Drivers of Membrane Fouling in the Non-aqueous Vanadium Acetylacetonate Redox Flow Battery

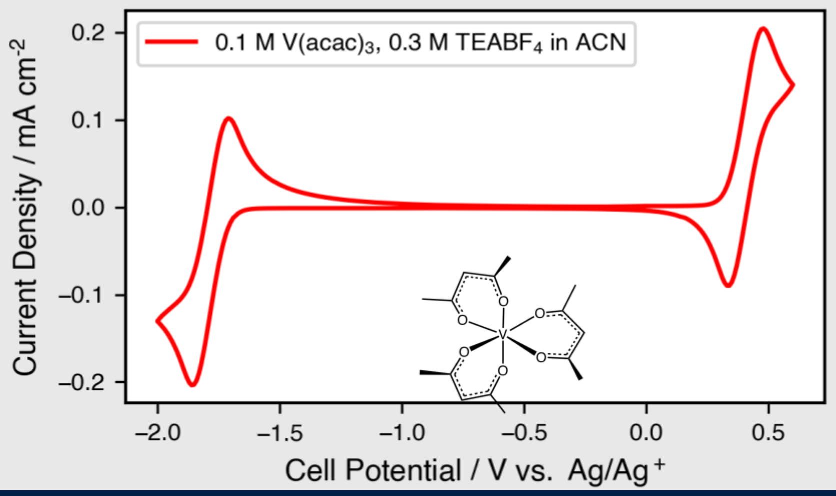
Rohit Rungta[1], Charles W. Monroe[1,2]

[1]*Department of Engineering Science, University of Oxford, Oxford, OX1 3PJ, United Kingdom*

[2]*The Faraday Institution, Harwell Campus, Didcot, OX11 0RA, United Kingdom*

(a) Development of the Nonaqueous $V(acac)_3$ Electrolyte

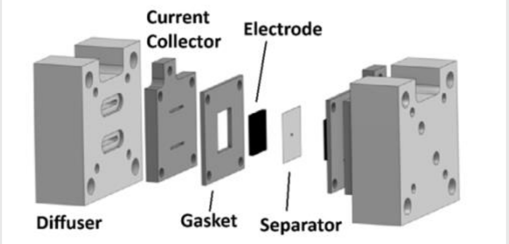
- Liu, Shinkle et al.[1] first synthesized $V(acac)_3$ and reported its kinetics
  - Fast kinetics
  - Wide voltage window of 2.20 V
  - Possible replacement of IEMs (\$500 m^{-2}) for microporous separators (\$10 m^{-2}).
- Escalante-García et al.[2] report poor chemical stability of $V(acac)_3$ during flow cell operation.
- Saraidaridis et al.[3] and Clegg et al.[4] have conflicting cycling results even after eliminating $V(acac)_3$ degradation.

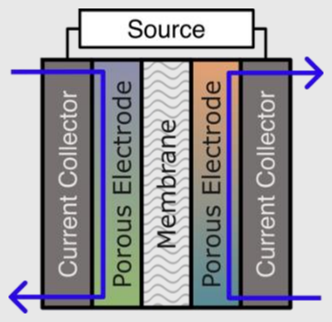


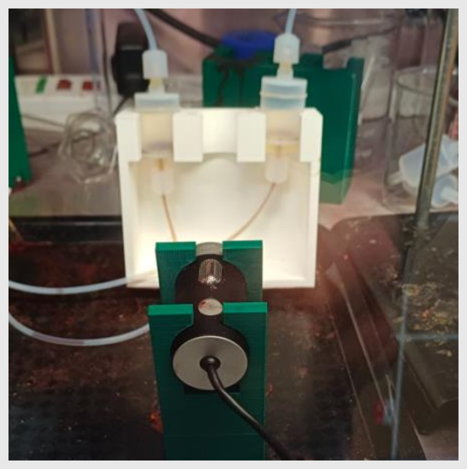
$2V(acac)_3 \leftrightarrow V(acac)_3^+ + V(acac)_3^-$

