

NMR studies of ionic mobility in polymer gel electrolytes for advanced lithium batteries

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Abstract

The NMR pulsed field gradient spin echo technique has been used to measure the self-diffusion coefficients of ^7Li , ^{19}F and protons in two polymer gel electrolytes, based on polyvinylidene fluoride (PVDF) and LiCF_3SO_3 with tetraglyme (TG) or *N,N*-dimethylformamide (DMF). Predicted values for the ionic conductivity were obtained from the NMR diffusivities using the Nernst–Einstein equation and compared with those from direct a.c. conductivity measurements to provide estimates of the degree of ionic association as a function of temperature and salt concentration. The results for the gel electrolytes are compared with those for the corresponding liquid electrolytes and are found to be very similar. There are, however, some small but significant differences between the behaviours of the gel electrolytes and the liquid electrolytes and these are discussed. The picture that emerges is of a two-phase material with regions of liquid electrolyte existing within a polymer gel rich matrix. This is consistent with measurements of the transverse relaxation time T_2 on these systems. The combination of high ionic conductivity with good mechanical properties of these polymer gel electrolytes is confirmed by their excellent performance in prototype battery systems. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In previous papers, pulsed field gradient (PFG) spin echo NMR measurements of the self diffusion coefficients of solvent molecules (^1H measurements), Li^+ cations (^7Li measurements) and CF_3SO_3^- anions (^{19}F measurements) have been reported for liquid electrolytes based on lithium trifluoromethanesulphonate (lithium ‘triflate’, LiT) and either *N,N*-dimethylformamide (DMF) or tetra(ethylene glycol) dimethyl ether (‘tetraglyme’, TG) [1,2]. In addition, measurements of the NMR longitudinal relaxation time T_1 have been reported for these systems [3]. In combination with measurements of ionic conductivity and viscosity, the NMR measurements have been shown to be extremely valuable in providing quantitative information on issues such as the degree of ionic association and the mechanisms of ionic mobility. Similar NMR studies have been reported by other groups [4,5].

Recent research at Leeds University has focused on the behaviour of gel electrolytes [6,7], where a polymer is dissolved in the liquid electrolyte at high temperatures. On cooling, a thermoreversible gel is produced where the

liquid electrolyte is now contained in a polymeric matrix. Such systems can show high levels of ionic conductivity and excellent mechanical properties. In the case of gel electrolytes based on PVDF, tough transparent materials are produced with room temperature conductivities approaching $10^{-2} \text{ S cm}^{-1}$ (DMF) and $10^{-3} \text{ S cm}^{-1}$ (TG).

The present paper describes PFG spin echo NMR measurements on PVDF gel electrolytes incorporating either DMF/LiT or TG/LiT liquid electrolytes. As might be expected, there are many similarities between the behaviour of the gel electrolyte and the corresponding liquid electrolytes but there are also some small but significant differences.

2. Experimental

2.1. Preparation of gel electrolytes

The materials required for the preparation of PVDF gel electrolytes were obtained from Aldrich and dried prior to use. DMF and tetraglyme were dried by storing over a 3 Å molecular sieve; PVDF (powder, molecular weight = 534,000) and lithium triflate were dried in a vacuum oven for at least 48 h prior to use at 100°C and 130°C, respectively.

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Initially, liquid electrolytes were prepared in a dry atmosphere by dissolving the appropriate amount of lithium triflate in either DMF or tetraglyme. Weighed amounts of PVDF were then added to each liquid electrolyte, which were heated and stirred intermittently until homogeneous mixtures were observed. Upon cooling, thermoreversible polymer gel electrolytes were formed.

For the NMR measurements, pieces of the gel electrolytes were placed in 7 mm diameter NMR tubes which were then heated until the gel melted; upon cooling a void-free, homogeneous gel electrolyte sample was obtained.

