Sri Lankan Journal of Physics, Vol. 12 (2011) 25-31

INSTITUTE OF PHYSICS - SRI LANKA

Research Article

Effect of the polymer host, Polyacrylonitrile on the performance of Li rechargeable cells

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Abstract

Gel electrolytes have emerged as potential candidates for various applications because they have appreciable ionic conductivities while having mechanical stability. In this study, the main objective was to find the role of Polyacrylonitrile (PAN) on performance of a gel polymer electrolyte in a Li rechargeable cell. A gel electrolyte was prepared using Ethylene Carbonate (EC), Propylene Carbonate (PC) and Lithium Trifluoromethanesulfonate ($LiCF_3SO_3$) with PAN. A Li rechargeable cell having a conducting polymer cathode was assembled with the electrolyte. To observe the effect of PAN, parent liquid electrolyte was also used in a similar cell. It was seen that both cells have equal capacities but the stability with a liquid electrolyte is very low. This means PAN provides only dimensional stability. Room temperature conductivity of few samples was measured varying PAN amount. When PAN amount was increased, conductivity reduced. It may be due to blocking of ion transporting channels. It was interested to note that both gel electrolyte and its liquid electrolyte show maximum conductivity at slightly different salt concentrations for many temperatures. We conclude that addition of PAN does not disturb the performance of gel electrolyte in a battery; But it provides the mechanical stability for the liquid electrolyte.

Keywords: Polyacrylonitrile; Ionic conductivity; Gel Polymer Electrolyte; Lithium Trifluoromethanesulfonate; Liquid Electrolyte

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1. INTRODUCTION

Gel polymer electrolytes generally consist with a polymer host, solvent/s and a salt. They show high ionic conductivities while having good mechanical stabilities. They have become promising candidates for many applications such as secondary cells[1], solar cells[2], artificial muscles[3] and electrochromic devices. The basic concept behind the gel polymer electrolytes is that they make the liquid electrolyte immobilized in a polymer host[4]. It is believed that due to the presence of a liquid electrolyte, gel polymer electrolytes show appreciable conductivities and polymer host provides the mechanical stability. Conventional polymer electrolytes have rather poor ionic conductivities at ambient temperatures. Efforts to enhance the ionic conductivity by different means become successful only at the expense of mechanical stability[5]. It is believed that polymers like polyethyleneoxide (PEO) tend to dissolve in different plasticizers which are used to enhance the conductivities. As far as polymer hosts like PAN are considered, they are not exhibiting such problems. It is believed that polymer hosts in gel polymer electrolytes are only acting as supporting matrices to hold the liquid electrolytes. But, some studies have shown that polymer hosts affect for conductivity and other properties as well in the gel polymer electrolytes. Hence, in this study, it was attempted to investigate the role of PAN in a gel polymer electrolyte when use in a Li rechargeable cell.

2. EXPERIMENTAL

A mixture of EC (ALDRICH, 98%) and PC (Bie and Berntsen A-S, 99%) of 1:1 (by weight) was dried over molecular sieves for 24 hrs. The composition selected was 15.01 mol% PAN : 41.84 mol% EC : 36.09 mol% PC : 7.06 mol% $LiCF_3SO_3$ which had given the maximum room temperature conductivity[1]. Then, the required amount of $LiCF_3SO_3$ (3M) was mixed in and purification was done by percolating through activated alumina. In a certain amount of so-prepared electrolyte, the corresponding quantity of PAN (ALDRICH) was dissolved with the aid of magnetic stirring. The mixture composing of PAN: EC : PC: $LiCF_3SO_3$ was heated at 140 ^{0}C for 1 hr in a Buchi model (T0-50) furnace. The resulting homogeneous, viscous hot mixture was poured between two well-cleaned glass plates and pressed. On cooling, transparent film membranes could be obtained which were free from bubbles and pinholes. All the preparation steps were carried out in side a glove box (Vacuum Atmospheres Corporation) purged with Argon (Ar).

