Experimental and characterisation

For the hydrolysis of ethoxy groups in APTES, a mixture of 2.21g of 3-aminopropyltriethoxysilane(APTES) and 18g of H_2O was stirred at room temperature for 24 hours [s1]. 0.98g of concentrated H_2SO_4 was dropwise added into the mixture at the rate of one drop per minute, and the mixture was then stirred for another 24 hours. The obtained solution is denoted as Si-solution. A Nafion membrane of 4×4 cm^2 surface area was heated at 140 °C for 30 minutes. Then the silica planting process was implemented by immersing this Nafion membrane into the Si-solution for a certain amount of time. Nafion membranes with planted sulfonated organic silica films with various thicknesses were obtained by controlling the planting time and were named Si-Nafion membranes. According to the planting time, the films were symbolised as Si-Nafion membranes (5 s), Si-Nafion membranes (20 s), Si-Nafion membranes (7 min).

The proton conductivity of the membranes was measured by a four-electrode ac impedance method from 0.1 Hz to 100 kHz, 10mV ac perturbation and 0.0V dc rest voltage. Impedance spectra were recorded using a Princeton Applied Research Model 273A Potentiostat (Model 5210 Frequency Response Detector, EG&G PARC, Princeton, NJ). The membranes were fixed in a measuring cell made of two outer gold wires to feed current to the sample and two inner gold wires to measure the voltage drops. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in liquid water. The proton conductivity (σ) of the membranes was calculated using the following equation:

$$\sigma = L / RA$$

where L, R and A denote the distance between the two inner gold wires, the resistance of the membrane, and the cross-sectional area of the membrane, respectively.

The methanol permeability of these membranes was determined with a glass diffusion cell. This glass cell consisted of two chambers each approximately 100 ml; one chamber of the cell was filled with 2M methanol solution, and the other with deionised water. The membrane (effective area 4.5 cm^2) was clamped between the two compartments which were kept under stirring during an experiment. The methanol concentration in the receptor chamber was measured versus time using a gas chromatograph (Shimazu GC-14B) (detect limitation:50ppm)equipped with a thermal conductivity detector. Ten hours was taken for the permeation experiment, and we test the methanol concentration in reservior B every two hours. The methanol permeability was calculated by the following equation:

$$C_B(t) = \frac{AP}{V_B L} C_A(t - t_0)$$

where $C_B(t)$ is the concentration of methanol measured in the receptor compartment as a function of time, V_B is the volume of the receptor compartment, and L and A are the thickness and the effective area of membrane, respectively. P is the methanol permeability and can be determined from the slope of the plot of methanol concentration in the receptor compartment versus time. The methanol detection limit of the GC is about 50 ppm. the amount of methanol molecules in the 100ml reservoir was calculated to be 2.78×10^{-4} mol. We suppose the methanol concentration of the

reservoir B reach the detection limit after ten hours testing, the maximal diffusion coefficient of the si-Nafion (7min) should be $3.19 \times 10^{-8} cm^2 s^{-1}$, which is even much lower than that of Nafion membrane ($6.0 \times 10^{-6} cm^2 s^{-1}$).

The morphology of the membranes was characterised by a LEO 1525 FE-SEM scanning electron microscope (SEM). Transmission electron microscopy (TEM) was performed by a FEI Tecnai G2 S-Twin instrument with a field emission gun operating at 200 kV, and images were acquired digitally on a Gatan multipole CCD camera. The sample was prepared by depositing the Si-solution onto a 300 mesh Cu grid, coated with a lacey carbon film.

The swelling properties of the Si-Nafion membranes were determined using water uptake measurements. The detailed procedure for water uptake and swelling property measurements was as follows. The first step was to completely dry the membrane at 80 °C for 3 hours before weighing and measuring it. After that, the membrane sample was placed into deionised water at ambient temperature for 3 hours to allow water uptake. The swollen membrane was then taken out of the water and quickly wiped using filter paper to remove the remaining water on both sides of the membrane; the swollen membrane was then weighed and measured. The quantity of water uptake inside the membrane was calculated according to Equation (1):

$$WaterUptake(\%) = 100 \frac{W_{wet} - W_{dry}}{W_{dry}}$$

where W_{wet} and W_{dry} are the weights of the membrane after and before the water uptake, respectively.

The changes in the width of the Si-Nafion membranes in water are

calculated by the following equation:

$$\Delta L(\%) = 100 \frac{L_{wet} - L_{dry}}{L_{dry}}$$

where L_{wet} and L_{dry} are the lengths of the membrane after and before water uptake, respectively.

[S1]. T. Tezuka, K. Tadanaga, Akitoshi Hayashi and M. Tatsumisago, *J. AM. CHEM. SOC.*, 2006, **128**, 16470-16471.