

CONTRACT SPC-93-4033
3rd two-month Progress Report
December 1993 - January 1994

Introduction

In this two month period, we have continued the investigation of the electrochemical properties of gel-type polymer electrolytes formed by the immobilization of liquid solutions in poly(acrylonitrile), PAN matrices. The aim was that of completing task (i) which is focused on the clarification and the understanding of the basic electrochemical properties of these new gel electrolytes. In particular in this report we discuss results related to the lithium ion transference number and to the electrochemical stability window.

Task (i) Determination of the lithium ion transference number and of the electrochemical stability window.

Experimental

The preparation of the PAN-based gel electrolytes has been described in the previous reports (1,2).

We have selected six representative examples of PAN-based gel electrolytes, namely electrolyte samples having the following molar composition:

- S-1) PAN: 16/PC : 23/EC:56.5/LiClO₄:4.5
- S-2) PAN: 16/PC : 23/EC:56.5/LiAsF₆:4.5
- S-3) PAN: 16/PC : 23/EC:56.5/LiAsF₆:4.5
- S-4) PAN: 16/BL : 79.5LiClO₄:4.5
- S-5) PAN: 16/BL : 79.5/LiAsF₆:4.5
- S-6) PAN: 21/BL:23/EC:56..5/LiN(CF₃SO₂)₂:4.5

These compositions were determined as the most suitable for ensuring complete miscibility the various components and thus, the full homogeneity of the final electrolytic membranes. The electrochemical stability of the electrolytes was determined by running a sweep voltammetry on a three-electrode cell where a stainless steel (SS 304)

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plate was the working electrode, a lithium disk was the counter electrode and a lithium strip, placed between two adjacent layers of gel electrolyte, was the reference electrode.

The techniques used for the determination of the lithium ion transference numbers of the various selected samples will be illustrated in the course of the discussion of the results (next session).

Results

1. Lithium transference number

It is today well established that the most promising positive electrodes in lithium rechargeable batteries are based on insertion compounds. Typical examples are transition metal dichalcogenides (e.g. TiS_2 , Nb_2S_3) and oxides (e.g. V_6O_{13} , V_2O_5). Since the electrochemical process of the electrodes consists of the intercalation and deintercalation of lithium ions throughout the host compound lattice, electrolytes with Li^+ transference number approaching unity ($t_{\text{Li}^+} \rightarrow 1$) are desirable for avoiding concentration gradient during the charge and discharge cycles. Therefore, the evaluation of this parameter is of great importance for the characterization of electrolyte materials designed for battery application. Various methods have been proposed for the determination of t_{Li^+} in polymer electrolytes, including d.c. polarizations, a.c. impedance spectroscopy, potentiometric analysis, as well as classical Tubandt gravimetric analysis. However, not all of these techniques can be correctly used since they may be affected by some operational problems which are specifically related to the nature and the characteristics of the polymeric electrolyte media, such as adhesion of the layers (which excludes Tubandt measurements) and reactivity toward the lithium metal electrode (which affects both d.c. and a.c. analyses).

Therefore, particular attention has been devoted in the past to identify and optimise experimental techniques which would be most suitable for correct transference number measurements in polymer ionics. In the specific case of poly(ethylene oxide) (PEO)-based electrolytes Bruce and Vincent (3) have recently shown that a method based on a combination of d.c.

polarization and a.c. analysis may effectively provide reproducible and reliable results. Therefore, we have considered this method also for the determination of t_{Li^+} in the PAN-based electrolytes examined in this report. Basically, the method consists of measuring by a.c. impedance and by d.c. chronoamperometry, respectively, the resistance of and the current across a symmetrical Li/electrolyte/Li cell, polarized by a d.c. pulse, V . The measurements are taken at the initial time of the applied d.c. voltage pulse ($t=t_o$, $R=R_o$, $I=I_o$) and under steady conditions ($t=t_s$, $R=R_s$, $I=I_s$). By using these values, the t_{Li^+} is given by the expression:

$$t_{Li^+} = \frac{I_s(V - I_o R_o)}{I_o(V - I_s R_s)} \quad [1]$$

where V is the value of the d.c. voltage pulse applied to the cell (in the case of this work $V=10mV$).

