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ANALYSIS OF DIELECTRIC, MODULUS, ELECTRO CHEMICAL STABILITY OF PVP – ABSA POLYMER ELECTROLYTE SYSTEMS

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ABSTRACT

Protons conducting solid polymer electrolytes comprising Poly vinyl pyrrolidone (PVP) and 2-amino benzene sulphonic acid (2ABSA) have been prepared by solution casting method with different compositions. A dielectric spectroscopy study has been carried out on the polymer electrolytes to identify the optimised salt composition, which is having high ionic conductivity. The ionic transference number has been estimated by Wagner's polarization method and the value is reported for all the samples (0.89-0.98). The dielectric behaviours of the samples have been analyzed using dielectric permittivity and electric modulus. The dielectric spectra show the low frequency dispersion, which implies the space charge effects arising from the electrode-electrolyte interface. Studies of frequency dependence of modulus formalism suggest that the ionic and polymer segmental motion are strongly coupled. The electrochemical stability of the polymer electrolyte has been studied by linear sweep voltammetry using stainless steel as the blocking electrodes and the film electrochemically stable in 2.5 V.

Key words: Poly vinyl pyrrolidone, Dielectric permittivity, Modulus, Transference number, Linerar sweep voltammetry.

INTRODUCTION

The dielectric properties of polymer materials play an important role in applications

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of electrochemical devices. The study of dielectric loss as a function of temperature and frequency has been used to characterize the molecular motion and dielectric relaxation behaviour of the polymer. In order to develop high ion conducting polymer electrolyte, poly (vinyl) pyrrolidone (PVP) has also been suggested as host polymer, because of it being an amorphous polymer, which can permit faster ionic mobility compared to other semi-crystalline polymers. Carbonyl group present in PVP is a proton acceptor. Some proton conducting polymer electrolytes have been reported based on PVP complexed with inorganic salts[1-3]. In the present work, the frequency dependent dielectric and modulus analysis of the PVP-2-Amino benzene sulphonic acid polymer electrolyte has been done for various temperatures and frequencies and the results are discussed. The total ionic transport number has been evaluated by polarizing the cell SS|PVP-2ABSA|MnO_2 and monitoring the potentiostatic current as a function of time and their electrochemical stability have been determined by linear sweep voltammetry analysis using stainless steel (SS) as blocking electrodes.

EXPERIMENTAL

Poly vinyl pyrrolidone K_{90} (Sd fine-chem. Limited, India), 2-amino benzene sulphonic acid (Tokyo Chemical Industry –Co. Ltd. Japan) – 99% pure were used as materials. Polymer electrolytes have been prepared with different concentrations of PVP complexed with 2-amino benzene sulphonic acid by solution casting technique using water as solvent. The dielectric and modulus measurement was carried out using a computer-controlled electrochemical work station (Biologic Science Instrument France Model – SP 300) in the frequency range of 100 Hz - 5MHz with an applied ac voltage of 100 mV at different temperatures. The total ionic transport number t_{ion} was measured using the Wagner's polarization technique. The electrochemical stability of the electrolyte was also determined by running linear sweep voltammetry measurements on the polymer membranes using stainless steel as blocking electrode at a scan rate of 10 mV/s.

RESULTS AND DISCUSSION

Dielectric analysis and modulus analysis

Fig. 1 (a) shows the ε' versus log ω plot for all PVP- 2ABSA based polymer electrolytes. The low frequency dispersion region is attributed to the contribution of charge accumulation at the electrode – electrolyte interface[4]. The higher values of ε' for PVP -9 mol% 2ABSA (higher σ) is due to enhanced charge carrier density at the space charge accumulation region, resulting in an increase in the equivalent capacitance. At higher frequencies, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. The polarization due to the charge accumulation decreases, leading to the decrease in the value of ε′.

