



Development and characterization of a new organic/inorganic hybrid ternary protonic conductive material for solid state cells



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ARTICLE INFO

Article history:

Received 5 March 2013

Received in revised form 9 November 2013

Accepted 20 December 2013

Available online 24 January 2014

Keywords:

Electrolyte material
Polyvinyl alcohol
Phosphotungstic acid
Protonic conductivity
Impedance spectrometry
Energy density

ABSTRACT

The advantages of using the ternary system based on the association of phosphotungstic acid (PWA) and orthophosphoric acid (H_3PO_4) in a polyvinyl alcohol (PVA) organic matrix as an interesting protonic electrolyte have been investigated in the frame of their applicability in all-solid state primary cell manufacturing. The developed electrolyte materials have been studied by X-ray diffraction (XRD), infrared Fourier transform spectrometry (FTIR) and electrochemical impedance spectrometry (EIS). High ionic conductivities ranging from 1.0 to $1.8 \cdot 10^{-2} \text{ S cm}^{-1}$ could be reached at room temperature for relative humidity ranging from 30 to 100% with a ternary PVA–PWA (40 wt.%)– H_3PO_4 (40 wt.%) complex. As a consequence of their overall good electrochemical but also mechanical properties, such materials have been used successfully as solid state protonic electrolyte in Zn– MnO_2 cell prototype development with an energy density up to 120 Wh kg^{-1} .

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1. Introduction

More and more recent electrical devices are powered by (primary or secondary) cells especially in mobile applications. These cells must be safe and stable. Historically, the first developed systems were generally based on liquid electrolyte containing devices. The liquid state led to very low internal resistance, and managed an excellent contact between the electrolyte and the electrodes.

However liquid state electrolytes result in risks of corrosion, leakage and spilling, which are easy to overcome when using solid state electrolytes. Among possible solid state electrolytes, protonic electrolytes are of major interest since the high mobility of protons results in highly conductive materials. Thus, uranyl hydrogenophosphate [1], montmorillonite [2] and phosphotungstic acid [3–7] have often been considered with interest in the past. With regard to its conductivity at room temperature, the latter is among the best ones of inorganic solid state electrolytes, with conductivities up to 0.19 S cm^{-1} for the $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$ phase.

Nevertheless, its application area is often limited as a consequence of the high sensitivity of its protonic conductivity to the ambient relative humidity [8]. In order to increase the resilience of this electrolyte against changes in the surrounding relative humidity (RH), its association with polymers such as PVA or PEO (polyethylene oxide) has been investigated. Polymer-based solid state electrolytes such as PVA or PEO have already shown interesting properties when combined with potassium hydroxide (KOH) [9–12], orthophosphoric acid [13–16] or

with PWA [17–22] as an inorganic load. But as far as we know, no study has been made up to now upon the ternary system PVA–PWA– H_3PO_4 . One must keep in mind that an inorganic acid such as PWA or H_3PO_4 to the PVA enhances the ionic conductivity but results in severe loss of mechanical properties. Beyond a concentration limit of mineral load, the binary complex becomes rigid or even brittle in the case of PWA or quasi liquid (forming a gel) in the case of H_3PO_4 at high values of RH. The use of both acids as a mineral load in a PVA matrix could result in the formation of a highly conductive ternary complex the mechanical properties of which remain however good enough for being used successfully as a solid state electrolyte. At this point, the most important objective consisted in optimizing the composition of the electrolyte complexes so as to keep the best possible conductivity in association with good solid state mechanical properties over the whole RH working range. Therefore, this study aims at examining more into details the effects of both charge carrier concentrations and relative humidity (RH) on such solid state electrolytes.

In this context, this contribution aims at examining the interest of associating both PWA and H_3PO_4 in the PVA matrix in order to improve the overall physico-chemical properties of the solid state electrolyte with regard to its potential applications in primary and secondary cells.

2. Experimental

2.1. Material preparation

The material has been prepared by following procedure: one first dissolves 1 g of PVA (polyvinyl alcohol, average molecular weight

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about $7 \cdot 10^4 \text{ g mol}^{-1}$, MERCK ref 843869) in boiling water (1 g PVA/100 mL H_2O) by stirring strongly the mix. This step requires about one hour to be completed. Once the PVA is completely dissolved, the appropriate amount of PWA ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$ type FLUKA ref 79690, wt.% PWA: 0–90) and/or H_3PO_4 (85% phosphoric acid, PROLABO, ref 87887.180: 0–60 wt.%) is added at 80°C to the previous solution. The dissolution of PWA is very fast. After the complete dissolution, the mix is evaporated at 80°C until the remaining liquid is reduced to about 20% of its initial volume.

The following step consists in the preparation of an electrolyte film for the material testing. Therefore, 10 mL of the previously viscous mix is poured into a 10 cm diameter PETRI's glass box and allowed to evaporate at room temperature and ambient atmosphere until constant weight is reached.

The obtained electrolyte film can then be withdrawn from the bottom of the glass vessel and cut with a 13 mm punch as circular samples for the required measurements.

2.2. XRD and FTIR studies

The characterization of the materials has been made by means of diffraction patterns as obtained on hand 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 $\text{K}\alpha$ line of a copper anticathode for 2 θ ranging from 5° to 70° and stepping by $0.01^\circ \text{ s}^{-1}$.

Fourier transform infrared spectrometry (FTIR) measurements have been performed on hand of an FTIR SHIMADZU 8400S spectrometer. The spectral range was 4000 cm^{-1} to 400 cm^{-1} and the resolution 2 cm^{-1} .

