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“Unexpected” behaviour of the internal resistance of a vanadium redox flow battery

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HIGHLIGHTS

- The internal cell resistance of vanadium redox flow batteries is studied.
- A theoretical battery model based on the Butler–Volmer equation is constructed.
- A decrease of the internal resistance versus the electric current is found.
- The energy efficiency versus the electric current is measured and calculated.

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ABSTRACT

This article presents the results of experimental and theoretical studies of energy losses owing to the internal resistance of vanadium redox flow batteries (VRFBs). A dependence of the internal cell resistance (ICR) on the electric current was measured and calculated. During the cyclic operation of a test battery, the internal resistance was halved by increasing the electric current from 3 A to 9 A. This is due to a strongly non-linear dependence of an over-potential of the electrochemical reactions on the current density. However, the energy efficiency does not increase due to a squared dependence of the energy losses on the increasing electric current. The energy efficiency of the test battery versus the electric current was measured and simulated. The deviation between the simulation results and experimental data is less than ±3.5%.

1. Introduction

The VRFB demonstrates attractive properties as a storage system for large amounts of electric energy by virtue of a relatively high efficiency, a low environmental impact, as well as the ability of operation in a power range up to MW-scales [1–3]. However, a long-term cyclic operation of the battery leads to a decrease of capacity and of energy efficiency [4], which was studied in our laboratory [5–7]. In these articles, we have presented some methods of on-line monitoring and compensation methods against capacity decreasing. In Ref. [8], we have presented the results concerning an in-situ regeneration of energy efficiency based on a reverse of battery polarity. It was found that the decrease of energy efficiency is caused by electric charge losses in side reactions and by an increase of the internal battery resistance. The first issue was studied in previous works, as cited above, the second one was discussed in Ref. [8]. The restrictions of battery operation efficiency caused by the electrolyte flow rate were studied in our article [9].

In Ref. [10], the heat generation in the VRFB was carefully studied and it was demonstrated that not only the ohmic resistance of the battery components, but also the over-potentials lead to a conversion of the electric energy into thermal energy, i.e. lead to energy losses. Therefore, in accordance with the concept declared above, the heat production in the battery can be represented by a generalized internal resistance comprising all relevant components. The internal resistance R_{in} of the battery consists of the ohmic resistance R_e of the cell components (planar and porous collectors), of the resistance R_i of the electrolytes and of a resistance R_η caused by over-potentials on the surface of the electrodes. Thus,

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the total ICR is given by Ref. $R_{in} = R_e + R_i + R_\eta$. The conductivity of the cell components, which is provided by the electrons, is stable during battery operation. The conductivity of the electrolytes is ionic and, therefore, depends on ion concentrations changing with the state of charge (SOC) of the battery. During operation, the over-potentials vary as well. As a result, the internal resistance periodically changes during charge and discharge cycles. Moreover, in accordance with the Butler–Volmer equation, the internal resistance depends on the rate of electrochemical reactions on the surface of the graphite collectors. A decrease of the reaction rate leads to an increase of the internal resistance [8]. These features concerning the internal resistance have to be studied in order to develop methods for the increasing of the energy efficiency of VRFBs.

In this article, we present the results of our studies concerning the battery's internal resistance behaviour during charging and discharging cycles at a constant electric current versus the current value.

2. Theoretical background

2.1. Internal resistance of the VRFB

During the operation of the VRFB, the following electrochemical reactions take place in the half-cells:

In the positive half-cell

$$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O, \tag{1}$$

in the negative half-cell

$$V^{2+} \rightleftharpoons V^{3+} + e^-. \tag{2}$$

Here, V^{2+}, V^{3+}, VO^+, and VO_2^+ denote the vanadium ions with different valence labelled as V^{2+}, V^{3+}, V^{4+}, and V^{5+} in the following text. By discharging, these reactions occur in forward direction and one H^+-ion with one electron is transported from the negative half-cell to the positive. By charging, they occur in reverse direction.

For the theoretical description, the parameters of the VRFB have to be defined in terms of mathematical expressions based on the laws of electrodynamics and of electrochemistry.

In accordance with Ohm's law, the generalized internal resistance R_{in} is determined by

$$R_{in} = \frac{E-U}{I}, \tag{3}$$

where E is the electromotive force (EMF), U is the cell voltage, and I is the electric current.

