

Ion solvation in lithium battery electrolyte solutions Part II*. Solvent effects on lithium-ion intercalation in niobium triselenide

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(Received February 6, 1991)

Abstract

Solvent effects on the intercalation of lithium ions in niobium triselenide electrodes have been investigated by cathodic polarization measurements in propylene carbonate (PC), acetonitrile (AN), 1,2-dimethoxyethane (DME), tetrahydrofuran (THF) and their 50% vol./vol. mixtures with PC, using 1 M LiClO₄ as the supporting electrolyte. The polarization follows the general order PC ≈ PC/AN ≈ PC/THF > THF > PC/DME > DME > AN which reflects the probable size of the solvated lithium ion. This suggests that intercalation of Li⁺ into the host lattice occurs without desolvation. Lattice diffusion coefficients of Li⁺ in NbSe₃ in the various solvents have been determined by an intermittent galvanostatic technique and found to be in the order AN > DME ≈ PC/DME > PC/AN > PC. This has also been explained in terms of solvation effects and the composition of the resultant Li⁺ solvation shell.

Introduction

The reactivity of lithium towards water necessitates the use of non-aqueous electrolyte solutions for the development of high energy density lithium batteries. Organic solvents offer a wide range of viscosities, ionic mobilities (conductivities), redox stabilities, and operating temperatures. However, the rational selection of solvents for lithium batteries requires an understanding of the influence of solvent effects on the relevant solution properties and also the thermodynamics and kinetics of the electrode processes [1].

The negative electrode (anode) in a lithium battery is either the metal itself or one of its alloys. Solvent effects on the thermodynamic potentials and electrode kinetics of lithium and its alloys have been the subject of numerous studies [1-5]. Likewise, many positive electrode (cathode) materials for lithium batteries have been investigated [2]. In particular, the transition metal chalcogenides MX_n (where: M = Ti, V, Nb, Mo or Cu; X = S or Se) have

*Part I, *J. Solution Chemistry*, in press.

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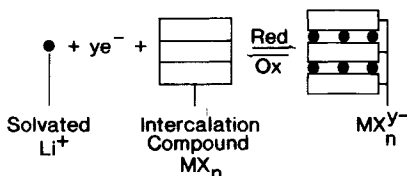


Fig. 1. Schematic representation of the reversible intercalation of lithium ions by a layered metal chalcogenide electrode during discharging and charging.

attracted considerable attention for rechargeable lithium batteries [6–8]. These compounds are of interest because their lattices can act as hosts for lithium ions. The Li^+ ions move reversibly in and out of the lattice when the positive electrode matrix (MX_n) undergoes a change in oxidation state as the battery discharges or charges [9]. This is illustrated schematically in Fig. 1.

Niobium triselenide (NbSe_3) has several properties that make it attractive as a lithium battery positive. These include: high gravimetric and volumetric energy densities; a rugged layer structure; fibrous morphology; and good electronic conductivity [6, 7, 10, 11]. It has been shown that NbSe_3 undergoes a topotactic reversible intercalation, incorporating up to 3 moles of Li^+ [6]. The mechanism of this intercalation is still not clearly understood [7, 8], however, and little is known about the effects of solvent. In particular, controversy exists in the literature [2, 8, 12–15] as to whether the intercalation of Li^+ occurs via the solvated or unsolvated ion. In this paper, we address this question and report the results of potentiometric and coulometric studies on the behaviour of the NbSe_3 electrode in propylene carbonate (PC), acetonitrile (AN), 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), and 50% vol./vol. mixtures of PC/AN, PC/DME, and PC/THF. These solvents are chosen because they are either currently used in commercial primary lithium batteries or are promising materials for low-temperature lithium batteries [1–4, 16–19]. A model for the intercalation of Li^+ into the NbSe_3 lattice is proposed.

