Element Species Determination in Polymer Electrolyte Membranes

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Polymer electrolyte membranes (PEM) are polymers which act as separator in an electrochemical cell and allow ionic charge flow to close the circuit. Widely used membranes are perfluorinated sulfonic-acid (PFSA) ionomers (e.g. Nafion™), a class of ion-conducting polymers with remarkable ion conductivity and chemical-mechanical stability. A nanoscopic water system around the sulfonic acid capped side-chains of the otherwise hydrophobic polymer allows the ion transport. Only *approx.* 14 molecules of water per sulfonic group are present in the fully hydrated state. In vanadium redox flow batteries (VRFB) ideally only protons are transported. The weak ion selectivity of Nafion™ is the main cause for the transportation of vanadium, briefly vanadium crossover, in VRFBs a system we have investigated more closely, lately. The consequences of crossover are a concentration imbalance and a self-discharge of the battery, which leads to a decrease of the capacity.

The development of efficient energy storage systems is crucial for the transformation towards a renewable energy based economy. The VRFB has a great potential as a commercial electrochemical energy storage system due to properties including, but not limited to, no cross-contamination, a long cycle-life and a theoretically unlimited capacity. VRFB consists of two half-cells, which are linked to electrolyte tanks and separated by a membrane. The membrane plays a major role in overall cell performance.

So far, vanadium transportation models, which include diffusion, migration, electroosmotic convection and pressure gradients, are inconsistent. There is no agreement in the literature on the diffusion coefficients of vanadium species (e.g. published diffusion coefficients of V^{2+} are located between $3.13 \cdot 10^{-12}$ m²s^{-1} and $9.44 \cdot 10^{-12}$ m²s^{-1}) indicate that the vanadium crossover is not well understood and there is a lack on a more fundamental level. Since the membrane transport is the rate-determining step of the crossover as well as of the proton exchange it is extremely important to understand these phenomena on a fundamental level. This will eventually allow us to design better membranes. Alternative materials need to show equivalent performance compared with Nafion™ and ideally be more selective regarding ion cross-membrane transport.

There are several options to approach the chemistry *i.e.* the interaction of dissolved and bound ions inside the confined water body of ionomeric membranes. Vanadium ions are a versatile model as UV/VIS data can be used to distinguish between the 5 species V^{2+}, V^{3+}, VO^{2+}, VO_2^{+} and $V_2O_3^{3+}$ of the electrolyte. Infrared spectroscopy has been applied to study the interaction of sulfonic groups and the ions. Molecular dynamic modeling is another approach to study the distribution and distances of ions. We now introduce X-ray absorption near edge structure spectroscopy (XANES) to study species and species changes inside Nafion™ and a novel membrane based on poly(1,1-difluoroethylene) (PVDF) [1]. We evaluated the methods and investigated the influence of irradiation, temperature and hydration on the measurements.

[1] Li, X.; dos Santos, A. R.; Drache, M.; Ke, X.; Gohs, U.; Turek, T.; Becker, M.; Kunz, U.; Beuermann, S. Polymer Electrolyte Membranes Prepared by Pre-Irradiation Induced Graft Copolymerization on ETFE for Vanadium Redox Flow Battery Applications. *J. Memb. Sci.* **2017**, *524* (15 February 2017), 419–427. https://doi.org/10.1016/j.memsci.2016.10.053