Overpotential measurements with reference electrodes in redox flow batteries

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The all-vanadium redox flow battery is a promising system which fulfills all the requirements of a storage device for electronic grid integration of renewables [1]. Due to the separation of energy storage and energy conversion, energy and power density can be scaled independently. Other advantages of the system are a high efficiency and fast response time. This paper deals with the investigation of overpotential distributions in all-vanadium redox-flow batteries (RFB).

It is important to measure the overpotential of each half-cell for understanding the losses arising from the electrodes. The efficiency of the electrodes is determined by their electric conductivity, their surface area and the electrochemical behavior towards the respective reactions i.e. oxidation and reduction of vanadium ions in acidic solution. Thermal treatment of the carbon based electrodes leads to oxidized surfaces which show in general a much better performance [2]. Current-voltage characteristics or so called polarization curves of the complete system (RFB) [3, 4] give only global information. These cannot be separated into the individual electrode contributions or the voltage drop due to the restistance.

In our work we added reference electrodes to our RFB test system. The system was built up with a test cell containing pristine or thermally treated SGL carbon material GFA 6 as electrode and a Nafion 117 membrane as separator. As electrolyte 1 M $VOSO_4$ dissolved in 4 M H_2SO_4 was used. By measuring the voltage between the reference electrode and each half-cell electrode it is possible to determine the potential of each electrode separately [Figure 1]. From this the overpotential of each side can be determined [Figure 2]. With the present setup the positive half-cell potential contains all the membrane losses, too. These can be estimated by measurements of the internal resistance of the cell by impedance spectroscopy during the experiment.

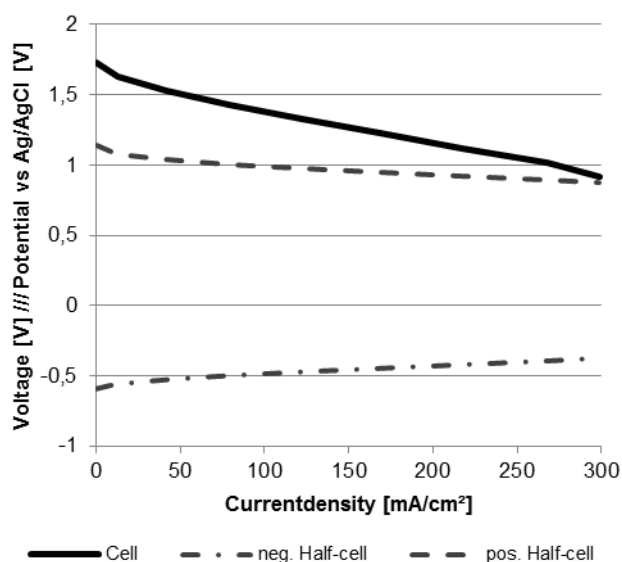With this setup we investigate the losses of variously treated electrodes and membranes.

Figure 1: Polarization curve of the RFB with cell voltage and potential of each half-cell.
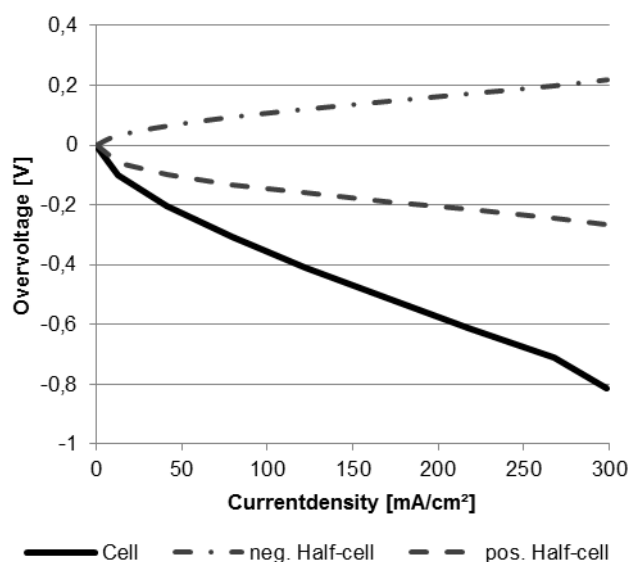

Figure 2: Overpotential of the cell an each half-cell. Cell and positive side overpotential is iR corrected.

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