Measurement and control of transport phenomena in nonaqueous flow batteries

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M-RHEX Battery/PV Workshop

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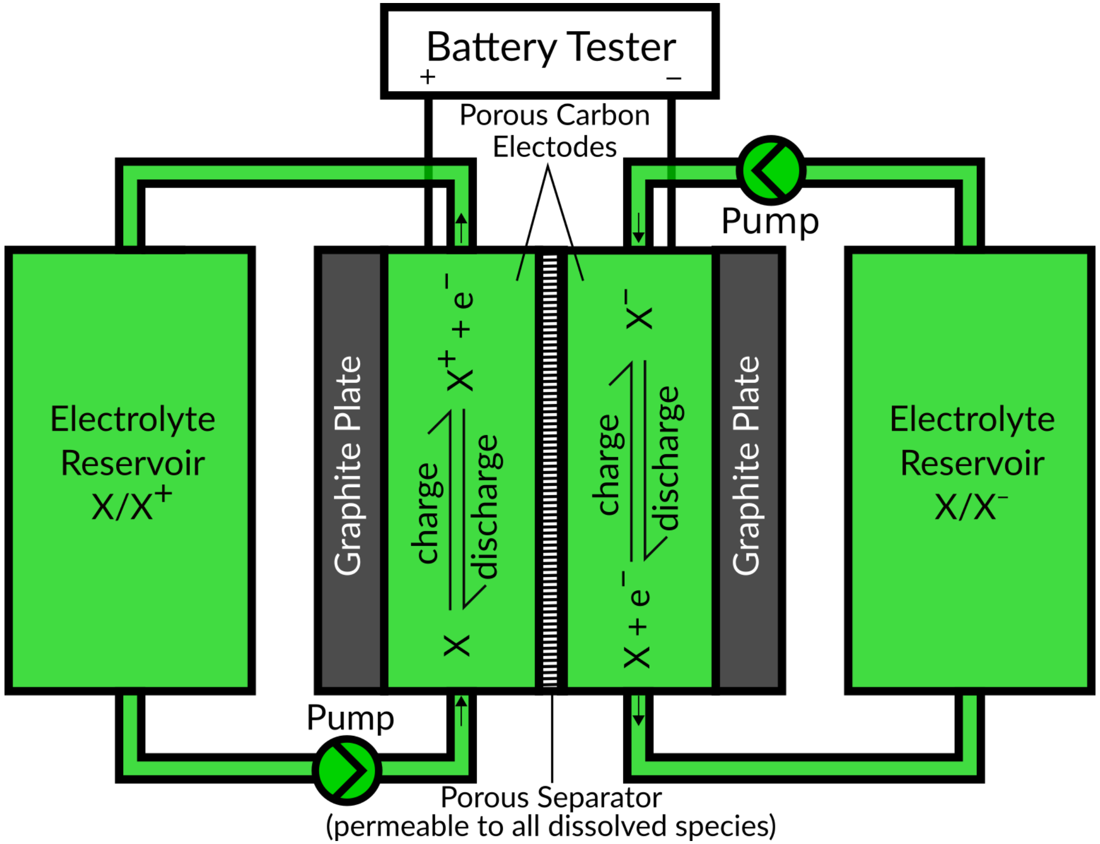
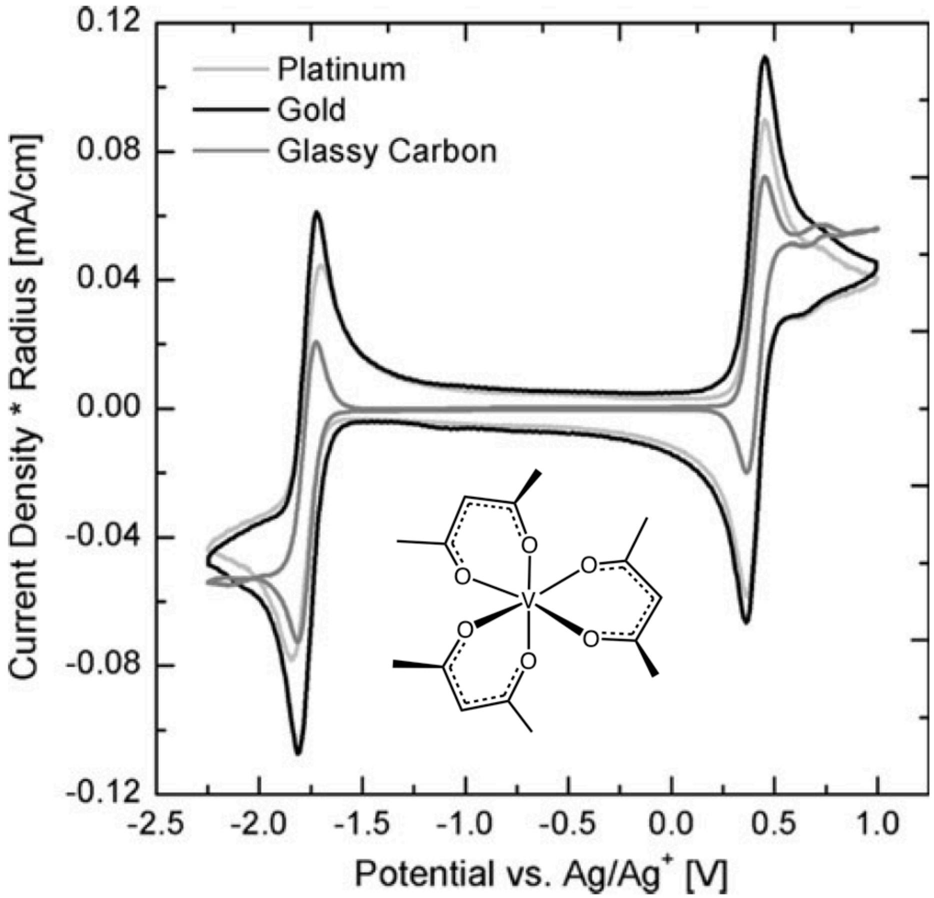
Disproportionation redox flow batteries (DRFBs)



