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New Plasticized Polymer Solid Electrolyte Material for Zn/MnO₂ Cell

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Solid polymer electrolytes based on polyvinyl alcohol (PVA) and plasticized with ethylene glycol (EG) and/or phosphoric acid (H₃PO₄) have been developed to increase their proton conductivities. This electrolyte material has been characterized using various experimental techniques such as X-ray diffraction, infrared Fourier transform spectrometry and electrochemical impedance spectrometry. An optimum ionic conductivity value of the plasticized polymer electrolyte film has been achieved to be of the order of 10⁻³ Scm⁻¹ at relative humidity equal to 100% for 45 wt.% EG and 5 wt.% H₃PO₄. The minimum activation energy of this ternary complex is found to be 9 kJmol⁻¹ for optimum conductivity condition. Using this ternary PVA-EG(45 wt.%)-H₃PO₄(5 wt.%) complex film as electrolyte, an "all solid state" Zn/MnO₂ cell was fabricated and its discharge characteristics profile has been studied. In fact, the specific capacity and energy exceeding 200 Ahkg⁻¹ and 250 Whkg⁻¹, respectively, have been observed experimentally in this cell.

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PACS/topics: electrolyte, plasticizer, discharge

1. Introduction

In recent years, solid polymer electrolytes, such as polyvinyl alcohol (PVA) and polyethylene oxide (PEO), have attracted considerable attention in view of their wide potential applications in various electrochemical devices, particularly in solid state batteries, sensors, fuel cells and supercapacitors [1, 2]. PVA has the advantage of being soluble in water and compatible with numerous mineral and organic additives which can confer to it the appropriate electrical and mechanical properties for these applications.

Since the ionic conductivity of this type of materials depends on the concentration of mobile charge carriers (H⁺) and their mobility [3, 4], we opted to add to the PVA a plasticizer (ethylene glycol: EG) and/or an acid (H₃PO₄). This choice is justified by the fact that the polymer matrix provides good mechanical properties while the additives increase the H⁺ concentration and their electrical mobility, which regulates the value of the ionic conductivity.

2. Experimental

2.1. Materials

The PVA-based complexes have been prepared according to the procedure described in [5]. First, 1 g of PVA (average mol. wt. $\approx 7 \times 10^4$ g mol⁻¹, MERCK) was

added to 100 cm³ of boiling water under vigorous stirring until a complete dissolution of the PVA was achieved. Once the PVA was completely dissolved, an appropriate amount of EG (BIOCHEM, wt.% EG: 0–50 wt.%) and/or H₃PO₄ (85% phosphoric acid, PROLABO: 0–10 wt.%) was added to the previous solution. The mixture was then maintained at 80 °C until a highly viscous gel was obtained, such that the remaining liquid was about 20% of its initial volume.

The formed gel was poured on a flat smooth surface of a cylindrical Petri glass box to obtain, after drying in ambient atmosphere for a few days, homogeneous films having comparable thicknesses (average of 0.20 ± 0.005 mm). The films thus obtained were cut to form circular samples of 13 mm in diameter which were stored under conditions appropriate to their required measurements.

2.2. Cell preparation

Zn/MnO₂ cell has been realized according to the procedure described in [5]. The cathodic electrode consists of 80 mg of a homogenized mixture of manganese dioxide powder (variety γ , Sedima) and carbon black (5 wt.%) and pressed to form a pellet with area of 1.3 cm² and the thickness of 0.01 mm using a hydraulic press.

The anodic working electrode contains 40 mg of mixture of metallic Zn, zinc ammonium sulfate (AZS: (NH₄)₂Zn(SO₄)₂·6H₂O) and carbon black (CB), in weight ratio (wt.%) of Zn:AZS:CB=65:35-*x*:*x*, where *x* was varied from 0 to 5. This mixture was carefully homogenized and pressed into a pellet with area of 1.3 cm² and thickness of 0.01 mm. The cell was then mounted as a five layer assembly: a flexible 0.25 mm graphite foil,

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the positive active mass, the electrolyte, the negative active mass and a second flexible graphite foil. The whole system was kept under moderate pressure using a Teflon screwing system.

2.3. Characterization

The XRD characterization of the materials has been carried out by means of a high resolution X ray MRD PANALYTICAL (ISM) diffractometer. The used wavelength has been set at $\lambda = 1.5418 \text{ \AA}$ by using the K_{α} line of a copper anticathode. 2θ was ranging from 5° to 70° and stepping was set to $0.01^{\circ} \text{ s}^{-1}$.

