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

Thomas Puleston[a], Giacomo Marini[b], Maria Serra[a], Ramon Costa-Castelló[a], Andrea Trovò[b], Massimo Guarnieri[b]

[a] Institut de Robòtica i Informàtica Industrial (IRI-CSIC-UPC), Polytechnic University of Catalonia, Barcelona, Spain.

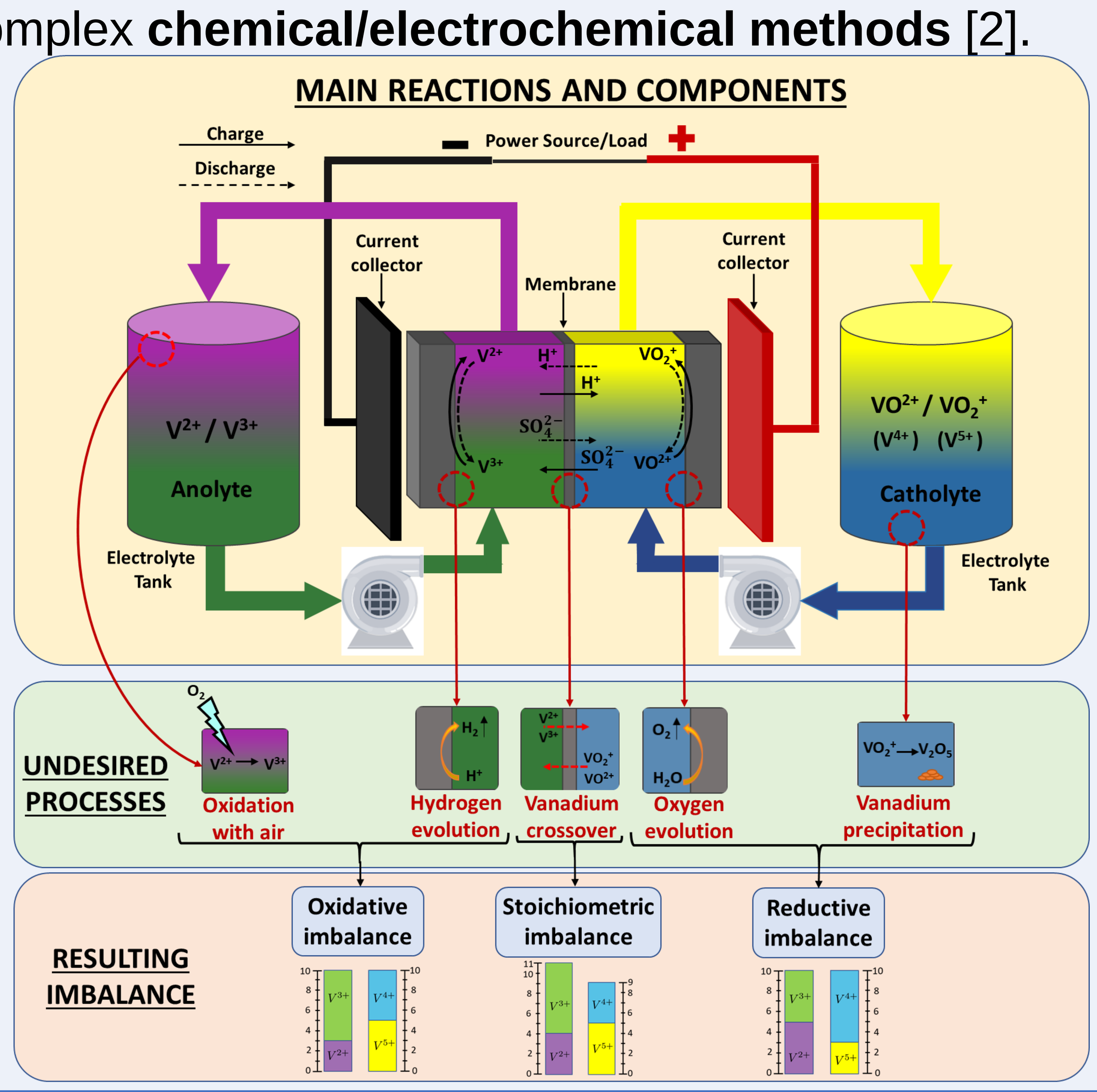
[b] Electrochemical Energy Storage and Conversion Laboratory (EESCoLab), Department of Industrial Engineering, University of Padua, Italy.

Email: thomas.paul.puleston@upc.edu (Thomas Puleston); giacomo.marini@unipd.it (Giacomo Marini)

INTRODUCTION

Electrolyte imbalance is the main cause of capacity loss in VFB:

- **Stoichiometric imbalance** ("mass imbalance"): originated by crossover through the membrane. It can be corrected by **remixing** the electrolytes and evenly splitting the resulting solution [1].
- **Faradaic imbalance** ("oxidative/reductive imbalance"): originated by side reactions that produce a shift in the ideal **Average Oxidation State** (AOS) of +3.5. It can only be reverted by means of more complex **chemical/electrochemical methods** [2].



