Selection of new Kynar-based electrolytes for lithium-ion batteries

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Abstract

New electrolyte solution compositions have been identified for use in lithium-ion batteries after gelling with an appropriate quantity of Kynar polymer. Since the Li^+ conducting medium is largely the liquid electrolyte component, the assessment of these solutions as suitable lithium-ion cell candidates were investigated before adding the polymer. Selected electrolyte solutions were then used in the preparation of polymer gels. The specific conductivities of Kynar-based gels were determined as a function of salt concentration and polymer concentration. Optimised self-supporting polymer films, based on mixtures of ethylene carbonate (EC), ethylmethyl carbonate (EMC) and lithium hexafluorophosphate ($LiPF_6$) or lithium tetrafluoroborate ($LiBF_4$), showed good high current density cycling performance when used as separators in coke and $Li_{1-x}Mn_2O_4$ (spinel) half-cells. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Lithium battery technology has developed to a stage where high output voltages are now available from lithium metal-free 'rocking-chair', or lithium-ion, cells [1]. The use of highly oxidising positive electrodes such as the $Li_{1-x}Mn_2O_4$ spinel, with their high charging voltages, requires electrolytes that are resistant to oxidation to above 4.5 V [2]. Further, the chosen electrolyte must have high conductivity and be compatible with the carbon negative electrode down to 0 V.

A promising approach to the development of compact lithium-ion batteries involves use of a lithium-ion conducting gel, in which a conventional non-aqueous liquid electrolyte is immobilised by a polymer matrix [3]. This combines the electrical properties of the high conductivity liquid electrolyte solution with the mechanical properties of the host polymer. Recently, a study of gels prepared using fluorinated copolymer blends was presented by Schmutz et al. [4] and Gozdz et al. [5]. Kynar™, a commercially available copolymer blend based on polyvinylidene fluoride (PVDF) and hexafluoropropylene (HFP), has been specifically designed for use in wire and cable constructions and other uses requiring high flexibility and good resistance to impact. Compared to vinylidene fluoride homopolymers, Kynar is easily processed and has better flexibility and stress crack resistance with high thermal stability.

In this paper, we describe the selection of suitable parent electrolyte solutions and their subsequent incorporation into a polymer matrix using different polymer/electrolyte ratios. Electrodes constructed using coke or $Li_xMn_2O_4$ (spinel) with Kynar-based gel electrolytes were tested for cyclability at high charge/discharge rates.

2. Experimental

Lithium battery grade ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), (all from

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Grant Chemicals), and ethylmethyl carbonate (EMC, Tomiyama), were used as received. Each binary solvent mixture was prepared by adding an appropriate weight of second solvent to EC. To each of these mixtures, an appropriate quantity of lithium hexafluorophosphate (LiPF$_6$, Morita) or lithium tetrafluoroborate (LiBF$_4$, Tomiyama) was added to make electrolyte solution concentrations of 0.9 or 1.0 mol kg^{-1}.

All conductance measurements were made using variable frequency ac impedance spectroscopy. Ac impedance measurements were made with a Solartron 1255 frequency response analyser coupled to a Solartron 1286 potentiostat under computer control. A glass dip-type cell with platinum electrodes was used for liquid conductance measurements. The cell compartment was made from glass, into which the connecting cap with electrodes was attached by a Quickfit™ joint. Each of these cells had a cell constant close to 1.0 cm^{-1}. After filling, the sealed cells were removed from the glove box and immersed in an oil bath under temperature control (Haake DC5 and EK30 cooler) at 25 ± 0.05°C.

For conductivity measurements, gel films with varying polymer concentration were prepared by suspending appropriate amounts of Kynar™ Flex-2801 (Elf Atochem) in 1 EC:1 PC binary mixture containing LiPF$_6$ (1 mol kg^{-1}). Each mixture was lightly pressed at 100°C for 1 min between polished aluminium sheets separated by approximately 0.3-mm thick polytetrafluoroethylene (PTFE). The final products were highly transparent, colourless self-supporting films. The macroscopic viscosity of each film was increased by varying the amount of Kynar added, up to a maximum of 50 wt.%. Gels with varying salt concentration were prepared by dissolving Kynar into the EC:PC binary liquid containing LiPF$_6$ at known concentrations in the range 0.01–1 mol kg^{-1}. Two gel electrolytes of this nature were prepared for experiments studying the salt concentration dependence of conductivity, with polymer concentrations of 20 wt.% and 40 wt.%, respectively.

For measurements of the conductivity of the gel electrolytes, a two-electrode cell configuration was used, constructed from a PTFE body housing 10-mm diameter stainless-steel electrodes. The electrodes were screwed into the cell, sandwiching the gelled film between them. The fully assembled cell was placed in a Buchi TO-51 furnace, and the temperature of the cell was monitored by a K-type thermocouple. The cells were left for at least 1 h at each temperature to allow thermal equilibrium to be reached before measurements were made.

Kynar gel electrolytes for galvanostatic cycling experiments were prepared by solvent casting. Kynar (1 g) was dissolved into 1 g anhydrous tetrahydrofuran (THF, Aldrich). To this was added 2.5 g of the appropriate parent liquid electrolyte solution, followed by stirring. The viscous slurry was cast onto a PTFE sheet, using a Doctor-blade set to 0.5-mm thickness, and allowed to dry for 20 min. The resulting film, which was approximately 100 μm

thick, was cut to size and placed into a closed vessel containing some parent solution, which allowed recovery of any evaporated solvent. All preparations were performed in an argon filled dry box, where H$_2$O and O$_2$ levels were maintained below 1 ppm.