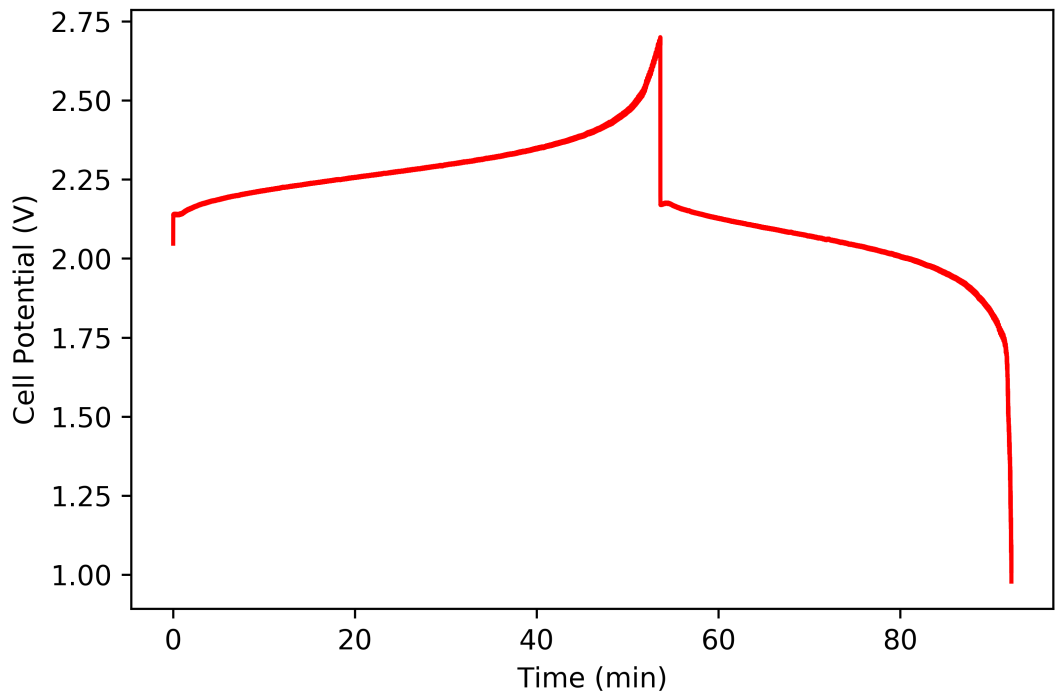
- Cell reaction: $2\,\mathrm{X} \rightleftharpoons \mathrm{X}^{+} + \mathrm{X}^{-}$
- Identical oxidation states in fully discharged reservoirs
- Tolerant of active-species crossover
- Allow use of porous separators

Vanadium acetylacetonate as a model chemistry



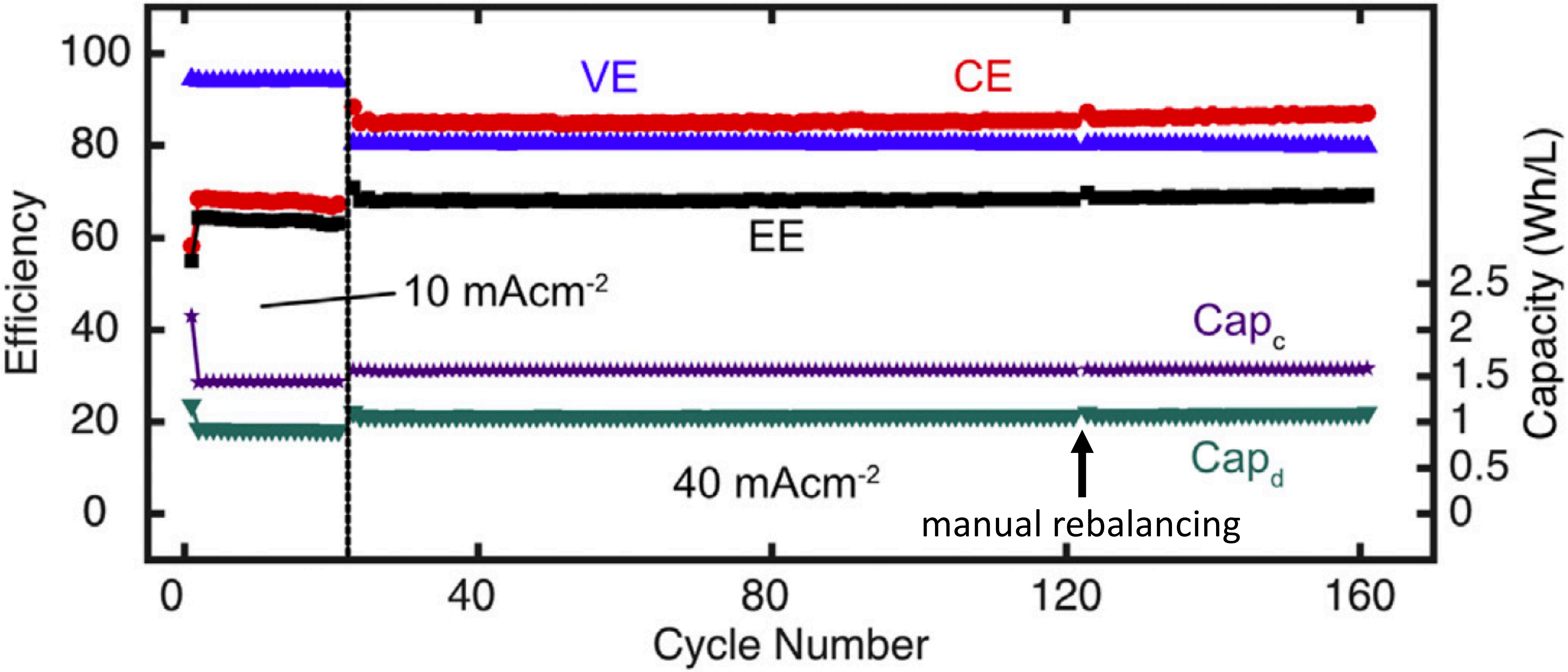
Shinkle *et al.* 2011, *Journal of Applied Electrochemistry*

