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Ionic Conductivity studies on Plasticized Proton conducting solid polymer electrolyte complexes PVA - NH₂SO₃H-PEG

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Abstract : An attempt was made in the present work to develop a new plasticized proton conducting polymer electrolytes comprising of Poly (vinyl alcohol) (PVA) - Sulfamic Acid (SA) - Poly ethylene glycol (PEG₄₀₀). The role of the plasticizer was studied in terms of dc conductivity (σ_{dc}), activation energy (E_a) and mobility of the charge carrier (μ) using ac impedance spectroscopy. The dc conductivity was enhanced by two order of magnitude for 48 mol % of PEG plasticized polymer electrolyte than the unplasticized polymer electrolyte at 313K. The low activation energy (0.445eV) and high mobility of the charge carrier ($4.42x10^{-8}$ cm²v⁻¹s⁻¹) were observed for the plasticized polymer electrolyte.

Keywords: Polymer electrolytes, Proton conductor, Poly (vinyl alcohol), Sulfamic acid, PEG₄₀₀, Impedance spectroscopy.

1. Introduction

Many proton conducting polymer electrolytes were studied extensively because of their potential application mainly in proton battery fabrication[1,2]. Polymer electrolyte should possess high ionic conductivity, good mechanical and thermal stability, non toxicity, ease of preparation with desire shapes, low electronic conductivity at ambient temperature and it should be less expensive. The polymers such as poly (ethylene oxide) PEO[3], poly (vinyl alcohol) PVA [1,2,4,5] and Poly (vinyl pyrrolidone) PVP[6] were widely used as host polymer to dissolve organic or inorganic salts. Usage of organic salts/acids as a proton donor causes low ionic conductivity and poor solubility in the polymer matrix. Attempts have already been made to use inorganic acids/salts[2,4,5] as proton donors to the polymer matrix and it shows good ionic conductivity while causes some serious problems of corrosion with electrode. Research is going on to identify a suitable electrolyte comprising polymer matrix and inorganic salt which will not corrode the electrode while maintaining the decent ionic conductivity. Polyvinyl alcohol (PVA) is selected as host polymer because of its good charge storage capacity, dopant dependent physical properties, low cost and it has many applications in materials, electrical and food industries. Several reports are available on organic/inorganic salts complexes with PVA to improve the ionic conductivity[7,8]. Sulfamic acid (NH₂SO₃H) (SA) is a dry nonhygroscopic, nonvolatile, non corrosive, low cost, highly stable. odorless solid and highly efficient green catalyst in organic synthesis. Several reports on co-polymarization, polymer blends, addition of plasticizer and addition of nano fillers are available for further enhancement of the conductivity of solid polymer electrolytes. Addition of Plasticizer is one of the best suitable

methods to increase the dissociation of salt which promote the higher ionic conductivity. Plasticizer is normally having high dielectric constant and low molecular weight solvent. Poly ethylene glycols (PEG), Dimethyl formamide (DMF), propylene carbonate (PC), Ethylene carbonate (EC) and sometimes water may be used as plasticizer. Poly ethylene glycol (PEG) with different molecular weights was widely used as plasticizer owing to their interesting features such as low viscosities, low toxicity and low cost. PEG with low molecular weight of 400g /mol was already reported as the best plasticizer[9]. In the present investigation, the effect of PEG as plasticizer on the conductivity of PVA-sulfamic polymer electrolyte complexes is studied and the results are presented.

2. Experimental

PVA (average Mw - 1, 25,000 g/mol) (degree of hydrolysation = 88%) (SDFCL), ionic dopant sulfamic acid (NH₂SO₃H) (FISCHER, 99%) and the plasticizer PEG₄₀₀ (Merck) were used as received. Polymer electrolyte films with different molar ratio of PVA-SA and 100-*x* (97 mol% PVA: 3 mol% SA): *x* PEG (*x*=10, 22.5,30,38 and 48 mol %) were prepared by solution casting technique using distilled water as solvent. The polymer electrolytes were sandwiched between two stainless steel electrodes which acted as blocking electrodes for ions. The electrical studies on the polymer electrolytes were measured in the temperature range of 303K - 343K over the frequency range of 42Hz- 1MHz using a computer controlled HIOKI 3532 LCR meter. Z View software package was used to fit the experimental data of polymer electrolyte system.

