diffusion-fundamentals
The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application
www.diffusion-fundamentals.org, ISSN 1862-4138; © 2005-2010

Proton Conductivity of Aluminium or Sulfonic Acid Functionalized Ordered Mesoporous Silica Materials

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Presented at the Bunsen Colloquium: Spectroscopic Methods in Solid State Diffusion and Reactions
September 24th – 25th, 2009, Leibniz University Hannover, Germany

Mesoporous SiO_2 materials of type Si-MCM-41 were functionalized in order to generate proton conductivity within the pores.

For the anchoring of sulfonic acid (SO_3H) groups on the inner walls two different synthesis routes are presented. The highest loading of Si-MCM-41 with SO_3H groups was reached via a co-condensation route, which turned out to be advantageous compared to subsequent grafting with mercaptosilane and oxidation. The direct *in situ* co-condensation route led to hybrid materials exhibiting proton conductivities up to 0.2 S/cm at 100% relative humidity and 413 K [1]. Especially at low humidities and under dry conditions, we show that the high group density of co-condensed materials is crucial for the proton transport. Experimental characterization, via impedance spectroscopy and water adsorption, and theoretical investigations of a simplified model system concordantly demonstrate the most important dependencies of the proton transport properties on the water content and on the density of SO_3H groups.

The distribution of SO_3H groups within the pore channels was found to be much more homogenous if the samples were prepared by co-condensation than it is the case after loading by grafting. In neutron scattering experiments the diffraction signals of the host are partially quenched by adsorption of a D_2O/H_2O mixture. Since for non-modified Si-MCM-41 the complete quenching was observed [2], this indicates the presence of non-modified regions in the channels. Probably the silanes are predominately anchored only at the pore mouths. This of course hinders very much the diffusion of the protons along the channels. For samples, formed by *in situ* co-condensation, however, the quenching of the neutron diffraction signals by an adsorbed D_2O/H_2O mixture was not possible because the homogenously modified pore walls exhibit an altered scattering-length density for neutrons. The such proven better homogeneity of the functionalization enhances the proton diffusion due to better hand-over of protons from one SO_3H group to the next.

Computational studies were performed including classical molecular dynamic (MD) simulation and free energy calculation with a quantum mechanical method, which are showing comparable trends to the performed proton conductivity measurements of the material. Furthermore, the water uptake of the functionalized material was studied by MD simulation finding the water density inside the porous system to be inhomogeneous in the case of low relative humidity.

In order to check the influence of Brønstedt acidic Al sites in the walls of mesoporous Si-MCM-41 materials on their proton conductivity, we also substituted some silica atoms in the walls by aluminium. For this different Al sources, *i.e.*, sodium aluminate, aluminium sulphate and aluminium isopropoxide (AIP) were added to the synthesis gel [3]. The successful synthesis of ordered mesoporous material with incorporated Al species was proven by X-ray diffraction, energy-dispersive X-ray spectroscopy, nitrogen adsorption, scanning electron microscopy and solid-state ^{27}Al MAS NMR. By realizing Si/Al-ratios of 8 to 40 it was found that the proton conductivity of the mesoporous aluminium silicates measured by impedance spectroscopy significantly increases with the Al content, reaching a conductivity of 3×10^{-3} S/cm at 140 °C (see Fig. 1). The increase of the proton conductivities compared to Al-free Si-MCM-41 results from (i) an improved hydrophilicity enhancing the water storage capability, (ii) a decreased particle size from the micrometer to the nanometer scale (50 – 100 nm) and (iii) the existing Brønstedt acidity in the mesoporous Al-MCM-41. The Al source $NaAlO_2$ gives clearly the best results because the entire Al incorporated within the framework is tetragonally coordinated, while for samples prepared with $Al_2(SO_4)_3$ or AIP also octahedral coordination of oxygen around the Al centers is observed by ^{27}Al MAS NMR.

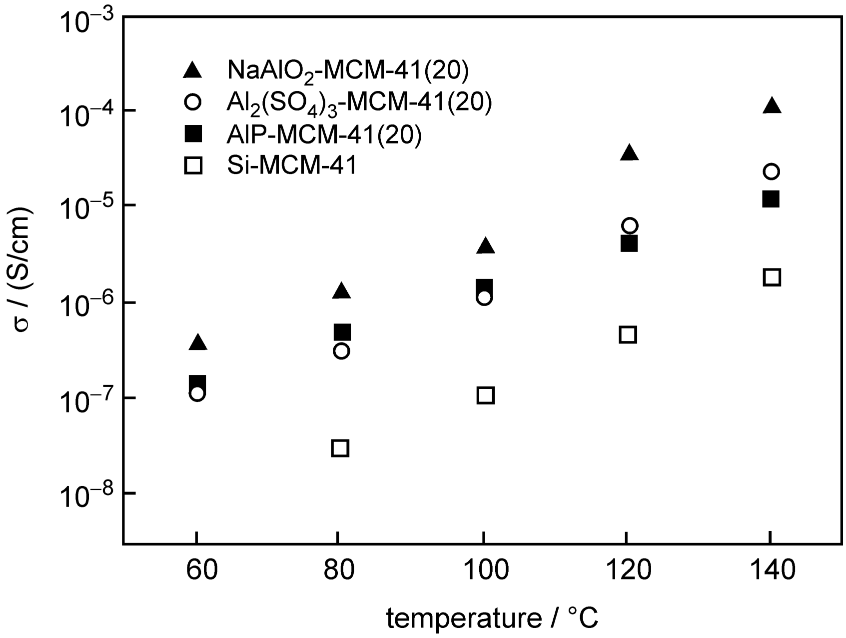

Fig. 1 Proton conductivities at 100% relative humidity of mesoporous MCM-41 materials with a Si/Al ratio of 20 compared to pristine Si-MCM-41.

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