Sulfonated poly(pentafluorostyrene)

Vladimir Atanasov and Jochen Kerres

University of Stuttgart, Institute of Chemical Process Engineering, Boeblinger Str. 78, 70199 Stuttgart, Germany

The global needs of new polymeric materials that can fulfill the requirements of the innovative technologies e.g. fuel cell, flow battery and water desalination is nowadays essential. Herein we present such a polymer which is based on a well known structure of polystyrene and possessing simultaneously excellent ion-conductive properties and high resistance to thermal and oxidative treatments.

Highly sulfonated poly(pentafluorostyrene) (sPFS) is obtained in three steps: (i) emulsion polymerization of the pentafluorostyrene, (ii) thiolation with metal sulfide and (iii) oxidation of the thiol-functions to the corresponding sulfonic acids. The advantages of the radical polymerization in emulsion in compare to commonly used polycondensation reaction, lie in the higher molecular weights (100 – 1000 kDa), the milder conditions (T = 90 °C in water) and the shorter reaction time (1-2 hrs). Structural analysis of sPFS confirmed a 100% sulfonation (each pentafluorostyrene unit is sulfonated), which gave us an access to polymer with extremely high ion-exchange capacity of 3.9 mequiv. g⁻¹. The contrivance is in the cumulative electron withdrawing effect of the fluorine functions. This simultaneously facilitates the thiolation reaction (ii) to the level of a "click-reaction" and enhances acidity of the finally obtained sulfonic acid. Beside the high resistance to oxidative and thermal treatment (T_{decomp} = 268 °C at 70% oxygen atm.), the most important consequence is the tremendous increase of the proton-conductivity being 35 mS cm⁻¹ (at 160°C, p = 10⁵ Pa water vapor pressure), which is an order of magnitude higher than those of Nafion measured under the same conditions. Moreover, sPFS showed very small dependence of the ion-conductivity onto the water content, which is extremely important for the performance of the polyelectrolyte in the fuel cells above 100 °C. This makes sPFS the best ion-conducting polymer besides disulfonated polyphenylenes of Morton Litt¹ and sulfonated polysulfones of Klaus-Dieter Kreuer².

All this makes us to believe in the very high potential of the sPFS as a polyelectrolyte for the fuel cell applications.

^{1.} S. Granados-Focil, M. H. Litt Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem. 2004, 49(2), 529.

^{2.} M. Schuster, C. C. de Araujo, V. Atanasov, H. T. Andersen, K.-D. Kreuer, J. Maier *Macromolecules* **2009**, *42*, 3129.