Positive electrodes were prepared by dissolving Kynar in *N*-methylpyrolidinone (NMP) followed by addition of ground Li$_{1-x}$Mn$_2$O$_4$ [6] and carbon Super-S, in a (80:10:10) mass ratio. The solution was stirred for 15 h under moderate heating. The casting of the slurry was performed using a K-control coater KCC 302 (Erichsen). The aluminium substrate (Aldrich) was set on a grooved plate connected to a vacuum pump, which maintained a flat surface. The slurry was cast by an adjustable micrometer blade, that controlled the thickness of the coating, and left to dry at room temperature for approximately 30 min, before vacuum drying at 70°C for 12 h. The thickness of each composite electrode was in the range of 40–50 μm. Coke electrodes, kindly supplied by Danionics, using ethylenepropylenediene monomer (EPDM) as the binder and cast with an active mass of 4.5 mg cm^{-2}, were dried for 12 h at 70°C under dynamic vacuum.

Galvanostatic cycling of three-electrode cells, with lithium metal reference electrodes, was performed using a Macpile system (Biologic). All voltages are quoted with respect to Li/Li$^+$.
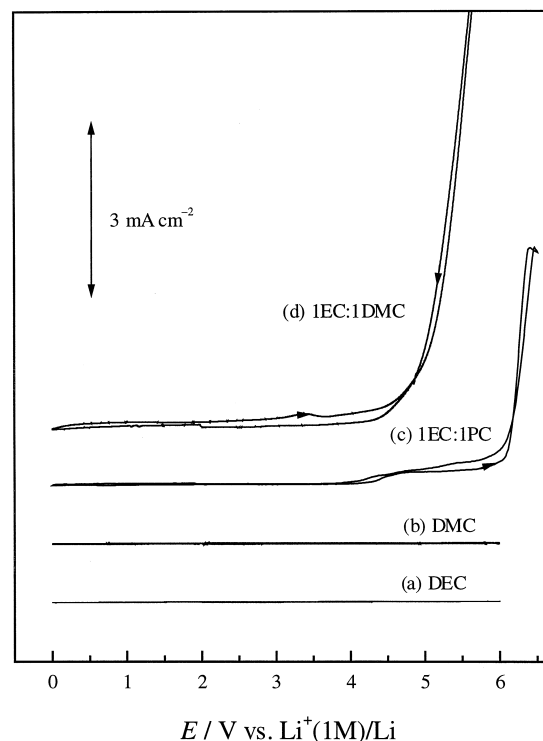

Fig. 1. Voltammograms of selected solvents and binary mixtures, without added electrolyte, at a Pt microelectrode. The curves represent (a) DEC (b) DMC (c) 1 EC:1 PC (d) 1 EC:1 DMC. Sweep rate = 200 mV s^{-1}.

Determinations of solvent stability windows were made using a two-electrode cell configuration consisting of a Li/Li$^+$ (1 mol kg^{-1}) counter-reference electrode, described elsewhere [7], and a 25 μm diameter Pt microworking electrode. These measurements were made using an Autolab PGSTAT-10 (Eco Chemie) with low current (ECD) module.
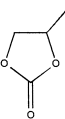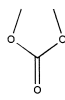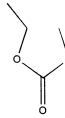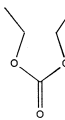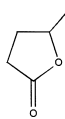
3. Results and discussion

3.1. Electrochemical stabilities of solvents

The cathodic ($E_{cathodic}$) and anodic (E_{anodic}) limits, at Pt, of a selection of non-aqueous solvents were determined by microelectrode cyclic voltammetry, over the voltage range 0 V → +6 V. Fig. 1 shows voltammograms of some solvents that are stable in this range. Each potential limit was determined as the potential at which a rapid rise in current was observed and continues to increase as the potential was swept in the same direction. Table 1 summarises the results from these experiments. For EC and PC, no cathodic breakdown occurred on sweeping to 0 V and the oxidation potentials were sufficiently high, at +5.5 V, to be acceptable for high voltage cathode materials [2]. The carbonate based solvents, DMC, diethyl carbonate (DEC) and EMC, all show no apparent electrochemical breakdown at Pt over a very wide potential range. The reason for this is unclear at this time, but it is thought that some passivating reaction may be occurring at the platinum electrode surface that may also be reflected in the good passivating behaviour observed on carbonaceous materials [8,9].

Table 1
Some physical properties of selected non-aqueous solvents

Solvent		b.p.	m.p.	$E_{cathodic}$	E_{anodic}
		°C		V vs. Li$^+$ (1M) / Li	
ethylene carbonate (EC)			35 - 38	0 [†]	+5.5
propylene carbonate (PC)		240		0 [†]	+5.5
dimethyl carbonate (DMC)		86 - 89		0 [†]	6 [†]
ethylmethyl carbonate (EMC)		109	−14	0 [†]	6 [†]
diethyl carbonate (DEC)		125 - 126		0 [†]	6 [†]
γ-valerolactone (GVL)		208	−31	+2.5	+4.5

[a] No solvent breakdown observed.
Electrochemical stability window was measured between 0 V and 6 V vs. Li$^+$/Li.
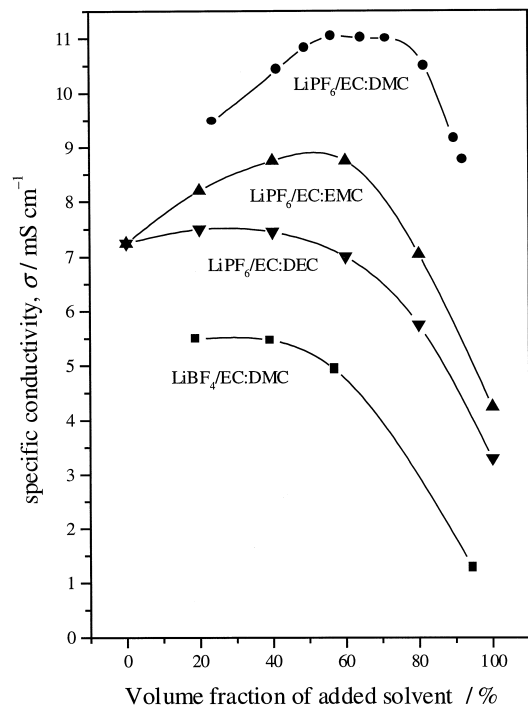
Fig. 2. The conductivity dependence of EC based electrolyte solutions with varying added second solvent component. Fractions are noted in percentage of total volume. All salt concentrations are 1 mol kg^{-1}.

