Polarization curve measurements combined with potential probe sensing for determining current density distribution in vanadium redox-flow batteries

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HIGHLIGHTS

- Solid phase potential probes are applied to a vanadium redox-flow battery (VRFB).
- A method for determining the felt resistance of the VRFB is presented.
- Effect of different carbon felt compression rates on felt resistance is shown.
- Known felt resistances allow the determination of localized current densities.

GRAPHICAL ABSTRACT
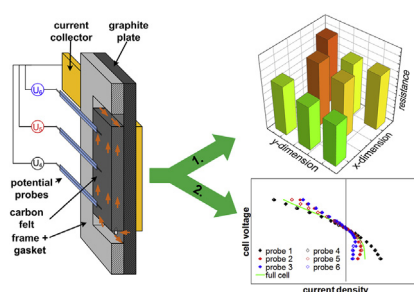
ABSTRACT

Potential probes are applied to vanadium redox-flow batteries for determination of effective felt resistance and current density distribution. During the measurement of polarization curves in 100 cm^2 cells with different carbon felt compression rates, alternating potential steps at cell voltages between 0.6 V and 2.0 V are applied. Polarization curves are recorded at different flow rates and states of charge of the battery. Increasing compression rates lead to lower effective felt resistances and a more uniform resistance distribution. Low flow rates at high or low state of charge result in non-linear current density distribution with high gradients, while high flow rates give rise to a nearly linear behavior.

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1. Introduction

The change in the production of electrical energy from fossil fuels to renewable energy sources increases the demand for electrical energy storage systems compensating the intermittent nature of renewable energy sources. Redox-flow batteries among others are promising devices due to their capability of separately customizing power and energy capacity by cell design and tank size, respectively. Although a number of redox couples are possible the all vanadium redox-flow battery (VRFB) is the most common one [1–3]. The VRFB electrolyte contains vanadium in four different oxidation states used as electrochemically active species that

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undergo redox-reactions during charging or discharging. While charging V^{3+} is reduced to V^{2+} at the negative electrode and VO^{2+} is oxidized to VO_2^+ at the positive electrode. The reverse reactions take place during discharging:

$$V^{2+} \rightleftharpoons V^{3+} + e^- \qquad (1)$$

$$VO^{2+} + H_2O \rightleftharpoons VO_2^+ + 2H^+ + e^- \qquad (2)$$
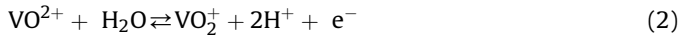
Although commercial VRFBs are already available, further cell improvement is necessary to reduce the power specific costs of the system. Besides new developments in the field of electrocatalysts [4–6], membranes [7–12] and electrolytes [13–16], flow field design and flow strategies become more important. Ma et al. studied the effect of switching the flow rate from a low to a high value, if the voltage increases to a specific threshold during charging or discharging, on the system efficiency [17]. Tang et al. modeled concentration overpotentials and pressure drop losses within a flow battery stack of 40 cells and found that a variable flow rate with a flow factor of 7.5 yielded the highest system efficiencies [18]. Rudolph et al. calculated the flow distribution within a multi inlet cell. The highest utilization was achieved using only one inlet and two outlet channels at the opposite endings of the cell [19].

Different flow field designs were investigated in several studies [20–25]. Xu et al. compared cells with serpentine and parallel flow fields to cells without flow fields by three dimensional modeling. The serpentine flow field design resulted in an even overpotential distribution across the cell, a good mass transport into the felt and a low pressure drop across the cell [20]. Yin et al. developed a three dimensional model to describe an interdigitated redox-flow battery, that predicts a homogenous flow distribution if the land width and flow rate become sufficiently high.

As modeling needs experimental validation, the measurement of current density distribution is essential to confirm homogenous current density and overpotential. While this is a relatively common tool in fuel cell research [26,27], there are only a few publications dealing with current density distribution in redox flow batteries.

