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5th two-month Progress Report

April-May 1994

Introduction

In this 5th two-month period we have synthesized and characterized new types of gel electrolytes formed by trapping solutions of lithium salts in a poly(methylmethacrylate), PMMA matrix. In this report we describe the conductivity, the lithium ion transference number and the electrochemical stability of these PMMA-base electrolyte membranes. In the following two-month period we will investigate the phenomena occuring at the interface between these membranes and the lithium metal electrode.

Task (iii) - Synthesis and test of 'new' gel-type lithium electrolytes.

Introduction.

The type and the unique properties of gel electrolytes obtained by trapping lithium salt solutions in a poly(acrylonitrile) PAN matrix have been already described in the past progress reports. In this last part of the Project we have undertaken a systematic investigation of gel electrolytes formed by replacing the type of the immobilizing polymer, namely by replacing PAN with PMMA. The main motivation is the investigation the role of the polymer constituent on the transport properties of the lithium ions, as well as on the stability and the kinetics of the lithium metal electrode.

Experimental.

Materials and samples preparation

Three representative samples of PMMA-based gel electrolytes have been considered in this work, namely the systems having the following molar composition:

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S-1) PMMA: 30/PC : 19/EC:46.5/LiClO$_4$:4.5

S-2) PMMA: 30/PC : 19/EC:46.5/LiAsF$_6$:4.5

S-3) PMMA: 30/PC : 19/EC:46.5/LiN(CF$_3$SO$_2$)$_2$:4.5

The preparation of these electrolyte samples involved the immobilization of a propylene carbonate-ethylene carbonate,PC-EC solution of the selected lithium salt in a poly(methylmetacrylate) PMMA matrix. In order to obtain homogeneous samples, particular care was devoted both to the purification of the components and to the synthesis procedure.

Lithium perchlorate, LiClO$_4$ (Fluka 99.5%), lithium hexafluoroarsenate, LiAsF$_6$ and lithium perfluorosulphonimide LiN(CF$_3$SO$_2$)$_2$ (3M reagent grade), were dried by annealing them under vacuum at 120°C, 70°C and 80°C, respectively, for 24 hours. Commercial PMMA (Aldrich, reagent grade) was dried by heating it under vacuum at 100°C for 10 hours. Care was taken in controlling the annealing temperature in order to avoid material decomposition.

Both propylene carbonate, PC and ethylene carbonate, EC (Fluka reagent grade) were purified by distillation under reduced pressure. Solid EC was mixed in the desired proportion with PC, and the resulting EC-PC liquid mixture was dried by storing it over molecular sieves.

All the components, namely the selected lithium salt and PMMA, were dissolved in the PC-EC solvent mixture at temperatures ranging between 40°C and 50°C. The solution was then slowly heated to 70-80 °C to favour gelification and finally cast between glass sheets to obtain the desired solid membranes, generally having a transparent, elastomeric appearance.

Sample characterization

The Arrhenius conductivity plots of the various electrolyte samples were determined by measuring the temperature dependence of the impedance of cells formed by sandwiching the given sample between two stainless steel (SS 304) blocking electrodes. The measurements were performed using a Solartron Model 1260 Frequency Response Analyser. A thermostatic bath with 0.1°C precision was utilized to control the temperature.

The electrochemical stability window was determined by running a sweep voltammetry on a three electrode cell where a nickel plate was the working electrode, a lithium disk was the counter electrode and a lithium strip placed between two adjacent layers of gel electrolyte, served as the reference electrode. The decomposition voltage limits were assumed to be those at which

current began to flow through the cell. The current-voltage curves were driven by a PAR, Model 273 potentiostat coupled with a PC computer.

The techniques used to measure the lithium ion transference number, t_{Li+} of the various selected samples, namely the impedance method described by Bruce and Vincent and the so called "time-of-fly" method described by Watanabe and co-workers, were illustrated in detail in a previous report (3rd two-month progress report).

Kinetics and stability of the lithium electrode

The kinetics of the lithium deposition-stripping process from PMMA-based electrolytes was evaluated by cyclic voltammetry (CV) curves obtained in three-electrode cells having a stainless-steel working substrate, a lithium counter and a lithum reference electrode. The CV curves were run and controlled by using a PAR, Mod.273 potentiostat and an IBM 70 computer.

The stability of the lithium interface was investigated by monitoring the time dependence of the impedance of symmetrical Li/PMMA-based electrolyte/Li cells utilizing the same instrumentation used in the case of the conductivity measurements.

The lithium cycling efficiency was determined by first depositing an excess of lithium on an "inert", stainless-steel substrate, then cycling a fraction of the deposited lithium and following the evolution of the overvoltage associated to the stripping process. The cycling life was considered to be concluded when the overvoltage tended to infinite. Under these conditions, the cycling efficiency, E, was evaluated using the equation:

$$E = \frac{Q_{cycl} - (Q_{dep}/n)}{Q_{cycl}} \qquad [1]$$

where Q_{dep} is the charge involved in the initial excess lithium deposition, Q_{cycl} is the charge used for cycling a fixed (10%) fraction of the deposited lithium and n is the number of cycles obtained up to infinite stripping overvoltage.

