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PFG NMR Studies of Diffusion in Sulfonic Acid Based Systems

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Polymer-electrolyte-membrane fuel cells (PEM-FCs) are considered as the most promising fuel cell technique for applications like automobiles or stationary power supplies. State-of-the-art separator materials in PEM-FCs are commonly sulfonic acid functionalized polymers, like the perfluorinated polymer Nafion. These materials show the required high proton conductivity only at high degree of hydration, i.e. high water content. Thermodynamically speaking, such electrolytes are two-phase systems containing liquid water as a nano-dispersed second phase. This water solvates the acidic protons of the sulfonic acid function and promotes proton mobility by structure diffusion and, particularly, vehicle-type transport, i.e. water is essential for the formation and mobility of protonic charges [1, 2].

The most obvious limitation of these systems is the low proton conductivity at low levels of hydration. Because of the poor connectivity (percolation) of the water structures in these polymers and the strong local retardation of the water diffusion, fast proton conduction according to a vehicle mechanism is not possible at such low degrees of hydration.

But there is experimental indication, that high proton conductivity in sulfonic acid based systems may be possible even at low hydration levels, provided that the sulfonic acid groups are spatially less separated. The observation, that the proton conductivity of aqueous highly concentrated sulfuric acid H_2SO_4 shows a non-linear behavior with decreasing water content [3], indicates another proton conduction mechanism appearing at low degrees of hydration, e.g. structure diffusion within hydrogen bonded network formed by sulfonic acid group and water. In order to clarify whether this is the case (structure diffusion at low degree of hydration), we started to analyze the diffusion, T_1 relaxation and conductivity data of different sulfonic acid model systems, including the methylsulfonic acid CH_3SO_3H (MSA), the triflic acid CF_3SO_3H and the sulfuric acid H_2SO_4 , at low degrees of hydration and over a wide range of temperature.

PFG NMR spectroscopy has been used to measure the mass transport on a macroscopic scale, while T_1 relaxation data allow identifying local transport processes. Complementary to diffusion studies, ac impedance spectroscopy has been applied to investigate charge transport. Comparison of conductivity and diffusion data via the Nernst-Einstein relation [4] provides valuable information about the conduction mechanism in hydrated sulfonic acid based systems.

In Fig. 1a the ^1H PFG NMR measurement of the sample MSA $\cdot$ 3 H_2O is exemplarily shown, featuring two ^1H signals corresponding to the two chemically different sorts of protons, the CH protons of the methyl group and the OH protons of the sulfonic acid functional group together with H_2O protons. From the apparently different attenuation of both signals it is evident that both, the CH and the OH protons diffuse differently, which is again shown in Fig. 1b. A distinctly higher OH proton diffusion coefficient compared to the CH proton diffusion indicates that structure diffusion is most likely the prevailing proton transport mechanism. The corresponding diffusion coefficients of CH and OH protons as a function of temperature are shown in Fig. 2, indicating an almost Arrhenius-like behavior. Measurements at different water levels of MSA and the comparison with results from triflic acid CF_3SO_3H and sulfuric acid H_2SO_4 reveal even more details about the transport mechanism.

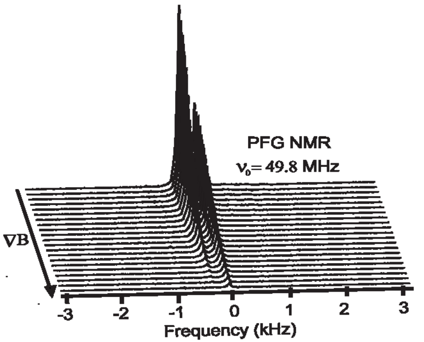

Fig.1a: 3D plot of the ^1H PFG NMR measurement of MSA · 3 H_2O at 379 K. With increasing magnetic field gradient strength, the signal intensity decreases due to diffusion effects.

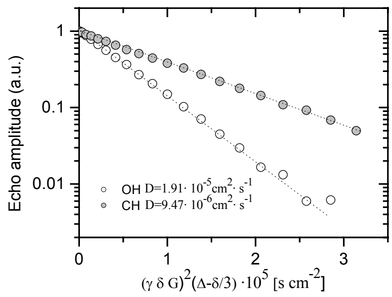

Fig.1b: Echo amplitude versus gradient strength of CH protons and OH protons. Latter belong to H_2O and protons of the $–SO_3H$ group of MSA.

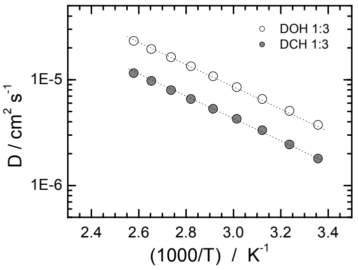

Fig. 2: ^1H self-diffusion coefficients for the MSA·3 H_2O sample versus temperature.

Conclusion

Diffusion, T_1-relaxation and conductivity measurements on CH_3SO_3H, CF_3SO_3H and H_2SO_4 at low degrees of hydration have been used to analyze the proton conduction mechanism in concentrated sulfonic acid based systems. The results indicate that with decreasing water content a change in the conduction mechanism appears, from mainly vehicle diffusion to predominantly structure diffusion.

References

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