Pyrrole (ALDRICH) was purified by distillation under Nitrogen (N_2) and stored in a refrigerator under dark. Sodium Dodecylbenzenesulfonate (SDBS)(ALDRICH) was used as received. Galvanostatic polyemrization of pyrrole was done on a polished stainless steel dice (of a brass sample holder) in a three-electrode cell where a platinum electrode and a saturated calomel electrode were served as counter and reference electrodes respectively. The monomer used consisted of 0.2 M pyrrole with 0.05 M SDBS. The current density used was 1 $mAcm^{-2}$. The time for polymerization was regulated in order to obtain a film of thickness of 1 μm upon the assumption that a charge of 240 mC cm^{-2} produces a film having thickness 1 μm[6]. Thickness value of PPy film was 1 μm. Polymerization process was done with the use of a computer controlled galvanostat / potentiostat. Films were thoroughly rinsed with distilled water after deposition to remove any existing monomer molecules. Cell preparation was done in side a glove box purged with Ar. A circular shape pellet was cut from the electrolyte membrane. A lithium electrode of the identical diameter was taken as the anode. A brass sample holder was used to house the cell assembly. When assembling cells using the liquid electrolyte, two porous polypropylene sheets were used with the liquid electrolyte. The cells were continuously charged and discharged using a computer controlled charge-discharge setup. For some further studies, samples were prepared varying the PAN amount in the gel electrolyte following the same method. Also, gel electrolyte and the corresponding liquid electrolytes were prepared for different salt concentrations. To obtain room temperature conductivities, samples were assembled in a brass sample holder using stainless steel electrodes and impedance data were collected using a computer controlled Solatron SI 1260 impedance analyser. The diameter and the thickness of the samples were measured with a micrometer screw gauge.

3. RESULTS AND DISCUSSION

The charge variation upon continuous cycling of the cell having the polymer gel electrolyte and the corresponding liquid electrolyte are shown in Figure 1 and Figure 2 respectively.

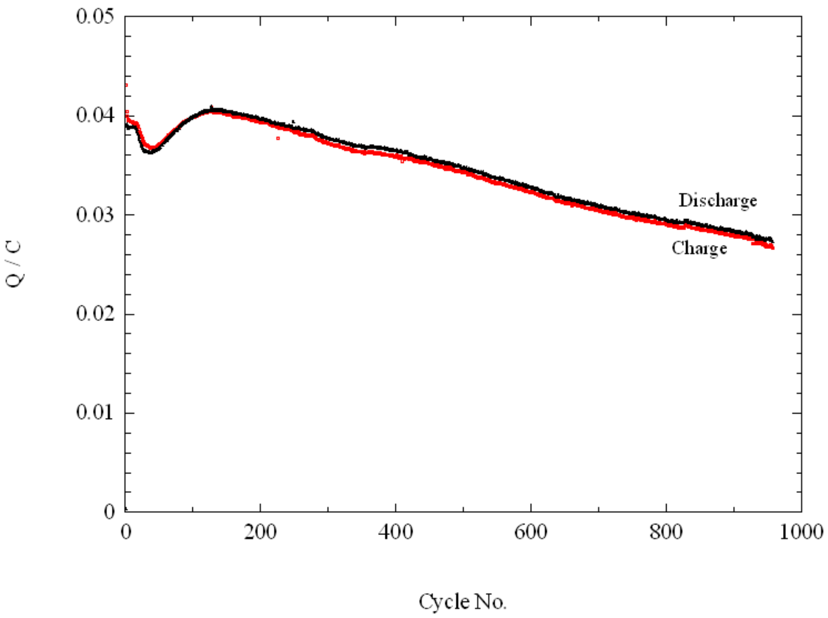

Figure 1: Continuous charge discharge behavior of the cell, Li / PAN : EC : PC : LiTf / PPy DBS

