

AD-A229 186

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. SECURITY CLASSIFICATION AUTHORITY NOV 05 1990		1c. DECLASSIFICATION/DOWNGRADING SCHEDULE D		2. DISTRIBUTION/AVAILABILITY OF REPORT Unclassified/Unlimited	
4. PERFORMING ORGANIZATION REPORT NUMBER ONR Technical Report #28				5. MONITORING ORGANIZATION REPORT NUMBER(S)			
5a. NAME OF PERFORMING ORGANIZATION Corrosion Research Center		5b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION Office of Naval Research, Resident Rep.			
5c. ADDRESS (City, State, and ZIP Code) University of Minnesota Minneapolis, MN 55455		5d. ADDRESS (City, State, and ZIP Code) Federal Building, Room 286 536 South Clark Street Chicago, IL 60605-1588		7b. ADDRESS (City, State, and ZIP Code) Federal Building, Room 286 536 South Clark Street Chicago, IL 60605-1588			
3a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Res. & the Def Adv Res Projects Agency		3b. OFFICE SYMBOL (If applicable) Code 1113		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract No. N00014-88-K-0360			
3c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000		10. SOURCE OF FUNDING NUMBERS		PROGRAM ELEMENT NO.		PROJECT NO.	
				TASK NO.		WORK UNIT ACCESSION NO.	
11. TITLE (Include Security Classification) Interfacial Stability of Lithium in Non-Aqueous Gel Polymer Electrolyte Cells							
12. PERSONAL AUTHOR(S) P.S.S. Prasad, B.B. Owens and W.H. Smyrl							
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM 1/1/89 TO 5/1/90		14. DATE OF REPORT (Year, Month, Day) 5/1/90		15. PAGE COUNT 3	
16. SUPPLEMENTARY NOTATION 178th Meeting of the Electrochemical Society, Seattle, Washington, October 1990							
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)					
FIELD	GROUP	SUB-GROUP					
		polymer electrolyte, solid state battery, interfacial impedance.					
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Solid polymer electrolytes (SPE) prepared by crosslinking non-aqueous gel polymer precursors in dimethyl sulfoxide-lithium salt media were investigated by a.c. conductivity measurements. These materials exhibit an ionic conductivity of about 10^{-3} S/cm at 25°C. Electrochemical cells of the type Li/SPE/Li and Li/SPE/M where M = Ni, Al & SS were fabricated. Cyclic voltammograms on the asymmetric cells indicate that the electrolyte decomposition potential is about 3.6 volts. The shape of the repetitive cyclic voltammograms within the stability domain indicated that the lithium plating/stripping process is more efficient in the case of Li/SPE/Ni & Li/SPE/Al than Li/SPE/SS asymmetric cells. The a.c. impedance measurements on symmetric Li/SPE/Li cells exhibited two well defined semi-circles with three intercepts on three real-axis. The observed increase in impedance with time was indicative of passivating film formation at the interface. The growth of the film stabilized at a finite value, permitting lithium cyclability.							
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS				21. ABSTRACT SECURITY CLASSIFICATION Unclassified			
22a. NAME OF RESPONSIBLE INDIVIDUAL Boone B. Owens/ W.H. Smyrl				22b. TELEPHONE (Include Area Code) (612) 625-1332; 0717		22c. OFFICE SYMBOL	

INTERFACIAL STABILITY OF LITHIUM IN NON-AQUEOUS GEL POLYMER ELECTROLYTE CELLS

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Solid polymer electrolytes (SPE) prepared by crosslinking non-aqueous gel polymer precursors in dimethyl sulfoxide-lithium salt media were investigated by a.c. conductivity measurements. These materials exhibit an ionic conductivity of about 10^{-3} S/cm at 25 °C. Electrochemical cells of the type Li/SPE/Li and Li/SPE/M where M = Ni, Al & SS were fabricated. Cyclic voltammograms on the asymmetric cells indicate that the electrolyte decomposition potential is about 3.6 volts. The shape of the repetitive cyclic voltammograms within the stability domain indicated that the lithium plating/stripping process is more efficient in the case of Li/SPE/Ni & Li/SPE/Al than Li/SPE/SS asymmetric cells.

