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# Low temperature electrolytes for Li-ion PVDF cells

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## Abstract

New electrolyte solutions based on ternary and quaternary solvent mixtures containing significant amounts of toluene (tol) have been evaluated. Liquid electrolytes containing $LiAsF_6$ and $LiPF_6$ exhibit electrolytic conductivities $> 1$ S $cm^{-1}$ down to $-50$°C. When incorporated into PVDF host matrixes, these multicomponent solutions exhibit reduced conductivities but still remain sufficiently high, yielding useful conductivities down to at least $-40$°C. $LiC_6$/PVDF-electrolyte/$LiCoO_2$ cells containing these multicomponent electrolyte solutions are stable and highly reproducible. Ambient temperature performance is essentially equal to comparative $LiC_6$/PVDF/$LiCoO_2$ cells containing ternary mixtures such as ethylene carbonate (EC):dimethyl carbonate (DMC):diethyl carbonate (DEC) and EC:ethylmethyl carbonate (EMC):DMC; but at $-20$°C, $-30$°C and $-40$°C, cells containing the quaternary mixed solvent EC:EMC:methyl acetate (MA):tol are clearly superior. Capacity retention of cells utilizing this quaternary solvent in PVDF at $-40$°C is 50% of nominal capacity at ambient temperatures.

*Keywords:* Low temperature electrolytes; Methyl acetate; Ethylene carbonate; Ethylmethyl carbonate; Toluene; Dimethyl carbonate; Diethyl carbonate; Propylene carbonate; PVDF; Li-ion cells; $LiAsF_6$; $LiPF_6$

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## 1. Introduction

There are a number of terrestrial and space applications for Li-ion polymer cells which require operation at temperatures well below 0°C. The development of liquid electrolytes, which exhibit high conductivities and which are stable at both anode and cathode, has been the subject of previous research over a number of years [1–6]. While considerable success has been achieved, particularly for operation of Li-ion cells down to $-20$°C, practical electrolytes capable of operating below $-20$°C remains a major problem. To add to the complexity of these requirements, the present research focuses on polymer electrolytes which exhibit diminished conductivities, particularly the PVDF-based electrolyte developed at Bellcore [7,8]. The use of PVDF-based hosts for electrolytes raises an additional problem, e.g., the solubility and swelling of these polymers in solvents such as PC, DMF, γ-BL, DEC and EC [9]. The present approach to developing low temperature electrolytes is a common one, i.e., the use of mixtures of various solvents to optimize both conductivity and stability. The use of an alkyl carbonate as initially reported in Ref. [10] is important to both promote stability of the passive anode film (e.g., EC, DMC, and EMC). In addition, the high dielectric constant of EC is an important property contributing to solubilities and conductivity by minimizing ion association. However, many of these carbonates have moderate to high viscosities and relatively high melting points as indicated in Table 1. Solvents such as MF and methyl acetate MA possess very low freezing points and very low viscosities which are important properties in developing a multicomponent electrolyte capable of exhibiting high conductivities at low temperatures (at least $1 \cdot 10^{-3}$ S $cm^{-1}$ at $-40$°C and below). However, as is well known (e.g., Refs. [1,10]), both MF and MA are ‘‘aggressive’’ solvents, and without additions of other solvents to protect the anode, cells with these esters do not cycle well. Cycling efficiency of Li-ion cells containing either MF or MA can be improved by including one or more carbonate solvent, but further improvements are still necessary for maximum stability. The present approach is to incorporate a hydrocarbon solvent such as toluene. Toluene has many desirable properties which include its large liquidus range (see Table 1) and its stability towards lithium. In fact metallic lithium can be stored in solvents

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Table 1
Physical properties of selected aprotic solvents[a]

| Solvent | $\varepsilon$ | $\eta$ (cP) | fp (°C) | bp (°C) |
|---|---|---|---|---|
| Toluene (tol) | 2.379 | 0.552 | $-95$ | 111 |
| Ethylmethyl carbonate (EMC) | 2.4 | 0.65 | $-55$ | 107 |
| Diethyl carbonate (DEC) | 2.82 | 0.748 | $-43$ | 126 |
| Dimethyl carbonate (DMC) | 3.12 | 0.585 | 0.5 | 90 |
| Propyl acetate (PA) | 6.00 | 0.551 | $-95$ | 102 |
| Ethyl acetate (EA) | 6.02 | 0.426 | $-84$ | 77 |
| Methyl acetate (MA) | 6.67 | 0.368 | $-96$ | 56 |
| Methyl formate (MF) | 8.90 | 0.328 | $-99$ | 36 |
| $\gamma$-Butyrolactone ($\gamma$-BL) | 41.77 | 1.727 | $-43$ | 202 |
| Propylene carbonate (PC) | 64.92 | 2.53 | $-49$ | 241 |
| Ethylene carbonate (EC, 38°C) | 89.6 | 1.85 | 36 | 248 |