In open circuit state, the electric current is equal to zero and the voltage is equal to the EMF. This voltage is called the open circuit voltage (OCV). However, during the charging/discharging process, the electric current causes a difference $\Delta U = E - U$ between the EMF and the voltage, which consists of a voltage drop ΔU_e in the ohmic resistance of the battery components, a voltage drop ΔU_i in the ohmic resistance of the electrolytes and over-potentials $\Delta U_\eta = \eta_1 + \eta_2$ of the electrochemical reactions leading to the corresponding resistances R_e, R_i, R_η and to the relation

$$R_{in} = \frac{\Delta U_e + \Delta U_i + \Delta U_\eta}{I} = R_e + R_i + R_\eta. \tag{4}$$

Let us consider the internal resistance $R_\eta = \Delta U_\eta / I$ caused by the over-potentials η_1 and η_2 of the reactions on the positive and on the negative collectors. In accordance with the Butler–Volmer equations, the values of η_1 and η_2 depend on the current densities j_1 and j_2 on the surfaces of the porous collectors:

$$j_1 = j_{01}\left(\frac{c_{05}}{c_5}\exp\left(-\frac{0.5F\eta_1}{RT}\right) - \frac{c_{04}}{c_4}\exp\left(\frac{0.5F\eta_1}{RT}\right)\right), \tag{5}$$

$$j_2 = j_{02}\left(\frac{c_{03}}{c_3}\exp\left(-\frac{0.5F\eta_2}{RT}\right) - \frac{c_{02}}{c_2}\exp\left(\frac{0.5F\eta_2}{RT}\right)\right), \tag{6}$$

where F is the Faraday constant, R is the universal gas constant, T denotes temperature, $j_{01} = k_1 F c_4 c_5$, $j_{02} = k_2 F c_2 c_3$ are the exchange current densities, k_1 and k_2 are the reaction rates of the reactions (1) and (2), respectively, c_k and c_{0k} ($k = 2,3,4,5$, corresponding to the valence of the ions) are the concentrations of the vanadium-ions in the electrolytes and on the surface of the collectors, respectively. The exponential dependence of the current density on the over-potential in the Butler–Volmer equation is caused by an activation energy, which an electron should have by transferring between the collector and the electrolyte during the electrochemical reaction. In accordance with the equations of chemical kinetics, this energy is needed to achieve the intermediate state by crossing the double electrical layer on the collector surface [11].

In Ref. [12,13], it was shown that the active C–OH groups on the surface of the graphite collectors provide the redox reactions (1) and (2). The surface concentration of these groups determines the reaction rates k_1 and k_2. In our work [8], we demonstrated that, during the cyclic operation of the VRFB, a passivation of the negative collector takes place. It was measured that the internal resistance of a test battery starting with new collectors is doubled in the course of 12 cycles (12.5 h). This could be explained on the basis of a decreasing surface concentration of active C–OH groups on the negative collector surface. Moreover, a method for the regeneration of the C–OH groups using a polarity inversion of the battery was developed. Thus, it was experimentally and theoretically confirmed that the passivation of the negative collector leads to a decreasing reaction rate k_2 in equation (6). To keep the current constant ($I = \text{const}$) during battery operation, the decreasing of k_2 has to be compensated by an increase of the over-potential η_2 in accordance with (6). On the one hand, this results in an increase of the internal resistance $R_\eta = \Delta U_\eta / I$ caused by an over-potential. On the other hand, this leads to a non-linear dependence of the internal resistance R_{in} on the electric current I, which will be discussed further in section 3.1.

Let us consider the ohmic internal resistances $R_e = \Delta U_e / I$ and $R_i = \Delta U_i / I$ caused by electronic conductivity of the collectors and by ionic conductivity of the electrolytes, respectively. To find these resistances, the current density distribution has to be analysed. This analysis given in Appendix A results in the following expressions for the electronic and the ionic resistance of the half-cell:

$$R_e = \frac{\rho_e l_{av}}{S}, \quad R_i = \frac{\rho_i (L - l_{av})}{S}, \tag{7}$$

where l_{av} is the average distance which the electrons are moved in the porous collector from the planar collector to the point of interaction with the ions on the surface of the porous collector.

It should be noted that there is an ionic resistance of the membrane between the half cells as an additional contribution to the total internal resistance. This is calculated as

$$R_{mem} = \frac{\rho_{mem} d_{mem}}{S_{mem}}, \tag{8}$$

where ρ_{mem} is the specific ionic resistance, d_{mem} is the thickness, S_{mem} is the active surface of the membrane. The value of ρ_{mem} is defined as a reciprocal value of the a specific conductivity of the