

Electrochemical rebalancing process for vanadium flow batteries: sizing procedure and economical assessment

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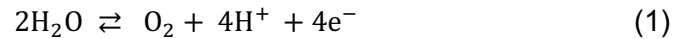
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Introduction

In all-vanadium flow batteries, electrolyte oxidation from atmospheric oxygen and/or hydrogen evolution due to operations at extreme states of charge may occur. After events like these, an electrolyte imbalance affecting the battery capacity appears that cannot be recovered by a simple mixing operation and a more complex rebalancing process must be undertaken. Among the different rebalancing processes which have been proposed in the literature, we consider here the electrochemical method that uses a specific electrolysis reactor to reduce V(V) in the positive electrolyte to the level of V(II) in the negative electrolyte, so as to equate the states of charge in the two tanks. We present a techno-economic model of this process allowing to investigate how the process and the reactor can be optimized from a technical and economical point of view.

Chemical Technologies (Pfinztal, Germany), consists in partially reducing V(V) to V(IV) in the positive tank, to equate it to V(II) in the negative tank, which has decreased after oxidation caused by hydrogen evolution or oxidation by air. The procedure uses a stack of electrolysis cells made with the same membrane and the same negative electrode of the main VFB cells, where the battery V(V) is reduced to V(IV). Instead, the positive electrode is made of titanium-iridium oxide cermet to catalyze the water oxidation that balances the electrochemical reaction [1]. The reactions which take place in each cell are:

At the positive half-cell:



At the negative half-cell:



Techno-economic model

The investment of this rebalancing process mainly consists of the stack of electrolysis cells, to which operational costs add on. The cost of the rebalancing stack depends on its size which is given by the number of cells N_r and their active area A_r . The products of these two parameters can be expressed as:

$$A_r N_r = \frac{\beta W}{\overline{\text{OCV}}_r j_r t_r} \quad (3)$$

where $\beta = \text{SOC}_+ - \text{SOC}_-$ is the imbalance between the two electrolytes (corresponding to the relative energy capacity decrease, that increases with time, cycle after cycle, as imbalance develop), βW is the rebalancing energy that must be processed in the rebalancing stack, $\overline{\text{OCV}}_r$ is the cell average Open Circuit Voltage during the process, j_r is the cell current density and t_r is the duration of the rebalancing process. The total energy $W_{reb,t}$ needed in a rebalancing process is the sum of energy consumed in the rebalancing stack (W_{rs}) and the energy consumed by the pump (W_{rp}) that circulates the positive electrolyte:

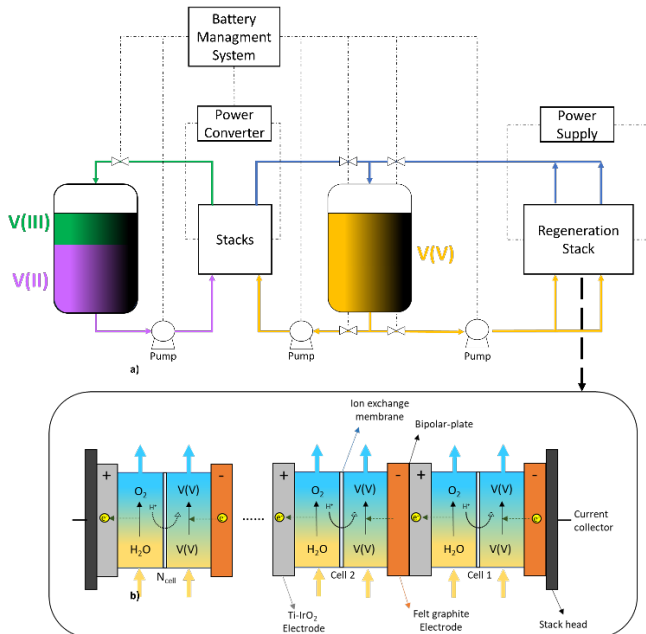


Figure 1: a) Process flow diagram of a VFB with the rebalancing system; b) Detail of the stack configuration of the rebalancing process.

Electrochemical rebalancing process

A specific electrochemical rebalancing method is here considered, as schematized in Fig.1. The strategy, developed at the Fraunhofer Institute of

$$W_{reb,t} = W_{rs} + W_{rp} = \beta W(1 + ASR_r j_r / \overline{OCV}_r + k_p) \quad (4)$$

where ASR_r is the area specific resistance of the electrolysis cell and k_p is the fraction of the pump energy with respect to the stack (usually $k_p = 3-4\%$).

