Electrochemical analysis of the performance loss in all vanadium redox flow batteries using different cut-off voltages

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ABSTRACT

The performance loss observed in vanadium redox flow batteries over time strongly depends on the material and the cycling conditions. We have chosen 1.65 V and 1.8 V as the cut-off voltages in order to compare the performance loss and the risk of evolving hydrogen on the negative side and CO_2 on the positive side. The 1.8 V experiment was expected to show stronger degradation because of the higher risk of hydrogen and CO_2 evolution due to the higher maximum half-cell potentials. To address this issue we implemented a reference electrode at the inlet of the negative half-cell of a 10 cm^2 test cell. The discharge process on the negative half-cell was assumed to be the process with the highest overpotential after running 50 charge and discharge cycles. After 50 cycles the reduction of V(II) remained the favored reaction compared to the HER in the negative side, even though the overpotentials for both reactions increased significantly. As for the positive half-cell, the risk of CO_2 evolution increased with increasing cut-off voltage. The higher cut-off voltage led to a higher rate of degradation, but it also showed a better overall performance. The potentials in the half-cells were changing dynamically with each cycle depending on the degradation rate of the electrode and the state of the electrolyte. An imbalance of the electrolyte could be observed by measuring the half-cell open circuit potential after each charge and discharge process. The obtained results can be used for the diagnostics and optimization of VRFB systems in order to achieve maximum system output at reasonable risks of parasitic reactions and degradation.

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1. Introduction

Redox flow batteries (RFB) are a promising technology for the rising share of renewable energies which are integrated in the electrical grid. The vanadium redox flow battery is one of the best known systems among various flow chemistries [1–4]. One advantage of the vanadium system compared to other redox flow systems is that only one element in different oxidation states is used in both half-cells. Therefore, a possible cross-contamination through the membrane does not lead to an unwanted side-reaction that could damage the cell and decrease its performance [4]. Redox flow batteries are supposed to be very durable systems with an expected life time of 10 years and several thousands of cycles [1]. But degradation mechanisms of system components, such as electrodes and membrane, are so far only scarcely addressed. The major reasons for performance loss are the degradation of the electrodes [5–7], the degradation of the membrane [8,9] and the imbalance of the electrolyte that can appear either due to

cross-over and drag-effects [10,11] or due to side reactions, which are expected to take place during the charge process. One of these side reactions is the hydrogen evolution reaction (HER) [12], which exhibits an onset potential of −0.5 V vs. Ag/AgCl (3 M KCl) in 2 M sulfuric acid but competes with the V(III) reduction at the negative side. The reduction of V(III) is the preferred reaction, which is why the onset potential of the HER is shifted towards more negative potentials in the presence of V(III). For the positive half-cell, in which the reaction V(IV) to V(V) takes place, the oxidation of carbon to CO_2 is one of the most important side reactions [13]. The degradation of the electrodes is attributed to the oxidation of the carbon surface, which causes a change of the surface functional groups and a loss of electrochemically active surface area [6]. These effects have a very strong impact on the performance of the negative half-cell [6,14]. The electrochemical degradation of the electrodes was found to cause a loss of electrode mass on the negative side. The reason is suspected to be the evolution of hydrogen damaging the fibers. Therefore, the cut-off voltage for charging is usually set to 1.6 V in order to prevent the negative half-cell from reaching more negative potentials [15]. This leads to the need to reduce the specific overpotentials of the half-cells in order to achieve higher states of charge (SOC). A major part of the

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appearing overpotentials can be ascribed to ohmic overpotentials [16,17], which are dominated by the membrane resistance, mass transport induced overpotentials that are controlled by the pump rate and kinetic overpotentials [18], which strongly depend on the electrode material. Since the ohmic resistance and the pump rate remain more or less constant throughout the experiment, it is the increase of the kinetic overpotentials, which decreases the overall cell performance. Therefore, an increased cell-voltage can result in different half-cell potentials for the chosen operating conditions, which can change over time, since the system is degrading. The rate determining process strongly depends on the operating conditions e.g. the flow rate of the electrolyte, the compression of the felt or the composition and concentration of the electrolyte [19–26]. Also the rate determining process can be changed over time due to degradation and imbalance of electrolyte. At the beginning of the experiment, ohmic losses and mass transport limitation are rate determining for the system. With operating time, the kinetic losses increase, especially for the negative half-cell, which leads to an additional loss of performance. G. Merei, S. Adler, D. Magnor, D.U. Sauer [25] have presented a model for the simulation of full systems including performance losses and the hydrogen evolution reaction. But so far, there is no reliable model which takes into account the degradation of the electrodes. M. j. Watt-Smith, P. Ridley, R. g. a. Wills, A. a. Shah, F. c. Walsh [19] have demonstrated a system with two cells in series. The first cell was used for cycling under varying conditions, while the second cell was used for monitoring the open circuit voltage. We present an alternative way of monitoring the state-of-health of the system without using a second cell. The correlation of different cut-off voltages and the dynamic development of the corresponding half-cell potentials can give an insight into the limiting processes as well as the degradation at specific operating conditions. The results could be used to develop new theoretical models and improve the risk/return spectrum for the VRFB by monitoring large scale (as well as lab-scale) VRFBs systems during cycling.

