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Two distinct lithium diffusive species for polymer gel electrolytes containing $LiBF_4$, propylene carbonate (PC) and PVDF

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Abstract

Polymer gel electrolytes have been prepared using lithium tetrafluoroborate ($LiBF_4$), propylene carbonate (PC) and polyvinylidene fluoride (PVDF) at 20% and 30% concentration by mass. Self diffusion coefficients have been measured using pulse field gradient nuclear magnetic resonance (PFG-NMR) for the cation and anion using 7Li and ^{19}F resonant frequencies respectively. It was found that lithium ion diffusion was slow compared to the much larger fluorine anion likely resulting from a large solvation shell of the lithium. Lithium ion diffusion measurements exhibited two distinct diffusive species, whereas the fluorine ions exhibited only a single diffusive species.

Keywords: NMR, polymer gel electrolyte, lithium ion diffusion

1. Introduction

Polymer electrolytes have their origins in research carried out by Armand[1] and Wright[2] and are of particular interest for commercial use in certain battery applications. In the early research, conductivities achieved were of the order $10^{-2}mS/cm$ [1], however, since this early research conductivities with orders of magnitude higher have been attained. This was achieved at Leeds University with the addition of solvent to make polymer gel electrolytes (PGE) based on poly(N,N-dimethyl acrylamide) containing lithium salt[3]. This was followed by PGEs based on PVDF[4] which were found

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to be stable under 4V, which is needed for use in battery applications[5]. These gels are important as they offer many properties that traditional lithium ion batteries do not exhibit. These features include enhanced safety as polymer gel electrolyte batteries do not contain free liquid outside the polymer structure and therefore do not leak even if punctured. Other desirable features include, high flexibility, thin film formation and processability. Due to easy fabrication by an extrusion lamination process[6], there is no need for external casing or a polymer separator to stop electrodes shorting[7]. For these reasons PGEs have become the focus of a significant amount of research by many groups worldwide [8, 9, 10, 11, 12, 13].

In this paper we further investigate thermo-reversible gel electrolytes produced from polyvinylidene fluoride (PVDF). These are semicrystalline, as distinct from gels formed from amorphous polymers such as poly (methyl methacrylate) (PMMA)[14, 15]. The semi crystalline gels form crystalline junctions within the solution below the melting temperature. The crystalline junctions will melt again if the melting temperature is exceeded due to the absence of chemical cross-links, allowing the gels to be thermo-reversible.

The solvent needs to exhibit a high dielectric constant. Propylene carbonate (PC) has a very high dielectric constant of 61.7 at 40°C[16], and is used here. However batteries cannot be produced from PC alone as it causes a passivation layer to the anode, resulting in the need for another solvent mixed with PC. Leeds have used ethylene carbonate (EC) which has been shown to eliminate this issue. However, for simplicity a one solvent system was examined in this paper. The salts used in the creation of polymer gel electrolytes require a large anion attached to the relatively small lithium cation. This uneven size distribution causes a somewhat dispersed charge, and hence low lattice energy and therefore favours dissociation.

Here we report on NMR pulse field gradient diffusion measurements of both liquid electrolytes and PGEs using lithium and fluorine resonant frequencies to aid understanding of the ionic motion within these electrolytes.

2. Methods

2.1. PGE Production

All samples were prepared in an oxygen-free nitrogen filled glove box. The liquid electrolytes were prepared by mixing $LiBF_4$ salt with PC solvent at different molar concentrations. The PC and $LiBF_4$ were purchased from Sigma-Aldrich. The PC solvent was sealed under vacuum and was 99.7% anhydrous. The gels were prepared by first making the liquid electrolyte and then adding polymer, in this case PVDF, and heating. The polymer concentrations used were 20% and 30% as a percentage of the combined mass of polymer and solvent. The thermo-reversible gels were produced under high temperature conditions of $160^\circ C$ and allowed to cool to ambient temperature.

2.2. NMR Diffusion

The diffusion coefficients were measured by using a 400MHz Bruker AVANCE II NMR spectrometer. Pulsed field gradient (PFG) NMR measurements were previously undertaken at Leeds[17] on model liquid electrolyte solutions in the polymer gel electrolyte system using an extensively modified Bruker SXP-100 spectrometer and a Stejskal-Tanner pulse sequence. The present research used a complex bipolar stimulated echo pulse field gradient (BPStE-PFG) originally designed by Cotts [18]. Cotts sequence was an adapted form of a Stejskal-Tanner pulse sequence which eliminates background magnetic fields. This method involves applying different gradient pulse strengths and then monitoring the resulting intensity of the signal.

