies obtained for a unperturbed EC molecule, to be directly observable, while all other shifts obtained computationally should be more difficult to detect. For the pure EC complexes ( $y = 0$ ) we focus on three regions: the ring bending mode found at 709 cm<sup>−1</sup>, the ring breathing mode at 900 cm<sup>−1</sup>, and the carbonyl stretch,  $\nu(\text{C}=\text{O})$ , at 1893 cm<sup>−1</sup>. The frequency for the stretch is clearly much too high, but this is expected due to the harmonic approximation

and the scale factor construction. For the mono EC complex with  $\text{Li}^+$  the computed shifts are large, +54, +6, and −134 cm<sup>−1</sup>, respectively, but for the more likely  $[\text{Li}(\text{EC})_4]^+$  complex the large shifts become on average more moderate, +12, +10, and −72 cm<sup>−1</sup>. The ring breathing mode seems essentially unaffected by the CN for  $\text{Li}^+$  and is not strongly shifted. Thus, the shift of this mode cannot be used for interpreting the prevailing CN for  $\text{Li}^+$ . However, we are primarily interested in obtaining correct directions of the shifts, while the absolute sizes of the shifts are of less importance for our characterization purposes.

For the PAN systems we simply look for shifts in the  $\nu(\text{C}\equiv\text{N})$  region (computed frequency  $\sim 2350$  cm<sup>−1</sup>): for  $[\text{Li}(\text{PAN})_1]^+$  there is a downshift of about 20 wavenumbers, but for the most stable mixed PAN complex  $[\text{Li}(\text{EC})_3(\text{PAN})_1]^+$  the shift is in the opposite direction ( $\sim +7$  cm<sup>−1</sup>).

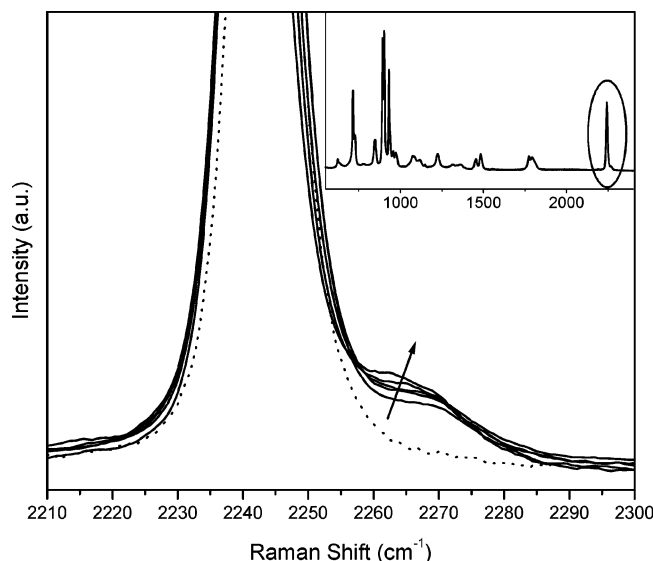
Finally, shifts for PMMA are expected, as for EC, primarily in the carbonyl stretch band,  $\nu(\text{C}=\text{O})$ , for pure PMMA the frequency was computed to 1820 cm<sup>−1</sup>. This band is calculated to be downshifted  $\sim 100$  cm<sup>−1</sup> in the most stable PMMA complex. Lithium ion induced shifts in almost all PMMA bands are found from the calculations on  $[\text{Li}(\text{PMMA})_1]^+$ .

**Experimental Vibrational Frequencies.** Many of the experimental results reported here have been observed before by others and we will therefore be brief in the description of the observations. For more thorough studies, such as derivations of assignments etc., we refer to refs 6 and 15–19. First we present results obtained at room temperature and then the spectra obtained at elevated temperatures.

