

Polymer and Colloid Highlights

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Structural Studies of Radiation-grafted Copolymer Proton Exchange Membranes

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The polymer electrolyte fuel cell (PEFC) is an electrochemical energy conversion device that is particularly attractive for applications including portable electronics, remote power sources, and electric vehicles. The heart of the PEFC device is an electrolyte membrane (proton exchange membrane, PEM), which has two primary roles: enable the transport of protons from anode to cathode and prevent the passage of the reactant gases and electrons. Radiation-grafted ion-containing copolymers are a potentially low-cost and versatile route for preparing PEM materials. The current focus regarding PEMs revolves around improving the membrane–electrode interface, the chemical stability, the mechanical integrity, and last but not least the proton conductivity. The optimization of PEMs requires a careful balance between these properties, and is intimately related to the nano-scale structure of the hydrophilic domains of the PEM. The characteristic scales of related heterogeneities range from nanometers to hundreds of nanometers, and therefore, we relied on small-angle neutron- and X-ray scattering to investigate the structure found in these polymer electrolytes. Structural findings, correlated with synthesis and fuel cell-relevant properties have been reported in a series of articles,^[1–6] and here we summarize our current understanding of the structure of pre-irradiation grafted copolymer PEMs.

Graft copolymers represent a class of polymers in which two dissimilar polymer constituents may be combined in a versatile way. The base polymer is usually a semi-crystalline commodity product, and the grafts are obtained by radical polymerization. Due to the processing conditions, the base polymer has a predefined anisotropic structure, which is preserved at moderate grafting level. However, upon increasing grafting, the grafted polymer chains swell the amorphous domains and deform the base film structure. Grafting takes place predominantly in the amorphous phase of the semi-crystalline base polymer, and therefore, the spatial distribution of ionic groups attached to the pendent chains is not uniform: certain domains of the PEM are rich in hydrophilic clusters, while un-grafted domains are devoid of them. The hydrophilic phase is thus not continuous, which has a negative impact on the connectivity of the aqueous phase – *i.e.* non-grafted crystalline domains impede the percolation of the hydrophilic domains – especially at low level of hydration. By optimizing the crystallinity and the distribution of crystallites in the base polymer we expect to improve the PEM, in which

proton conductivity is strictly proportional to water. The proton conductivity is governed by the percolation, the connectivity, and the tortuosity of the aqueous phase, which are found to be rather disordered, which explains the rapid loss in proton conductivity at lower water content: the tortuosity rapidly increases. This highlights that the water content of the aqueous phase cannot be decreased without losses in conductivity. In contrast, the tortuosity of well-defined domains (*e.g.* cylindrical) is independent of the volume fraction, as the geometry-limited self-diffusion coefficient approaches the same value in the long-range limit. Therefore, it can be expected that the dependence of the long-range proton diffusion coefficient on the volume fraction of well-defined aqueous domains is not as critical as in disordered domains (Fig. 1).

To conclude, structural studies have provided insights into fundamental properties of radiation-grafted copolymer PEMs, and pointed out new potentials in the development of these materials.

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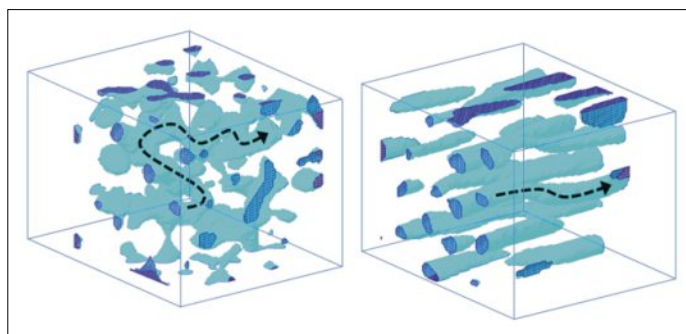


Fig. 1. Left: the aqueous phase is highly irregular, and the transport of protons is slowed down. Right: the aqueous network is formed by rather parallel channels, which facilitates the transport.

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