Results

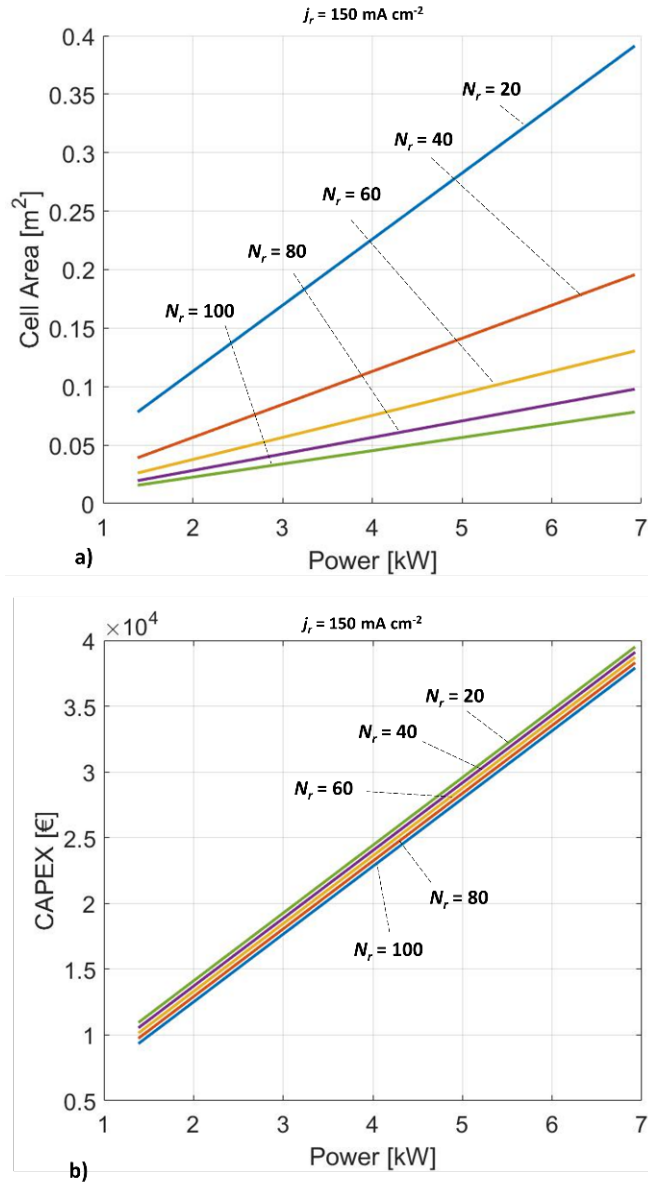


Figure 2: a) Cell area A_r as function of the rebalancing power and number of cells N_r , with a current density of $j_r = 150 \text{ mA cm}^{-2}$; b) Capital expenditure CAPEX of the rebalancing stack as function of the rebalancing power $P_{reb,s}$ and the cell area N_r , with a current density of $j_r = 150 \text{ mA cm}^{-2}$.

References

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- [3] M. Guarnieri, A. Trovò, A. D'Anzi, P. Alotto, Developing vanadium redox flow technology on a 9kW 26 kWh industrial scale test facility: design review and early experiments, Appl. Energy 230 (2018) 1425-1434

According to eq. (3), the size of the rebalancing stack depends on the power demand of the electrolysis process $P_{reb,s} = W_{reb,s} / t_r$ and, consequently, on the duration t_r of the rebalancing process. Fig. 2a shows the correlation between number of cells N_r and cell area A_r as function of the stack power $P_{reb,s}$ for a current density $j_r = 150 \text{ mA cm}^{-2}$ and for a specific kW-class VFB plant (specifically, a 9kW/27kWh VRFB system in operation at the University of Padua). The figure shows the linear correlation between $P_{reb,s}$ and A_r for 5 values $N_r = 20, 40, 60, 80, 100$. At $j_r = 150 \text{ mA cm}^{-2}$ and $N_r = 20$, the cell area A_r varies between 800 cm^2 and $\approx 4000 \text{ cm}^2$ as the power ranges between $\approx 1.4 \text{ kW}$ and 7 kW . The same figure shows that, always at $j_r = 150 \text{ mA cm}^{-2}$ and with $N_r = 100$, the cell area reduces between $\approx 200 \text{ cm}^2$ and 800 cm^2 . If we consider a number of 40 cells, which is a number of cell in VFB stack often found in the literature and manufacturer designs [2, 3], the cell area ranges between ≈ 400 to 2000 cm^2 . From the economic side, Fig. 2b shows a basically linear correlation between capital expenditure and stack power, at different cell numbers. Overall, increasing N_r and reducing $P_{reb,s}$ (i.e. increasing t_r) has a beneficial effect on the CAPEX. The insights above do not constitute design choices for a specific rebalancing system. Instead, they indicate that the designer has a number of variables (β , A_r , N_r , t_r , j_r) to choose in order to optimize the cost and performance of the rebalancing systems to specific service needs.

Conclusions

The battery capacity can be fully restored by a rebalancing process that reduces SOC_+ at the level of SOC_- , by using an electrochemical rebalancing reactor where the reduction of V(V) and the oxygen evolution reaction takes place in the negative and positive electrodes respectively. The sizing of an electrochemical reactor performing such rebalancing has been investigated. For a VFB system with a given rated energy, the size of the rebalancing reactor (cell area A_r and number N_r) depends on different factors: the relative oxidative imbalance between the two electrolytes β , the cell current density j_r and the rebalancing duration t_r .