Synthesis and Characterization of PVA-based Proton Conducting Membranes

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Proton conducting polymer membranes have attracted much attention for application in fuel cells. In particular, preparation of methanol selective membranes represents a primary goal for application in practical devices such as in Direct Methanol Fuel Cells (DMFC). Indeed, the crossover of methanol is one of the main causes of overpotential losses in DMFC based Nafion[®] membrane.

In this work we have prepared polyvinyl alcohol (PVA) based composite membranes having Al_2O_3 or SiO_2 as ceramic filler. The membranes were prepared by casting using an aqueous solution as the dispersing medium for the ceramic components. The proton conductivity was obtained by soaking the membranes into an acidic solution.

The SiO₂ nanosized filler assures high porosity to the PVA membranes, which then can be easily swelled by the HA solutions up to 250 % weigh percent.

The thermal characteristics of the PVA-based composite membranes were studied using DSC analysis. Figure 1 reports the DSC spectra of different PVA-SiO₂ membranes soaked in H_3PO_4 and H_2SO_4 solutions respectively. The thermal features of the polymer are modified by the presence of the strong acidic media. In fact, in the swelled membranes the melting peak of the PVA occurs at lower temperature than in the PVA native membrane.

The conductivity of the membranes was determined using impedance spettroscopy. Figure 2 reports the Arrhenius plot of membranes swelled in H_2SO_4 showing a quite high conductivity at room temperature ($\sigma = 1*10^{-2}$ S/cm). The decrease of conducibility at 80 °C is probably associated to the loss of water in the swelled membranes.

In order to increase the conducibility and the thermal stability of the membranes we have modified the PVA-based membranes by the use of proper crosslinking compounds [1]

For example the conductivity of membranes prepared from ethylene glycol as interchain ligand is very high ($\sigma = 1*10^{-1}$ S/cm) and stable up to 100°C. Moreover, it is possible to further improve the chemical and electrochemical properties of the PVA systems functionalizing the backbone of the polymer by reacting some –OH groups with R-SO₃H reagents [2]. In this way one may create an ionomeric structure.

References

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[2] Y.H.Chu, J.E.Lim, H.S.Han,H.chang, Y.G.Shul, 202 ECS Meeting, October 20-24 (2002), abs 834.

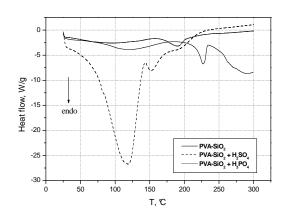


Fig. 1: DSC spectra of PVA-SiO₂ membranes swelled in H_3PO_4 2M and H_2SO_4 2M. Thermal scan 10 °C/min.

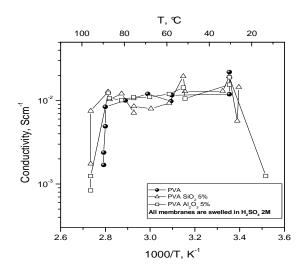


Fig. 2: Arrhenius plot of the PVA based membranes.