The gel electrolytes reported in this paper each contained 30% PVDF by weight with respect to the solvent alone (irrespective of salt concentration). Salt concentrations with respect to the solvent are O:Li = 3:1, 6:1 and 15:1 for the PVDF/DMF/LiT gel electrolytes and O:Li = 12:1 and 18:1 for the PVDF/TG/LiT gels.

2.2. Proton NMR spin echo measurements of transverse relaxation time, T_2

A Carr–Purcell–Meiboom–Gill pulse sequence [8], which takes the form:

$$\pi/2(+x) - \tau - [\pi(+y) - 2\tau]_n$$

has been used to monitor the proton NMR transverse relaxation in PVDF gel electrolytes and their incorporated liquid electrolytes.

Each of the proton transverse relaxation measurements were taken at 35°C using a MARAN benchtop pulse NMR analyser, manufactured by Resonance Instruments, UK, operating at 20 MHz.

2.3. Pulsed field gradient spin echo NMR measurements of self-diffusion coefficients

Self-diffusion coefficients for solvent molecules, Li^+ cations and CF_3SO_3^- anions in polymer gel electrolytes were determined separately by use of the PFG spin echo NMR technique [9], applied to ^1H , ^7Li and ^{19}F nuclei, respectively. Each diffusion measurement was obtained using an extensively modified Brüker SXP-100 spectrometer, operating at 100.5 MHz for protons, 95.6 MHz for ^{19}F and 39.1 MHz for ^7Li , with the aid of a commercially available pulse programmer/data acquisition system run from a PC. The gradient coils were calibrated on a sample of distilled water using the diffusion data reported by Mills [10] and could deliver a maximum field gradient of 2 T m^{-1} to an accuracy of 1 part in 4096.

In each PFG NMR experiment, the spin echo is formed at time 2τ by the application of a $\pi/2(+x)$ r.f. pulse at time zero, followed by a $\pi(+y)$ r.f. pulse at time τ . In all experiments, a gradient pulse width of $\delta = 3$ ms, a gradient pulse separation of $\Delta = 40$ ms and $\tau = 30$ ms was used. Using these parameters, for each of the ^1H and ^{19}F

measurements, a single diffusion coefficient was obtained, relating to the solvent and triflate ion diffusion, respectively, and showed that the contribution from the PVDF molecules had significantly decayed by the time of the spin echo due to the shorter transverse relaxation time of proton and fluorine nuclei in PVDF.

For each gel electrolyte system investigated, diffusion measurements were taken at 10°C intervals in the temperature range 35°C to 75°C. The range of salt concentrations was limited to those where the NMR signal intensity allowed measurements of the diffusion coefficient of all three nuclei to be determined, namely concentrations above O:Li of 15:1 for PVDF/DMF/LiT gel electrolytes and above 18:1 for PVDF/TG/LiT gel electrolytes. In general, the experimental uncertainty in the proton diffusion coefficients was better than 3%, with uncertainties of 5–10% being estimated for the lithium and fluorine diffusion measurements.

2.4. Ionic conductivity measurements

Bulk ionic conductivities were measured using a Solartron SI 1260 impedance/gain-phase analyser in the frequency range 1 Hz to 400 kHz. The gel electrolytes were melt cast between two stainless steel blocking electrodes and a constant thickness in the range 0.3 to 2.0 mm was maintained using a PTFE spacer [6].

3. Results and discussion

3.1. Measurements of proton NMR transverse relaxation time T_2

Proton T_2 measurements were undertaken on the PVDF gel electrolytes and on the corresponding DMF/LiT and TG/LiT liquid electrolytes. The decays of the echo heights $M(t)$ for the gel electrolytes with the corresponding liquid electrolytes are shown in Fig. 1 for the DMF system (salt concentration of O:Li = 3:1) and for tetraglyme TG (O:Li = 12:1) in Fig. 2. In both cases, the decay of $M(t)$ for the liquid electrolyte is well-described by a single exponential decay, but $M(t)$ for the gel electrolytes is described by a bi-exponential decay with two T_2 values shown in Table 1. The slower decay component, accounting for the majority of the signal, is due to the protons with the greatest mobility associated with the liquid electrolyte component; the faster component is due to ^1H in a gel rich phase which includes the PVDF protons. The proportion of protons in the slowly decaying component is less than expected if all the solvent molecules ($\sim 85\%$ for the DMF gel) contributed to the decay. The reduction is attributed to the partial solvation shell of solvent around amorphous parts of the PVDF.

