

Hydrated antimononic acid as a solid electrolyte

Oleksii Kosohin*, Oleksandr Matvieiev and Olga Linyucheva

National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute",
Prospect Peremohy, 37, Build 4, Kyiv-56, 03056, Ukraine.

ABSTRACT

The literature data on the methods of obtaining hydrated antimononic acid, which can be used as a solid electrolyte in fuel cells and gas sensors, were analyzed. Samples of antimononic acid were obtained experimentally, with electrical conductivity ranging from $0.1 \cdot 10^{-2} \Omega^{-1} \cdot \text{m}^{-1}$ to $2 \cdot 10^{-2} \Omega^{-1} \cdot \text{m}^{-1}$. The effect of relative humidity on the electrical conductivity of antimononic acid is shown.

KEYWORDS: solid electrolyte, polyantimononic acid, conductivity.

1. INTRODUCTION

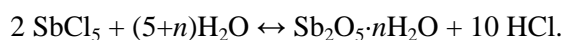
Solid electrolytes are widely used in high-performance fuel cells, electrochemical sensors and electrochromic systems [1, 2]. One of the most promising materials with high electrical conductivity is hydrate of antimononic acid [3] (hydrate of antimononic pentoxide, polyantimononic acid, PAA). PAA has proton-conducting [4] and ion-exchange [5] properties. In the general case, the structural formula is written as $\text{Sb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, where the degree of hydration n can vary in the range of 1-5. Amorphous hydrate of antimononic pentoxide has the electrical conductivity higher than crystalline, due to a greater degree of hydration, but is not stable over time; it gradually loses water and turns into a crystalline modification. According to the literature, a temperature increase accelerates the crystallization process [3]. However, most of the known methods are aimed at obtaining ion-exchange material, while the actual electrical

conductivity for PAA has not been studied enough.

2. MATERIALS AND METHODS

PAA was synthesized both by the well-known method [6] - sample PAA-1, and by the modified method based on [7] - sample PAA-2.

Preparation PAA-1: to 200 times the excess of cold water pure antimononic pentachloride is added dropwise, while the reaction proceeds:



The resulting suspension is boiled for several hours to complete the hydrolysis. Then, the precipitate is washed from the chloride ion by decantation. The precipitate is filtered and dried in air at 25 °C for about 5 days to constant weight.

Preparation PAA-2: Polyantimononic acid was obtained by a modified method of hydrolysis of antimononic pentachloride. To perform this, hydrolysis was carried out in a 100-fold excess of water. To reduce the dispersion of amorphous PAA, a part of hydrogen chloride was neutralized with lithium carbonate. After that, the precipitate was filtered, dried on a steam bath and treated at a temperature of $(290 \pm 10) \text{ }^\circ\text{C}$. To oxidize antimony (IV) compounds, which could have been formed at elevated temperatures [8], PAA was treated with 50% HNO_3 , thoroughly washed with distilled water, and dried on a steam bath.

The electrical resistance of the obtained PAA sample was determined on the samples made from a mixture of 0.5 g PAA with 0.1 g of polytetrafluoroethylene powder, and pressed between two plates made of titanium powder.

*Corresponding author: o.kosogin@kpi.ua

The effort of layer-by-layer pressing was 36 MPa, and the final pressing force was 360 MPa. Resistance was measured using an impedance meter R5010 at an alternating current frequency of 2 kHz. Different relative humidity of the air was created in sealed vessels containing various saturated salt solutions.

Electronic photographs of the PAA samples were obtained on a scanning electron microscope with energy microanalyzer REM 106Y in the Center for Electron Microscopy (Faculty of Physical Engineering, Igor Sikorsky Kyiv Polytechnic Institute). The determination of the chemical and phase composition of PAA samples was performed

on multipurpose X-ray diffraction system Ultima-IV in the Center for X-ray analysis RIGAKU (Faculty of Physical Engineering, Igor Sikorsky Kyiv Polytechnic Institute).

3. RESULTS AND DISCUSSION

The obtained PAA-1 samples were a white crystalline powder with a high degree of amorphism. During storage, there was a gradual transformation of the ordering of the structure and the formation of crystalline structures (Figure 1).