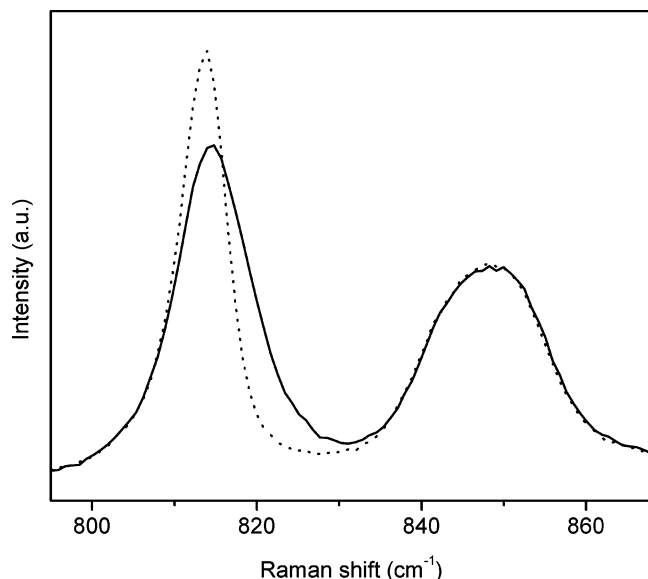
For the spectra of the mixed solvent blend (EC/PC) new peaks arise upon salt addition. Those due to the anion are not of prime interest here, however, the high-frequency weak shoulder for the symmetric  $\text{ClO}_4^-$  A<sub>1</sub> stretching mode (932 to 937 cm<sup>−1</sup>) is used to detect ion pairing.<sup>20</sup> The pure ring bending mode of EC/PC (the two different contributions cannot be resolved) is found at  $\sim 717$  cm<sup>−1</sup> and is shifted to  $\sim 729$  cm<sup>−1</sup> for the electrolyte. Similarly the EC breathing mode at 894 cm<sup>−1</sup> is shifted to 904 cm<sup>−1</sup>. For the much less intense PC breathing mode at 849 cm<sup>−1</sup>, we cannot locate a shifted peak, probably due to a too low intensity or overlapping peaks. In the carbonyl stretch region 1750–1800 cm<sup>−1</sup> Fermi resonance (FR) affects the EC mode,<sup>21</sup> and we find two peaks due to EC and one due to PC in the blend. For a thorough analysis of the FR effects we refer to ref 21, however, made for a different choice of salt and concentration. In the present study salt addition changes the relative intensities of the two EC peaks, but no observable shifts are obtained. We will thus in the analysis preferably use the ring EC modes.

For the PAN gel electrolytes not many changes compared to salt-free EC/PC/PAN gels are obtained. The main change is found in the nitrile stretch region, where a lithium ion induced weak shoulder with higher frequency is obtained (2243 to 2268 cm<sup>−1</sup>) (Figure 3). The PAN polymer itself has relatively few strong features in the spectra.





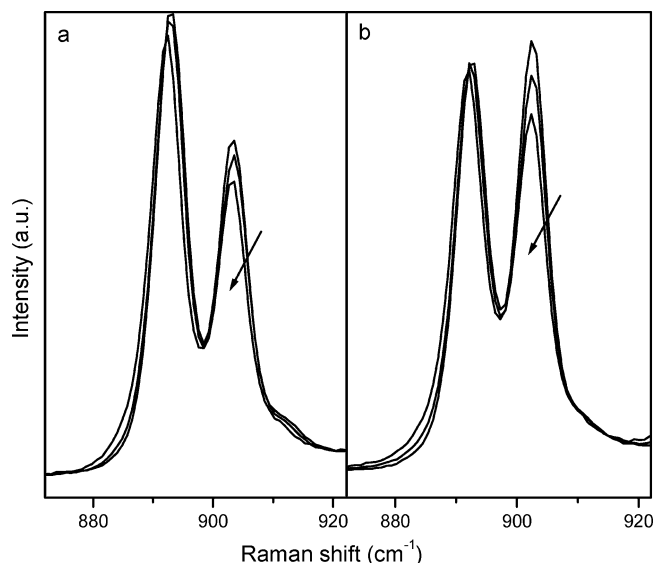
**Figure 3.** FT Raman spectra of the PAN gels in the  $\nu(\text{C}\equiv\text{N})$  region. The insert shows the overall location and band strength. The dotted line shows the salt-free PAN gel at room temperature. The arrow indicates change with increased temperature.



**Figure 4.** Room-temperature FT Raman spectra of the PMMA gels in the  $\text{O}=\text{C}-\text{O}$  bending region. The dotted line shows the salt-free gel.

The PMMA gels are richer in information than the PAN gels, but upon addition of salt no marked influence on the PMMA peaks is seen. Kim and Oh<sup>18</sup> reported a shifted  $\nu(\text{C}=\text{O})$  peak on the low-frequency side, observed at  $1702\text{ cm}^{-1}$ . No such effect was obtained here, but their PMMA concentration was much stronger. What may be a sign of  $\text{Li}^+$ -PMMA interaction is a small effect on the  $815\text{-cm}^{-1}$   $\text{O}=\text{C}-\text{O}$  bending band, a high-frequency shoulder compared to the salt-free EC/PC/PMMA sample appears (Figure 4). Unfortunately, Kim and Oh do not report this region in their study. No other PMMA bands undergo changes of the same magnitude. However, there are some intensity differences for the pure EC bands and the lithium ion induced shifted EC bands as compared to the pure liquid electrolyte.