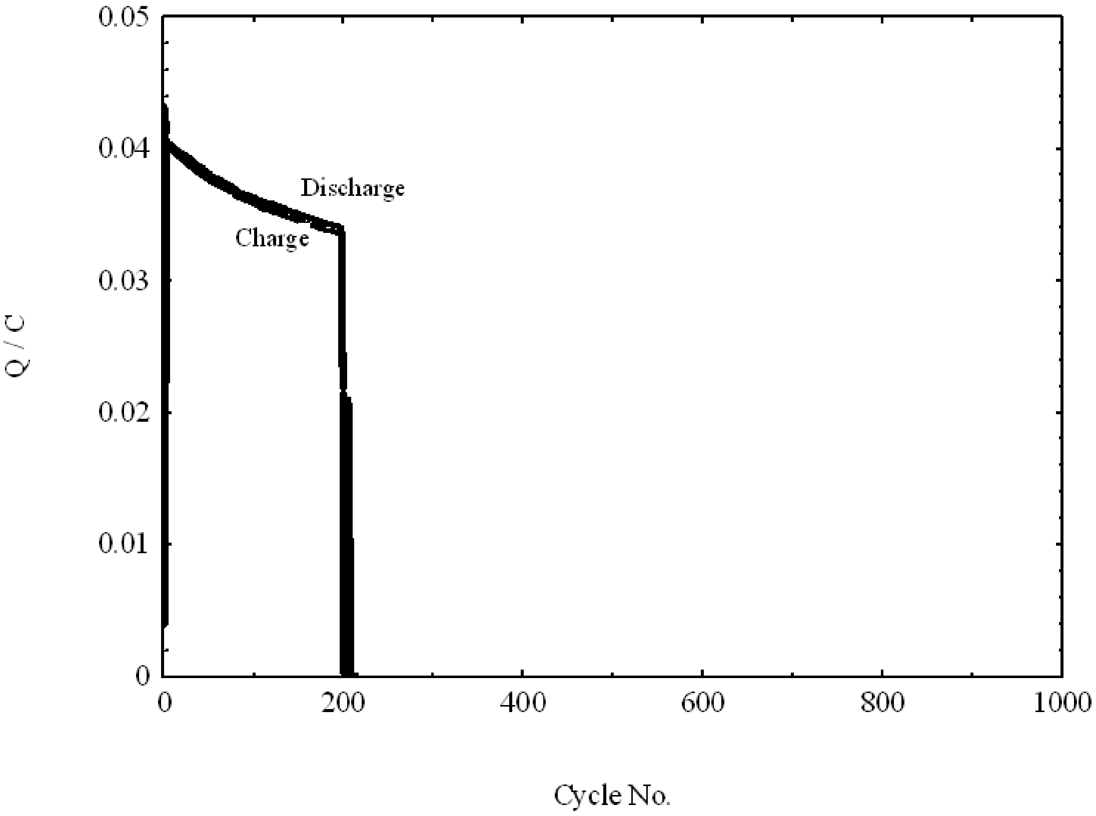

Figure 2: Continuous charge discharge behavior of the cell, Li / EC : PC : LiTf / PPy DBS

PAN / Liquid electrolyte ratio was maintained at 0.1. It is seen that in the two graphs, the charge available in the cell at the start is same. In the liquid electrolyte based cell, the charge decrement is more rapid. It has failed after about 200 cycles. But, the cell with the gel polymer electrolyte was functioning without a failure though charge was decreasing. This shows clearly that cells with gel polymer electrolytes are more stable than the cells with liquid electrolytes and the reason may be the presence of the polymer, PAN that traps the liquid electrolyte inside the polymer matrix. To prove this fact further, room temperature conductivities were measured varying the PAN concentration of the gel electrolyte and salt concentration of gel polymer and its liquid electrolyte. The results are shown in Figure 3 and Figure 4 respectively.