3 Results and discussion

3.1 Concentration dependent conductivity analysis

DC conductivity of polymer electrolytes is extracted from conductance spectra (not shown) by using Jonscher's power law, $\sigma(\omega) = \sigma(0) + A\omega^n$. where $\sigma(0)$ is the dc conductivity of the sample, A is the dispersion parameter and n is the dimensionless frequency exponent. The variation of log σ_{dc} with PEG₄₀₀ concentration expressed as mol% at 313K is shown in Fig.1. The ionic conductivity of the PVA-SA is found to be 9.07 x 10⁻⁸ S cm⁻¹ at 313K and it increases with plasticizer concentration reaching to the maximum value of 3.83×10^{-6} S cm⁻¹ for 48mol % of PEG. It is clearly observed that the dc conductivity of plasticized polymer electrolyte (PVA-SA-PEG) increases by two orders in magnitude compare with unplasticized polymer electrolyte 97mol% PVA - 3mol% SA. The increase of dc conductivity with increase of PEG concentration upto 30 mol% is due to the plasticising effect that leads to increase of flexibility of the polymer matrix and raises the ionic mobility in the polymer matrix.



Figure 1 dc conductivity at various concentration of PEG at 313K

Further increase of PEG beyond 30 mol%, the dc conductivity decreases which is due to the interaction between PVA and PEG .This interaction is reduce the segmental motion of the polymer chain⁵. But, 48 mol % of PEG enhances conductivity further. This may be caused by the mobility of the charge carriers are through PEG rather than PVA.

3.2 Impedance Analysis

Figures 2a and 2b show the typical Cole - Cole (Z' vs Z'') plot and corresponding equivalent circuits for PVA-SA and PVA - SA- PEG polymer electrolyte at 313K. In both electrolytes, the plot shows two well defined regions, namely, depressed semi circle in the high frequency region and inclined straight line in the low frequency region. The depressed semicircle is due to the parallel combination of resistance (R1) and capacitance (C_d) and low frequency inclined straight line is due to the formation of electrical double layer capacitance (C_e) at the electrode-electrolyte interface. The inclined straight line and depressed semicircle indicate the distributed microscopic properties of the materials, which is represented by constant phase elements (CPE)[10,11]. Here, two constant phase elements (CPE) are used to fit instead of C_d and C_e.



Figure 2a the impedance plot of PVA-SA polymer electrolyte at 313K and its corresponding equivalent circuit.

The equivalent circuit indicates the parallel combination of resistance R1 and constant phase element CPE1, while the low frequency inclined straight line can be represented by CPE2. The impedance of a CPE is expressed by $Z_{CPE}=1/C_d(j\omega)^{\alpha}$, where α is related to the deviation from the vertical of the line in the -Z'' vs Z' plot. $\alpha = 0$ indicates a perfect capacitance and lower α value directly reflect the roughness of the electrode used[9,10]. Table1 shows the fitted data from Z View software for PVA- SA and PVA-SA- PEG at 313K.



Figure 2b the impedance plot of PVA-SA-PEG polymer electrolyte at 313K and its corresponding equivalent circuit.

Elements	97mol%PVA-3mol %SA (PVA- SA)	48mol % of PEG 52mol % (97mol%PVA-3mol %SA) (PVA-SA- PEG)
R1	50391Ω	952.4Ω
CPE1-T	3.71 X10 ⁻⁹ F	3.55X10 ⁻⁹ F
CPE1-P	0.78	0.82
CPE2-T	1.61 X10 ⁻⁵ F	4.92 X10 ⁻⁵ F
CPE2-P	0.42	0.62

Table 1. Some parameters estimated from Figs. 2a, 2b using the equivalent circuit for PVA- SA and PVA-SA- PEG at 313K.

