Optimal electrolyte flow distribution in hydrodynamic circuit of vanadium redox flow battery

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A B S T R A C T

This article presents the results of studies of the electrolyte flow configuration in a vanadium redox flow battery (VRFB). The flow structure is formed by a system of inlet and outlet channels and of porous collectors of the battery. This configuration is considered as a hydrodynamic circuit. The theoretical models, which were used to simulate the flow behaviour, are based on conservation laws of mass and of electric charge. The electrolyte flow was analysed on the basis of three theoretical models: total flow, depending on the electric current; flow distribution in the inlet/outlet channel system; flow distribution in a half-cell. For the test battery a capacity availability was calculated and measured in a wide range of the flow rate and of the electric current. The flow distribution in the porous collector was calculated and the efficiency by the different flow configurations in the half-cells was measured. The parameters and the configuration of the electrolyte inlet/outlet channels were optimized to obtain the uniform distribution of the electrolyte flow to each half-cell.

1. Introduction

The fundamental principles of operation of the VRFB are developed since 1986 [1]. This kind of battery is very attractive as energy storage system due to the following properties: relatively high efficiency, low environmental impact, ability of operation in power range up to MW-scale [2,3]. Therefore, the studies of the redox flow batteries were very intensive in the last years [4–7].

Long-term operation of the VRFB demonstrates several problems, concerning the capacity losses, the imbalance of the electrolytes, the collector corrosion, etc., that leads to decreasing energy efficiency. Some of these effects were studied and methods of their elimination were developed in our laboratory [8–11].

The energy efficiency of the battery depends on the charging/discharging conditions, which are determined by the values of electric current, voltage, electrolyte volume in the tanks, electrolyte flow rate in the battery, etc. In this article we present an analysis of the electrolyte flow rate and of the flow configuration in the VRFB regarding the operation efficiency. The studies are based on the conservation laws of mass, of electric charge and of energy. The conservation law of electric charge allows to establish that the charge, received from the battery, is restricted by the value of the charge, delivered to the battery from the storage tank by the electrolyte flow. Therefore, the effective transfer of the charge from the electrolyte to the collectors can occur only by the electrolyte flow rate, fitted to the electric current, and by accurate distribution of the flow in the battery cells.

In [12] an optimization of the electrolyte flow rate in accordance with the state of charge of the battery was provided, and the capacity of the battery was increased by 8%. But this increase of the flow rate leads to increasing energy consumption of the electrolyte pumping and, consequently, to decreasing energy efficiency. In [13] it was shown also that the increasing electrolyte flow rate results in increasing useful capacity of the battery. In [14] a serpentine electrolyte flow configuration in cell was proposed to increase the operation efficiency of the battery.

The main goal of this article is the theoretical and experimental analysis the electrolyte flow rate and of the flow configuration in the VRFB regarding the operation efficiency.

2. Theoretical background

The analysis of the battery operation is based on the following characteristics of the battery: capacity, state of charge, charging/

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discharging energy, energy efficiency. These parameters should be defined as the mathematical expressions to use them for the simulations of the battery operation.

A battery with N_c cells, connected electrically in-series, is considered. The electrolytes from the storage tanks are pumped through the positive and the negative half-cells separately. Each half-cell contains a planar collector, a porous collector, and a PVC frame with an inlet and an outlet channel for the electrolyte flow (Fig. 1). Between the positive and the negative half-cells a proton exchange membrane is placed to prevent cross-mixing of the electrolytes. Uniform electrolyte flow rate in each cell of the battery is carried out by an common inlet channel, formed by holes in the frames and in the planar collectors.

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

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

in the negative half-cell

$$V^{2+} \rightleftharpoons V^{3+} + e^-. \tag{2}$$
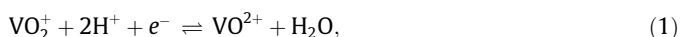
Here V^{2+}, V^{3+}, VO^+, VO_2^+ are the vanadium ions with different valence, labelled in the following text as V^{2+}, V^{3+}, V^{4+}, V^{5+}. By discharging the reactions occur in the forward direction and one H^+-ion with one electron is transported from the negative half-cell to the positive, by charging – in the reverse direction. At the same time in the VRFB some side reactions can occur [15]. These effects were studied in our laboratory and the results are published in [9]. The theoretical model, presented in this article, is simplified to allow an analytical solution of the equations. Therefore, the side reactions were not taken into account and it was assumed that the battery has 100% current efficiency. Additionally, it was assumed that the internal cell resistance is constant. Only in this case, the Ohm's law can be used for the battery. Therefore, an analytical solution of the equations is possible.