E° = 2.2 V with acetonitrile as solvent, $TEABF_4$ as salt



- Cycled from 1.0 - 2.7 V
- At 40 mA/cm^2, 0.1 M $V(acac)_3$:
  - Energy efficiency > 70%
  - Energy density > 75% of theoretical
  - > 200 mW/cm^2 peak power density

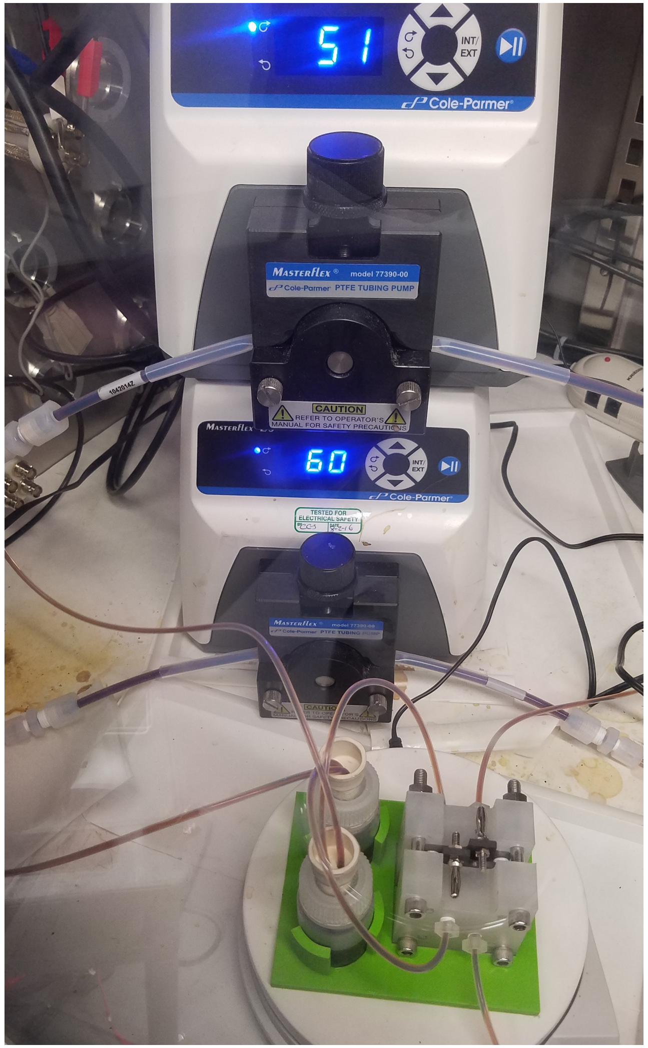
Vanadium acetylacetonate cycles stably

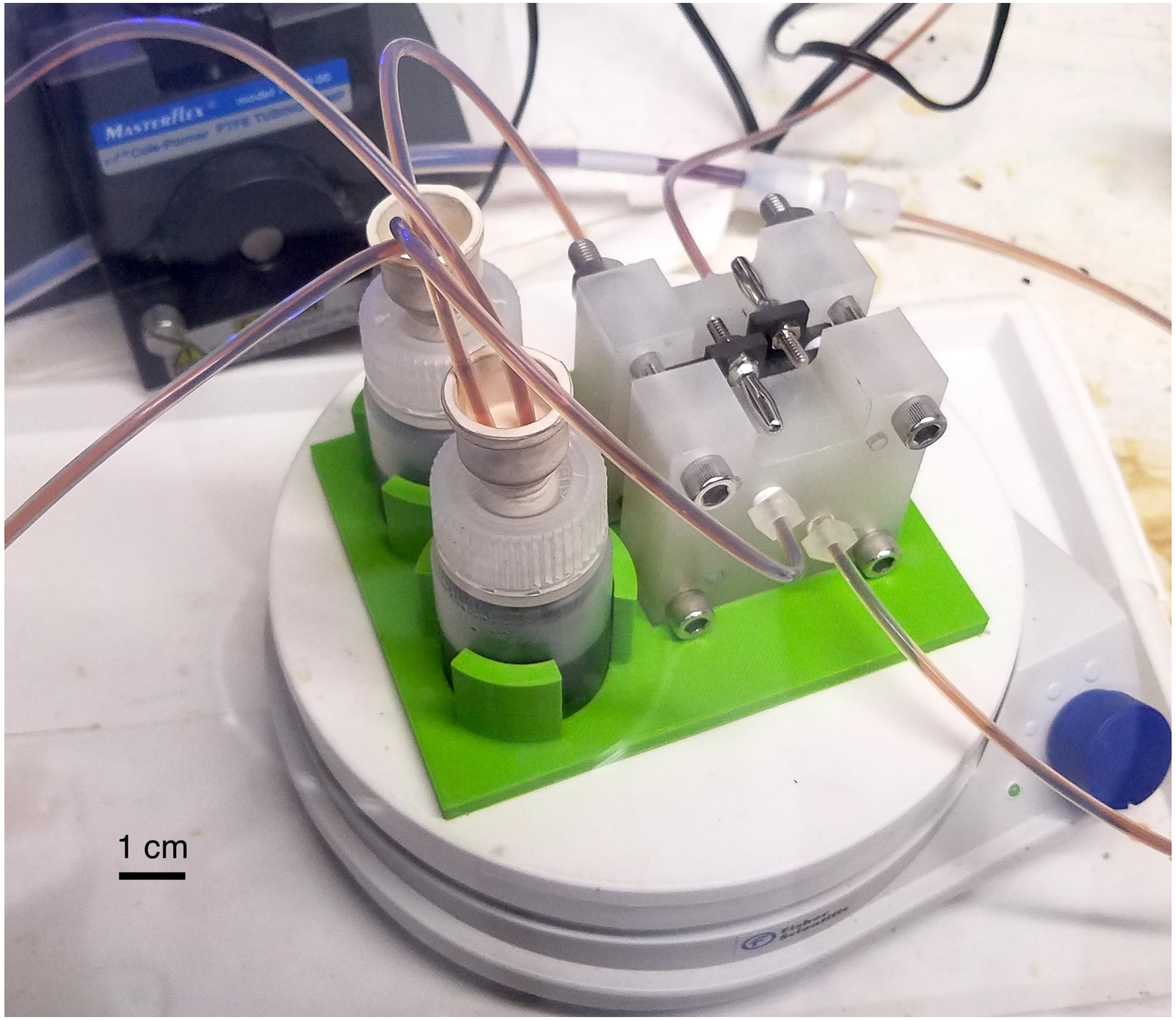


