

## Cation and anion diffusion coefficients in a solid polymer electrolyte measured by pulsed-field-gradient nuclear magnetic resonance

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1993 J. Phys.: Condens. Matter 5 153

(<http://iopscience.iop.org/0953-8984/5/2/003>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 12:48

Please note that [terms and conditions apply](#).

## Cation and anion diffusion coefficients in a solid polymer electrolyte measured by pulsed-field-gradient nuclear magnetic resonance

S Arumugam††, J Shi†, D P Tunstall‡ and C A Vincent†

† Centre for Electrochemical and Material Sciences, Department of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, UK

‡ Department of Physics and Astronomy, University of St Andrews, St Andrews, Fife KY16 9ST, UK

Received 9 October 1992

**Abstract.** Diffusion of  $\text{Li}^+$ -based and  $\text{PF}_6^-$ -based species in an amorphous polymer electrolyte has been explored by pulsed-field-gradient (PFG) nuclear magnetic resonance. The experiments were undertaken over a range of salt concentrations and temperature extending to lower values of both variables than in previous studies. Features of the results include a demonstration of different mechanisms for anion and cation transport at high concentration, as shown by their different temperature dependences, a reduced sensitivity of cation diffusion to salt concentration and a failure of the Nernst–Einstein relationship. Cation hopping between ionic clusters and the diffusion of neutral ion pairs are advanced as microscopic mechanisms to explain the data.

### 1. Introduction

Polymer electrolytes are ionically conducting phases formed by dissolving salts in suitable high-molecular-weight polar polymers. Such materials can be fabricated as thin films and offer an attractive alternative to conventional non-aqueous liquid electrolytes for practical electrochemical devices such as high-energy power sources or electrochromic displays [1]. Over the past ten years extensive measurements have been made on the electrical conductivity of polymer electrolytes [2], but there have been few reports of measurements of diffusion coefficients in such systems. Together with conductivities, diffusion coefficient data are of key importance in attempts to assess the state of the electrolyte in the polymer and to understand the mechanism of ion transport.

Radiotracer studies have been undertaken by Chadwick and co-workers [3–6] and a number of attempts have been made to interpret nuclear magnetic resonance (NMR) line broadening and spin relaxation times in terms of diffusional processes. Neither of these techniques has been particularly successful: the radiotracer studies are experimentally very difficult and non-linear penetration profiles cause problems in interpretation; the NMR experiments probably give information on short-range motional disorder, rather than on long-range diffusion. In addition, the latter experiments can be interpreted reliably only for crystalline solids with symmetric structures. Pulsed-field-gradient (PFG) NMR experiments give a direct measure of the

diffusion coefficient and there are a number of reports in the literature of use of this technique to study polymer electrolytes [7–12]. Until now, however, its use has been limited to systems with a relatively high concentration of salt and at elevated temperatures.

In this paper we describe the use of a Bruker MSL-500 NMR spectrometer in conjunction with a PFG probe manufactured by Doty Scientific, here using field gradient strengths of up to  $4 \text{ T m}^{-1}$ ; this system has enabled us to study electrolytes with concentrations down to  $0.25 \text{ mol dm}^{-3}$  at temperatures from  $25^\circ\text{C}$  to  $100^\circ\text{C}$ .

## 2. Experimental details

### 2.1. Materials

$\text{LiPF}_6$ , lithium hexafluorophosphate (Aldrich Chemical Co.) was dried at  $80^\circ\text{C}$  for 48 h. The host polymer was an oxymethylene-linked poly(oxyethylene) prepared after the method of Craven *et al* [13], purified by dialysis and carefully dried as described previously [14]. The number-averaged molecular weight was  $1 \times 10^5$  with a dispersion index of 1.34. Polymer electrolytes with a range of salt concentrations having an ethylene oxide to salt molar ratio varying from 100:1 to 20:1 (i.e. approximately  $0.25 \text{ mol dm}^{-3}$  to  $1.25 \text{ mol dm}^{-3}$ ) were prepared by solvent casting followed by pumping at  $90^\circ\text{C}$  for 12 h. All of the final products were completely amorphous above room temperature.

