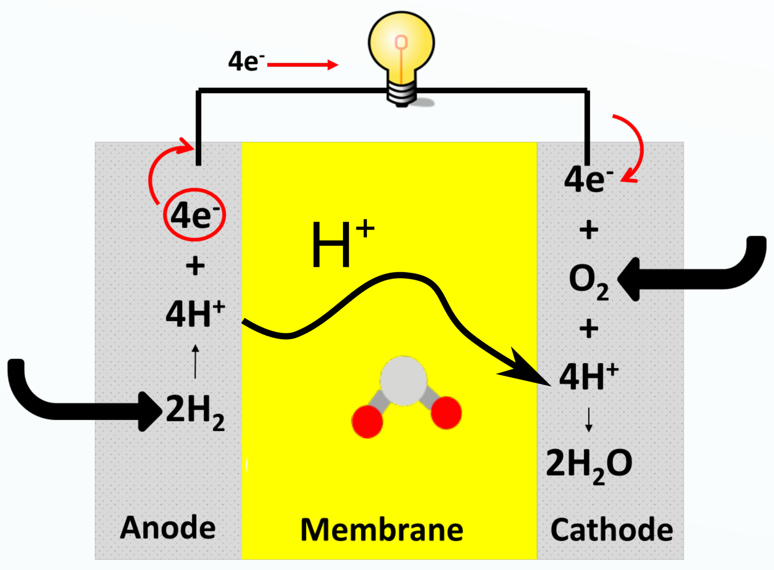
Water behavior in Fuel cell proton exchange membrane

Xiao Ling, Sapun H. Parekh and Katrin F. Domke
Department of Molecular Spectroscopy, Max Planck Institute for Polymer Research, Mainz, Germany
ling@mpip-mainz.mpg.de

Proton exchange membrane fuel cell[1]



Water transport

↓

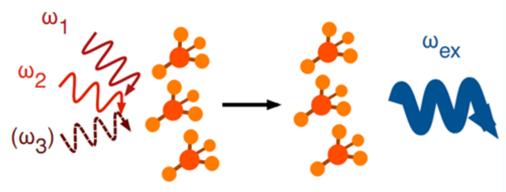
Proton transport

↓

Performance

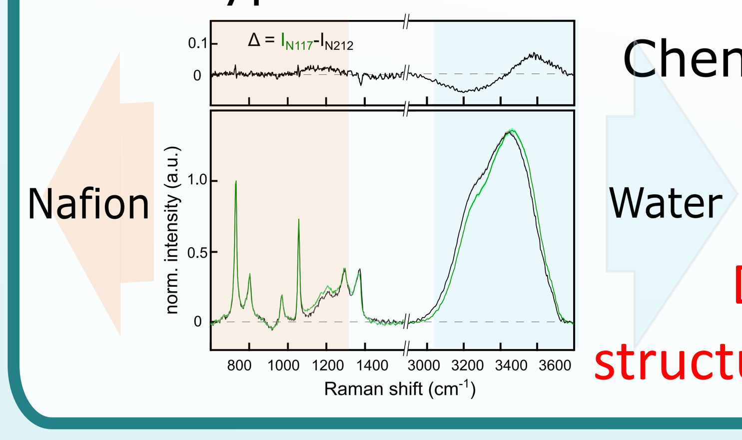
Coherent anti-Stokes Raman scattering (CARS)

Nonlinear analogue of Raman scattering



- High signal intensity, label free, nondestructive
- Chemical information, (sub)μm spatial resolution;
- Fast mapping: (ms) temporal resolution.

Two types of Nafion membrane: N117 and N212



Chemically identical; produced via different processes

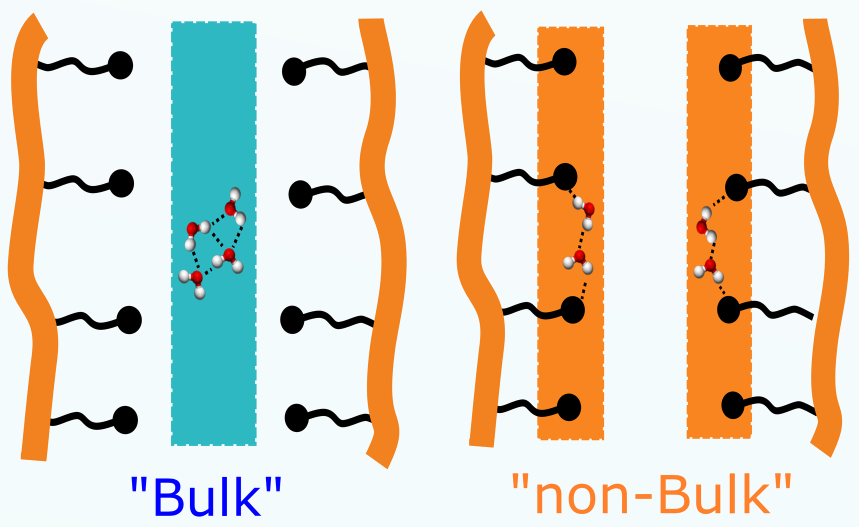
Proton conductivity: N117 > N212

OH peak in N117 blue shifts compare to N212

Do different membranes have different water structures that lead to different macroscopic properties?

