

### Atomic Force Microscopy Studies of Conductive Nanostructures in Solid Polymer Electrolytes

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Solid polymer electrolytes are a key component in fuel cell as ion conducting barrier between the two electrochemical reactive electrodes and their conductivity significantly determines the performance of the cells.

The conductivity of the electrolyte membranes is typically based on a nanoscale phase separation that results in an ionic conductive network and a stabilizing matrix. In sulfonated ionomers the sulfonic acid groups are solvated and a hydrophilic proton conducting aqueous ionic phase is formed in a self-assembling process upon solidification of the membrane. The hydrophobic polymer back-bones which may be perfluorinated as in case of Nafion-type molecules or aromatic as in case of multi-block copolymers provide mechanical stabilization.

Upon solidification of the polymer solution /dispersion a surface layer with a structure different from the bulk equilibrium structure is formed that depends on the surface energies of polymer and the adjacent material, i.e. humid air or platinum [1]. Consequently, the membrane properties at or close to the surface may differ from the bulk of the membrane and its structure and conductivity are crucial as interface between membrane and electrode/catalyst.

Different types of sulfonated membranes, perfluorinated Nafion<sup>®</sup> (long-side chain molecules) and Aquivion<sup>®</sup> (short side chain molecules) membranes, and aromatic multiblock copolymer membrane named JST (JSR Corp., Japan) have been investigated. Beside the investigation of surfaces freshly cut cross section from Nafion and Aquivion samples have been examined.

For analysis material-sensitive and conducting atomic force microscopy was used to map local adhesion forces, stiffness, deformation, conductivity and surface potential with nanoscale resolution. The following issues will be addressed:

1. Change of the conductivity upon current flow.
2. Size and distribution of conductive area at the surface for different membrane types.
3. Existence and thickness of a surface layer for different membranes.
4. Difference in membranes structure close to the surface (Fig. 1).
5. Ionic structure of the bulk for Nafion<sup>®</sup> and Aquivion<sup>®</sup>
6. Shape of aqueous phase in the bulk of Nafion<sup>®</sup> and Aquivion<sup>®</sup>.
7. Molecular structure of Nafion<sup>®</sup> (Fig. 2) and Aquivion<sup>®</sup>.

8. Deposition of platinum inside a Nafion<sup>®</sup> membrane after accelerated degradation (Fig. 3) [2].
9. Comparison of models for Nafion<sup>®</sup> nanostructure with AFM results.

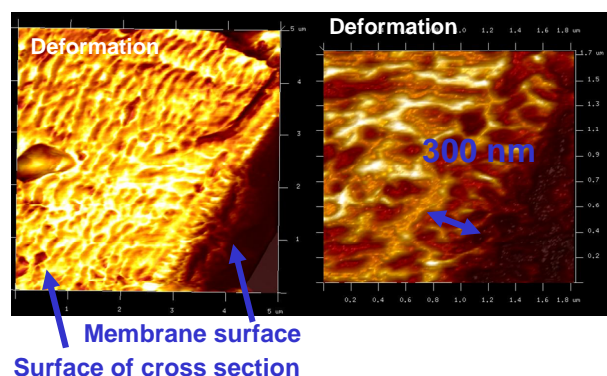


Figure 1: Cross section deformation image of Nafion<sup>®</sup> 112 and zoom into edge structure.

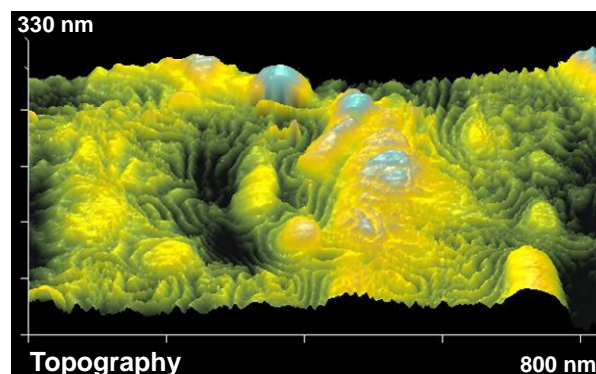


Figure 2: High resolution topography on cross section of Nafion<sup>®</sup> 112

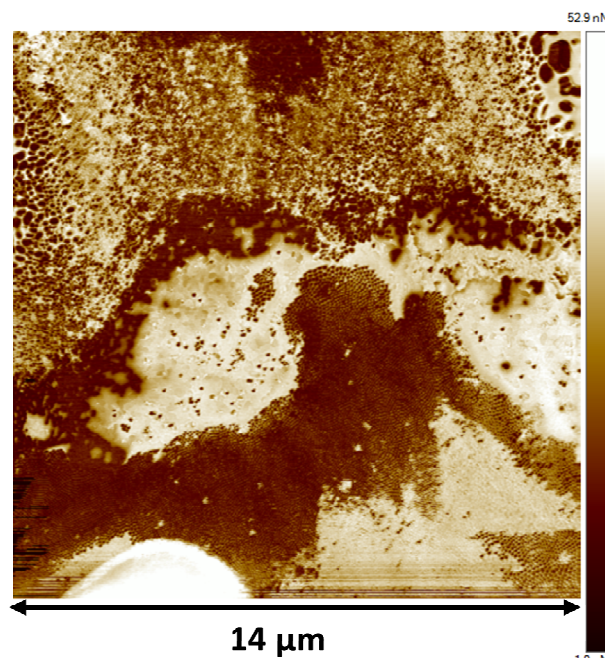


Figure 3: Adhesion image of cross section of Nafion<sup>®</sup> 112 membrane after 1600 h of accelerated degradation under open circuit voltage

- [1] M. Bass, A. Berman, A. Singh, O. Konovalov, V. Freger, *J. Phys. Chem. B* 114, 3784–3790 (2010).  
[2] S. Helmly, R. Hiesgen, T. Morawietz, X.-Z. Yuan, H. Wang, K.A. Friedrich, *J. Electrochem. Soc.* 160, F687-F697 (2013).