

Optimised partial remixing procedure for mitigating capacity loss in imbalanced vanadium flow batteries

Thomas Puleston^{1*}, Giacomo Marini², Andrea Trovò², Maria Serra¹, Ramon Costa¹, Massimo Guarnieri²

¹Institut de Robòtica i Informàtica Industrial, Polytechnic University of Catalonia, Barcelona, Spain

²Department of Industrial Engineering, University of Padua, Padua, Italy

*Email: thomas.paul.puleston@upc.edu

Introduction

Electrolyte imbalance is the main cause of capacity loss in Vanadium Flow Batteries (VFB). Imbalance can be classified into “stoichiometric imbalance” (or “mass imbalance”) and “faradaic imbalance” (or “oxidative/reductive imbalance”) [1]. The former is a consequence of vanadium crossover and electrolyte transfer through the membrane, that result in a different amount of vanadium moles on each side of the system. The latter is caused by several side reactions (oxidation with air, hydrogen/oxygen evolution, etc.), that result in a deviation from the ideal overall Average Oxidation State (AOS) of +3.5. Stoichiometric imbalance can be corrected in a simple way, by total or partial remixing the tanks’ contents [2]. In contrast, faradaic imbalance can only be reverted by means of more complex chemical or electrochemical methods [3]. Typically, both types of imbalance are addressed independently. To overcome this limitation, this work presents a novel strategy that considers their interaction for recovering the capacity of imbalanced VFB.

Analysis of imbalance effects

In our previous work [4], we obtained a theoretical expression that allows to calculate the State of Health (SoH) of VFBs that suffer from simultaneous faradaic and stoichiometric imbalance. In particular, the ratio between the total capacity of an imbalanced VFB (Q_M) and the ideal total capacity corresponding to a balanced VFB (Q_M^N) can be expressed as follows:

$$SoH = \frac{Q_M}{Q_M^N} = \frac{\min\{M_2, M_5\} + \min\{M_3, M_4\}}{M_t/2}, \quad (1)$$

where M_i is the number of vanadium moles with oxidation state $+i$ and M_t is the total number of vanadium moles in the system: $M_t = M_2 + M_3 + M_4 + M_5$. Then, to explicitly decouple the effects of both imbalance types, we define a “Stoichiometric Imbalance Index” (Δm) that quantifies the difference of the number of moles between the positive and the negative electrolyte; and a “Faradaic Imbalance Index” (Δq), that quantifies the deviation of the AOS from its ideal value of +3.5.

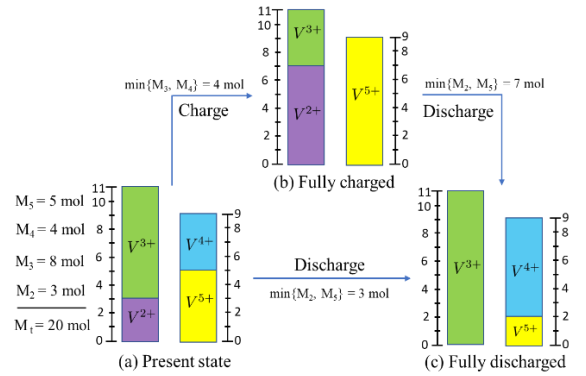
$$\Delta m = 2 \times \frac{(M_4 + M_5) - (M_2 + M_3)}{M_t} \quad (2)$$

$$\Delta q = 2 \times \left(\frac{2M_2 + 3M_3 + 4M_4 + 5M_5}{M_t} - 3.5 \right) \quad (3)$$

Accordingly, we rewrite (1) in terms of Δm and Δq , obtaining the following picewise expression:

$$SoH = \begin{cases} 1 - \max\left\{\Delta q - \Delta m, \frac{\Delta m}{2}\right\}, & \Delta m \leq 2\Delta q \\ 1 - \max\left\{\Delta m - \Delta q, -\frac{\Delta m}{2}\right\}, & \Delta m > 2\Delta q \end{cases} \quad (4)$$

An illustrative example of the utilisation of Eqs (1) and (4) is presented in Fig.1 and Fig.2, respectively. Note that both yield the same results for calculating the SoH of the battery, but (4) allows to more clearly appreciate the combined effects and interactions of both types of imbalance.



$$SoH = \frac{\min\{M_{2,(a)}, M_{5,(a)}\} + \min\{M_{3,(a)}, M_{4,(a)}\}}{M_t/2} = \frac{\min\{M_{2,(b)}, M_{5,(b)}\}}{M_t/2} = \frac{7 \text{ mol}}{10 \text{ mol}} = 70\%$$

Figure 1. Illustration of generalised SoH equation (1).

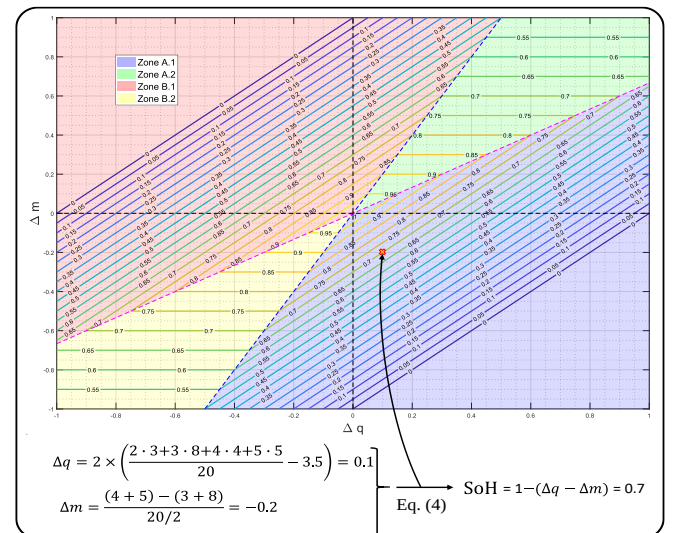


Figure 2. Representation on the $\Delta q - \Delta m$ imbalance plane obtained from (4) of the example of Fig. 1.