The a.c. impedance measurements on symmetric Li/SPE/Li cells exhibited two well defined semi-circles with three intercepts on the real-axis. The observed increase in impedance with time was indicative of passivating film formation at the interface. The growth of the film stabilized at a finite value, permitting lithium cyclability.

INTRODUCTION

The investigation of solid polymer electrolyte rechargeable batteries was directed towards three types of materials that are classified as (a) Plasticized salt polymer electrolytes (b) Mixed polymer electrolytes and (c) Lithium non-aqueous gel electrolytes. Of these three categories, solid polymer electrolytes prepared by cross-linking non-aqueous gel polymer precursors in dimethyl sulfoxide-lithium salt media were found to exhibit a high ionic conductivity of 3.3×10^{-3} S/cm at 25 °C, with good thermal stability over the temperature region -100 to +200 °C. Preliminary results on conductivity measurements in the latter material (SPE) and the performance of the electrolyte in a Li/SPE/V₆O₁₃ cells were already reported [1]. On charge-discharge cycling, the coulombic efficiency initially increased with cycle number, but suddenly decreased to a low value at the 10th cycle. This was attributed to one of the following possibilities: (a) utilization of a low conducting (PEO)₈-LiCF₃SO₃ electrolyte phase in the preparation of the composite cathode; (b) instability at the interface due to possible formation of multiphase electrolyte compositions; (c) growth effects of a passivating thin film at the solid polymer electrolyte/electrode interface.

Hence the present study evaluates the electrochemical stability domain of the SPE, the stability of the SPE in different electrode configurations, passivating film growth at the electrode/electrolyte interface, stability of the interface with time and the stability of the electrolyte in terms of degradation into poorly conducting compounds. Cyclic voltammetric and a.c. impedance measurements were performed on different types of cell configurations and the results were related to the interfacial stability of lithium in non-aqueous gel electrolytes.

EXPERIMENTAL

The electrochemical cells were fabricated in a dry room with less than one percent relative humidity and carefully transferred to an argon gas dry box. Both sealed and unsealed cells were fabricated to test the dry box atmosphere effect on the electrochemical properties. Impedance measurements were performed in the frequency range 10 mHz-1.0 MHz using a Solartron 1260 impedance gain/phase analyzer instrument controlled by an IBM PC/XT computer. An EG&G PARC model 175 universal programmable sweep generator, a model 173 constant potentiostat/galvanostat source and an X-Y recorder were used to perform cyclic voltammetric experiments.

a.c. IMPEDANCE MEASUREMENTS

The solid polymer electrolyte was placed between different types of metallic electrode disks and electrical conductivity measurements were performed to determine the stability of the electrolyte. The electrolyte was found to be stable in symmetric cells of the type M/SPE/M, where M = Ni, Al or SS (stainless steel). When M was lithium, growth of a passive film was observed.

In the case of the asymmetric cell Li/SPE/Ni, lithium deposition on nickel was observed from the nature of the variation of the impedance plots with time. The components of the impedance such as double layer capacitance and charge transfer resistance were considered in determining the value of the bulk electrolyte impedance.

Figure 1 shows the impedance plot of the SS/SPE/SS cell soon after fabrication. Fig. 2(a) shows the corresponding impedance plot of a fresh Li/SPE/Li cell. There are two distinct semi-circles with the bulk electrolyte resistance centered at 000 ohms and the interfacial resistance at 900 ohms. After 24 hours, the measured impedance as shown in Fig. 2(b) shows a very similar behaviour with the bulk electrolyte resistance centered at 2600 ohms and the interfacial resistance increased to 2200 ohms. A distinctively observed difference is the nature of the semi-circle. In Fig. 2(a), both the semi-circles are symmetrical with approximately the same radius. After 24 hours, the semi-circle due to the double layer capacitance & interfacial charge transfer resistance increases by two times indicating that there is predominantly an increase in the interfacial resistance thus indicating the formation of a passive film. Impedance plots recorded after 48, 96 and 200 hours indicated that the interfacial resistance stabilized at an intermediate value, with no further effect on the nature of the impedance plot. The experimentally determined bulk and interfacial resistances were plotted against time (Fig. 3(a)). Fig. 3(b) shows that the bulk electrolyte resistance remained almost constant with time in the SS/SPE/SS cell of Fig. 1.