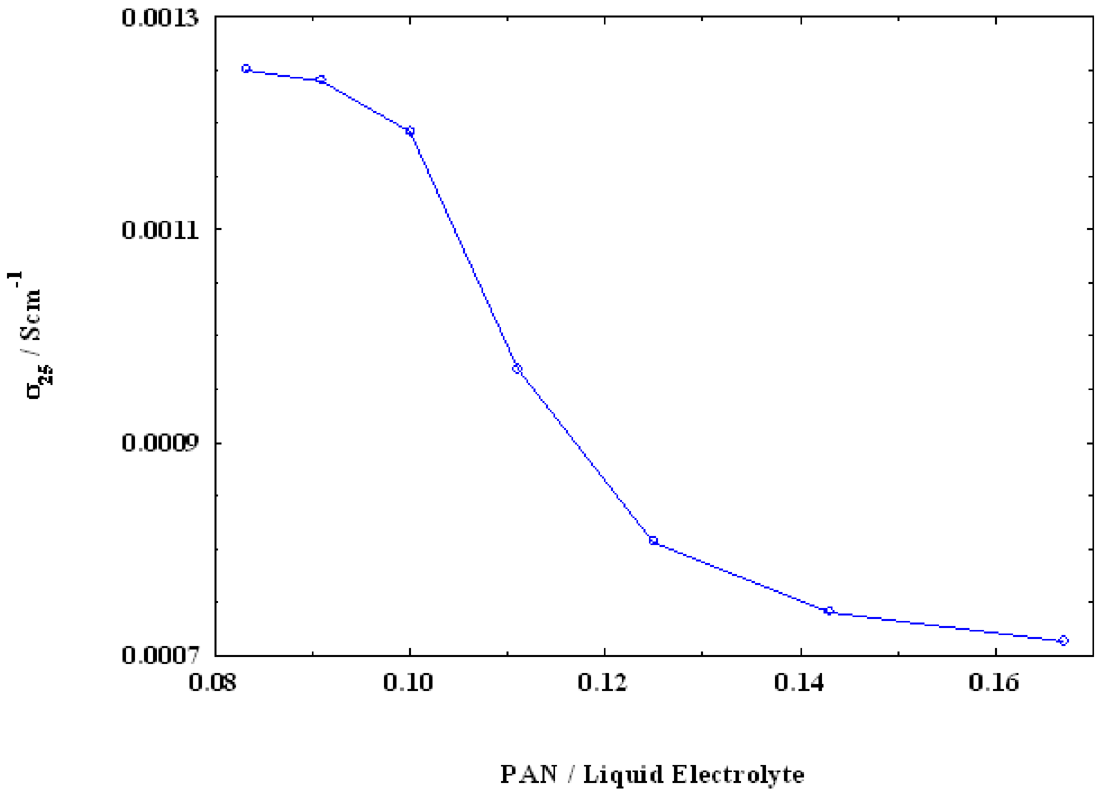

Figure 3: Room temperature conductivity vs PAN / liquid electrolyte ratio for the gel polymer electrolyte PAN : EC : PC : LiTf

It is clear that when the amount of PAN in the liquid electrolyte is increased, the conductivity goes down. This behaviour has been reported by others as well[7]. The reason may be blocking of channels for ion transport by the presence of PAN. Due to this effect, paths for ionic motion may become tortuous lowering the ion transport and then, ionic conductivity reduces. Though the conductivity is higher at low amounts of PAN, the electrolytes are more or less close to liquid phase. This is a problem in handling them for applications. With the compromise of conductivity and the mechanical stability, the suitable value of PAN / liquid electrolyte was 1/10 in this study.