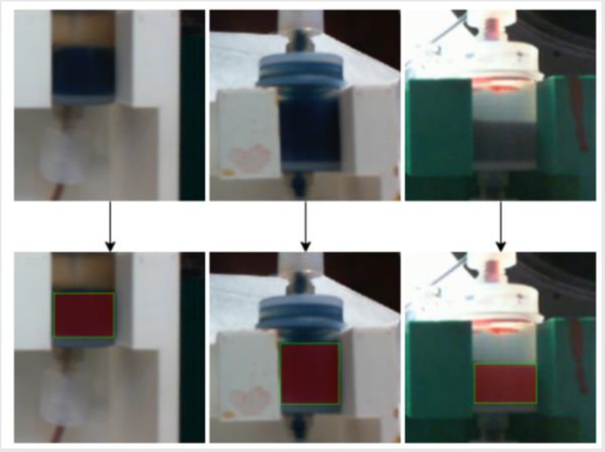
(b) Flow Cell Design and Experimental Setup

- Reactor design is largely inspired from the Brushett group, with slight modifications.
  - 2.20 cm^2 geometric active area ; flow-through configuration ; 20 mA/cm^2 current density ; 20 mL (total) electrolyte sealed in PFA reservoirs ; counter-current flow configuration
- All experiments are conducted with a modified reservoir balancing system developed by Smith et al.[5]
- CV scans of the fresh and spent electrolytes are conducted to confirm its purity.



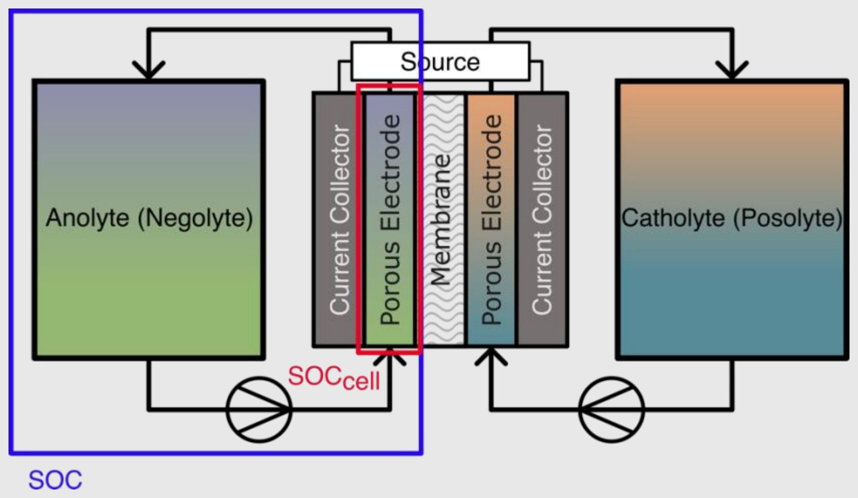






(d) Crossover Estimation During Cell Operation

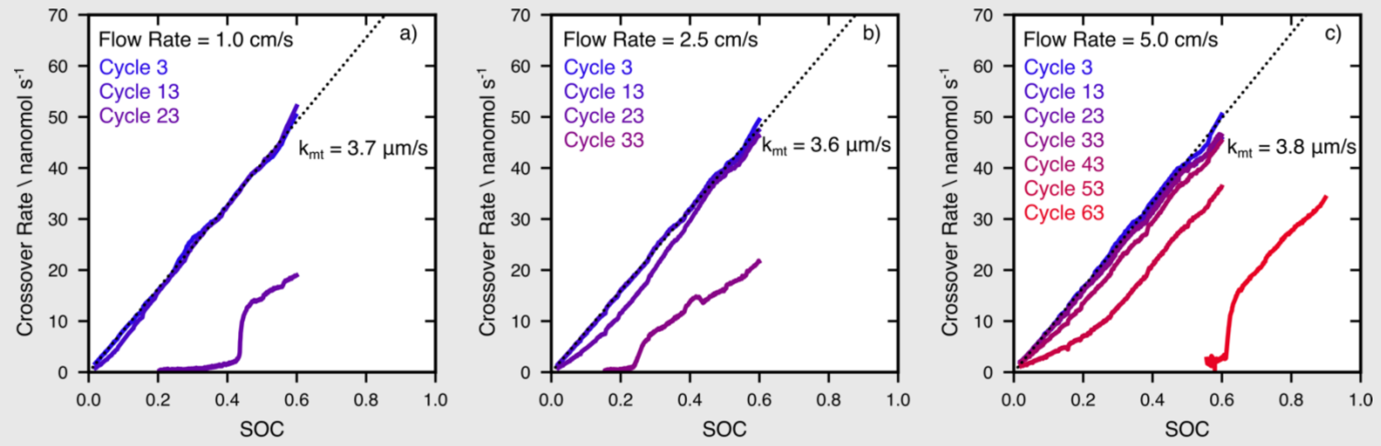
- An isothermal lumped parameter model developed by Ascencio et al.[5] is used to define an adaptive observer which does not make any assumptions regarding the relationship between the crossover rate (Q_x) and SOC.
- If we assume first-order simple Fickian diffusion across the membrane, Q_x has a linear relationship with SOC such that $Q_x = k_{mt}A_xc_0SOC_{cell}$