The variation of ε″ (b) as a function of logω for 91 mol% PVP–9 mol% 2ABSA polymer electrolyte at different temperatures reveals that the two prominent relaxation processes: the low frequency α-relaxation peak; pronounced at higher temperatures, may be caused by the movement of main segments and the other at high frequency side, the so-called β-relaxation may be caused by side group dipoles and the nearest part of the backbone[5]. The relaxation peaks appear to be broad due to different mechanisms associated with local molecular motions.

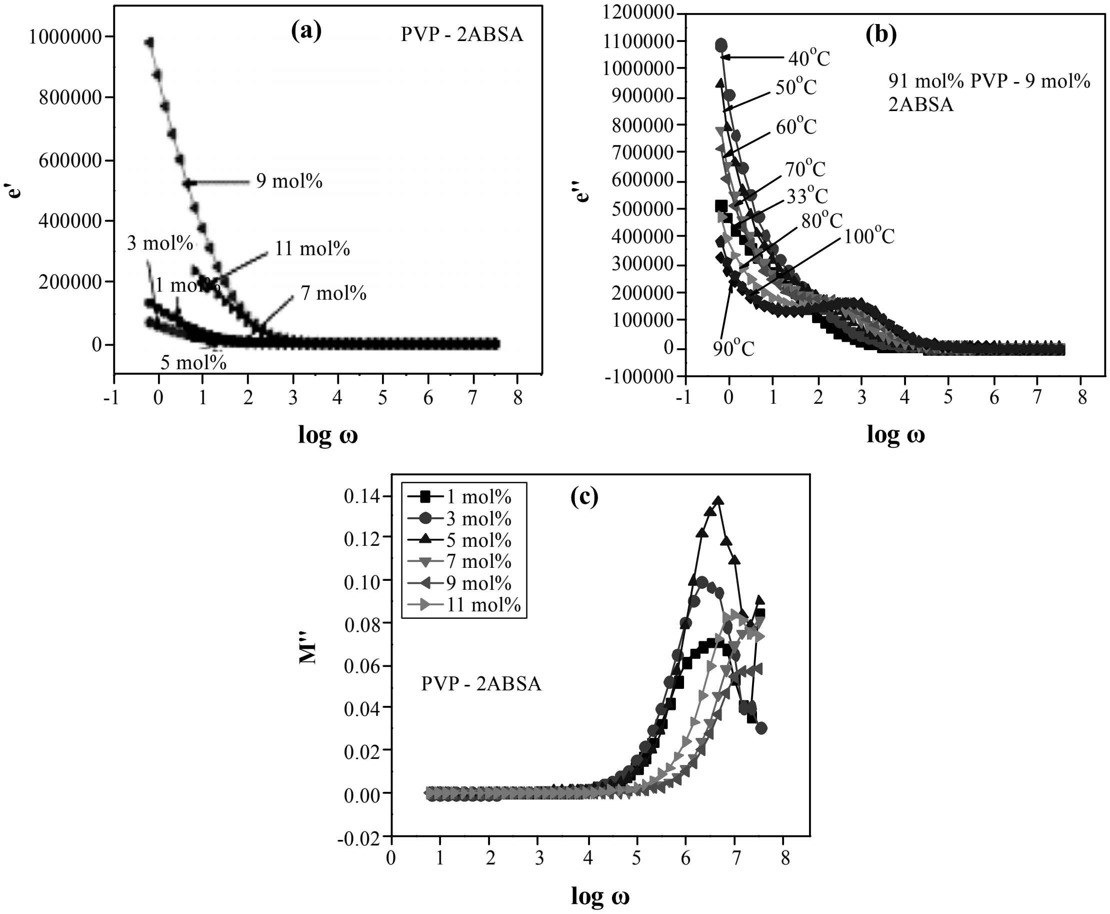

Fig. 1: Dielectric and modulus spectra of PVP -2ABSA

The imaginary parts of the modulus at different compositions of the system are shown in Fig 1(c). At low frequencies, imaginary parts of the modulus approaches zero indicating the fact that the electrode polarization phenomenon makes a negligible contribution. The long tail at lower frequencies is due to the large capacitance associated with the electrodes. The presence of peak in the imaginary modulus formalism at higher frequency for the polymer electrolyte system indicates that ionic conduction motion and polymer segmental motion are strongly coupled in the polymer electrolyte systems[6, 7].

