Characterization of Poly(vinyl alcohol)/Potassium Chloride Polymer Electrolytes for Electrochemical Cell Applications

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A solid polymer electrolyte system based on poly(vinyl alcohol) (PVA) complexed with potassium chloride (KCl) salt was prepared by using solution cast technique. The complexation of KCl salt with the polymer was confirmed by X-ray diffractrometer and Fourier transform infrared spectroscopy. Differential scanning calorimetry was used to determine the melting temperatures and crystallinity of the pure PVA and complexed films. Ionic conductivities of the electrolytes have been determined by AC impedance studies in the temperature range 303–373 K. The conductivity was found to increase with the increase in dopant concentration and temperature. Transference number data suggests that the charge transport in this polymer electrolyte system is mainly due to ions. Optical absorption studies were made in the wavelength range 200–800 nm on pure and KCl doped PVA films. The absorption edge, direct band, and indirect band gap values were evaluated. It was found that the energy gaps and band edge values shifted to lower energies on doping. Electrochemical cells were fabricated with the configuration of K/(PVA + KCl)/(I2 + C + electrolyte) and discharge characteristics were studied under a constant load of 100 kΩ. Various cell parameters, such as open circuit voltage, short circuit current, power density, and energy density were determined. POLYM. ENG. SCI., 52:1685–1692, 2012. © 2012 Society of Plastics Engineers

INTRODUCTION

In recent years, there has been an increasing interest to develop the polymer electrolytes for various applications, such as high energy density batteries, fuel cells, electrochemical capacitors, solar cells, gas sensors, etc. due to their versatility and dimensional stability [1–3]. The advantages of polymer electrolytes over other solid electrolytes are due to their unique mechanical and electrical properties; ease of fabrication into films of desirable sizes and interactions to strengthen the electrode–electrolyte contact. The study of polymer electrolytes was launched by Fenton et al. [4] in 1973, but their technological significance was not appreciated until the research undertaken by Armand et al. [5, 6], a few years later. Initially, polyethylene oxide-(PEO) based electrolytes were investigated. However, PEO-based polymer electrolytes showed ionic conductivity of the order of $10^{-10} \text{ S cm}^{-1}$. Due to the poor performance of this electrolyte, much effort has been devoted to improve the ambient ionic conductivity of polymer electrolytes by improving the cation migration in the amorphous domain. Since ions primarily transport in amorphous phase, many investigations, which aimed to improve ionic conductivity have focused on increasing the amorphous phase of the material. Many attempts have been made on various polymers such as poly (methyl methacrylate) (PMMA), poly (vinyl chloride) (PVC), polyacrylonitrile (PAN), and poly(vinyl alcohol) (PVA) for the purpose of designing polymer electrolyte systems.

In this study, we report solid polymer electrolyte films of pure PVA and PVA complexed with KCl systems. Several experimental techniques like X-ray diffractometer (XRD), Fourier transform infrared (FTIR), differential scanning calorimetry (DSC), transference number were carried out to characterize these polymer electrolytes. Using these electrolytes, electrochemical cells were fabri-
cated and their discharge characteristics were evaluated at a constant load of 100 kΩ.

EXPERIMENTAL

Films of pure PVA and various compositions of complexed films of PVA with KCl salt were prepared in weight percent ratios (95:05), (90:10), and (85:15) by solution cast technique using distilled water as a solvent. The solutions were stirred for 10–12 h to get a homogeneous mixture. The mixture solution was cast on to polypropylene dishes and allowed to evaporate slowly at room temperature. The final product was dried thoroughly to remove all traces of the solvent. The dried composite polymer electrolyte films were peeled off from the polypropylene dishes and stored inside a dry vacuum box.

The XRD patterns of the films were taken using SEIFERT 3003TT X-ray diffractometer with CuKα radiation and graphite monochromator at room temperature. FTIR spectra of these films were recorded using EO-SXB IR spectrometer with resolution of 4 cm⁻¹. The morphology of the polymer films have been observed using CARL ZEISS EVO 25 scanning electron microscope. DSC thermograms of pure PVA and KCl complexed PVA polymer electrolytes were recorded using SDT Q600 V20.9 in the range 303–483 K. The AC impedance measurements were performed by a computer controlled PSM 1700 (phase sensitive multimeter) in the frequency range 10 Hz to 1 MHz and temperature range 303–373 K. Optical absorption studies were carried out at room temperature in the wavelength region 200–800 nm using Perkin Elmer UV-Vis-NIR (model 3100) spectrophotometer. Electrochemical cells were fabricated with the configuration K (anode)/(PVA + KCl)/(I₂ + C + electrolyte) (cathode) and their discharge profiles were monitored at a constant load of 100 kΩ.