Results.

1. Conductivity and electrochemical tests

Figures 1 illustrates the dependence of the conductivity of two rapresentative samples of PMMA-based gel electrolytes (i.e., samples S-1 and S-2). The related Arrhenius plots show that the electrolytes reach conductivities of the order of 0.5×10^{-3} S cm^{-1} at 60°C and that even at low temperatures (e.g., down to -20°C) the conductivity remains quite high (i.e. in the range of 10^{-4} Scm^{-1}).
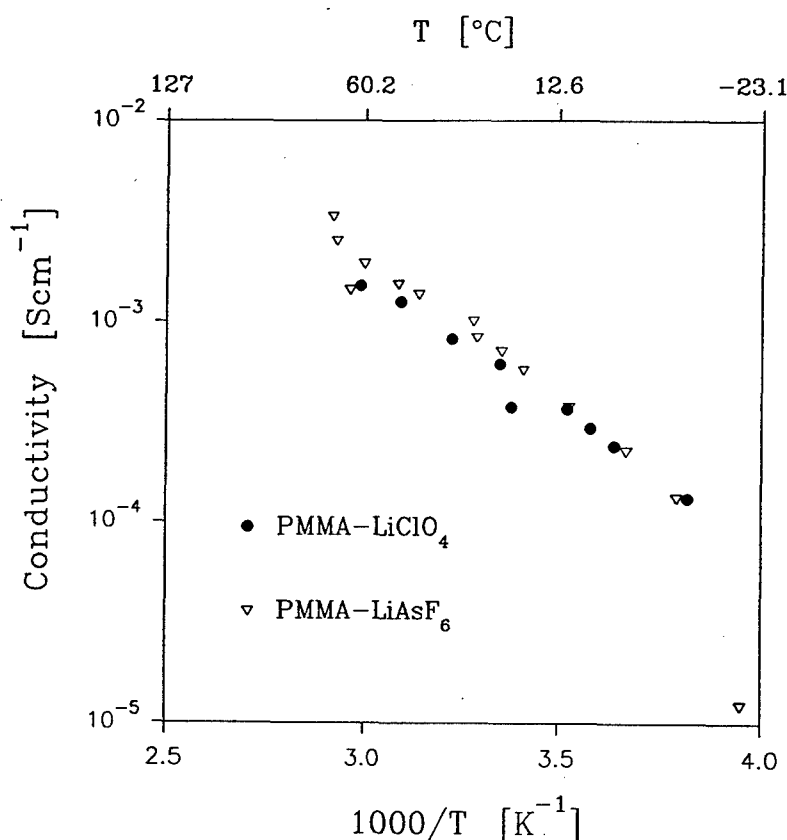

Figure1-   Arrhenius plot of the PMMA-PC/EC- LiClO$_4$ (sample S-1) and of the PMMA-PC/EC- LiAsF$_6$(sample S-2) electrolytes.

Figure 2 compares the conductivity of a PMMA-PC/EC- LiAsF$_6$ (sample S-2) electrolyte with that of a PAN-PC/EC- LiAsF$_6$ one. The figure clearly shows that the two electrolytes have a similar conductivity behaviour with only a slight difference in the activation energy. Therefore, in terms of conductivity, the PMMA-based electrolytes can be easily interchanged with the PAN-based ones.
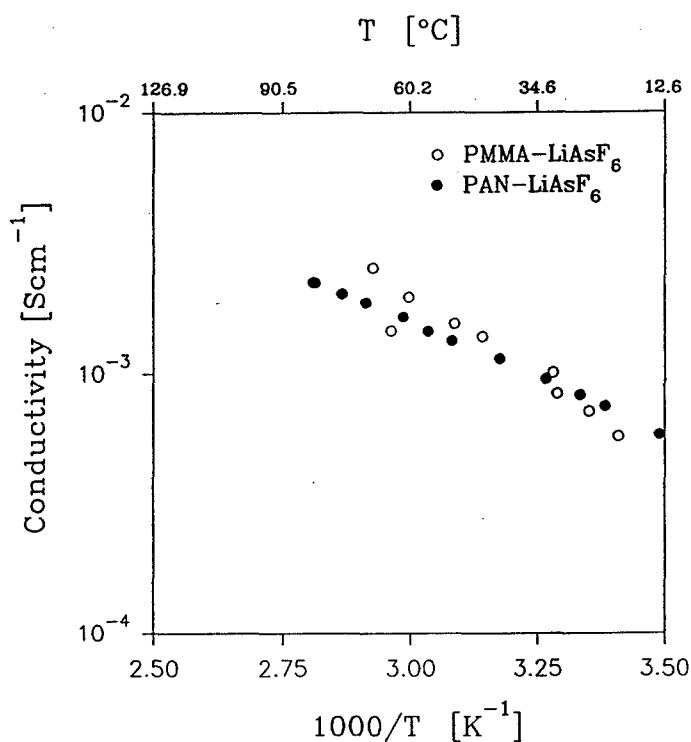
Figure 2- Arrhenius plots of a PMMA-PC/EC- LiAsF$_6$ (sample S-1) and of a PAN-PC/EC- LiAsF$_6$ analogue having the composition PAN:16/PC:23/EC:56.5/ LiAsF$_6$:4.5.