STATE OF HEALTH

We derive an expression for the **State of Health** (SoH) that considers **both types of imbalances** [3]:

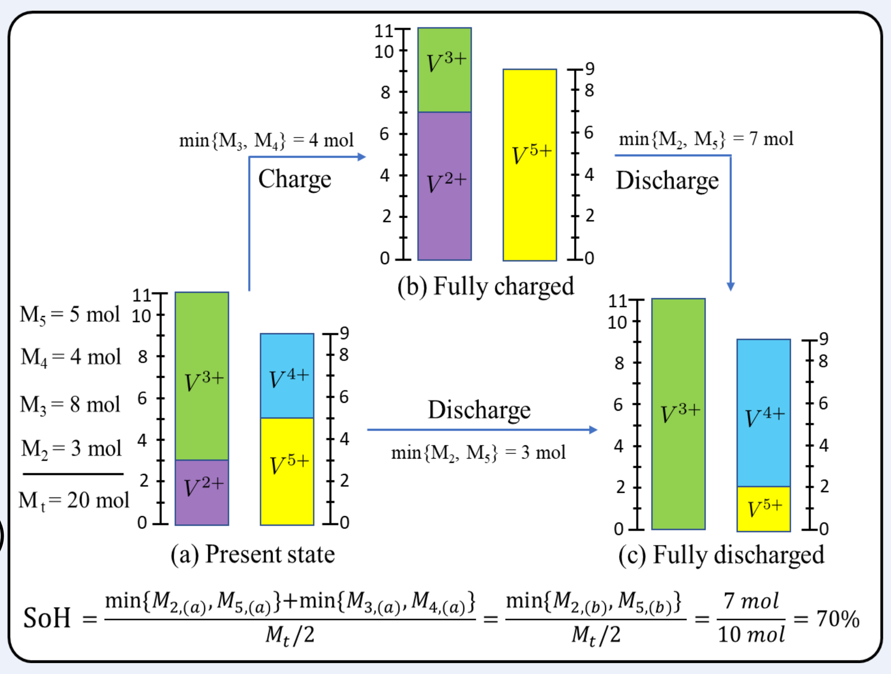
$$\mathrm{SoH} = \frac{Q_M}{Q_M^N} = \frac{\min\{M_2, M_5\} + \min\{M_3, M_4\}}{M_t/2}$$

Q_M: Total capacity of an imbalanced VFB.

Q_M^N: Ideal total capacity of a balanced VFB with the same number of moles.

M_i: number of vanadium moles with oxidation state $+i$.

M_t: total number of moles ($M_t = M_2 + M_3 + M_4 + M_5$)



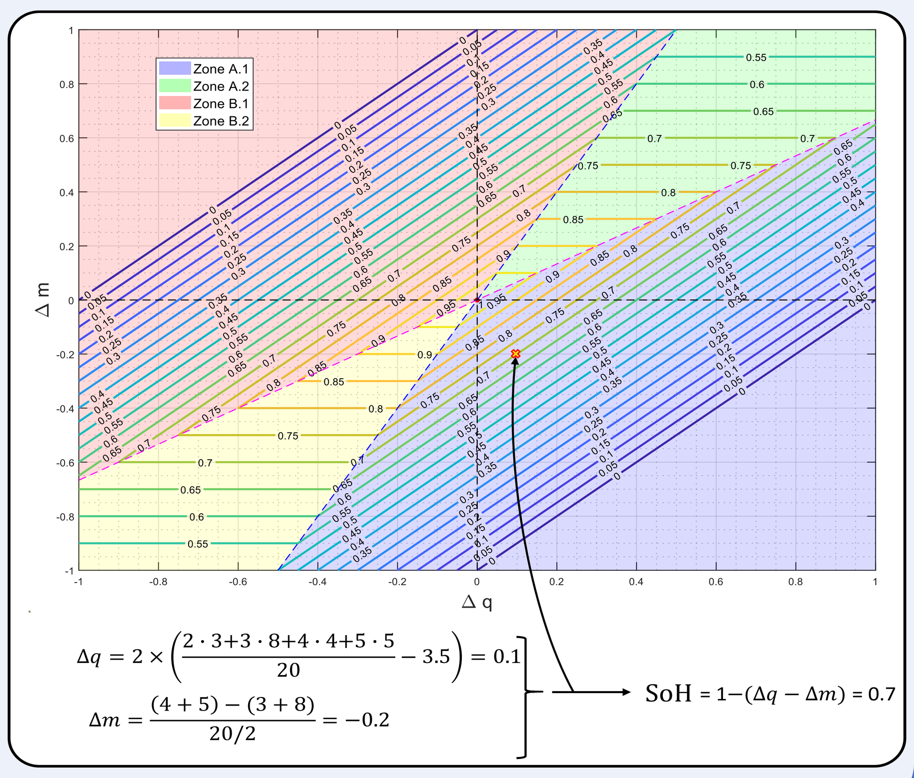
To **decouple** both sources of imbalance, we define a "**Stoichiometric Imbalance Index**" (Δm), and a "**Faradaic Imbalance Index**" (Δq):