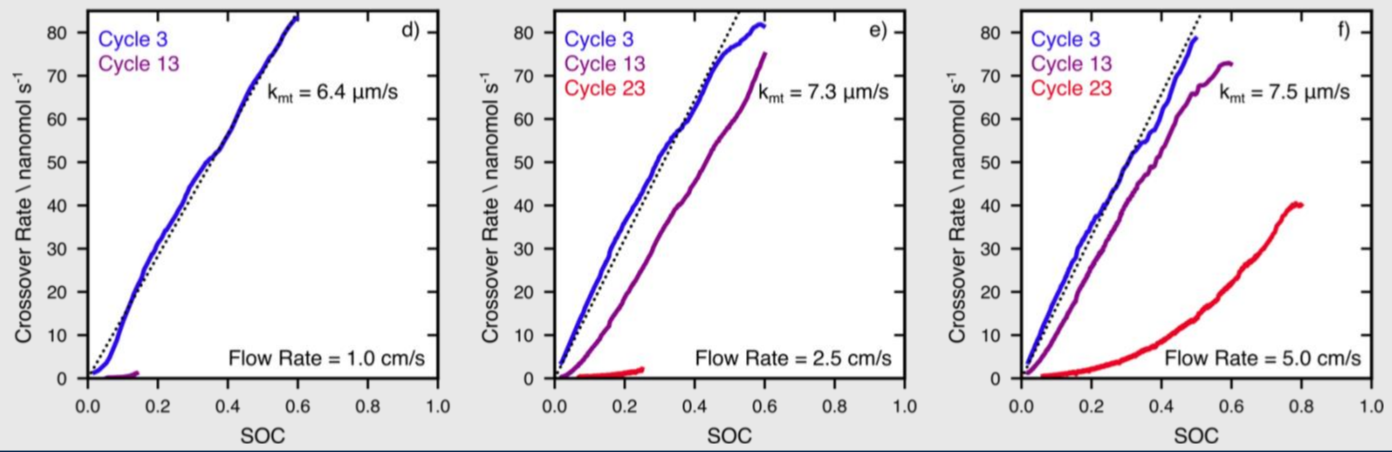
$$V_{out}(t) = \underbrace{E^0_{cell} + \frac{2\mathcal{R}\mathcal{T}}{\mathcal{F}} \ln\left(\frac{SOC_{cell}(t)}{1-SOC_{cell}(t)}\right) + V_R(t)}_{\Gamma(SOC_{cell}(t), I(t))}$$

$$\begin{bmatrix} \frac{dSOC}{dt}(t) \\ \frac{dSOC_{cell}}{dt}(t) \end{bmatrix} = \underbrace{\begin{bmatrix} 0 & 0 \\ \frac{Q(t)}{\epsilon V_{cell}} & -\frac{Q(t)}{\epsilon V_{cell}} \end{bmatrix}}_{A(Q(t))} \begin{bmatrix} SOC(t) \\ SOC_{cell}(t) \end{bmatrix} + \underbrace{\begin{bmatrix} -\frac{1}{c_0 V_{res}} \\ -\frac{1}{\epsilon c_0 V_{cell}} \end{bmatrix}}_{E} \boxed{Q_x(s(t))} + \underbrace{\begin{bmatrix} -\frac{1}{c_0 V_{res}\mathcal{F}} \\ -\frac{1}{\epsilon c_0 V_{cell}\mathcal{F}} \end{bmatrix}}_{B} I(t)$$