[a] Temperature is 25°C unless stated otherwise.

containing large amounts of aliphatic and aromatic hydrocarbons such as found in kerosene. In addition, the solubilities of lithium oxides, carbonates, fluoride compounds and alkoxides which are the basic compounds found in the passivating anode films are highly insoluble in these solvents. This property is expected to increase the stability of the passive anodic film by both significantly decreasing its solubility and by producing a thinner and more compact passive film. In addition, hydrocarbon solvents such as toluene do not generally solubilize or excessively swell polymers such as PVDF which are important factors in long-life and highly stable Li-ion PVDF-based batteries. To insure high solubilities of Li-salts in solvent mixtures with high toluene content, it is necessary to select co-solvents which are completely miscible with toluene and which can dissolve sufficient electrolyte without phase separation over the desired temperature range. This problem is solvable by noting that many hydrocarbons such as toluene are completely miscible with carboxyl-containing organic solvents such as esters and ethers (e.g., see Refs. [11–15]).

Based on the above concepts, MaxPower has carried out a series of studies based on multicomponent solvent mixtures containing toluene as a major component. Initially, the properties of ternary and quaternary liquid mixtures containing EC, EMC, MA and tol were determined over the temperature range of $-60$°C to ambient with $LiAsF_6$ and $LiPF_6$ electrolytes. Selected mixtures were then incorporated into PVDF-based electrolytes and the conductivities of these polymer electrolytes determined. Finally, the electrochemical properties of Li-ion pouch cells were determined. Cells of the type

$$\begin{aligned}&|\text{MCMB} - \text{based anodes}\ (-'\text{ve Cu current collector})\\&\quad\times|\ \text{polymer electrolyte}|\quad \text{LiCoO}_2\ \text{cathode}\\&\quad\times(+'\text{ve Al current collector})| \qquad (1)\end{aligned}$$

constructed by adaptation of the Bellcore technology were used for these studies. Where possible, comparisons were made between the new data presented here and literature data.

## 2. Experimental

### 2.1. Materials

The active material for anodes is MCMB obtained from Osaka Chemicals. $LiAsF_6$ and $LiPF_6$ were obtained from Foote Minerals and Mitsubishi Chemicals, respectively. Toluene was obtained from Burdick & Jackson (''Distilled in Glass'' grade) and treated with type 3 Å molecular sieves before use. Methyl acetate, 99.5% pure, was obtained from Aldrich Chemicals) and treated with type 3 Å molecular sieves before use. All other solvents were high purity materials obtained from both Grant Chemicals and Mitsubishi Chemicals. Solutions were prepared in a dry box (less than 1 ppm $O_2$ and $H_2O$) located in a dry room with a capability of $< 1$% relative humidity. All conductivity and Li-ion cells were prepared in the dry room.

### 2.2. Conductivities

For liquid conductivities, a YSI Model 3200 conductivity meter was used with dip type conductivity cells sealed in glass ampoules with silicone rubber O-rings. The cells with nominal cell constants of 0.1 $cm^{-1}$, 1 $cm^{-1}$ and 10 $cm^{-1}$ were calibrated with standard KCl solution. For temperatures above 0°C, conductivity cells were thermostated in a Polyscience water bath capable of $\pm 0.05$ K reproducibility. For temperatures at and below 0°C, conductivity cells were thermostated in a Model TJR Tenney Environmental Chamber capable of reaching temperatures to $-75$°C with a reproducibility of $\pm 1$ K. The conductivities of the polymer electrolytes were measured by impedance spectroscopy by sandwiching the membranes between two identical stainless steel blocking electrodes whose surfaces were previously polished to metallographic grade using an alumina paste. The conductivities were measured with a Solartron 1255 FRA coupled to a Solartron 1286 potentiostat in a two-electrode configuration.