Background magnetic field gradients manifest due to inhomogeneities in the magnetic field. This produces cross terms of the applied magnetic gradients and the background magnetic gradients. This introduces the relation for intensity of signal in the form of equation 1.

$$I \propto \exp\left(-\left(G^2 + aGG_0 + bG_0^2\right) D\delta^2 \left(\Delta - \frac{\delta}{3}\right)\right) \quad (1)$$

G is the gradient field strength, G_0 is the background magnetic field gradient, Δ is the time between subsequent gradient pulses, δ is the gradient pulse duration, a and b are arbitrary constants. As there is no need to know every constant term, the G_0^2 term can just be incorporated into the constant of proportionality. The GG_0 term makes it difficult

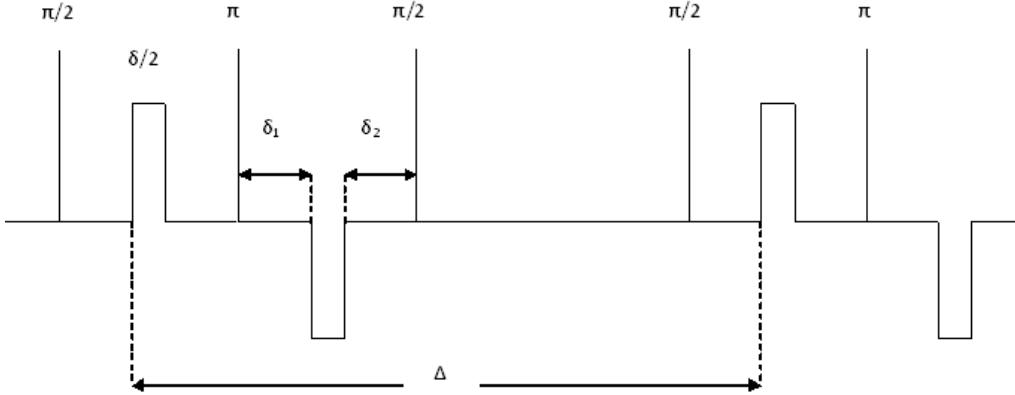


Figure 1: Cotts pulse sequence used with all diffusion measurements. This pulse sequence contains two sets of two gradient pulses (bipolar) which are separated by a time Δ . The radio frequency pulses consist of two π pulses and three $\frac{\pi}{2}$ pulses.

to measure the diffusion coefficient as one would also need to know the background magnetic field gradient. However, the introduction of bipolar pulses resolves this problem and allows measurement of the self diffusion coefficients. The Cotts pulse[18] shown in figure 1 has incorporated bipolar pulses in order to eliminate these cross terms.

The bipolar pulses (i.e. where the gradient is split into two gradient pulses of equal size with opposite sign) are used in order to eliminate the background gradient field. This background field occurs due to the heterogeneities within the magnetic field causing a distribution of magnetic field gradients throughout the sample, causing a nonuniform magnetisation in the sample. The different nuclei were isolated by applying radio frequency pulses corresponding to the resonant frequency of the nucleus. The NMR parameters used were $\Delta = 40ms$, $\delta = 10ms$ and $\delta_1 = 1ms$. δ_1 and δ_2 are the times between radio frequency (rf) and gradient pulses shown in figure 1, which in order to eliminate cross terms the condition $\delta_1 = \delta_2$ must be satisfied. These values were used as they have been proven to work previously with this type of measurement[17]. The value of the $\frac{\pi}{2}$ pulse was $18.5\mu s$ and $19.6\mu s$ at a power level of 3dB for 7Li and ${}^{19}F$ respectively. The typical recycle delay (RD) used here was taken as $5T_1$ with the number of transients being 16 in each case. With the cross terms eliminated the decay curves can be fitted to

equation 2.

$$I = I_0 \exp\left(-4\pi^2\gamma^2\delta^2G^2D\left(\Delta - \frac{\delta}{3}\right)\right) \quad (2)$$

Here both liquid and PGEs self diffusion coefficients for the anion and cation were measured using ^{19}F and ^7Li resonant frequencies respectively. The values of the spin-lattice relaxation times were also measured, but not reported here (to be published at a later date by Richardson *et al*). The T_1 values are in the high temperature (low correlation time) regime, in which the T_1 values are determined by the T_2 relaxation. The T_1 s were found to be of the order of seconds which means that $T_1 \gg \Delta$, suggesting there is no decay during diffusion measurements.

