Physical theory of ionomer aggregation in water

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Chemical degradation of ionomer molecules causes continuous changes in microstructure and transport properties of polymer electrolyte membranes (PEMs) [1]. These changes are associated with decreases in electrochemical performance, mechanical robustness and lifetime of polymer electrolyte fuel cells. Ionomer degradation mainly results from chemical attack by radicals, which are formed during fuel cell operation at metal ions or platinum deposits in the membrane. Radical reactions lead to the shortening of hydrophobic backbones or the loss of terminal ionic groups. These chemical processes transform the thermoelastic and electrostatic properties of the membrane. A systematic understanding of ionomer aggregation is vital to connect the primary chemical architecture to elastic, electrostatic and transport properties of the PEM.

In this talk, we will present a physical theory of ionomer aggregation in water. The analytical formulation of the model accounts for interaction terms between hydrophobic polymer groups, ionic groups, protons, and water. Their interplay governs the equilibrium state of polymer aggregates and the corresponding proton distribution in the surrounding electrolyte. As a first approximation ionomer molecules are described as a stiff rod, justified by the exceptional persistence length of polytetrafluoroethylene-derived polymers with sidechains and charged end groups. We have devised two models to explore various limits. Their main difference is whether electrolyte is absorbed into or expelled from bundles. The presence of electrolyte within the bundle induces a non-uniform charge distribution at the surface of the rods. With these models in hand, we determine the size of the most stable aggregates as a function of ionomer density in water, grafting density of sidechains, sidechain length. Results on ionomer bundle formation will be discussed in view of implications for water sorption properties and degradation effects of PEM.

[1] L. Ghassemzadeh, et al., *J. Power Sources 196*, 2490 (2011); M. Danilczuk, et al., *Macro Lett. 1*, 280 (2012); R. Borup, et al., *Chem. Rev. 107*, 3904 (2007); M. Rodgers, et al., *Chem. Rev. 116*, 6075 (2012); C. Lim, et al., submitted to *J. Power Res.* (2013).