



ROLE OF POLYMER MATRIX IN GEL ELECTROLYTE MORPHOLOGY

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ABSTRACT

Polyacrylonitrile (PAN), Polyurethane (PU), PAN- Polyethylene oxide (PEO) gels were synthesized and their morphology is correlated with syneresis effect. A porous morphology was observed in PAN and PAN-PEO based gel electrolytes and a platelet morphology in the case of PU based gel electrolytes. Syneresis is found to be more than 25% in the case of PAN and PAN-PEO and 3.5% in PU based gel electrolytes over a period of 30 days. The DC conductivity of polymer gel electrolytes for all the polymer matrices at room temperature was of the order of 10^{-3} S/cm. The correlation studies suggest that PU based gel electrolytes has more potential applicability over PAN and PAN-PEO based gel electrolytes.

Keywords: Gel electrolyte, syneresis, conductivity, morphology

1. INTRODUCTION

Polymer gel electrolytes are receiving considerable attention in advanced application such as rechargeable lithium batteries because of their high ionic conductivity. Polymer gel electrolytes are made by immobilizing lithium salts and plasticizing organic solvents in polymer matrices^{1,2,3}. The enhanced ionic conductivity by the addition of plasticizing organic solvents is a favorable characteristic of polymer gel electrolytes. Even though polymer gel electrolytes show a high ionic conductivity that is comparable to that of liquid electrolytes, other factors such as solvent retention ability, mechanical strength, and sub-ambient temperature conductivity should be considered further for practical applications. Nonetheless, solvent loss either by evaporation or permeation is inevitable in these multi-component systems^{4,5}. The solvent loss over a period of time, which is referred to as syneresis⁶, may result in failure of the electrode-electrolyte contact as well as decrease in ionic conductivity. However, syneresis can be effectively controlled by increasing the affinity between the polymer matrix and plasticizing solvent. Apart from this, the polymer-solvent affinity also plays an additional key role in determining the mechanical strength and sub-ambient temperature conductivity of the gel electrolyte. The prime concern in this work is the polymer-solvent affinity in polymer gel systems. The degree of interaction of polymer matrices with solvent has been obtained by correlating the morphology of the gel electrolytes with syneresis study. Moreover, syneresis effect in polymer gel electrolyte has not been well studied. Therefore systematic study has been carried out to explore the syneresis effect in polymer gel electrolytes based on three different polymer matrices namely PAN, PAN-PEO and PU. The plasticizing solvent for the above matrices was fixed as propylene carbonate (PC). The polymers differ in the functional groups and crystallinity, thereby carrying a different degree of affinity for organic carbonates.

2. EXPERIMENTAL

Polymer gel electrolytes were prepared by solution casting technique. For all the three compositions, polymer matrices were fixed at 35 wt% and also keeping constant the mole ratio of carbonyl group in PC (Spectrochem, India) to the cation in LiClO_4 salt (Aldrich) as 1:12.

2.1 Preparation of PU based gel electrolytes

Polyurethane gel was prepared from polyethylene glycol (PEG) and 1, 4-methylenedi (phenyl methane diisocyanate) (MDI). PEG (Huntsman, India) with an average molecular weight of 5500, used as the soft segment, was dried at 75 °C in a vacuum oven for 48 hours. MDI (Huntsman, India), used as the hard segment was vacuum dried at 75 °C for 24 h. To the liquid electrolyte PEG was added at room temperature followed by MDI. The final solution was dissolved thoroughly and kept at room temperature for 24hrs to complete the polymerization.

2.2 Preparation of PAN and PAN-PEO based gel electrolytes

PAN, PEO and LiClO_4 (Aldrich, USA), Propylene carbonate (PC) (Spectrochem) were used for the preparation of the gels. The polymers were dissolved in a solution of LiClO_4 in PC and subsequently gelled at 433 K for 30 minutes. The final gel was cast on a teflon plate and excess solvent was removed at 60°C over a period of 12 hours.

3. MEASUREMENTS

Frequency dependent conductivity was measured with an Alpha high resolution analyzer coupled to a Novocool temperature control system (Novocontrol GmbH, Germany) in the frequency range of 10^{-1} Hz to 10^7 Hz and the temperature range of –80 to +50 °C. A perfect contact between gels and electrodes for different composition was ensured by casting gels of the same thickness. The microstructure of the polymer gel electrolyte was identified by Environmental Scanning Electron Microscopy (ESEM). Syneresis effect was studied by observing the weight loss as a function of time.

