VANADIUM REDOX FLOW BATTERY - MEMBRANE SELECTION AND CHARACTERIZATION

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The increasing share of renewable energy sources in the total energy production emphasizes the need for a reliable and cheap stationary energy storage. Such a tool allows to baffle hardly predictable non-stabilities in output power of photovoltaics or wind turbines on the power transmission level. Vanadium redox flow battery (VRFB) appears as a promising solution for the stationary energy storage as it offers high efficiency (80% DC-DC), foolproof arrangement of decoupled power (kW) to capacity (kWh), extended durability and fast demand response. However, the broader commercialization of the technology is still obstructed by relatively high investment costs.

In redox flow batteries, electrolytes are not stored in the battery construction but in an external tank and are continuously pumped through the battery stack where electrical energy is transformed on inert electrodes into chemical during charging and conversely during discharging. Battery stack is composed of several serially connected cells. Each cell consists of positive and negative half-cells which are mutually separated typically by ion-exchange membrane. In VRFB, both electrolytes comprises vanadium salts dissolved in diluted sulfuric acid (i.e., (VO₂)₂SO₄ and VOSO₄ in positive electrolyte and VSO₄ and V₂(SO₄)₃ in negative electrolyte). Price of the ion-exchange membrane, one of the key components of the battery stack, represents 5 - 15 % of the overall costs typically. Long term durability of membrane in acidic electrolytes is vitally necessary for VRFB function.

In our contribution we present the results of the broad systematic study focused on the effect of membrane properties (charge, equivalent weight, thickness, method of preparation, homogeneity) on VRFB operation. The various types of commercially available ion-exchange membranes were characterized with the respect to the properties relevant for VRFB operation such as: i) through-plane ionic conductivity in the environment of VRFB cell, ii) permeability for vanadium ions of different oxidation states, iii) performance in VRFB single-cell under well-defined conditions (i.e., vanadium and sulfuric acid concentration, constant temperature) and iv) durability in the presence of oxidizing V^v electrolyte.

The results obtained from permeation measurement indicate that effective diffusion coefficient of V³⁺ ions is significantly lower than of VO²⁺ ions in all studied ion-exchange membranes. It was found that the difference



Figure 1 – Energy efficiency of VRFB cells comprising Nafion membranes of different thicknesses and operating at different current densities.

between effective diffusion coefficients of both vanadium forms is dependent on inner structure of hydrophobic and hydrophilic domains in ion-exchange membrane. The battery energy efficiency of cells comprising different membranes was evaluated from charge discharge cycles at different current densities. Optimal membranes for VRFB both with the respect to the energy efficiency of charging discharging cycle and maximal power output were identified. Considering Nafion perfluorinated cation-exchange membranes of different thicknesses, the energy efficiency as a function of membrane thickness and cell current density is shown in Figure 1. Perfluorinated cation-exchange membranes are the solution when high power and long durability is required. Anion-exchange membranes show lower vanadium crossover and thus appears more suitable for the application when low maintenance is required.