



Measurement, simulation and in situ regeneration of energy efficiency in vanadium redox flow battery



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ABSTRACT

In this article the energy and efficiency losses during cyclic operation of vanadium redox flow battery (VRFB) are studied. A theoretical model, based on the equation system of fluid dynamics, including convective and diffusive transfer of species in electrolytes, and electrochemical interaction of ions, is developed. The reaction rates are calculated on the basis of the Butler–Volmer equation. The electric field distributions in half-cells are found by solving of the equation system, which is obtained by Ohm's law. A test battery was constructed. The parameters of the battery – voltage, current, power, energy and capacity during cyclic operation are measured and calculated. The numerical model was validated with the experimental data. The results of the calculation and of the measurement agree within $\pm 2\%$, which corresponds to the measurement accuracy. The decreasing of the energy efficiency during cyclic operation of the battery is observed and simulated. It was found that the capacity decrease is caused mainly by the imbalance of the positive and the negative electrolytes. The increasing of the internal resistance depends on the passivation of the negative collector surface. An in situ regeneration of the energy efficiency, based on an inverse electric potential in the negative half-cells during the cyclic operation, was developed. The reduction of the internal resistance approximately of 2.4 times was measured after the reactivation of the negative collector surface.

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1. Introduction

In the last years the VRFBs in the power range of 100 kW and more with an energy capacity up to 6 MWh have been constructed (for example, [1–3]). But long-term operation of the battery is accompanied by some processes that cause disequilibrium of concentration of species in the positive and the negative half-cell electrolytes [4], leading to increasing energy and capacity losses [5]. In our laboratory the effects were studied experimentally and the methods of on-line measuring [6] and compensating [7] of the capacity losses were developed. It was suggested that the capacity losses in the VRFB are caused by parasitic oxidation effects of V^{2+} -ions in the negative half-cells [4]. The increasing of the internal resistance [7] was measured as well.

The total electric energy, received from the battery by the discharging process, is less than the energy, that was used to charge the battery, mainly because of two kinds of losses: the first

one is caused by the imbalance of the state of charge (SOC) of the positive and the negative electrolytes that leads to the reduction of the SOC-operation range and to incomplete discharge of the electrolytes; the second one is caused by increasing of the internal resistance of the battery during the operation.

The modelling of the operation of the VRFB enables the possibility for the analysis of the internal parameters of the battery, which cannot be measured in the experiment. In the recent years, a number of theoretical models of operation of redox flow cell (RFC) have been developed [4,8–16]. Some of the models are based on the equations of fluid dynamics, taking into account the electrochemical reactions. They allow to calculate the distributions of concentrations of the species, of the electrical fields and of the temperature. The solution of the equation systems of the models can be realised, using some standard computer codes, for example, COMSOL Multiphysics package, or by means of numerical methods [17]. This allows controlling the accuracy of the calculations, to optimise the space and time steps etc. In this article the numerical simulation of the VRFB operation, including the mechanisms of increasing of capacity and energy losses, is realized, taking into account the measured operation behaviour of the battery.

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2. Theoretical model of VRFB

The operation of a single cell of the VRFB is simulated on the basis of a theoretical model, including the equations of fluid dynamics, electrostatics and electrochemistry. This model is able to simulate the operation of a single cell as well as an assembly of all. Yet, the increasing of the total number of cells in the numerical model leads to increasing of the required computational resources. Therefore, we present the simulation of the battery operation, based on the numerical model of a single cell. The parameters of the battery are calculated as a sum of corresponding parameters of N_{cell} equivalent operating single cells. For example, the flow rate of the electrolyte V_t is calculated as the sum of flow rates in the single cells $V_{t,i}$ as

$$V_t = \sum_{i=1}^{N_{cell}} V_{t,i}. \quad (1)$$

The other parameters of the battery are calculated in Section 2.5.

2.1. Theoretical background of RFC model

The scheme of the RFC is presented in Fig. 1. Each half-cell consists of a porous graphite collector, which is confined by a planar graphite collector from one side and by an ion-exchange membrane from the other side. The positive and the negative electrolytes, which are stored in the external tanks, are pumped through the half-cells.

The theoretical description of the RFC operation can be provided in 2D-formulation [8–10] and in 3D-formulation [13–15]. Large gradients of concentrations and of parameters of electric field in the half-cells take place in direction along the fluid flow in a half-cell due to an electrochemical interaction (OY-axis in Fig. 1) and in direction, which is perpendicular to the membrane (OX-axis in Fig. 1) due to an ion exchange across the membrane. The flow velocity distribution along OZ-axis, which is not showed in Fig. 1, should be uniform for optimal operation of the cell. Therefore, 2D-formulation of the problem can be used to solve the problem with adequate accuracy using minimal computational resources.