CYCLIC VOLTAMETRIC MEASUREMENTS

Additional details about the interface characteristics and electrochemical decomposition potential of SPE were obtained from cyclic voltammetry. The observed results were related to the kinetic and thermodynamic processes that occur at the electrode/electrolyte interface. The redox scan in the potential region -4.0 to +4.0 volts vs Li/Li⁺ was obtained for a Li/SPE/SS asymmetric cell to determine the active cathodic and anodic potential regions of the electrolyte. The lithium redox process was observed over the -0.4/+0.4 volt region. The evaluation of this plating/stripping process at various sweep rates indicated the most appropriate rate at which the electrode kinetics matched with the sweep rate. A 1.0 mV/s sweep rate cyclic voltammogram in the potential range -0.4/+2.2 volts vs Li/Li⁺ performed on the above cell is shown in Fig. 5. A second oxidation/reduction peak of unknown electrochemical species was observed at about 1.5 volts (anodic) and 0.8 volts (cathodic). The electrochemical process seems to be controlled more by electrode kinetics than by thermodynamic aspects.

A cyclic voltammogram was recorded to determine the electrochemical window and the decomposition potential of the electrolyte. Fig. 6 shows the extended region of Fig. 4, where two major peaks were encountered in the curve, indicative of an electrochemical parasitic reaction of the electrolyte with fresh deposition of lithium. The second one indicates a partial decomposition phenomena occurring at a potential somewhat higher than 3.6 volts vs Li/Li⁺. The reverse scan was affected by decomposition products and hence could not be analyzed. However, the electrochemical window extended to 3.6 volts vs Li/Li⁺ and thus this electrolyte is of interest for applications with various positive electrodes such as V₆O₁₃, MnO₂, Cr₂O₃ and TiS₂.

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CONCLUSIONS

The relationship between cyclic behaviour in an electrochemical cell and the lithium ion stability, both in the bulk solid polymer electrolyte and the metal/electrolyte interface has been investigated. In the case of a thin film lithium/SPE battery, the overall interfacial impedance may be expected to provide a larger contribution to the overall battery impedance than that of the bulk electrolyte.

ACKNOWLEDGMENTS

The authors wish to acknowledge the financial support of the Office of Naval Research (ONR) and the Defense Advanced Research Projects Agency (DARPA).

REFERENCES

- (1) P S S Prasad, M Z A Munshi, B B Owens and W H Smyrl, Solid State Ionics, 40/41 (1990) In Press.

FIGURES

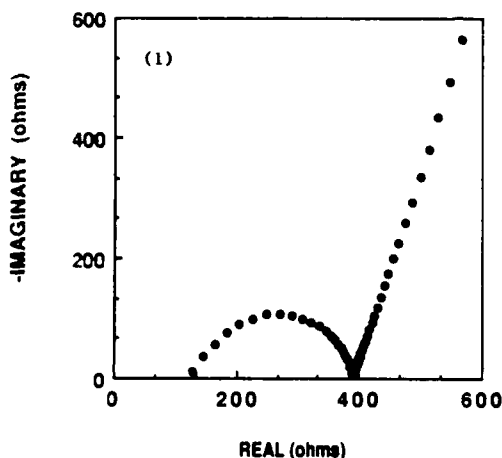


Fig. 1 : Impedance plot of a lithium non-aqueous gel electrolyte in SS/SPE/SS cell configuration at 25 °C.

