EVALUATION OF THE PYROCHLORNE (H₃O)SbTeO₆ AS A CANDIDATE FOR ELECTROLYTIC MEMBRANES IN PEM FUEL CELLS

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Abstract

(H₃O)SbTeO₆ pyrochlore is an excellent fast proton conductor, due to its open crystalline structure and suitable porosity. According to literature it presents a conductivity of 1x10⁻² S/cm at 30°C in a saturated water vapor atmosphere. Recently we have described the crystal structure of this pyrochlore, where we have been able to locate the H₃O⁺ species from neutron powder diffraction data. In this work we present the results of conductivity as a function of temperature and relative humidity, as well as a NMR characterization of this appealing compound. At low temperatures the conductivity of the pyrochlore does not vary much, but above 100 °C this magnitude increases exponentially. At 160 °C σ= 1.8x10⁻¹ S/cm. At 30°C, the conductivity is 5.0x10⁻³ S/cm, in contrast with the value reported literature.
1. Introduction

The development of fuel cells in the temperature range 100-300° C relies on the availability of solid electrolyte materials with a high proton conductivity, in the range of $10^{-2}$ S cm$^{-1}$. For temperatures below 100°C Nafion developed by Du Pont is widely known and used. However, several technical obstacles hinder their widespread commercialization. These include inadequate water and heat management, the intolerance to impurities such as CO and sluggish electrochemical cathode kinetics. Moreover, its high cost is still prohibitive in many commercial applications. Among the most promising candidates to replace Nafion, the antimonic acids (of general stoichiometry HSbO$_3$·nH$_2$O or Sb$_2$O$_5$·nH$_2$O) show a relatively high proton conductivity of $\sim 10^{-4}$ S cm$^{-1}$ at room temperature [1], and some yttrium-doped derivatives reach conductivities as high as $10^{-3}$ S cm$^{-1}$ [2]. An even better $\sigma$ value of $10^{-1}$ S cm$^{-1}$ at 30°C under saturated water vapor partial pressure was described by Turrillas et al. [3] for an original derivative of the antimonic acid, obtained by partial replacement of Sb by Te, giving rise to a well-defined oxide with pyrochlore structure and composition (H$_3$O)SbTeO$_6$ [3]. The pyrochlore structure is very appealing in terms of ionic conductivity, given its open structure containing three-dimensional interconnected channels. The most general pyrochlore oxides, A$_2$B$_2$O$_6$O’, can be described as made up of a covalent B$_2$O$_6$ skeleton of BO$_6$ corner-sharing octahedra; the A$_2$O’ sublattice forms an interpenetrating network with little interaction with the former. In fact, both A cations and O’ oxygens may be partially absent, giving rise to defect pyrochlores of stoichiometry A$_2$B$_2$O$_6$ or even AB$_2$O$_6$ [4,5]. Recently, we have described a full characterization of the crystal structure of the (H$_3$O)SbTeO$_6$ pyrochlore, performed by neutron diffraction: the location of the protons in the framework, randomly distributed over crystallographic positions with a large multiplicity, accounts for the high mobility of the H$^+$ ions across the material [6].

2. Experimental

The precursor K$_2$SbTeO$_6$ pyrochlore was obtained by solid state reaction between analytical grade K$_2$C$_2$O$_4$, Sb$_2$O$_3$ and TeO$_2$, heated in air with intermediate grinding at increasing temperatures from 823 K to 1123 K for 12 h. The hydronium exchange was accomplished in a subsequent treatment of the potassium precursor powder (5 g) in concentrated sulfuric acid (50 cc) in excess at 453 K for 12
h. The resulting white powder was filtered, washed with acetone and dried in air at room temperature. The KSbTeO$_6$ sample was characterized by XRD; a Rietveld refinement according to the model described in Ref [4] allowed us to assess the sample quality and stoichiometry. XRD patterns were collected at 295 K with Cu K$_\alpha$ radiation in a Brucker D8 powder diffractometer, by step-scanning from 10 to 120° in 2Θ, in increments of 0.02° and a counting time of 10 s each step.