2.1. Capacity and operation efficiency, depending on electrolyte flow rate

The maximal electric charge, which can be brought in the electrolyte by the charging process, is defined as the total capacity of the electrolyte Σ_0, and this is determined by the electrolyte volume V and by the concentration of the vanadium ions C_0 in the electrolyte
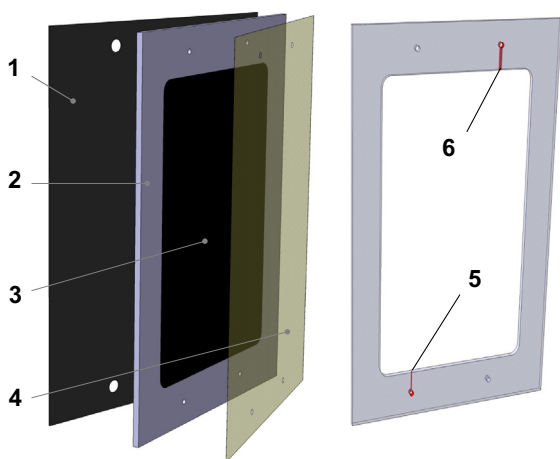

Fig. 1. Construction of a VRFB half-cell: 1 – graphite planar collector, 2 – PVC frame, 3 – graphite felt, 4 – membrane, 5 – inlet channel, and 6 – outlet channel of PVC frame.

$$\Sigma_0 = C_0 \cdot V \cdot F, \tag{3}$$

where $F = 96{,}485$ C/mol is the Faraday's constant. The total capacity is measured in coulombs (C) or in ampere $\cdot$ hours (1 Ah = 3600 C).

A state of charge (SOC) of the electrolyte in the positive half-cell (catholyte) is determined as

$$SOC_c = \frac{C_5}{C_{05}}, \tag{4}$$

where C_5 is the actual value and C_{05} is the maximal value of the V^{5+}-ion concentration. It is supposed that in the fully charged catholyte all of the vanadium ions are arrived the V^{5+}-state: $C_{05} = C_0$.

For the electrolyte in the negative half-cell (anolyte) the SOC is determined as

$$SOC_a = \frac{C_2}{C_{02}}, \tag{5}$$

and the maximal V^{2+}-ion concentration C_{02} is accepted to be equal C_0 also because of the identical initial concentration of the vanadium ion in both of the electrolytes.

The actual value of the charge Σ in the catholyte is defined by the SOC as

$$\Sigma = C_5 \cdot V \cdot F = \frac{C_5}{C_{05}} C_{05} \cdot V \cdot F = SOC_c \cdot C_{05} \cdot V \cdot F = SOC_c \cdot \Sigma_0. \tag{6}$$

For the maximal effective operation of the VRFB SOC = 100% should be reached by charging and SOC = 0% – by discharging. But in the real charging/discharging cycle the operation range of the SOC is restricted by some minimal and maximal values $SOC_{min} > 0\%$ and $SOC_{max} < 100\%$. To calculate these values we proposed the following approach.

The charging/discharging cyclic operation of the battery is carried out with a constant electric current.

At the end of the charging process the SOC of the electrolyte can reach 100% in the outlet channel only. Therefore, the SOC of the electrolyte in the inlet of the battery is less than 100%. This maximal value of the $SOC_{in,max}$ in the inlet channel is equal to the maximal value in the tank and this has to be calculated.

The difference between the V^{5+}-ion concentrations in the outlet and in the inlet of the battery is determined by the total amount of the electrons $q_e = I_{ch} \cdot N_c/F$ (mol/s), which were taken away from the V^{4+}-ions in the catholyte per time unit, and by the electrolyte flow rate V_t (m^3/s) as

$$\Delta C = C_{out} - C_{in} = \frac{q_e}{V_t} = \frac{I_{ch}N_c}{V_t F}. \tag{7}$$

By charging C_{out} cannot exceed the value C_{05} and, therefore, the maximal value of SOC of the electrolyte in the tank is

$$SOC_{c,in,max} = \frac{C_{in}}{C_{05}} = \frac{C_{05} - \Delta C}{C_{05}} = 1 - \frac{I_{ch}N_c}{C_{05}V_t F}. \tag{8}$$

The difference between the total value of capacity Σ_0 and the maximal value of the electric charge Σ_{max} of the electrolyte in the tank, named as a deficit of the capacity, is calculated as

$$\Delta\Sigma = \Sigma_0 - \Sigma_{max} = \frac{I_{ch}N_c V}{V_t}. \tag{9}$$

The value $\Delta\Sigma$ characterizes the unused range of the total capacity by the charging process. The expression (9) shows that this value can be decreased by increasing flow rate V_t or by decreasing current I_{ch}.

At the end of the discharging process the minimal value of $SOC_{in,min}$ of the electrolyte in the tank cannot reach 0% also due to the difference of the V^{5+}-ion concentrations by the inlet C_{in} and by the outlet C_{out} of the battery. The calculation of the value $SOC_{in,min}$ is more complicate in comparison with the calculation