### 2.3. Cell cycling studies

100 mA h pouch type cells (Eq. (1)) were constructed in the dry room and cycled at C/5 and C/10 rates between the voltage limits of 3.0 to 4.15 V. For all temperatures between $-40$°C and 25°C, the Tenny Environmental Chamber was used for thermostating. All cells were anode limited having a cathode/anode capacity ratio of 1.2–1.3. Anodes (38.7 $cm^2$) contained between 70 and 80 mass% active material (MCMB-1028), 3.5 and 4.5% Super P carbon black and 17 and 24% PVDF: typical thickness of this anode is 0.012 cm. Cathodes (38.7 $cm^2$) contained between 70 and 75 mass% active material ($LiCoO_2$), 5 and 10% Super P carbon black, and 17 and 24% PVDF: typical thickness of this cathode is 0.021 cm. The polymer host-matrix for the electrolyte contained be-

Table 2
Electrolyte conductivities, $10^3\ \sigma$, as a function of temperature[a]

| | −65°C | −50°C | −40°C | −20°C | 0°C | 25°C | 40°C |
|---|---|---|---|---|---|---|---|
| LiPF$_6$ EC:DMC:DEC (5:4:1 v/o) | s | s | s | 2.825 | 5.913 | 10.872 | 14.183 |
| LiPF$_6$ EC:DMC:DEC (1:1:1 v/o) | s | s | nd | 2.896 | 5.705 | 10.010 | 12.793 |
| LiPF$_6$ EC:DMC:DEC (1:1:1 v/o)[d] | 0.02[b] | nd | 1.01 | 2.9 | 5.6 | 9.7 | nd |
| LiPF$_6$ EC:DMC:MA (1:1:1 v/o) | 0.140 | 0.680 | 1.830 | 5.786 | 9.878 | 15.808 | 19.130 |
| LiPF$_6$ EC:EMC:DMC (1:1:1 v/o) | s | 0.680 | 1.400 | 3.320 | 6.280 | 10.820 | nd |
| LiPF$_6$ EC:EMC:DMC (1:1:1 v/o)[e] | s | s | 1.120 | 3.110 | 5.730 | 10.510 | nd |
| LiAsF$_6$ EC:EMC:MA:tol (1:1:1:1 v/o) | s | 1.100 | 1.830 | 3.260 | 4.940 | 6.870 | nd |
| LiPF$_6$ EC:EMC:MA:tol (1:1:1:1 v/o) | 0.260 | 1.130 | 1.860 | 3.690 | 6.070 | 8.060 | nd |
| LiAsF$_6$ PC:MA:tol (1:1:1 v/o) | 0.530 | 1.310 | 2.080 | 3.320 | 4.720 | 6.640 | nd |
| LiAsF$_6$ EC:MA:tol (1:1:1 v/o) | s | s | 1.190[c] | 4.590 | 8.030 | 12.900 | nd |
| LiAsF$_6$ EMC:tol (1:1 wt/o) | 0.105 | 0.373 | 0.624 | 1.153 | 1.811 | 2.660 | nd |
| LiAsF$_6$ EC:EMC:tol (1:1:1 wt/o) | 0.150 | 0.373 | 0.700 | 3.060 | 6.250 | 9.920 | nd |
| LiPF$_6$ EC:EMC:MA:tol (0.5:0.5:1:1 v/o) | 0.35[c] | 1.28[c] | 2.35 | 4.53 | 7.15 | 9.45 | nd |
| LiPF$_6$ EC:EMC:MA:tol: (0.5:1:1:1 v/o) | 0.41[c] | 1.26 | 2.06 | 3.62 | 5.45 | 6.82 | nd |
| 0.5 M LiPF$_6$ EC:EMC:MA:tol (1:1:1:1 v/o) | 0.30[c] | 1.16[c]? | 2.36 | 4.13 | 6.48 | 8.40 | nd |

[a] All concentrations are 1 mol dm$^{-3}$ unless stated otherwise. Conductivity units are S cm$^{-1}$. In the table, s indicates freezing of the solution, and nd indicates not determined. The compositions of the solvent mixtures in either mass or volume% are given in parentheses.

[b] − 60°C.

[c] Phase separation.

[d] Ref. [5].

[e] Refs. [3,4].

tween 55 and 65 mass% PVDF and 35 and 45% silica, and thicknesses were typically around 0.0085 cm. Cell components containing PVDF were initially prepared using dibutylphthalate (DBP) to plasticize the polymer, and after lamination the DBP was extracted using ethyl ether. The completed structure was then placed in pouch type cells, electrolyte added (average between 4 and 5 ml), and finally sealed.

## 3. Results

### 3.1. Conductivities of liquid and polymer electrolytes

Table 2 lists the electrolytic conductivities ($\sigma$, S cm$^{-1}$) of various multicomponent electrolyte systems determined in the present research. Selected literature data are also included for comparisons.