RESULTS AND DISCUSSION

XRD Analysis

To investigate the influence of salt on polymer structure, X-ray diffraction studies were performed for pure PVA, (PVA + KCl) complexed polymer electrolyte films and KCl salt. Figure 1 represents the XRD patterns of pure PVA, KCl salt, and PVA complexed with KCl salt. From Fig. 1, it is clear that a broad peak around 23.6° is found in the XRD pattern of pure PVA. The relative intensity of this peak decreased with the increase in the dopant concentration. This shows a decrease in the degree of crystallinity of polymer after the addition of KCl. Absence of peaks corresponding to KCl salt, in these polymer complexes indicates the complete dissolution of salt in the polymer matrices. Hodge et al. [8] established correlation between the intensity of the peak and degree of crystallinity. They observed that the intensity of XRD pattern decreases as the amorphous nature increases with the addition of dopant. No sharp peaks were observed for higher concentrations of KCl salt in the polymer, indicating that the amorphous phase was dominant [9]. This amorphous nature results in greater ionic diffusivity with a high ionic conductivity, which can be obtained in amorphous polymers that have flexible back bone [10].

FTIR Spectral Studies

The FTIR spectra for pure PVA, KCl complexed PVA of different compositions, and KCl salt are shown in Fig. 2. The following changes in the spectral features have been observed after comparing the spectrum of complexed PVA with that of pure PVA and KCl. The inter molecular hydrogen bonded O–H stretching frequency of PVA appearing in the range of 3540–3060 cm⁻¹ is shifted to 3536–3173 cm⁻¹, 3502–3171 cm⁻¹, and 3513–3150 cm⁻¹ in the complexed PVA films respectively. In addition to this, the C–H stretching of CH₂ exhibited at 2844 cm⁻¹ in pure PVA is shifted to 2919, 2908, and 2998 cm⁻¹, respectively upon doping. The C–H bending of CH₂ in pure PVA exhibited absorption at 1470 cm⁻¹ is shifted to 1450, 1440, and 1420 cm⁻¹ in the complexed PVA films, respectively. Deformations coupled to C–H wagging and gives rise to a peak at1300 cm⁻¹ in pure PVA. It is shifted to 1270, 1250, and 1230 cm⁻¹ in the complexed films. C–C stretching occurring at 1130 cm⁻¹ in pure PVA is shifted to 1140, 1130, and 1120 cm⁻¹ in complexed films. All these changes in the FTIR spectra are clear indications for the complexation of PVA [11, 12].

Morphological Studies

Scanning electron microscopy (SEM) is often used to study the compatibility between various components of
the polymer electrolytes through the detection of phase separations and interfaces [13, 14]. The compatibility between the polymer matrix and the inorganic dopants has great influence on the properties (mechanical, thermal, ionic conductivity) of the polymer electrolytes.

The morphology of the pure PVA and KCl doped polymer electrolytes, studied by SEM technique, is a uniform type but with different degrees of roughness. Figure 3 shows the surface morphology of complexed polymer electrolytes with different concentrations of KCl salt. When KCl salt is added to the polymer, the surface morphology of pure PVA changes from rough to smoother and the reductions of rumples are also found. This indicates the semi-crystalline nature of pure is reduced by the addition of salt. As the KCl salt concentration increases, the surface morphology is further improved. The rumples of pure PVA are gradually decreased and the rough surface becomes even smoother than pure PVA membrane.

The smooth surface morphology indicates that salt was completely dissolved in the polymer matrix. This dissolution is due to the interaction of salt with the polymer host. These observations were supported by XRD and FTIR studies reported in the previous sections.