Table 1- Lithium transport numbers at 25.4°C

electrolyte	solvent/salt ratio		sample	t_{Li^+}	t_{Li^+}
PC-LiClO ₄	liquid			0.4	
PEO-LiClO ₄	polymer			0.2	
LiClO ₄ -PC/EC-PAN	17.6:1		S-1	0.6 ^a	0.5 ^b
LiAsF ₆ -PC/EC-PAN	17.6:1		S-2	0.7 ^a	0.6 ^b
LiN(CF ₃ SO ₂) ₂ -PC/EC-PAN	17.6:1		S-3	0.8 ^a	0.7 ^b
LiClO ₄ -BL-PAN	17.6:1		S-4	0.6 ^a	0.4 ^b
LiAsF ₆ -BL-PAN	17.6:1		S-5	0.7 ^a	0.6 ^b
LiN(CF ₃ SO ₂) ₂ -BL/EC-PAN	17.6:1		S-6	0.6 ^a	0.6 ^b

a) calculated using impedance technique

b) calculated using pulse technique

Table 1 reports the values obtained for the six PAN-based electrolytes and, for comparison purpose, also values for common liquid organic and PEO-based polymer electrolytes. The sequence of the values is logical since t_{Li^+} increases as the size of the anions progressively increase, namely passing from $LiClO_4$ -based, to $LiAsF_6$ -based and finally, to $LiN(CF_3SO_3)_2$ -based electrolytes. However, the values of the transference numbers of the PAN-electrolytes are much higher than those usually obtained for the parent liquid and for PEO-based polymer electrolytes (see Table 1). Although, this difference could possibly be related to a specific role of the polymeric matrix on the lithium ion transport mechanism, one has to be aware that the technique used for the t_{Li^+} determination may be affected by a certain degree of uncertainty especially in highly concentrated solutions where the extent of ion-ion and ion-solvent association is unpredictable. It may be of interest to point out that high values of t_{Li^+} have also been reported for other types of low-viscous polymer electrolytes. For instance t_{Li^+} values of the order of 0.4-0.5 have been found by Abraham and Alamgir (4) for poly[bis-(methoxy ethoxy ethoxy) phosphazene], MEEP-based polymer electrolytes. Furthermore, Matsuda et.al (5) have reported a value of $t_{Li^+}=0.56$ for the case of a PEO-PMMA/PC- $LiClO_4$ (where PMMA=polymethylmethacrylate) system, namely of a gel electrolyte similar to those examined in this work. We have also attempted to determine t_{Li^+} using a different technique, namely the so called "time of fly" method described by Watanabe and co-workers (6). Basically, the method consists of polarizing a "blocking" electrode cell (e.g. SS/electrolyte sample/SS (SS=stainless steel) cell) for a reasonably long time (typically one hour) in order to promote accumulation of charge at the interface, and then monitoring the current flowing through the same cell immediately after inverting the polarity of the applied voltage. The idea is that of promoting separation of the ionic charge carriers during the initial long polarization period and then of detecting the different peak times associated to the different mobility of the ions when they migrate in opposite directions following the reversal polarization pulse. In this way the lithium transference number may be evaluated by the expression:

$$t_{Li^+} = \frac{\mu^+}{\mu^+ + \mu^-} = \frac{\tau^+}{\tau^+ + \tau^-} \quad [2]$$

Where μ is the mobility of the ion given by the expression:

$$\mu = \frac{d^2}{\Delta v \tau} \quad [3]$$

where d is the cell thickness and τ is the peak time of the ion crossing the cell.

The t_{Li^+} values obtained with this method are generally lower than those obtained with the Bruce and Vincent's method (see Table 1). This discrepancy confirms the limitations of the experimental techniques and the qualitative character of the data of Table 1.