These results confirm that the gel electrolytes contain a liquid-like phase which is very similar to that in the

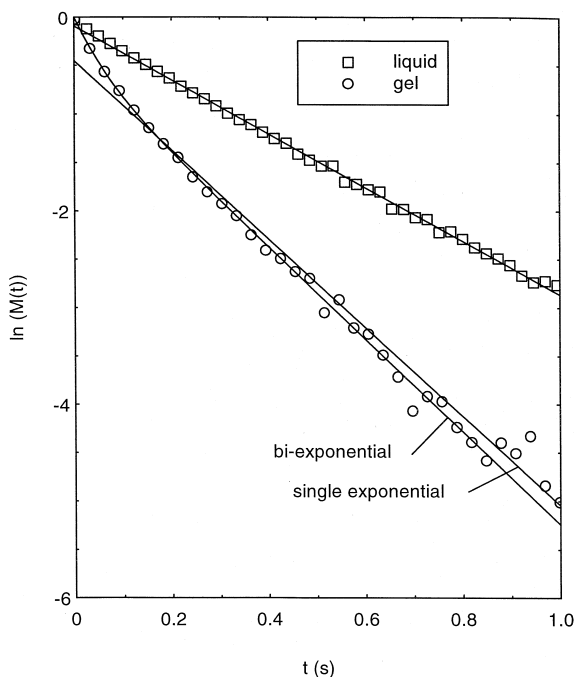


Fig. 1. Plot of $M(t)$ against time for a Carr-Purcell-Meiboom-Gill NMR pulse sequence for a DMF/LiT liquid electrolyte and a 30 wt.% PVDF/DMF/LiT gel electrolyte, each at a salt concentration of O:Li = 3:1.

corresponding liquid electrolyte and confirm that the PFG spin echo diffusion measurements to be reported refer to the liquid electrolyte phase in the gel electrolyte.

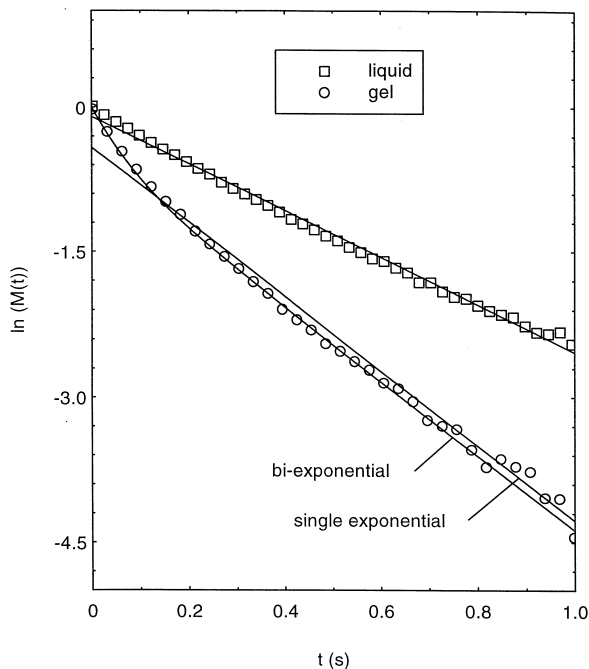


Fig. 2. Plot of $M(t)$ against time for a Carr-Purcell-Meiboom-Gill NMR pulse sequence for a TG/LiT liquid electrolyte and a 30 wt.% PVDF/TG/LiT gel electrolyte, each at a salt concentration of O:Li = 12:1.