**Thermal Studies**

DSC is used to measure the enthalpy changes that occur in a sample as a function of either time or temperature. Using this technique, the glass transition temperature...
As well as melting temperature \( T_m \) and degree of crystallinity of the material can be identified. Figure 4 shows the typical plot of the DSC curves of pure PVA and different concentration of the doped KCl polymer electrolytes, respectively. An endothermic peak has been observed around 465 K which corresponds to the melting of PVA. A slight shift of \( T_m \) towards lower temperatures on the addition of salt to the host polymer reveals the disruption of crystallinity of the host polymer. This clearly indicates that the micro movement of the PVA chain becomes easier by the addition of the salt, presumably owing to the decrease in crystallinity of these electrolytes. The relative percentage of crystallinity \( \chi_c \) has been calculated by using the equation:

\[
\% \chi_c = \frac{\Delta H_m}{\Delta H^0_m} \times 100
\]

where \( \Delta H_m \) and \( \Delta H^0_m \) are the melting heat of the doped polymer electrolytes and host polymer, respectively, obtained from DSC results.

From the Table 1, it is clear that \( T_m \) values and relative crystallinity decreasing of polymer electrolytes with the increase of salt content which causes an increase in the amorphous phase. The \( T_m \) and \( \chi_c \) has been found to be low for 15 wt% KCl doped polymer electrolytes system. The low values of \( T_m \) and \( \chi_c \) represents the highly amorphous nature of the above mentioned polymer electrolyte as confirmed from the XRD result.

### Electrical Conductivity

The ionic conductivity of pure and doped polymer electrolyte films has been determined from the complex impedance analysis using the cell with blocking electrodes. The typical impedance plot of PVA + KCl (90:10) at different temperatures is shown in Fig. 5. The complex impedance diagram shows two well-defined regions. The high frequency region semicircle, which is due to the bulk effect of the electrolyte, and the linear region in low frequency range, that is attributed to the effect of the blocking electrodes. In ideal case at low frequency, the complexed impedance plots should show the straight line parallel to the imaginary axis, but the double layer at the blocking electrodes causes the curvature [15]. The ionic migration and bulk polarization are physically in parallel and therefore, the semi circle at high frequency can be observed in all the samples.

The bulk resistance was measured from the high frequency intercept on the real axis. The ionic conductivity of the electrolytes was calculated from the equation:

\[
\sigma = \frac{L}{R_b A}
\]

where \( L \) is the thickness of the polymer electrolytes (cm), \( A \) is the area of the blocking electrodes (cm\(^2\)), and \( R_b \) is the bulk resistance of the polymer electrolytes.

The bulk resistance decreases with increasing temperature. The decrease in bulk resistance of the polymer ele-

<table>
<thead>
<tr>
<th>Polymer system</th>
<th>( T_m ) (K)</th>
<th>Relative crystallinity (%) ( \chi_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PVA</td>
<td>465</td>
<td>—</td>
</tr>
<tr>
<td>PVA + KCl (95 + 05)</td>
<td>462</td>
<td>79.6</td>
</tr>
<tr>
<td>PVA + KCl (90 + 10)</td>
<td>461</td>
<td>47.5</td>
</tr>
<tr>
<td>PVA + KCl (85 + 15)</td>
<td>459</td>
<td>39.5</td>
</tr>
</tbody>
</table>

**FIG. 5.** COLE-COLE plots of PVA + KCl (90 + 10) at different temperatures: (a) 303 K, (b) 313 K, (c) 323 K, (d) 333 K, and (e) 343 K.
trolyte is due to enhancement of the ionic mobility and the number of carrier ions with concentration of the dopant [16]. Table 2 shows the conductivity values of the polymer electrolytes at room temperature.

Figure 6 shows the Arrhenius plots of logarithmic conductivity versus inverse temperature of pure PVA and different compositions of PVA + KCl polymer electrolytes. It is observed that as temperature increases, the conductivity also increases for all complexes which is in agreement with the theory established by Armand et al. [17]. This can be rationalized by considering the free volume model [18], when the temperature is increased, the vibrational energy of a segment is sufficient to push against the hydrostatic pressure imposed by its neighboring atoms and create a small amount of space surrounding its own volume in which vibrational motion can occur [19]. Thus the free volume around the polymer chain causes the mobility of ions and polymer segments. Hence the increment of temperature causes the increase in conductivity due to the increased free volume and their respective ionic and segmental mobilities.

The conductivity values do not show any abrupt jump with temperature which indicates that these electrolytes exhibit a completely amorphous structure [20]. This type of behavior is observed in a number of PVA-based electrolyte systems [20–22]. The increase in conductivity with temperature can be linked to the decrease in viscosity and thus, to increased chain flexibility [23]. Since the conductivity–temperature data obeys an Arrhenius relationship, the nature of cation transport is quite similar to that occurring in ionic crystals, where ions jump into neighboring vacant sites and hence increase the ionic conductivity [24].