Saraididis and Monroe 2019, *Journal of Power Sources*

6 days of cycling shown

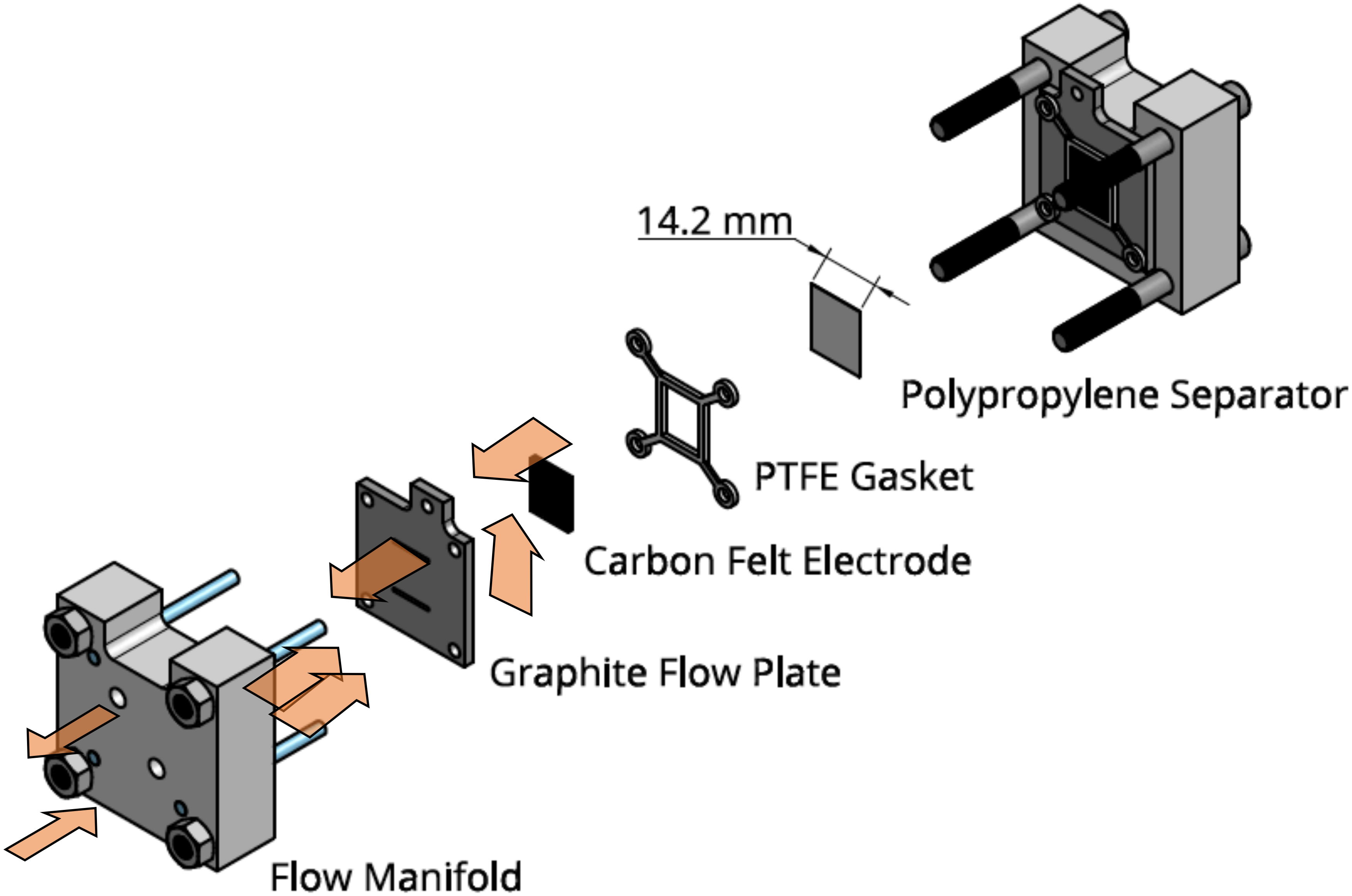
Experimental setup for nonaqueous DRFBs





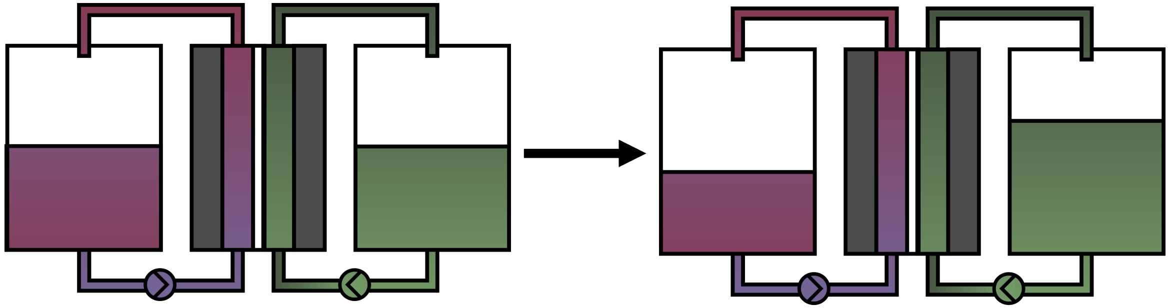
Adapted from Milshtein *et al.* 2016, *Energy & Env. Sci.* and Saraidaridis and Monroe 2019, *Journal of Power Sources*

