Investigation on Vanadium Crossover in Nafion™ and Novel PVDF-Based Membranes for Vanadium Redox Flow Batteries

Christian Lutz[1], Sabine Beuermann[2], Thomas Turek[3], Ulrich Kunz[3], Ana Guilherme Buzanich[4], Martin Radtke[4], and Ursula Elisabeth Adriane Fittschen[1]

[1] Clausthal University of Technology, Institute of Inorganic and Analytical Chemistry, 38678 Clausthal-Zellerfeld, Germany.
[2] Clausthal University of Technology, Institute of Technical Chemistry, 38678 Clausthal-Zellerfeld, Germany.
[3] Clausthal University of Technology, Institute of Chemical and Electrochemical Process Engineering, 38678 Clausthal-Zellerfeld, Germany.
[4] Federal Institute for Materials Research and Testing (BAM), 12489 Berlin, Germany.

email address: christian.lutz@tu-clausthal.de

Vanadium redox flow batteries (VRFB) are currently one of the most promising candidates for stationary energy storage. For large scale applications the ion conducting membranes currently in use need to be improved. Ideally, they need to become more cost efficient and selective regarding the vanadium crossover. For a better understanding of the vanadium crossover, the development of reliable analytical methods and procedures, that elucidate uptake and transport of vanadium ions in the membrane, is necessary [1].

First, we present the uptake of V^{2+}, V^{3+}, VO^{2+}, VO_2^{+} and $V_2O_3^{3+}$ in Nafion™ and in a novel membrane based on poly(1,1-difluoroethylene) (PVDF). In preliminary discharge/charge experiments the ETFE-based membrane, the precursor of PVDF-based membrane, performed comparable to Nafion™ [2]. The methods of choice for speciation are UV/Vis and X-ray absorption near edge structure spectroscopy (XANES). According to the results, $V_2O_3^{3+}$, formed from VO^{2+} and VO_2^{+}, diffuses also into the membrane. In present models, the diffusion of $V_2O_3^{3+}$ is neglected.

In addition, we study whether reactions could take place inside the membranes' nanoscopic water body using XANES. Exposing Nafion™ from one site with V^{3+} and from the other site with VO_2^{+} realized the experiment. The results verified that VO^{2+} was formed inside the membrane. However, in present models reactions inside the membrane are neglected, too.

[1] Lutz, C.; Fittschen, U. E. A. Entwicklung neuer Prozeduren zur Elementbestimmung und Speziation in Vanadium Redox Flow Batterien, *Tagungsband 3. Niedersächsisches Symposium Materialtechnik* **2019**, 229-240. https://doi.org/10.21268/20190312-0
[2] 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