Development of solid proton conductors based on doped polyvinyl alcohol

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The different ammonium salts are added in polyvinyl acetate to increase the proton conductivity. Amongst all the added salts, ammonium nitrate salt addition gives maximum conductivity with minimum activation energy. Salt addition increases the amorphismity in turn the molecular weight. Enhanced conductivity with increased hydrogen concentration and relative humidity suggest H⁺ mobility through complex polymer electrolyte.

Keywords: Polymer complexes, Proton conductors, Complex impedance spectroscopy, Glass transition

1 Introduction

During last few years, the proton conductors have received the much attention due to their potential applications as electrolytes in fuel cells, supercapacitors, smart windows and other electrochromic devices (ECDs). The polymer electrolyte fuel cell (PEMFCs) viewed as promising source of electrical power for transportation, residential and portable applications. The polymer complexes based on polyethylene oxide (PEO) have been extensively investigated to increase protonic conductivity. In recent past, much of the efforts have been directed to develop amorphous polymers with high ionic conductivity at room temperature as well as good mechanical, optical and thermal properties. Dissolving salt in the immobilized polymer matrix has been one of the methods to obtain amorphous electrolyte. The electrical and optical properties of the polymers can be suitably modified by the addition of salts. The polymers with high concentration of polar groups and high chain flexibility have been preferred for better salt-solvation.

Polyvinyl alcohol (PVA) is an exceptional polymer having high dielectric strength, good charge storage capacity and dopant-dependent electrical and optical properties. It has been a known semi-crystalline material, which exhibited certain physical properties due to crystal-amorphous interfacial effect. According to literature, several combinations of PVA with acids or salts such as phosphoric acid, hypophosphorous acid, heteropolyacid (HPA), dipotassium phosphate (K₂HPO₄) and sulphasuccinic acid (SSA) have been studied to improve the proton conductivity of the PVA membranes.

More recently, the ammonium salts have been viewed as excellent proton donors to the polymer matrix. The protonic transport in these polymer electrolytes, generally, has been due to motion of groups like H⁺, NH₄⁺, H₂O⁺, OH⁻, etc. In addition to the motion of protons, the conductivity has also been associated with the segmental motions of the polymer chain. A detailed literature survey revealed that the PVA complexed with ammonium salts has been less attended so far from proton conducting polymer electrolyte viewpoint. The preparation and characterization of proton conducting polymer electrolytes have been studied in the present paper. Particularly, polymer complexes using different ammonium salts i.e., NH₄NO₃, CH₃COONH₄, (NH₄)₆Mo₇O₂₄, 4H₂O, ((NH₄)H₂PO₄), ((NH₄)₂SO₄), with fixed concentration in PVA polymer matrix were synthesised to develop proton conducting solid polymer electrolyte.

2 Experimental Details

The initial reagents polyvinyl alcohol (PVA) with a degree of hydrolysis more than 99% and average molecular weight of 146000, NH₄NO₃ (AN), (NH₄)₆Mo₇O₂₄.4H₂O (AMTH), (NH₄)H₂PO₄ (ADP) and (NH₄)₂SO₄ (AS) were procured from Aldrich, USA. CH₃COONH₄ (AA) was procured from Merck, India. Initially, aqueous solution of 80PVA:20NH₄NO₃ was stirred thoroughly for 8-10 h at 343 K using magnetic stirrer for homogeneity. The homogenous viscous gel solution was then casted on the glass plate and dried for one week. Similar
procedure was followed to prepare polymer complexes mentioned in Table 1.

All the prepared samples were characterized using X-ray diffraction (PANalytical X’pert PRO (Philips, the Netherlands)). The thermal analysis was carried out using differential thermogravimetric analysis/differential thermal analysis (TGA/DTA) (Perkin Elmer, Diamond TGA/DTA). The Fourier transform infrared (FTIR) spectra were recorded in the range 600-4000 cm\(^{-1}\) at room temperature using Perkin Elmer, FTIR with HATR sampling accessory. The density was measured following Archimedes principle with the help of Mettler XS105 dual range viscometry technique. Micro-hardness number was measured by Vickers indentation technique (HMV-2 micro-hardness tester, Shimadzu, Japan). Furthermore, the molecular weight of polymer complex was determined following viscometry technique.

The circular film of diameter 9 mm was punched out from the casted polymers for complex impedance spectroscopy studies. A thin platinum coating on both the flat surfaces of the circular polymer film was obtained by dc sputtering and resulted in a good ohmic contact. The real and imaginary parts of complex impedance were measured as a parametric function of frequency (20 Hz to 1 MHz) and temperature (263 to 373 K) during the heating cycle using Agilent 4284A LCR meter. The required hydrogen partial pressure around the film was maintained using electronic mass flow meters (Teledyne-Hastings, USA). Nitrogen gas with purity \(\approx 99.99\%\) was used to dilute the \(H_2\) gas. In order to see the effect of relative humidity on the conductivity, the mixture of hydrogen and nitrogen gases was humidified with the help of hot water bubbler. The relative humidity in the conductivity cell was measured using Rotronic (USA) hygrometer.