Fig. 1 summarizes the present studies for the electrolytic conductivities of 1 mol dm$^{-3}$ LiAsF$_6$ in binary, ternary and quaternary solvent mixtures containing toluene. Based mainly on the observations that at −40°C the electrolytic conductivities of LiPF$_6$ and LiAsF$_6$ in the quaternary solvent mixtures are the highest obtained ($> 1.8 \cdot 10^{-3}$ S cm$^{-1}$), our cell studies reported below focus on these particular quaternary solvent mixtures. Fig. 2 summarizes results for this quarternary system with LiPF$_6$, where the EMC and toluene compositions are varied in addition to the salt concentration. As for the case with LiAsF$_6$ systems (Fig. 1), the 1:1:1:1 v/o system appears superior, particularly at ambient temperatures.

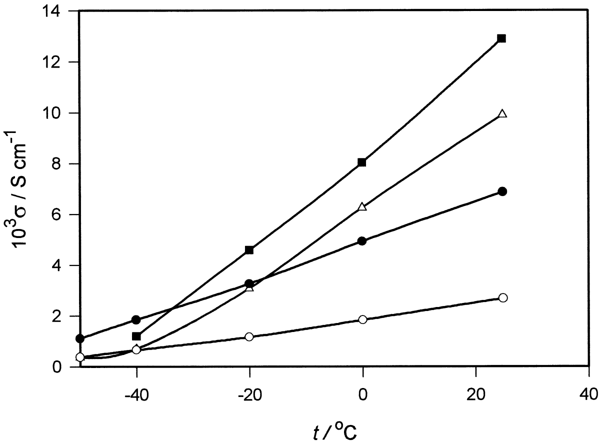

Fig. 1. Electrolyte conductivities ($\sigma$) for 1 mol dm$^{-3}$ LiAsF$_6$ in various solvent mixtures. ■ EC:MA:tol (1:1:1 v/o); △ EC:EMC:tol (1:1:1: wt/o); ● EC:EMC:MA:tol (1:1:1:1 v/o); ○ EMC:tol (1:1 wt/o).

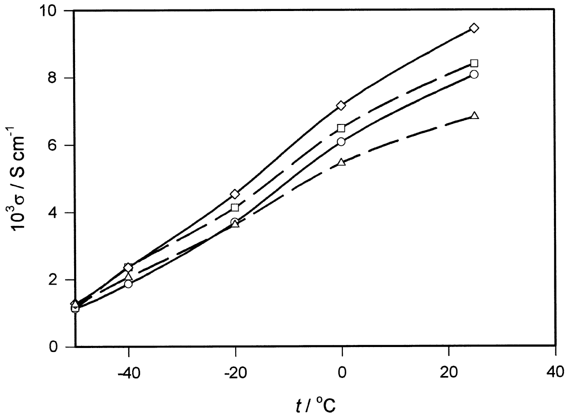

Fig. 2. Electrolyte conductivities ($\sigma$) for LiPF$_6$ in EC:EMC:MA:tol (v/o). ◇ 1.0 mol dm$^{-3}$ LiPF$_6$ in 1:1:1:1 solvent mixture. □ 0.5 mol dm$^{-3}$ LiPF$_6$ in 1:1:1:1 solvent mixture. ○ 1.0 LiPF$_6$ in 0.5:1:1:0.5 solvent mixture. △ 1.0 LiPF$_6$ in 0.5:1:1:1 solvent mixture.

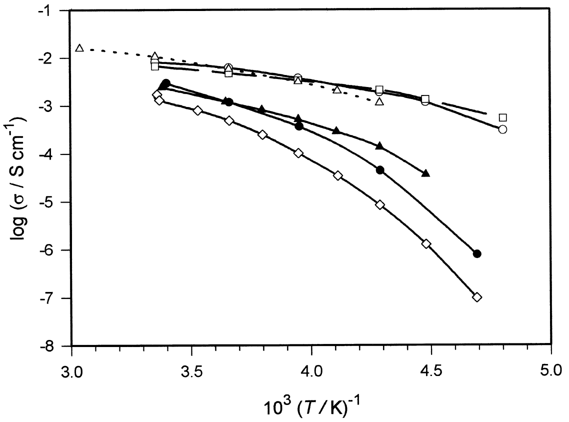

Fig. 3. Arrhenius plots of conductivities of 1 mol dm$^{-3}$ solutions in liquid and polymer electrolytes. □ $LiAsF_6$ in PC:MA:tol (1:1:1 v/o). ○ $LiPF_6$ in EC:EMC:MA:tol (1:1:1:1 v/o). △ $LiPF_6$ in EC:EMC:DMC (1:1:1 v/o), from Refs. [3,4]. ▲ $LiPF_6$ in PVDF/EC:EMC:MA:tol (1:1:1:1 v/o). ● $LiPF_6$ in PVDF/EC:DMC:MA (1:1:1 v/o). ◇ $LiPF_6$ in PVDF/PC:MA:tol (v/o).