Table 1- Lithium transport numbers at 24°C of various lithium electrolytes.

electrolyte	solvent/salt ratio	sample	tLi+ (a)	tLi+ (b)
PC-LiClO$_4$	liquid		0.4	0.25
PEO-LiClO$_4$	polymer		0.2	
PMMA-PC/EC- LiClO$_4$	14.6:1	S-1		0.4
PAN-PC/EC- LiClO$_4$ (f)	17.6:1		0.6	0.5
PMMA-PC/EC- LiAsF$_6$	14.6:1	S-2		0.6
PAN-PC/EC- LiAsF$_6$ (e)	17.6:1		0.7	0.6
PMMA-PC/EC-LiN(CF$_3$SO$_2$)$_2$	14.6:1	S-3		0.7
PAN-PC/EC-LiN(CF$_3$SO$_2$)$_2$ (f)	17.6:1		0.8	0.7

a) calculated using Bruce and Vincent impedance technique
b) calculated using Watanabe pulse technique

Table 1 reports the lithium ion transference number values obtained for the three PMMA-based electrolyte samples and, for comparison purpose, also the values for common liquid organic, PEO-based and PAN-based polymer electrolytes. Again, the values for the PMMA systems are comparable with those for the PAN systems. This confirms that the two classes of gel electrolytes have comparable transport characteristics. It is interesting to note from Table 1 that these electrolytes seem to have Li^+ transference numbers considerably higher than those usually obtained for the parent liquid and PEO-based polymer electrolytes. This suggests that the role of the polymer component (PMMA or PAN) is much more complex than simply acting as a porous solid matrix for the liquid (LiX in PC/EC) solutions. Therefore the term "hybrid electrolytes" often used for these gel systems is not strictly appropriate. We propose here the introduction of the term "gelionics" as a more representative identification of the PMMA-based and, generally, of the entire class of these liquid-immobilizing ionic membranes.
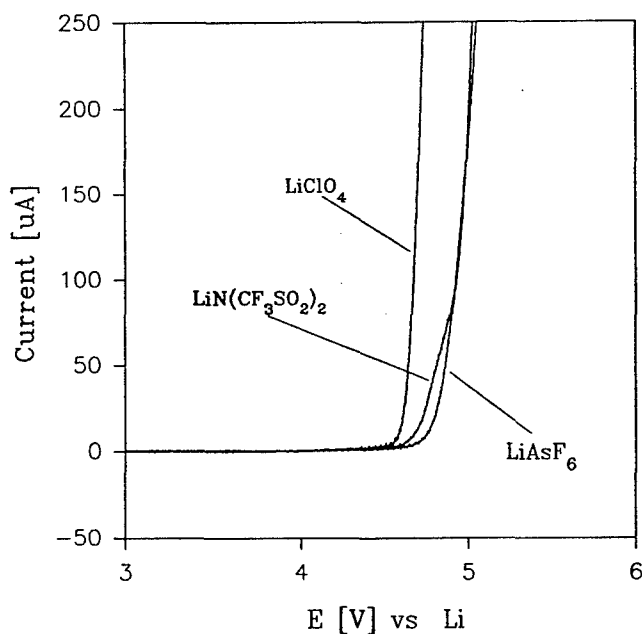

Figure 3- Current-voltage response at 25°C of a stainless-steel electrode in PMMA-PC/EC-LiClO$_4$ (sample S-1), PMMA-PC/EC-LiAsF$_6$ (sample S-2) and in PMMA-PC/EC-LiN(CF$_3$SO$_2$)$_2$(sample S-3),electrolyte cells. Scan rate: 1 mV s^{-1}.

Figure 3 illustrates the current-voltage curves obtained by sweeping an "inert" stainless steel eletcrode in cells using alternatively the three PMMA-based electrolyte samples. As already described in the experimental session, one may assume as the anodic decomposition limit of the electrolyte the voltage at which current flows through the cell. Under this assumption, Figure 3 suggests that the three PMMA electrolytes have anodic stability higher than 4.5V vs. Li (Table 2) and thus, that they can withstand high-voltage electrodic couples, such as the $Li-V_6O_{13}$ or $Li_xC_6-LiMO_2(M=Co$ or Ni) couples.

Table 2- Anodic decomposition voltage at 25 °C of PMMA and PAN lithium gel electrolytes.

electrolyte	sample	decomposition voltage (volt)
$PMMA-PC/EC/LiClO_4$	S-1	4.6
$PAN-PC/EC-LiClO_4$		4.8
$PMMA-PC/EC/LiAsF_6$	S-2	4.8
$PAN-PC/EC-LiAsF_6$		4.5
$PMMA-PC/EC-LiN(CF_3SO_2)_2$	S-3	4.9
$PAN-PC/EC-LiN(CF_3SO_2)_2$		4.6