

# $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ Kynar gels at carbon negative electrodes

Lynn Christie<sup>\*</sup>, Alasdair M. Christie, Colin A. Vincent

*School of Chemistry, University of St. Andrews, St. Andrews, Fife, KY16 9ST, Scotland, UK*

## Abstract

Electrolyte solutions, comprising of  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  dissolved in solvent mixtures of ethylene carbonate (EC) and either dimethyl carbonate (DMC) or ethylmethyl carbonate (EMC), were used to prepare films after gelling with an appropriate quantity of Kynar<sup>TM</sup> polymer. The specific conductivity of each film is comparable with liquid electrolyte solutions at ambient temperatures. Half-cells assembled with each gel film and graphite from different sources are shown to have good cyclability with practical capacities of around  $350 \text{ mA h g}^{-1}$  at C/8. Cells constructed using coke as the active electrode material were also cycled successfully at a high charge/discharge rate of C/4 ( $1 \text{ mA cm}^{-2}$ ) with practical capacities of greater than  $200 \text{ mA h g}^{-1}$ . An EC:EMC:Kynar-based cell was successfully cycled at  $0^\circ\text{C}$  using this electrode material. Although an increase in the resistance of the passivating layer was observed at  $0^\circ\text{C}$ , the cell sustained a capacity of  $230 \text{ mA h g}^{-1}$  at a rate of C/50. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Graphite; Coke; Gel; Kynar; Lithium imide

## 1. Introduction

The salts commonly used in lithium battery electrolytes such as lithium hexafluorophosphate ( $\text{LiPF}_6$ ), hexafluoroarsenate ( $\text{LiAsF}_6$ ) and lithium tetrafluoroborate ( $\text{LiBF}_4$ ) have poor thermal stability and may have toxic by-products. Any replacement salt must possess certain electrochemical characteristics in addition to properties such as stability, safety and low cost. In particular, electrolytes for lithium ion cells must be resistant to electrochemical oxidation to above 4.5 V, and be compatible with carbon negatives down to 0 V vs.  $\text{Li}^+/\text{Li}$ , while exhibiting high conductivity in an appropriate solvent.

Lithium trifluoromethanesulphonate ( $\text{LiCF}_3\text{SO}_3$ ), known as lithium triflate, and lithium bis (trifluoromethanesulphonyl) imide ( $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ), known as lithium imide, fulfill most of these requirements [1–6]. Lithium imide, although relatively expensive, has certain particularly favourable electrochemical characteristics, including high specific conductivity, which are likely to make it an electrolyte of choice for small rechargeable cells for portable applications and in biomedicine. In this paper, we describe the suitability of lithium imide-based gelled electrolytes as candidates for use in lithium ion battery technology.

## 2. Experimental

Lithium battery grade ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), all from Grant Chemicals, and ethylmethyl carbonate (EMC) (Tomiya), were used as received. Kynar<sup>TM</sup>-flex 2801 (Elf-Atochem) was dried under dynamic vacuum at  $70^\circ\text{C}$  for 24 h. 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  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  (3 M) was added to make electrolyte solution concentrations of  $0.9 \text{ mol kg}^{-1}$ .

Kynar gel electrolytes were prepared by both solvent casting and thermal casting methods. The solvent casting method was described previously [7]. The thermal method involved suspending 1 g of Kynar in 2.5 g of the parent liquid electrolyte. The mixture was lightly pressed at  $70^\circ\text{C}$  for 1 min between polished aluminium sheets separated by an approximately  $100 \mu\text{m}$  thick PTFE spacer. In each case, the final product was a highly transparent, colourless self-supporting film. The films were cut to size and placed in a closed vessel containing some of the parent liquid electrolyte.