By the method of X-ray phase analysis (Figure 2), it has been found that in the process of this synthesis, it is possible to obtain a PAA of

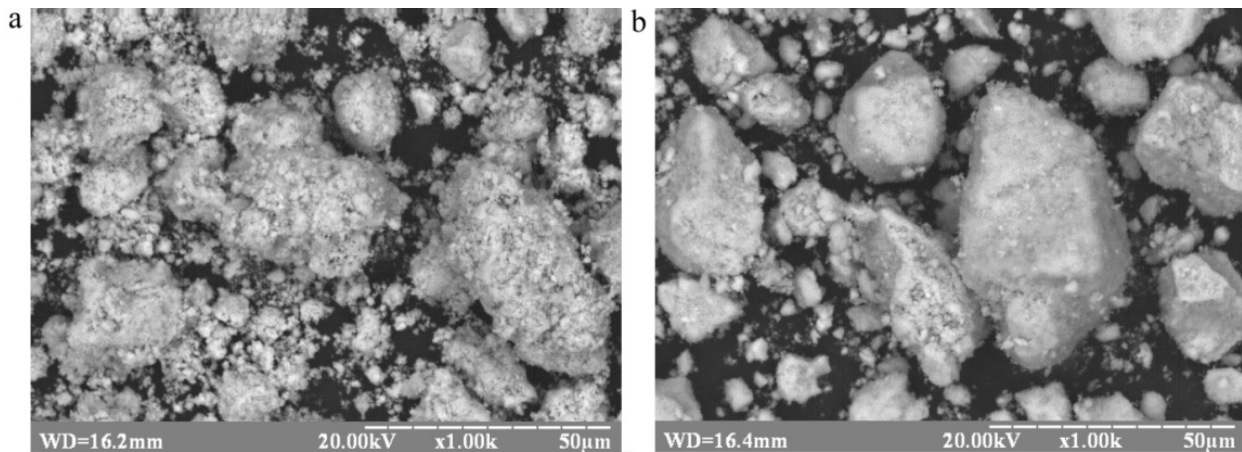


Figure 1. SEM of PAA-1 sample after production (a) and 6 months later (b).

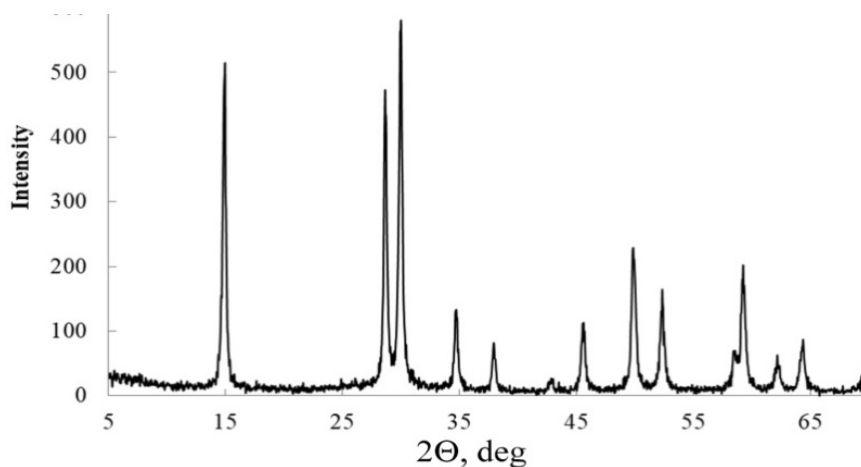


Figure 2. X-ray diffraction pattern of a PAA-1 sample.

composition $\text{H}_2\text{Sb}_2\text{O}_3(\text{OH})_6$ with the space group $\text{Fd}\bar{3}\text{m}$.

Sample PAA-2 (Figure 3) had a yellowish tint that indicates the presence of antimony (IV) compounds, which are formed during partial decomposition when the antimony (V) compounds are heated. Also, the obtained PAA-2 had a much more orderly structure and dispersion compared to PAA-1, which changed insignificantly during storage. X-ray phase analysis shows (Figure 4) that the obtained sample has a pyrochlore structure ($\text{Fd}\bar{3}\text{m}$) as well, but is characterized by the formula $\text{Sb}_3\text{O}_6(\text{OH})$ (or $\text{Sb}_2\text{O}_5 \cdot \text{SbO}(\text{OH})$), which indicates the inclusion of antimony in lower degrees of oxidation.

Both samples demonstrated a similar character of the dependence of electrical resistance on humidity (Figure 5); however, for sample PAA-2, the values of electrical conductivity were established much slower, especially when the humidity decreased. Also, for the sample PAA-2, the electrical conductivity changed less critically when the relative humidity is above 80%.

