HIGH PROTON CONDUCTING ANTIMONY-PHOSPHATE GLASS

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Introdustion

Materials exhibiting high proton conductivity can find very attractive applications. They can be use as membranes for fuel cells, sensors or proton pumps. Fuel cells are electrochemical devices that convert the chemical energy of a reaction directly into electrical energy. Recently, they have been extensively investigated as a key technology for solving global energy and environmental problems. They do not involve transformation of chemical energy to heat. Therefore, their efficiency is not limited by Carnot theorem. Moreover, they produce water vapor as the only primary exhaust.

The most common classification of fuel cells is by the type of electrolyte used in the cells and includes: proton exchange membrane (polymer) electrolyte fuel cell (PEMFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC). These fuel cells are listed in the order of approximate operating temperature, ranging from ~80°C for PEFC, ~100°C for AFC, ~200°C for PAFC, ~650°C for MCFC, and 800°C to 1000°C for SOFC.

Among several types, PEMFCs have been regarded as a promising option for electric vehicles and on-site power generation for its superior efficiency and less environmental impact. However, the use of current PEM fuel cells is restricted by complicated and thus expensive water management. A major limitation of the cell working at temperatures below 90°C comes from the need of using the Pt anode electrocatalysts which are easy to be poisoned by CO even at levels about 5 to 10 ppm. The solution is a higher operating temperature when CO tolerance of the Pt catalyst is much higher (up to 0.5%) and also passivation of the catalyst by other condensable species can be avoided. Moreover, the intermediate temperature could eventually allow direct use of reformable fuels such as methanol [1].

Chemical sensors are increasingly used in numerous applications, such as analysis setups, chemical processes, food industry, environmental control (water, air, industrial wastes, combustion monitoring, etc.), and biomedical applications (analysis and monitoring). Other new fields of applications could arise in the near future; for instance, integrated home systems. Therefore, the development of specific and sensitive gas sensors became very important. Electrochemical sensors are particularly attractive because the chemical quantities to be measured are directly transformed in electrical signals. Two types of sensors can be distinguished: active sensors, which give a voltage (potentiometric sensors), and passive sensors, for which an electric source is necessary to apply a signal, the response of which is analyzed afterwards (amperometric, coulometric, and conductometric sensors) [2].

Especially, for the fuel cells, the membrane should exhibit proton conductivities at least 1 S/m at operating temperature. To achieve high proton conductivity the material must contain a sufficient concentration of functional groups that easy dissociate protons. In case of phosphate glass the –OH groups are the proton generating species.

For application in the fuel cell operating in the temperature range 100-200°C, the dependence of proton conductivity on relative humidity (r.h.) should be minimal.

One of the promising materials seems to be a hybrid organic-inorganic membrane containing organic polymer bonded to inorganic moiety on a molecular level. The organic part brings membrane elastic and hydrophobic properties and the inorganic component high proton conductivity along with hydrophilic behavior. To develop such material, we started the synthesis of the inorganic part for the hybrid membrane and focused

our interest on a phosphate glass stabilized with antimony. In the following sections we describe the preparation and properties of the high proton conducting antimony-phosphate glass.

Experimental

Glass Synthesis

Prepared glasses should contain high concentration of –OH functional groups. Therefore our material should be synthesized at relatively low temperatures comparing with usual melting temperatures of glass. For this reason we developed a two-step preparation procedure. The first step is based the acid-based reaction between the melt of orthophosphoric acid (Fluka) and liquid antimony pentachloride (Fluka) at 80°C, schematically:

$$H_3PO_4 + SnCl_5 \leftrightarrow PO(OH)_2\text{-}O\text{-}SnCl_4 + HCl \qquad (1)$$

The next step was a controlled hydrolysis of the product from Eq.(1):

$$PO(OH)_2\text{-}O\text{-}SnCl_4 + 4H_2O \leftrightarrow PO(OH)_2\text{-}O\text{-}Sn(OH)_4 + 4HCl \qquad (2)$$

followed by the condensation of OH groups and H_2O elimination resulting in the formation of 3-D network connected with bridging oxygen atoms (e.g., P-O-Sb, Sb-O-Sb, or P-O-P). Using this procedure, we made four samples having different Sb/P molar ratio listed in Table 1.

