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Characterization of plasticized proton conducting polymer electrolyte and its application in primary proton battery

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Abstract : The effect of poly ethylene glycol (PEG₄₀₀) as plasticizer on the conductivity of proton conducting solid polymer electrolytes comprising of poly (viny pyrrolidone) (PVP) - sulfamic acid (SA) was studied. A complex formation between polymer, salt and plasticizer was confirmed by Fourier transform infrared spectroscopy (FTIR). The optical band gap energies of unplasticized and plasticized polymer electrolytes were investigated by using UV-VIS spectroscopy and it was observed that the plasticized polymer electrolyte had low band gap energies compared with unplasticized polymer electrolyte. AC impedance spectroscopy measurement was used to investigate the conductivity of the polymer electrolytes. The highest dc conductivity was found as $1.99 \times 10^{-7} \text{ Scm}^{-1}$ for 3 mol % SA doped with 97mol% PVP .The conductivity was enhanced by four times with addition of 37 mol % of PEG and was calculated as $8.23 \times 10^{-7} \text{ Scm}^{-1}$. A primary proton battery was fabricated and its discharge characteristics were studied. The open circuit voltage and cell impendence were measured for fresh and after discharge.

Keywords: PVP, Sulfamic acid, PEG400, Proton battery, Polymer electrolytes

1. Introduction

Polymer electrolytes are more extensively used in the fabrication of solid state devices such as Li-ion, Zn-air and proton batteries[1-3]. Polymer electrolyte possesses high ionic conductivity, good mechanical and thermal stability, non toxicity and ease of preparation with desire shapes at ambient temperature. It is also less expensive compare with other solid electrolytes. To further improve the ionic conductivity of polymer electrolyte, addition of plasticizer and/or nano inert fillers are proposed to incorporate with the polymer electrolyte. The plasticized electrolytes are normally obtained by adding small amount of some organic solvent with high dielectric constant and low molecular weight to a polymer-salt complex. The plasticized polymer electrolytes help to reduce the electrode-electrolyte interfacial problem. In the present work, polyvinyl pyrrolidone (PVP) is selected for host polymer because of its high amorphous nature, biocompatible and low cost. Sulfamic acid (SA) is a dry inoraganic salt to donate proton to the polymer matrix. The ionic conductivity of poly aniline has been enhanced five orders of magnitude by doping with SA[4]. Poly ethylene glycol (PEG) with different molecular weights has been widely used as a plasticizer because of their low viscosity, low melting point and low cost. PEG₄₀₀ has also been reported as better plasticizer effect compare with other molecular weights of PEG[5]. The aim of this work is to develop a new plasticized proton conducting polymer electrolyte based on PVP with high ionic conductivity, good mechanical stability and less expensive. The

detailed ac impedance spectroscopic, vibrational and optical studies of PVP doped with SA and plasticized polymer electrolytes are studied. The solid state proton battery is fabricated and discharge characteristics are also studied.

2. Experimental

Thin films of polymer electrolyte comprised of pure PVP-K90 (SDFCL -99%) and ionic dopant, sulfamic acid (NH₂SO₃H) (FISCHER, 99%) have been prepared with different molar ratio (99:01) (98:02) (97:03) (96:04) , (95:05) and (93:07) by solution casting technique using distilled water as solvent. The sample which shows high conductivity have been plasticized with PEG ($_{400}$) (Merck) with different molar ratio of (87.3:2.7:10), (75.2:2.3:22.5), (67.9:2.1:30) and (61.1:1.9:37). FTIR spectra were recorded for the polymer complexes using JASCO FTIR-4100 spectrometer in the wave number range of 400 cm⁻¹ - 4000 cm⁻¹. The UV-VIS spectra were recorded in the wave length range of 200-800 nm using SHIMADZU (UV-2600) UV-VIS Spectrophotometers. AC impedance spectroscopic studies on the polymer electrolytes were carried out in the temperature range of 30° C- 70° C over the frequency range of 42Hz-1MHz using a computer interfaced HIOKI-3532 LCR meter. The polymer electrolyte films were sandwiched between two stainless steel electrodes which acted as blocking electrodes for ions. The compositions of the cathode and anode for proton batteries were 0.8g MnO₂: 0.15g activated carbon: 0.05g poly (vinyledene fluoride) (PVdF) and 0.5g Zn: 0.40g ZnSO₄.7H₂O: 0.05g activated carbon: 0.05g PVdF respectively. The mixture of the raw materials was grounded and made in to a pellet. The proton battery was discharged using Bio-Logic electrochemical work station by Galvanostatic mode at constant current of 0.5 μ A.