2. Electrochemical stability window

An important parameter for the characterization of any electrolyte, designed for battery applications is the extent of its electrochemical stability window. For instance, in the case of 'conventional' rechargeable lithium batteries (i.e. batteries based on common intercalation cathodes, e.g. V_6O_{13}) the stability window of the electrolyte should be at least 4V vs. Li. Even wider, i.e. exceeding 4.5 vs. Li, should be the stability window when highly oxidizing cathode materials, such as the layered $LiMO_2$ ($M=Ni,Co$) or the spinel-type $LiMn_2O_4$ compounds currently of interest for the development of high-energy lithium batteries of high-voltage lithium rocking chair batteries are used.

For the determination of the anodic limit of the gel electrolytes considered in this Project we have used the generally accepted procedure, namely the determination of the current-voltage response of an "inert" test electrode (in our case, a stainless-steel (SS) electrode).

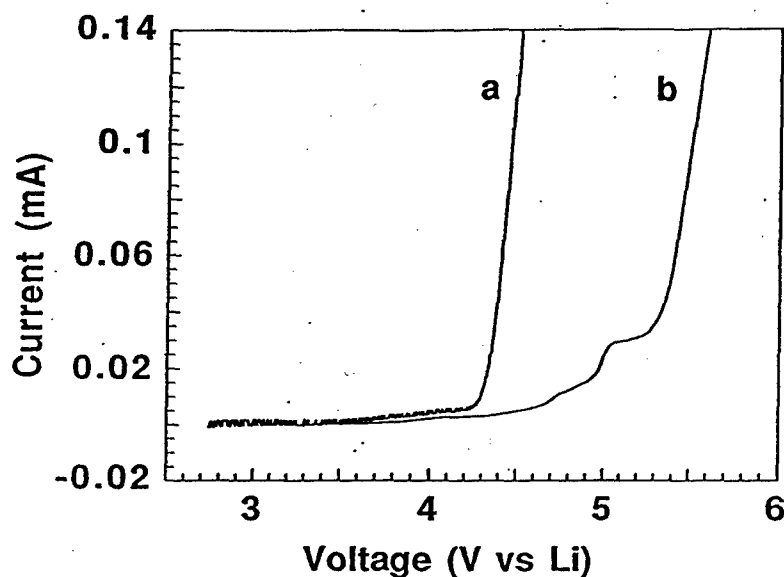


FIGURE 1- Current-voltage response at 20°C of a stainless-steel electrode in a LiAsF₆-PC/EC PAN (sample S-2) electrolyte (curve a) and in a LiAsF₆-PC liquid solution (curve b). Scan rate: 1 mV s⁻¹.

Figure 1 illustrates the current-voltage response obtained in a LiAsF₆-PC/EC-PAN (sample S-2) gel electrolyte cell and, for comparison purposes, that obtained under the same sweeping conditions in a parent liquid solution. Clearly, the anodic limit of the former (about 4.5 V vs. Li) is lower than that of the latter (about 5.2 V vs. Li). A similar trend has also been found for the other PAN-based gel electrolytes examined in this work. The results are illustrated in Figure 2 and summarised in Table 2. The addition of PAN seems to influence the oxidation kinetics. However, although narrower than that of the liquid solution, the stability window of the PAN-based gel electrolytes is still wide enough to allow safe operation with the majority of the lithium battery electrode couples.

Table 2- Anodic decomposition potential.

electrolyte	sample	decomposition potential (volt)
LiClO ₄ -PC/EC-PAN	S-1	4.8
LiAsF ₆ -PC/EC-PAN	S-2	4.5
LiN(CF ₃ SO ₂) ₂ -PC/EC-PAN	S-3	4.6
LiClO ₄ -BL-PAN	S-4	5.0
LiAsF ₆ -BL-PAN	S-5	4.6
LiN(CF ₃ SO ₂) ₂ -BL/EC-PAN	S-6	4.7