### 2.2. Conductivity measurements

Conductivities at each salt concentration were determined as a function of temperature by mounting the polymer electrolyte films in a thermostatted constant-volume cell with stainless steel electrodes, and studying its response to small-signal and variable-frequency alternating current. Analysis in the complex plane provided the bulk conductivity.

### 2.3. Diffusion coefficient measurements

Diffusion coefficients were determined using a Bruker MSL-500 spectrometer operating at 194.366 MHz for  $^7\text{Li}$  and 202.458 MHz for  $^{31}\text{P}$ , with an associated PFG probe from Doty Scientific. The typical stimulated echo pulse sequence is shown in figure 1:  $\delta$  is the duration of the field gradient pulse and  $\Delta$  the time interval between the two pulses. The maximum field gradient used was  $3.53 \text{ T m}^{-1}$  although a value of  $2.92 \text{ T m}^{-1}$  was normal; the gradient pulse rise/fall time was approximately  $50 \mu\text{s}$ . When measuring  $^7\text{Li}$ ,  $\delta$  was varied from 0.5 ms to 6 ms, while  $\Delta$  was kept constant; for  $^{31}\text{P}$ ,  $\Delta$  was varied from 200 to 900 ms while  $\delta$  remained constant. Values of  $D$  were obtained using the relationship [15]

$$\ln[A(\tau)/A(0)] = -\gamma^2 G^2 \delta^2 D (\Delta - \sigma/3) \quad (1)$$

where  $A(\tau)$  and  $A(0)$  are the echo amplitudes with and without application of the pulsed field gradient respectively,  $\gamma$  is the gyromagnetic ratio and  $G$  is the strength of the field gradient pulse, by plotting  $\ln[A(\tau)/A(0)]$  against  $\delta^2(\Delta - \delta/3)$  and measuring the slope of the resulting straight line. A typical plot is shown in figure 2.

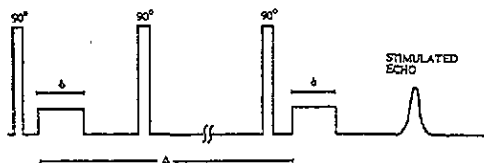


Figure 1. Schematic stimulated echo pulse sequence used for pulsed-field-gradient NMR experiments.

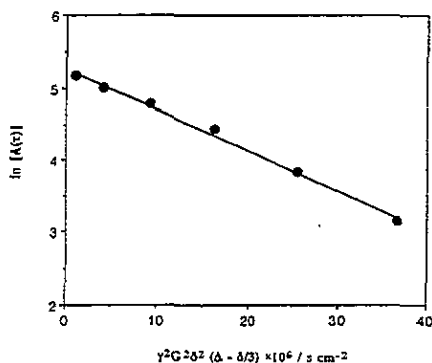


Figure 2. Typical plot of  $\ln[A(\tau)]$  against  $\gamma^2 G^2 \delta^2 (\Delta - \delta/3)$ .

### 3. Results and discussion

Conductivities, shown plotted as  $\log_{10} \sigma$  against  $1/T$  in figure 3, followed the empirical Vogel–Tamman–Fulcher (VTF) relationship

$$\sigma = A \exp[-B/(T - T_0)] \tag{2}$$

where  $A$ ,  $B$  and  $T_0$  are fitted constants. This behaviour is almost universal for ionic conductivities in amorphous polymer electrolytes [2]. Diffusion coefficient data for PF<sub>6</sub><sup>-</sup>-based species are given on a similar plot in figure 4, and for Li<sup>+</sup>-based species in figures 5(a) and (b).