A pellet of 13 mm dia. and 0.6 mm width, weighing 200 mg, was prepared from 90% of (H$_3$O)SbTeO$_6$ powdered pyrochlore, 10% of ligant, and 2 ml acetone. The pellet was compacted under an uniaxial load of 10 ton. The conductivity measurements were carried out in a Agilent 4294A Precision Impedance Analyzer in a frequency range from 40 Hz to 100 MHz. The conductivity was measured at different temperatures and relative humidities. The ohmic resistance was obtained from the Nyquist diagrams. The conductivity was calculated from the ohmic resistance $R$ as:

$$\sigma = \frac{1}{R} \times \frac{l}{S}$$

where $\sigma$ is the conductivity (S/cm), $R$ is the resistance (ohm), $l$ is the thickness in cm and $S$ is the contact surface with the electrode (cm$^2$), which in this case is 0.618 cm$^2$. The pellet was enclosed in an autoclave together with 100 ml of distilled water, in order to provide a relative humidity of 100%. The temperature of the autoclave was varied between 25 and 170 °C. After this experiment the resistivity was also recorded in the cooling run from 170 to 25 °C, in order to check the possible hysteresis of these measurements. The effect of the relative humidity was investigated following the method of Aparicio et al [7], by introducing saturated solutions of different salts within the autoclave, which provide different relative humidities at a given temperature.

$^1$H MAS-NMR spectra were recorded with an Avance-400 (Bruker) spectrometer. The frequency used in this work was 400.13 (external magnetic field, 9.4 T). In MAS experiments, the rotor was of Andrew type and spinning rates used were 4 and 10 kHz. Spectra were recorded after a $\pi/2$ radiofrequency pulse (4 µs). The number of scans amounted to 100 and the interval between scans, 1s, was chosen to avoid saturation effects. In spectra deconvolution, intensity, position and
linewidths of components were determined by using the WIN-NMR (Bruker) software package. Chemical shift values of NMR components are referred to that of the TMS compound.

3. Results and Discussion

3.1. Structural study

The powder sample of \((H_3O)SbTeO_6\), obtained by ionic exchange from K\(\text{SbTeO}_6\), exhibited an excellent crystallinity, as shown by the sharpness of the XRD reflections (Figure 1). The XRD pattern could be indexed in a cubic unit cell with \(a = 10.1510(1) \, \text{Å}\), characteristic of a pyrochlore structure.

![XRD pattern of \(H_3O(SbTe)O_6\), refined by the Rietveld method in the cubic pyrochlore structure described in the text.](image)

The \((H_3O)SbTeO_6\) crystal structure is constituted [6] by a network of randomly distributed Sb\(^{VI}\)O\(_6\) and Te\(^{VII}\)O\(_6\) octahedra linked by their corners with (Sb,Te)-O1-(Sb,Te) angles of 136.2\(^{\circ}\) (Fig. 2a). Hydronium ions are located off-center around the large 8\(a\) cages of the pyrochlore (Fig. 2b). As shown in Fig. 2b, the geometry of the \((O_2)\)-H\(_3\) units is that of an almost regular tetrahedron, with O\(_2\) atoms at the center and the three H atoms in three of the vertices; the fourth vertex is supposed to be occupied by the O\(_2\) lone pair. The relatively large thermal factors of O\(_2\) and H, of 2.5 and 3.7 \(\text{Å}^2\), respectively, suggest that both kinds of atoms are not static at fixed positions but could be dynamically fluctuating between crystallographically equivalent sites.
Fig. 2. Views of the structure of the (H₃O)SbTeO₆ pyrochlore along the [110] direction, highlighting a) the open structure of the covalent (SbTe)O₆ network of octahedra, containing three-dimensional interconnected channels and b) the location of H₃O⁺ units within the cavities formed by 6 (Sb,Te)O₆ octahedra.

3.2. Transport properties

Figure 3 shows the conductivity of the pyrochlore with temperature. It does not vary much at low temperatures, but above 100 °C, the conductivity increases exponentially. At 160 °C $\sigma = 1.8 \times 10^{-1}$ S/cm. At 30°C, the conductivity is $5.0 \times 10^{-3}$ S/cm, in contrast with the value reported literature of $1.0 \times 10^{-2}$ S/cm [3].

It is interesting to compare the conductivity of (H₃O)SbTeO₆ with that of Nafion (Fig. 3); at high temperatures they exhibit a comparable magnitude and, above 160° C, the pyrochlore would overcome the Nafion values.
Fig. 3. Thermal evolution of the conductivity of (H$_3$O)SbTeO$_6$ at 100% humidity, compared with that of Nafion in the same temperature range.

In the cooling run we obtained a similar conductivity curve. The good reversibility of the process seem to indicate that there is no adsorption that could influence the conductivity value. After the cooling run we observed that the pellet exhibits the same color as initially, also indicating the absence of any adsorbed substance.

Fig. 4. Hysteresis effect of the conductivity in the (H$_3$O)SbTeO$_6$ pyrochlore
The behavior of the \((H_3O)SbTeO_6\) pyrochlore with the relative humidity is as expected: the conductivity diminishes with the humidity as shown in the following Table; it seems that the mobility of the protons is significantly affected by the water contents of the external atmosphere.

