Influence of the solvent on PEEK membranes characteristics for medium temperature PEFC.

A. Carbone, I. Gatto, R. Pedicini, A. Saccà and E. Passalacqua
CNR-ITAE, Institute for Advanced Energy Technologies "N. Giordano"
Via Salita S. Lucia sopra Contesse, 5 – Messina, ITALY

The recent research of PEFC has been devoted to the development of membranes based on non-perfluorinated polymers as an alternative to the high cost, low thermal stability and mechanical strength of perfluorosulphonic membranes [1]. In general these polymers consist of polyaromatic or polyetherocyclic repeat units like polyetheretherketone (PEEK), polysulphone (PSF); polyethersulphone (PES) and others. These polymers should have a fundamental property to find an application in a medium temperature PEFC: the temperature stability of the original polymer, wich has to be sulphonated to give the material the characteristics necessary for protonic conduction. PEEK is a thermoplastic polymer that maintains its unaltered structure until reaching a temperature of about 500°C. After the sulphonation reaction (s-PEEK) this temperature decreases until about 300°C, but in any case it is sufficient to operate in a medium temperature (over 100°C) PEFC. For this reason s-PEEK polymer has been chosen as a probable candidate. The final characteristics of the membranes prepared by s-PEEK essentially depend on the chemical nature of the polymer backbone and secondarily on the molecular weight and the nature of the solvent used for membrane preparation. In fact, the possible presence of the residual solvent in the final membrane could condition the conductivity and the mechanical strength.

In this work a s-PEEK polymer with a sulphonation degree (DS) of about 50-60% (determined by CHNS-O elemental analysis) was prepared following a standardized preparative procedure [2]. A commercial PEEK (Victrex 450PF) was used as starting material and 96% H_2SO_4 as sulphonating agent. The DS was regulated operating on temperature and time during the sulphonation reaction. To evaluate the influence of the casting solvent on the chemical physical and electrochemical properties, membranes of s-PEEK were prepared from a 6% polymer/solvent solution with three different solvents: DMAc, DMF and DMSO. These solvents have different physical characteristics such as a dielectric constant, dipole moment and boiling point. Membranes with a thickness of about 70-90 μm were obtained and characterized in terms of water uptake (Wup) and IEC. The Wup was determined by the water absorption after immersion for 24 hrs at room temperature and the IEC value by titration of H^+ with NaOH.

In Tab. 1 the chemical physical characteristics are reported.

Tab. 1 Chemical physical data

Polymer-solvent	Thickness μm	Wup %	IEC meq/g
s-PEEK/DMA	70	31	1.70
s-PEEK/DMF	70	31	1.70
s-PEEK/DMSO	90	30	1.71

The water retention and IEC characteristics of the membranes are very similar.

Electrochemical characterizations were performed in a 5 cm^2 commercial single cell at a temperature range between 80 and 130°C, in humidified H_2/air, and pressures of 3.0 abs. bar. MEAs (membrane/electrodes assemblies) were prepared by using electrodes with 0.5 mg_{Pt}/cm^2 developed at CNR-ITAE [3]. A commercial 30% Pt/Vulcan (E-TEK) catalyst and a 5% Nafion dispersion (Aldrich) were used for the catalyst layer preparation. The maximum performance was recorded at 100°C for all the membranes. In fig. 1 the polarization curves at 100°C are shown.

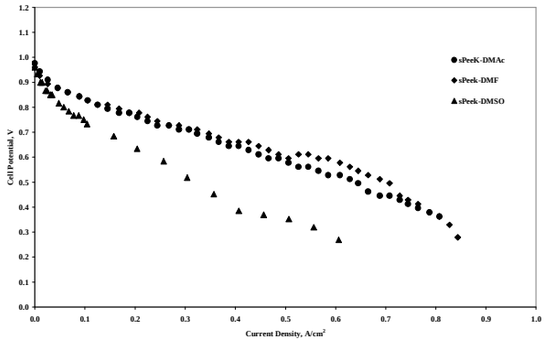

Fig. 1. Polarization curves of s-PEEK at T=100°C (P=3abs. bar) in humidified H_2/air

Despite, the chemical physical characteristics being very similar the electrochemical behaviour is different. The low performance for the sPeek-DMSO membrane could be attributed to a residual presence of solvent (BP = 189°C) wich in these cell operative conditions is probably eliminated with a consequent membrane structure collapse. This influence of solvent presence is not evident in chemical physical data because a thermal treatment undervacuum was carried out on the samples to determine the Wup and IEC values. Starting with the promising electrochemical results on sPeek-DMAc and sPeek-DMF membranes a new membrane was prepared using the same polymer powder and a DMAc/DMF mixture (50%/50% wt) as a solvent. This membrane was tested at 130°C in humidified H_2/air with a RH = 85% for both gases.

In fig. 2, the performances of the membrane compared to the commercial N112 are shown.

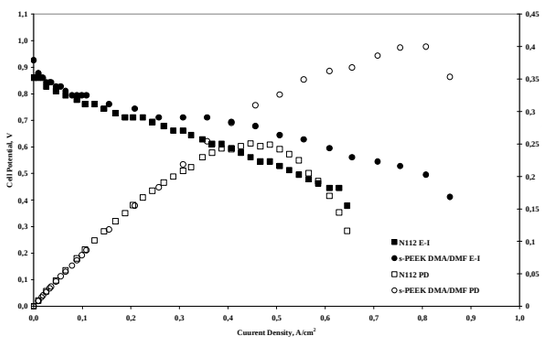

Fig.2- Power density of s-PEEK at T=130°C (P=3abs. bar) in humidified H_2/air

Very high performances were recorded for sPeek-DMAc/DMF membrane with a maximum power density of about 400 mW/cm^2 at about 0.5 V against a power density of about 270 mW/cm^2 at the same potential for N112.

References

[1] J. Roziere, D. J. Jones, Annu. Rev. Mater. Res. 2003, 33: 503-55

[2] J.Kerres, A.Ullrich, TH.Haring, M.Baldauf, U.Gebhardt, W.Preidel, Journal of New Materials for Electrochemical Systems,3,129-239 (2000)

[3] F. Lufrano, E. Passalacqua, G. Squadrito, A. Patti, J. Appl. Electrochem., 29**,** 445 (1999)