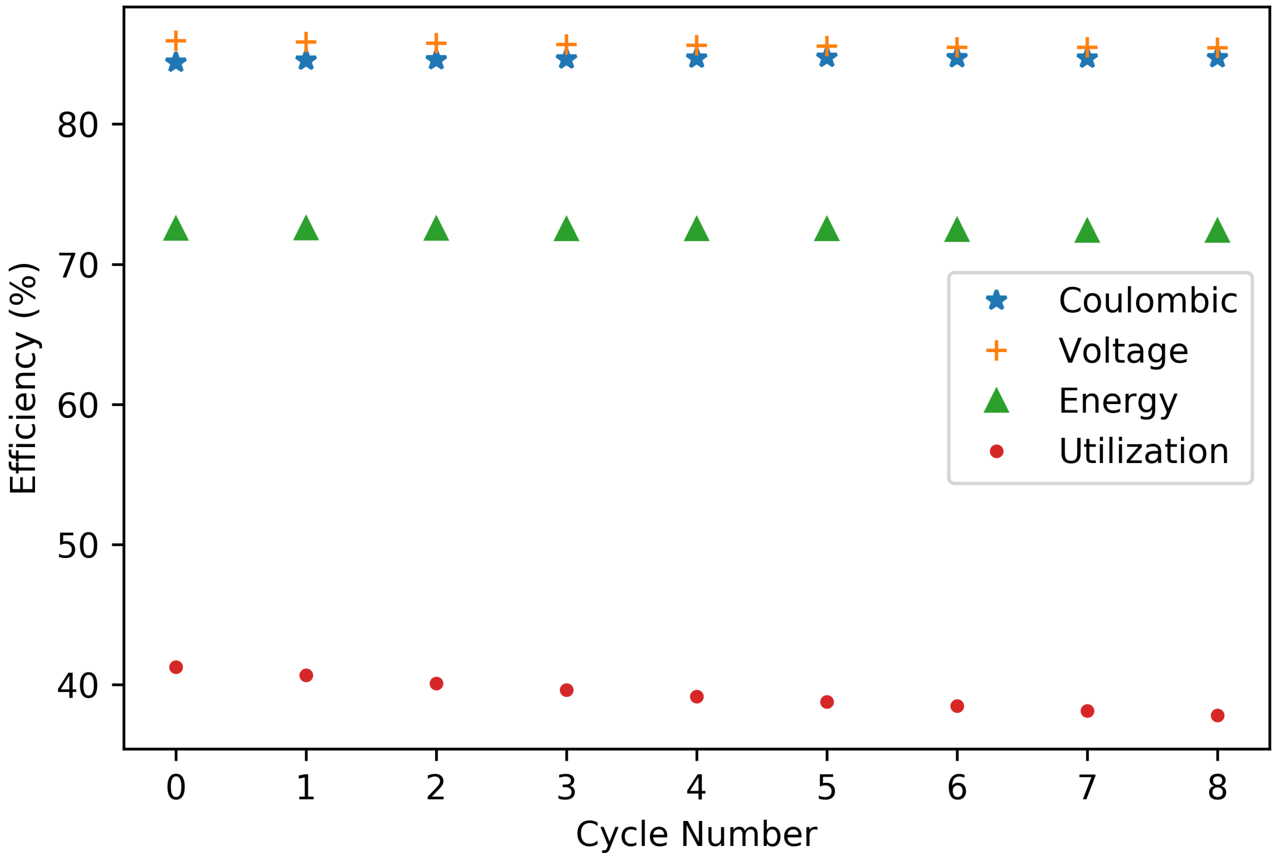
Leak-free reactor design



Adapted from Milshtein *et al.* 2016, *Energy & Env. Sci.* and Saraidaridis and Monroe 2019, *Journal of Power Sources*

Imbalance limits capacity and repeatability



