

**SPECTROSCOPIC AND ELECTROCHEMICAL PROPERTIES OF PROTON CONDUCTORS IN THE  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-P}_2\text{O}_5$  SYSTEM**

A. MORIN<sup>a,b</sup>, S. DEABATE<sup>b</sup>, R. MOSDALE<sup>a</sup>, L. GAUTIER<sup>c</sup>, D. J. JONES<sup>b</sup>, and J. ROZIERE<sup>b</sup>

a CEA-Grenoble, DRT/DTEN/SCSE/LHPAC, 17 Avenue de Martyrs, 38054 Grenoble (France), Cedex 09

b Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques, UMR CNRS 5072, Université Montpellier II, Pl. E. Bataillon, 34095 Montpellier (France), Cedex 05

c EDF, Centre des Renardières, 22-30 Avenue de Wagram, 75382 Paris (France), Cedex 08

Even though reliable fuel cell stacks have already been used to power cars or buses, the cost of this technology must be brought down in order to be commercially viable. Operating a PEMFC above 150°C could lead to significant system simplification regarding heat management and to improvements in performance, due to the more rapid oxygen reduction reaction kinetics. Moreover, since the tolerance of catalysts to CO poisoning would be increased, the use of low grade reformat containing up to a few percent of CO as a fuel would be possible. The use of inorganic, solid, proton conductors as electrolytes working at high temperatures would be also attractive from the point of view of cogeneration of heat and for their use in Direct Methanol Fuel Cells (DMFC).

Boron phosphate ( $\text{BPO}_4$ ) has been used as an acid catalyst and more recently its proton conduction properties have been described. The proton conductivity of this material can reach  $5 \cdot 10^{-2} \text{ S.cm}^{-1}$  at room temperature and 100% relative humidity (RH) and remains high even under low relative humidity. However, its relative water solubility limits its use as an electrolyte in fuel cells.  $\text{SiO}_2$  can be added to  $\text{BPO}_4$  via a sol-gel process in order to obtain a material with satisfactory conducting properties and chemical stability in the presence of water.

X-ray amorphous glass ceramic monoliths of the ternary  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-P}_2\text{O}_5$  system were obtained using a three step sol-gel synthesis, and studied with multinuclear MAS-NMR and ATR-IR (infrared spectroscopy). In this system,  $\text{SiO}_4$ ,  $\text{BO}_4$  and  $\text{PO}_4$  tetrahedra are mutually connected with surface hydroxyl groups. The environment of the tetrahedra changes with the amount of boron and phosphate and the thermal treatment temperature as shown in figures 1 and 2. Indeed, as these two parameters increase, the tetrahedra seem to organise into amorphous domains of  $\text{SiO}_2$ ,  $\text{BPO}_4$  and fully condensed phosphate.

Chemical stability in presence of water also depends on composition and thermal treatment. ATR-IR spectra show that for high amounts of boron phosphate, hydrolysis of B-O-P bonds occurs in ambient conditions, leading to the formation of hydroxyl groups (Figure 3). Moreover, materials heat treated at 400°C are more easily hydrolysed than those heated up to 650°C.

The mechanical stability of the monoliths in presence of water seems to be linked to the pore structure. Since this compound is very hydrophilic, water is absorbed and create stress due to capillary pressure. Monoliths heat treated at 400°C crack in the presence of water whereas those heat heated up to 650°C are mechanically stable. This is ascribed to the collapse of the micropores during calcination which reduces the capillary pressure.

The proton conductivity increases with the amount of boron phosphate. As a consequence, a compromise between high stability and high proton conductivity must be found in order to obtain a material which can be used as an electrolyte for fuel cells. At the present time, chemically stable monoliths have been obtained. They exhibit a high proton conductivity up to  $5 \cdot 10^{-3} \text{ S.cm}^{-1}$  at 150°C at 100% relative humidity (RH). The conductivity remains rather high even at low RH:  $5 \cdot 10^{-4} \text{ S.cm}^{-1}$  at 150°C and 25% RH. Spectroscopic investigations are correlated to the electrolyte composition and thermal treatment, and to the conductivity measurements in order to find the best compromise.

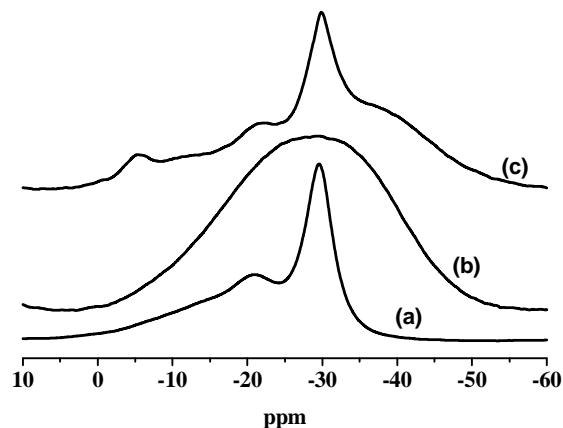


Fig. 1:  $^{31}\text{P}$ -MAS NMR spectra of  $\text{SiO}_2\text{-}0.25\text{B}_2\text{O}_3\text{-}0.25\text{P}_2\text{O}_5$  heat treated up to (a) 230°C, (b) 400°C, (c) 650°C.

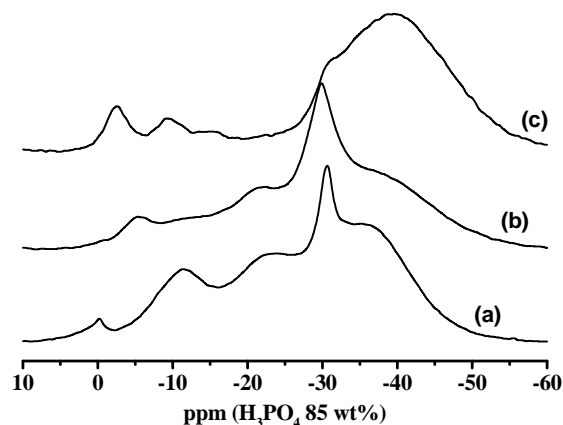


Fig. 2:  $^{31}\text{P}$ -MAS NMR spectra of  $\text{SiO}_2\text{-}x\text{B}_2\text{O}_3\text{-}x\text{P}_2\text{O}_5$  calcined at 650°C,  $x =$  (a) 0.15, (b) 0.25, (c) 0.62.

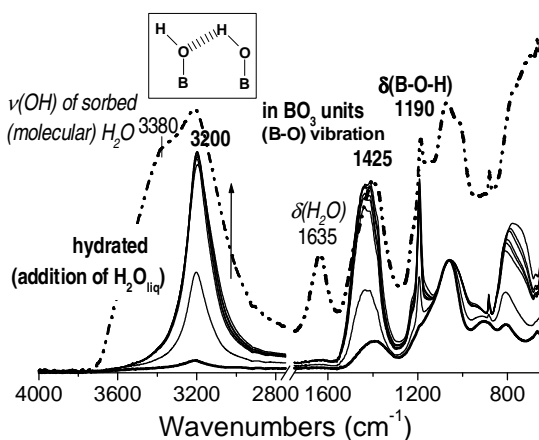


Fig. 3: ATR-IR spectra of  $\text{SiO}_2\text{-}1.25\text{B}_2\text{O}_3\text{-}1.25\text{P}_2\text{O}_5$  as a function of exposure to air (water vapour) for progressively increasing periods, at room temperature.