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SOLID POLYMER ELECTROLYTES BASED ON NATURAL RUBBER AND POLY(ETHELENE)OXIDE (PEO) AND THEIR APPLICATION IN RECHARGEABLE LITHIUM BATTERIES

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ABSTRACT

Hybrid solid electrolyte films have been prepared by incorporating various proportions of natural rubber into $(PEO)_9$-$LiCF_3SO_3$ solid polymer electrolyte. Rubbery electrolyte membranes with as much as 50% by weight of natural rubber could be prepared without significantly reducing the ionic conductivity of the polymer electrolyte. The possibility of using these electrolyte membranes in solid state lithium batteries with V_6O_{13} cathode has been demonstrated.

1. INTRODUCTION

Solid polymer electrolytes are complexes between metal salts and high molecular weight polymers containing solvating heteroatoms.Solid polymer electrolytes based on poly(ethylene)oxide(PEO) complexed with lithium salts have been widely studied due to the possibility of using them in rechargeable lithium batteries, and becuase good lithium cyclability has been found in most of these complexes[1-4]. In order to look for the possibility of incorporating naturalrubber(NR) into these polymer electrolytes, we have synthesised and characterised hybrid polymer electrolytes with 12%, 20% and 50% by weight of natural rubber and $(PEO)_9$-$LiCF_3SO_3$ solid polymer electrolyte. Charge/discharge behaviour of rechargeable solid state cells incorporating these elastic electrolyte membranes has also been investigated.

2. EXPERIMENTAL

Natural rubber latex stabilised with NH_4OH was first coagulated by adding CH_3COOH. The solid rubber coagulum was subsequently washed thoroughly with distilled water and dried in vacuum for three days. Electrolyte films, containing the pure $(PEO)_9$-$LiCF_3SO_3$ solid polymer electrolyte as well as those with 12%, 20% and 50% by weight of natural rubber were prepared by solvent casting method using dichloromethane (CH_2Cl_2) as the common solvent. The films were subsequently dried in vacuum for at least 24 hours prior to conductivity measurements.

Ionic conductivity of the thin electrolyte films was measured at various temperatures up to 110°C using complex impedance technique in the frequency range 20 Hz to 10 MHz by means of the HP4192A complex impedance meter. The dc polarisation test was performed on the samples at 90°C under 2V bias potential. Solid state cells were fabricated using the electrolyte membrane $(PEO)_9$-$LiCF_3SO_3$ + 50% by weight of natural rubber, and Li as the anode and V_6O_{13} as the cathode. Constant load discharge characteristics were obtained for these cells operating at 110 °C. This temperature was chosen in order to minimise the effect of moisture and also to make use of the higher conductivities of the polymer electrolyte. In order to test the cyclability of the cells, constant current charge/discharge characteristics were obtained at the same temperature using an automated potentiostat and a chart recorder. After fully discharging the cells, their capacities were estimated.

3. RESUTS AND DISCUSSION

Ionic conductivity of the pure $(PEO)_9$-$LiCF_3SO_3$ solid polymer eklectrolyte at 110 ° C is 1.20×10^{-4} S cm^{-1}. This value is consistent with the values reported in the literature for this material. Out of the three samples prepared by incorporating 50% by weight of NR, the highest conductivity obtained is 2.55×10^{-5} S cm^{-1} at the same temperature. The dc polarisation tests performed at 110 °C showed the predominently ionic nature of both these electrolytes.

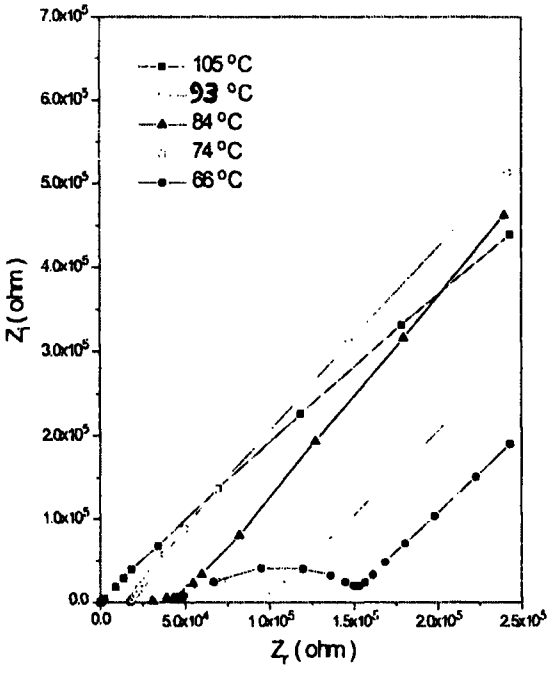

Fig.1. Impedance plots of pure $(PEO)_9$-$LiCF_3SO_3$ polymer electrolyte at various temperatures