For all samples the effects of raising the temperature was studied. As the solvation of salts in polymeric systems often is sensitive to entropy effects, notable changes in the Raman spectra might be expected. Nicotera *et al.* studied in depth the



**Figure 5.** FT Raman spectra of the EC ring breathing mode at 23, 60, and  $100\text{ }^{\circ}\text{C}$  for (a) the PMMA gel and (b) the PAN gel. The arrows indicate changes with increased temperature.

thermoreversibility of a  $\text{LiClO}_4/\text{EC}/\text{PAN}$  gel system with emphasis on mechanical properties but also presented Raman spectra.<sup>22</sup> Their results will therefore be compared to ours below. In general the peaks are slightly widened and shifted toward lower frequencies due to softening of the materials.

In the liquid electrolyte the EC shoulder at  $904\text{ cm}^{-1}$  decreases in intensity compared to the main EC breathing mode peak upon heating. At the same time the lithium ion affected  $\text{ClO}_4^-$  mode at  $937\text{ cm}^{-1}$  increases. Thus the ion pair formation increases with increasing temperature. For the EC ring breathing mode the PMMA gels behave similarly to the liquid electrolyte, however, with a lower amount of  $\text{Li}^+$ -affected EC molecules already at room temperature, while the PAN gels have a more pronounced temperature behavior (Figure 5). PAN interacts by itself with EC already at room temperature,<sup>19</sup> resulting in a decreased relative concentration of “pure” EC (Figure 5) and a virtual higher salt concentration and thereby amount of ion pairs (not shown). However, the ratio of ion pairs to free anions increases slower for the PAN gels than for both the pure electrolyte and the PMMA gels upon heating. This is most probably due to the occurrence of increasing  $\text{Li}^+$ -PAN interactions with temperature (Figure 3), even if the statistics in this region were bad, which may partly be due to slow kinetics. PMMA behaves almost identically to the liquid electrolyte with respect to ion pair formation. In the work by Nicotera *et al.* the ring breathing mode of EC, the  $\text{ClO}_4^-$  mode at  $934\text{ cm}^{-1}$ , and the  $\text{C}-\text{N}$  stretching region were studied.<sup>22</sup> In contrast to our results, they note (for an  $\text{O}/\text{Li}$  ratio = 10) increasing satellite bands to the EC modes when the temperature is increased. In agreement with our present data they observe an increased tendency for ion pair formation via the shoulder at  $939\text{ cm}^{-1}$  and increased interaction with the nitrile group via observing the shoulder at  $2267\text{ cm}^{-1}$  with temperature. Thus, in their study, Raman bands arising from all possible  $\text{Li}^+$  perturbed species (anions, solvent, and polymer) all increase with temperature. The explanation given involves increased solvation (coordination) numbers for  $\text{Li}^+$  with increased temperature but yet basically supports our notion of increased  $\text{Li}^+$ -nitrile group interactions. An increased coordination number is not supported in the literature.<sup>5-9,15-17</sup> However, using our present data, there is no need for any increases in the coordination number for  $\text{Li}^+$ .

## Discussion

The many interactions present in the gels, as outlined above, make a single, unambiguous interpretation cumbersome. Focus is here, however, only on the strongest interactions present and especially on the different possibilities for solvent and polymer cation coordination.

The possibility of mixed solvent and polymer coordination in the gel systems means that simple relationships to individual coordination properties of the components do not necessarily hold. As an example, with only pure EC ( $x = 1$ ;  $y = 0$ ) or only the polymers as ligands ( $x = 0$ ;  $y = 1$ ), the interaction strengths obtained from the binding energies follow  $\text{EC} > \text{PMMA} > \text{PAN}$ , while experimentally PAN gels are known to be more active than PMMA gels.<sup>19</sup> Below, the necessity of using mixed complexes not only for a correct treatment of the energetics involved but also for a proper modeling of experimental spectra will be emphasized.

The computed and theoretical shifts due to lithium ion coordination probe the interactions and clarify, together with the binding energies, which of the computed complexes that should be regarded as likely to occur. In the liquid electrolyte we focus on two shifts, the EC ring bending and ring breathing, which are shifted 12 and 10  $\text{cm}^{-1}$ , respectively. For the  $[\text{Li}(\text{EC})_4]^+$  complex identical shifts, compared to pure EC, are obtained (12 and 10  $\text{cm}^{-1}$ ). As this complex is expected to largely dominate as the lithium ion containing species in the solution, the observation as such is trivial, but that the shifts are calculated so exactly is encouraging, partly though fortuitous cancellation of errors.

