



Investigation of crossover processes in a unitized bidirectional vanadium/air redox flow battery



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HIGHLIGHTS

- Crossover in a VARFB is investigated using ICP-MS and *in situ* UV/Vis spectroscopy.
- Coulombic efficiency of a VARFB is lowered by crossover (mainly O₂ permeation).
- Vanadium crossover which limits the cycle life of VARFB is quantified.
- Diffusion coefficients of V²⁺ and V³⁺ through Nafion® 117 are determined.

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ABSTRACT

In this paper the losses in coulombic efficiency are investigated for a vanadium/air redox flow battery (VARFB) comprising a two-layered positive electrode. Ultraviolet/visible (UV/Vis) spectroscopy is used to monitor the concentrations $c_{V^{2+}}$ and $c_{V^{3+}}$ during operation. The most likely cause for the largest part of the coulombic losses is the permeation of oxygen from the positive to the negative electrode followed by an oxidation of V²⁺ to V³⁺. The total vanadium crossover is followed by inductively coupled plasma mass spectroscopy (ICP-MS) analysis of the positive electrolyte after one VARFB cycle. During one cycle 6% of the vanadium species initially present in the negative electrolyte are transferred to the positive electrolyte, which can account at most for 20% of the coulombic losses. The diffusion coefficients of V²⁺ and V³⁺ through Nafion® 117 are determined as $D_{V^{2+}, N117} = 9.05 \cdot 10^{-6} \text{ cm}^2 \text{ min}^{-1}$ and $D_{V^{3+}, N117} = 4.35 \cdot 10^{-6} \text{ cm}^2 \text{ min}^{-1}$ and are used to calculate vanadium crossover due to diffusion which allows differentiation between vanadium crossover due to diffusion and migration/electroosmotic convection. In order to optimize coulombic efficiency of VARFB, membranes need to be designed with reduced oxygen permeation and vanadium crossover.

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1. Introduction

In the past years, redox flow batteries (RFB) have gained increasing attention as promising candidates for stationary electricity storage applications. They show advantageous characteristics such as high cycle life (>12,000 [1]) and good round-trip efficiencies ($\eta_E \approx 80\%$ [2]). However, as redox flow batteries are generally based on electroactive materials (e.g. metal cations) dissolved in a solvent (e.g. water) with a limited solubility, the energy density of RFB is low compared to other battery systems (e.g.

25–30 Wh kg⁻¹ for the all-vanadium redox flow battery (VRFB) [3]).

Different approaches have been proposed to enhance the energy density of RFB including increasing the solubility of the electrolytes by using additives [4,5] or following alternative concepts such as solid/liquid hybrid redox flow batteries [6,7]. The substitution of the positive half cell (i.e. the VO²⁺/VO³⁺ redox couple) by a bidirectional air electrode was disclosed in a patent in 1992 [8] and holds the potential for roughly doubling the energy density in relation to a VRFB. A modular VARFB system (i.e. two separate reaction units for charging and discharging) was described by Hosseiny et al. [9] and a system for discharging only was reported by Noack et al. [10] and Menictas et al. [11].

In our previous paper [12] we introduced a concept for a

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unitised bidirectional VARFB utilising a two-layered positive electrode. Figure 1a depicts the setup of the VARFB. The negative electrode of the battery comprises a current collector (②) and a graphite felt electrode (③) through which the V^{2+}/V^{3+} containing electrolyte (①) is circulated. For brevity we denote the electrolyte in the negative electrode as “negative electrolyte” (analogous for the “positive electrolyte”). The positive electrode is composed of two electrodes that are pressed together: An IrO_2 -modified graphite felt (⑤) serves as electrode for the charging reaction (oxygen evolution reaction, OER; $2H_2O \rightarrow O_2 + 4e^- + 4H^+$), while a platinum-containing gas diffusion layer (⑥) which is fed with air through the flow-field/current collector (⑦) supports the discharging reaction (oxygen reduction reaction, ORR; $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$). Negative and positive electrode are separated from each other by a Nafion® 117 membrane (④). The VARFB was operated for several cycles and an energy efficiency $\eta_E = 39\%$ at $21^\circ C$ and 40 mA cm^{-2} was achieved [12].

However, comparably low coulombic efficiencies ($\eta_C = 55.0\%$ at 15 mA cm^{-2} and $\eta_C = 87.6\%$ at 40 mA cm^{-2}) were obtained which also decreased with each consecutive cycle. The coulombic efficiency η_C is the ratio of the amount of electric charge delivered during discharging ($Q_{\text{discharge}}$) to the charge consumed during charging (Q_{charge}):

$$\eta_C = \frac{Q_{\text{discharge}}}{Q_{\text{charge}}} \quad (1)$$

The capacity of the VARFB depends exclusively on the capacity of the negative electrolyte because the reagents of the positive electrode are O_2 and H_2O which are not limiting in our setup (Fig. 1b). Therefore, a decrease of η_C must only consider all side reactions that influence the capacity of the negative electrolyte. Fig. 2b shows the cell reactions occurring in a VARFB. The main