The electrochemical interaction between the electrolytes is carried out by means of H^+ -ion exchange across the membrane. The reduction and oxidation reactions take place in half-cells by operation of the battery: in the positive half-cell



in the negative half-cell

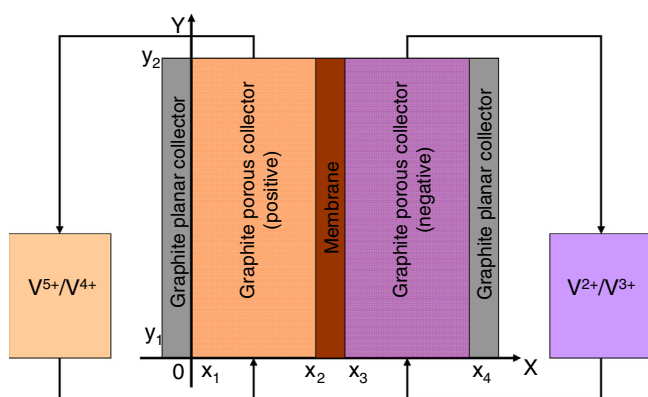


Fig. 1. Structure of RFC in Cartesian coordinate system.

V^{2+} , V^{3+} , VO_2^+ , VO^{2+} are the vanadium ions with different valence, labelled in the following text as V^{2+} , V^{3+} , V^{4+} , V^{5+} .

The processes in the RFC are described by the equations of fluid mechanics, electrostatics and electrochemistry. The electrolyte flow through the porous collectors and the diffusion of ions can be described by the conservation laws of mass and of momentum. The distribution of the electric potential in the RFC can be obtained by solving of the Poisson equations. The electrochemical interaction of the species in the cell is described by the Nernst equation and by the Butler–Volmer equation. An interference of these processes makes the solution of the equations complicate. But the calculations can be separated in several steps because of different time scales t_i of the processes.

The electrolyte flow in the cell can be considered as a stationary fluid dynamics problem (the time scale is $t_1 \rightarrow \infty$). The electric field distribution in the electrolyte and in the collector system is established with the velocity of the electromagnetic waves ($t_2 \rightarrow 0$). The concentrations of the ions in the cell are changed during the flow of the electrolyte through the cell ($t_3 = L/v$), where L is the length of cell, v is the flow velocity. This approach leads to three calculation steps for the simulation of the battery operation.

2.2. Fluid dynamics equations

The first calculation is based on the conservation law of mass for electrolyte flow as non-compressible liquid

$$\text{div } \vec{v} = 0. \quad (4)$$

The flow velocity \vec{v} in the porous collector is determined by Darcy's law

$$\vec{v} = -\frac{k}{\mu \varepsilon} \text{grad} p, \quad (5)$$

where p is the pressure, k is the permeability of the porous collector, ε is the porosity of the porous collector and μ is the dynamic viscosity of the electrolyte. The permeability of the porous collector is calculated by the Carman-Kozeny equation [18]

$$k = \frac{d_f^2 \varepsilon^3}{16k_{CK}(1-\varepsilon)^2}.$$

A combination of these expressions gives the Laplace equation for the pressure distribution

$$\frac{\partial^2 p}{\partial x^2} + \frac{\partial^2 p}{\partial y^2} = 0. \quad (6)$$

The second calculation describes the convective and diffusive transfer of the ions in the cell

$$\text{div}(\varepsilon C_k \vec{v}) - D_{eff,k} \left(\frac{\partial^2 C_k}{\partial x^2} + \frac{\partial^2 C_k}{\partial y^2} \right) = J_k, \quad k = 1, \dots, N_{sp}, \quad (7)$$

where c_k are the molar concentrations of ions, $D_{eff,k}$ are the effective diffusion coefficients, J_k are the rates of the electrochemical reactions, N_{sp} is the number of the species in the electrolytes. The effective diffusion coefficient in liquids in the porous media is smaller than in the pure liquid and can be calculated by the Bruggemann correction [19]

$$D_{eff,k} = \varepsilon^{3/2} D_k.$$

2.3. Equations of electrochemistry

In the third calculation the rates of the electrochemical reactions are obtained. The equations, presented in this article, are done for the discharging process. An electrochemical reaction

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