The complex impedance plots for the pure $(PEO)_9$-$LiCF_3SO_3$ solid polymer electrolyt e at various temperatures are shown in Fig. 1 and that for the electyrolyte with 50% by weight of NR are shown in Fig.2.

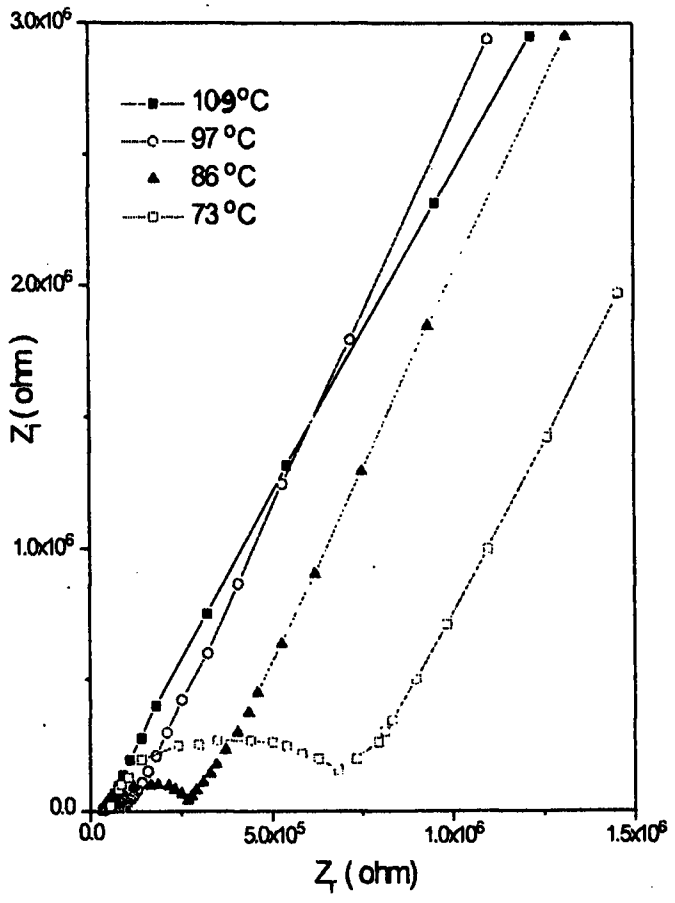

Fig. 2. Impedance plots of $(PEO)_9$-$LiCF_3SO_3$ + 50% by weight of Natural Rubber at various temperatures

Table 1 gives the ionic conductivity values of three different samples of $(PEO)_9$-$LiCF_3SO_3$ + 50% by weight of NR at various temperatures along with pure $(PEO)_9$-$LiCF_3SO_3$ electrolyte for comparison.

Table 1. Conductivities (in S cm^{-1}) of three polymer electrolyte samples $(PEO)_9$-$LiCF_3SO_3$ + 50% by weight of NR (samples A,B C) and pure $(PEO)_9$-$LiCF_3SO_3$ electrolyte at various temperatures.

