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Ion and Solvent Dynamics in Gel Electrolytes Based on Ethylene Oxide Grafted Acrylate Polymers

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Multinuclear pulsed field gradient NMR measurements and rheological viscosity measurements were performed on three series of polymer gel electrolytes. The gels were based on a lithium salt electrolyte swollen into a copolymer matrix comprising an acrylate backbone and ethylene oxide side chains. In each series the side chains differed in length and number, but the acrylate-to-ethylene oxide ratio was kept constant. It was found that the self-diffusion coefficient of the cations was much lower than that of the anions, and that it decreased rapidly when the side chains got longer. In contrast, the self-diffusion coefficient of the anions was found to be independent of chain length. In the gel electrolytes, the diffusion coefficients of the solvent molecules are relatively constant despite an increased viscosity with increasing length of the side chains. However, in salt-free gels made for comparison, the diffusion coefficients of the solvent molecules decreased with increasing length of the side chains, which is consistent with an increased viscosity.

Introduction

In the development of new high-energy-density secondary lithium batteries, the electrolyte is of crucial importance. In particular, a useful electrolyte must be able to act as a mechanical separator, an electronic insulator, and a good ionic conductor. Solid polymer electrolytes (SPE) are one class of electrolytes with potential applicability in many electrochemical devices; however, the classical SPE based on a lithium salt dissolved in poly(ethylene oxide) (PEO), has a rather low ionic conductivity at ambient temperature (10^{-5} S/cm) due to a low ion mobility in the PEO matrix. To improve the ionic conductivity, gel-based electrolytes have come into focus as potentially useful electrolytes for lithium batteries. In these electrolytes, the polymer matrix provides the system with mechanical strength, while the relatively large amount of solvent allows rapid transport of the ions and hence gives conductivities of the order of 10^{-3} S cm^{-1}. Typical examples of polymers used as matrixes for this type of electrolyte are poly(methyl methacrylate), PMMA, polyacrylonitrile, PAN, and polyvinyldifluoride, PVdF. Gel electrolytes based on these polymers have been widely studied by experimental techniques such as Raman, a.c. impedance, and NMR spectroscopies,[1–6] etc. The liquid components of the gel electrolytes are most often a mixture of two or more solvents, e.g., ethylene carbonate (EC) and propylene carbonate (PC), γ-butyrolactone (gBL), or dimethyl carbonate (DMC). The lithium salt may be LiPF$_6$, LiClO$_4$, or LiCF$_3$SO$_3$. The challenge has been, and still is, to optimize all components in order to achieve the best combination of materials for the application. For example, the gel should be stable at the gel–electrode interphases, and the matrix should be almost inert with respect to ionic entities although still providing a good solvent retention. Earlier studies of PMMA-based electrolytes have shown, however, that too weak interaction between the polymer matrix and the other components in the gel electrolyte might lead to phase separation,[7] which can cause leakage problems in an application.

In the present work we have studied the properties of gel electrolytes based on a copolymer with ethylene oxide chains grafted on an acrylate backbone. This combination of an inert acrylate backbone with active ethylene oxide side chains has been synthesized in order to obtain a polymer matrix that has strong enough interactions with the other constituents to prevent phase separation, but still weak enough interactions to maintain the relatively high ionic transport characteristic of gel electrolytes. Raman studies of these gel electrolytes, based on polymers with different length of the EO side chains (1, 2, 5, 9, and 45 EO units), showed that the preferred interaction is altered from being mainly Li–solvent for short side chains, toward being predominantly Li–polymer with increasing length of the side chains.[8,9] Therefore, by careful control of the length of the side chain it should be possible to design a polymer matrix that optimizes the properties of the system. The benefit of the increased interaction on solvent retention, however, may have a negative impact on lithium ion mobility (and hence lithium

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ion conductivity) because this species is primarily responsible for the enhanced interactions through its coordination both to the solvent molecules and to the ether oxygens in the side chains. In this study we have therefore investigated the diffusion coefficient and the transport number of the cation, anion, and solvent species in the gel electrolytes as a function of length of the polymer side chains using multinuclear pulsed field gradient NMR spectroscopy. In addition, the macroscopic viscosity was also determined for all systems in order to correlate changes in ionic and molecular diffusivity with macroscopic changes in system mobility. This allowed the effects originating from changes in viscosity to be separated from those resulting from changes in interactions within the different gels.

