

Degradation Induced Changes in Structure-Property Relationship of Perfluorosulfonic-acid (PFSA) membranes

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Perfluorosulfonic-acid (PFSA) membranes are the most widely studied ionomers for their common use in polymer-electrolyte fuel-cell (PEFC) applications as well as in other electrochemical energy storage and conversion devices such as redox flow batteries. Nafion[®] membrane, a commercial PFSA ionomer, has been considered as the benchmark material for understanding the role of ion-conductive polymers in PEFCs but also for developing alternative materials. Nafion[®] membrane's high proton conductivity and good mechanical stability are critical factors for achieving the desired cell performance and durability, respectively. In PEFCs, the chemical and mechanical stressors are synergistically influenced by each other as well as the temperature and humidity, making it difficult to characterize the role of individual stressors on overall properties. Nevertheless, transport and mechanical properties are strongly correlated through the chemical interactions, water uptake, and membrane morphology. Thus, changes in these properties during operation (e.g., degradation) could be better understood by investigating the changes in the nanostructure.

Our goal in this talk is to demonstrate a (nano)structure-property map for membranes that were aged and failed in various degradation modes based on accelerated-stress testing (AST) protocols. To eliminate the chemical stressors from the environmental effects during a degradation process, membranes that were hygro-thermally aged in similar environments are also studied. Therefore, we will present and compare the changes in the membrane's structure and properties due to various mechanisms: ex-situ vs. in-operando, and hygro-thermal ageing vs. chemical degradation (e.g., AST modes).

The nanostructure of membranes degraded or aged via various protocols are studied using Small- and Wide-Angle X-Ray Scattering (SAXS/WAXS) technique from which the characteristic domain spacing of the membrane are identified. Moreover, changes in the crystallinity of the membrane due to degradation are explored by analyzing the WAXS patterns. In addition, the water-uptake behavior was also studied by measuring the weight change as well as the equivalent weight of the samples to assess accurate values for water content. Aged and degraded membranes' nanostructural features and water-uptake properties are correlated, and then compared against fresh membranes to identify the effect of chemical and mechanical stressors on the membrane's structure-property relationship. Lastly, how these structural, chemical, and mechanical properties are affecting each other and the membrane's macroscopic properties are discussed by means of a membrane model that uses the concept of thermodynamic equilibrium. With the help of the model and based on the experimental evidence, we will elaborate how chemical/mechanical stressors could control the failure mechanisms and explain the observed differences in the nanostructure due to different degradation modes, and then discuss the potential implications of our findings for optimizing the membrane performance-durability relationship.

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