The ionic conductivity measurements have been carried out on a Solartron 1260 type impedance-meter connected to a micro computer driven SOLARTRON 1287 interface controlled by Zplot and Zview software. For the electrical conductivity measurements, the tested frequency range was 1 to 10^6 Hz and the applied voltage was varied between 10 mV for the highest conductivity to 50 mV for less conductive materials.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffractograms of PVA, PVA-EG(50 wt.%) and PVA-EG(45 wt.%) $\text{-H}_3\text{PO}_4$ (5 wt.%) complexes are shown in Fig. 1. The PVA film diffraction pattern (Fig. 1a) presents a broad peak at $2\theta = 20^{\circ}$ characteristic for the amorphous structure of the polymer [6, 7]. Similarly, the shape of the diffraction pattern of PVA-EG(50 wt.%) (Fig. 1b) and PVA-EG(45 wt.%) $\text{-H}_3\text{PO}_4$ (5 wt.%) (Fig. 1c) complexes is similar to that of PVA. Nevertheless, the height of the characteristic peak of the polymeric phase becomes smaller with the addition of the plasticizer. On the other hand, the substitution of 5 wt.% of ethylene glycol by an equivalent quantity of orthophosphoric acid engenders a more important effect on the height and the width of the characteristic peak. This shows clearly that the amorphous character of the studied complexes becomes more pronounced with the addition of EG and H_3PO_4 . This observation is in good agreement with literature data [8, 9].

3.2. Conductivity studies

Figure 2 shows the effect of the surrounding relative humidity on the ionic conductivity of the PVA-EG binary complexes with different plasticizer contents. This figure shows the effect of both amount of the plasticizer in the complex and the hydration on the ionic conductivity of these materials.

The ionic conductivity of all studied complexes increases with increasing the amount of ethylene glycol in the complex and also with the increasing surrounding relative humidity. In fact, the protonic conductivity of PVA (Fig. 2a) increases from $3.0 \times 10^{-10} \text{ Scm}^{-1}$ at 10% RH to $3.0 \times 10^{-4} \text{ Scm}^{-1}$ at 100% RH, this corresponds to an improvement by a factor of 10^6 [5].

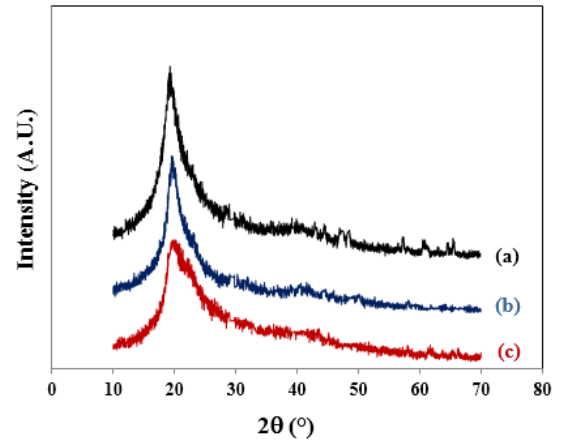


Fig. 1. X-ray diffraction patterns of: (a) PVA, (b) PVA-EG(50 wt.%) and (c) PVA-EG(45 wt.%) $\text{-H}_3\text{PO}_4$ (5 wt.%).

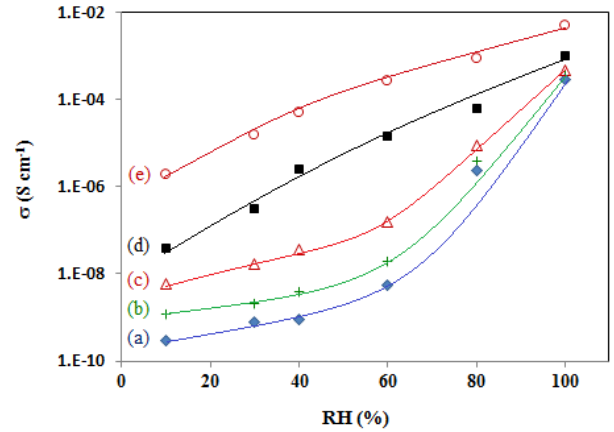


Fig. 2. Evolution of ionic conductivity as a function of RH of samples: (a) PVA, (b) PVA-EG(10 wt.%), (c) PVA-EG(30 wt.%), (d) PVA-EG(50 wt.%) and (e) PVA-EG(45 wt.%) $\text{-H}_3\text{PO}_4$ (5 wt.%).