Experimental

Working electrode discs were made from NbSe_3 prepared by the method developed by Carides and Murphy [20]. Microscopic and X-ray diffraction examination indicated that the material was pure NbSe_3 with the fibrous structure described by Trumbore [7]. The felt-like morphology of NbSe_3 made homogenization to a uniform particle size impossible. Consequently, approximately 3 g of fibres were mechanically broken into small pieces, pressed under 5000 kg cm^{-2} into a disc ($<0.5 \text{ mm}$ thick), and mounted onto a Teflon cylinder containing an electrical contact lead. A sleeve of heat-shrink Teflon was sealed over this to eliminate seepage of solvent. This reduced the exposed surface of the electrode to 0.15 to 0.33 cm^2 , and the

effective weight of NbSe_3 exposed to the electrolyte to ~ 0.04 g. The electrical conductivity of NbSe_3 is known to be reasonably high (0.344 S cm^{-1}) [7] and the resistance of the cathode disc was calculated to be negligible ($< 1 \text{ m}\Omega$).

A schematic diagram of the cell used for measuring galvanostatic polarization of NbSe_3 in various solvents is shown in Fig. 2. Counter and reference electrodes were discs constructed from Li-Al alloy (10% Li, Foote Chemical Co.). The counter electrode (1 cm diameter) was machined to fit tightly into a Ke1-F support that was fitted into the bottom of a modified small-volume (2 ml) Metrohm cell. The reference electrode was a 5 cm long rectangular rod suspended in a separate compartment. This was fitted with an angled capillary tip positioned 0.5 mm from the surface of the working electrode. The working NbSe_3 electrode was suspended vertically from the cell cap, 1.5 cm above the counter electrode. Before each experiment, the electrodes were removed for cleaning and polishing in an argon-filled glove bag. Both the cell and the reference electrode compartment were filled with the solvent (pure or mixed) under study containing 1 M LiClO_4 .

After introducing the cleaned lithium electrodes, the argon-filled cell was removed to the bench and filled with electrolyte solution. The cell was maintained at 25 ± 0.05 °C. All experiments were conducted under a positive

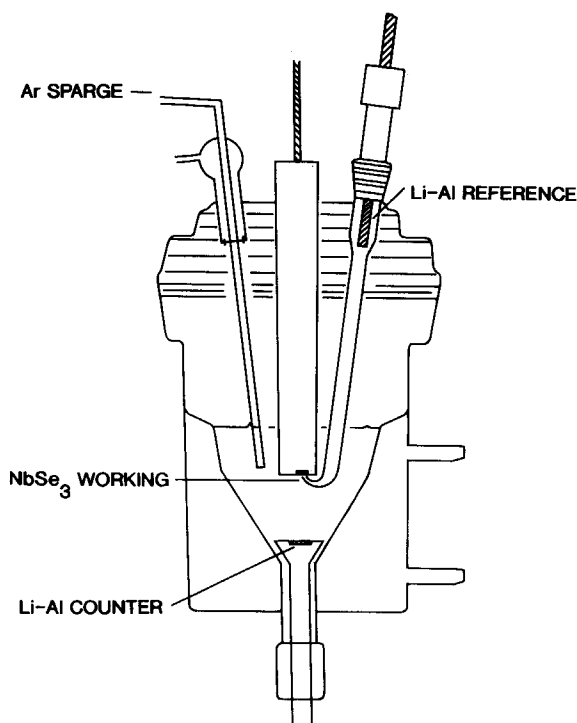


Fig. 2. Diagram of cell used for galvanostatic polarization of NbSe_3 in solutions of 1 M LiClO_4 in various solvents.

argon atmosphere. The system was left to equilibrate on open-circuit voltage (OCV) until the variation was less than 10 mV h^{-1} . The cell was then discharged for 3 min at a fixed current; NbSe_3 was reduced with concurrent intercalation of Li^+ ions to maintain the charge balance. The current was then interrupted and the cathode allowed to relax to a nominal OCV for 10 min. A series of galvanostatic steps between 5 and $50 \mu\text{A}$, following the same pattern, was then instituted. Cathode voltages were followed on a Hewlett-Packard 3495a digital multimeter and a Rikadenki dual-channel chart recorder with a d.c. offset. The galvanostat was of local construction.