Structure and binding of water in Nafion

Two types of water species in fully hydrated Nafion membrane[2]



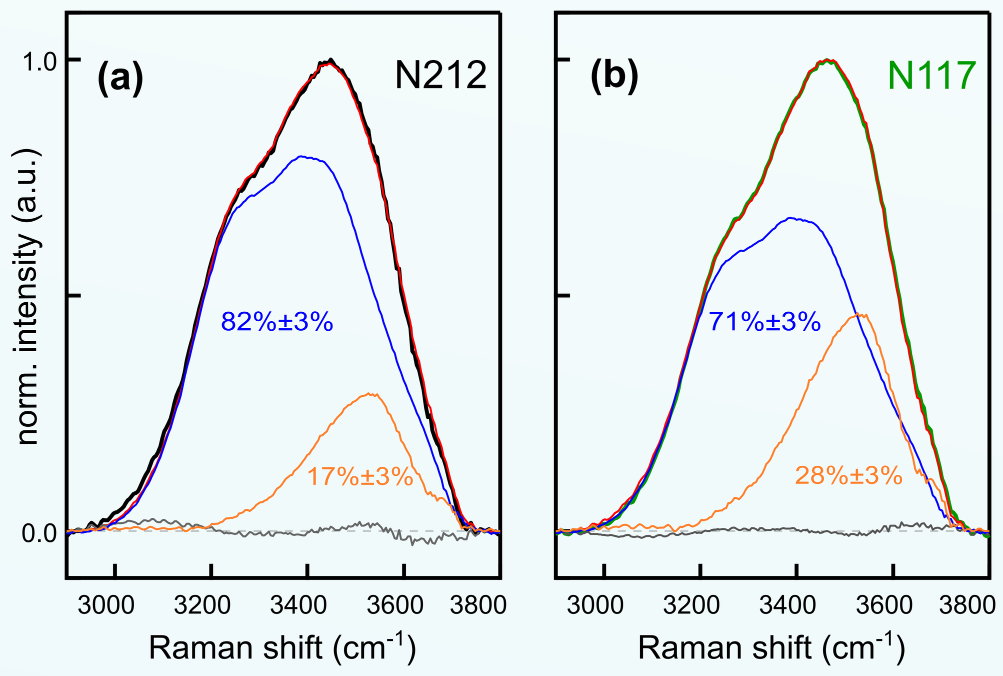
"bulk" water: water molecules that are completely surrounded by - and hydrogen bonded to - other water molecules

"non-bulk" water: water molecules that interact (or at least partially) with Nafion membrane, therefore less with other water molecules.

Different contribution of water species: N212 vs N117

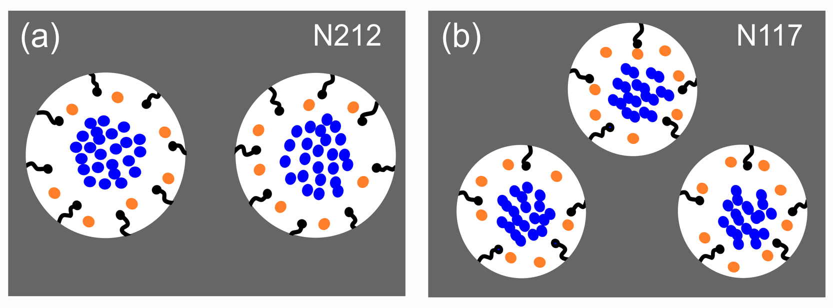
We decomposed the OH region using a constrained classical least-squares (CCLS) fitting routine to identify the different contribution of water species

"Non-bulk" water:
N212 (17%) < N117 (28%).
N117 accommodates less bulk water.



Why do N212 and N117 (identical chemical composition) have different relative contributions of bulk and non-bulk water?

