

Investigation of the Hydrogen Evolution in All-Vanadium Redox Flow Battery

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Efforts have been made toward improving the VRFB performance with modifying electrodes, membranes, electrolytes and cell configuration. However, self-discharge induced by vanadium ion crossover and asymmetrical valence of vanadium ion in positive and negative electrolytes caused by side reaction were observed during charge-discharge cycling. These studies investigated the mechanisms for the capacity fade of the system as well as provide further insights for optimizing the long-term operation. Recently, vanadium crossover through the membrane has been effectively reduced by alternating the polymer morphology or employing the anion exchange membrane. However, the impact on the side reaction in the VRFB from an electrode perspective was not extensively discussed.

We have recently successfully demonstrated the possibility to integrating a reference electrode into the VRFB. The presence of a reference electrode allowed studying the processes in positive and negative electrode individually. One of our important findings was that the potential of the negative electrode lays c.a. 350 mV below that of a dynamic hydrogen reference electrode at 50% state of charge (SoC). The lower potential suggests the possibility for hydrogen evolution and V^{2+}/V^{3+} reactions co-existence on the negative side of the cell. Moreover, we also observed a significant amount of gas generated by plunging a piece of platinum foil into the negative electrolyte. The magnitude of the driving force of this reaction, however, partly depends on the proton concentration and the SoC according to the Nernst equation. Since the vanadium ions are typically dissolved in the concentrated (3-5 M) sulfuric acid, the Nernst potential for the hydrogen evolution shifts positively due to the high proton concentration. For the V^{2+}/V^{3+} couple, the Nernst potential becomes more negative as the SoC increases and therefore increases the driving force.

In this work, we demonstrate a simple protocol to evaluate in a quantitative manner the impact of the carbon paper electrode material on the gas evolution side reaction. The protocol is based on an adequate combination of characterization techniques (electron microscopy, gas adsorption, electrochemical surface area, x-ray photoelectron spectroscopy) to probe the crucial material properties (surface area and chemistry) affecting the rate of the side reaction by buoyancy measurements.

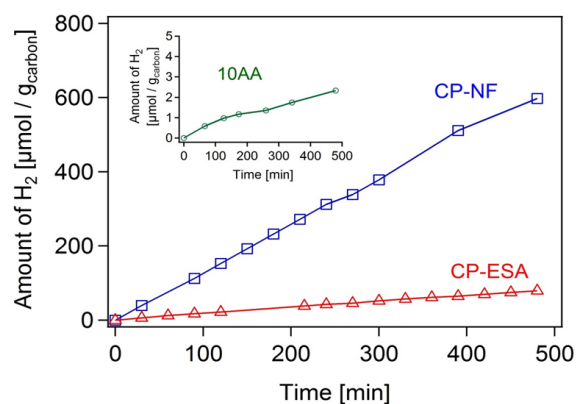


Figure 1. Amounts of hydrogen in moles that are generated as a function of time for CP-NF, CP-ESA and 10AA.

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