The ohmic potential drop (iR) between the working electrode and the tip of the reference electrode capillary was calculated to be less than 2 mV for an applied current of $25 \mu\text{A}$ and is therefore negligible.

Results and discussion

Solvent effects on open-circuit voltage

The observed equilibrium (open-circuit) voltages (OCVs or E_o) of the Li_xNbSe_3 ($\delta = 1 \times 10^{-4}$) electrode relative to the Li-Al reference electrode in various solvents are recorded in Table 1. Since the free energies of transfer of Li^+ from PC to the other solvents are known (Table 1), it is possible to express the open-circuit voltages with respect to the common reference electrode Li-Al/1 M LiClO_4 PC (within the validity of the assumption necessary to obtain the free energies of transfer of a single ion). These data are also noted in Table 1. The values vary in the range 2.326 to 2.546 V.

Solvent effects on cathode polarization

Kinetic information on Li^+ intercalation can be obtained from the polarization behaviour of NbSe_3 in the solvents of interest. These data are

TABLE 1

Open-circuit voltages (OCV) of a pressed disc Li_xNbSe_3 electrode^a

Solvent ^b S	OCV ^c (V)	$\Delta_1 G(\text{Li}^+)_{\text{PC} \rightarrow \text{S}}$ ^d (kJ mol ⁻¹)	OCV ^e (V)
PC	2.315	0	2.315
AN	2.377	+4.9	2.326
DME	2.448	-5.4	2.504
THF	2.444	-5.5	2.501
PC/AN	2.433	+2.8	2.405
PC/DME	2.372	-6.3	2.437
PC/THF	2.493	-6.1	2.546

^a $\delta = 1 \times 10^{-4}$.

^bSolvent mixtures 50% vol./vol.

^cvs. Li/Al, 1.0 M LiClO_4 , S.

^dData from ref. 21.

^evs. Li/Al, 1.0 M LiClO_4 , PC corrected from column 2 using $\Delta_1 G(\text{Li}^+)_{\text{PC} \rightarrow \text{S}}$ from column 3, see text.

shown in Fig. 3. It can be seen that the polarization follows the general order: $PC \approx PC/AN \approx PC/THF > THF > PC/DME > DME > AN$.

Two mechanisms for the intercalation of Li^+ into the $NbSe_3$ host lattice are possible:

- (i) the solvated lithium ion sheds its solvation shell prior to intercalation;
- (ii) the solvated ion retains its solvation shell throughout the intercalation process.

The first mechanism would require energy for the desolvation step and therefore the cathodic polarization would be directly related to the free energy of solvation. As can be seen from the values of $\Delta_s G(Li^+)_{PC \rightarrow S}$ given in Table 1, however, there is no correlation between the transfer free energies and the observed polarization behaviour. Thus, the first mechanism can be ruled out.

If the second mechanism is operative, the polarization should be related to the rate of diffusion of the solvated lithium ions within the host lattice. The rate of diffusion, in turn, is inversely proportional to the size of the solvated ion. Thus, the polarization should be inversely related to the ionic size.