- Crossover estimation with Daramic 175

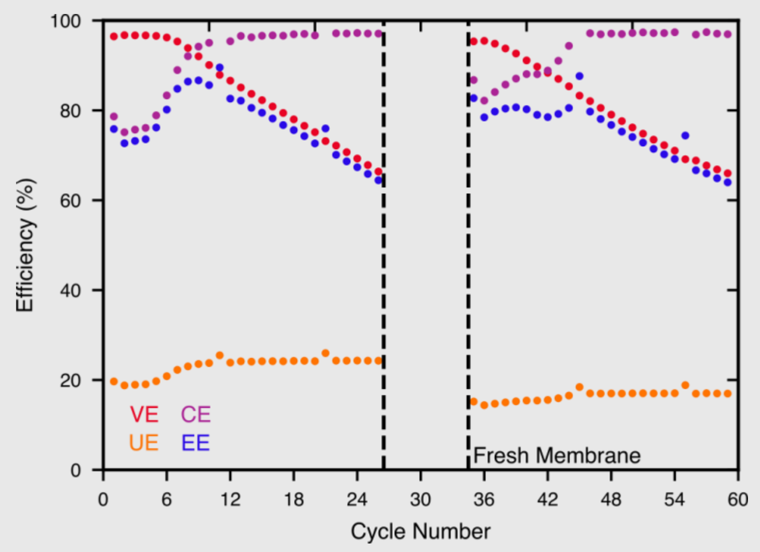


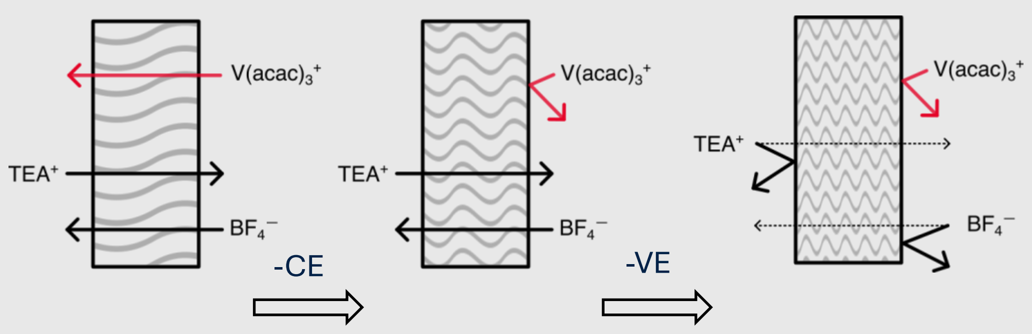
- Crossover estimation with Celgard 4560 – a different mode of degradation