Table 2
Conductivity maxima of optimised solutions prepared from Li salts dissolved in mixtures of selected electrochemically stable solvents

Salt	Solvent mixture components		σ_{max} (mS cm^{-1})
	1	2	
LiPF$_6$[a]	EC $(1-y)$	DMC $y = 0.4–0.8$	11.0
LiPF$_6$	EC $(1-y)$	DMC $y = 0.3–0.8$	11.0
	EC $(1-y)$	EMC $y = 0.3–0.6$	9.0
	EC $(1-y)$	DEC $y = 0.2–0.4$	7.5
LiBF$_4$	EC $(1-y)$	DMC $y = 0.2–0.4$	5.5
	EC $(1-y)$	EMC $y = 0.2–0.4$	5.5
	EC $(1-y)$	DEC $y = 0.2–0.4$	4.3

[a]Data taken from Ref. [2].

3.2. Parent electrolyte conductivities

The variation in the ambient temperature conductivity of a mixture of the high dielectric constant solvent EC with the low viscosity solvent DMC is shown in Fig. 2. The maximum conductivity was observed for the EC:DMC solvent composition with volume ratios 3:2 to 1:4 for the LiPF$_6$ solution, and 4:1 to 3:2 for the LiBF$_4$ solution. The conductivity maximum for LiPF$_6$ solutions was also observed by Tarascon and Guyomard [2] over a similar composition range. The figure shows that the higher boil-
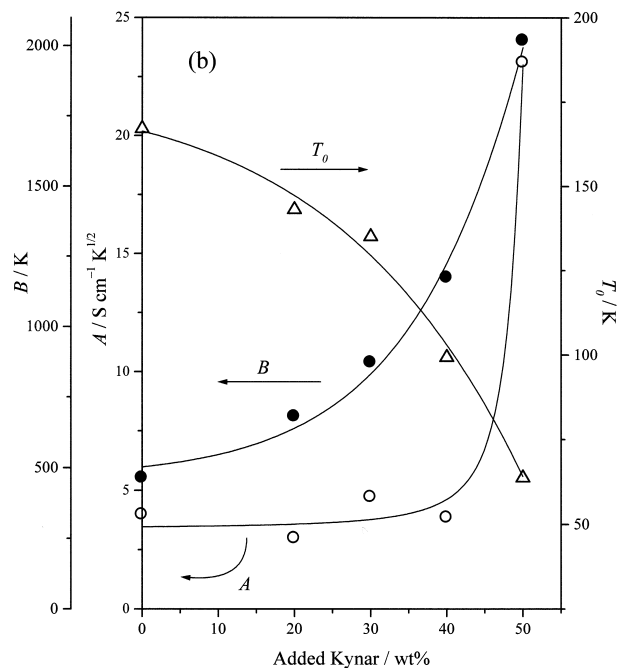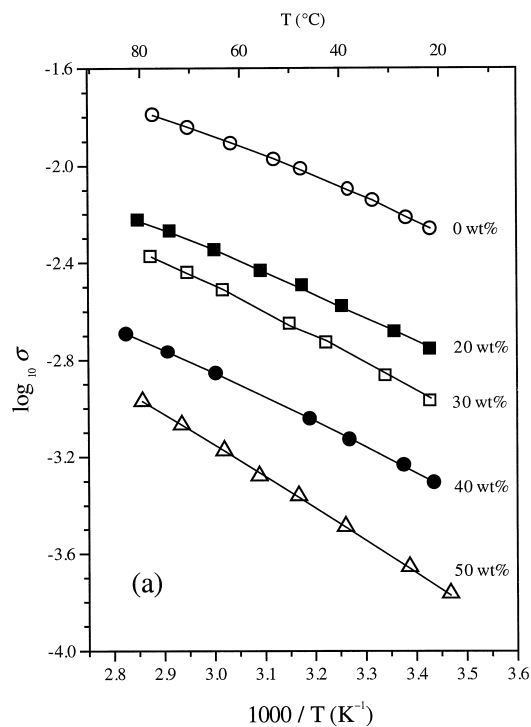

Fig. 3. (a) Arrhenius plots of experimental conductivity (σ) for gels of LiPF$_6$ (1 mol kg^{-1}): 1 EC:1 PC: Kynar (x wt.%). The solid lines indicate the fits according to the VTF Eq. (1); (b) Plots of the VTF fitted parameters T_0, A and B of Eq. (1) as a function of added Kynar (wt.%).

ing point EMC can replace the DMC component in each case without significantly reducing its conductivity. The compositions of each electrolyte solution with conductivity values close to the maximum are listed in Table 2. It is evident that on increasing the alkyl group chain length from DMC to EMC to DEC, the conductivity maximum σ_{max} decreases and the maximum occurs at a lower fraction of added solvent to EC. This is an important factor, since a high boiling point solvent is more likely to remain entrapped within the polymer matrix at prolonged higher temperatures without significant loss of solvent.

3.3. Polymer content

Fig. 3a shows the conductivity of a $LiPF_6$:1 EC:1 PC solution and gels of this electrolyte containing varying amounts of added Kynar as a function of temperature. As observed with viscous electrolytes and many polymeric systems [3], the profile of the log σ vs. $1000/T$ shows deviation from the Arrhenius behaviour. The thermal dependence of this conductivity must therefore be described by a non-Arrhenius relationship, such as the empirical expression of the form

$$\sigma \cdot \sqrt{T} = A \cdot \exp\{-B/(T - T_0)\} \qquad (1)$$

where A, B and T_0 are fitted parameters. This equation is related to the empirical Vogel–Tammann–Fulcher (VTF) [10] expression and may be related to the free volume-based theories of mobility. The results of the fits to Eq. (1) over a range of Kynar polymer concentration are summarised in Table 3. The observed values of B are smaller than those of PEO-based polymer electrolytes but are comparable with other gels [3].