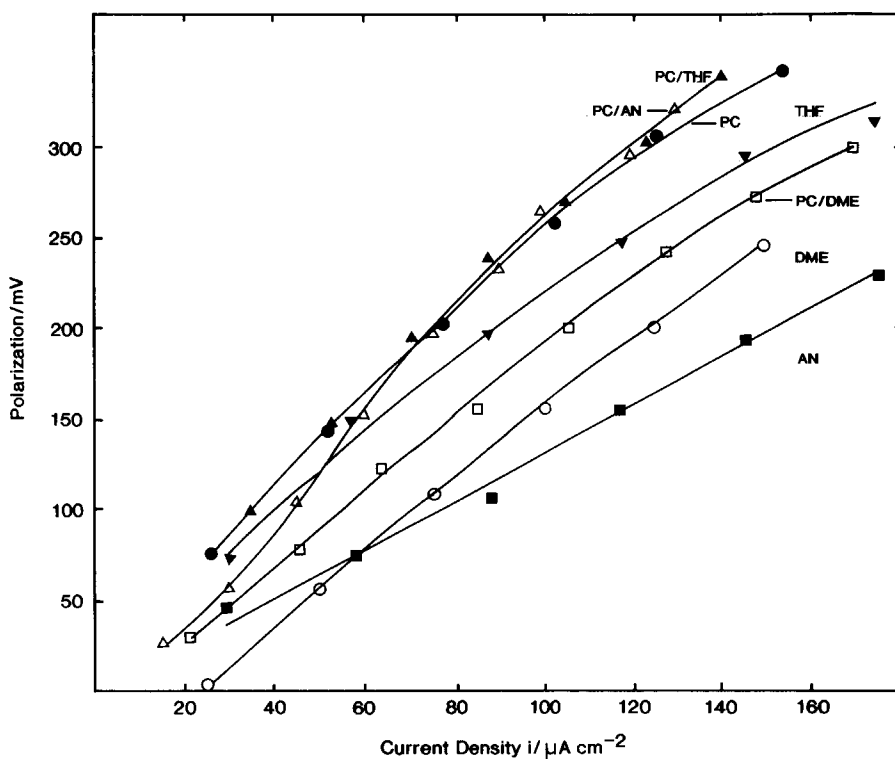


Fig. 3. Cathodic polarization of $NbSe_3$ (1 M $LiClO_4$) in various solvents at different current densities.

It is difficult to establish the 'true' sizes for solvated ions in solution. For example, solvation numbers differ widely according to the technique chosen [22]. In the strongly coordinating PC, THF and DME, however, the radius of the solvated lithium ion (r_s) may be taken, as a first approximation, to be the crystallographic radius of the ion itself (r_{Li^+}) plus the diameter of a coordinated solvent molecule. Thus for PC, THF and DME, the situation may be of the type illustrated in Fig. 4. Note, the position of Li^+ -AN is less obvious: AN is a weak solvator of Li^+ , thus the lithium ion in AN will be essentially 'bare' and hence its effective solvated radius will be smaller than in the other solvents.

Thus, based on the above model, the radius of the solvated lithium ion is expected to be in the order: Li^+ -PC > Li^+ -THF > Li^+ -DME > Li^+ -AN. This order matches exactly that of the polarization values (Fig. 3). The fact that the observed polarization behaviour is consistent with the estimated size of the solvated ion suggests that the second mechanism (see above) for intercalation is indeed operative, at least in pure solvents.

Consider now the observed behaviour in mixed solvents. In this case, the composition of the ionic solvation shell composition is related to the relative coordinating abilities of the component solvents in the mixture [13]. The values of the free energies for transfer of Li^+ ions (i.e., $\Delta_t G(Li^+)$) from PC to PC/AN, PC/THF or PC/DME mixtures (Table 1) indicate that the coordinating strength of the various cosolvents is: DME > THF > PC > AN. Thus, in PC/DME, the solvation shell is expected to be rich in DME. Hence, in this solvent mixture, due to the presence of both the solvents in the solvation shell, the size of the solvated lithium ion would be larger than that in pure DME, but smaller than in pure PC (cf., Fig. 4). A similar argument

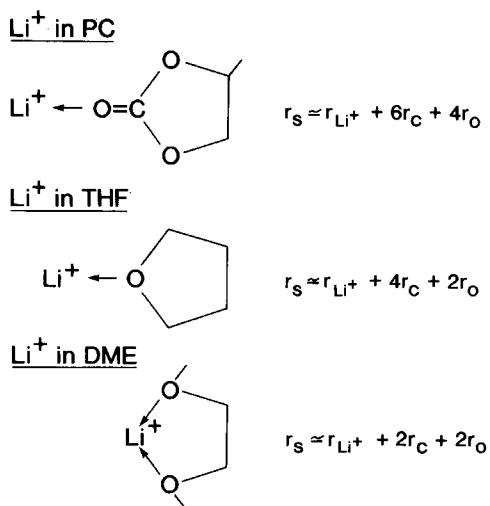


Fig. 4. Approximate radius of solvated lithium ion (r_s) in PC, THF and DME. The summed atomic radii are purely indicative; double bonds and hydrogen atoms have been ignored.