3. Results and Discussion

3.1 FTIR analysis

FTIR spectroscopy provides the molecular interaction between host polymer and salt. FTIR spectra of pure PVP, SA, PEG, PVP-SA and PVP-SA-PEG complexes are shown in Fig. 1. The N-H stretching vibration of NH₂SO₃H is noted around 3110 cm⁻¹ corresponding to zwitterion formation of salt. The vibrational band observed at 1441 cm⁻¹ and 1538 cm⁻¹ correspond to the NH deformation modes of NH₃⁺. The vibrational bands situated at 1060 cm⁻¹ and 1005 cm⁻¹ impute the SO₃ symmetric stretching and rocking mode vibration of NH₃⁺ respectively. The above results confirm the existence of zwitterionic nature of NH₂SO₃H in solid form[6]. The vibrational bands observed at 2923 cm⁻¹, 1494 cm⁻¹, 1642 cm⁻¹ and 1437 cm⁻¹ are attributed to C-N stretching band in pyridine ring, C-H bending of CH₂, C=O stretching and CH₂ wagging of pure PVP respectively[3,7]. The SO₃ stretching vibrational band of NH₂SO₃H is affected when it is dissolved in PVP and it is shifted towards lower wave number side in PVP-SA polymer complex. In pure PEG₄₀₀ the vibrational bands at 848 cm⁻¹,941 cm⁻¹, 1296 cm⁻¹ and 1350 cm⁻¹ are assigned for C-C vibration, C-OH out of plane bending, C-O sym.stretching and C-H bending respectively[8].



Figure 1. FTIR spectra of pure SA, PVP, PEG, PVP-SA and PVP- SA- PEG

In plasticized polymer electrolyte, vibrational bands of C-O symmetric stretching and C-H stretching of pure PEG are shifted to 1287 cm⁻¹ and 2882 cm⁻¹ respectively. CH₂ wagging vibrational band at 1437 cm⁻¹ of pure PVP is shifted to1421cm⁻¹ in plasticized polymer electrolyte. These changes in the wave number confirm the complex nature of plasticized polymer electrolyte (PVP-SA-PEG).

3.2 UV-Visible analysis

UV-Visible analysis was used to analyze the characteristic electronic band structure of polymer electrolytes. The optical band gap energy and absorption coefficient (α) are determined from the spectra using Beer-Lambert's law, α =2.303(A/d), where d and A are the thickness of the polymer film and absorbance of the sample, respectively. The optical band gap energy (E_g) can be calculated from the following relation $\alpha(\nu)h\nu$ =B(hv-Eg)ⁿ, where hv is the proton energy, B is a constant and n is the power factor and its values are 0.5, 2, 1.5 and 3 corresponding to allowed direct, indirect, forbidden direct and forbidden indirect transition respectively⁹.



Figure 2 Direct and i	indirect bandgap energy	in PVA-SA	and PVA-SA-PEG.
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Samples	Direct bandgap energy	Indirect bandgap energy	
	(\mathbf{E}_{gd}) (eV)	(\mathbf{E}_{gid}) (eV)	
Pure PVP	4.61	4.52	
PVP-SA	2.24	2.11	
PVP-SA-PEG	1.97	1.86	

Table 1 Direct and indirect band gap energies in PVP, PVP-SA, and PVP-SA-PEG.

The width of the direct and indirect bandgap (E_{gd} and E_{gid}) are calculated from the plot of hv vs (α hv)² and hv vs (α hv)^{0.5} and extrapolation of the straight line to (α hv)²=0 and(α hv)^{0.5}=0, gives the value of direct and indirect bandgap energy respectively as shown in Fig. 2 and these values are tabulated in the Table 1. It is observed that the value of E_{gd} and E_{gid} of pure PVP decreases upon doping of salt and the addition of plasticizer. The decreases of optical bandgap energy are due to formation of charge transfer complexes¹⁰. It leads to increase in mobile charge carries and increase of the amorphous nature of the polymer electrolyte.

3.3 Concentration dependence of conductivity

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.

Figure 3a shows the variation of logarithmic dc conductivity as a function of SA concentration expressed in mol% at 30°C. The conductivity value is extracted from conductance spectra. It is observed that the conductivity increases with increase of SA concentration up to 3 mol%. The increase of conductivity is due to the increase of mobile charge carriers and all ions contribute to charge transport in the presence of an applied field.