Experimental Section

Materials. Three series of gel systems were made: one salt-free, one with lithium hexafluorophosphate, and one with lithium perchlorate. The electrolyte solutions used for the salted gels consists of 1 M $LiPF_6$ or 1 M $LiClO_4$ dissolved in a 2:1 (mol/mol) mixture of ethylene carbonate (EC)/γ-butyrolactone (gBL). The copolymers used as gel matrixes in this investigation consisted of a poly(methyl methacrylate-*co-tert*-butylacrylate) backbone carrying ethylene oxide side chains with different length (1, 2, 5, and 9 EO units per side chain). The monomer feed of methyl methacrylate was varied to keep the total content of EO units constant in the polymer ($\sim$25 wt %). The preparation of the copolymers is described in detail in a recent study.[9] All the $(EO)_n$ side chains were CH_3-capped. The polymer was mixed with the electrolyte solution in a 50 wt % ratio, and was thereafter kept at room temperature for 48 h in order for the polymer to be homogeneously dissolved/gelled into the solvent mixture. In the salt-free and the $LiClO_4$-containing series, 4 gels were made, based on the polymers with 1, 2, 5, and 9 EO units per side chain, while in the series of $LiPF_6$, 3 gels were made based on the polymers with 1, 2, and 5 EO units per side chain. The salted samples all correspond to a Li:EO ratio of 1:6, where EO corresponds to the ethylene oxide units in the polymer. At ambient conditions this mixture is not a mechanically stable gel, rather a high-viscosity liquid. All samples were prepared in a dry argon atmosphere in order to prevent contamination. The samples were sealed under dry argon in 5 mm diameter liquid NMR tubes prior to the measurements. In addition, NMR tubes containing pure solvents and electrolytes were prepared for comparison.

Pfg-NMR. ^{19}F, ^7Li, and ^1H pfg-NMR diffusion measurements were performed on a Varian CMX Infinity spectrometer, operating at proton frequency 400 MHz, using the stimulated spin−echo (STE) pulse sequence.[10] The spectrometer was equipped with a double resonance diffusion probe capable of producing linear gradients up to 3.4 T/m. Pulse lengths of 90° were 12.8 μs (^1H), 13.5 μs (^{19}F), and 15.0 μs (^7Li), respectively, and the waiting time between experiments were typically 3−5 T_1. The temperature was 25 °C and controlled to ±0.5 °C by means of a heated air stream passing the sample. Typically, 20 experiments were performed for each diffusion measurement, in which the gradient strength was varied while keeping all the other parameters constant. The self-diffusion coefficient was then determined from the peak-amplitude attenuation according to the Stejskal-Tanner diffusion equation.[11] Diffusion coefficients were determined in this way for three different diffusion times, Δ = 15, 60, and 240 ms, to exclude anomalous diffusion.[12] No systematic trend was found for the self-diffusion coefficients with Δ, and effective diffusion was therefore assumed. The reported diffusion data are mean values from the
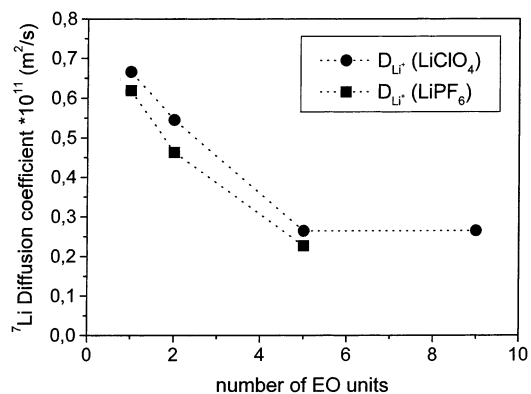

Figure 1. The Li^+ diffusion coefficients as a function of length of the grafted side chains, measured at room temperature. Circles denote the $LiClO_4$-containing samples, and squares denote the $LiPF_6$-containing samples.

measurements with the three different Δ. Calibration has been made on water, and substances with lower diffusion coefficients has been tested in the same way as described by Holz et al.[13] It should be noted that the transport numbers determined with pfg NMR techniques are obtained under equilibrium conditions in the absence of an electrical field. For a recent discussion of electrophoretic NMR on similar systems, we refer to Zawodzinski et al.[14,15]

Viscosity. A Stress Tech rheometer (Rheological Instruments AB, Lund, Sweden) was used for the viscosity measurements. A parallel plate system with a diameter of 15 mm was used, and the gap between the plates was set to 1 mm. The viscosity was measured at 25 °C as a function of shear rate for all samples.