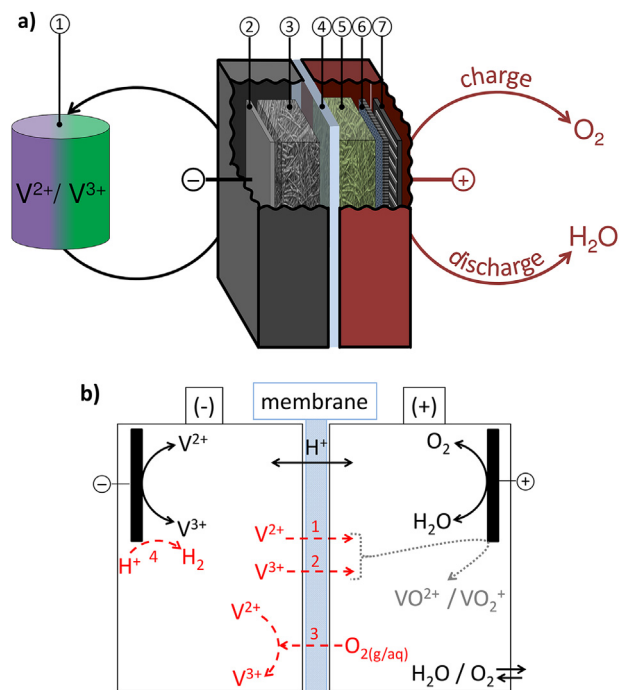


Fig. 1. a) The VARFB test cell comprising a two-layered positive electrode. ① = negative electrolyte tank; ② = current collector; ③ = graphite felt; ④ = membrane; ⑤ = IrO_2 -mod. graphite felt; ⑥ = gas diffusion electrode; ⑦ = current collector with flow field. b) Possible chemical reactions in the VARFB. Main reactions (—), η_C reducing crossover and side reactions (---) and subsequent chemical reaction (· · ·). 1, 2 = vanadium crossover; 3 = oxygen crossover; 4 = hydrogen evolution.

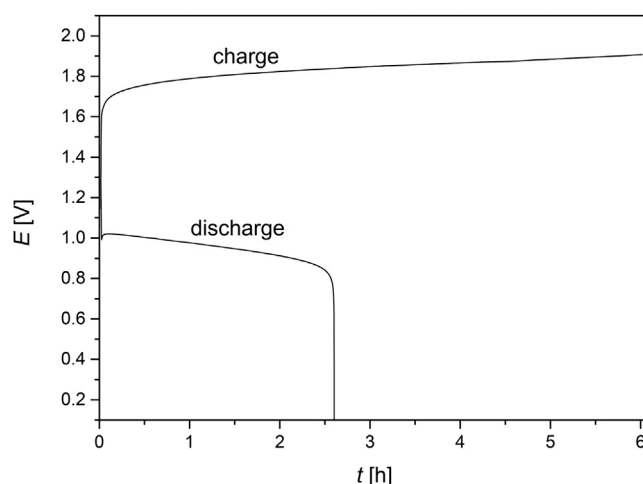


Fig. 2. Charge/discharge curve of the VARFB test cell ($j = 15\text{ mA cm}^{-2}$, $21^\circ C \pm 1^\circ C$).

reactions are shown as black solid line, side reactions reducing η_C are numbered and highlighted by red dashed lines. Processes 1 and 2 illustrate the crossover of V^{2+} and V^{3+} from the negative to the positive electrode. After crossing the membrane, V^{2+} and V^{3+} can be oxidized at the positive electrode to VO^{2+} (“ V^{4+} ”) and/or VO_2^+ (“ V^{5+} ”) due to the potential of the positive electrode or due to oxygen present in the positive electrode chamber. This reaction (gray dotted arrow) does not influence η_C because the capacity is determined by the capacity of the negative electrolyte. Process 3 depicts the oxygen crossover and the subsequent homogeneous oxidation of V^{2+} to V^{3+} by O_2 which reduces η_C because V^{2+} is consumed. Hydrogen evolution reaction (HER; process 4) would also lower η_C . The chemical follow-up reaction has no influence on η_C and thus depicted as gray dotted line.

For conventional VRFB the crossover of vanadium species through the membrane has been reported to contribute to η_C losses and was investigated in several studies [13–18]. This crossover (i.e. the transport of ions through the membrane) is caused by one or more of the three processes: migration (in the electric field during battery operation), electroosmotic convection (EOC; caused by electroosmotic flow of water through the membrane) and/or diffusion [19]. Recently, these processes were studied in detail for VRFB by Darling et al. [20] and Yang et al. [19] by modeling approaches. Yang et al. [19] found that V^{3+} net transfer from the negative to the positive electrode is much more pronounced during discharging than during charging due to superposition of the three processes. During charging the direction of the diffusive part (negative to positive) is opposite to the direction of migration and EOC (positive to negative).

The transport of vanadium cations through the cation exchange membrane is influenced by the interactions of the cations with the negatively charged sulfonate groups of the membrane [21,22]. The transport mechanisms of vanadium ions through a Nafion® membrane on a molecular level have been investigated and discussed in several publications [22–25]. Vijayakumar et al. [22] reported about two fouling mechanisms of Nafion® membranes due to vanadium cations that blocked the sulfonic acid groups. Recently, the interaction between triflic acid (F_3C-SO_3H) as a reference system for Nafion® and vanadium cations was investigated with hybrid density functional theory [21]. The influence of absorbed V^{2+} and V^{3+} on the local structure of Nafion® was examined by molecular dynamics [26].

Diffusion coefficients for vanadium species through diverse (pristine and modified) membranes were investigated in several

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