Optimal partial remixing method

The main outcome of Eq. (4) is that, for any level of faradaic imbalance, there will be an optimal

stoichiometric imbalance that maximises the VFB capacity. Specifically, this maximum is located at the line $\Delta m = 2/3\Delta q$, i.e., at the border between zones A.1 and A.2, and zones B.1 and B.2 of Fig.2, respectively. In other words, the condition $\Delta m = 0$ will only be desirable if Δq is also equal to 0. From (4) it is obtained that $SoH = 1 - |\Delta q|$ if $\Delta m = 0$, while $SoH = 1 - 1/3|\Delta q|$ if $\Delta m = 2/3\Delta q$. Thus, in a faradaic imbalanced VFB ($\Delta q \neq 0$), it is expected that at $\Delta m = 2/3\Delta q$, the capacity loss will be only one third of the capacity loss with $\Delta m = 0$, namely, with perfectly balanced electrolyte masses.

The current value of Δq can be determined from (3) if the concentrations and volumes are being measured. Alternatively, it can be obtained by performing firstly a total remixing and then solving (4) assuming $\Delta m = 0$. Once Δq has been determined, the optimal partial remixing can be conducted by transferring a calculated volume of electrolyte in order to reach the target $\Delta m = 2/3\Delta q$.

Experimental Results

The proposal was validated in the Flow Battery-Cell Testing Facility (FB-CTF), of the Electrochemical Energy Storage and Conversion Laboratory (EESCoLab) at the University of Padua. In the tests, 290 ml of electrolyte with a total vanadium concentration of 1.6 M is placed in each tank. The VFB starts from a perfectly balanced condition and undergoes 50 CC/CV cycles, during which the battery becomes progressively imbalanced. To accelerate the process of oxidation and avoid extremely lengthy tests, no nitrogen purge is applied to the tanks. Once these 50 cycles are finished, a total remixing is performed, and two more cycles are conducted. Finally, an optimal remixing followed by two final cycles is performed.

Fig. 3 shows the capacity evolution throughout the complete test. Note that, as a result of the imbalance, the capacity gradually decreases from an original 11.1 Ah (SoH=100%) at point “1” to an exiguous 0.55 Ah (SoH=5%) at point “2”. Since oxidation constitutes the main source of imbalance, the total remixing leads to a limited capacity recovery, up to 4.1 Ah (SoH=37%) at point “3”. Finally, the optimal remixing is conducted by

transferring 64 ml of electrolyte to the positive side, which results in a dramatic capacity recovery, reaching a value of 8.2 Ah (SoH=78%) at point “4”.

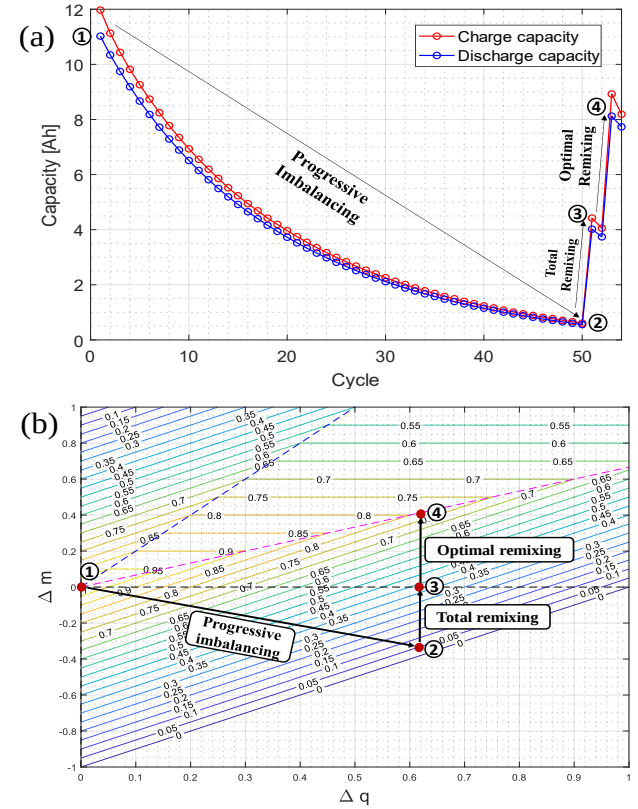


Figure 3. a) Capacity evolution as the battery becomes progressively imbalanced and subsequent recovery attained by total and optimal remixing. b) Trajectory of the system on the $\Delta q - \Delta m$ imbalance plane.

Conclusion

This work presented a cost-effective optimal partial remixing method that allows to recover two-thirds of the capacity loss of a VFB suffering from faradaic and stoichiometric imbalance. To the best of our knowledge, this is the first experimentally validated method that allows to mitigate the capacity loss associated to oxidation without resorting to any additional equipment beyond the one required for a total remixing. This allows to reduce the frequency of scheduled chemical/electrochemical servicing in commercial VFBs and, furthermore, eliminates the need to take the battery out of service in the event of unforeseen issues, such as an accelerated oxidation due to imperfect tank sealing.

Acknowledgements

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