Hybrid Proton Conducting Membranes based on Short Side Chain Perfluorosulfonic Acids and Organically modified Zirconium Phosphate

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Organically modified ZrP bearing surface alkyl chains was used as a filler material in the preparation of a series of hybrid proton conducting membranes based on EW 830 and 700 short side chain perfluorosulfonic acid (PFSA) with the aim of mechanically reinforcing the hydrophobic component of the PFSA. ZrP particles of nanometric size were prepared according to a recent work which allows the quick formation of gels in aliphatic alcohols of solvent-intercalated ZrP nanoparticles[1], which were then functionalized by reacting them with 1,2 epoxydodecane[2]. To make the filler more stable under fuel cell conditions and more compatible with the PFSA, a fluorinated epoxydodecane was also used.

Hybrid membranes, with filler loadings up to 10 wt%, were obtained by a solvent-casting procedure and characterized by thermogravimetric analysis, mechanical tests and conductivity measurements. The hybrid materials were stable up to 250°C and their mechanical properties were improved in comparison with those of the neat PFSA in terms of elastic modulus (E) and yield stress (Y), both at room temperature (ΔE/E up to +54%, ΔY/Y up to +22%) and at 80°C / 70% RH (ΔE/E up to +110%, ΔY/Y up to +50%).

The proton conductivity was determined by in-plane impedance measurements as a function of RH in the range 80 - 110°C. Surprisingly, the proton conductivity of the materials was not compromised by the hydrophobic character of the nanofiller and all the hybrid membranes exhibited higher conductivity than the pristine cast PFSA. In particular, fig.1 shows the in-plane conductivity at 100°C as a function of RH for hybrid membranes made of EW 830 PFSA and organically modified zirconium phosphate bearing hydrogenated alkyl chains ($ZrP(C_{12})_{0.9}$).

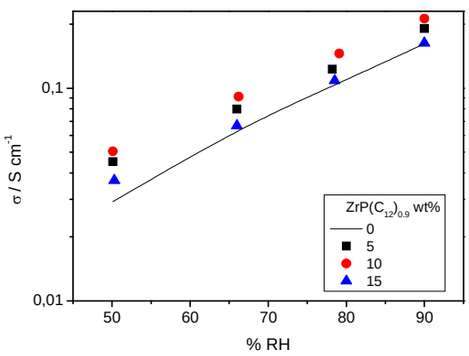

Figure 1. In-plane conductivity at 100°C as a function of RH for hybrid membranes of EW 830 PFSA filled with the indicated amounts of $ZrP(C_{12})_{0.9}$.

A hybrid membrane containing 10 wt% of ZrP bearing fluorinated alkyl chains presented a conductivity of 0.4 S cm^{-1} at 110°C and 95% RH. This result is consistent with the good performance of the membrane in single fuel cell tests.

References

1. M. Pica et al, *Inorg. Chem.* 50 (2011) 11263-11630.
2. M. Casciola et al, *Inorg. Chem.* 49 (2010) 3329 3336.

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