<table>
<thead>
<tr>
<th>% Relative Humidity</th>
<th>Conductivity* (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>5.80E-03</td>
</tr>
<tr>
<td>88</td>
<td>9.71E-04</td>
</tr>
<tr>
<td>70</td>
<td>6.11E-04</td>
</tr>
<tr>
<td>43</td>
<td>1.28E-04</td>
</tr>
</tbody>
</table>

* Conductivity measured at 40 ºC

In Figure 5 we illustrate the huge difference observed between the \(\sigma\) value measured at 100% of relative humidity and those for the lower values, which are not significantly different among them.

![Fig. 5. Conductivity of \((H_3O)SbTeO_6\) Pyrochlore at different relative humidity values at 40 ºC](image)
3.3. Proton NMR

The $^1$H NMR spectrum of $(\text{H}_3\text{O}^+)\text{SbTeO}_6$ was recorded with the MAS technique to improve the resolution. The $^1$H MAS-NMR spectrum was formed by two signals centred at 12 and 7 ppm and the corresponding spinning side bands associated with the rotation of the sample around an axis inclined 54º47’ with respect to the external magnetic field. In general, chemical shift values of proton signals are comprised between 0 and 10 ppm with respect to the TMS standard. Chemical shift values of two detected components, 7 and 12 ppm, differ considerably from that of molecular water at 4.8 ppm and could correspond to protons of OH groups having different charge density. In particular, the component at 12 ppm is at the limit of the spectral range ascribed for protons, could correspond to protons of very acidic OH groups.

On the other hand, the signal at 7 ppm is located between those of acidic OH groups at 12 ppm and that of water molecules, what could be ascribed to protons of H$_3$O$^+$ species. Chemical shift values of H$_3$O$^+$ groups could be estimated by assuming the existence of exchange processes between both species with the expression

$$\delta (\text{H}_3\text{O}^+) = \frac{n_{\text{H}(\text{OH})}\delta(\text{OH}) + n_{\text{H}(\text{H}_2\text{O})}\delta(\text{H}_2\text{O})}{n_{\text{H}(\text{OH})} + n_{\text{H}(\text{H}_2\text{O})}}$$

where $n_{\text{H}(\text{OH})}$ and $n_{\text{H}(\text{H}_2\text{O})}$ are the amount of protons in two exchanging species and $\delta(\text{OH})$ and $\delta(\text{H}_2\text{O})$ are chemical shift values of OH groups and water molecules. In this case, chemical shift values of H$_3$O$^+$ should be 7.2 ppm what are near to that observed in $^1$H NMR spectra.

On the other hand, the formation of H$_3$O$^+$ species has been associated with the detection of three broad lines (triplet) with an external separation of 13.6 Gauss ($\sim$ 60 kHz). In $^1$H NMR spectrum, the modulation of the experimental envelope by spinning side bands separated 4 kHz, should cover a more extended region that observed experimentally. This observation indicates that intramolecular interactions present in H$_3$O$^+$ are considerably reduced as a consequence of local mobility of these groups. This result agrees with structural information deduced from ND study, where the thermal factors of protons and oxygen atoms are too large to correspond to fixed species. Local rearrangements of H$_3$O$^+$ would explain the partial cancellation of dipolar H-H
interactions and the enlargement of thermal factors measured at room temperatures. In the case of OH groups, dipolar interactions are considerably reduced, what explains the smaller spectral region covered by spinning side bands of this species.

In a future work, the temperature dependence of $^1$H NMR spectra will be analyzed. The analysis of $^1$H NMR spectra recorded at low and high temperatures will permit to deduce local mobility and proton hoping processes between H$_3$O$^+$ groups. This information will be correlated with proton mobility deduced from proton conductivity deduced as a function of water adsorbed this sample.

4. Conclusions

The (H$_3$O)SbTeO$_6$ pyrochlore contains hydronium units within the large cavities conformed by the covalent (SbTe)O$_6$ network of octahedra, which are interconnected giving rise to three-dimensional channels where protons have been demonstrated to be highly mobile. An excellent conductivity has been recorded for the (H$_3$O)SbTeO$_6$ pyrochlore at 100% humidity, both in the heating and cooling runs, reaching $\sigma$ values that overcome that of Nafion in the high-temperature range (around 160º C). The conductivity decreases at lower relative humidities. The analysis of $^1$H MAS-NMR spectra recorded at room temperature showed the presence of two lines at 12 y 7 ppm. These components could be tentatively ascribed to acidic OH groups and H$_3$O$^+$ species. In the first case, the partial cancellation of nuclear dipolar interactions produces spinning sideband patterns formed by equally spaced components. In the second case, motions probably associated with local rearrangements of H$_3$O$^+$ species and/or proton hopping between equivalent sites results in a more efficient cancellation of the dipolar interactions.

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References