Since no lithium ion induced changes are seen in the PMMA gels compared to the liquid electrolytes, we regard the mixed complexes of PMMA to be of less importance. For the PAN gels we note the interaction with the lithium ion in the  $\nu(\text{C}\equiv\text{N})$  region, and the most stable complex involving PAN,  $[\text{Li}(\text{EC})_3(\text{PAN})_1]^+$ , should therefore be regarded as a possible structure present in the PAN gels. For this complex there is a small shift to higher frequency for the nitrile stretch (+7  $\text{cm}^{-1}$ , experimentally +25  $\text{cm}^{-1}$ ).

Experimentally there also seems to be differences in the temperature behavior of the PMMA and PAN gels. For the PMMA gels a temperature increase does not inflict any serious changes as compared to the liquid electrolytes, the PMMA matrix is only a bystander. As for the liquid electrolyte a temperature increase leads to a decrease in the  $\text{Li}^+$  affected EC modes and to an increase in the amount of ion pairs, as detected at 937  $\text{cm}^{-1}$ . PMMA does not seem to even influence the amount of temperature behavior of the contained electrolyte.

For the PAN gels the situation differs; when the temperature is raised the decrease in the  $\text{Li}^+$  affected EC modes is pronounced, but no significant increase in the amount of ion pairs can be detected. Instead the lithium ion affected nitrile stretch increases in intensity. As the temperature is lowered this intensity decreases again, and the EC modes are strongly affected again, thus being a reversible process.

The reason for PAN being a stronger ligand than PMMA in the mixed complexes, while being a weaker ligand for  $x = 0$ ;  $y = 1$ , is probably due to steric hindrances. The PAN ligand has a narrow penetration edge and thus does not disturb an EC coordination shell as much as the PMMA monomer does. In addition, the equilibrium distance for  $\text{Li}^+$  to the nitrile nitrogen atom is longer than the corresponding  $\text{Li}^+$  to the carbonyl oxygen atom distance.

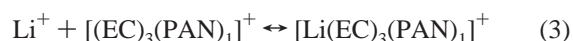
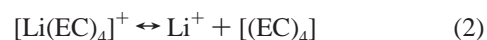
In contrast, for all the complexes using only oligomers of PAN or PMMA ( $x = 0$ ), the latter are much preferred as ligands

already as monomers, and as the length of the PMMA oligomer increases the binding energy increases by 74 (CN 1  $\Rightarrow$  2) and 21% (CN 2  $\Rightarrow$  3), respectively. This is reminiscent of pure EC coordination (82 and 32%). For PAN, however, the increases are only 47 and 24%. This is probably due to the larger flexibility of the PMMA oligomers, where four bonds between each of the coordinating groups participate in adjusting to obtain the optimal coordination geometry to the lithium ion. For the less flexible PAN backbone, only two backbone bonds are useful this way.

By using the higher level single-point calculations and the three most likely complexes we will try to explain some of the experimental observations from the thermodynamics involved. For PAN we will look at the reaction



which simply can be treated as two virtual steps each corresponding to a binding energy in Table 1



Using  $\Delta E = \Delta U_{0\text{K}}$  and  $K_{\text{T}} = e(-\Delta U_{0\text{K}}/RT)$ , it is possible to calculate the driving force at 0 K and the equilibrium constant for reaction 1 at the experimental turning point temperatures (296 and 373 K). The driving force is +6  $\text{kJ mol}^{-1}$  (−619 + 625) and the  $K_{\text{T}}$  values become 0.087 and 0.14, respectively. Thus the energy difference between the complexes is large enough to make the pure solvent (EC)  $\text{Li}^+$  coordination dominant but also small enough to allow a significant portion of the lithium ions to be transferred to the mixed EC/PAN complex  $[\text{Li}(\text{EC})_3(\text{PAN})_1]^+$  upon heating. The large energy difference between the  $[\text{Li}(\text{EC})_3(\text{PAN})_1]^+$  and  $[\text{Li}(\text{EC})_2(\text{PAN})_2]^+$  complexes makes sequential nitrile group coordination considerably less likely. A still open question is that of coordination of polymer fragments in other ways than sequential, *i.e.*, from different polymer chains. However, the gel materials as such do not make such coordination situations probable; the mesh size, as recently measured by small-angle neutron scattering (SANS), gives a polymer–polymer distance of 9.2 Å for a  $\text{LiClO}_4\text{:EC:PC:PMMA}$  (5:48:19:28) gel.<sup>23</sup>

A similar calculation for PMMA, using the  $[\text{Li}(\text{EC})_3(\text{PMMA})_1]^+$  complex, results in a larger energy difference, +17  $\text{kJ mol}^{-1}$ , enough to heavily favor pure EC coordination both at 296 K ( $K = 0.001$ ) and at 373 K ( $K = 0.004$ ). Thus no detectable changes in the temperature interval of our experiments are expected.