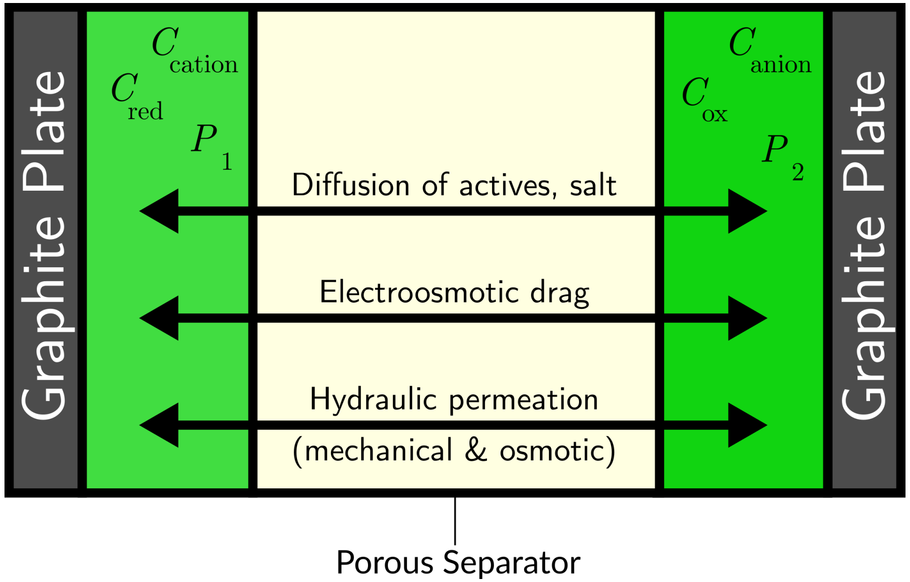


constant

decreasing

Multiples sources of crossover and imbalance

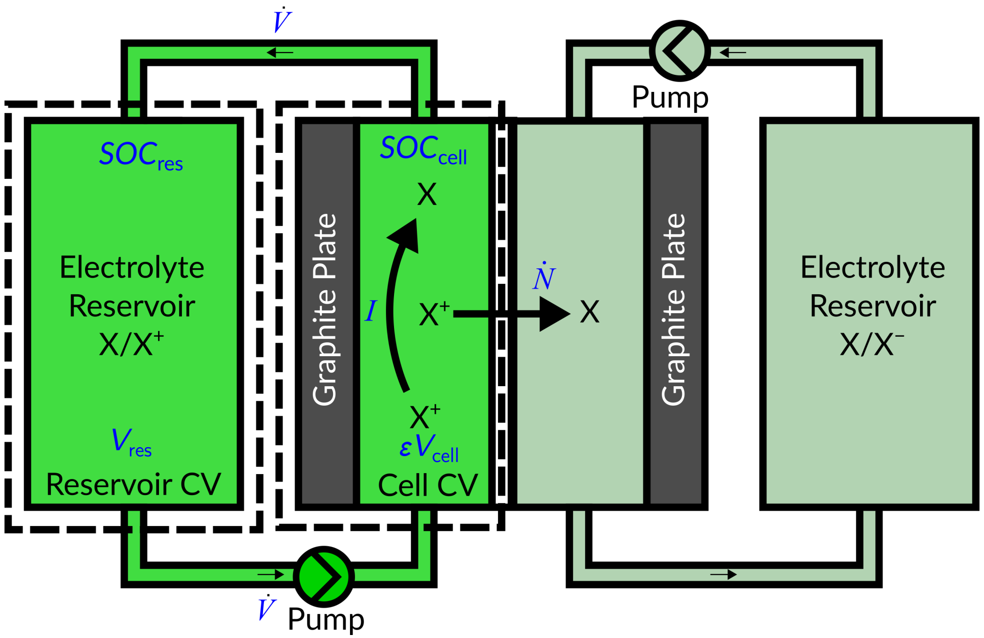
$$\mathrm{V(acac)_3}^{+} + \mathrm{V(acac)_3}^{-} \longrightarrow 2\,\mathrm{V(acac)_3}$$