Membrane structure determines water structure



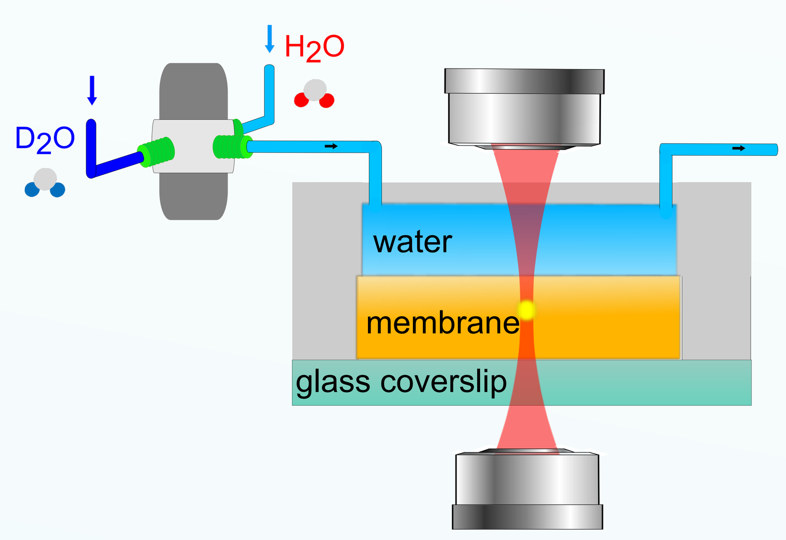
Small angle scattering experements have shown the radius of water channels in N117 is smaller than that in N212[3].

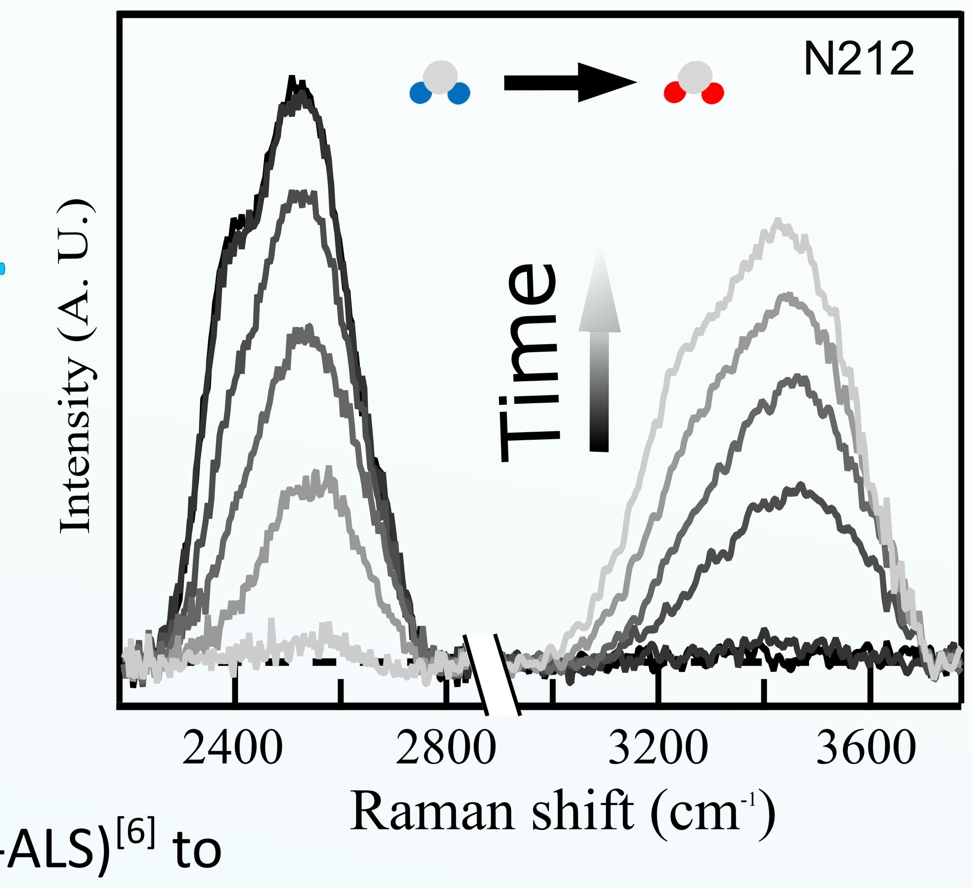
Thus, the area-to-volume ration (A/V) of N117 is larger than N212, assuming the total length of the channels is the same and much larger than the channel radius in both membranes. The water molecules interact more with the membrane structure in N117, and therefore, a larger proportion water is non-bulk water in N117

X.Ling, M.Bonn, S.H.Parekh, K.F.Domke. Angew. Chem. Int. Ed. 2016, 55, 4011 –4015