Results

Figure 1 shows the Li^+ self-diffusion coefficients as determined from ^7Li pfg-NMR measurements. In the case of both $LiClO_4$- and $LiPF_6$-containing systems, the diffusion coefficient decreases with increasing length of the side chains, n (where n is the number of EO units), up to 5 EO units. In the case of $LiClO_4$, the lithium ion diffusion then seems to plateau for $n >$ 5. These sets of data indicate that an interaction between the lithium ion and the ether side chains is favored for increasing values of n, consistent with previous Raman data.[8,9] On the other hand, the diffusion coefficient of the anion, as measured by ^{19}F pfg-NMR, does not appear to be affected by changes in the polymer structure. These data therefore suggest a lack in significant interaction between the anion and the polyether side groups. Figure 2 presents these data as a function of length of the side chains for the $LiPF_6$-containing samples.

Figure 3 shows the ^1H diffusion coefficients for the two solvents, EC and gBL, as a function of n. The diffusion coefficients of both solvents are independent of the nature of the salt for a given length of ether chains on the polymer backbone. The mobility of the gBL species is slightly lower than of the EC species, in all samples. For the salt-free gels, the diffusion coefficient decreases with increasing length of the side chains. In contrast, when a lithium salt is present, the increasing length of EO units results in a slight enhancement of the solvent diffusion coefficient for both gBL and EC. Whereas pfg-NMR measurements presented thus far probe the molecular motions of the individual species, the bulk dynamics of these materials was probed using viscosity measurements. The results are shown in Figure 4 for both salt-free and $LiClO_4$-containing gels as a function of n. These data represent the viscosity values at room temperature (298 K). The viscosity is

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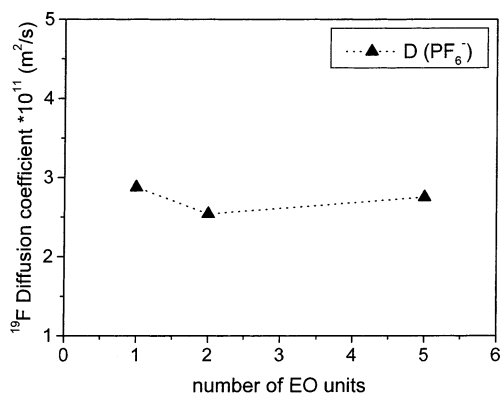*J. Phys. Chem. B, Vol. 106, No. 47, 2002* **12121**

Figure 2. The PF_6^- diffusion coefficients as a function of the length of the side chains, measured at room temperature for the LiPF$_6$-containing samples.
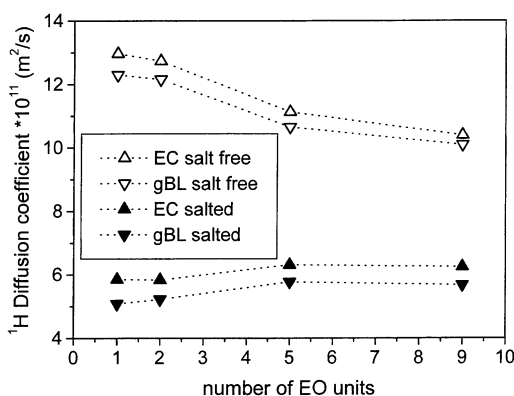

Figure 3. The ^1H diffusion coefficients measured at room temperature for the two solvents, EC and gBL, for all three series.
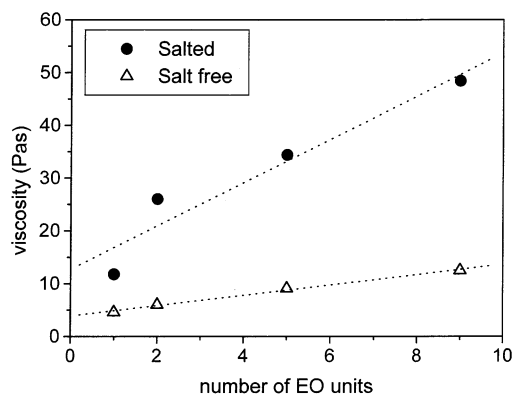

Figure 4. The viscosity of the gels as a function of length of the side chains, for both the salt-free and salted series.

observed to increase from 12Pas to 45Pas when salt is present, whereas only a slight increase in viscosity is observed with increasing side chain length in the absence of salt.