Hsieh et al. used shunt resistors with gold-plated current collector segments or divided segments within the bipolar plate to measure the current density distribution during charging and discharging experiments [28]. The measurement setup using divided segments of the bipolar plate seemed to be beneficial for a higher accuracy by decreasing the amount of lateral currents but also lowered the cell performance, due to higher contact resistances. Clement et al. used a printed circuit board with segmented shunt resistors for determining the current density in each segment [29]. These authors used a serpentine flow field bipolar plate which was partially segmented by machining a grid from the back side of the bipolar plate. This reduced the lateral currents and allowed a precise measurement of current density distributions within cells made of different carbon paper electrodes. In a split cell setup the difference between a heat treated electrode and an untreated electrode containing 5% of PTFE was very significant. However, the expensive setup, the susceptibility to corrosion in case of electrolyte leakages and the challenging application to large cells are drawbacks of these methods.

Our approach is the development of a more robust, inexpensive method to measure the current density distribution based on potential probes. Aaron et al. used dynamic hydrogen reference electrodes to investigate the in-situ kinetics of a VRFB [30]. A quite similar setup was applied by Ventosa et al. through sandwiching a silver–silver sulfate reference electrode between two layers of membrane separating the positive and negative electrode [31]. Liu et al. studied the electrolyte phase potential distribution in the positive electrolyte using platinum wires covered by a layer of PTFE [32], which allowed to localize the main reaction zone within the porous electrode. The potential probes used in these three works allowed to measure the liquid phase potential and to determine overpotentials as well as ionic resistances. These experimental data are viable for improving the kinetics but they are not necessarily helpful to check for a homogeneous current density distribution, since the liquid potential is a function of felt resistance, electrolyte resistance, mass transport, kinetics and, depending on the setup, of membrane resistance.

Therefore we decided to measure the solid phase potential by probes based on long carbon fibers that were inserted into the cell as an array. The solid phase potential only depends on the local felt and monopolar plate resistance as well as on the local current density distribution. The dependency can be described using Ohm's law (3), where the potential difference φ is a result of the local current density j and the sum of the electrical resistances of felt R_{felt} and monopolar plate $R_{\text{monopolar plate}}$, respectively.

$$\varphi = \left(R_{\text{felt}} + R_{\text{monopolar plate}} \right) \cdot j \qquad (3)$$

Because the measured solid phase potential is neither directly influenced by electrolyte resistance, mass transport, kinetics nor membrane resistance, it provides more accurate and reliable data than measurement of the liquid phase potential. Furthermore, the method is very inexpensive and easily applicable to large cells or cell stacks.

2. Experimental

2.1. Material

The vanadium electrolyte (1.6 mol/L vanadium concentration and 4 mol/L total sulfate concentration) was purchased from GfE (Gesellschaft für Elektrometallurgie, Germany). The initial electrolyte was a 1:1 mixture of V(III) and V(IV) resulting in a state of charge (SoC) of −50%. The sulfuric acid 95%–98% (Ph. Eur.) and phosphoric acid 85% (Ph. Eur.) purchased from Carl-Roth (Germany) was diluted with Milli-Q water (18.2 MΩ cm) to concentrations of 1 M. Volumetric standard solutions of 0.02 M potassium permanganate were purchased from Carl Roth. 0.1 M Fe(II) solutions were prepared using ammonium iron (II) sulfate hexahydrate (p.a., Carl Roth) dissolved in 1 M sulfuric acid.

2.2. Cell construction

The cells consisted of 7 mm thick PPG86 monopolar plates (Eisenhuth GmbH & Co. KG, Germany) and a single layer of untreated GFD4.6 EA carbon felt (SGL Carbon GmbH, Germany) with uncompressed dimensions of $100 \times 100 \times 4.6$ mm^3 resulting in an active cell area of 100 cm^2. Silicon gaskets and polymethylmethacrylate (PMMA) frames of different thicknesses were used to assemble three cells with carbon felt compression rates of 9%, 28% and 42%, respectively. The gaskets and frames had inner dimensions of 120×100 mm^2 to provide a sufficient supply channel of 10 mm in height for an even electrolyte distribution across the cell. The inlets were placed on the bottom left and the outlets were placed at the top right position of the cell. Two 2 mm thick brass plates served as current collectors connected to the monopolar plates via a gold plated nickel mesh to reduce contact resistances. The positive and negative electrodes were separated by a Nafion® 117 membrane. Prior to cell assembly the membrane was swelled for at least 24 h in 1 wt.-% sulfuric acid. Two 22 mm thick end plates of PMMA yielded a homogeneous compression of the carbon felt and permitted a back fed electrolyte supply as well as