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On-line controlled state of charge rebalancing in vanadium redox flow battery

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ABSTRACT

This article presents results of studies, carried out on chemical and electrochemical processes, resulting in energy and capacity losses in vanadium redox flow battery (VRFB). Two mechanisms, concerning losses, were evaluated: hydrogen evolution and imbalance of vanadium ions in electrolytes. Capacity losses of the battery were measured as the reduction of total electric charge, obtained from battery in discharging process, during charging/discharging cycle operation. Charge losses were verified using chronoamperometry measurements, where the electric current was measured and used to quantify the losses while keeping the battery at constant voltage. Methods for compensation of capacity losses and rebalancing of the battery were investigated and discussed. An electrolysis cell was developed to compensate the losses of charge in one half-cell only and, therefore, to rebalance the electrolytes.

1. Introduction

Vanadium redox flow batteries (VRFB) have recently been proposed as large scale energy storage systems [1,2]. Long-term operation of the VRFB, however, has shown some processes, which cause concentration disequilibrium of vanadium species in positive and negative half-cells [3]. Furthermore, volumetric disequilibrium can occur as well [4,5]. It is thought that these phenomena are due to the transport of ions across the proton exchange membrane between half-cells, favoured by the built up of an electric field. This, in turn, can lead to self-discharging reactions [6] and other side reactions [7,8], which are considered to be the basis of these undesirable side processes, resulting in energy and capacity losses [9].

In [6] effects of ion diffusion and side reactions, resulting in capacity losses, are discussed. One effect described is the transfer of vanadium ions across one half-cell to the other. The ions interact chemically without the exchange of electrons through the collectors. Another effect, described in [6], that causes losses of charge, is gas evolution, predominately hydrogen. Through these gassing reactions in negative half-cell electric charge and protons are lost from the electrolytes, thus leading to the imbalance of the state of electric charge between half-cells. A third effect thought to take place is the interaction with oxygen in the air leading to the oxidation of V^{2+}, also leading to imbalance of the state of charge of electrolytes between two half-cells [10].

To counteract these effects and to rebalance the two half-cells of the VRFB, [6,10] present two methods: (1) remixing of electrolytes and (2) partial reduction of V^{5+} via the addition of organic compounds to the catholyte. However, remixing results in energy losses requiring the pre-charging of the electrolytes before restarting battery operation, making it in terms of energy non-efficient. Furthermore, it was shown that remixing failed after the third attempt to restore the battery capacity [10]. This short-term positive effect from remixing can be interpreted by decreasing of internal resistance of battery, which will be discussed in Section 4.2.1. Further increasing of imbalance can be explained by following effect: by remixing of balanced positive and negative electrolytes the vanadium ions react chemically with each other reaching an oxidation state $V^{3.5+}$ (50% V^{3+} and 50% V^{4+}). If the electrolytes are imbalanced, some V^{x+}-state ($x \neq 3.5$) of the ions is reached. And by pre-charging, started with this initial state, the SOC = 100% is obtained only in one electrolyte – either positive or negative. This effect is discussed in Section 4.2.1.

As second method of rebalancing [10] the usage of organic compounds was suggested. This method though leads to a volumetric imbalance between the catholyte and analyte and might be difficult to realise in large scale battery systems.

Recently a new method was developed to rebalance the positive electrolyte using hydrogen [11]. The main idea of this method is to feed the hydrogen, lost in the anolyte through side reactions, back to the catholyte and use it to reduce V^{5+} with help of a catalyst. The

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drawback of this method is the slow reaction rate between V^{5+}-ions and H_2.

In our article following processes are considered to result in capacity and efficiency losses: gassing of hydrogen, the imbalance of vanadium ion concentration, and self-discharging of the battery due to the cross-contamination of vanadium ions across the membrane. These effects were studied and two methods were developed to compensate these losses and, thus, to rebalance the battery – firstly, by remixing small defined amounts of the electrolytes to increase efficiency by H^+-ion balancing, and, secondly, reintroducing lost hydrogen ions and charge into the electrolyte by using a self-built electrolysis cell.