#### 3.1. Anion diffusion

The <sup>31</sup>P diffusion coefficients vary with temperature according to the VTF equation at all concentrations studied (figure 4). Data for electrolytes more dilute than 50:1 were not recorded because of the excessive spectrometer time required. At any temperature, the diffusion coefficient of the 50:1 sample is approximately four

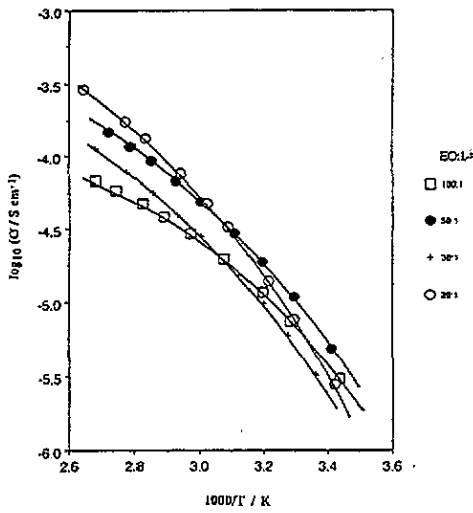


Figure 3. Conductivity of  $\text{LiPF}_6$ -based electrolytes as a function of temperature for ethylene oxide to salt ratios of 100:1 ( $\square$ ), 50:1 ( $\bullet$ ), 30:1 ( $+$ ) and 20:1 ( $\circ$ ).

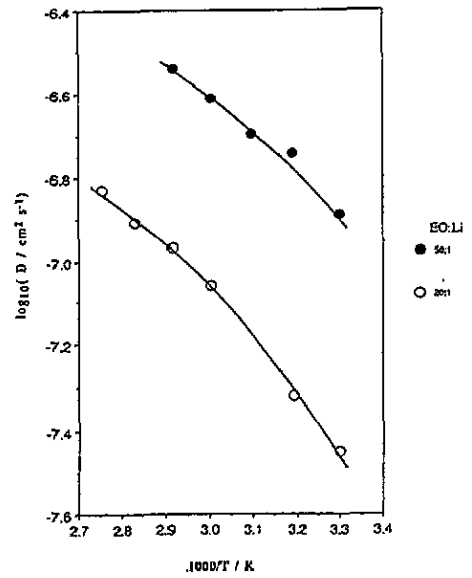


Figure 4. Diffusion coefficients of  $^{31}\text{P}$  as a function of temperature for ethylene oxide to salt ratios of 50:1 ( $\bullet$ ) and 20:1 ( $\circ$ ).

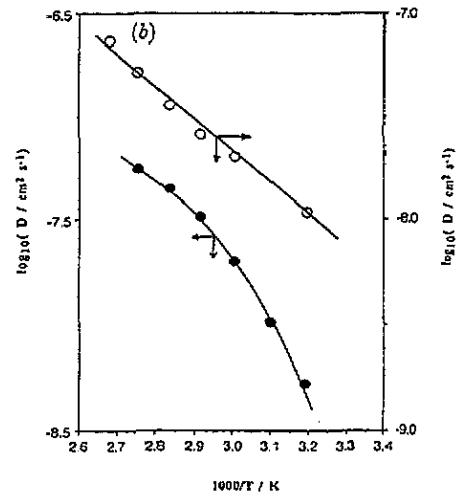
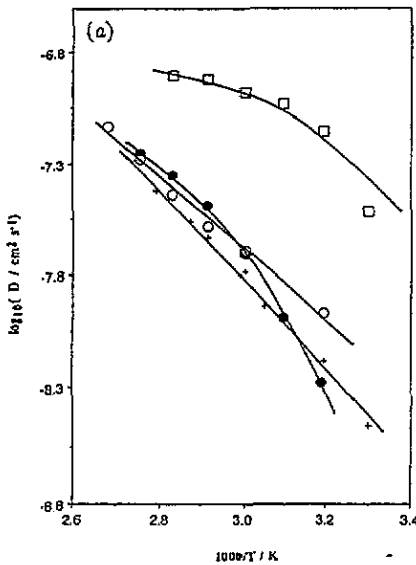


Figure 5. (a) Diffusion coefficients for  $^7\text{Li}$  as a function of temperature for ethylene oxide to salt ratios of 100:1 ( $\square$ ), 50:1 ( $\bullet$ ), 30:1 ( $+$ ) and 20:1 ( $\circ$ ). (b) Diffusion coefficient data for  $^7\text{Li}$  for 50:1 ( $\bullet$ ) and 20:1 ( $\circ$ ) plotted to show different forms of temperature dependence.

times higher than that of the 20:1 sample. This is consistent with the idea that the segmental motion of the polymer is reduced by transient ionic cross-links, as is also

demonstrated by, for example, the increase in the glass transition temperature. Little consideration has so far been given to the description of anion motion in a polymer electrolyte. Anions do not form strong ion-polymer bonds, as cations do, in ether-based systems, and it is therefore assumed that transport processes involving anions (and also negative triple ions) will not be thermally activated in the normal sense, but will depend simply on the rate of polymer rearrangements. The latter have been described in terms of configurational entropy or free volume theories, both of which predict a VTF-like temperature dependence [16].