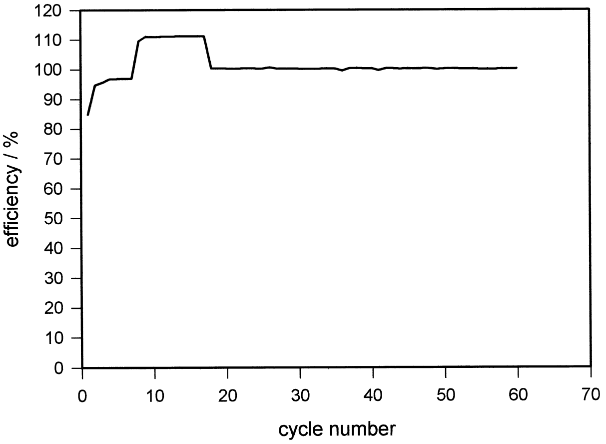

Fig. 4. Room temperature ( ~ 25°C) cycling behavior of PVDF electrolyte cell 35. Cycles 1–7: preconditioning at C/5. Cycles 8–17: overcharged at C/10 and discharged at C/5. Cycles 18–60: charged and discharged at C/5.

In Fig. 3, conductivity results for both liquid and polymer electrolytes are compared. Not included in Fig. 3 are data for $LiN(CF_3SO_2)_2$ in pure MA and EA (from Plichta and Slane [2]) which were analyzed for comparison purposes. To help in interpreting these data, we used the Vogel–Fulcher–Tammann equation

$$\sigma = A(T)^{-1/2} \exp\left\{ \frac{-E}{R(T-T_0)} \right\} \qquad (2)$$

which, strictly speaking, is valid for glass-forming liquids which are similar to the highly concentrated solutions used for battery electrolytes (e.g., see Ref. [16]). The results of these analyses are given in Table 3.

Most noteworthy in this table are the approximate activation energies, $E$, and the glass transition temperatures, $T_0$. Values of $E$ for the liquid electrolytes are generally smaller than those for the polymer systems. These results are reasonable noting that the PVDF electrolyte is an ''electrolyte starved membrane'' where the magnitude of the conductivity is dependent upon polymer porosity. However, the PVDF electrolytes still appear to behave as liquids based on the similarities in glass transition temperatures for comparable liquid and polymer systems. For all systems containing EC, MA and toluene, the glass transition temperature is around 170 K which is consistent, even for the polymer system. The electrolyte based on EC:DMC:EMC has the highest glass transition temperature, and the electrolyte based on PC:MA:tol has a distinctly lower glass transition temperature than any of the other solvent systems. In view of our use of graphite anodes (MCMB), cell studies utilizing solvent mixtures containing PC were not carried out.

### 3.2. Cell cycling studies

A series of 100 mA h pouch type cells (Eq. (1)) were fabricated and evaluated using our quaternary solvent mixture and compared with solvent mixtures presently used in several commercial Li-ion cells. All cells reported below were initially subjected to between five and seven ''conditioning'' charge/discharge cycles before data were

Table 3
Arrhenius parameters for selected liquid and PVDF-based electrolytes[a]

| System | $A$ | $E$ (cal mol$^{-1}$) | $T_0$ (K) |
|---|---|---|---|
| 1.0 mol dm$^{-3}$ $LiPF_6$ in PVDF (EC:EMC:MA:tol) | 0.744 | 717.4 | 172.9 |
| 1.0 mol dm$^{-3}$ $LiPF_6$ in PVDF (EC:DMC:MA) | 3.82 | 1064 | 171.1 |
| 1.0 mol dm$^{-3}$ $LiPF_6$ in PVDF (EC:MA:tol) | 7.70 | 1486 | 165.1 |
| 1.0 M $LiPF_6$ in EC:EMC:DMC | 0.818 | 335.4 | 190.6 |
| 1.0 mol dm$^{-3}$ $LiPF_6$ in EC:EMC:MA:tol | 0.639 | 386.2 | 170.3 |
| 1.0 mol dm$^{-3}$ $LiAsF_6$ in PC:MA:tol | 0.517 | 431.9 | 156.5 |
| 1.37 mol dm$^{-3}$ $LiN(CF_3SO_2)_2$ in pure MA | 0.854 | 271.9 | 170.2 |
| 1.20 mol dm$^{-3}$ $LiN(CF_3SO_2)_2$ in pure EA | 0.651 | 305.5 | 167.6 |

[a] Equal volume mixtures for the mixed solvents. The PVDF-based electrolytes contained 84 mass% liquid electrolyte.