Graphite negative electrodes were prepared by dissolving Kynar in THF followed by the addition of the selected graphite (Johnson Matthey and Timcal) in a (95:5) mass ratio. Coke, supplied by Danionics, negative electrodes were prepared in the same manner, using either Kynar or PVDF as the binder and the addition of carbon Super-S

<sup>\*</sup> Corresponding author. Telefax: +44-1334-462543

(3 M), in a (80:10:10) mass ratio. The electrode casting method was described previously [7]. The thickness of each composite electrode was in the range of 40 to 50  $\mu\text{m}$ . Other ready-cast coke electrodes, supplied by Danionics, were also used, incorporating ethylenepropylenediene monomer (EPDM) as the binder and cast with an active mass of 4.5  $\text{mg cm}^{-2}$  onto a nickel substrate. These were dried for 12 h at 70°C under dynamic vacuum.

All electrochemical experiments were described in another paper [7].

### 3. Results and discussion

The electrochemical stability of lithium imide gels at Pt were determined by microelectrode cyclic voltammetry over the potential range 0 V  $\rightarrow$  +6 V. 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. Fig. 1 shows the voltammogram of the solvent cast 2EC:1DMC:Kynar gelled electrolyte containing 0.9  $\text{mol kg}^{-1}$  lithium imide and less than 30 wt.% Kynar, at a 25  $\mu\text{m}$  diameter Pt microelectrode at a sweep rate 100  $\text{mV s}^{-1}$ . On sweeping cathodically, several low current peaks are observed corresponding to trace water reduction at +0.4 V and other processes, including anion reduction and the onset of underpotential deposition (UPD) of lithium, at potentials lower than +0.6 V. These have all been observed previously in liquid electrolyte systems and other gels [8]. The overall stability of the gelled electrolyte is good with no electrochemical oxidation occurring until potentials greater

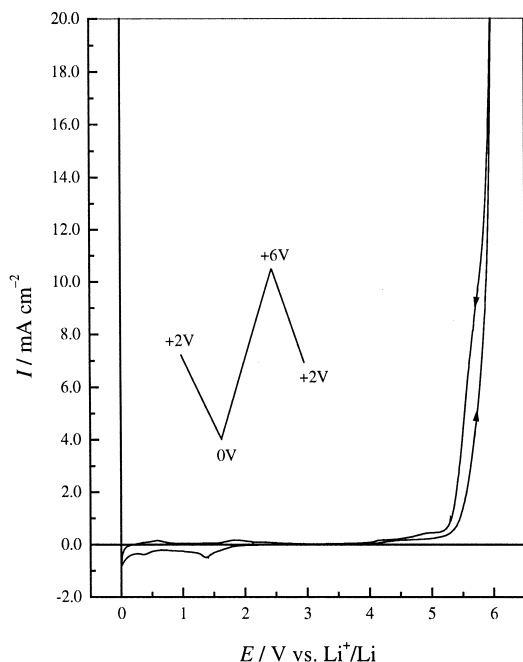


Fig. 1. Cyclic voltammogram of Li imide/2 EC:1 DMC:Kynar gelled electrolyte at 25  $\mu\text{m}$  Pt microelectrode, sweep rate = 100  $\text{mV s}^{-1}$ .

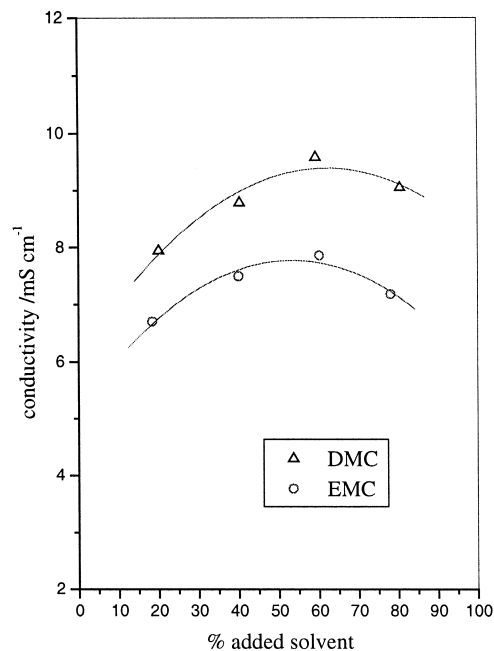


Fig. 2. Variation in ambient temperature conductivity for mixtures of EC/DMC and EC/EMC containing 0.9  $\text{mol kg}^{-1}$  Li imide.

than +5 V are reached. This has also been observed with gelled electrolytes containing the  $\text{LiPF}_6$  and  $\text{LiBF}_4$  salts [7].