Table 1

Proton NMR transverse relaxation time T_2 (ms) for the gel and liquid electrolytes

| | Liquid | | Gel | |
|-----|------------|---------------------------------|--------------------------|---------------------------------|
| | T_2 (ms) | T_2 slow decay component (ms) | slow decay component (%) | T_2 fast decay component (ms) |
| DMF | 348 | 209 | 64 | 48 |
| TG | 389 | 261 | 60 | 61 |

The percentage of the slow decay component is also given.

3.2. Proton, ^7Li and ^{19}F self diffusion measurements

Figs. 3 and 4 show the variation with temperature of the self diffusion coefficients for the protons, Li^+ ions and CF_3SO_3^- ions in the PVDF/DMF/LiT and PVDF/TG/LiT gel electrolytes, respectively, at selected salt concentrations.

A similar pattern of behaviour is observed for both the polar solvent DMF and the less polar solvent TG. First, the diffusion coefficients for the solvent molecules are always greater than for the Li^+ and CF_3SO_3^- ions. This is exactly the same as the behaviour observed previously for the liquid electrolytes [1,2] and is attributed to the fact that the proton signal is predominantly due to free solvent molecules which are not solvating the salt, at least in the time scale of the NMR experiment (~ 40 ms).

Secondly, the diffusion coefficients of the cation and anion are very similar, with the fluorine values slightly greater than the lithium values at lower salt concentrations and virtually identical at the highest salt concentrations.

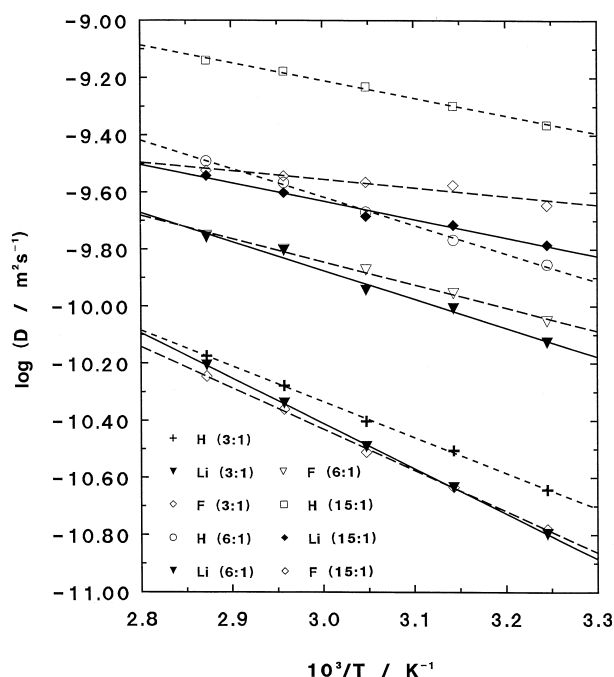


Fig. 3. Arrhenius plot of proton, lithium and fluorine diffusion coefficients for PVDF/DMF/LiT gel electrolytes. The solid lines represent the best fit lines of the data to the Arrhenius equation.

