

## Composite fuel cell materials studied by MAS PFG NMR diffusometry and MAS NMR spectroscopy

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Proton exchange membrane (PEM) fuel cells are considered to be one of the most promising energy conversion systems for replacement of conventional energy sources based on fossil fuels for automobiles and mobile devices [1]. An often used membrane material facilitating the proton transport is a Nafion polymer membrane, which has been an industrial standard for many years. However, amongst disadvantages for the practical use of Nafion are its stability at temperatures  $>90$  °C and maintaining high relative humidity at these temperatures. Incorporation of inorganic–organic additives into the polymer membrane is a promising approach to overcome the stability issues at elevated temperatures for future generations of membranes for PEM fuel cells. As a host system, mesoporous silicas can be utilized for creating hybrid organic–inorganic composites by functionalization them with organic moieties.

In our contribution, we prepared mesoporous Si-MCM-41 and KIT-6 materials [2], which were subsequently functionalized by co-condensation from tetraethyl-orthosilicate and mercaptopropylmethoxysilane with a following thiol-oxidation to  $\text{SO}_3\text{H}$  by  $\text{H}_2\text{O}_2$ . In our earlier work [1], we showed that low proton conductivity of pristine Si-MCM-41 ( $2 \times 10^{-6}$  S  $\text{cm}^{-1}$  at 373 K and 100% of relative humidity) can be drastically improved (up to  $2 \times 10^{-2}$  S  $\text{cm}^{-1}$ ) by functionalizing the pore surface with sulfonic groups by  $\sim 40\%$ . The conductivity of the sample KIT-6 reaches a value of the same order.

Further, magic-angle spinning (MAS) pulsed field gradient (PFG) NMR diffusometry has been applied for investigating the nature of the conductivity in these materials. In addition, MAS NMR spectroscopy provided structural analysis of the synthesized materials. The use of high-resolution  $^1\text{H}$  MAS PFG NMR was necessary, since the  $^1\text{H}$  NMR spectrum consists of the signal of mobile hydroxy species and the non-decaying signals of the fixed methylene groups (Fig.1). Self-diffusion coefficients in the order of magnitude of  $4 \times 10^{-9}$   $\text{m}^2\text{s}^{-1}$  were obtained and compared with diffusion coefficients derived from conductivity data. The deconvolution of the  $^{29}\text{Si}$  MAS NMR spectra showed that Si atoms of the functionalizing silane are linked to the MCM-41 framework via three or two  $\equiv\text{Si-O-Si}\equiv$  bonds.  $^{13}\text{C}$  cross-polarization MAS spectroscopic experiments confirmed that the majority of the organic functional groups remained intact after the oxidation [3].

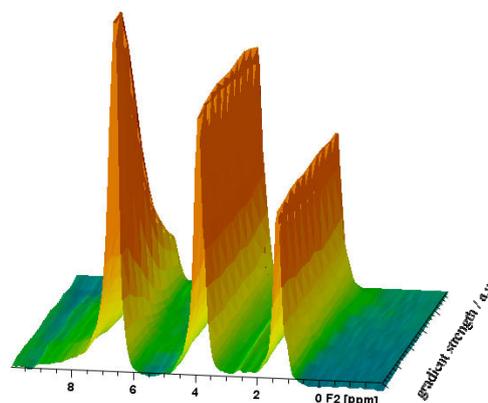


Figure 1: NMR signal decays with linearly increasing strength of the gradient pulses for KIT-6 with 20 % functionalization by sulfonic groups loaded with water vapour at 373 K.

### References

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