For comparison, the NMR data of the pure solvents and electrolytes are given in Table 1. The diffusion coefficients of both the cation and the solvent molecules are found to be independent of the nature of the anion (PF_6^- and ClO_4^-). It can also be seen that the diffusion coefficient of the lithium ion species is about half that of the anions, while the anions and the solvent are diffusing at approximately the same rate. This is consistent with the work of Capiglia et al. who showed that the Li transport number in an EC/DMC solution with LiPF$_6$, LiBF$_4$, or LiN(CF$_2$SO$_3$)$_2$ is between 0.37 and 0.49 depending on the salt concentration as well as the ratio between the two solvents.[16] Table 2 presents transport numbers, τ^+ and τ^-, for

TABLE 1: The Self-Diffusion Coefficients for the Different Species in the Three Liquid Electrolytes[a]

	$D_{Li^+} \times (10^{10})$ [m^2/s]	$D_{PF_6^-} \times (10^{10})$ [m^2/s]	$D_{EC} \times (10^{10})$ [m^2/s]	$D_{gBL} \times (10^{10})$ [m^2/s]
EC/gBL			6.57 ± 0.2	6.48 ± 0.2
EC/gBL/LiClO$_4$	1.39 ± 0.02		3.16 ± 0.04	2.80 ± 0.08
EC/gBL/LiPF$_6$	1.41 ± 0.02	2.67 ± 0.002	3.2 ± 0.07	2.95 ± 0.012

[a]The errors are the standard deviation from the three measurements with different Δ.

TABLE 2: Transport Number for the Liquid Electrolyte and the 3 First Gels Containing LiPF$_6$.

	EC/gBL/LiPF$_6$	Gel 1 (1 EO)	Gel 2 (2 EO)	Gel 3 (5 EO)
τ^+	0.35	0.18	0.15	0.08
τ^-	0.65	0.82	0.85	0.92

the cation and the anion as determined from the diffusion constants in a binary electrolyte approach:

$$\tau^+ = \frac{D_{Li}^+}{D_{Li}^+ + D_{PF6}^-} \qquad (1)$$

It can be seen that the transport number (as defined above) of the cation is rapidly decreasing with increasing length of the side chains.

Discussion

The lithium diffusion coefficients (Figure 1) for the two series with different salts follow the same trend, although the values are slightly lower for the gels with LiPF$_6$. The finding that the lithium ion mobility is the same for the gels with $n = 5$ and $n = 9$, respectively, indicates that the average mobility of the lithium ions is independent of chain length when a critical value of n is reached, in this case when $n \approx 5$. It should be stressed that the total number of ethylene oxide units are the same in all polymers, i.e., increasing *length* of the side chains results in a decreasing *number* of side chains in the polymer matrix. Furthermore, the ratio of lithium ions to ethylene oxide units is the same in all gels, Li:EO = 1:6, as described above. This means that in the system with $n = 5$, nearly all side chains are occupied by a lithium ion, although it is possible that each side chain is involved in coordinating more than one lithium ion and that the lithium ion coordination sphere comprises oxygens from more than one side chain, i.e., interchain ionic cross-linking as observed in polyether systems.[17,18]

The decrease in lithium ion mobility is accordingly attributed to the increased interaction between the ions and the side chains of the polymer with increasing chain length, as have been seen previously by Raman spectroscopy.[8,9] This interaction in turn also explains the increased macroscopic viscosity observed with increasing length of the side chains, Figure 4. It is, however, acknowledged that the greater distance between the side chains might slow the interchain transfer of the lithium ions, which also would contribute to an overall decrease in the lithium ion mobility. The anions, on the other hand, are not affected by the changes in the polymer matrix, Figure 2. This indicates that the anions in these gels experience a similar environment independent of the polymer matrix. The lack of correlation between the anion diffusivity and the bulk viscosity is also consistent with a lack of significant anion−cation and/or anion−polymer interaction. In other words, the anion mobility is decoupled from the polymer matrix motions, whereas the lithium cation appears to become increasingly more coupled to the polyether segments with increasing n. As a consequence, the

cation transport number is seen to decrease rapidly with increasing length of side chains as would be expected for a change in preferred interaction from being mainly cation–solvent to predominantly cation–polymer.