applies for PC/THF. In PC/AN mixtures, however, since PC is more strongly coordinating than AN, the solvation shell of the lithium ion will contain mainly PC and the size of the solvated ion should be essentially the same as in PC. Thus, in the solvent mixtures, the radius of the solvated Li^+ ion is expected to be in the order $\text{PC/AN}(= \text{PC}) > \text{PC/THF} > \text{PC/DME}$. The observed polarization behaviour (Fig. 3) is again consistent with this order. Such an observation lends further support to the proposal that the lithium ion enters the NbSe_3 lattice with its solvation shell intact.

Lattice diffusion coefficients of Li^+

The solid-state diffusion coefficients for Li^+ in a NbSe_3 lattice were measured by the galvanostatic intermittent titration technique developed by Weppner and Huggins [23–26]. In this method, a galvanostatic current pulse is applied to the cathode (NbSe_3). The consequent potential transient is measured over the period of this pulse.

For a solid-state diffusion-controlled process, the potential (E) versus time (t) relationship is:

$$\frac{dE}{d\sqrt{t}} = \frac{2V_m}{Fz_i} \times \frac{dE_s}{d\delta} \times \frac{1}{\sqrt{\pi D_{\text{Li}^+}}} \times \frac{I_0}{S} \quad (1)$$

where V_m = molar volume of NbSe_3 ($51.52 \text{ cm}^3 \text{ mol}^{-1}$); F = Faraday constant, C mol^{-1} ; z_i = charge on diffusing species; E_s = steady-state (equilibrium)

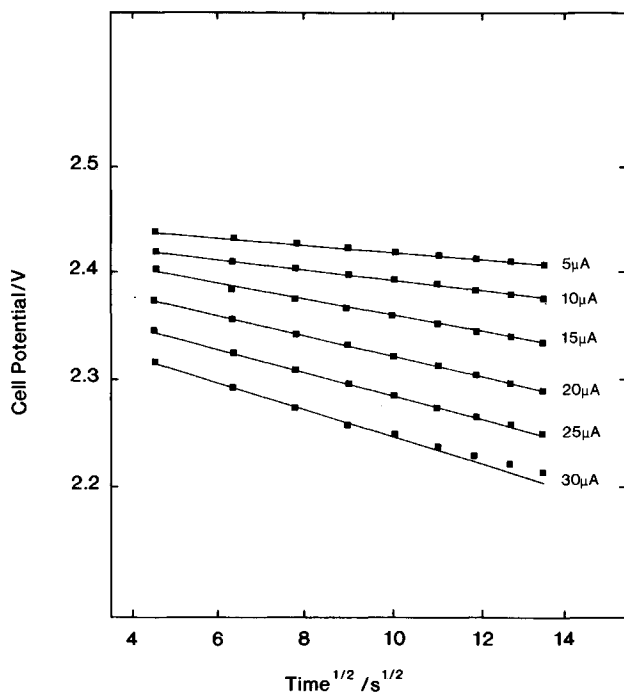


Fig. 5. Cell potential during discharge at various constant currents (1 M LiClO_4 in AN).