Table 1. *Theoretical and Analyzed Molar Ratio Sb/P of Prepared Glass, Conductivity at 25°C, and Water Content.*

Glass	Sb/P		σ_{25}	H_2O
	Theoretical	Analysis	(S/m)	(mass%)
SP1	0.35	0.49	4.5	23
SP2	0.40	0.55	1.8	21
SP3	0.50	0.70	1.3	19
SP4	0.60	0.84	0.9	18

Glass Characterization

A degree of structural units ordering in the prepared materials was investigated by X-ray powder diffraction (XRD) with X´PERT PRO diffraction meter using Cu-K_α radiation and the scan rate 2° 2Θ/min (Figure 1). Water content, glass transition and crystallization were studied by thermogravimetry (TG) and differential thermal analysis (DTA) in air with the heating rate 10°C/min and Al_2O_3 as a reference. The existence of OH groups was verified by IR spectroscopy with the IR Microscope DRIFTS.

To determine a room temperature proton conductivity of our glass samples, we used the two-probe impedance measurement with cylindrical graphite or Pt electrodes that were immersed into samples before their final polymerization and solidification. The electrodes had radius 0.25 mm and their distance was 16 mm. The dependence of sample impedance on frequency was measured with Tesla BM529 RLCG impedance meter at 9 frequencies from 100Hz to 20 kHz. The obtained impedance spectrum was analyzed using an equivalent circuit (see Figure 4) and bulk resistance (R_v) was determined. From the bulk resistance and the

conductivity cell constant we calculated total conductivity of samples. The measurements were performed in air atmosphere with r.h. about 30%.

Because we measured the total conductivity, we needed to know its electronic part to determine the protonic (ionic) conductivity. To measure electronic contribution, we used amperometry with constant polarizing voltage 100 mV.

What was the most interesting for us, it was the studying the dependence of proton conductivity at elevated temperatures up to 150°C in air atmosphere with r.h. below 30%. This experiment was done using a horizontal tube furnace, were the disks of our glass were placed between two Pt disk electrodes. The conductivity was calculated from the impedance of sample at frequency 20 kHz by similar procedure as in the case of the room temperature measurements.

Stability of the glass in reducing conditions was tested by cyclic voltammetry in the potential region from +1.5 to –1.5V using the potentiostat AUTOLAB.

Results and discussion

The prepared material was colorless and transparent. All the samples were not hygroscopic showing a good stability in laboratory atmosphere (with r.h. approximately 30%). Their elasticity increased with the decreasing Sb/P ratio.

The XRD experiments reveled that all the prepared materials were amorphous exhibiting a flat and diffused XRD pattern (see Figure 1). The TG and DTA curves in Figure 2 showed that the first endothermic minimum corresponds to the loosing of water starting at approximately 40°C. The water content in our samples, determined from TG curves, is listed in Table 1. It shows that the water content increases with the decreasing Sb/P ratio. The following slight decline of the TG curve probably reflects condensation of OH groups and elimination of H_2O. The next endothermic DTA minimum represents glass transformation followed by crystallization (exothermic effect) and melting of crystalline components (endothermic effects). After the glass transformation, the TG curve decline is steeper because the glass structure is more relaxed and the condensation of OH groups is thus easier. The amorphous character of samples together with the existence of glass transformation gave evidence that the prepared materials are of the glass nature.

