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Lithium Electrode/Polyacrylonitrile Based Polymer Electrolyte Interface

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13. ABSTRACT (Maximum 200 words) Preparation of solid-state polymer lithium electrolytes based on polyacrylonitrile (PAN) have achieved room temperature conductivities equal to that of liquid organic electrolytes. Polymer films of ethylene carbonate, propylene carbonate, PAN, and lithium salts have yielded conductivities as high as 0.004 S/cm at 25 deg C. These high conductivities make the use of polymer electrolytes a viable possibility in advanced lithium batteries. Besides a high ionic conductivity, chemical stability of the polymer with lithium is another consequential property to make an electrolyte successful in a practical battery configuration. It is shown that the growth of the interfacial resistance between lithium and the solid polymer electrolyte (SPE) can be reduced by the addition of dimethyl carbonate, or ground molecular sieves, or by reducing the solvent to salt ratio. Reported here are the film preparation technique, conductivities from -70 to +70 deg C, and the time evolution of the impedance responses of Li/SPE/Li cells.				
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INTRODUCTION

The use of solid polymer electrolytes (SPE) in rechargeable lithium batteries is currently being widely investigated. Polymer electrolytes can be prepared into very thin films possessing large surface areas yielding high power densities. An energy advantage of a solid flexible electrolyte is its ability to enable the design of more volume efficient battery configurations. In an electrochemical cell, especially in a reversible cell, a flexible electrolyte can accommodate the volume changes that occur with charge/discharge cycles. Polymer electrolytes can increase cell safety by preventing ignition, by acting as a shutdown separator, if thermal runaway should occur within a cell. A thin Li^+ ion conducting polymer film acts as both the electrolyte and a separator between the lithium anode and a lithium insertion compound as the cathode. The use of high energy cathode films of reversible compounds such as LiCoO_2 , LiNiO_2 , LiMn_2O_4 , V_2O_5 , or V_6O_{13} with thin lithium foil anodes and the structural flexibility of polymer electrolytes make the lithium polymer battery a promising candidate for advanced battery systems for electric vehicles (EV) or consumer/military electronics applications.

One of the first polymer electrolyte chemistries consisted of poly(ethylene oxide) PEO-LiX complexes (1,2) which need to operate at around 100°C . New multiphase systems involve adding plasticizing solvents to PEO-LiX or trapping liquid electrolyte solutions in a polymer matrix to form a "gel" electrolyte. The latter more "liquid-like" chemistries can operate at room temperature and therefore are of interest for further research. One of the basic fundamental problems in the development of solid state ionic materials based on polymers is the conductivities of these materials. Recently, room temperature conductivities as high as $10^{-3} \text{ S cm}^{-1}$ have been reported by Abraham and Alamgir (3) for polyacrylonitrile (PAN) based lithium salt complexes.

Electrolyte solvents PC (propylene carbonate) and EC (ethylene carbonate) which are currently being utilized as plasticizers with PAN are known to form passivating layers on metallic lithium in liquid electrolytes (4). Continuous growth of this layer will effect battery performances such as cyclability, reliability and safety. It is the aim of this study to evaluate the compatibility of the lithium anode with PAN based electrolytes and to study what effect, if any, compositional changes have on the resistive film growth. An identification of a suitable equivalent circuit for the purpose of interpretation of the interfacial phenomena is not made in this study but has been proposed elsewhere (4,5).

EXPERIMENTAL

The preparation of the solid gel electrolytes involved the immobilization of LiAsF_6 in ethylene carbonate (EC) and propylene carbonate (PC) mixtures with PAN. The LiAsF_6 (Lithco "Lectro-salt") was dried under vacuum at 60°C for 24 h. PC

(Burdick and Jackson) was dried with type 4A molecular sieves for 48 h then distilled under vacuum. EC (Fluka AG) was fractionated under vacuum. Dimethyl carbonate (DMC) (Burdick and Jackson) was fractionated in an argon atmosphere. Karl Fisher titration for EC, PC, and DMC indicated water contents of < 24 ppm. Poly(acrylonitrile) (Polyscience Inc.) with an average molecular weight of 150,000 was dried under vacuum at 60°C for 48 h. Molecular sieves, type 3A, were ball-milled for 24 h then dried under vacuum at 60°C for 24 h.