Fig. 3b shows the variation of the fitted parameters T_0, A and B obtained from the conductivity data as a function of added Kynar, for thermally cast gels. Evidently, some change occurs in the conduction pathways of the gel at approximately 30–35 wt.% of Kynar. This feature was also observed by Bohnke et al. [3,11] in $LiClO_4$:PC:PMMA gels, who attributed it to two conduction paths. As polymer is added, the effective high conductivity path decreases resulting in an increase in A and B, while T_0
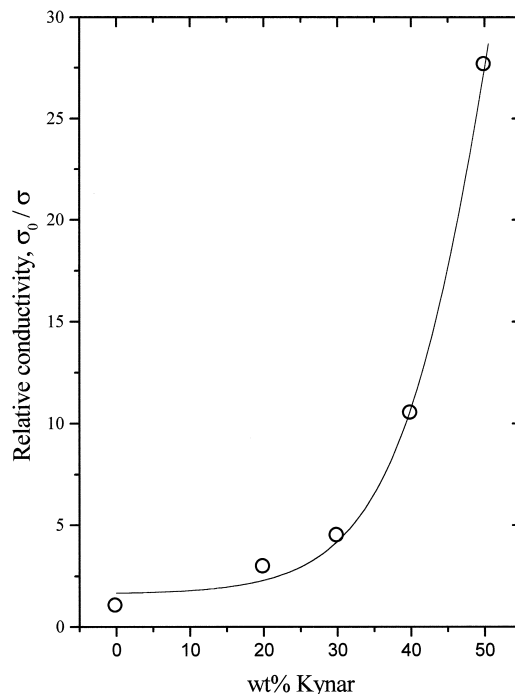

Fig. 4. Variation of the relative conductivity (σ_0/σ_x) at 25°C of $LiPF_6$:1 EC:1 PC:Kynar as a function of added polymer.

decreases. This feature may also be seen in Fig. 4, where the relative variation in specific conductivity (σ_0/σ) at 25°C vs. the gel composition is plotted (σ_0 is the conductivity of the liquid electrolyte at 25°C). The conductivity decreases very slightly for gels containing small amounts of Kynar, but decreases rapidly for polymer concentrations above 30–35 wt.% of added polymer.

For low polymer concentrations (< 30 wt.%) the gelled electrolyte may be considered to be a liquid electrolyte entrapped in a polymer matrix. The matrix is likely to have very little effect on the electrolyte and hence on the conduction, as shown in Fig. 4, leading to an almost constant pre-exponential factor, A (Fig. 3b). Similarly, the value of B increases only slightly suggesting that ion migration is not influenced to any significant level.

On increasing the polymer content beyond 35 wt.% strong interactions between the polymer chains and the

Table 3
Fitted parameters obtained from conductivity data for $LiPF_6$ (1 mol kg^{-1})/1 EC:1 PC/Kynar (x wt.%)

Kynar added (wt.%)	T_0 (K)	A (S cm^{-1} $K^{1/2}$)	B (K)
0	167 ± 8	4.0 ± 0.6	464 ± 45
20	143 ± 18	3.0 ± 1.0	681 ± 144
30	135 ± 5	4.7 ± 0.5	873 ± 43
40	99 ± 23	3.9 ± 2.0	1174 ± 241
50	64 ± 7	23 ± 5	2019 ± 109

Table 4
The Casteel–Amis parameters at 25°C for $LiPF_6$ (1 mol kg^{-1}):1 EC:1 PC/Kynar (x wt.%) electrolytes, where x is the percentage of polymer added

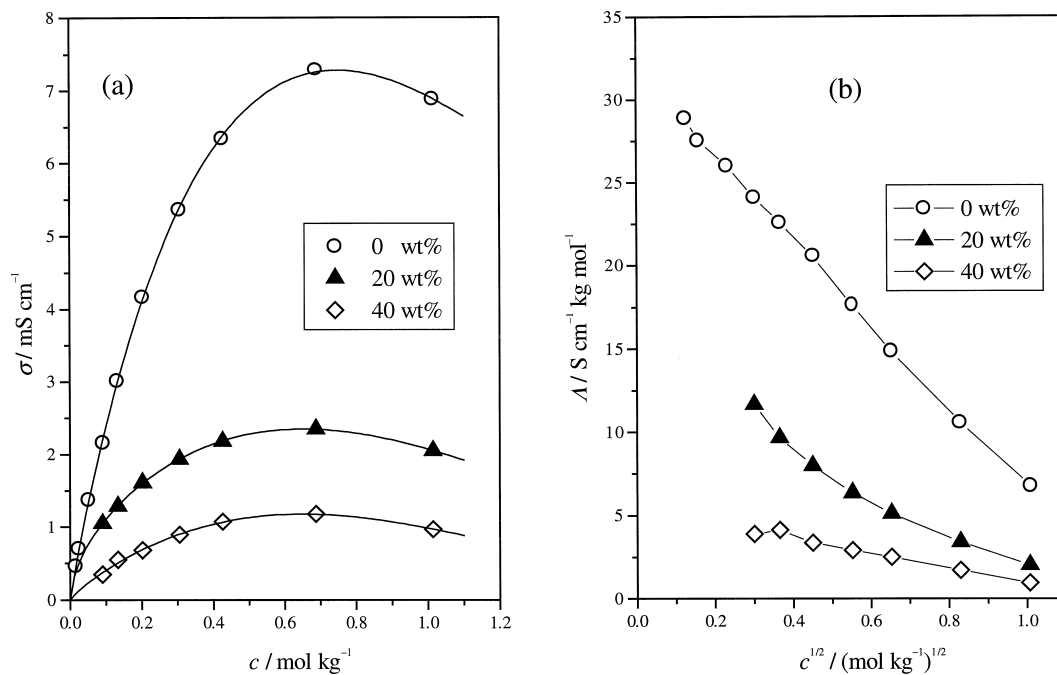| Kynar added (x wt.%)	σ_{max} (mS cm^{-1})	c_{max} (mol kg^{-1})	a	b (mol kg^{-1})^2
0	7.3	0.75	0.95	−0.08
20%	2.4	0.65	0.58	−0.52
40%	1.2	0.65	0.82	−0.76