The IR spectra in Figure 3 exhibited relatively narrow absorption bands with maximum at 3619 cm^{-1} that corresponds to the absorption of bonded OH groups [3]. The bands with maximum at 2885 cm^{-1} probably also represents the OH groups but in this case their H atoms are strongly bonded to the non-bridging oxygens by the hydrogen bond. The original O-H bond is thus weaker and we observe the maximum at lower wavenumber (i.e., at lower energy). Therefore, these H^+ ions should be more mobile [4]. This absorption band and thus the mobile H^+ ions concentration increase with the decreasing Sb/P, which corresponds to the increase of σ_{25} presented in Table 1.

A typical impedance spectrum of the prepared glass samples together with the corresponding equivalent circuit and the bulk resistance (R_v) estimation are illustrated in Figure 4. All samples exhibited high protonic conductivity at 25°C at low r.h. (about 30%).

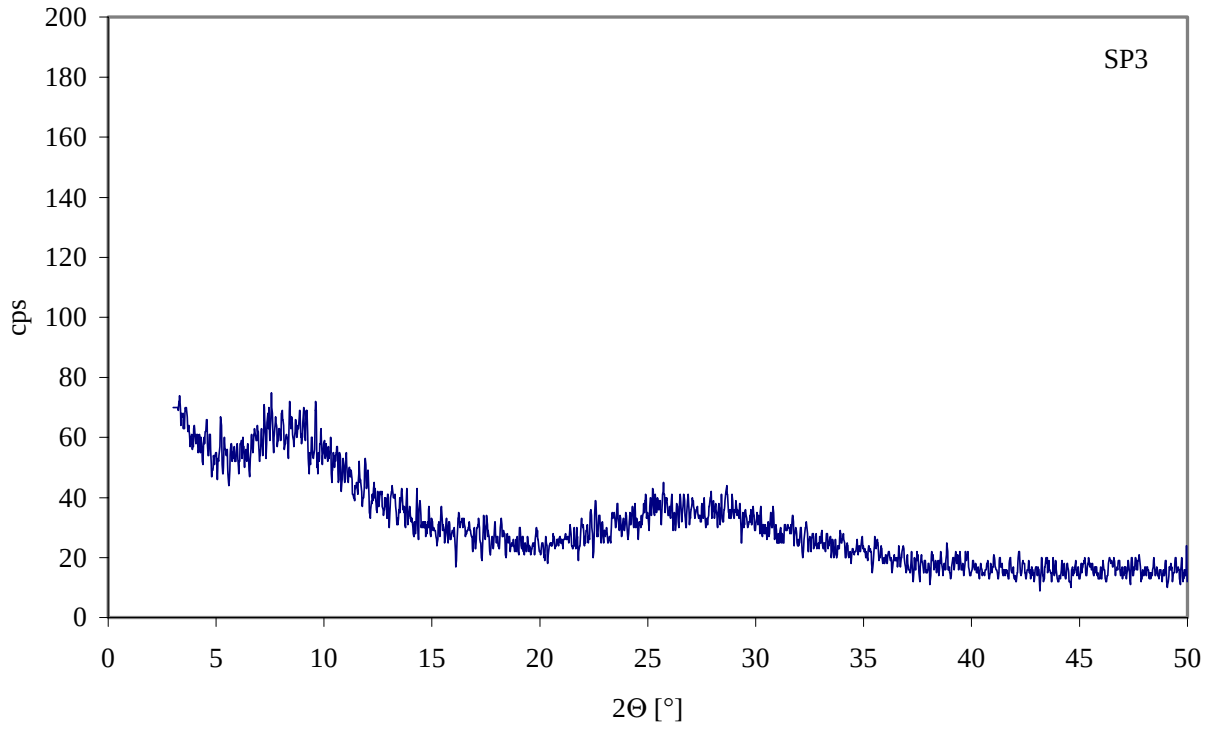

Fig. 1. *XRD Pattern of Amorphous Sample SP3.*

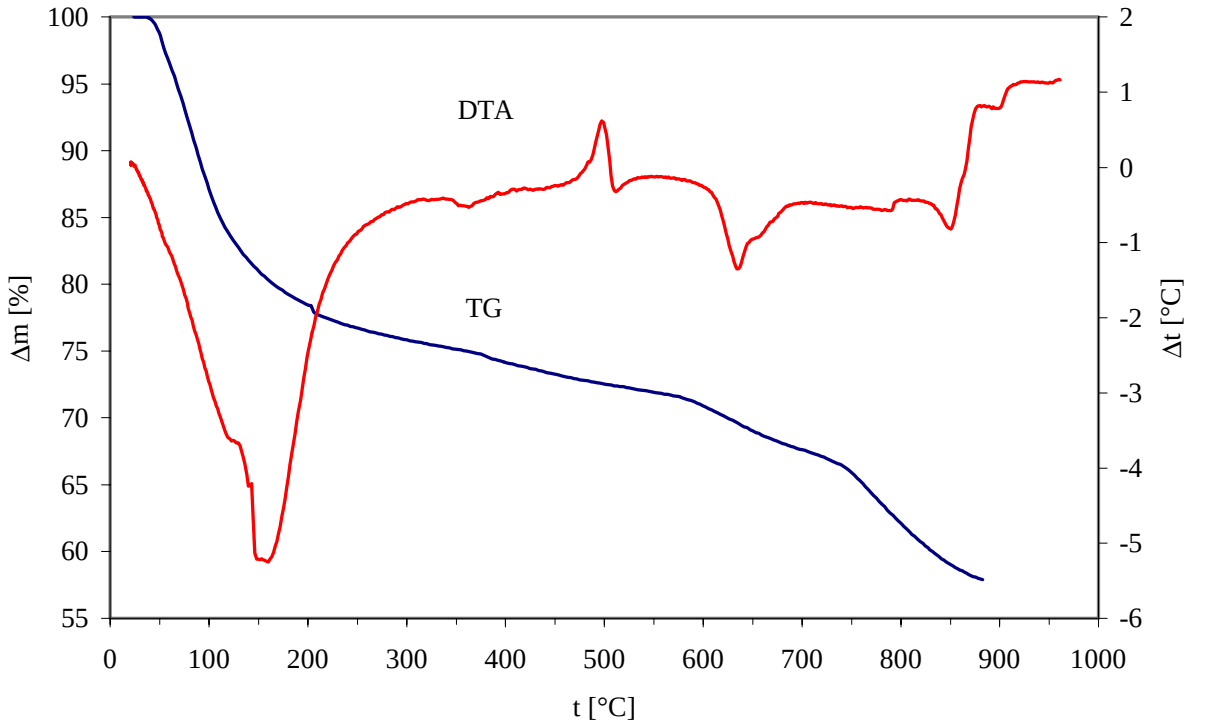