The activation energy ($E_a$) which is a combination of the energy of defect formation and of the energy of defect migration can be calculated from log $\sigma$ versus $1000/T$. Fig. 6 plots using the following Arrhenius equation:

$$\sigma = \sigma_0 \exp \left( \frac{-E_a}{kT} \right)$$

where $\sigma_0$ is a constant, $E_a$ is the activation energy, $k$ is the Boltzmann constant, and $T$ is absolute temperature. The low activation energy for potassium ion transport is due to the completely amorphous nature of polymer electrolyte that facilitates the fast $K^+$ ion motions in the polymer network. The amorphous nature also provides a bigger free volume in polymer electrolyte system with increase in temperature.

**Transference Numbers**

The conductivity measurements are inadequate if performed without the information on the possible type of charge carriers. The transference numbers corresponding to ionic ($t_{ion}$) and electronic ($t_{ele}$) of the polymer electrolytes are evaluated with the Wagner’s polarization technique [25]. In this technique, the direct current is monitored as a function of time on the application of a fixed DC potential of 1.5 V across (K/electrolyte/C) cell. The transference numbers were calculated using the following equation:

$$t_{ion} = l - \frac{I_f}{I_i}$$

$$t_{ele} = l - t_{ion}$$

where $I_i$ is the initial current and $I_f$ is the final residual current.

Figure 7 shows the variation of current as a function of time upon the application of a DC voltage of 1.5 V.
across the (K/electrolyte/C) cell. The transference numbers were evaluated from the plots and are given in Table 2. The total ionic transference number was found to be in the range 0.94–0.96 in these polymer electrolyte systems. This suggests that the charge transport in these polymer electrolytes is predominantly due to ions, with negligible contribution from the electrons.

Optical Properties

The study of optical absorption gives information about the band structure. Insulators/semiconductors are generally classified into two types: (a) direct band gap semiconductors and (b) indirect band gap semiconductors. In direct band gap semiconductors, top of the valance band and bottom of the conduction band lie at the same zero crystal momentum (wave vector). If the bottom of conduction band does not correspond to zero crystal momentum, then it is called indirect band gap semiconductor. In an indirect band gap semiconductor, transition from valance band to conduction band should always be associated with a phonon of right magnitude. Davis and Shalliday [26] reported that near fundamental band edge both direct and indirect transitions occur and can be observed by plotting $x^1/2$ and $x^2$ as a function of energy $hν$. The analysis of Thutupalli and Tomlin [27] is based on the following relation:

$$ (hνx)^2 = C_1(hν - E_{gd}) \tag{6} $$

$$ (hνx)^{1/2} = C_2(hν - E_{gi}) \tag{7} $$

where $hν$ is the photon energy, $E_{gd}$ is the direct band gap, $E_{gi}$ is the indirect band gap, $n$ is the refractive index, $x$ is the absorption coefficient, and $C_1$ and $C_2$ are constants.

The absorption coefficient ($x$) was calculated from the absorbance ($A$). After correction for reflection, $x$ was determined using the relation:

$$ I = I_0 \exp(-x) $$

Hence,

$$ x = \frac{2.303}{x} \log \left( \frac{I}{I_0} \right) = \frac{2.303}{x} A \tag{9} $$

where $A$ is absorbance and $x$ is thickness of the sample.

To determine the nature and width of the band gap $x$, $(xhν)^2$ and $(xhν)^{1/2}$ were plotted as a function of photon energy ($hν$). The position of the absorption edge was found by extrapolating the linear portions of $x$ versus $hν$ curves (Fig. 8) to the zero absorption value. It is observed that the absorption edge for pure PVA lies at 5.23 eV while for complexed films, 5.04, 4.97, and 4.92 eV, respectively.

When a direct band gap exists, the absorption coefficient has the following dependence on the energy of incident photon [27–29].

$$ (xhν) = C(hν - E_{gd})^{1/2} \tag{10} $$
where $E_g$ is the direct band gap, $C (=4\pi\sigma_d/nc\Delta E)$ is a constant dependent on the specimen structure.

The direct band gap values were obtained by plotting $(\alpha h\nu)^2$ versus $h\nu$ curves (Fig. 9). For pure PVA, the optical band gap was observed to be 5.08 eV while for complexed films the values lies at 5.03, 4.96, and 4.88 eV, respectively.