Figure 3 a), 3 b) Variation of dc conductivity of the PVP doped with different SA and PEG concentration at 30°C.

The decreasing trend of the conductivity is observed beyond 3 mol% SA doped electrolyte and this is due to the formation of ion pairs which cannot move in the polymer matrix in the presence of an external electric field. The high conducting unplasticized polymer electrolyte is added with different concentration of PEG at 30°C as shown in Fig. 3b. The increase of ionic conductivity is found upto 37 mol% PEG in polymer electrolyte and the conductivity of plasticized polymer electrolyte is found as $8.23 \times 10^{-7} \text{ Scm}^{-1}$.

3.4 Conductivity analysis

The variation of logarithmic ac conductivity with logarithmic angular frequency at various temperatures for PVP- SA and PVP – SA- PEG is shown in Fig.4a, 4b respectively.

Both conductance spectra of PVP-SA and PVP-SA-PEG consist of two distinct regions: 1) low frequency plateau region and 2) high frequency dispersion region. The low frequency plateau region is due to mobile ions which are jumping from one site to another vacant site effectively and contribute to dc conductivity. It is noted from the experimental data that ionic conductivity is enhanced with increase of temperature. At high frequency region, the conductivity dispersion is observed and is due to the forward and backward hopping of mobile ions in their sites.



Figure 4 Conductance spectra of a) 97 mol% PVP- 3 mol% SA and b) 61.1 mol% PVP-1.9 mol% SA-37 mol% PEG at various temperatures

This high frequency dispersion corresponds to bulk relaxation of the material. The dc conductivity extracted from ac conductance spectra at various temperatures and the conductivity value is tabulated in the table 2.

Temperture(°C)	PVP: SA	PVP-SA-PEG
	$\sigma_{d.c}$ (S cm ⁻¹)	$\sigma_{d.c}$ (S cm ⁻¹)
30	1.99 x10 ⁻⁰⁷	8.23 x 10 ⁻⁰⁷
40	6.34x 10 ⁻⁰⁷	2.54 x 10 ⁻⁰⁶
50	2.05 x 10 ⁻⁰⁶	7.46 x 10 ⁻⁰⁶
60	3.51x 10 ⁻⁰⁶	2.425 x 10 ⁻⁰⁵
70	5.98x 10 ⁻⁰⁶	4.26x 10 ⁻⁰⁵

Table 2 Dc conductivity of PVP-SA and PVP-SA-PEG at various temperatures

3.5 Characterization of solid state proton battery

The discharge characterization of the cell configuration of $(Zn+ZnSO_4.7H_2O+C+PVdF)/61.1 \text{ mol}\%$ PVP-1.9 mol% SA-37 mol% PEG/(MnO₂+C+PVdF) at constant current of 0.5µA at room temperature is shown in Fig.5. The detailed cell configuration was discussed elsewhere³.



Figure 5 Discharge characteristics curve for PVP-SA-PEG at 0.5 µA at room temperature.

It is observed that the open circuit voltage of the cell is almost constant (1.36V)(not shown). The initial sharp decrease in the voltage upon given constant load current of 0.5 μ A has been noticed. Then for a given constant load current, the voltage is fixed at 1.28 V for at least 2 hrs. Then it starts decreasing upon increase of time. The voltage is still maintained even for 4.4 hrs of discharge with 0.5 μ A. The work is also aimed to discharge the battery with higher constant current. From the result, it is confirmed that PVP-SA-PEG is capable as solid electrolyte for solid state proton battery.



Figure 6 Impedance plot of fresh and after discharge at $0.5\mu A$ for solid state proton battery based on PVP-SA-PEG

The ac impedance spectra are measured for fresh cell and after discharge at 0.5μ A at room temperature as shown in Fig.6. From the figure, it shows that the cell impedance a fresh cell is less compare with after discharge. Similar trend of impedance spectra is also noticed for fresh and after discharge cell.

4. Conclusion

The new proton conducting polymer electrolytes based on PVP-SA, PVP-SA-PEG were prepared by using solution casting technique. The complex behaviour was studied by using FTIR analysis. The optical bandgap energies of PVP-SA-PEG were found to be less compared with PVP-SA. The influence of plasticizer in the polymer electrolyte was discussed and conductivity of PVP-SA was increased by four times upon the addition of plasticizer. The open circuit voltage and the discharge characteristics of the cell using PVP-SA-PEG as solid electrolyte were studied. The cell impedance of fresh and after discharge was measured.

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