The liquid electrolyte EC:PC:LiX was prepared in a vial with a stirring bar. PAN powder was then added and the mixture stirred to ensure wetting of the PAN. The mixture was heated slowly in an oil bath to 100°C, avoiding overheating and decomposing the PAN. The mixture turned to a clear highly viscous gel and was cast between glass plates, with 0.25 mm spacers, and allowed to cool. The resulting polymer electrolyte was an elastomeric mechanically stable film. Two general film compositions were prepared with mole percentages of 40EC:34.75PC:21PAN:4.25LiX (17.6:1 EC + PC:LiX) and 38EC:33PC:21PAN:8LiX (8.8:1 EC + PC:LiX). Variations to these compositions include the use of DMC with EC/PC mixtures and the addition of ground molecular sieves to form a composite film.

Electrolyte conductivities and lithium/electrolyte interfacial corrosion were determined from ac impedance measurements using an EG&G PAR model 388 impedance system with a frequency range of 5 Hz to 1000 kHz. The conductivity measurements were performed with a test cell with an electrode configuration of SS/SPE/SS. A thermocouple was in close proximity to the SPE in the cell. The cell assembly was inserted into a wide-mouthed glass reaction vessel packed with molecular sieves, and argon bubbled through. The temperature testing (70°C to -70°C) was performed in a Tenney environmental chamber. The corrosion measurements were performed on a Li/SPE/Li cell at 25°C. Chemical storage, film casting, and cell assembly were performed in a Vacuumatmospheres Inc. argon-filled dry box.

RESULTS AND DISCUSSION

For polymer electrolytes to be of practical use, Li-ion mobility must be high enough to enable useful rate capabilities in lithium batteries. The PAN-based electrolyte films demonstrate conductivities approaching that of the liquid and a significant increase in ion mobility over the PEO-based electrolytes. It is this result, first demonstrated by Abraham and Alamgir for this chemistry (3), that makes a mechanically stable freestanding film a possible battery electrolyte. Having established that PAN-based films can be prepared with PC and produce ionic conductivities close to liquid organic electrolytes, further studies of Li-ion mobility in these types of electrolytes were performed.