Fig. 5. Salt concentration dependence of (a) specific conductivity, with fits according to the Casteel–Amis equation, and (b) molal conductivity of 1 EC:1 PC:Kynar (wt.%) at 25°C containing LiPF$_6$.
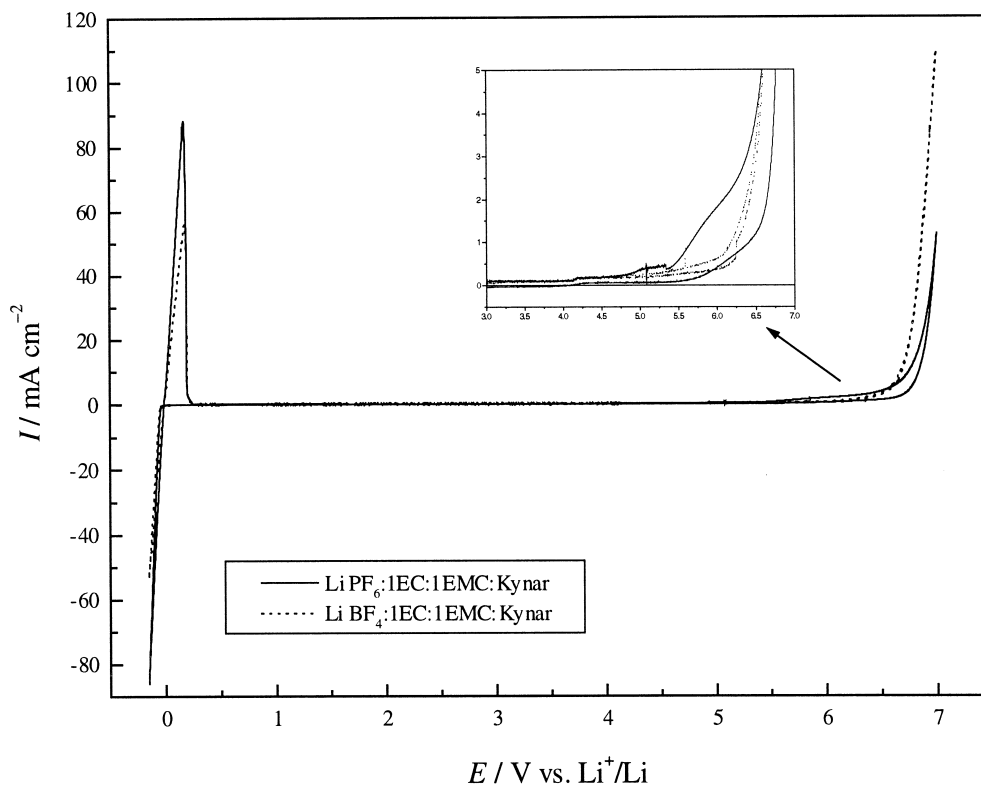

Fig. 6. Voltammograms of 1 EC:1 EMC:Kynar gel films containing 0.9 mol kg^{-1} LiPF$_6$ and LiBF$_4$, respectively, at a 25-μm diameter Pt microelectrode (sweep rate = 20 mV s^{-1}).

electrolyte may result in a decrease in the number of charge carriers and an increase in B as well as a decrease in T_0 as the free volume decreases.

Attention is now drawn to two polymer concentrations: above and below the 30–35 wt.% 'cross-over' point. The specific conductivity σ generally passes through a maximum at a salt concentration characteristic of the solvent and solute. In recent years, interest in σ_{max} values for a range of solution mixtures has proved its importance in the development of high energy density lithium rechargeable battery systems [12]. The specific conductivity values σ for the gels were analysed using the semi-empirical Casteel–Amis equation [13], where c_{max} is the concentration corresponding to the maximum specific conductivity. The constants a and b are arbitrarily chosen and are adjusted during the non-linear least-squares (NLLS) fit along with σ_{max} and c_{max}. Experimental points for the $LiPF_6$:1 EC:1 PC: Kynar (x wt.%) gels at 25°C are presented in Fig. 5a with Casteel–Amis fits shown as solid lines. The fitted parameters are listed in Table 4 for each of the electrolyte systems. The maximum conductivity values σ_{max} for each

of the gel systems decrease in the order $x = 0$ wt.% (7.28 mS cm^{-1}) $> x = 20$ wt.% (2.35 mS cm^{-1}) $> x = 40$ wt.% (1.18 mS cm^{-1}).