However, the PVA-EG complex containing 50 wt.% of EG presents better electrical properties than those of the PVA (Fig. 2d). Its ionic conductivity increases from $3.9 \times 10^{-8} \text{ Scm}^{-1}$ to $9.9 \times 10^{-4} \text{ Scm}^{-1}$ when RH varies between 10 and 100%. This corresponds to an improvement by a factor of 2.5×10^4 .

At low relative humidity (10%), PVA-EG(50 wt.%) complex is about 130 times more conductive than the PVA, whereas at high RH (100%) the conductivity of the PVA-EG(50 wt.%) complex is only three times stronger than that of the PVA. The two binary complexes of PVA-EG(10 wt.%) (Fig. 2b) and PVA-EG(30 wt.%) (Fig. 2c) have intermediate ionic conductivity between those of the PVA and PVA-EG(50 wt.%) complexes. This can be explained by the fact that the presence of plasticizer in the complex increases the electrical mobility of the charge carriers (H^+) [8].

Although the ionic conductivity of the PVA-EG binary complexes is better than that of the pure PVA over the entire studied interval of relative humidity, the electrical properties of these complexes are not sufficient for their use as solid electrolyte proton conductor in electrochemical cells. In order to improve this ionic conductivity, the mixture of PVA and EG with a mineral acid in small amounts was studied. These new complexes should have adequate electrical and mechanical properties for their application in cells.

In fact, the ternary PVA-EG- H_3PO_4 complexes seem to be an excellent combination to obtain a relatively high protonic conductivity with suitable mechanical and hygroscopic properties. Moreover, these complexes may be less corrosive for the active material of negative electrode if their acid content remains relatively low [5, 10].

The ternary complex PVA-EG(45 wt.%) - H_3PO_4 (5 wt.%) presents at room temperature a protonic conductivity of $5.2 \times 10^{-3} \text{ S cm}^{-1}$ at RH= 100% (Fig. 2e). This represents a protonic conductivity respectively 17 and 5 times better than those of PVA and PVA-EG(50 wt.%) complex. Such electrical performance is satisfactory for the use of this complex in the field of cells. Therefore, this complex will be used as an electrolyte to evaluate the electrochemical performances of the “all-solid” Zn/ MnO_2 cells.

Figure 3 shows the temperature-dependent conductivity of different PVA-based complexes. From the plot it is evident that as the temperature increases, the ionic conductivity also increases for all these complexes. The increase in the conductivity with temperature may be due to the increased mobility of charge carriers [8, 11].

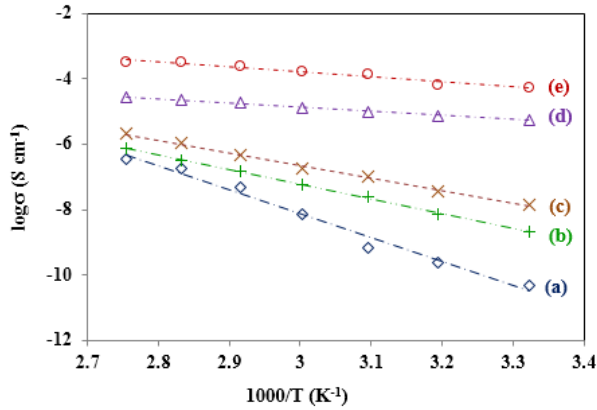


Fig. 3. Evolution of $\log(\sigma)$ as a function of the inverse temperature at RH=40%: (a) PVA, (b) PVA-EG(10 wt.%), (c) PVA-EG(30 wt.%), (d) PVA-EG(50 wt.%) and (e) PVA-EG(45 wt.%) - H_3PO_4 (5 wt.%).

These complexes exhibit an Arrhenius-type temperature dependence of the protonic conductivity, suggesting thermally activated proton conduction. The activation energy is obtained for each complex from the slope of the Arrhenius plots. The values of the activation ener-

gies of these complexes at different RH are grouped in Table I. All of these results are comparable to those reported in the literature for PVA-based complexes under similar conditions [8, 11].