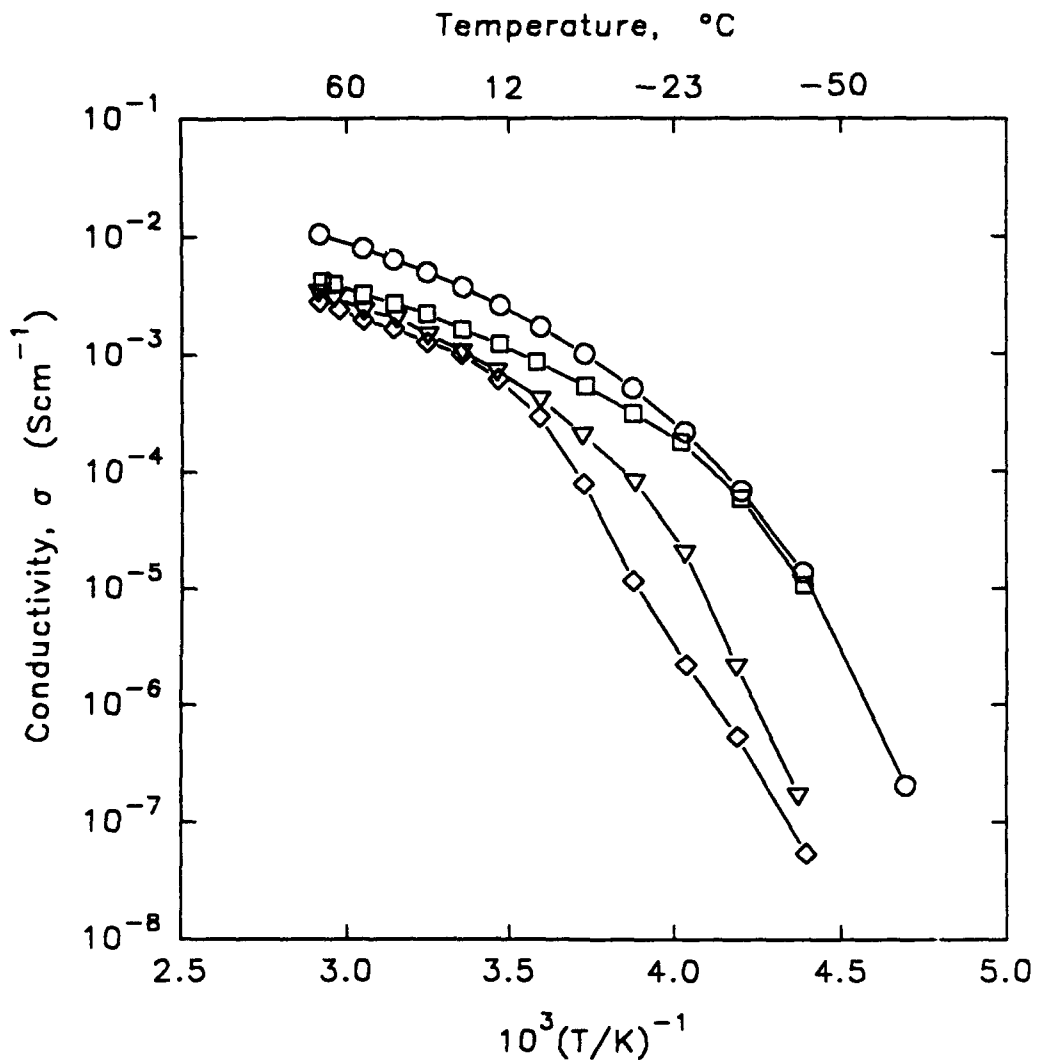
The Arrhenius plots in Figure 1 show the conductivities of four chemical variations of the EC:PC: PAN:LiAsF₆ electrolyte. Changing the solvent to LiAsF₆ ratio from 17.6:1 to 8.8:1 (i.e., doubling the amount of salt while holding the PAN concentration at 21 mole percent) lowers the conductivity over the whole temperature range. This is a viscosity effect on the ionic mobility. The addition of DMC in liquid organic electrolytes makes the solvent more stable with the lithium metal anode and improves lithium cycling efficiency (6). This is due to the formation of a thin compact film such as lithium ethyl carbonate on the lithium surface (7). In the polymer, addition of DMC lowers the conductivity at lower temperatures due to its high melting point. This result has also been demonstrated in liquid electrolytes.

The addition of ceramic materials such as γ -LiAlO₂ dispersed in PEO-based polymer electrolytes has been reported to increase ionic conductivity and reduce interfacial corrosion (8). It is believed the LiAlO₂ particles decreased the polymer crystallinity and absorbed impurities such as water that are reactive with lithium. In this study, type 3A molecular sieves were ground and dispersed in a mixture of EC:PC: PAN:LiAsF₆. The effect on conductivity was to lower slightly the ionic mobility at higher temperatures. In general, the change in salt concentration, the addition of DMC, and the composite film formation with the sieves had little effect on conductivity at room temperature and above.

The time evolution of the ac impedance responses of Li/SPE/Li cells with the 17.6:1 and 8.8:1 (EC + PC;LiAsF₆) electrolytes is shown in Figure 2. The curves reveal an increase in resistance with time indicating an interfacial film growth due to the corrosion of lithium. A decrease in the amount of EC + PC results in a significant reduction of interfacial film resistance. Summarized in Figure 3 are the interfacial resistance growth for 35 days of the four PAN electrolytes studied. All three electrolyte modifications lowered the film growth. Lowering the solvent to salt ratio, in effect having less solvent exposed to the lithium, reduced the corrosion. The addition of DMC, which is less reactive toward lithium, also reduced the film formation. Adding ground molecular sieves lowered the film resistance indicating that trace water is absorbed in the sieve pores preventing its exposure to the metallic lithium electrode.

CONCLUSIONS

It can be concluded from this study that solid gel polymers based on PAN and LiX salt complexes possess adequate ionic conductivities to be used in lithium rechargeable batteries. The reduction of resistive film growth due to the corrosion of the lithium anode with the electrolyte can be achieved by various chemical modifications without significant loss of ionic conductivity. The addition of ground molecular sieves to form a composite electrolyte seems to be of particular interest for future studies. While it has less of a negative effect on conductivity and a



- 40EC:34.75PC:21PAN:4.25LiAsF₆
- 40EC:34.75PC:21PAN:4.25LiAsF₆ w/5wt% 3A sieves
- ▽ 38EC:33PC:21PAN:8LiAsF₆
- ◇ 33EC:28PC:13.5DMC:20PAN:5.5LiAsF₆

Figure 1. Arrhenius plot of electrolyte conductivities.