The effect of ion association can be seen by plotting the molal conductivity Λ as a function of the square root of lithium salt concentration for the liquid and gelled electrolytes, as shown in Fig. 5b. The profiles in all three show a fall in molal conductivity with increasing salt concentration. This has been attributed to the increasingly significant presence of neutral ion-pairs formed by the association of cations and anions that can no longer participate in conduction [14]. The difference in Λ between the liquid and gels may be attributed to an increase in the microscopic viscosity. Estimates of the molal conductivities at infinite dilution Λ_0 can be made by extrapolation of the linear function at low salt concentrations. The values of Λ_0 obtained in this way were 31.97, 18.85 and 7.41 S cm^{-1} kg mol^{-1} for the liquid EC:PC electrolyte, 20 wt.% Kynar gel and 40 wt.% Kynar gel, respectively. As the concentration of Kynar is increased to 40 wt.% the possibility of cross-linking between polymer chains becomes more likely,
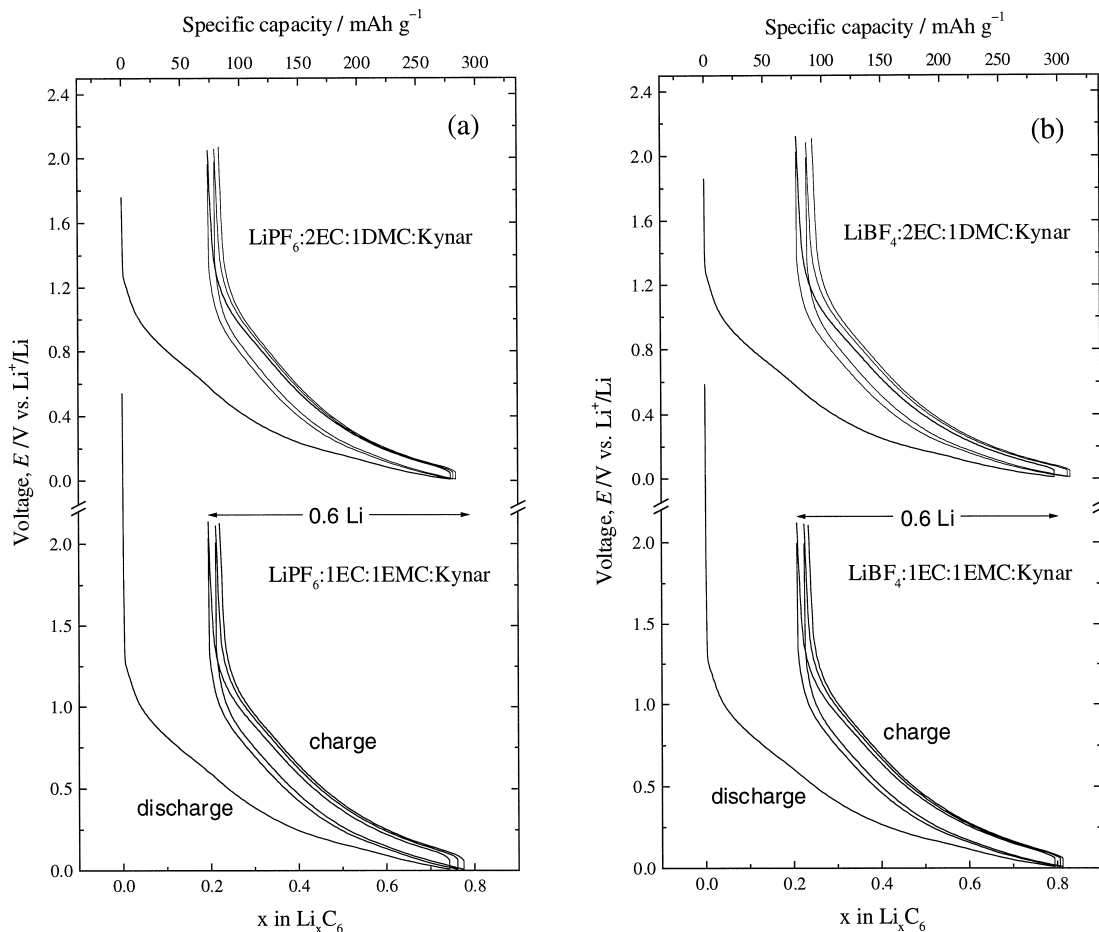

Fig. 7. The galvanostatic charge/discharge profiles of coke electrodes shown as a comparison of the first three cycles from (a) $LiPF_6$:2 EC:1 DMC:Kynar and $LiPF_6$:1 EC:1 EMC:Kynar gels, and from (b) $LiBF_4$:2 EC:1 DMC:Kynar and $LiBF_4$:1 EC:1 EMC:Kynar.
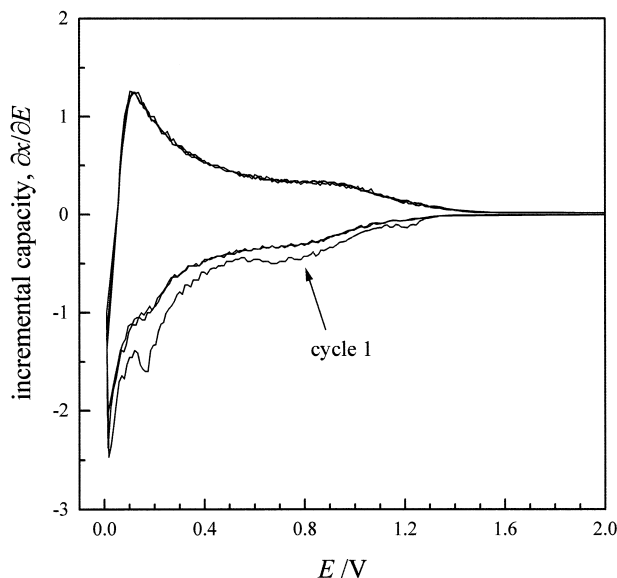
Fig. 8. Incremental capacity plot for the first three cycles of coke in $LiBF_4$: 1 EC:1 EMC:Kynar gel.

cations are predominantly surrounded by polymer chains, shielding from anion association takes place with a corresponding decrease in the slope of the Λ vs. $\sqrt{c}$ profile.

3.4. Electrochemical behaviour of Kynar gelled films

Fig. 6 shows voltammograms of 1 EC:1 EMC:Kynar gelled electrolytes containing $LiPF_6$ and $LiBF_4$ at a 25 μm diameter Pt microelectrode (sweep rate = 100 mV s^{-1}). The cathodic window is limited by the deposition and subsequent stripping of lithium at around 0 V. The stability of each electrolyte is very good, with no electrochemical oxidation occurring until a potential of greater than $+5$ V is reached. The $LiPF_6$ based film shows a pre-oxidation wave starting at about 5.25 V. However, as in the case of the $LiBF_4$ electrolyte, breakdown does not take place until nearly 6 V.

