Direct Sulfonation of Fluoropolymers: A New Approach for the Manufacturing of Cheap and High-Performance Proton-Conducting Polymer Membranes for Fuel Cells

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Manufacturing of proton conductive polymer membranes for low-temperature fuel cells is a challenging task. Because of the highly oxidising environment the membranes need to have excellent oxidation stability. In addition, the ion conductivity should be higher than 10 mS/cm and the membrane thickness less than 100 µm. Consequently, the membranes ought to have very good mechanical properties so that they can fulfil also the barrier demands with respect to mixing of the reactant gases.
Our approach has been the combination of irradiation treatment and direct sulfonation.[1] The matrix material is used in film form. We have tested such fluorinated polymers as poly(vinyl fluoride)[1-3] and poly(ethylene-co-tetrafluoroethylene). As the fluoropolymers are usually inert they need to be activated for the sulfonation reaction. Our method for this has been irradiation with heavy charged particles. E.g., accelerated protons and helium ions create cylindrical tracks with high reactivity to sulfonation when traversing polymer films.[1] Consequently, sulfonation of e.g. proton irradiated polymer films produces membranes in which the sulfonic acid groups form continuous channels for proton conduction through the membrane.[2,3]
According to our results irradiation by means of accelerated heavy charged particles and subsequent sulfonation produces membranes with necessary ion conductivity, mechanical properties and very good oxidation stability. In addition, cost analysis showed that manufacturing of membranes on a large scale by means of direct sulfonation is highly economic.

1) M. Paronen, F. Sundholm, E. Rauhala, T. Lehtinen, S.Hietala, Effects of irradiation on sulfonation of Poly(vinyl fluoride), *J.Mater. Chem.*, 1997, **7**, 2401
2) M. Paronen, M. Karjalainen, K. Jokela, M. Torkkeli, R. Serimaa, J. Juhanoja, D. Ostrovskii, F. Sundholm, T. Lehtinen, G. Sundholm, L. Torell, Structure of Sulfonated Poly(vinyl fluoride), *J. Appl. Polym. Sci.*, 1999, **73**, 1273
3) D. Ostrovskii, M. Paronen, F. Sundholm, L. Torell, State of Water in Directly Sulfonated Poly(vinyl fluoride) Membranes: a FTIR study, *Solid State Ionics*, 1999, 116, 301

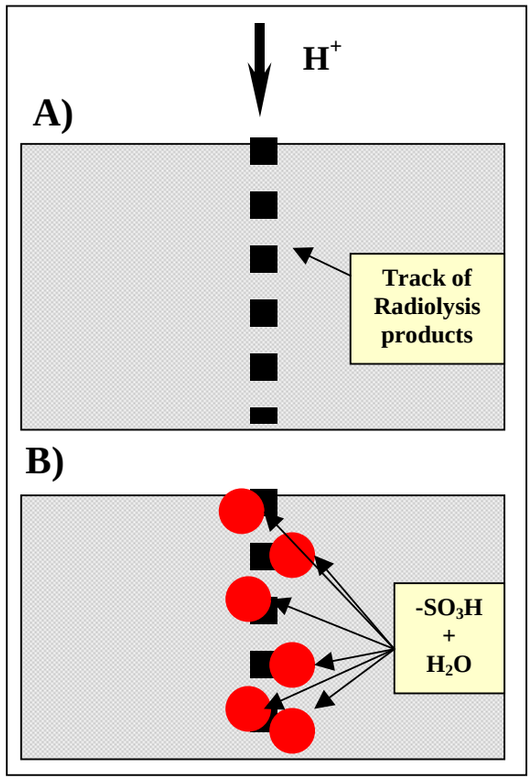

Fig 1: A) Model for the formation of reactive sites in polymer upon irradiation with protons.
B) Model for the distribution of sulfonic acid groups in a proton irradiated and subsequently sulfonated polymer.

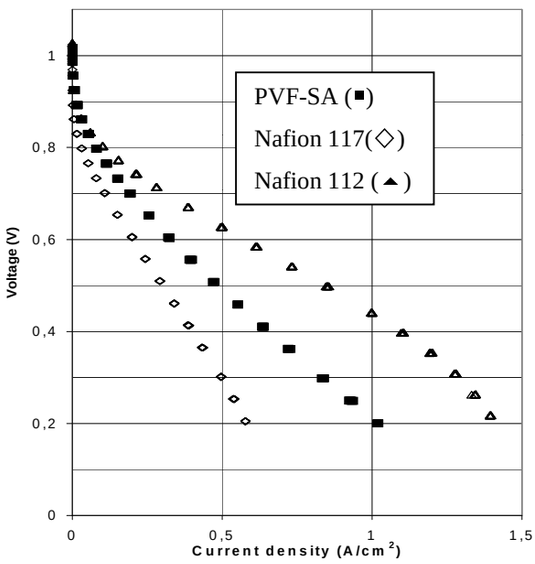

Fig. 2: Fuel cell performance of a direct sulfonated poly(vinyl fluoride) membrane compared to Nafion 117 and 112. Test temperature with PVF-SA was 50 °C and 70 °C with Nafion membranes. All the other essential test parameters were the same for both type of membranes.