2.3. Electrical and electrochemical characterisation

The ionic conductivity measurements have been carried out on an SOLARTRON 1260 type impedance-meter connected to a micro computer driven SOLARTRON 1287 interface on hand of Zplot and Zview software. The tested frequency range was 1 to 10^6 Hz and the applied voltage was 10 mV for the highest conductivities to 50 mV for less conductive materials.

2.4. Cell assembly

The cathodic electrode is made of 80 mg chemically prepared Faradiser γ -type manganese dioxide MnO_2 . The anodic working electrode contains 40 mg of a mixture of metallic zinc (65 wt.%) and zinc-ammonium sulfate (double salt: $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, 35 wt.%) [23].

The assembling of such a cell has been managed by preparing separately, with a stainless steel hydraulic press (800 MPa cm^{-2}), both negative electrode and positive electrode as 13 mm solid disks. The cell is then mounted as a five layer assembly: a flexible 0.25 mm graphite foil, the positive electrode, the electrolyte, the negative electrode and a second flexible graphite foil. The whole system is kept under moderate pressure by a Teflon screwing system. The collectors are made of stainless steel in contact with the graphite foils.

3. Results and discussion

3.1. X-ray diffraction

The PVA film diffraction pattern (Fig. 1a) shows a broad peak at $2\theta = 20^\circ$ which corresponds to an average diffraction distance of about 0.45 nm. Several authors [19,21,24–27] consider this signal to be characteristic for amorphous PVA. In any case, if PVA contains some more or less ordered zones, the broad peak they give rises to indicate that they are small sized and/or not clearly defined. On the other hand, the diffraction pattern of the phosphotungstic acid (PWA, Fig. 1d) shows well defined diffraction lines corresponding to the crystalline Keggin's structure [19,21,24,27–29].

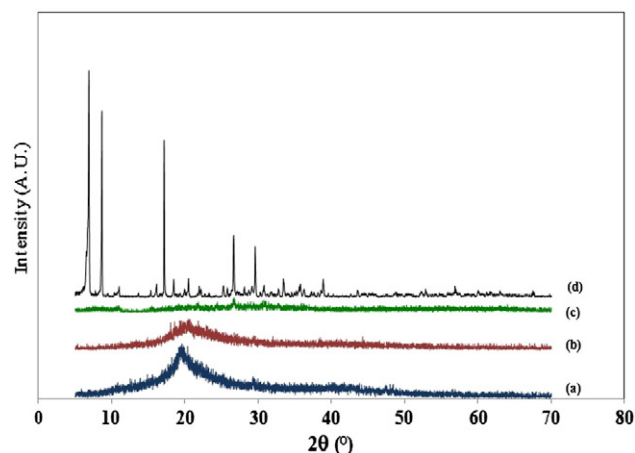


Fig. 1. X-ray diffraction patterns of: (a) PVA, (b) PVA–PWA (50 wt.%), (c) PVA–PWA (40 wt.%)– H_3PO_4 (40 wt.%) and (d) pure PWA. Legend.

Mixing PVA and PWA (50 wt.%) results in a similar to PVA XRD pattern (Fig. 1b) in which, as expected, the contribution of PVA is decreased by nearly 50% but in which the crystalline structure of PWA has completely disappeared. This gives evidence of the very fine dispersion (or even dissolution) of PWA in the PVA matrix.

In the ternary complex (Fig. 1c) obtained by mixing PVA (20 wt.%)–PWA (40 wt.%)– H_3PO_4 (40 wt.%) the broad peak of PVA are completely absent. The presence of acid in the complex renders the material more amorphous. This can be attributed to a plasticising effect of the acid. This observation gives clear evidence for the complete disorganization of PVA by the addition of phosphoric acid H_3PO_4 . Since the molecular weight of phosphoric acid (98 g mol^{-1}) is lighter than the molecular weight ($2880.17 \text{ g mol}^{-1}$) of PWA, the presence of phosphoric acid leads to a contribution to the total acidity of the complex nearly thirty times higher than the contribution of PWA. Thus, the observed effects of the addition of phosphoric acid on the XRD patterns can probably be attributed to the high acidity of this mix, which is strongly interacting with the oxygen atoms (OH groups of PVA) of the present molecules. Further, Fig. 1c as well as Fig. 1b no longer shows any diffraction line of the crystalline phase of the PWA, nor any other new diffraction line which could possibly show the presence of any new crystalline phase. That means that all components of the mix are completely dissolved in the PVA matrix. Further the presence of orthophosphoric acid does not result in the formation of any new crystalline phase. These remarks are in good agreement with the visual inspection of both binary and ternary obtained complexes, which show a perfectly homogeneous phase, indicating a total mixing of all inorganic compounds within the PVA matrix. Moreover, the amorphous character of all obtained solid state mixes seems to increase with increasing concentration of the inorganic compounds in the PVA matrix. This observation is also in good agreement with already existing bibliographic data [24,30].

3.2. Fourier transform infrared spectrometry (FTIR)

The structure of $\text{PWA} \cdot n\text{H}_2\text{O}$ is built upon a heteroacidic anion ($\text{PW}_{12}\text{O}_{40}$)^{3−} generally known as Keggin's anion in which a central P atom is tetraordinated with oxygen atoms of phosphate (PO_4)^{3−} groups. Each phosphate tetrahedron (PO_4) is bound to 12 WO_6 octahedrons (Fig. 2). The structure stability results from the presence of protonic species which are linked to Keggin's anions by hydrogen bonds [31]. In the structure of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, the oxygen atoms are located on 4 different sites a, b, c and d. Oxygen atoms O_a are located at the summits of PO_4 tetrahedrons, O_b are shared between W_3O_{13} groups where they are located at a summit shared by two octahedrons, O_c are located on common edges inside W_3O_{13} groups and O_d when located at an end position.

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