The variation in the ambient temperature conductivity of a mixture of the high dielectric constant solvent, EC, with the low viscosity solvents, DMC and EMC, are shown in Fig. 2. The maximum conductivities were observed for the EC:DMC and EC:EMC solvent compositions with volume ratios 3:2 to 1:4. These are similar values to those reported for electrolytes containing  $\text{LiPF}_6$  or  $\text{LiBF}_4$  salts [7]. While the specific conductivity of the  $\text{LiN}(\text{CF}_3\text{SO}_2)_2/2\text{EC}:1\text{DMC}$  parent liquid electrolyte was 9.6  $\text{mS cm}^{-1}$  at 25°C, previous reports [3] have indicated that a specific conductivity of 12.5  $\text{mS cm}^{-1}$  is possible for the imide salt in a 1PC:1DME mixed solvent system. After gelling, a specific conductivity of 2.25  $\text{mS cm}^{-1}$  was observed for the 2EC:1DMC system. This is higher than the value of 1.1  $\text{mS cm}^{-1}$  reported previously for the lithium imide/EC:DMC:PMMA gelled system [2].

#### 3.1. Graphite half-cells

Two types of graphite, from Timcal (TC) and Johnson Matthey (JM), were used to study the cycling behaviour of the  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  gelled electrolytes. Fig. 3 shows an example of an incremental capacity plot for a solvent cast film at JM graphite. Both EC:DMC and EC:EMC systems exhibited an irreversible loss of capacity, as is generally encountered on the first intercalation of  $\text{Li}^+$  into carbonaceous materials [9], followed by rapid and reversible intercalation of approximately 0.9 Li ions per six carbons ( $\text{Li}_{0.9}\text{C}_6$ ). The percentage losses on the first cycle of both

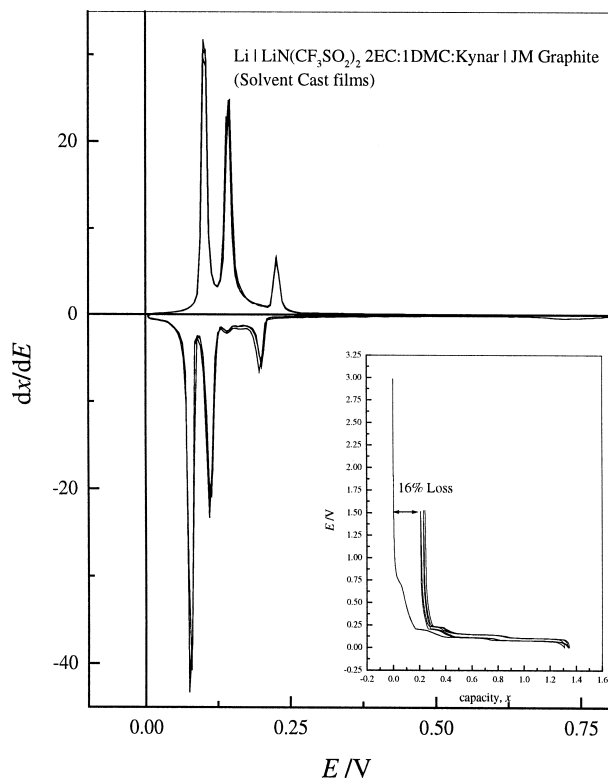


Fig. 3. Incremental capacity plot for Li imide/2EC:1DMC:Kynar (solvent cast) at JM graphite.