4. CONCLUSIONS

The obtained samples of hydrated antimony acid have a sufficiently high electrical conductivity that non-linearly depends on the relative humidity of the environment. Heat treatment makes it possible to speed up the process of formation of

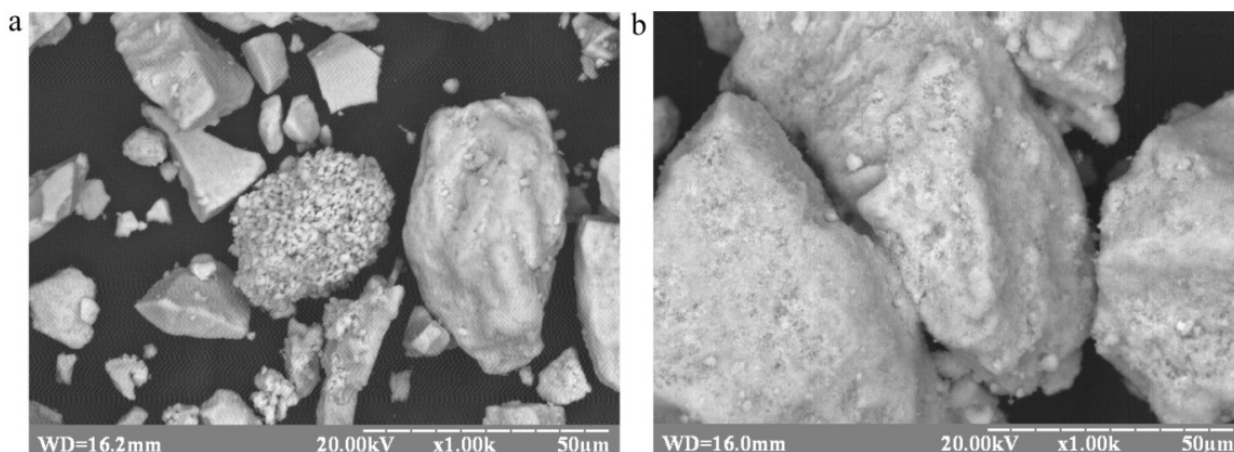


Figure 3. SEM of PAA-2 sample after production (a) and 6 months later (b).

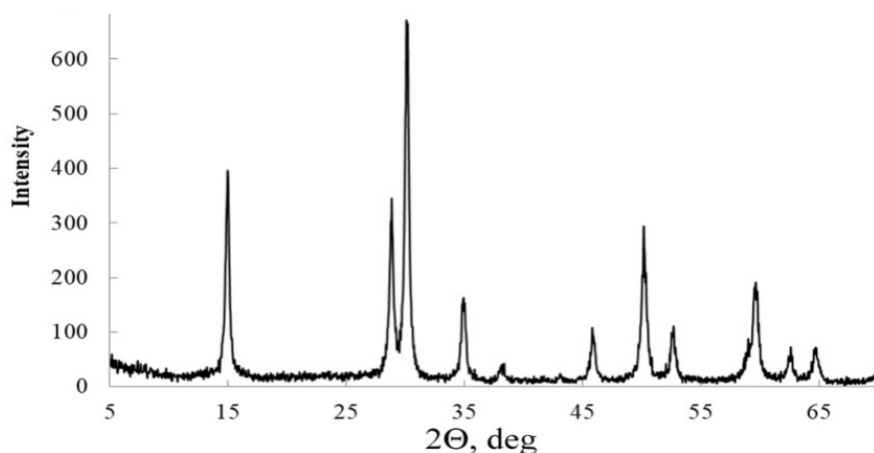


Figure 4. X-ray diffraction pattern of a PAA-2 sample.

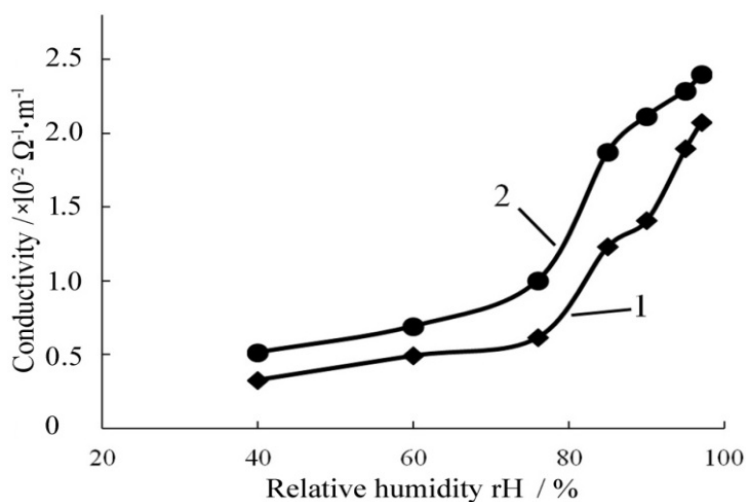


Figure 5. Change in conductivity of the sample PAA-1 (1) and PAA-2 (2) at 290 K.

the pyrochlore structure, and the use of lithium carbonate at the stage of preparation of antimonite acid gel reduces dispersion and increases the yield of the product.

CONFLICT OF INTEREST STATEMENT

There are no conflicts of interest.

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