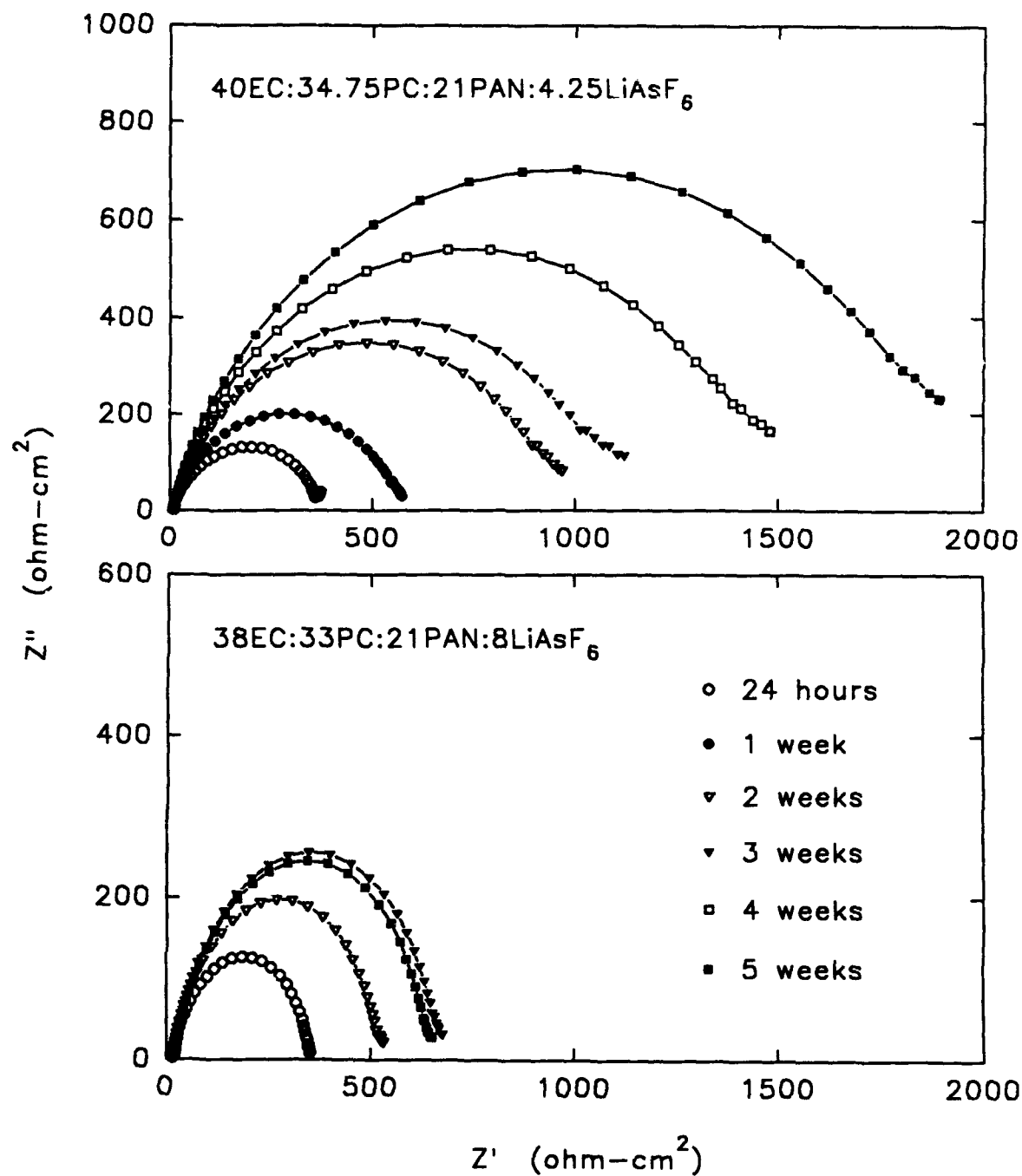


Figure 2. Time evolution of the impedance response of Li/SPE/Li cells.

