

Ion transport properties in modified  $P_2O_5$ - $SiO_2$  glassy protonic electrolytes

M. Siekierski, M. Mroczkowska-Szerszeń, R.

Letmanowski, D. Zabost, M Struzik, M. Piszcz

Warsaw University of Technology faculty of Chemistry  
Polymer Ionics Research Group

Noakowskiego 3, 00-664 Warsaw, Poland

Oil and Gas Institute, ul. Lubicz 25a, 30-350 Cracow,  
PolandWarsaw University of Technology, Faculty of Physics, ul.  
Koszykowa 75, 00-662 Warsaw, Poland

Superprotonic conductors with high ionic conductivity in middle range temperatures ( $>100^\circ\text{C}$ ) are an area of interest to researchers due to their applicability as membranes in fuel cells. A relatively new idea in this field are glassy composite membranes with conduction mechanism allowing proton conduction even in low humidity regime which can be realized through the application of e.g. phosphate glasses.

The  $30P_2O_5$ - $70SiO_2$  glassy electrolyte prepared by the accelerated sol-gel process [1] can be modified by several kinds of polymer additives which can cause changes in mechanical properties of the glasses (e.g. flexibility and stability). The series of glasses with PVA (poly (vinyl alcohol)) or PEO poly(ethylene oxide)) additive has been synthesized and studied with a set of complimentary methods. Another modification of the base glass is related to doping it with  $TiO_2$  additive in the form of nanopowder or nano dispersion obtained *in situ* in the sol-gel processes to improve the chemical stability of the membrane.

FT-IR studies show that the process can be tailored in such a way that none of the additives influences the progress of the hydrolysis reaction and the yield of the product. On the other hand, SEM testing constitutes a proof that additives decrease the number of cracks and fractures on surface of the resulting membrane.

Thanks to the Arrhenius-like behavior it was also possible to determine Diens temperatures from the Meyer-Nedel rule [10] for the samples. The value of this temperature corresponds to the temperature of the order-disorder transition occurring in the ionic lattice. In this case, the temperature is equal to  $430\pm 20^\circ\text{C}$ . This value lays between temperatures of the melting point for two polymorphs of the phosphorus pentoxide ( $340$  and  $542^\circ\text{C}$  for standard and the so called "O" polymorph respectively), and is consistent with values of order-disorder temperatures found for various ionically conductive phosphates [2]. The increase of the  $T_d$  in comparison with pure  $P_2O_5$  (in its basic form) can be explained either by additional immobilization of phosphorous sublattice due to its interactions with the silicate part or to partial formation of the "O" polymorph. It must be stressed that the geometrical arrangement of the "O" polymorph is similar to that observed in silicates, thus, the formation of this type structure can be promoted by the presence of the silicate sublattice. It is also important to notice that this temperature lays in vicinity (within the experimental error) of the previously unidentified endothermic transition observed in the DTA traces.

In the next step an analysis based on Jonscher's universal power law of dielectric response [3] was used to study the correlation between dielectric properties of the sample and its morphology. The most pronounced differences can be observed between samples  $30P_2O_5$ - $70SiO_2$  + 0,5% PVA + 5%  $TiO_2$  (TEOT) and  $30P_2O_5$ - $70SiO_2$  + 0,5%

PVA where a significant increase in the conductivity value and an increase of two orders of magnitude in the specific surface area are correlated with the significant decrease of the power factor  $n$  (see Table 1). In addition, the latter (and better conducting) sample exhibits two times higher effective concentration of charge carriers. This parameter varies in its temperature dependence as well. In the first case, it is monotonically decreasing with the increase of temperature, while in the second it remains constant. In the case of  $30P_2O_5$ - $70SiO_2$  + 0,5% PVA + 5%  $TiO_2$  (nanopowder) the  $n$  values are placed between the ones for the first two samples. This can be easily correlated with the intermediate value of specific surface for this system. The temperature-induced decrease of the  $k$  value is similar to the  $30P_2O_5$ - $70SiO_2$  + 0,5% PVA + 5%  $TiO_2$  (TEOT) sample allowing us to correlate this phenomenon with the presence of titanium in the system. This observation can be attributed to the formation of the Ti-O-P moieties according to scheme  $P-O-H + Ti-O-H = Ti-O-P + H_2O$  decreasing the number of mobile protons. The equilibrium of chemical reaction of this kind is shifted to the right by water evaporation upon heating. Taking into consideration the  $30P_2O_5$ - $70SiO_2$  + 0,5% PVA (Ultras.) sample, we can observe that the  $n$  value is low similarly to the one for the other titanium-free one  $30P_2O_5$ - $70SiO_2$  + 0,5% PVA). The value of charge carriers concentration is the highest among all four samples which correlates with the highest overall conductivity.

The correlation between the value of the parameter  $n$  and the surface area of samples can be based on the fractional dimensionality of the porous sample. If the homogenous sample is taken into consideration, the conductivity is occurs in the bulk. Thus, the dimensionality of the process equals 3. In the opposite situation when conductivity is predominantly a surface phenomenon (e.g. grain boundaries, surfaces of pores) the dimensionality ascribed to it is equal to 2. In all the intermediate cases the process has a mixed character depicted by the presence of fractional dimension (in range between 2 and 3). As was stated previously  $n$  can be correlated with  $d$ . This stays in agreement with the fact that samples of lower surface area exhibit more bulk conductivity while the high surface area ones are characterized with lower  $n$ , and thus, dimensionality values.

Table 1 Dielectric relaxation parameters of glasses

Sample	n	K	$\Delta K$ upon heating
$30P_2O_5$ - $70SiO_2$ +0,5% PVA+5% $TiO_2$ (TEOT)	0,99-1,02	$8,4 \times 10^{-8}$	-14%
$30P_2O_5$ - $70SiO_2$ +0,5% PVA	0,77-0,79	$1,4 \times 10^{-7}$	0%
$30P_2O_5$ - $70SiO_2$ +0,5% PVA+5% $TiO_2$ (nanopowder)	0,90-0,92	$3,05 \times 10^{-7}$	-27%
$30P_2O_5$ - $70SiO_2$ +0,5% PVA (Ultras.)	0,78-0,80	$6 \times 10^{-7}$	+10%

## Bibliography:

1. Shih-Ping Tung, Bing-Joe Hwang, Journal of Membrane Science 241 (2004) 315–323
2. Ph. Colomban, A. Novak, Journal of Molecular Spectroscopy 177 (1988) 277
3. A. Jonscher, in: "Dielectric Relaxation in Solids," Chelsea Dielectric Press, London, 1983