### Table 1—Comparison of density (\(\rho\)), molecular weight, micro-hardness number (\(HV\)), glass transition temperature (\(T_g\)), melting temperature (\(T_m\)) and the activation energy for different salts in PVA.

<table>
<thead>
<tr>
<th>Samples</th>
<th>(\rho) (g/cm(^3))</th>
<th>Molecular weight</th>
<th>HV</th>
<th>DSC (T_g) (K)</th>
<th>(T_m) (K)</th>
<th>DTA (T_g) (K)</th>
<th>(T_m) (K)</th>
<th>(E_a) (eV)</th>
<th>(E_p) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PVA</td>
<td>1.475</td>
<td>996620.92</td>
<td>16.909</td>
<td>356</td>
<td>504</td>
<td>355</td>
<td>503</td>
<td>0.479</td>
<td>1.103</td>
</tr>
<tr>
<td>PVA+(NH(_4))(_2)SO(_4)</td>
<td>1.597</td>
<td>6903590.141</td>
<td>14.637</td>
<td>339</td>
<td>497</td>
<td>337</td>
<td>496</td>
<td>0.543</td>
<td>0.869</td>
</tr>
<tr>
<td>PVA+ NH(_4)H(_2)PO(_4)</td>
<td>1.605</td>
<td>11337283.32</td>
<td>13.321</td>
<td>338</td>
<td>494</td>
<td>336</td>
<td>493</td>
<td>0.413</td>
<td>0.813</td>
</tr>
<tr>
<td>PVA+ (NH(_4))(_6)Mo(_2)O(_24). 4H(_2)O</td>
<td>1.638</td>
<td>14396336.85</td>
<td>7.383</td>
<td>337</td>
<td>492</td>
<td>335</td>
<td>491</td>
<td>0.391</td>
<td>0.789</td>
</tr>
<tr>
<td>PVA+ CH(_3)COONH(_4)</td>
<td>1.640</td>
<td>17201249.69</td>
<td>6.737</td>
<td>336</td>
<td>491</td>
<td>334</td>
<td>490</td>
<td>0.356</td>
<td>0.608</td>
</tr>
<tr>
<td>PVA+ NH(_4)NO(_3)</td>
<td>1.712</td>
<td>19588219.46</td>
<td>4.336</td>
<td>333</td>
<td>489</td>
<td>333</td>
<td>488</td>
<td>0.321</td>
<td>0.588</td>
</tr>
</tbody>
</table>

### 3 Results and Discussion

#### 3.1 X-ray diffraction (XRD)

The X-ray diffraction patterns of pure PVA and complexed with 20 mole% of different ammonium salts are shown in Fig. 1 (a-f). Evidently, Fig. 1 (a) exhibits the broad peak in the 2\(\theta\) range from 18 to 22\(^\circ\), which matched well with the (110) reflection due to pure PVA reported in the literature\(^{25-27}\). The broadened (110) peak not only shifts after complexing with salts but also reduces the intensity of the peak. The broadening of the (110) peak due to addition of ammonium salts indicates increased amorphocity of polymer electrolyte. Hodge et al\(^{25}\) have also reported similar results. Four broad peaks of the PVA membrane located at 2\(\theta\) = 18, 23, 42 and 68\(^\circ\), indicate the low crystallinity of PVA membrane\(^{18}\). According to literature, there is a correlation between the intensity of the peak and the degree of crystallinity\(^{25}\). The absence of peaks corresponding to ammonium salts confirms the complete dissociation of it in the polymer matrix\(^{26}\).

The density, molecular weight and hardness number of all polymer complexes are compared in Table 1. As seen, with the salt addition, the density of polymer complex increases and also, molecular weight increases commensurately. The variation of both these parameters is attributed to an increase in degree of polymerization. In contrast, the mechanical strength of PVA polymer complexes decreases on salt addition. The decreased hardness value after addition of ammonium salts is attributed to the decrease in crystallinity as well as increased plasticization.

#### 3.2 Thermal properties (TG/DTA)

The TG/DTA curve for 80PVA:20AN is shown in Fig. 2 which reveals that initially the weight loss is negligible up to 423 K, thereafter the rate of weight loss increases. The peak around 488 K coincides with...
the melting temperature observed in DTA curve (Fig. 2). The results indicate the polymer complex under study retains the water up to 423 K, which would allow the proton conduction without any appreciable change. Consequently, the operating temperature of the fuel cell can be extended up to 488 K using this complex system. The comparison of transition and melting temperatures obtained from DTA and DSC of all samples under study is given in Table 1 which indicates that the glass transition temperature obtained from the DSC and DTA curves matches well. Furthermore, glass transition temperature decreases due to the addition of ammonium salts in PVA complexes. Vargas\textsuperscript{16} and Pandian\textsuperscript{28} have reported similar results. The plasticization of PVA polymer due to the addition of ammonium salts weakens the dipole-dipole moment of PVA chains, therefore, the decrease in the $T_g$ and $T_m$.