1. Molecular diffusion, from:
   a) Concentration gradient of active species/salt ions
   b) Solvent migration, from electro-osmotic drag of actives and salt ions [1]
2. Pressure-driven permeation, from:
   a) Difference in hydraulic head across half-cells [2]
   b) Osmotic pressure from concentration differences

[1] Weber *et al.* 2011, *J. Appl. Electrochem*, [2] Li *et al.* 2014, *ChemSusChem*

DRFB model for separator characterization



Reservoir: $$\frac{dSOC_{res}}{dt} = \frac{\dot{V}}{V_{res} - \varepsilon V_{cell}}(SOC_{cell} - SOC_{res})$$

Half-cell: $$\frac{dSOC_{cell}}{dt} = \frac{\dot{V}}{\varepsilon V_{cell}}(SOC_{res} - SOC_{cell}) - \frac{I}{\varepsilon V_{cell} c_0 F} - \dot{N}$$

Output cell potential: $$\theta = E^\circ + \frac{2RT}{F}\ln\left(\frac{SOC_{cell}}{1 - SOC_{cell}}\right) + \eta(I)$$

SOC_{cell} uniform in cell

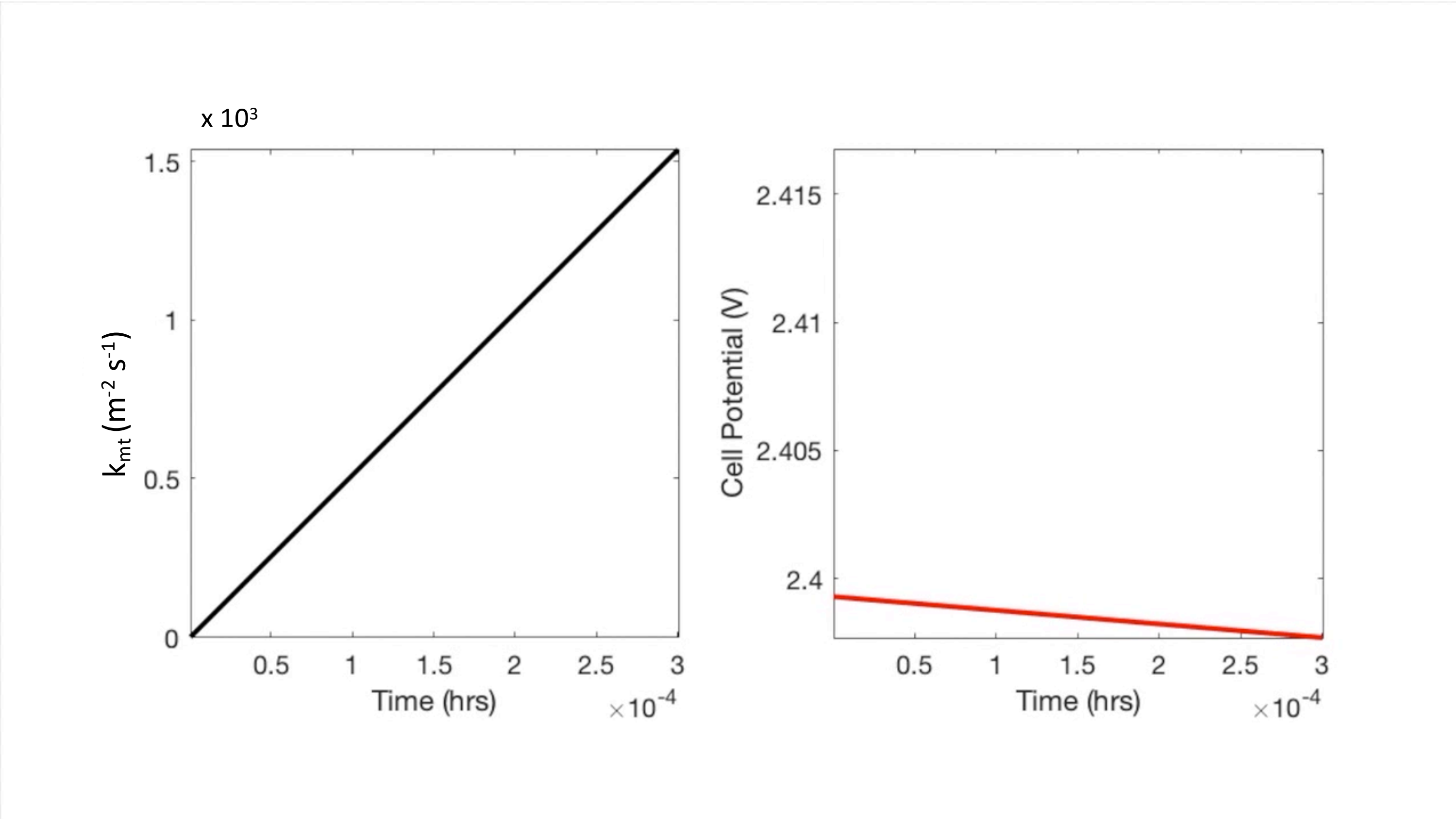
- Higher crossover due to porous separator
- Lower coulombic efficiency: ≈ 85%
- SOC via coulomb counting impractical
- Need for model which quantifies SOC and self-discharge simultaneously