The increase in viscosity with increasing n is generally expected to cause a reduced solvent diffusion coefficient. However, the mobility of the solvent molecules remains almost constant, or even increases for the salted gels while it decreases as a function of n for the salt-free gels. These observations suggest that the increasing viscosity with increasing n is due to interchain ionic cross-links and that the interaction between the solvent molecules and the polymer matrix is rather weak, which is consistent with what has been found in PMMA-based gels.[19] However, in the salt-free case, a small increase in viscosity, and a small decrease in the mobility of the solvent molecules with increasing n are detected, although the relative increase in viscosity is almost twice as high as the decrease in solvent mobility. This suggests that the weak interaction between the polymer matrix and the solvent molecules increases with increasing length of the side chains. On the other hand, when the lithium salt is present, the solvent is known to interact with the lithium ion and the reduction of these interactions in favor of lithium–polymer interactions with increasing n will free the solvent, which should result in a higher diffusion coefficient. There are now two competing effects that govern the solvent diffusion; the reduction in solvent–lithium interactions and the increasing viscosity due to polymer–lithium interactions. The net result is an almost invariant solvent diffusion coefficient with increasing n in the salted system.

The conductivity of these samples has been previously measured as a function of n in the case where the solvent-to-polymer ratio was 0.7:0.3.[9] It is possible to determine the level of ion–ion interactions by comparing the measured conductivity with the conductivity calculated from the diffusion coefficients of the ionic species. This is often done by calculating the Haven ratio.[20–23] The Nernst–Einstein equation can be used to calculate the ionic conductivity, σ_{calc}, from the diffusion coefficients of the cation, D_{Li^+}, and anion, $D_{PF_6^-}$

$$\sigma_{calc} = \frac{Nq^2}{kT}[D_{Li^+} + D_{PF_6^-}] \qquad (2)$$

where N is the number of ions per unit volume, and q is the charge of the ions. Since the salt concentration in the gels is about 0.5 M, σ_{calc} is found to be 10^{-2} S cm^{-1}, varying only weakly with n. This is approximately an order of magnitude higher than the measured value, even for a system where a higher solvent content is present (this would lead to significantly higher conductivities for a given salt concentration). Usually, this discrepancy between σ_{calc} and σ_{meas} would lead to the conclusion that significant cation–anion interactions or associations are present.[20–23] However, the previously reported Raman data did not indicate any ion pairing in these systems and so the discrepancy cannot be due to contact ion pairs.[8] Nevertheless, correlated motions of entities of loosely interacting ions will also contribute to pfg diffusion coefficients but not to conductivity. Additional evidence for such long-range interactions comes from the fact that the anion diffusion coefficient is significantly lower than the solvent diffusion, although it is decoupled from the cation behavior. Furthermore, since the diffusion coefficient for the anions is almost constant as a function of n in these gels and about 10 times higher than that for the cations, the calculated conductivity for all the gel samples is nearly independent of n. This is in agreement with the conductivity data discussed above, where the conductivity at

ambient temperatures is approximately the same for all samples.[9] This underlines the finding that the conductivity of these gel systems is mainly due to diffusion of the anions.

From the discussion above it can be concluded that the polymer matrix restricts the lithium-ion mobility, and this therefore becomes decoupled from the solvent diffusion. This is in contrast to gels based on PMMA, where it has previously been reported that the conductivity is closely related to the diffusive motion of the low molecular weight solvents within the gel system.[24] In solid polymer electrolytes, however, the conductivity has been shown to be strongly linked to the segmental mobility of the polymer.[25] In our case there seems to be a combination of these two processes. The solvent–lithium interaction is strong for short n, while the polymer–lithium interaction becomes predominant for larger n. It is also evident that in this system the anion is still coupled to the motions of the solvent, even if it is restricted by the low mobility of the lithium ions.

Conclusions

The ^7Li diffusion coefficient of the gels (both LiClO$_4$- and LiPF$_6$-containing systems) appears to decrease as a function of length of the side chains up to 5 EO units, and thereafter, in the case of LiClO$_4$, reach a plateau. On average, the mobility of the lithium ions therefore seems to be independent of chain length when a critical value of n is reached, in this case when $n = 5$. On the other hand, the diffusion coefficient of the anion does not appear to be significantly affected by changes in the polymer structure, suggesting a lack in significant interaction between the anion and the polyether side groups.

The self-diffusion coefficients of both solvents are independent of the nature of the salt for a given length of ether chain on the polymer backbone. In the case of the salt-free gels the diffusion coefficient decreases with increasing length of the side chains, consistent with the increase in viscosity. In contrast, when the lithium salt is present, the increasing length of EO units results in a slight enhancement of the solvent diffusion coefficient for both gBL and EC. This is attributed to the two competing effects in this system: the reduction of cation–solvent interaction in favor of lithium–polymer interaction, which will free the solvent molecules, and the increasing viscosity due to polymer–lithium interactions. The net result of these two effects is an almost constant solvent diffusion coefficient with increasing n in the salted system.

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