From a comparison of the values in figures 4 and 5, it is seen that anion diffusion is significantly faster than cation diffusion in the same system. Taking the 50:1 electrolyte as an example, the mean diffusion coefficient of PF<sub>6</sub><sup>-</sup>-based species is  $3.7 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  at 90 °C compared with  $0.58 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  for Li-based species. At lower temperatures this difference is even more marked, becoming approximately two orders of magnitude at 25 °C. A further feature of this comparison is the relative insensitivity of cation diffusion to salt concentration at high values of the latter.

### 3.2. Cation diffusion

Cations form strong ion-polymer bonds: it is the magnitude of the cation-polymer interaction that compensates largely for the lattice energy of the salt enabling its dissolution and the formation of the polymer electrolyte [1,2]. In the conductivity model proposed by Ratner and co-workers (see, for example, [16] and references therein) long-range cation transport is seen to involve a combination of local segmental motion of the polymer host (to which cations are attached by dative electrostatic bonds) and occasional independent transitions of ions themselves between suitable coordinating sites which may be located on different polymer strands. Cations thus percolate between sites which are constantly forming and disappearing. A prerequisite for cation conductivity in high-molecular-weight polymer electrolytes is a dissociation step which permits these ionic transitions between sites.

It is clear from figure 5 that at concentrations of 50:1 and below (i.e. at higher ethylene oxide to salt ratios), cations show somewhat similar VTF (equation (2)) behaviour to anions—i.e. any thermally activated dissociation step is not dominant in the determination of the rate. The need for such a step, however, may explain why cations have net diffusion coefficients that are lower than those of anions in the same electrolyte.

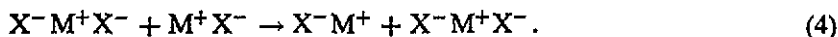
At higher concentrations, however, a new thermally activated mechanism takes over. The fitted rectilinear function for the 30:1 sample has a confidence factor of 0.990. Thus, as the salt concentration is raised it seems that a competing process becomes relatively faster than the segmental motion/site percolation mechanism. At these higher concentrations there is persuasive spectroscopic and electrical evidence for the existence of increasing concentrations of ion-associated species [17]. A consistent mechanism for cation transport at 30:1 and above might therefore involve activated ion transitions between ion clusters such as



as proposed previously by ourselves [18] and by Teeters and Frech [19]. The relative independence of cation diffusion coefficient from salt concentration for concentrations above 50:1 at any given temperature is striking. It has been well established that at these high concentrations ionic crosslinking of the polymer strands significantly

reduces segmental motion: this process explains the reduction in the anion diffusion coefficients when the concentration was raised from 50:1 to 20:1 as shown in figure 4. The implication is therefore that the dominant mechanism for cation transport at high concentration, such as that suggested in equation (3), is largely independent of the segmental mobility.

The question that now arises is why a similar mechanism is not seen for anions, i.e.



Two reasons may be given. First the competitive 'normal' diffusion mechanism for anion-based species is very much faster than that observed for the onset of the activated cation transitions. Further, the much larger size of  $PF_6^-$  in comparison with  $Li^+$  may make activated anion transitions of this sort much less probable.

In a previous study of  $LiCF_3SO_3$ -based polymer electrolytes it was suggested that  $Li^+$  ion motion followed Arrhenius behaviour at all concentrations [11, 20]. It was also proposed that as a result of this, cation transport as measured on a PFG timescale might be determined by polymer diffusion, involving, for example, activated reptation steps [21]. This now seems a less likely explanation.