Conclusion and further work

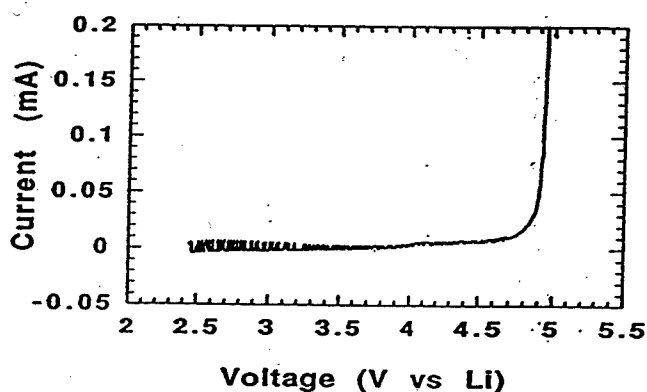
The results described in this and in the previous progress reports indicated that the PAN-based electrolytes have the following electrochemical characteristics.

- i) Very high ionic conductivity, namely of the order of 10^{-3} Scm^{-1} at room temperature (1st. Progress Report).
- ii) Reasonably high value of lithium ion transference number, i.e. of the order of 0.5-0.6 (this Report).
- iii) Stability window with anodic limits extending up to about 4.5 V (this Report)).
- iv) Poor interfacial characteristics resulting in the passivation of the lithium electrode (2nd Progress Report).

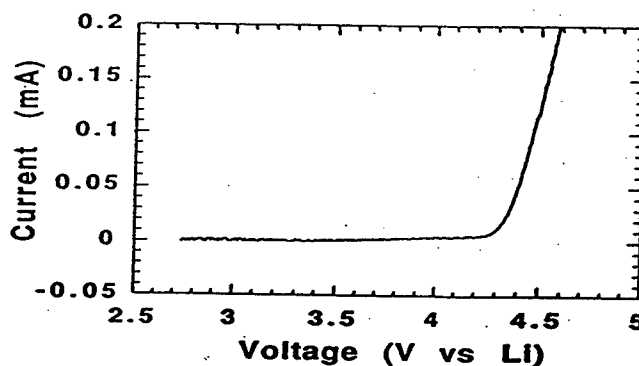
While points i) to iii) are all beneficial in terms of battery applications (since they would assure low IR drops, low concentration polarizations and a wide choice of cathode materials, respectively), point iv) is detrimental (since it would affect cyclability). However, the impedance analysis discussed in the 2nd Progress Report (2) indicates that the kinetics and the type of passivation seems to vary from one electrolyte to another, suggesting a definite role of the electrolyte salt in controlling the phenomenon. Therefore, one may foresee that by the selection of a proper solvent and of a proper salt, the extent of the passivation may be

limited to such a level to assure acceptable stability of the interface and thus, good lithium cyclability. In view of this provision, we will focus our future work to the characterization of alternative gel electrolyte systems, namely to the completion of task III (see 1st Progress Report for task identification and description).

a)



b)



c)

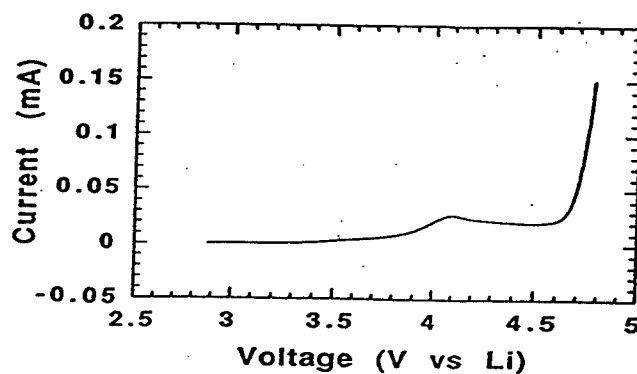


FIGURE 2- Current-voltage response at 20°C of a stainless-steel electrode in PAN gel electrolytes. Scan rate: 1 mV s⁻¹.
 LiClO₄-PC/EC-PAN (sample S-1, curve a)
 LiAsF₆-PC/EC-PAN (sample S-2, curve b)
 LiN(CF₃SO₂)₂-PC/EC-PAN (sample S-3, curve c).

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