Further, the CPE can be expressed by two parameters CPE-T and CPE-P where CPE-T indicates the value of capacitance of the CPE elements. CPE1-P indicates the change of depressed semicircle from an ideal semicircle and CPE2-P indicates the slope of the low frequency straight line. CPE-P is a parameter equal's n in the above equation[10].

The value of CPE2-P is 0.42 and 0.62 for PVA-SA and PVA - SA- PEG respectively and is smaller than 1 which represents more rough surface contact in the SS/SPE/SS structure.

3.3 Temperature dependent conductivity analysis

The variation of dc conductivity with inverse of temperature is depicted in the Fig. 3 for PVA - SA and PVA - SA- PEG. The dc conductivity is found to be temperature dependent and obeying the Arrhenius relation, $\sigma T = \sigma_0 \exp(-E_a/kT)$, where σ_0 is a pre-exponential factor, E_a is the activation energy, T is the absolute temperature in Kelvin and k is the Boltzmann constant.



Figure 3 Arrhenius plot for PVA - SA and PVA - SA- PEG.

It is noted from the experimental data that ionic conductivity has been enhanced with increase of temperature. From the slope of the straight line, the activation energy has been calculated to be 0.62 eV and 0.45eV for PVA - SA and PVA - SA- PEG respectively. It shows that plasticized polymer electrolyte having less activation energy compare to unplasticized polymer electrolyte.

3.4 Mobility of charge carrier analysis

In microscopic point of view, the ionic conductivity of the polymer electrolyte is given as $\sigma = nq\mu$, where n is number of charge carrier, q is the charge of the mobile carrier and μ is the mobility of the carrier.

Transport parameters	97mol%PVA-3mol %SA	48mol% PEG - 52mol %
		(97mol%PVA-3mol%SA)
σ (S/cm)	3.96×10^{-8}	1.32×10^{-6}
$E_a(eV)$	0.62	0.45
v (cm/sec)	1.08×10^{6}	9.22x10 ⁵
τ (sec)	9.21×10^{-14}	1.08×10^{-13}
$n (cm^{-3})$	3.05×10^{21}	1.86×10^{20}
$\mu (cm^2 v^{-1} s^{-1})$	8.09x10 ⁻¹¹	4.42×10^{-8}

Table 2 Transport parameters of PVA-SA and PVA-SA-PEG polymer electrolyte at 303K.

The transport parameters of each polymer electrolyte were calculated from Rice and Roth model[12]. In this model, the conductivity can be expressed as:

$$\sigma = \frac{2}{3} \left[\frac{\left(Ze \right)^2}{kTm} \right] n E_a \tau \exp \left(\frac{-E_a}{kT} \right)$$

where Z, e, m, n and τ are the valency of the conducting species, electronic charge ,mass of the charge carrier, number density of charge carriers and travelling time of ions, respectively. The value of τ was calculated from the equation:

$$\tau = \frac{l}{v}$$

where *l* is the jump distance between two complexation sites, which is 10^{-9} m and *v* is the velocity of mobile ions which is calculated using,

$$v = \sqrt{\frac{2E_a}{m}}$$

The ionic mobility, μ is calculated using the value of n. $\mu = \sigma/ne$

All the transport parameters are tabulated in the Table 2. The results show that the high mobility of the free charge carriers are presented in plasticized polymer electrolyte compare with unplasticized polymer electrolyte. It is clearly noticed that the charge carriers are bound to the PEG and the motion of the charge carriers through the PEG backbone. The dc conductivity of PVA-SA-PEG is high due to the mobility of charge carries even though the value of 'n' is less.

4. Conclusion

Proton conducting polymer electrolytes comprising of 100-*x*(PVA-NH₂SO₃H)-*x*PEG (0, 10, 22.5, 30, 38, and 48 mol %) have been prepared for different compositions by solution casting technique. It is clearly observed that the ionic conductivity of the plasticized polymer electrolyte increases by two orders in magnitude compare with unplasticized polymer electrolyte at 313K. The equivalent circuit is also used to determine the roughness of the electrode-electrolyte interface. The plasticized polymer electrolyte has shown less activation energy for conduction and high mobility of the charge carriers compared with unplasticized polymer electrolyte.

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