TABLE I

Values of the activation energy in kJ mol^{-1} of the studied complexes for different values of relative humidity (RH).

| RH [%] | 40 | 60 | 80 | 100 |
|--|------|------|------|------|
| PVA | 105 | 97.7 | 45.0 | 40.8 |
| PVA-EG(10 wt.%) | 66.0 | 52.4 | 32.7 | 30.2 |
| PVA-EG(30 wt.%) | 43.6 | 36.0 | 33.4 | 28.9 |
| PVA-EG(50 wt.%) | 21.0 | 20.5 | 20.0 | 18.6 |
| PVA-EG(45 wt.%) - H_3PO_4 (5 wt.%) | 20.4 | 18.5 | 13.4 | 9.0 |

The results of Table I show a decrease in the activation energy of the studied complexes with RH. This is expected since the plasticizing effect of the hydration water has been already proved [5, 12]. However, the PVA-EG(45 wt.%) - H_3PO_4 (5 wt.%) complex has the highest protonic conductivity and the lowest activation energy. In addition, the activation energy values of this ternary complex are of the order of 10 kJ mol^{-1} under relative humidities between 80 and 100%. This later result and the high values of the ionic conductivity make of this complex a good electrolyte material for cells in such hydration conditions.

3.3. Discharge characteristics

Figure 4 shows a typical discharge curve recorded on a two electrodes cell: Zn-AZS(33 wt.%) - NC(2 wt.%) / PVA-EG(45 wt.%) - H_3PO_4 (5 wt.%) / MnO_2 - NC(5 wt.%), compared to that of Zn/PVA-PWA(40 wt.%) - H_3PO_4 (40 wt.%) / MnO_2 cell [5]. This discharge was carried out at a constant current density of 0.1 mA cm^{-2} with lower cut-off voltage of 0.9 V.

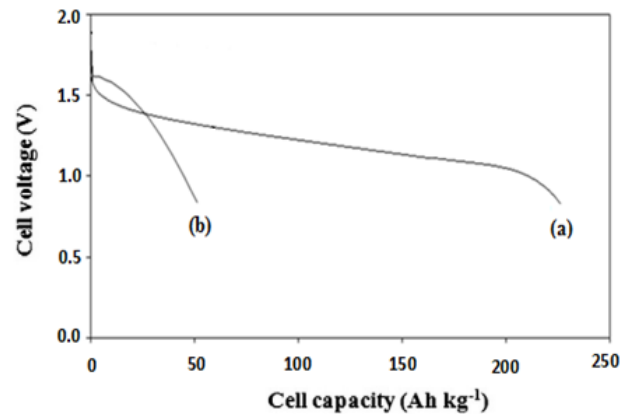


Fig. 4. Evolution of cell voltage of: (a) Zn-AZS(35 wt.%) - NC(2 wt.%) / PVA-EG(45 wt.%) - H_3PO_4 (5 wt.%) / MnO_2 - NC(5 wt.%) and (b) Zn/PVA-PWA(40 wt.%) - H_3PO_4 (40 wt.%) / MnO_2 [5] at regime discharge of 0.1 mA cm^{-2} and RH= 100%.

The open-circuit voltage for this cell has reached a high value of 1.8 V. When the cell delivers a current, the cell voltage decreases due to the ohmic drop and the polarization of electrodes. Then, a pseudo-plateau, around 1.4 V, is established during the major part of the discharge. Its shape is characteristic of cells based on MnO₂.

At the end of discharge, the cell voltage drops sharply showing an accentuated impoverishment of one of electrode/electrolyte interfaces. This cell provides an experimental specific capacity and energy, specific to the unit of the negative active mass, exceeding 222 Ahkg⁻¹ and 286 Whkg⁻¹, respectively. These performances are significantly higher than those reported in the literature [5, 10, 13] for comparable systems.

4. Conclusions

Plasticized polymer electrolyte films containing PVA, EG and H₃PO₄ have been prepared and the effect of plasticizer on polymer electrolytes has been studied using such experimental techniques as XRD and SIE. The polymer electrolyte developed from a mixture of 45 wt.% EG and 5 wt.% of H₃PO₄ has achieved an ionic conductivity of 5.2×10^{-3} Scm⁻¹ and an activation energy of 9 kJmol⁻¹ at RH= 100% and at room temperature with appropriate mechanical properties, regarding especially the flexibility. These results suggest that this material is a good candidate electrolyte for “all-solid” state Zn/MnO₂ cell. In fact a capacity of 220 A h kg⁻¹ and a specific energy of 286 W h kg⁻¹ have been observed experimentally in this cell.

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