EC:EMC and EC:DMC systems are very similar at approximately 16%.

Fig. 4 shows the plot of specific capacity vs. cycle number for each Kynar film at graphite with a charge/discharge current density of  $0.25 \text{ mA cm}^{-2}$  (C/6). It can clearly be seen that although each gel cycles with a high specific capacity at TC graphite, the cells begin to fail after only 10 cycles. A higher cost graphite (JM) was used for comparison; for the solvent-cast gelled electrolytes, in particular those based on 2EC:1DMC, a higher than theoretical capacity was observed. Although the reason for this is unclear, it may be caused by a reaction between an electrolyte component and the electrode. If so, then the reaction seems to be reversible since the capacities are sustainably high at  $377 \text{ mA h g}^{-1}$  after 300 h of cycling. Previous studies of liquid systems at carbon electrodes have sometimes reported higher than theoretical capacities, some as high as  $1000 \text{ mA h g}^{-1}$  [10–12]. Sato et al. [10], who reported discharge capacities of  $680 \text{ mA h g}^{-1}$ , suggested that disordered carbon permits both ionic and covalent-bonded Li to occupy sites in the carbon structure. It is possible that the graphite electrode material (both TC and JM) used in this study is not fully ordered and that cavities exist into which Li ions can be inserted, a theory also proposed by Tran et al. [6].

The experiments with the JM graphite cells were repeated using thermally prepared gel systems, in which a practical capacity of  $334 \text{ mA h g}^{-1}$  after 200 h was

observed, indicating that the presence of the casting solvent does, indeed, influence the observable graphite capacity.

These and other investigations indicate that gelled electrolytes at graphite containing lithium imide consistently produce higher and more sustainable practical capacities than electrolytes based on either  $\text{LiPF}_6$  or  $\text{LiBF}_4$ . Matsuda et al. [1] have reported high, sustainable specific capacities of  $275 \text{ mA h g}^{-1}$  for the lithium imide salt in EC liquid systems. It is well-known that EC reduction at potentials positive to the intercalation potential produces compact Li alkyl carbonate surface films. Ein-Eli et al. [5] reported a greater cycling performance for the lithium imide salt over the  $\text{LiPF}_6$  salt in EC solutions, reflecting a strong influence of the salt reduction on the formation of surface films. These authors suggest that the stability of the Li-alkyl carbonate film decreases in the presence of  $\text{LiPF}_6$ , an observation also reported by others [13,14].

### 3.2. Coke half-cells

Coke electrodes prepared with either EPDM, PVDF or Kynar 2801 binders were cycled using lithium imide gelled electrolytes. After an initial irreversible loss of capacity, approximately 0.6 Li ions per six carbons ( $\text{Li}_{0.6}\text{C}_6$ ) were reversibly intercalated. Fig. 5 shows the plot of practical capacity vs. cycle number for each gel film at coke with a charge/discharge current density of  $1 \text{ mA cm}^{-2}$  (C/2). Although in each case a specific capacity of around  $200 \text{ mA h g}^{-1}$  was obtained, it can be seen that the coke EPDM systems cycled more efficiently. These values are similar to those reported recently for  $\text{LiPF}_6$  and  $\text{LiBF}_4$  in both the EC:DMC and EC:EMC systems [7].

AC impedance measurements were made to investigate the temperature dependence of a cell based on lithium imide:1EC:1EMC:Kynar gelled electrolyte at open circuit potentials down to  $2^\circ\text{C}$  (Fig. 6). The high frequency intercept, representing the bulk electrolyte resistance ( $R_b$ ),

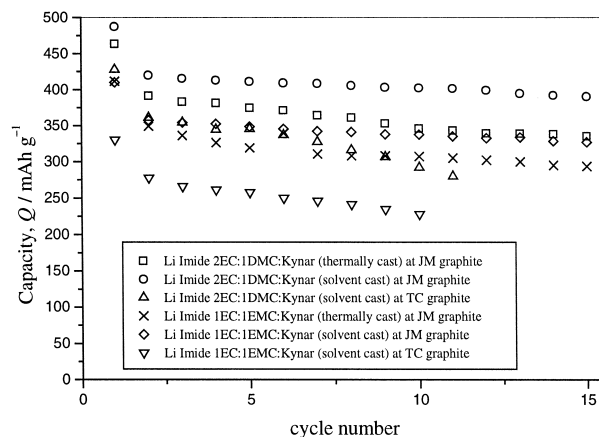


Fig. 4. Specific capacity vs. cycle number of each gelled electrolyte graphite.