Fig. 2. *TG and DTA Curves for Sample SP1.*

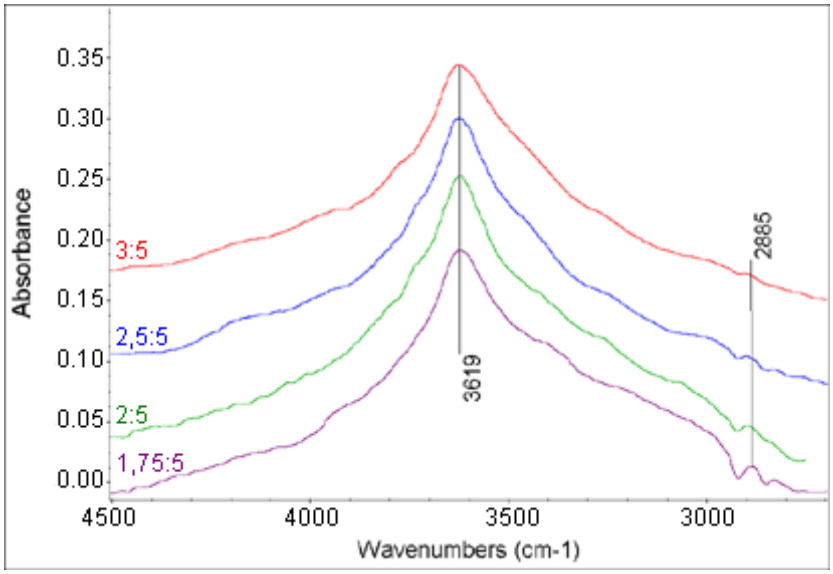

Fig. 3. *IR Spectra of Prepared Glasses with Different Theoretical Sb:P Ratio*.

From Table 1 it follows that the decreasing Sb/P ratio had a positive effect on σ_{25}. The observed increase could be caused by the increasing concentration of more mobile potons along with the increased content of water. Electronic contribution to the total conductivity was 10^{-6} $S \cdot m^{-1}$, therefore; the total conductivity practically represents the ionic (protonic) conductivity.

The highest σ_{25} was achieved by SP1 glass. Its conductivity at elevated temperature is plotted in Figure 5. Up to 120°C the conductivity increased; at 150°C the sample cracked and we observed a sudden decrease of conductivity. Even though the material was loosing water at elevated temperature, the conductivity increased. Therefore, we suppose that the glass contains enough OH groups close to each other that their protons can hop from one available site to another and they do not need water molecules for the fast transport. The hopping mechanism is facilitated by a higher temperature because ions have more energy and hence a higher probability to overcome energy barriers as they migrate.

Cyclic voltammetry results revealed that our glass samples did not show any current maxims were in the studied potential window and were stable in reduction conditions.

Conclusions

The prepared antimony-phosphate glass is a good protonic conductor with conductivity from 1 to 10 S/m at low relative humidity. Its conductivity increased with the increasing temperature at relative humidity less than 30%. The material was not hygroscopic, was stable in reducing conditions and exhibited negligible electronic conductivity. Therefore, the glass is suitable for the construction of sensors based on proton reactions and also as a highly conductive inorganic component for hybrid organic-inorganic membranes. Such membranes can be useful in the fuel cells operating at temperatures from 90 to roughly 150°C without a complicated and expensive water management and fuel purification.