### 3.3. The relationship between conductivity and diffusion coefficients

For strong electrolytes at infinite dilution, transport of ions due to (i) an electric field (migration) and (ii) a concentration, or better activity gradient (diffusion) are simply related by the Nernst-Einstein relation

$$\sigma_i = z_i c_i F^2 D_i^0 / RT \quad (5)$$

where  $D_i^0$  is the diffusion coefficient,  $z_i$  the charge,  $c_i$  the concentration and  $\sigma_i$  the contribution to the total conductivity of the ionic species  $i$ , extrapolated to infinite dilution.  $F$  is Faraday's constant,  $R$  the gas constant and  $T$  the absolute temperature. For a strong 1:1 electrolyte the total conductivity is then given by

$$\sigma = c F^2 (D_+^0 + D_-^0) / RT \quad (6)$$

where  $c$  is the concentration of the salt. At real concentrations but in circumstances where equations (5) and (6) can serve as a realistic approximation, measurement of  $D_i$  and  $\sigma$  enables a number of useful parameters to be derived. For example, the term  $D_+ / (D_+ + D_-)$ , known as the electric transport number, is a measure of the relative conductance of the cations or of the proportion of current carried by them. Further, in situations where some of the diffusing ions are immobilised in low-energy traps, evaluation of  $c_i$  permits the determination of the proportion that is active in transport. The Nernst-Einstein relationship fails, however, for a number of reasons. First, and of minor importance in the present study, the electrophoretic and relaxation field effects operate in a different manner for diffusion and migration and hence the absolute mobilities of ions in diffusion vary differently with concentration from their mobilities in electrolytic conduction. A much more important limitation of the Nernst-Einstein equation relates to the requirement that at the concentration of interest, the species involved in diffusion must also be responsible for electric conduction.

In solution (whether based on a conventional liquid or solid polymer host), a salt such as  $\text{LiPF}_6$  can exist as a number of distinct species—free  $\text{Li}^+$  and  $\text{PF}_6^-$  ions, ion-pairs ( $\text{LiPF}_6$ ), ion-triples ( $\text{Li}_2\text{PF}_6^+$  and  $\text{Li}(\text{PF}_6)_2^-$ ), etc. A conductance measurement determines the effect of the sum of the transport of all the *charged* species,

$$\sigma = \sum_i n_i q_i u_i$$

where  $n_i$  is the concentration of species  $i$ ,  $q_i$  its charge and  $u_i$  its mobility. Ion pairs and higher uncharged clusters (whether mobile or immobile) do not contribute to the conductance. A diffusion coefficient measurement, on the other hand, gives the mean value for the diffusion of all the species present which contain the nucleus in question, irrespective of charge.

**Table 1.** Experimental and calculated conductivities of 50:1 and 20:1 polymer electrolytes at 40 °C–80 °C.

	50:1		20:1	
	$\sigma_{\text{exp}}$ ( $\text{S cm}^{-1}$ )	$\sigma_{\text{calc}}$ ( $\text{S cm}^{-1}$ )	$\sigma_{\text{exp}}$ ( $\text{S cm}^{-1}$ )	$\sigma_{\text{calc}}$ ( $\text{S cm}^{-1}$ )
40 °C	$1.88 \times 10^{-5}$	$2.48 \times 10^{-4}$	$1.40 \times 10^{-5}$	$1.92 \times 10^{-4}$
60 °C	$4.89 \times 10^{-5}$	$3.28 \times 10^{-4}$	$4.90 \times 10^{-5}$	$3.53 \times 10^{-4}$
80 °C	$1.04 \times 10^{-4}$	$4.11 \times 10^{-4}$	$1.33 \times 10^{-4}$	$5.08 \times 10^{-4}$

In table 1 values of conductivity calculated using equation (6) are compared with experimental data for 20:1 and 50:1 electrolytes at three temperatures. In all cases the experimental values are significantly lower than those predicted assuming strong electrolyte behaviour. The discrepancy is higher at low temperatures. At first sight this might be interpreted as suggesting that a significant percentage of the ions were trapped and not involved in long-range motion. Such an explanation is, however, unlikely in the system under investigation, since there was no evidence from the PFG spectra of any second peak which could be interpreted as signifying the presence of an immobile (or differently mobile) species. Within the timescale of the experiment there must therefore have been rapid exchange between the different species present, including trapped species, if indeed they did exist. It is more probable that the reason for the discrepancy involves the facile diffusion of uncharged species such as ion pairs, motion of which contributes to the measured mean diffusion coefficients but not to the conductivity. Gross deviations from the Nernst–Einstein equation are well documented for a number of other systems; for example molten salts, where it is also considered that diffusion may occur partly through displacement of uncharged ion pairs, or indeed by ‘coordinated jumps’ of oppositely charged ions.