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

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

Rearranging, we obtain that:

$$\mathrm{SoH} = \begin{cases} 1 - \max\left\{\Delta q - \Delta m, \frac{\Delta m}{2}\right\}, & \Delta m \le 2\Delta q \\ 1 - \max\left\{\Delta m - \Delta q, -\frac{\Delta m}{2}\right\}, & \Delta m > 2\Delta q \end{cases}$$



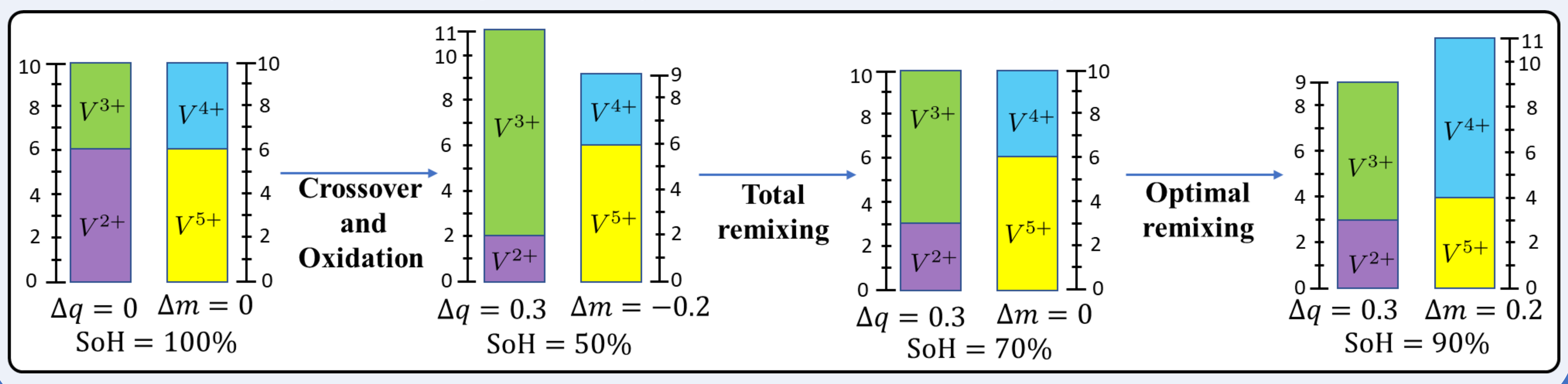
OPTIMAL REMIXING METHOD

From the SoH imbalance plane, it is obtained that for **any level of faradaic imbalance**, there will be an **optimal stoichiometric imbalance** that **maximises the VFB capacity.** This maximum is located at the line $\Delta m = 2/3\Delta q$:

If $\Delta m = 0$ → $\mathrm{SoH} = 1 - |\Delta q|$

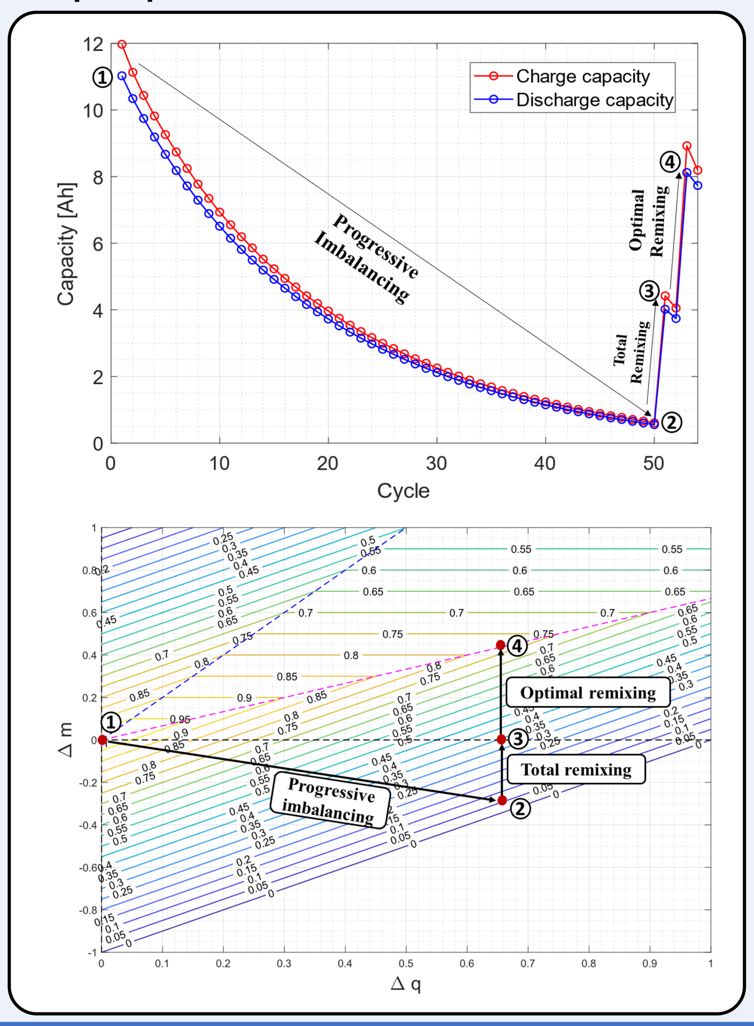
If $\Delta m = 2/3\Delta q$ → $\mathrm{SoH} = 1 - 1/3|\Delta q|$

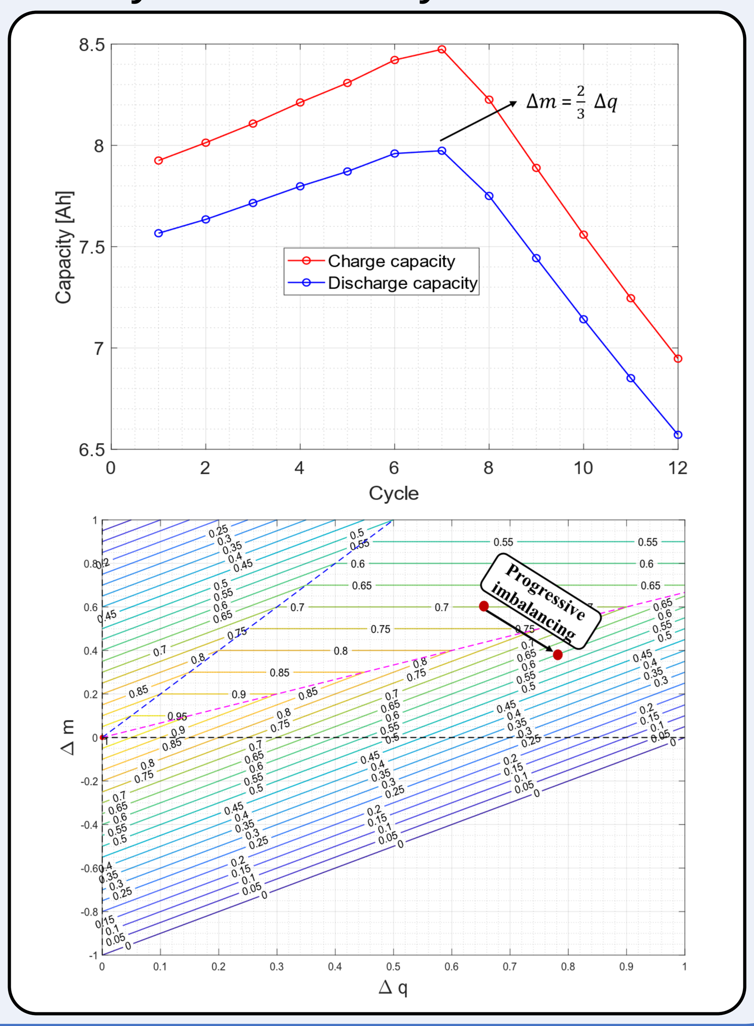
The optimal remixing method consists of transferring a calculated volume of electrolyte in order to reach target asymmetric distribution: $\Delta m = 2/3\Delta q$. The **capacity loss** will be only **one-third** of the loss with $\Delta m = 0$, namely, with perfectly balanced electrolyte masses.



EXPERIMENTAL RESULTS

The proposal was validated at a laboratory-scale facility at EESCoLab.





CONCLUSION

- Theoretical predictions of **capacity recovery** through optimal mass imbalance were **experimentally verified**.
- Total remixing is **counterproductive** under certain conditions.
- **Optimal remixing** allows to recover a 67% of the capacity loss of VFB associated to oxidative/reductive imbalance without resorting to any chemical/electrochemical methods.
- Optimal remixing is **a very simple procedure**; it could be easily implemented in **large-scale** VFBs.

REFERENCES & ACKNOWLEDGEMENTS

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