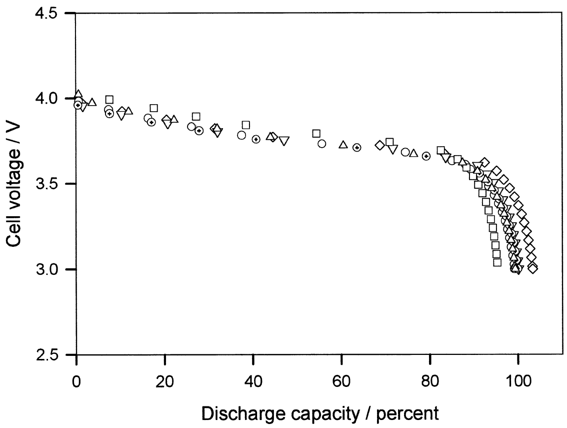

Fig. 5. Discharged curves for various 1 mol dm$^{-3}$ PVDF electrolyte cells at room temperature. ◇ and ▽ $LiPF_6$ in EC:DMC:MA (1:1:1 v/o). ⊕ and ○ $LiPF_6$ in EC:EMC:DMC (1:1:1 v/o). □ and △ $LiAsF_6$ in EC:EMC:MA:tol (1:1:1:1 v/o).

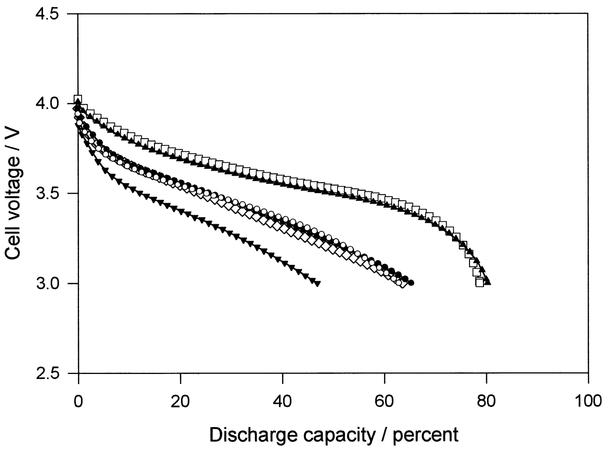

Fig. 7. Discharge curves for various 1 mol dm$^{-3}$ PVDF electrolyte cells at −30°C (note: all cells charged and discharged at C/10 at −30°C). ◇ $LiPF_6$ in EC:DMC:MA (1:1:1 v/o). ● $LiPF_6$ in EC:DMC:MA (1:1:1 v/o). ▼ $LIPF_6$ in EC:DMC:DEC (5:4:1 v/o). ○ $LiPF_6$ in EC:EMC:DMC (1:1:1 v/o), cell 20. □ $LiAsF_6$ in EC:EMC:MA:tol (1:1:1:1 v/o), cell 21. ▲ $LiAsF_6$ in EC:EMC:MA:tol (1:1:1:1 v/o), cell 22.

analyzed and compared. At ambient temperatures, cells were generally charged and discharged at the C/5 rate (~ 0.45 mA cm$^{-2}$), and at −30°C and −40°C, cells were generally charged and discharged at the C/10 rate. A typical result for cells containing 1 mol dm$^{-3}$ $LiPF_6$ in the 1:1:1:1 quaternary mixture is shown in Fig. 4. First cycle capacity losses generally amounted to no more than 15%, and excellent reproducibility is obtained. The room temperature experiment shown in Fig. 4 also demonstrates the ability of these Li-ion cells to withstand abuse: note that while charged to 110% above its nominal capacity, the cell resumed normal cycling behavior when charging was returned to standard procedure (starting with cycle 18). Note that during overcharge, the total cell potential did not exceed 4.1 V. This cell was cycled around 160 times without noticeable loss in capacity before the experiment was terminated. The discharge capacities of cells with PVDF containing various electrolytes at 25°C, −20°C, −30°C and −40°C are shown in Figs. 5–8, respectively (these discharge curves were obtained immediately following the preconditioning regime of 5–7 cycles).

Examination of these figures reveals the following properties.