4. RESULTS AND DISCUSSION

Frequency dependent conductivity spectra obtained for PAN, PAN-PEO and PU systems at various temperatures are shown in figure 1. The frequency dependent conductivity plots show two distinct regions; an almost frequency independent plateau region at low frequencies and a dispersion at high frequencies. The high frequency dispersion is predominant at lower temperatures and with increase in temperature it shifts towards the high frequency region. Finally the high frequency dispersion region almost disappears at higher temperatures, since the jump frequency of the charge carriers increases with temperature. The dc plateau and the extended conductivity dispersion at higher frequencies usually follow Jonschers power law.

$$\sigma(\omega) = \sigma_0 + A\omega^n \quad (1)$$

where, $\sigma(\omega)$ is the conductivity at a particular frequency, σ_0 the dc conductivity of the sample at zero frequency, A and n are weakly temperature dependent parameters and n is the power law exponent that varies from zero to one ($0 < n < 1$).

The variation with temperature of the dc conductivity (obtained from the Jonschers power law) of the gels prepared by different polymer matrices are shown in the Arrhenius plot of figure 2. The Arrhenius plot indicates that the ionic conduction obeys the VTF relation which describe the transport properties in a viscous matrix⁷.

$$\sigma = AT^{-1/2} \exp (-B/T-T_0) \quad (2)$$

Where A is the temperature independent constant, B is the pseudo activation energy related to polymer segmental motion, T_0 may also be compared with the glass transition temperature, T_g . The DC conductivity at room temperature, activation energy and ideal glass transitions are shown in the table 1.

The extent of phase separation according to the polymer-solvent affinity is examined by ESEM. Figure 3a & 3b corresponds to the cross-sectional ESEM image of PAN and PAN-PEO based gel electrolytes. A macroscopic phase separation between the dense and porous layer is noticed. The ESEM morphology shown in figure 3c was obtained with PU based gels electrolytes. A platelet morphology was observed in this gel electrolyte. The entire cross-sectional region is totally uniform without any phase separation.

Gel polymer electrolytes may undergo solvent exudation upon long storage. This phenomenon, known as the syneresis effect, has been encountered in many gel polymer electrolyte systems^{8,9}. Figure 4 illustrates the decrease in weight as a function of time for all the three polymer matrices of the gel. The weight loss was seen merely a 3.5% for PU based gel electrolyte. Whereas more than 25% weight loss was seen in both PAN and PAN-PEO based gel electrolytes. The presence of pores in the case of PAN and PAN-PEO indicates solvent loss through the pores leading to high syneresis. The solvent loss, more prominently observed in the gels made with the low affinity polymers. On the other hand, the absence of pores in the case of PU based gels suggest a strong interaction between the PU and PC makes the organic solvent difficult to exude from the polymer matrix.

5. CONCLUSIONS

The Arrhenius plot indicates that the ionic conduction obeys the VTF relation which describes the transport properties in a viscous matrix. Ionic conductivity of these gels are of the order of 10^{-3} S/cm at room temperature. The relative order of polymer affinity for organic carbonates was compared between three polymer matrices. When polymer gels were made with the low affinity polymers, i.e., PAN and PAN-PEO, there appears a microscopic phase separation in the gels which leads to porous morphology. The absence of pores in the case of PU based gels suggests a strong interaction between the PU and PC makes the organic solvent difficult to exude from the polymer matrix. The low syneresis makes PU based polymer gel electrolytes better candidate than other polymer matrices. Because of the transparent nature of PU gel electrolytes, these can also be used in electrochromic devices.

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Table 1: VTF parameters of Polymer gel electrolytes

Composition	σ at RT ($\times 10^{-3} \text{S/cm}$)	To (K)	B (kJ/mol)
PAN	2.13	152	2.641
PAN-PEO	2.11	131	2.512
PU	2.53	128	2.319