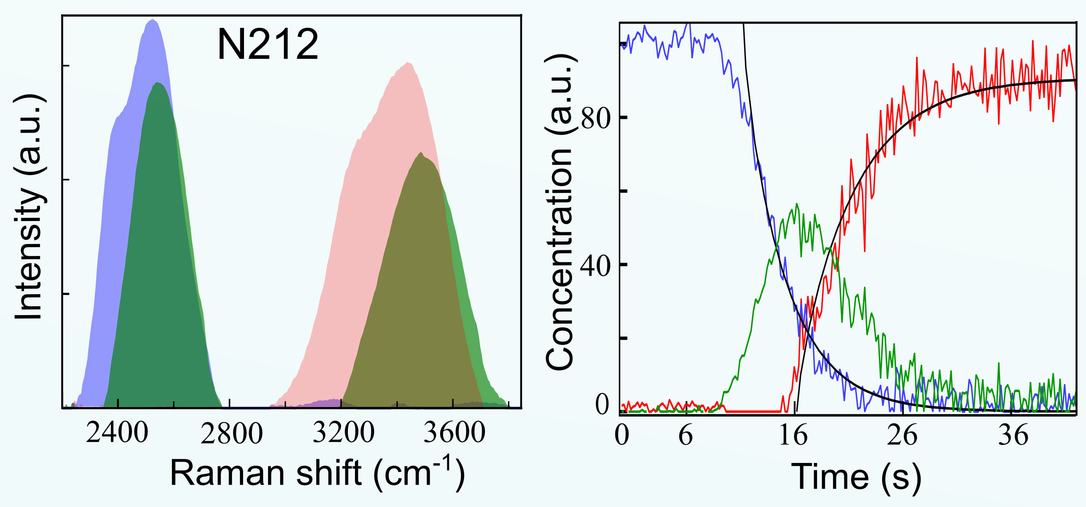
Water transport in Nafion membrane

H_2O/D_2O exchange





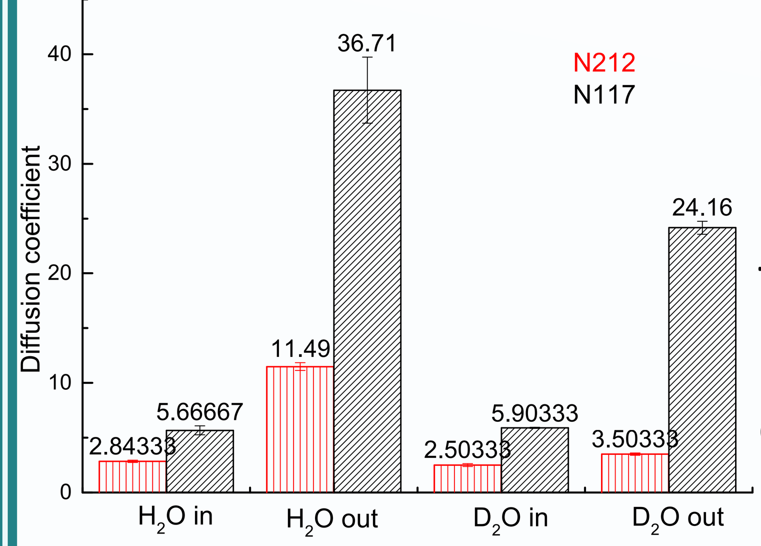
Mutlivariate Curve Resolution-Alternating Least Square (MCR-ALS)[6] to reslove the spectral signature of water species (H_2O, D_2O, HOD).



Left: spectral signatures obtained by MCR-ALS
Right: concentration profile by CCLS using the spectral signatures

The analytical solution to Fick's second law reported by D. T. Hallinan is applied to the concentration profile and the diffusion coefficient is obtained.[7] In N212: (H_2O diffuses in) D = 2.84×10^{-10} m^2/s; (D_2O diffuses out) D = 3.50×10^{-10} m^2/s

Faster water transport in N117 than in N212



In both N212 and N117:
H_2O (diffuses in) < H_2O (diffuses out),
D_2O (diffuses in) < D_2O (diffuses out)
The formation/deformation of HOD speciese is likely the main reason that causes the difference between water diffuses in and out.

The diffusion coefficient of water in N117 is significantly larger than that in N117. The larger propotion of non-bulk water in N117 likely contributes to the differences in transport properties

Summary

Nanoscale chemical constitution and corresponding molecular-scale water–membrane interaction, are significantly different for N117 and N212. The nanoscale architecture of N117 is correlated to faster water tranport and higher proton conductivity.

References:[1]S. Tsushima, et al. Energy Comb. Sci. 37 (2011) 20;[2]M. Falk, Can. J. Chem. 1980, 58, 1495–1501; [3]M. Kim et al. Macromolecules 2006,39, 4775–4787; [5]A. d. Juan et al. Nat. Protocol 10 (2015) 2;[6]Daniel T.Hallinan, et al. Macromolecules 43 (2010) 4667-4678.

We thank M. J. Van Zadel, F. Fleissner, J. Hunger and P. Schäfer for general technical and scientific support and Anke Kaltbeitzel for proton-conductivity measurements.
We gratefully acknowledge funding through FINON-ITN#607842