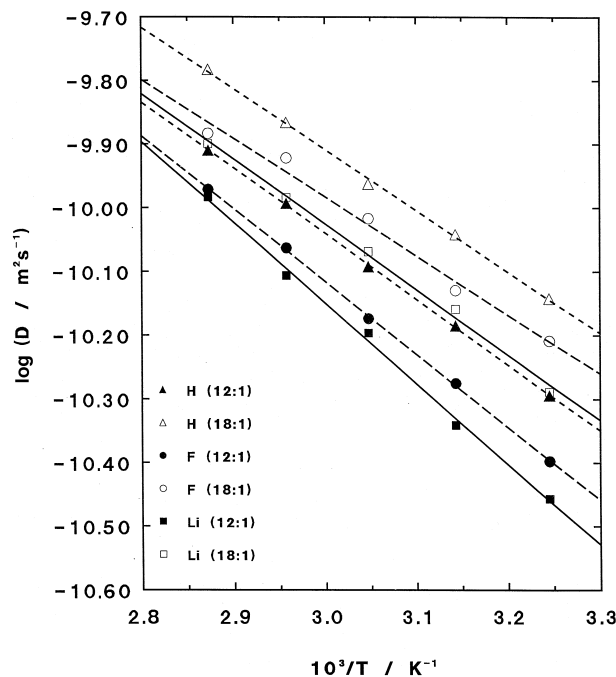


Fig. 4. Arrhenius plot of proton, lithium and fluorine diffusion coefficients for PVDF/TG/LiT gel electrolytes. The solid lines represent the best fit lines of the data to the Arrhenius equation.

This could be due either to increasing ionic association so that ion pairs are being observed where the Li^+ and CF_3SO_3^- ions move as a single species, or to correlated motion of the ions as suggested previously for LiT/polyethylene glycol electrolytes [11–13].

Figs. 3 and 4 show that the temperature dependence of self diffusion for ^1H , ^{19}F , and ^7Li is Arrhenius:

$$D = D_0 \exp\left[\frac{-E_D}{RT}\right] \quad (3)$$

The activation energies for the diffusion of each nucleus in the gel electrolytes, as for the corresponding liquids [1,2] increase with increasing salt concentration due to the increased interactions; and, as for the liquids, for each salt concentration the activation energy for lithium diffusion is greater than that for either proton or fluorine, reflecting stronger interactions involving lithium ions than either triflate ions or the solvent molecules.

The activation energies for the diffusion of each species are very similar between the DMF-based gel and liquid electrolytes at equivalent salt concentrations. This indicates similar mechanisms for diffusion for each diffusing species (solvent, anion, cation) and between the gels and the corresponding liquid electrolytes; this supports the picture of regions of liquid electrolyte within the gel.

A similar picture emerges in the TG based electrolytes, although in this case, the activation energies for the diffusion of each species are consistently around 10–20% higher in liquid electrolytes than in gel electrolytes, possibly as a result of an increase in dielectric constant of the electrolyte system in the presence of PVDF, or to an

Table 2

Comparison of Δ values calculated from the Nernst–Einstein equation for PVDF/DMF/LiT gel electrolytes and DMF/LiT liquid electrolytes

| O:Li | Δ (35°C) | | Δ (75°C) | |
|------|-----------------|-------|-----------------|-------|
| | Liquid | Gel | Liquid | Gel |
| 3:1 | 0.701 | 0.924 | 0.745 | 0.813 |
| 6:1 | 0.610 | 0.614 | 0.663 | 0.552 |
| 15:1 | 0.439 | 0.422 | 0.500 | 0.198 |

increase in the interaction of the salt-solvent species with the PVDF.

3.3. Ionic association: use of Nernst–Einstein equation

For fully dissociated ions, the Nernst–Einstein equation can be used to calculate the ionic conductivity, σ_{calc} , from the diffusion coefficients of the cation and anion ($D(\text{Li}^+)$ and $D(\text{CF}_3\text{SO}_3^-)$, respectively) as:

$$\sigma_{\text{calc}} = \frac{nq^2}{kT} [D(\text{Li}^+) + D(\text{CF}_3\text{SO}_3^-)] \quad (4)$$

where n is the number of anions and/or cations per unit volume of solution and q is the charge on each ion.

Generally, calculated values of σ_{calc} are greater than those measured directly, σ_{meas} , due to ionic association and the formation of species which contribute to the diffusion but not to the conductivity measurements. A quantitative measure Δ of ionic association is calculated from:

$$\sigma_{\text{meas}} = \sigma_{\text{calc}}(1 - \Delta) \quad (5)$$

Values of Δ for the PVDF/DMF/LiT and the PVDF/TG/LiT gel electrolytes are given in Tables 2 and 3, respectively, and are compared as a function of salt concentration and temperature, with those obtained from the corresponding liquid electrolytes [14,15]. In the PVDF/DMF/LiT gel electrolytes, Δ , and therefore the degree of ionic association, increases with increasing salt concentration similar to that observed for the DMF/LiT liquid electrolytes, but for this system, Δ increases more sharply with salt concentration in the gels than in the liquid electrolytes.