For indirect transitions, which require phonon assistance, the absorption coefficient has the following dependence on photon energy [27–29]:

$$a h\nu = A(h\nu - E_g + E_p)^2 + B(h\nu - E_g - E_p)^2$$  \hspace{1cm} (11)

where $E_p$ is the energy of the photon associated with the transition of constants $A$ and $B$ depending on the band structure.

The indirect band gap values were obtained from the plots of $(z h\nu)^{1/2}$ versus $h\nu$ shown in Fig. 10. For pure PVA, the indirect band gap lies at 4.96 eV while for complexed films its value lies at 4.74, 4.67, and 4.53 eV, respectively. All these values of absorption edge, direct band gap, and indirect band gap are tabulated in Table 2.

From the table, it is clear that the band edge, direct band gap, and indirect band gap values showed a decrease with the addition of dopants. Similar behavior can also be seen in the activation energies obtained from the conductivity data as shown in Table 2. The magnitudes of the activation energies obtained from conductivity data are small in comparison with optical band gap energies. This is due to the fact that the activation energy corresponds to the energy required for conduction from one site to another, while the optical band gap corresponds to the interband transition [29].
TABLE 3. Cell parameters of K/(PVA + KCl)/(I2/C/electrolyte) polymer electrolytes.

<table>
<thead>
<tr>
<th>Cell parameters</th>
<th>(PVA + KCl) (95 + 05)</th>
<th>(PVA + KCl) (90 + 10)</th>
<th>(PVA + KCl) (85 + 15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Open circuit voltage (V)</td>
<td>2.58</td>
<td>2.61</td>
<td>2.71</td>
</tr>
<tr>
<td>Short circuit current (µA)</td>
<td>350</td>
<td>420</td>
<td>546</td>
</tr>
<tr>
<td>Area of the cell (cm²)</td>
<td>1.168</td>
<td>1.168</td>
<td>1.168</td>
</tr>
<tr>
<td>Weight of the cell (g)</td>
<td>1.32</td>
<td>1.31</td>
<td>1.34</td>
</tr>
<tr>
<td>Discharge time for plateau region (h)</td>
<td>95</td>
<td>111</td>
<td>130</td>
</tr>
<tr>
<td>Current density (µA cm⁻²)</td>
<td>299</td>
<td>359</td>
<td>467</td>
</tr>
<tr>
<td>Power density (W kg⁻¹)</td>
<td>0.684</td>
<td>0.836</td>
<td>1.104</td>
</tr>
<tr>
<td>Energy density (Wh kg⁻¹)</td>
<td>64.98</td>
<td>92.88</td>
<td>143.54</td>
</tr>
<tr>
<td>Discharge capacity (µA h⁻¹)</td>
<td>3.68</td>
<td>3.78</td>
<td>4.20</td>
</tr>
</tbody>
</table>

Electrochemical Cell Discharge Characteristics

Solid-state electrochemical cells with the configuration K (anode)/(PVA + KCl)/(I2/C/electrolyte) (cathode) were fabricated and their discharge profiles were studied and are shown in Fig. 11. There was an initial rapid decrease in the voltage, which could be due to polarization and/or the formation of a thin layer of potassium salt at the electrode–electrolyte interface. The open circuit voltage (OCV), short circuit current (SCC), and other cell parameters of these cells are listed in Table 3. From Table 3, it is clear that the SCC and the discharge time for the plateau region are found to be greater in PVA + KCl (85 + 15) cell compared with the other two complexed cells. This has been explained in terms of high ionic conductivity and more amorphosity as observed in PVA + KCl (85 + 15) electrolyte system compared to the other two complexed systems.

CONCLUSIONS

Polymer electrolytes based on PVA + KCl of different compositions was prepared using solution cast technique. The structural and complexation behavior have been studied by XRD and FTIR. DSC spectra revealed the thermal stabilities, melting temperatures, and crystallinity of the samples. Using impedance spectroscopy, the conductivity was found to increase with the increase in temperature as well as dopant concentration. Optical absorption edge and optical energy gaps (both direct and indirect) showed a decreasing trend with increasing dopant concentration. It was observed that these values shifted to lower energies on doping. Electrochemical cells were fabricated and the discharge characteristics were studied. Among these cells, PVA + KCl (85 + 15) was found to be more stable than the other two cells.

REFERENCES