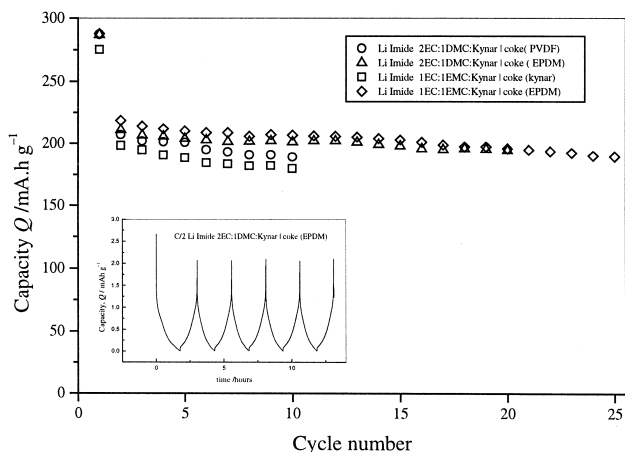


Fig. 5. Specific capacity vs. cycle number for each gelled electrolyte at coke.

increases with decreasing temperature. The semi-circle is associated with the passive layer at the carbon surface, where the diameter represents the resistance ( $R_e$ ). While the value of  $R_e$  increases with decreasing temperature, the capacitance associated with this semi-circle does not vary significantly from  $7.5 \mu\text{F cm}^{-2}$ . This indicates that the passivating layer remains a constant thickness and the lithium ionic conduction through the layer decreases with temperature. Similarly, the gelled electrolyte film resistance increases, as indicated by the shift in the high frequency intercept.

At  $2^\circ\text{C}$ , the resistance of the passivating layer ( $117 \Omega$ ) would at first indicate that it would be difficult to cycle the cell. However, it was found that by decreasing the charge/discharge rate to C/50, a practical capacity of  $224 \text{ mA h g}^{-1}$  was possible after 500 h of cycling. This was

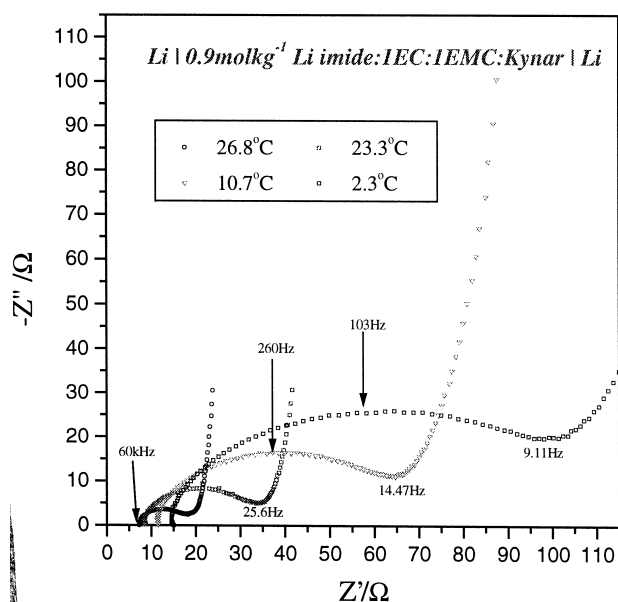


Fig. 6. Temperature-dependent AC impedance spectra for Li imide in 1EC:1EMC:Kynar at coke with Kynar binder.