In the case of the PVDF/TG/LiT gel electrolytes, the behaviour with salt concentration is identical to that found for the corresponding liquid electrolytes, with a decrease in Δ with increasing salt concentration consistent with increasing ionic melt-like behaviour [1,2,12,13].

Table 3

Comparison of Δ values calculated from the Nernst–Einstein equation for PVDF/TG/LiT gel electrolytes and TG/LiT liquid electrolytes

| O:Li | Δ (35°C) | | Δ (75°C) | |
|------|-----------------|-------|-----------------|-------|
| | Liquid | Gel | Liquid | Gel |
| 12:1 | 0.821 | 0.830 | 0.855 | 0.814 |
| 18:1 | 0.854 | 0.882 | 0.879 | 0.840 |

However, for both the DMF and tetraglyme systems, the decrease of Δ with temperature in the gel electrolytes is precisely the opposite to that found for the liquid electrolytes. The increase in ionic association with temperature in liquid electrolyte systems is well-established [1,13,14] and is consistent with Raman studies of ion pairing [16,17]. The fall in the value of Δ and hence, the level of ionic association, with increasing temperature for the gel electrolytes, could be due either to the release of ions from crystalline regions of the gel into regions of liquid electrolyte or to the precipitation of neutral associated species onto PVDF regions increasing the proportion of dissociated ions in the liquid electrolyte component. In either case, the results show that the PVDF does interact with the solvent electrolyte in these gels and affect the conductivity over and above the presence of the PVDF simply increasing the tortuosity for ionic diffusion.

4. Conclusions

The technique of PFG NMR has been used to measure the diffusion coefficients of protons, fluorine and lithium nuclei in PVDF/DMF/LiT and PVDF/TG/LiT gel electrolytes containing 30% PVDF by weight with respect to the solvent. Proton diffusion coefficients in the range $(2.28 \text{ to } 72.6) \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ for the PVDF/DMF/LiT electrolytes and $(5.08 \text{ to } 16.5) \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ for the PVDF/TG/LiT electrolytes were obtained, with higher diffusion coefficients being measured at low salt concentrations and high temperatures.

The predominant overall effect of the PVDF gels is to reduce the ionic conductivities and diffusion coefficients of protons, fluorine and lithium, to about half that of the corresponding liquid electrolytes. The similarities in the behaviour of the liquid and gel systems are greater than the differences: the proton diffusion coefficient is greater than that for fluorine and lithium in both liquid and gel electrolytes; the temperature dependence of the diffusion is Arrhenius with similar activation energies in the gel and liquid systems; and the degree of ionic association Δ and the variation with salt concentration is similar for the liquids compared to the gels. It appears that the overall mechanism for diffusion and conduction are the same in the gel and liquid electrolytes and supports the view that the gel electrolyte behaviour is predominantly determined by the liquid electrolyte component, consistent with the picture from the T_2 measurements of regions of liquid electrolyte within the gel electrolyte framework.

However, there are clear differences in the behaviour of the gels compared with the liquid electrolytes: the lower

activation energies for the diffusion of each species in the tetraglyme gel electrolyte compared with the corresponding liquids; the greater range of the ionic association parameter Δ and sharper increase with salt concentration for the PVDF/DMF/LiT gel electrolytes compared to the corresponding liquid electrolytes; and most strikingly, the decrease in ionic association with temperature for PVDF gel electrolytes is in marked contrast to the increase in the liquid electrolytes previously observed. This is strong evidence to suggest that the PVDF in some way interacts with the liquid electrolyte component to modify the properties of the gel electrolytes.

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