Temperature (°C)	Sample A	Sample B	Sample C	($PEO)_9$-$LiCF_3SO_3$
40	$1.99x10^{-8}$	$8.30x10^{-9}$	$5.27x10^{-8}$	$3.57x10^{-9}$
57	$8.08x10^{-8}$	$3.67x10^{-8}$	$6.08x10^{-8}$	$3.11x10^{-8}$
70	$1.92x10^{-6}$	$1.39x10^{-6}$	$2.09x10^{-6}$	$1.87x10^{-5}$
85	$3.36x10^{-6}$	$3.37x10^{-6}$	$3.54x10^{-6}$	$3.55x10^{-5}$
97	$1.05x10^{-5}$	$9.33x10^{-6}$	$7.20x10^{-6}$	$6.08x10^{-5}$
108	$2.08x10^{-5}$	$2.55x10^{-5}$	$2.26x10^{-5}$	$1.20x10^{-4}$

Conductivity Arrhenius plots for pure $(PEO)_9$-$LiCF_3SO_3$ polymer electrolyte as well as for the $(PEO)_9$-$LiCF_3SO_3$ + 50% by weight of NR (Sample B) hybrid electrolyte are shown in Fig.3.

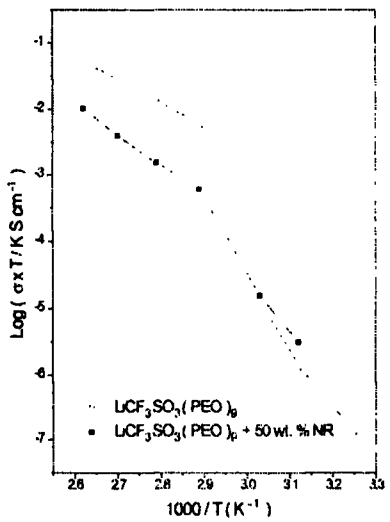

Fig. 3. Conductivity Arrhenius plots for pure $(PEO)_9$-$LiCF_3SO_3$ polymer electrolyte as well as for the $(PEO)_9$-$LiCF_3SO_3$ + 50% by weight of NR (Sample B) hybrid electrolyte

As can be seen from this Figure, at temperatures below the crystalline to amorphous phase transitiontemperature of 60 °C of PEO, the conductivity of the natural rubber incorporated electrolyte is higher than that of the pure $(PEO)_9$-$LiCF_3SO_3$ electrolyte. This may be attributed to the elastomeric nature of the environment introduced by the natural rubber matrix which can facilitate lithium ion migration. However, above 60 °C, the presence of the natural rubber matrix appears to have a negative effect on ionic conductivity. This may be due to the blocking effect caused by the rubber matrix on lithium ion migration as the amorphous phase of the PEO is more favourable for ionic migration.

Constant current charge/discharge curves of the cells, Li / $(PEO)_9$-$LiCF_3SO_3$ + 50% wt of NR/V_6O_{13} are shown in Fig. 4 for two different currents, 50 μA and 25 μA. Due to the higher IR drop caused by the lower conductivity, the current drawn from these cells were lower than those from a similar cell without natural rubber.

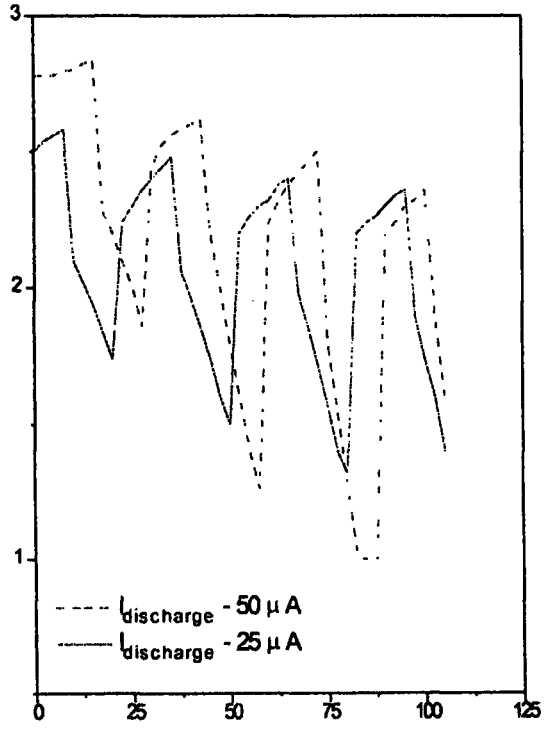

Fig.4. Charge/discharge curves of the solid state cells Li / $(PEO)_9$-$LiCF_3SO_3$ + 50% wt of NR/V_6O_{13}

The cell capacity was calculated after allowing the cell to discharge fully. The calculated capacity is 7.4×10^3 J kg^{-1}.

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