#### 4. Conclusions

Diffusion coefficients of  $\text{Li}^+$ -based and  $\text{PF}_6^-$ -based species in amorphous PMEO-based polymer electrolytes have been measured for a range of concentrations and the data have been compared with conductivity measurements in the temperature range 30 °C–100 °C. This study has extended diffusion measurements in polymer electrolytes to lower concentrations and temperatures than in previous investigations.



Failure of the Nernst–Einstein relationship is ascribed to a strong influence of neutral ion-pair diffusion on the NMR data. A change in the cation diffusion mechanism from a process controlled by VTF kinetics to a thermally activated mechanism is noted as the salt concentration is increased. It is suggested that the latter process, which does not affect anion motion, may involve cation hopping between ionic clusters.

### Acknowledgment

We thank the Science and Engineering Research Council (UK) for a grant to purchase the Bruker MSL-500 spectrometer.

### References

- [1] Gray F M 1991 *Solid Polymer Electrolytes: Fundamentals and Technological Applications* (New York: VCH)
- [2] MacCallum J R and Vincent C A (ed) 1987/9 *Polymer Electrolyte Reviews* 1, 2 (London: Elsevier)
- [3] Chadwick A V, Strange J H and Worboys M R 1983 *Solid State Ion.* 9/10 1155
- [4] Bridges C, Chadwick A V and Worboys M R 1988 *Br. Polym. J.* 20 207
- [5] Al-Mударis A A and Chadwick A V 1988 *Br. Polym. J.* 20 213
- [6] Chadwick A V, Al-Mударis A A and Bridges C 1989 *Polym. Prepr.* 30 418
- [7] Minier M, Berthier C and Gorecki W 1984 *J. Physique* 45 739
- [8] Mali M, Roos J and Brinkmann D 1984 *Proc. XXII Congress Ampère (Zürich, 1984)* ed K A Muller, R Kind and J Roos
- [9] Gorecki W, Andreani R, Berthier C, Armand M B, Mali M, Roos J and Brinkmann D 1986 *Solid State Ion.* 18/19 295
- [10] Bhattacharja S, Smout S W and Whitmore D H 1986 *Solid State Ion.* 18/19 306
- [11] Gorecki W, Donoso P, Berthier C, Mali M, Roos J, Brinkmann D and Armand M B 1988 *Solid State Ion.* 28/30 1018
- [12] Lindsay S E, Whitmore D H, Halperin W P and Torkelson J P 1989 *Polym. Prepr.* 30 442
- [13] Craven J R, Mobbs R H, Booth C and Giles J R M 1986 *Macromol. Chem. Rapid Commun.* 7 81
- [14] Gray F M 1990 *Solid State Ion.* 40/41 637
- [15] Fukushima E and Roeder S B W 1981 *Experimental Pulsed n.m.r.—a Nuts and Bolts Approach* (London: Addison-Wesley)
- [16] Ratner M A 1987 *Polymer Electrolyte Reviews* 1 ed J R MacCallum and C A Vincent (London: Elsevier) p 173
- [17] Kakihama M, Sandahl J, Schantz S and Torell L M 1989 *2nd Int. Symp. on Polymer Electrolytes* ed B Scrosati (London: Elsevier) p 1
- [18] Vincent C A 1987 *Prog. Solid State Chem.* 17 145
- [19] Teeters D and Frech R 1986 *Solid State Ion.* 18/19 271
- [20] Armand M B 1989 *Discuss. Faraday Soc.* 88 91
- [21] Ratner M A 1989 *Discuss. Faraday Soc.* 88 91