In this work, we compared the operation of a $10 \, cm^2$ cell with different cut-off voltages in order to determine the half-cell potentials [27] and the risk of hydrogen evolution on the negative side and CO_2 evolution on the positive side. Using the reference electrode we could show that the risk of evolving hydrogen does not solely depend on the cut-off voltage, because the V(III) reduction is the preferred reaction compared to the HER on heat-treated carbon felt electrodes. The degradation of the felts that appears during cycling is compared for both cut-off voltages. Even though a higher cut-off voltage led to higher electrode degradation and also a higher probability for CO_2 evolution, the overall performance of the system was better comparing the first 50 cycles. This relationship might change if more than 50 cycles would be considered. However, the reference electrode provided valuable data during cycling, which allowed us to determine the status of the individual half-cells.

2. Experimental

The hydrogen evolution reaction (HER) was investigated in a three electrode setup. GFA6 felts (by SGL Carbon, Germany) were heat-treated at $400 \, °C$ for 25 h in air atmosphere (thermal oxidation) [28] and used as the electrode. The working electrode (WE) and the counter electrode (CE) consisted of a carbon felt that was pulled over a glassy carbon rod. The WE usually had a size of $0.25 \, cm^2$ $(5 \times 5 \times 6 \, mm^3)$ and the CE was at least 5 times larger than the WE. A saturated calomel electrode (SCE) with 230 mV vs. standard hydrogen electrode (SHE) was used as the reference electrode (REF).

The activity of the carbon felt towards the HER was first investigated with a linear sweep protocol in 2 M sulfuric acid.

Afterwards the felts were measured in 0.16 M V^{3+}, 2 M H_2SO_4, 5 mM H_3PO_4 solution, which was prepared by charging 1.6 M V^{3+}/V^{4+}, 2 M H_2SO_4, 0.05 M H_3PO_4 commercial electrolyte (by GfE mbH, Germany) with a 50 cm^2 flow-by cell and diluting it with 2 M sulfuric acid.

The felts that were investigated underwent different pretreatments. The freshly heat-treated felt was measured 2 h after thermal oxidation of the carbon felt at $400 \, °C$ in air atmosphere. The second sample was the heat-treated felt, which was stored in air atmosphere and at room temperature for 90 days. The electrochemically degraded felts underwent a charge/discharge cycling protocol that is described below. Before measuring the cycled felt, it was washed with deionized water and dried in air atmosphere.

2.1. Cycling experiment

A Micro flow cell® with flow-through design (by Electrocell A/S, Denmark) with $10 \, cm^2$ electrodes was used for cycling. The electrodes were heat-treated GFA 6 felts. Heat-treatment was performed in air atmosphere at $400 \, °C$ for 25 h. All cycling experiments were conducted with a Nafion® 117 membrane (by DuPont) and 1.6 M V^{3+}/V^{4+} in 2 M H_2SO_4 and 0.05 M H_3PO_4 aqueous solution (by GfE GmbH, Germany) at room temperature. The membrane was used as received. The volume of the electrolyte was 100 mL per tank. The current collector plates were glassy carbon (GC) plates (by HTW GmbH, Germany). An Ag/AgCl (3 M KCl, 215 mV vs. SHE) reference electrode (by Metrohm AG, Switzerland) was introduced at the inlet of the negative side as described by J. Langner, J. Melke, H. Ehrenberg, C. Roth [29]. The reference electrode was used to record the half-cell potentials during cycling and for further half-cell experiments. The electrolyte tanks contained a magnetic stirrer and were refilled with argon every 24 h.

Cycling was performed with a Scribner 857 test bench (by Scribner Associates inc., USA). The current density was 50 mA cm^{-2} for all cycling experiments. The cut-off voltage was 0.8 V to 1.65 V (experiment 1) and 0.8 V to 1.8 V (experiment 2). The flow rate of the electrolyte was 50 mL min^{-1} during cycling and 100 mL min^{-1} during UI polarization curve measurement. After 50 cycles the electrolyte was renewed and 3 additional cycles were recorded. The polarization curves were measured with fresh electrolyte before and after cycling at a SOC of 50 % (Open circuit voltage = 1.4 V). Full-cell EIS measurements have been carried out after each charge and discharge step with 0.01 V AC and 0 V DC voltage in a frequency range between 10 kHz to 0.1 Hz.

3. Results and discussion

3.1. Comparing the rate of degradation with different cut-off voltages

The overall cell voltage that was measured during galvanostatic cycling results from the individual half-cell potentials. And the half-cell potentials strongly depend on the activity of the electrode material towards the respective reaction and the overpotentials that appear due to the membrane resistance and mass transport limitation. By varying the cut-off voltage we can study the overpotentials of the half-cells and explain which particular reaction suffers the most from the decrease in performance due to degradation of the electrode.

In Fig. 1a) the input and output energy are plotted against the corresponding cycle. Both experiments exhibited a loss of performance over 50 cycles. The output energy decreased by 76 % to 78 % after 50 cycles. That includes all side reactions and possible electrolyte imbalance. By exchanging the electrolyte, we can neglect the losses caused due to an imbalance of the