The cycling behaviour of coke half cells with 2 EC:1 EMC:Kynar and 1 EC:1 EMC:Kynar separators, containing $LiPF_6$ or $LiBF_4$ in each, are compared in Fig. 7a and b, respectively. After an irreversible loss of capacity, which is generally encountered on the first intercalation of Li$^+$ into carbonaceous materials [15], each electrolyte allowed rapid and reversible intercalation of 0.6 Li ions per six carbons ($Li_{0.6}C_6$). This feature may be seen more clearly in Fig. 8, where the incremental capacity, $(\partial x / \partial E)$, vs. potential, E, for the $LiBF_4$:1 EC:1 EMC:Kynar film is
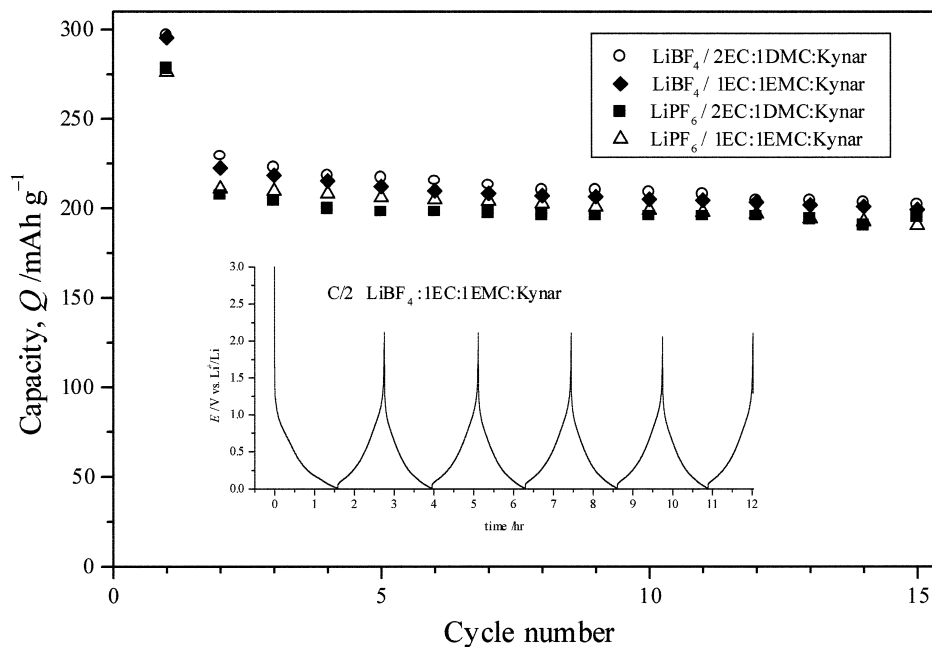
leading to a decrease in the ionic motion. The free volume decreases with increasing polymer concentration and the mode of ionic solvation will eventually change. Since the

Fig. 9. Specific capacity vs. cycle number of coke with Kynar gel electrolytes based on (i) $LiBF_4$:2 EC:1 DMC, $I = 0.73$ mA cm^{-2}; (ii) $LiBF_4$:1 EC:1 EMC, $I = 0.73$ mA cm^{-2}, (iii) $LiPF_6$:2 EC:1 DMC; $I = 0.51$ mA cm^{-2} and (iv) $LiPF_6$:1 EC:1 EMC, $I = 0.73$ mA cm^{-2}. All rates are at C/2. The inset shows the first five chronopotentiogram cycles for the new $LiBF_4$:1 EC:1 EMC:Kynar gel.

shown. On the first cycle, the irreversible peaks are believed to be due to electrolyte reduction and the formation of passivating films at the surface of the carbon [8]. The capacity loss of 26.2% on the first cycle for the EC:EMC based gels is slightly lower than 26.4% seen with the EC:DMC electrolytes. It has been reported recently that the behaviour of graphite anodes in EC:EMC solutions is slightly better than, or similar to, EC:DMC mixtures [16]. The surface layer formed on carbon at low potentials is composed of a mixture of lithium carbonate, lithium alkyl carbonates and salt reduction products. It is thought that EMC is superior to DMC at forming a stable protecting film due to the greater presence of Li_2CO_3 at the surface.
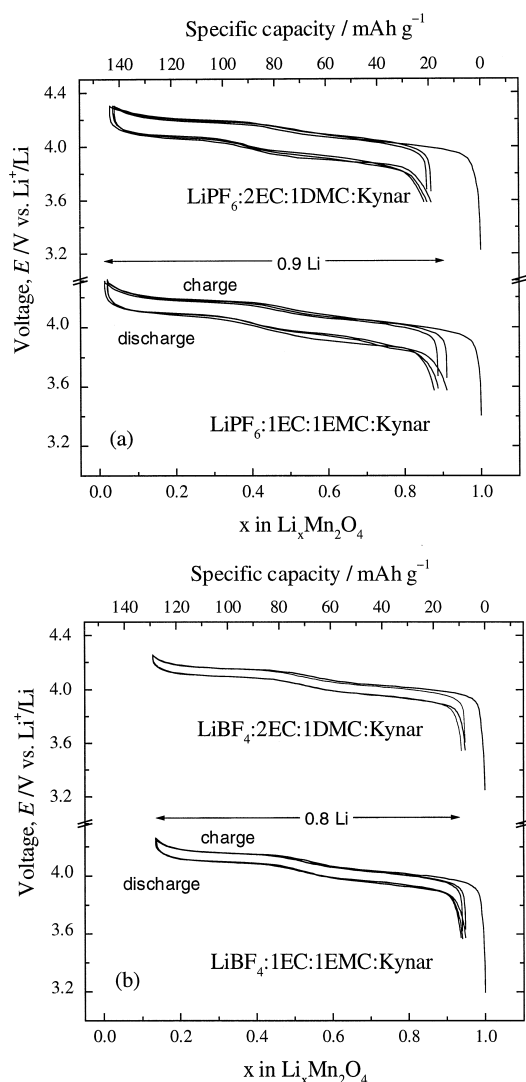
Fig. 9 shows the plot of specific capacity vs. cycle number for each Kynar film at coke with a charge/discharge current density of 1 mA cm^{-2} (C/2). In each case, a specific capacity of more than 200 mA h g^{-1} was obtained.