For these gels the stability seems partly due to the mixed solvent and polymer coordination of cations (dynamic cation cross-links). We note that the PAN gels, where the polymer is found to interact more strongly with the cation than in the PMMA based gels, often are more mechanically stable. However, the PAN gels are also less conductive than the PMMA based, which may be due to a slower exchange rate of lithium ions. We therefore propose here that these two properties are difficult to improve simultaneously using the prevailing gel approach.

## Conclusions

Although PMMA and EC both should attract lithium ions using their carbonyl groups, the latter species are strongly preferred as ligands. Results based on using only one of the

components, polymer or solvent, as the coordinating species in the modeling does not ensure a correct picture of the complex coordination in the gel materials, for this the present mixed solvent and polymer complexes are needed. Both experimental and calculated data show the PAN gels to be more active in the cation coordination. The observed temperature behavior of both PMMA and PAN gels is supported by the thermodynamic results based on the binding energies. In the PMMA gels, as for the liquid electrolyte, the  $[\text{Li}(\text{EC})_4]^+$  complex dominates as the lithium ion containing species. In PAN gels the  $[\text{Li}(\text{EC})_4]^+$  complex also dominates, but the  $[\text{Li}(\text{EC})_3(\text{PAN})_1]^+$  complex is of importance, especially at elevated temperatures. The dynamic cross-linking offered by the mixed solvent and polymer cation complexes seems to relate to both the advantageous mechanical properties of the PAN gels and to the ionic conductivity.

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## References and Notes

- (1) Ratner, M. A.; Johansson, P.; Shriver, D. F. *MRS Bull.* **2000**, *3*, 31.
- (2) Svanberg, C.; Adebahr, J.; Ericson, H.; Börjesson, L.; Torell, L. M.; Scrosati, B. *J. Chem. Phys.* **1999**, *111*, 11216.
- (3) Capiglia, C.; Saito, Y.; Kataoka, H.; Kodama, T.; Quartarone, E.; Mustarelli, P. *Solid State Ionics* **2000**, *131*, 291.
- (4) Adebahr, J.; Forsyth, M.; Gavelin, P.; Jacobsson, P.; Orädd, G. *J. Phys. Chem. B* **2002**, *106*, 12119.
- (5) Blint, R. J. *J. Electrochem. Soc.* **1995**, *142*, 696.
- (6) Klassen, B.; Aroca, R.; Nazri, M.; Nazri, G. A. *J. Phys. Chem. B* **1998**, *102*, 4795.
- (7) Wang, Y.; Nakamura, S.; Ue, M.; Balbuena, P. B. *J. Am. Chem. Soc.* **2001**, *123*, 11708.
- (8) Soetens, J.-C.; Millot, C.; Maigret, B. *J. Phys. Chem. A* **1998**, *102*, 1055.
- (9) Li, T.; Balbuena, P. B. *J. Electrochem. Soc.* **1999**, *146*, 3613.
- (10) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.
- (11) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (12) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (13) Titan version 1.0, Wavefunction, Inc., Schrödinger, Inc., 1999.
- (14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (15) Hyodo, S.-A.; Okabayashi, K. *Electrochim. Acta* **1989**, *34*, 1551.
- (16) Hyodo, S.-A.; Okabayashi, K. *Electrochim. Acta* **1989**, *34*, 1557.
- (17) Deng, Z.; Irish, D. E. *Faraday Trans.* **1992**, *88*, 2891.
- (18) Kim, C. S.; Oh, S. M. *Electrochim. Acta* **2000**, *45*, 2101.
- (19) Ostrovskii, D.; Brodin, A.; Torell, L. M.; Appetecchi, G. B.; Scrosati, B. *J. Chem. Phys.* **1998**, *109*, 7618.
- (20) Pereygin, I. S.; Mikhailov, G. P. *Zh. Prikl. Spektrosk.* **1988**, *49*, 65.
- (21) Ostrovskii, D.; Edvardsson, M.; Jacobsson, P. *J. Raman Spectrosc.* **2003**, *34*, 40.
- (22) Nicotera, I.; Oliviero, C.; Ranieri, G.; Spadafora, A.; Castriota, M.; Cazzanelli, E. *J. Chem. Phys.* **2002**, *117*, 7373.
- (23) Svanberg, C.; Pyckhout-Hintzen, W.; Börjesson, L., unpublished results.