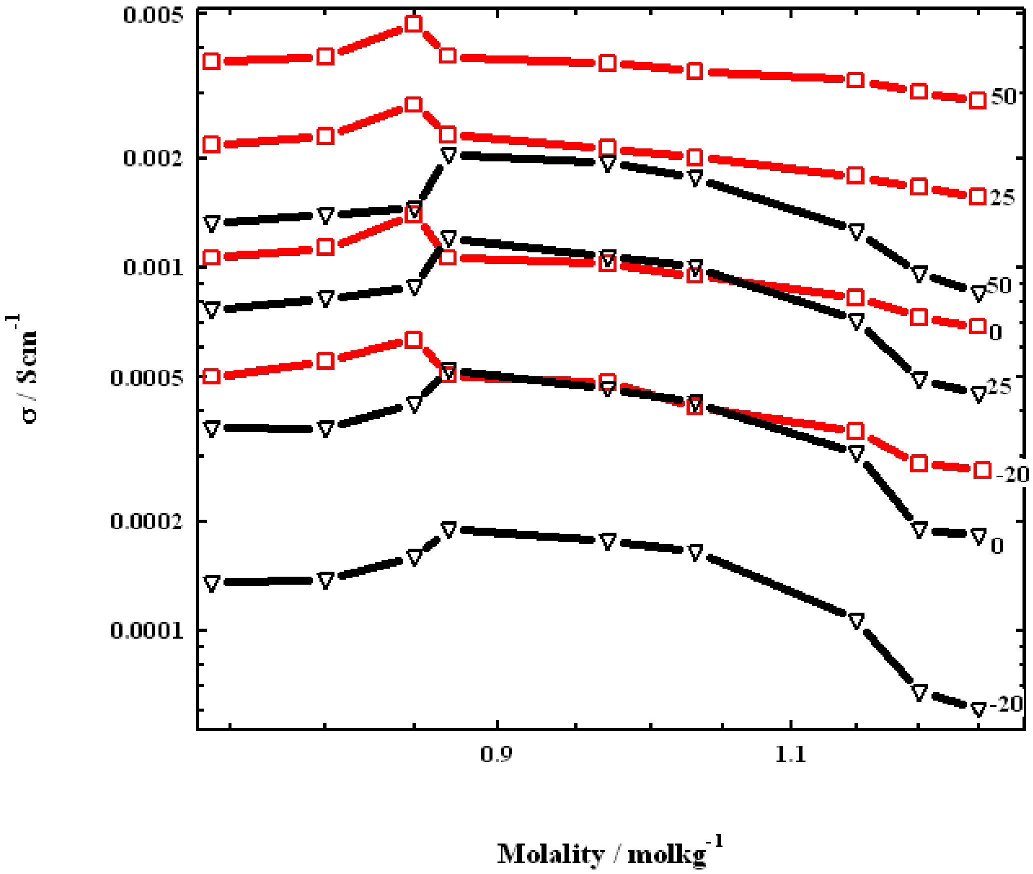

Figure 4: Conductivity vs salt concentration for the gel polymer electrolyte PAN : EC : PC : LiTf and liquid electrolyte EC : PC : LiTf at different temperatures.
(Temperatures are given in ^{0}C, □ Liquid electrolyte, ∇ Polymer electrolyte)

It is seen that liquid electrolytes show higher conductivity values than the gel polymer electrolytes at all temperatures. As described in the previous section, blocking of conduction paths by PAN may cause lower conductivity values. The other feature that can be envisaged from the graph is that salt concentration corresponding to the conductivity maximum has slightly shifted to a higher value upon introduction of PAN. The maximum room temperature conductivity of 1.21 x 10^{-3} S cm^{-1} has been obtained at the salt concentration of 0.87 mol kg^{-1} in the gel polymer electrolyte. The PAN / liquid electrolyte ratio was 0.1. A similar value has been reported by Ho Suk Ryu, et al.[8]. With the liquid electrolyte, a maximum room temperature conductivity of 2.8 x 10^{-3} S cm^{-1} was available at the salt concentration of 0.85 mol kg^{-1}. This can be taken as an evidence for the involvement of the polymer in the ion conduction mechanism[9]. From the results, it is clear that PAN does take part in the conduction mechanism to some extent. But, its main role is providing a matrix for the liquid electrolyte to trap in. At the expense of good mechanical stability available due to PAN, the conductivity reduction is not a serious issue. Also, when the gel polymer electrolyte is used for Li rechargeable cells, PAN provides a plus point for the cell performance by providing a mechanical stability. This fact has been mentioned in the literature too[10].

ACKNOWLEDGEMENTS

We wish to offer our sincere thanks to Prof. Steen Skaarup and Prof. Keld West for their utmost assistance. Also, the International Program for Physical Science (IPPS), Sweden is acknowledged for their financial assistance and physical resources.

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