3. Results

3.1. NMR Self Diffusion

Figure 2 shows the diffusion decay curves for a liquid electrolyte, 20% and 30% polymer gel electrolytes all containing LiBF_4 1.0M. Each of the decay curves in figure 2 has been fitted to equation 2 in order to find the self diffusion coefficients (dashed line). All fitting has been carried out using Bruker topspin1.5 software which utilises an iterative process based on the Levenberg-Marquardt algorithm. In each case the integrated intensities were used. It can be seen that in the case of the liquid (0% PVDF), equation 2 provides a good fit to the data. However, the polymer gel electrolytes (20% and 30% PVDF) cannot be fitted to this equation. Therefore, a sum of two exponentials of the form of equation 2 was fitted to the data for the PGEs (solid line), giving a good fit. This result suggests the presence of two unique diffusive species within the polymer gel electrolytes. Two environments have been previously reported [19] with spin-spin and spin-lattice relaxation parameters for lithium in similar systems, however, no dual fit was applied to the diffusion measurements.

Within the liquid electrolyte there are different arrangements of lithium ions, including lone ions, ions solvated by several different number of PC molecules [20], neutral pairs of lithium and fluorine ions, among many others. It is assumed that the single diffusion coefficient represents an average of all these different species. Since two diffusive species are only present in the PGEs, this suggests that the lithium ion is in some way interacting with the polymer structure.

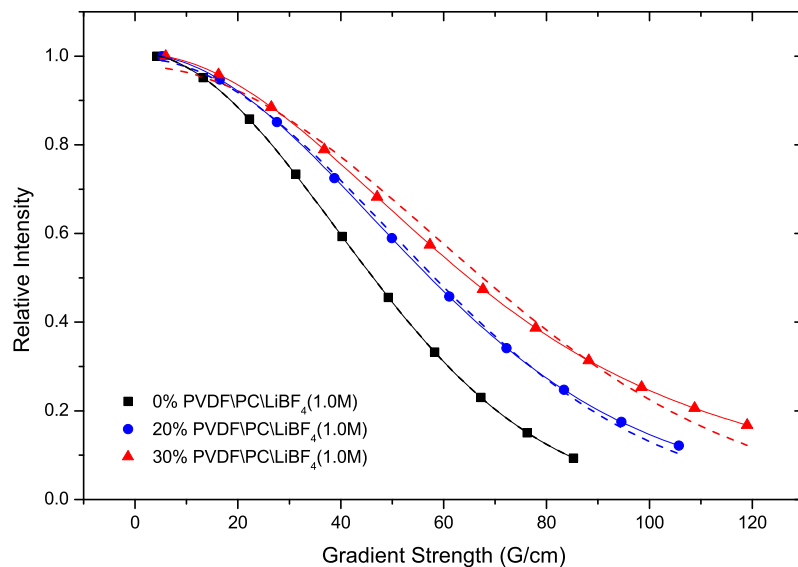


Figure 2: Lithium self diffusion decay curve for liquid electrolyte (0%) and PGEs (20% and 30%) PVDF/PC/ $LiBF_4(1.0M)$. The single (dashed line) and dual (solid line) fits have been applied here. Measurements carried out at 293K.

Table 1 shows the diffusion coefficients obtained for the liquid and PGEs along with the I_0 values. Since the intensity values of the diffusion decay curves are normalised the value of I_0 was unity. In the case of the PGEs the sum of I_{0_1} and I_{0_2} is also unity. It can be seen that the faster of the two diffusive species in the polymer gel electrolytes is of a similar value to that measured for the liquid electrolytes. Since these polymer gel electrolytes are believed to form by phase separation, yielding essentially a porous polymer structure with the liquid electrolyte flowing throughout, it is plausible that the faster component is due to the movement of the lithium ions within the liquid channels. Therefore, the liquid electrolyte and faster polymer gel diffusion coefficients being of a similar value is intuitively reasonable. There is still the issue of the slower moving lithium entity in the polymer gel electrolytes. It is thus suggested that the slower moving diffusive species is slowed down by association with the polymer in some manner. However, at this stage it is not possible to give the exact reason for the second diffusion coefficient.