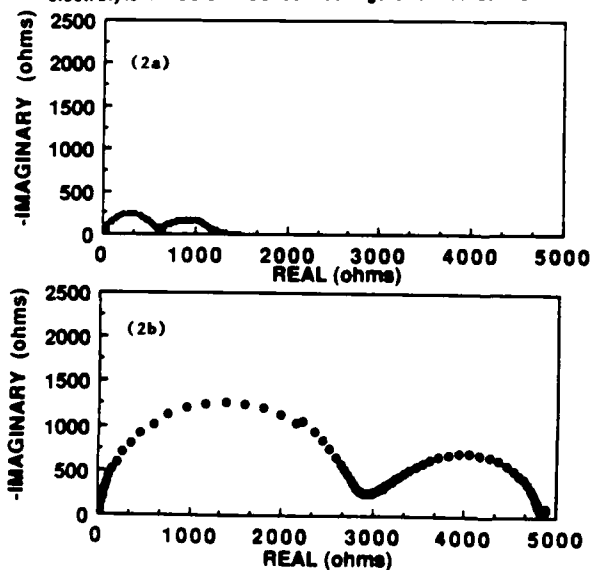


Fig. 2 : (a) Impedance plot of lithium non-aqueous gel electrolyte in the Li/SPE/Li cell configuration at 25 °C soon after fabrication and (b) after 24 hours.

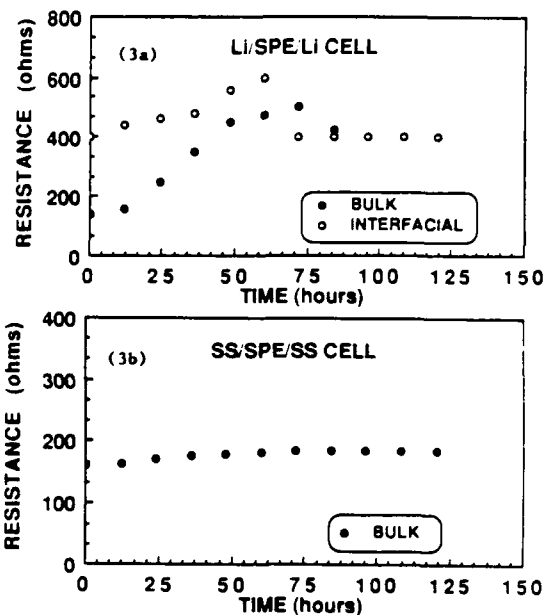


Fig. 3 : Variation of bulk & interfacial resistance with time in (a) Li/SPE/Li cell and (b) SS/SPE/SS cell.

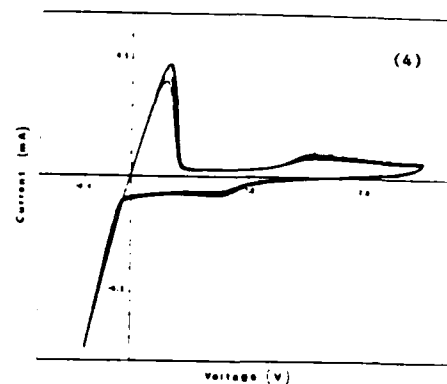


Fig. 4 : Cyclic voltammogram of the lithium non-aqueous gel polymer electrolyte in a Li/SPE/SS cell configuration.

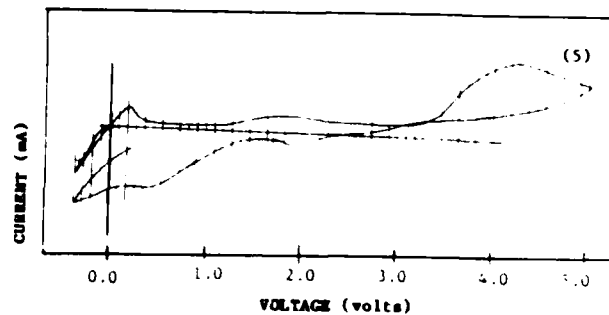


Fig. 5 : Cyclic voltammogram of the lithium non-aqueous gel electrolyte, in the extended potential region of Fig. 4.