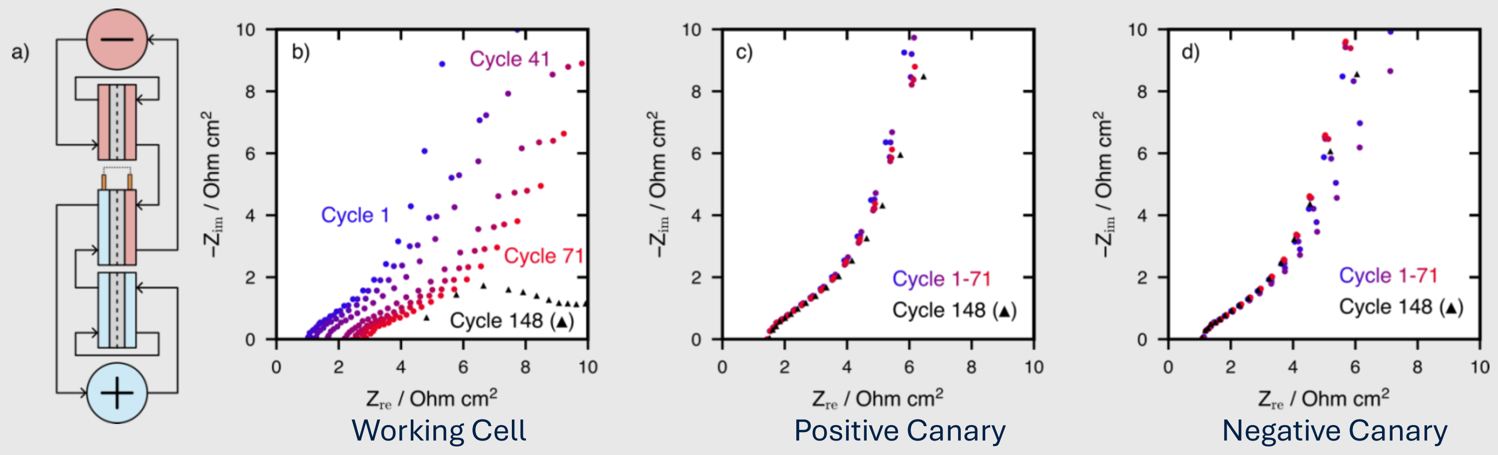
(c) Pore-clogging in Porous Separators

- Performance in a flow reactor

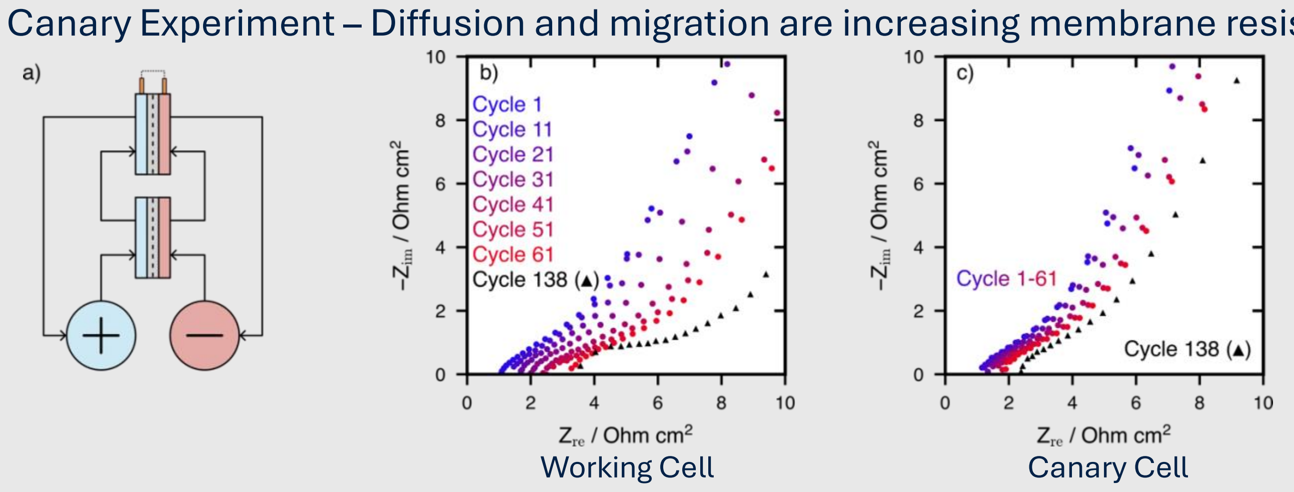




- 3 Cell Canary Experiment – Membranes are stable in both negolyte and posolyte



- 2 Cell Canary Experiment – Diffusion and migration are increasing membrane resistance



(e) Conclusions

- Increase in CE is a result of membrane fouling.
- Impedance measurements during cycling helps identify transient battery properties.
- Adaptive observer elucidates transient crossover mechanisms.

(f) References

[1] A. A. Shinkle, A. E. Sleightholme, L. T. Thompson, C. W. Monroe, Electrode kinetics in non-aqueous vanadium acetylacetonate redox flow batteries, J. Appl. Electrochem. (2011).

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[5] K. P. Smith, C. W. Monroe, Image-based mechanical balancing of reservoir volumes during benchtop flow battery operation, Front. Chem. Eng. (2021).

[6] P. Ascencio, K. Smith, C. Monroe, D. Howey, Adaptive observer for charge-state and crossover estimation in disproportionation redox flow batteries undergoing self-discharge, ACC (2019).

[7] R. Rungta, K. Smith, C. Monroe, Drivers of membrane fouling in the vanadium acetylacetonate flow battery, JMS Letters (2024).