Table 1 also shows that there is a reduction in the diffusion coefficient with the

Polymer (%)	I_{0_1}	D_1 ($\times 10^{-10} m^2 s^{-1}$)	I_{0_2}	D_2 ($\times 10^{-10} m^2 s^{-1}$)
0	—	—	1.00 ± 0.01	0.86 ± 0.01
20	0.28 ± 0.04	0.27 ± 0.02	0.72 ± 0.04	0.67 ± 0.02
30	0.39 ± 0.01	0.17 ± 0.01	0.61 ± 0.01	0.66 ± 0.01

Table 1: Lithium Intensity and diffusion coefficients for liquid electrolyte (0%) and PGEs (20% and 30%) PVDF/PC/*LiBF*₄(1.0M).

addition of 20% polymer, although there is no further reduction when the polymer concentration is increased to 30%. However, the intensity of the fit is dependent on the polymer concentration. Table 1 shows that the intensity of the slow diffusive species (I_{0_1}) was always less than that of the faster diffusive species (I_{0_2}). In the 20% gels, the value of I_{0_1} was around 0.3 increasing to 0.4 in the 30% gels. This is understandable, as the greater the polymer concentration in the gels, the more the lithium ions can interact with the structure. This result suggests that the structure of the gels contains multiple phases with a predominant liquid phase, accounting for 70% and 60% of the lithium signals in the 20% and 30% gels respectively.

Figure 3 shows the fluorine decay curve for liquid electrolytes and PGEs. Unlike the lithium ions, the fluorine only exhibits a single diffusion coefficient in both liquids and PGEs, suggesting that the fluorine ions do not interact with the polymer. This difference in behaviour between the lithium and fluorine ions can be understood due to the fact that the polymer contains fluorine on its backbone which will be slightly negatively charged, where as the lithium ion is positively charged. It is therefore logical to hypothesise that the two could be electrostatically interacting in some manner.

Table 2 shows the fluorine diffusion coefficients for liquid electrolytes and PGEs. As with the lithium data shown in table 1 there is a decrease in the diffusion coefficient with the addition of polymer.

The fact that the lithium data does not fit to a single exponential could potentially be due to restricted diffusion, this however has been dismissed here. If the polymer structure has small enough pores then it would be possible for the lithium ions to undergo restricted

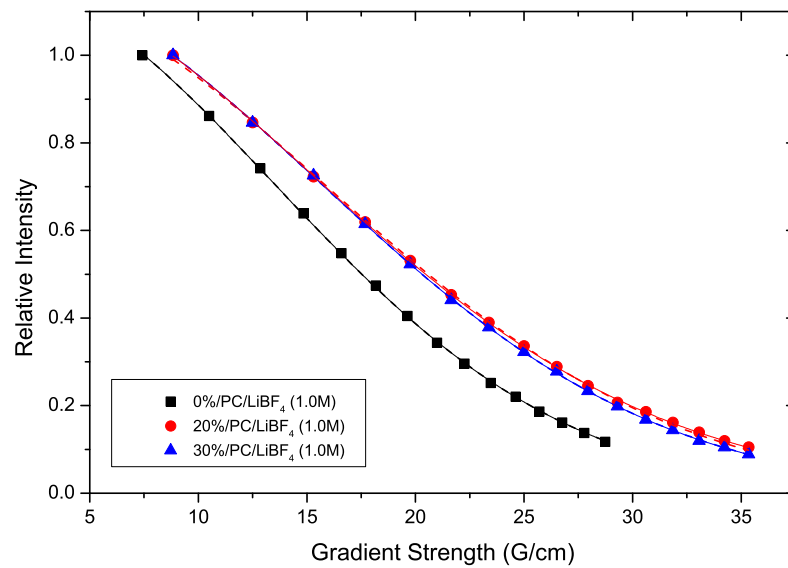


Figure 3: Fluorine self diffusion decay curve for liquid electrolyte (0%) and PGEs (20% and 30%) PVDF/PC/ $LiBF_4(1.0M)$. The single (dashed line) and dual (solid line) have been applied here. Both fits overlap suggesting that in the the case of the fluorine there is only a single diffusive species. Measurements carried out at 293K.