2. Theoretical background

2.1. Diffusion of ions across the membrane and related losses

Fig. 1 shows the schematic structure of a redox flow cell (RFC). Each half-cell consists of a graphite porous collector and is bound by a graphite bipolar planar collector from one side and an ion-exchange membrane from other side. The positive and negative electrolytes, stored in external tanks, are pumped through each half-cell separately. The membrane, used in RFC, prevents cross-mixing of the positive and negative half-cell electrolytes, but allows the transport of hydrogen-ions to complete the electric circuit during the operation of VRFB. Following reduction and oxidation reactions take place in the half-cells during charging and discharging processes:

in the positive half-cell (cathode)

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

in the negative half-cell (anode)

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

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

The distribution of the electric field in RFC is determined by a number of parameters: concentrations of ions, electric current, flow rate of electrolyte, etc. A distribution of electric potentials along X-axis in the graphite felt φ_s and in the electrolytes φ_l during charging process is shown qualitatively in Fig. 1.

The electric field E in the membrane, which is responsible for the transport of ions, is calculated as

$$E = \frac{\Delta\varphi}{d_{memb}}, \qquad (3)$$

where $\Delta\varphi = \varphi_{l2} - \varphi_{l1}$ is the difference of electric potentials between catholyte and analyte at the surface of the membrane and d_{memb} is the thickness of the membrane. For the open circuit state of the battery $\Delta\varphi = 0$, therefore the electric field does not cause ion transport across the membrane. During the charging/discharging cycle operation of the battery current density j in the membrane is defined by Ohm's law

$$j = \sigma E, \qquad (4)$$

where σ is the electric conductivity of the membrane.

This approach views an idealised situation. But detailed analysis of electric field distribution shows that the model requires some improvements.

The graphite felt in each half-cell of the battery is used to increase the surface area of the collector on which the electrochemical reactions can take place. Electric conductivity in the porous collector is derived from electrons, but the conductivity of electrolyte and of the membrane is ionic. Electric charge exchange between collector and electrolyte is realised via electrochemical reactions. It can be said that the potential difference $\Delta\varphi$ between opposite collector fibres near to the membrane is close to the electromotive force of the cell ($EMF = 1.256$ V). Taking into account the thinness of the membrane ($d_{memb} \approx 20 - 100\ \mu$m) it is estimated that the electric field E' is in the order of $10^4 - 10^5$ V/m between two opposite graphite porous collectors. This is the case when the distance between graphite fibre and membrane at the contact point is comparable with the thickness of double electrical layer on the graphite collector surface. This additional local field E' exists at any time, whether the battery is operating or not. As a result, an additional force is present acting on the ions in the membrane. This can cause migration of positive ions (vanadium and hydrogen ions) from catholyte to anolyte, leading to disequilibrium of ion concentrations and to polarisation effects.

2.2. Side reactions and related losses

Another effect, leading to capacity losses, is connected to undesired reactions of H^+-ions in the anolyte [10,13]. In [10] it is suggested that the production of hydrogen molecules in the negative half-cell leads to the oxidation of V^{2+}-ions into V^{3+}-ions without the transfer of electrons to the collector. In terms of electric charge conservation law the following could take place: two hydrogen ions receive two electrons from two V^{2+}-ions. This could lead to loss for the electrochemical reactions (2) during the discharge of the battery and the loss of two H^+ ions, as the gaseous hydrogen

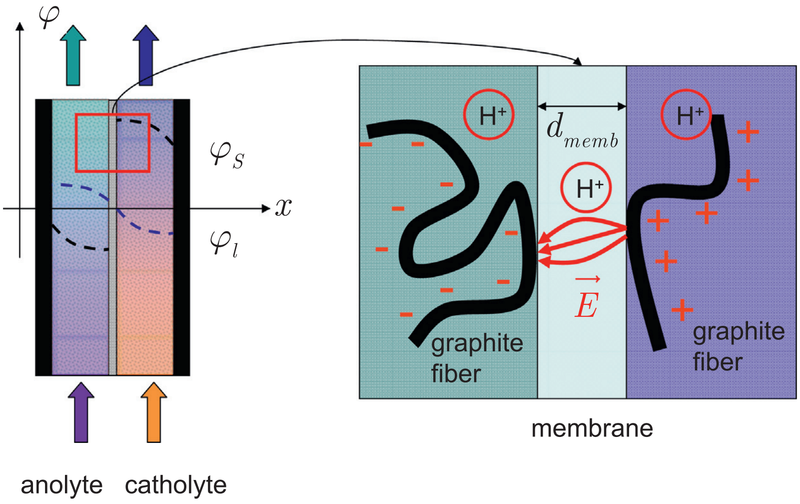

Fig. 1. Microscopic structure of membrane area of RedOx flow cell.