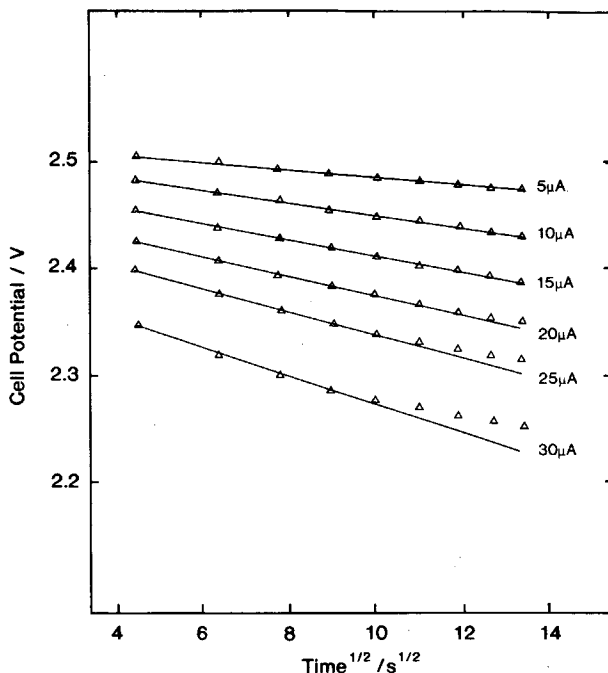


Fig. 6. Cell potential during discharge time at various constant currents (1 M LiClO₄ in PC/AN 50% vol./vol.).

potential of Li₃NbSe₃, V; δ = moles of Li⁺ intercalated into NbSe₃ during time t ; D_{Li^+} = diffusion coefficient of Li⁺ in NbSe₃ lattice, cm² s⁻¹; I_0 = applied current, A; S = area of NbSe₃ exposed to electrolyte, cm².

From eqn. (1), a plot of $dE/d\sqrt{t}$ versus I_0/S will be linear with a slope given by:

$$\text{slope} = \frac{2V_m}{Fz_i} \times \frac{dE_s}{d\delta} \times \frac{1}{\sqrt{\pi D_{\text{Li}^+}}} \quad (2)$$

This permits calculation of D_{Li^+} . Alternatively, D_{Li^+} can be calculated from eqn. (3) which is a rearranged form of eqn. (1):

$$D_{\text{Li}^+} = \frac{4}{\pi} \left[\frac{V_m}{SFz_i} \right]^2 \times \left[\frac{dE_s}{d\delta} \times I_0 \right]^2 \times \left[\frac{dE}{d\sqrt{t}} \right]^2 \quad (3)$$

Figures 5 and 6 show typical E versus $t^{1/2}$ plots for various currents in AN and PC/AN mixtures. In agreement with eqn. (1), the slope of the E versus $t^{1/2}$ plots is proportional to I_0 (Fig. 7), thus indicating that the experimental data are consistent with the theory upon which eqn. (1) is based. (Note, in the case of THF and PC/THF, the E versus $t^{1/2}$ plot was linear only at low currents (5–10 μA .)

The calculation of D_{Li^+} from eqn. (3) requires values for $dE_s/d\delta$. These have been determined for a small range of lithium stoichiometries in NbSe₃, and therefore allow the calculation of initial D_{Li^+} into a virgin NbSe₃ structure

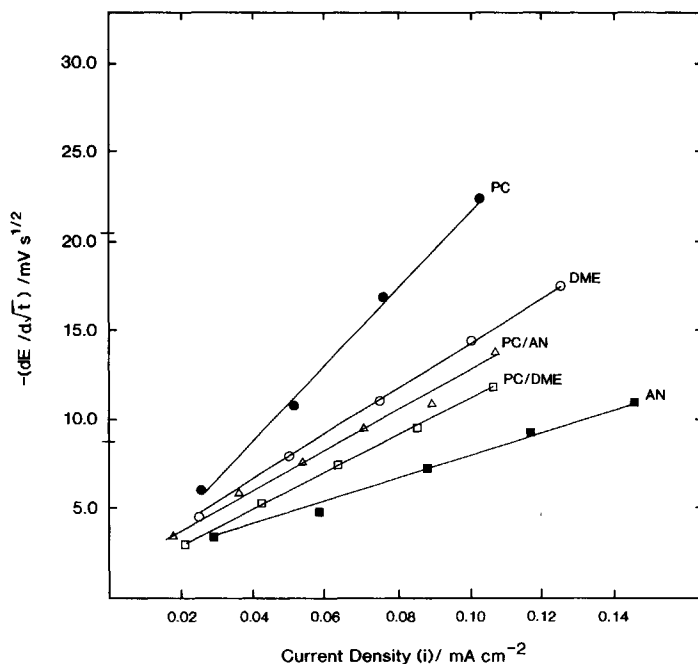


Fig. 7. Slope of polarization potential vs. \sqrt{t} as a function of applied current density.