Polymer (%)	$D(^{19}F)$ ($\times 10^{-10} m^2 s^{-1}$)
0	1.19 ± 0.01
20	0.86 ± 0.01
30	0.86 ± 0.02

Table 2: Fluorine diffusion coefficients for liquid electrolyte (0%) and PGEs (20% and 30%) PVDF/PC/ $LiBF_4$ (1.0M).

diffusion due to confinement and in this instance, equation 1 would not be valid. So, fitting two diffusion coefficients in the manner suggested above would not be correct.

In order to investigate this the lithium diffusion has been measured for 30% PVDF/PC/ $LiBF_4$ (1.0M) at varying diffusion times (Δ). Figure 4 shows the fast and slow diffusion coefficients for 30% PVDF/ PC / $LiBF_4$ (1.0M) PGE at varying diffusion times (Δ). The values of both species is independent of diffusion time suggesting there is no evidence of restricted diffusion. Values of Δ ranging from 16ms up to 200ms were used which correspond to distances (r) traveled by the ions of around $3\mu m$ to $11\mu m$ using a random walk argument, equation 3.

$$r = \sqrt{6D\Delta} \quad (3)$$

It is possible for the pore size to be smaller than $3\mu m$, however, since the fluorine exhibits only one diffusion coefficient in both liquids and PGEs and diffuses faster than the lithium ions, restricted diffusion can be disregarded and the two diffusing species are assumed real.

4. Conclusions

Polymer gel electrolytes (PGEs) have been prepared using $LiBF_4$, PC and PVDF. PFG-NMR Diffusion measurements have been taken for liquid electrolytes and PGEs using both 7Li and ^{19}F nuclei to determine anion and cation diffusion.

Here we report the observation of two unique diffusive species of the lithium ions within the PGEs. Liquid electrolytes only showed a single diffusion coefficient leading to

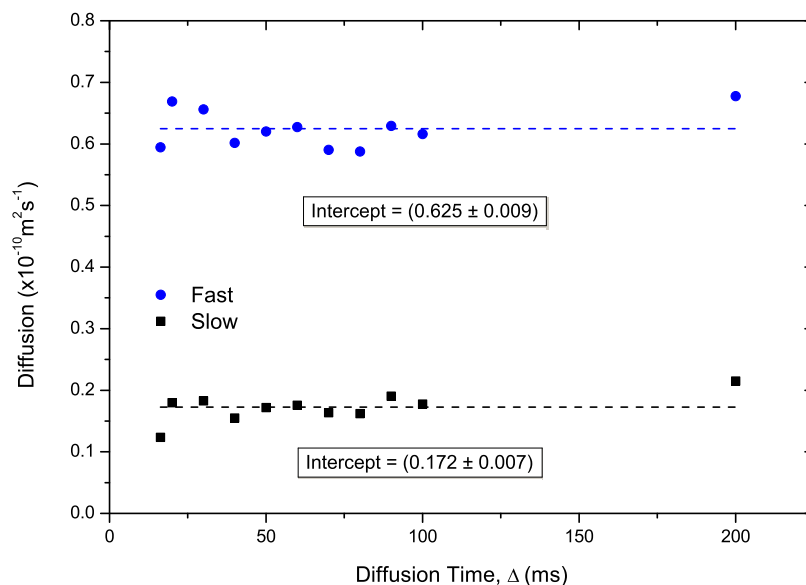


Figure 4: Lithium self diffusion for 30%PVDF/PC/LiBF₄(1.0M) polymer gel electrolyte at varying diffusion times (Δ) for both fast and slow diffusing species. The diffusion values for both species are unaffected by the change in diffusion times. Measurements carried out at 303 K.

the hypothesis of the lithium ions interacting with the polymer structure in some manner. The fluorine ions only exhibited a single diffusion coefficient in both liquid electrolytes and PGEs. The faster of the two lithium diffusive species yields a diffusion coefficient comparable to that of the liquid electrolyte, suggesting that these ions are in a liquid phase within a porous polymer structure. The source of the slower diffusive species could be explained as due to electrostatic interaction with the polymer or due to ions within the amorphous regions of the polymer structure.

It was observed that the intensity of the slow diffusive species was always less than that of the faster diffusive species. However there is an increase in the intensity of the slower diffusive species with increasing polymer concentration. This has attributed to there being a larger amount of polymer in the 30% gels allowing more of the lithium ions to interact with the polymer structure.

The implications of this research for industrial use is to understand how the motion of ions is affected by the addition of polymer, with the aim of enhancing the performance of the final rechargeable batteries.

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