Cells prepared using $Li_{1-x}Mn_2O_4$ (Fig. 10) as the working electrode were cycled at relatively high current densities (0.7 mA cm^{-2}), representing a C/2 rate. The cells were initially charged (extraction of Li^+) to 4.3 V then discharged to 3.5 V. On comparison of the charge/discharge curves for each electrolyte film, it is seen that the Kynar films containing $LiPF_6$ can remove $x = 0.9$ Li from the spinel material and than those with $LiBF_4$ can only remove $x = 0.8$ Li. This is seen more clearly in the specific capacity vs. cycle number plot (Fig. 11), where both the $LiPF_6$ Kynar films show discharge capacities of about 130 mA h g^{-1}, leveling off at 122 mA h g^{-1}. The $LiBF_4$ films show initial discharge capacities of 120 mA h g^{-1}, decreasing to about 110 mA h g^{-1} after 20 cycles. These results indicate similar performance of the macroscopically solid Kynar films as their parent liquid electrolytes.

4. Conclusions

In this paper, the electrochemical stability of a series of solvents was determined, followed by conductivity measurements of combinations of those solvents that were stable over the range 0 V → +5 V vs. Li^+/Li. Selected electrolyte solutions, optimised for conductivity, were used as parent electrolytes in the preparation of polymer gels. The polymer content has been shown to have an effect on the conduction properties of the electrolyte film. Specific conductivities of EC:PC:Kynar based gels were determined as a function of salt concentration, polymer concentration and temperature. As with other polymeric systems, the weight of Kynar should be kept below approximately 30 wt.% to maintain a liquid-like conduction mechanism while providing mechanical properties at the macroscopic level similar to those of conventional polymer electrolytes. The ambient temperature conductivities of gels based on 2 EC:1 DMC and 1 EC:1 EMC containing $LiPF_6$ or $LiBF_4$ were all above 2 mS cm^{-1}.

These Kynar gel films were used as electrode separators in half-cells using coke as the carbon based anode material and $Li_{1-x}Mn_2O_4$ (spinel) as the cathode material. In general, Kynar films based on EC electrolytes containing either DMC or EMC as a second component performed in a similar manner to their parent liquid solutions. Cells containing the new Kynar films based on the higher boiling point EC:EMC binary solvent mixture, were shown to
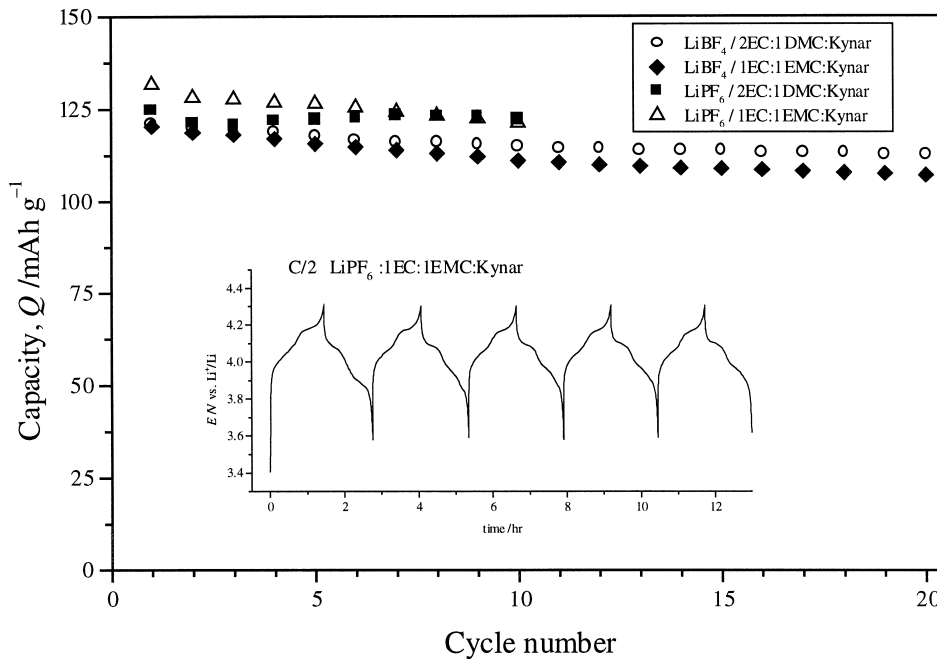

Fig. 10. The galvanostatic charge/discharge profiles of $Li_{1-x}Mn_2O_4$ electrodes shown as a comparison of the first three cycles from (a) $LiPF_6$:2 EC:1 DMC:Kynar and $LiPF_6$:1 EC:1 EMC:Kynar gels, and from (b) $LiBF_4$:2 EC:1 DMC:Kynar and $LiBF_4$:1 EC:1 EMC:Kynar.

Fig. 11. The specific capacity vs. cycle number of $Li_{1-x}Mn_2O_4$ with Kynar gel electrolytes based on (i) $LiBF_4$:2 EC:1 DMC, $I = 0.73$ mA cm^{-2} (ii) $LiBF_4$:1 EC:1 EMC, $I = 0.73$ mA cm^{-2} (iii) $LiPF_6$:2 EC:1 DMC, $I = 0.51$ mA cm^{-2} (iv) $LiPF_6$:1 EC:1 EMC, $I = 0.73$ mA cm^{-2}. All rates are at C/2. The inset shows the first five chronopotentiogram cycles for the new $LiPF_6$:1 EC:1 EMC:Kynar gel.

cycle well with coke and spinel electrodes at high current densities of around 1 mA cm^{-2}.

Acknowledgements

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