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Novel composite membranes for Direct Methanol Fuel Cells

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Abstract – Novel composite membranes using cost competitive materials and technologies are being developed for direct methanol fuel cells. The membranes consist of chemically modified zeolites and a hydrophobic polymer binder. The chemical modification of zeolites includes: i) dealumination to improve the acid stability and to increase the water up-take, and ii) surface grafting of moieties containing sulfonic acid groups to improve the proton conductivity. The membranes are prepared by blending the zeolites with a melted polymer binder (Fig. 2a). The zeolite funtionalization and the membranes' properties will be discussed. Membranes with 80wt% of zeolite filler showed constant conductivity values for more than 1200h, even after wetting and drying cycles (Fig. 2b)..

Direct methanol fuel cells (DMFCs) cover a vast range of applications, from portable electronics to backup power. DMFCs operating with Nafion 117 (DuPont) membrane are inefficient and unsuitable for operation with concentrated methanol: the permeation of methanol from the anode to the cathode through the electrolyte membrane decreases the fuel and voltage efficiencies.

In this work it will be presented our strategy and results on the development of composite membranes for DMFCs using cost competitive materials and technologies. The composite membranes consist of 3-D framework zeolites melt mixed with a polymer binder impermeable to methanol. It was recently demonstrated that porous silicates with proton exchange properties have a potential as membrane materials for DMFCs [1]. In this work Faujasite zeolites were chosen because they are commercially available in a wide range of compositions, have very high surface area (600-800 m^2/g), and their surface composition can be easily modified. Two strategies are being pursued to tailor their properties and to improve proton conductivity: dealumination by acid leaching and surface grafting of moieties containing sulfonic acid groups.

The proton conductivity of Faujasites (H form) is closely related to the water absorption capacity as shown in Figure 1a). Dealumination can be used to increase the number of micropores and surface area and thus the water up-take, but also improves the zeolites' acid stability. The functionalization with sulfonic acid groups is carried out by reacting the surface silanol groups with silane agents such as 3-mercaptopropyltrimethoxysilane. The functionalization increases the proton conductivity of the zeolites by at least one order magnitude. However, this process presents several challenges such as the competition between the silane grafting and silane polymerization reactions, and the control of the extent of grafting without the complete occlusion of the pores.

Figure 2 a) shows a SEM image of a composite membrane with 80 wt% Al-rich zeolite (non functionalized) and 20 wt% of hydrophobic polymer binder; the two components were mixed in a Brabender mixing chamber. The films are very homogeneous and the process is reproducible. The membranes' proton conductivity in 0.5M H_2SO_4 was measured in function of time. Figure 2 b) presents the conductivity data recorded up to 1200 h for two membranes prepared from independent batches and stored separately in water and acid solution up to 1200h. The membranes' resistance decreased significantly during the first 20 min due to the dealumination process but then it remained constant. These membranes were further submitted to drying-wetting cycles and the same values of water up-take and conductivity were measured.

These results clearly show the potential associated with this type of composite membranes and their preparation process for fuel cells applications.

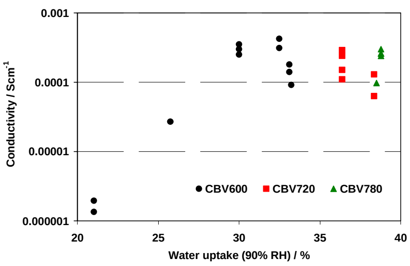

Figure 1: Proton conductivity in function of water up-take (90%RH) of Faujasites with different Si/Al ratio; as received and dealuminated samples.

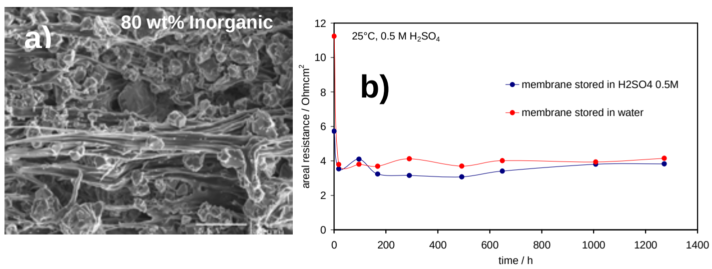

Figure 2: a) SEM image of a 80wt% Al-rich zeolite membrane; b) areal resistance of two membranes measured in 0.5M H_2SO_4; the membranes were stored separately, one in water and one in 0.5M H_2SO_4;

References

[1] Z.Chen, B.Holmberg, W.Li, X. Wang, W. Deng, R .Munoz , Y. Yan, *Chem Mater.* 18 (2006) 5669