3.3 Fourier-transform infrared spectroscopy (FTIR)

The FTIR spectra of PVA complexed with different ammonium salts are shown in Fig. 3(a-f). The absorption band at 2942 cm$^{-1}$ corresponds to asymmetric $-\text{CH}_2$ stretching and aliphatic C-H stretching of PVA. These $-\text{CH}_2$ and C-H bands shift to 2940, 2939, 2910, 2906 and 2902 cm$^{-1}$ for 80PVA:20AS, 80PVA:20ADP, 80PVA:20AMTH, 80PVA:20AA, and 80PVA:20AN, respectively. The relative intensity of other characteristic bands of PVA decrease a little with increasing NH$_4^+$ content. For instance, the band at 3541 cm$^{-1}$ is the characteristic band of alcohols and phenols (–O-H) band in pure PVA. This (OH) band shifts to 3267, 3251, 3220, 3216 and 3203 cm$^{-1}$ for 80PVA:20AS, 80PVA:20ADP, 80PVA:20AMTH, 80PVA:20AA, and 80PVA:20AN, respectively. Shift in hydroxyl band towards the lower wave number with the addition of ammonium salts indicates the interaction in the polymer matrices. Similar results in case of PVA complexed with LiBF$_4$ have also been reported in literature\textsuperscript{26}. While the peaks at 1439 and 1376 cm$^{-1}$ are the bending vibrations of $-\text{CH}_2$-OH. The band corresponding to C-H rocking vibration of PVA appears near 850 cm$^{-1}$. The absence of absorption peak for the complexes at 970 cm$^{-1}$ suggests the formation of intermolecular hydrogen bonds between the salts and PVA. The peak at 1100 cm$^{-1}$ assigned to C-O stretching of the secondary alcohols of PVA not only shifts to lower wave numbers but also its intensity decreases in the complexes. This shift is attributed to the decrease in number of C-O groups in the complexes and the specific interaction in the polymer matrices. The FTIR results, in general, suggest complete dissociation of salts in polymer matrix.
3.4 Ionic Conductivity

Typical complex impedance plots of 80PVA:20AN at 283, 293 and 303 K are shown in Fig. 4 which reveals the presence of two semicircular arcs. The high frequency semicircle is attributed to the proton migration through the polymer matrix, i.e. the bulk conductivity of the polymer film. The low frequency semicircular arc is due to the electrode-electrolyte interfacial impedance.

The variation of bulk conductivity as a function of temperature for all polymer complexes under study is shown in Fig. 5. All the samples below and above \( T_g \) obey the Arrhenius law (Eq. 1):

\[
\sigma T = (\sigma T)_0 \exp \left( \frac{-E_a}{kT} \right)
\]

where \((\sigma T)_0\), \(k\), \(T\) and \(E_a\) are pre-exponential factor, Boltzmann constant, absolute temperature and activation energy, respectively. From the Fig. 5, it can be noted that the maximum conductivity is obtained for ammonium nitrate doped PVA amongst all samples under study. The increase in conductivity with temperature is understood to be due to thermally activated defects. The proton conductivity, however, is due to hopping mechanism wherein intermolecular protons transfer rapidly (hopping) down to a chain of hydrogen bonds. At hydrogen bonds, the proton transfer events are highly correlated, and undergo a reorientation of alcohol / phenols dipoles in such a way that it produces a configuration favourable for the next hopping event. The increase in proton conductivity due to addition of ammonium salts is attributed to the decrease in degree of crystallinity and increase in amorphocity (XRD results). As the amorphous region increases, however, the polymer chain acquires faster internal modes thereby, bond rotations produce segmental motion and, thus, the increase in conductivity.

The Arrhenius plots for 80PVA:20AN in the presence of two different hydrogen partial pressures (0 and 4%) at 283, 293 and 303 K are shown in Fig. 6. Suggest increase in conductivity with increase in hydrogen partial pressure. The proton conductivity increases linearly with increasing relative humidity within entire range of hydrogen partial pressures under study (Fig. 7). Here, depleted water from polymer electrolyte film under very low relative humidity results in decrease in conductivity. In
contrast, water accumulation in polymer at relatively high humidity favors proton (H\(^+\)) transport thereby, the enhancement in bulk conductivity. The increased H\(_2\) partial pressure at porous Pt-electrode is responsible for increased H\(^+\) concentration across Pt-electrolyte interface. Concurrently, more mobile charge carriers (H\(^+\)) are available for transport through the polymer electrolyte thereby, the conductivity.

4 Conclusions
The different ammonium salts addition in polyvinyl acetate (PVA) increases the proton conductivity. Amongst all the added salts, the ammonium nitrate salt addition gives maximum conductivity with minimum activation energy. The amorphocity of PVA increases due to salt addition, whereby the molecular weight. The density of polymer complex enhances due to plasticization of PVA after addition of salts. Enhanced conductivity with increased hydrogen concentration and relative humidity suggests H\(^+\) mobility through complex polymer electrolyte.

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References