TABLES AND FIGURES

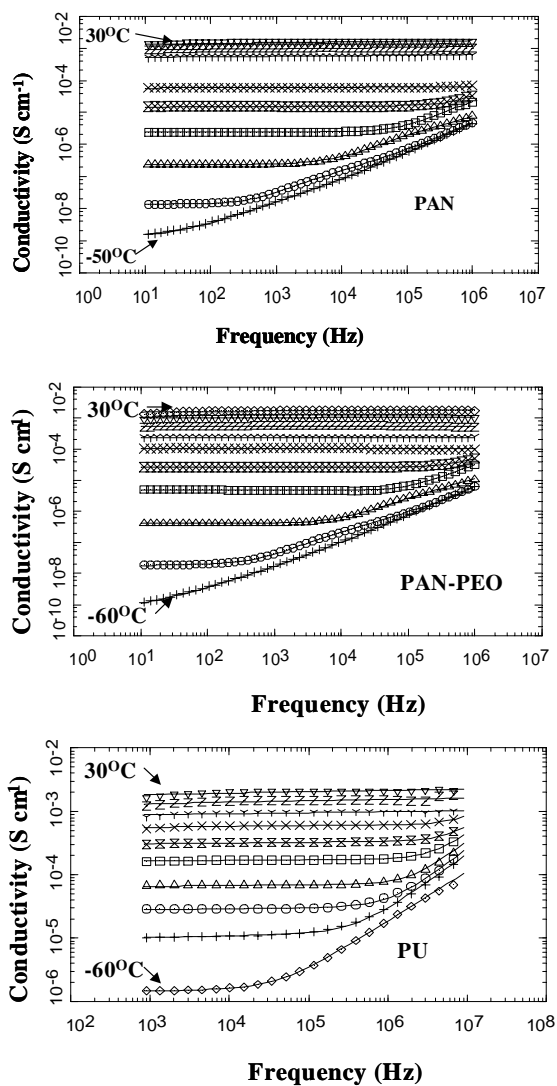


Figure 1. Frequency dependent conductivity spectra of gel polymer electrolytes

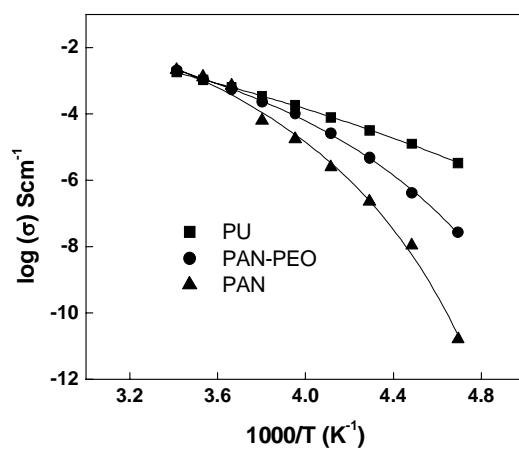


Figure 2. Arrhenius plot of the gel polymer electrolytes. Solid lines are VTF fit to the data

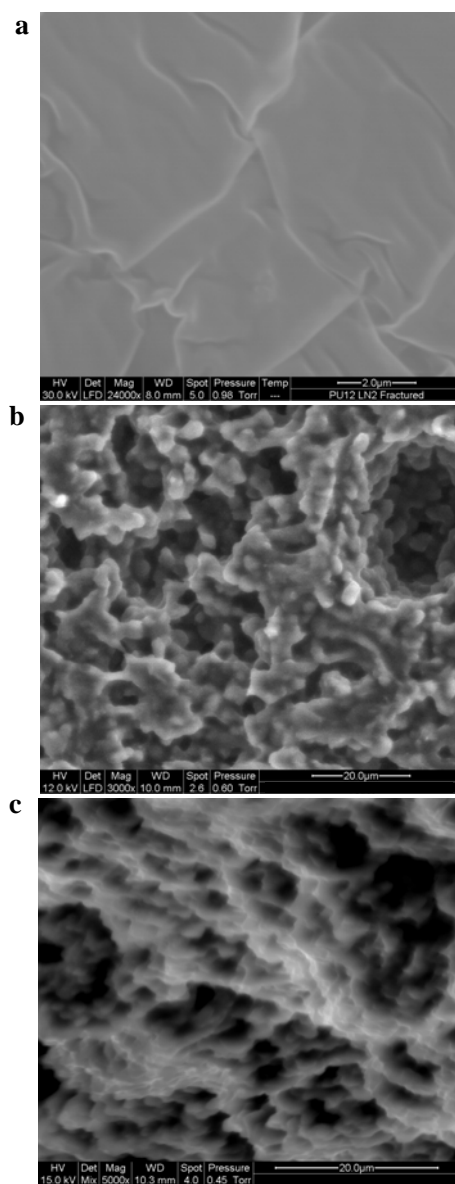


Figure 3. Esem micrograph of a)PU, b)PAN and c) PAN-PEO

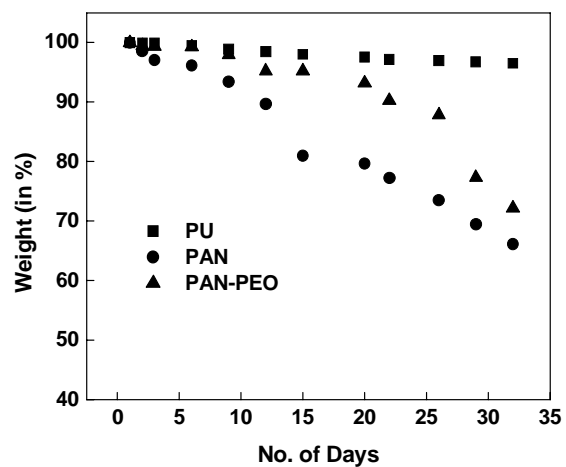


Figure 4. Syneresis effect on polymer gel electrolytes