(i) At room temperature (~ 25°C), all discharge curves are highly reproducible and delivered capacities are all close to 100%, i.e., PVDF-electrolyte compositions have

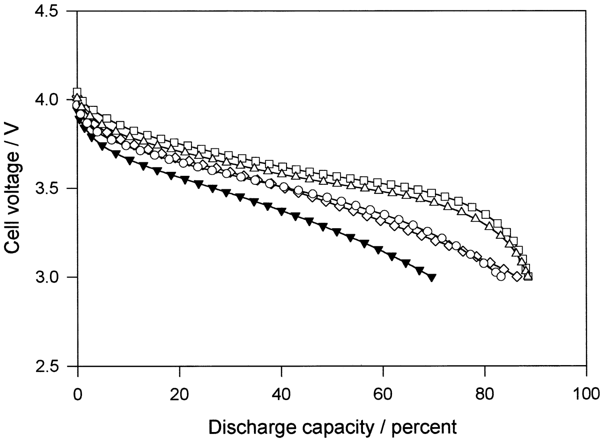

Fig. 6. Discharge curves for various 1 mol dm$^{-3}$ PVDF electrolyte cells at −20°C (note: all charged and discharged at C/5 at −20°C). ◇ $LiPF_6$ in EC:DMC:MA (1:1:1 v/o): identical results obtained for $LiPF_6$ in EC:EMC:DMC (1:1:1 v/o), cell 10. ▼ $LIPF_6$ in EC:DMC:DEC (1:1:1 v/o). ○ $LiPF_6$ in EC:EMC:DMC (1:1:1 v/o), cell 20. □ $LiAsF_6$ in EC:EMC:MA:tol (1:1:1:1 v/o), cell 21. △ $LiAsF_6$ in EC:EMC:MA:tol (1:1:1:1 v/o), cell 22.

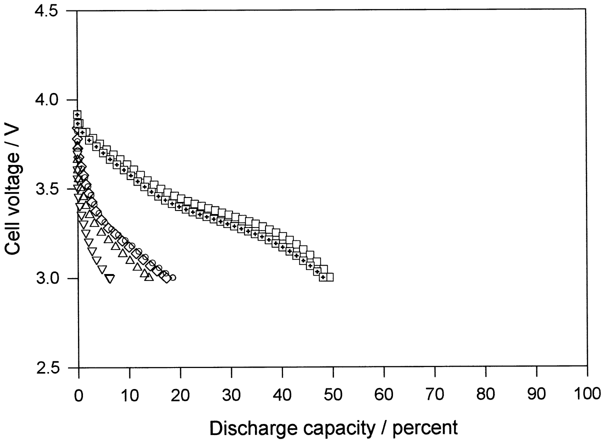

Fig. 8. Discharge curves for various 1 mol dm$^{-3}$ PVDF electrolyte cells at −40°C (note: all cells charged and discharged at C/10 at −40°C). ◇ $LiPF_6$ in EC:DMC:MA (1:1:1 v/o). ○ $LiPF_6$ in EC:DMC:MA (1:1:1 v/o). ▽ $LIPF_6$ in EC:EMC:DMC (1:1:1 v/o). △ $LiPF_6$ in EC:EMC:DMC (1:1:1 v/o). □ $LiPF_6$ in EC:EMC:DMC:tol (1:1:1:1 v/o), cell 21. ⊞ $LiAsF_6$ in EC:EMC:MA:tol (1:1:1:1 v/o), cell 22.

minimal effect on delivered capacities. Extended cycling behavior of the ternary EC:DMC:MA solvent/electrolyte has not been carried out, but the initial cycling behavior (less than 10 cycles) is reproducible.

(ii) At −20°C, differentiation becomes apparent and is reproducible as seen in Fig. 6. Cells with PVDF-electrolytes containing the quaternary solvent mixture (EC:EMC:MA:tol) not only exhibit higher capacities above 90%, but do so with greater capacity retention at a high mid-point voltage (see Figs. 9 and 10 below). Cells containing PVDF electrolytes with either EC:EMC:DMC or EC:DMC:MA yield almost identical results, but with a decrease in delivered capacity (below 90%) and at lower mid-point potentials as compared to cells containing the quaternary electrolyte. Cells containing EC:DMC:DEC electrolytes are distinctly inferior.

(iii) At −30°C, the differences first noted in (ii) above become still more dramatic, and the PVDF electrolyte containing EC:DMC:MA is beginning to outperform that based on EC:EMC:DMC.

(iv) At −40°C, cells utilizing the (EC:DMC:DEC) electrolyte did not deliver useful capacity. Cells containing the quaternary electrolyte deliver capacities approaching 50% whereas all other cells exhibited capacities below 20% and at much lower mid-point cell potentials (see Figs. 9 and 10).

Figs. 9 and 10 summarize capacity retention and mid-point voltages obtained immediately following the 5–7 preconditioning charge/discharge cycles. All salt concentrations are 1 mol dm$^{-3}$. For temperatures between 25°C and −20°C, cells were charged and discharged at the C/5 rate. For temperatures between −30°C and −40°C, cells were charged and discharged at the C/10 rate. There is a rapid decrease in useful capacities when cells are discharged at the C/5 rate for these two lowest temperatures.