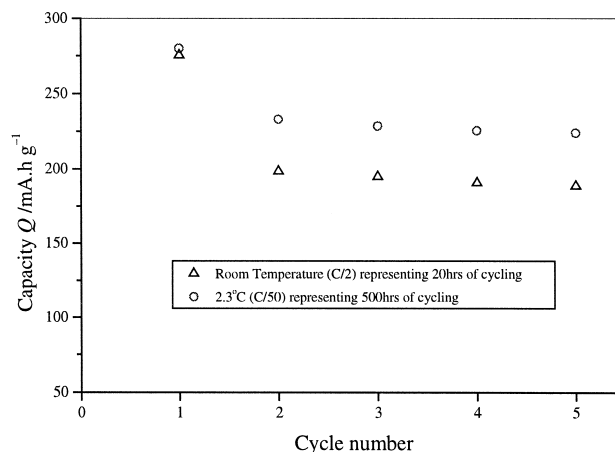


Fig. 7. Comparison of specific capacities obtained for Li imide in 1EC:1EMC:Kynar 1 coke at room temperature and  $2^\circ\text{C}$ .

indeed a higher practical capacity than was attained at room temperature after 20 h of cycling (Fig. 7). The initial irreversible capacity loss of only 16% was much lower than the 26% observed at room temperature (Fig. 8). Several authors [1,5,15] have reported increased cycling efficiency at lower temperatures, due to the differing natures of the surface films formed at each temperature. At higher temperatures, surface films on the lithium metal are chemically and morphologically irregular, allowing some dendritic deposition of lithium, leading to poor coulombic efficiency on cycling. At lower temperatures, anion reduction is less pronounced and the passive layers become more compact, well-ordered and homogeneous, allowing

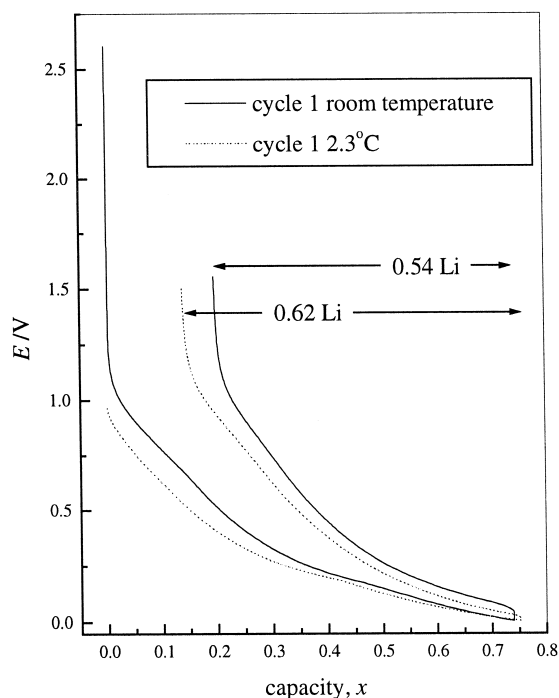


Fig. 8.  $E$  vs.  $x$  for the first cycle of Li imide in 1EC:1EMC:Kynar at coke at room temperature and  $2^\circ\text{C}$ .

Li-ion migration while suppressing dendritic deposition and, in turn, leading to higher cycling efficiency.

#### 4. Conclusions

It can be seen from this study that gelled electrolytes prepared from lithium imide and Kynar, in either EC:DMC or EC:EMC solvent systems, are very promising candidates for Li-ion electrolytes. Higher and more sustainable practical capacities were achieved at both graphite and coke electrodes than for LiPF<sub>6</sub> electrolyte systems. Low temperature cycling has been shown to be sustainable for long periods of time with capacities greater than those observed at ambient temperatures. We have also shown that capacities of 120 mA h g<sup>-1</sup> can be obtained at LiCoO<sub>2</sub> cathodes with the imide gelled systems [16], so that complete lithium ion cells based on this system are now a practical proposition.

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