TABLE 2

Initial Li^+ diffusion coefficients (D_{Li^+}) in the NbSe_3 lattice at 25 °C

Solvent	$dE/d\sqrt{t}$	Slope ^a	$dE/d\delta$	$10^7 \times D_{\text{Li}^+}$ ^b
PC	5.96	208.4	68.5	0.4
AN	3.47	64.1	66.3	3.6
THF	15.6	139.5 ^c	35.5	0.3
DME	4.53	125.6	112.3	2.8
PC/AN	3.40	113.0	76.9	1.7
PC/THF	6.80	162.7 ^c	93.9	1.2
PC/DME	3.07	103.3	90.9	2.9

^aSlope of $dE/d\sqrt{t}$ vs. I_0/S ; units, $\text{V cm}^2 \text{s}^{1/2} \text{A}^{-1}$.

^bUnits, $\text{cm}^2 \text{s}^{-1}$.

^c E vs. \sqrt{t} not truly linear except at 10 μA .

via eqn. (2). The $dE_s/d\delta$, $dE/d\sqrt{t}$, and calculated D_{Li^+} values are given in Table 2. With the exception of THF, it can be seen that D_{Li^+} generally follows the order predicted from the polarization measurements. This confirms that the electrode process is indeed controlled by the diffusion of solvated Li^+ ions. The measured diffusion coefficients in the various solvents (Table 2) are in the order: $\text{AN} > \text{DME} \approx \text{PC/DME} > \text{PC/AN} > \text{PC}$.

It is encouraging that the values for D_{Li^+} in DME and PC/DME are exactly the same since, in both solutions, the solvation sheath of Li^+ is

predominantly DME. Although the results for THF and PC/THF are anomalous, it should be remembered that the values in these solvents are estimates only, because E versus $t^{1/2}$ plots were not strictly linear as required by the model. The initial D_{Li^+} values in the investigated solvents range from 4×10^{-8} to $3 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. These values are generally an order of magnitude higher than those reported in the literature for TiO_2 , MoO_2 (framework lattice) and TiS_2 (layered lattice) [27]. The host lattice structure is known to play an important role in ion diffusion [7, 27]. For example, Winn [28] has shown that values for Na^+ diffusion in TiS_2 vary between 10^{-6} to $10^{-10} \text{ cm}^2 \text{ s}^{-1}$; the higher values are for a Na_yTiS_2 sample with an almost exact 1:2 ratio of Ti:S. Given that the fibrous structure of NbSe_3 [7] is very different to that of other electrode materials, the observed faster diffusion of Li^+ is not surprising.

When comparing the observed D_{Li^+} values with those reported in the literature, it must be remembered that diffusion coefficient data for polycrystalline material include a number of unknown parameters such as: effective surface area; particle size and orientation; diffusion pathway radius; pore size; influence of mobility in the liquid state [29]. Furthermore, diffusion in a polycrystalline sample is not uni-directional and the active surface area is greater than the geometric cross-sectional area. Thus, quantitative comparisons are not straightforward.

Conclusions

The present polarization and diffusivity results for NbSe_3 in various solvents provide important evidence in support of the proposal that, during discharge of lithium batteries, Li^+ is intercalated into NbSe_3 as a solvated rather than a desolvated ion.

Acknowledgements

This work was supported in part by the Australian Research Council. P. Atkins acknowledges with thanks the support of a Commonwealth of Australia Postgraduate Award.

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