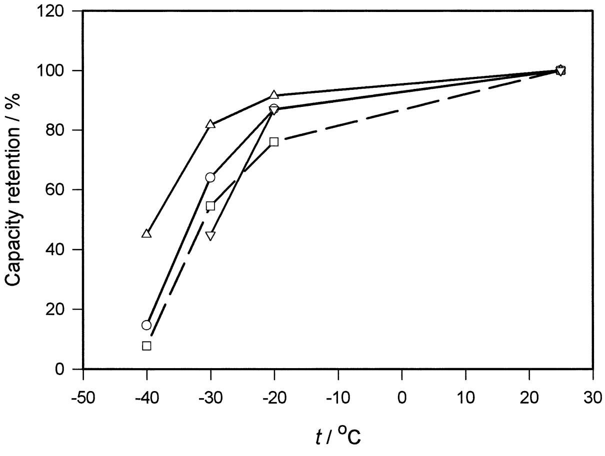

Fig. 9. Capacity retention of Li-ion PVDF electrolyte cells as a function of temperature. All results obtained immediately following the 5–7 preconditioning charge/discharge cycles. All salt concentrations are 1 mol dm$^{-3}$. For temperatures between 25°C and −20°C, cells charged and discharged at the C/5 rate. For temperatures between −30°C and −40°C, cells charged and discharged at the rate C/10 rate. △ $LiAsF_6$ in EC:EMC:MA:tol (1:1:1:1 v/o). ○ $LiPF_6$ in EC:DMC:MA (1:1:1 v/o). □ $LIPF_6$ in EC:EMC:DMC (1:1:1 v/o). ▽ $LiPF_6$ in EC:DMC:DEC (1:1:1 v/o).

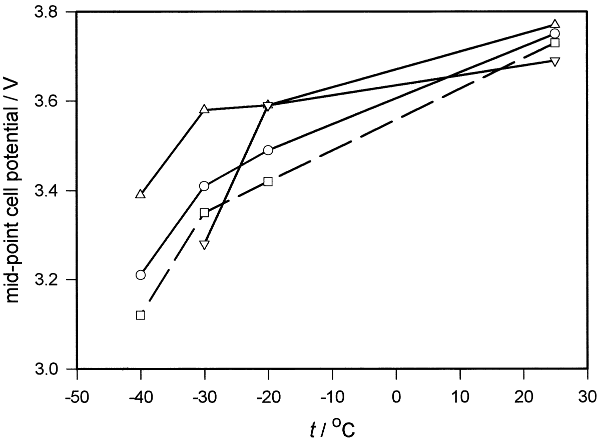

Fig. 10. Mid-point voltages of Li-ion PVDF electrolyte cells as a function of temperature. All results obtained immediately following the 5–7 preconditioning charge/discharge cycles. All salt concentrations are 1 mol dm$^{-3}$. For temperatures between −30°C and −40°C, cells charged and discharged at the C/10 rate. △ $LiAsF_6$ in EC:EMC:MA:tol (1:1:1:1 v/o). ○ $LiPF_6$ in EC:DMC:MA (1:1:1 v/o). □ $LIPF_6$ in EC:EMC:DMC (1:1:1 v/o). ▽ $LiPF_6$ in EC:DMC:DEC (1:1:1 v/o).

## 4. Conclusions

The present results show that highly conductive ($> 1 \cdot 10^3$ S cm$^{-1}$) solutions can be prepared for electrolytes in solvent mixtures containing large amounts of a hydrocarbon such as toluene. Salt solubilities and miscibility problems can easily be avoided by varying mixture compositions, e.g., MA is particularly effective in preventing phase separation. Li-ion/PVDF polymer/$LiCoO_2$ cells containing the quaternary electrolyte cycle well and the presence of significant amounts of MA do not have deleterious effects on anode stability. This is attributed to toluene additions to the mixed solvent, in addition to the anodic film stabilizing properties of EC and EMC. Our tentative conclusion is that toluene additions to these mixed solvents not only increases the stability of the anodic film (the SEI), but also reduces the solubility and swelling of PVDF. While the cells containing the quaternary solvent mixture are clearly significantly superior at temperatures ≤ −20°C, at −30°C and −40°C, useful capacities at rates C/5 and higher were not obtained. However, improvements in rate and capacity retention at these lower temperatures appears to be realizable by optimization of the compositions of these mixed solvents and by varying salt concentrations. The transfer of this electrolyte technology to Li-ion cells containing liquid electrolytes also appears to be a promising area for future exploration.

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