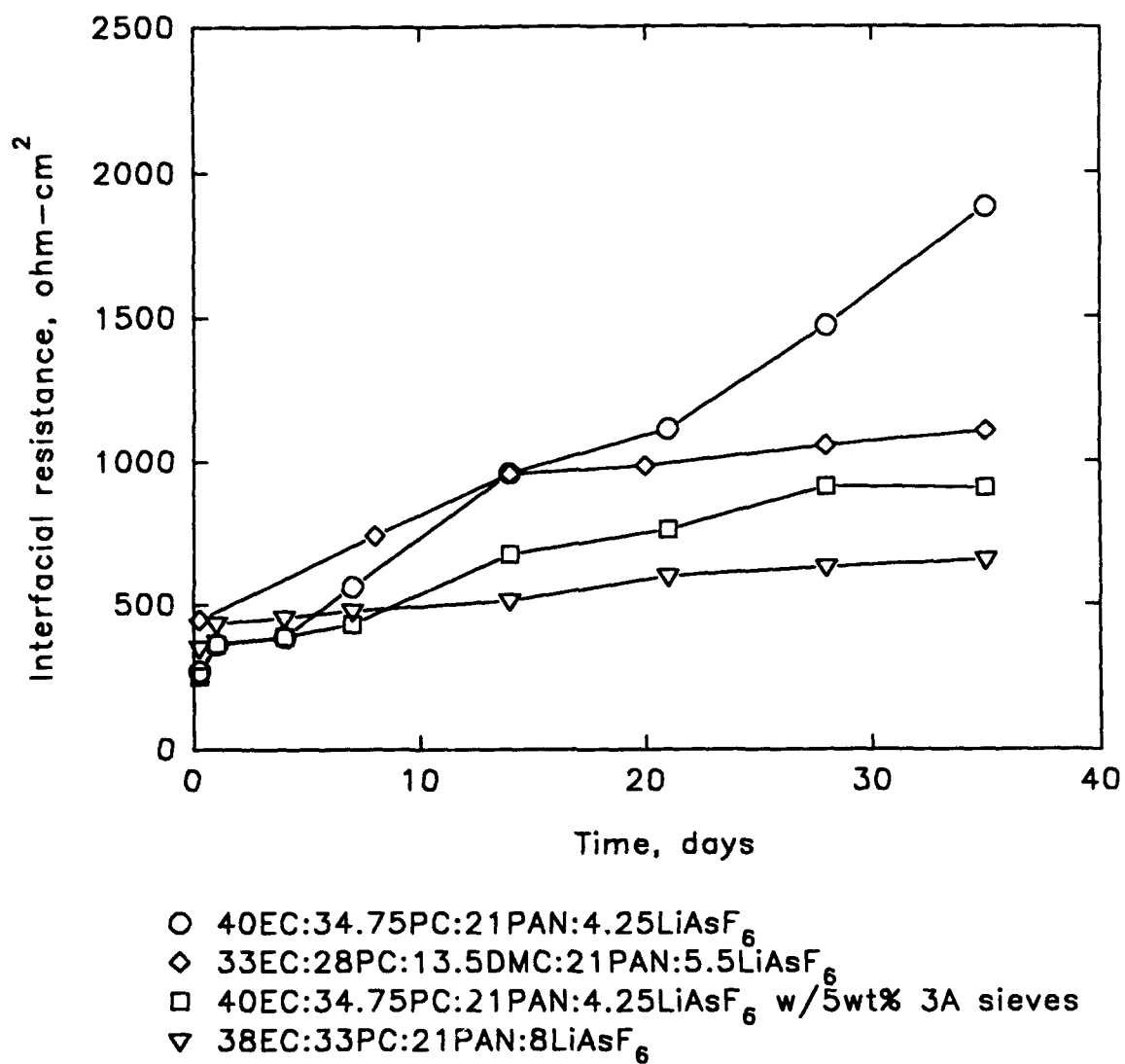


Figure 3. Interfacial resistance of Li/SPE/Li cells

beneficial effect on the lithium interface, the addition of ceramic powders may enhance the mechanical stability of a film. The conductivity of this electrolyte at low temperatures is equal to that of the electrolyte without the sieves, indicating possibly that the sieves are preventing crystallization of the polymer. The next obvious step in the development of PAN-based electrolytes is the study of their performance in full cell configurations.

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