Transference number and LSV study

The polarization current has been monitored as a function of time on application of dc potential (1V) across the cell stainless steel/electrolyte/MnO_2-C. The transference numbers has been calculated from the polarization current versus time plot (Fig. 2a) using the equations. $t_{ion} = (I_i - I_f)/I_i$ where I_i is the initial current and I_f is the final residual current. For all compositions of the PVP-2ABSA electrolyte systems, the values of the ionic transference numbers (t_{ion}) has been found to be in the range of 0.89-0.98. This suggests that the charge transport in these polymer electrolyte films is predominantly due to ions. The high transference number may be associated with the effect of ion–ion and polymer–ion interactions on the macroscopic transport parameters[8, 9].

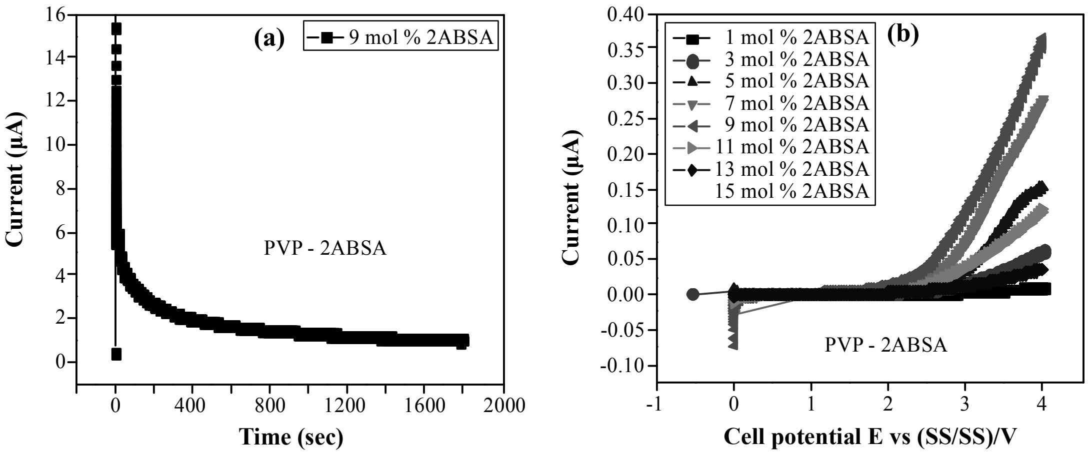

Fig. 2: Transference number (a) and LSV study (b) for PVP - 9 mol% 2ABSA

Fig. 2b shows the current–voltage response of a stainless steel/polymer electrolyte/ stainless steel cell by using linear sweep voltammetry. The scan rate of voltage was 10 mV/s. The onset current flow is associated with the decomposition voltage of the electrolyte. The figure shows that the current flow is very small when the voltage is below the decomposition voltage and then the current increases sharply[6]. The decomposition voltage depends on the salt concentration of the isomers. The decomposition voltage of PVP-2ABSA system is found to be 2.5 V.

CONCLUSION

In this paper we discussed about the dielectric, modulus, t_{ion} measurements and electrochemical stability of the PVP-2ABSA based polymer electrolyte. The low frequency dispersion of dielectric constant reveals the space charge effects arising from the electrodes. The M″ at higher frequency indicates that ionic conduction motion and polymer segmental motion are strongly coupled. The t_{ion} measurements reveal that the charge transport in the PVP complexed with 2ABSA polymer electrolyte films are predominantly due to ions and also the electrochemical stability is 2.5 V.

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