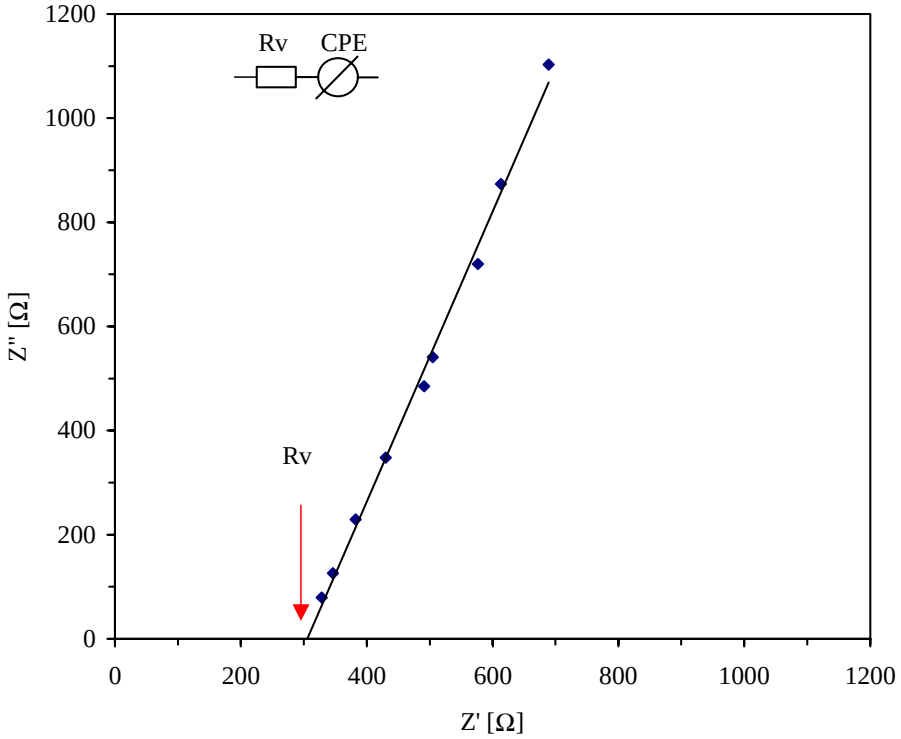

Fig. 4. *Impedance Analysis in the Complex Plane with Equivalent Circuit and Estimation of Bulk Resistance.*

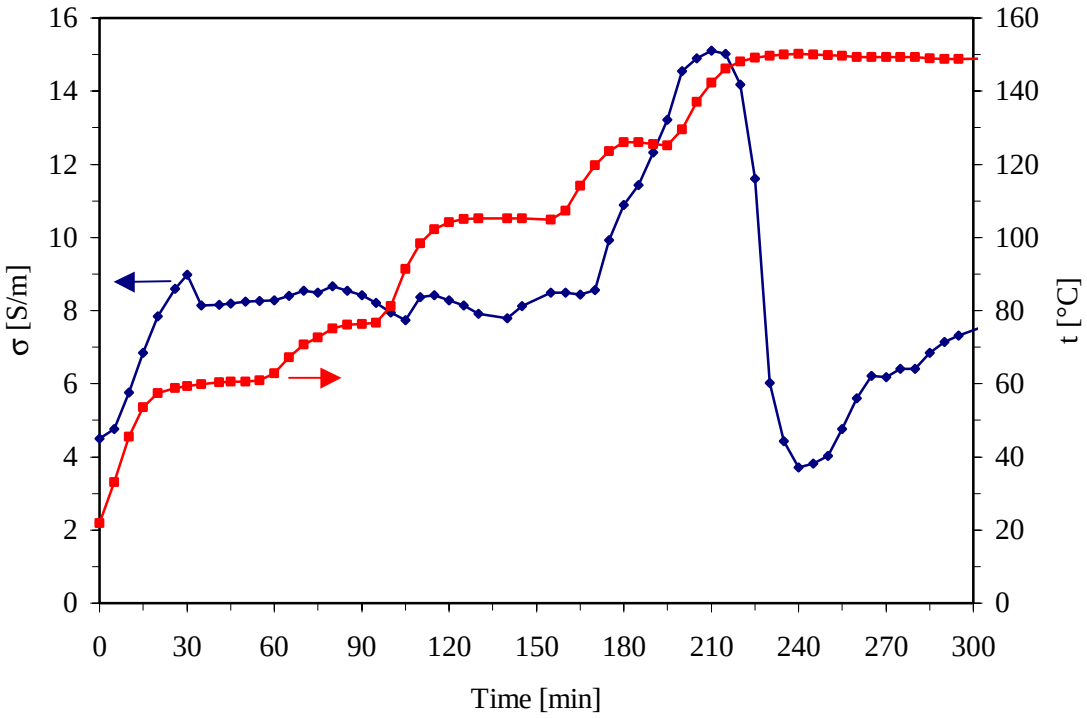

Fig. 5. *Conductivity of Sample SP1 at Elevated Temperature*.

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References

1. J.H. Hirschenhofer, D.B. Stauffer, R.R. Engleman, and M.G. Klett, *Fuel Cell Handbook*, DOE/FETC-99/1076, 1998.
2. G. Alberti, M. Casciola, *Solid State Ionics* **145**, 3, (2001).
3. Private communication with Dr. M. Novotná from the Laboratory of Molecular Spectroscopy at the Institute of Chemical Technology, Prague.
4. Y. Abe and M. Maeda: *J. Electrochem. Soc.*, **147**, 787 (2000).