SOC_{res}	reservoir state-of-charge	-	F	Faraday's constant	C/mol
SOC_{cell}	cell state-of-charge	-	$\dot{N}$	self-discharge	s^{-1}
I	applied current	A	ε	electrode porosity	-
V_{res}	reservoir volume	L	V_{cell}	cell volume	L
c_0	$V(acac)_3$ concentration	M	$\dot{V}$	volumetric flowrate	L/s
E°	standard potential	V	θ	cell potential	V

Adaptive observer: real-time estimation of *SOC* and $\dot{N}$

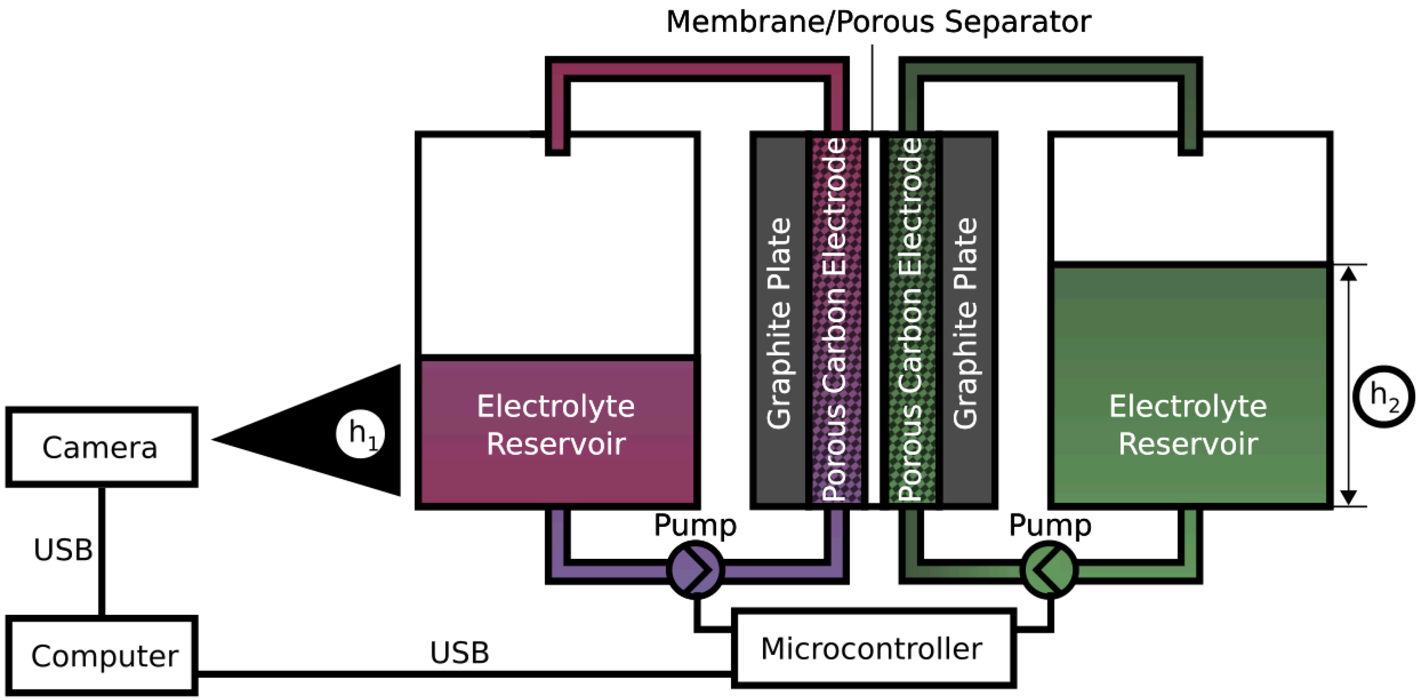
$$k_{\mathrm{mt}} = \frac{\dot{N}}{A_{\mathrm{cell}} SOC_{\mathrm{cell}}}$$

$\dot{N}$	self-discharge	s^{-1}
k_{mt}	mass-transfer coefficient	$m^{-2}\ s^{-1}$
A_{cell}	cell area	m^2
SOC_{cell}	cell state-of-charge	-

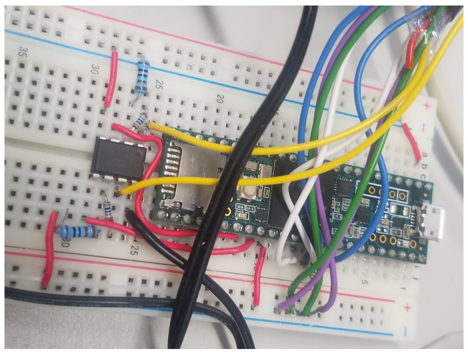


Ascencio *et al.* 2019, *American Control Conference*

PID reservoir balancing control schematic



$$\Delta\omega_{\text{pump}} = f(\Delta h)$$



Goal: equalize hydraulic heads in half-cells in order to balance reservoirs

Electrolyte level sensing: USB camera and Python

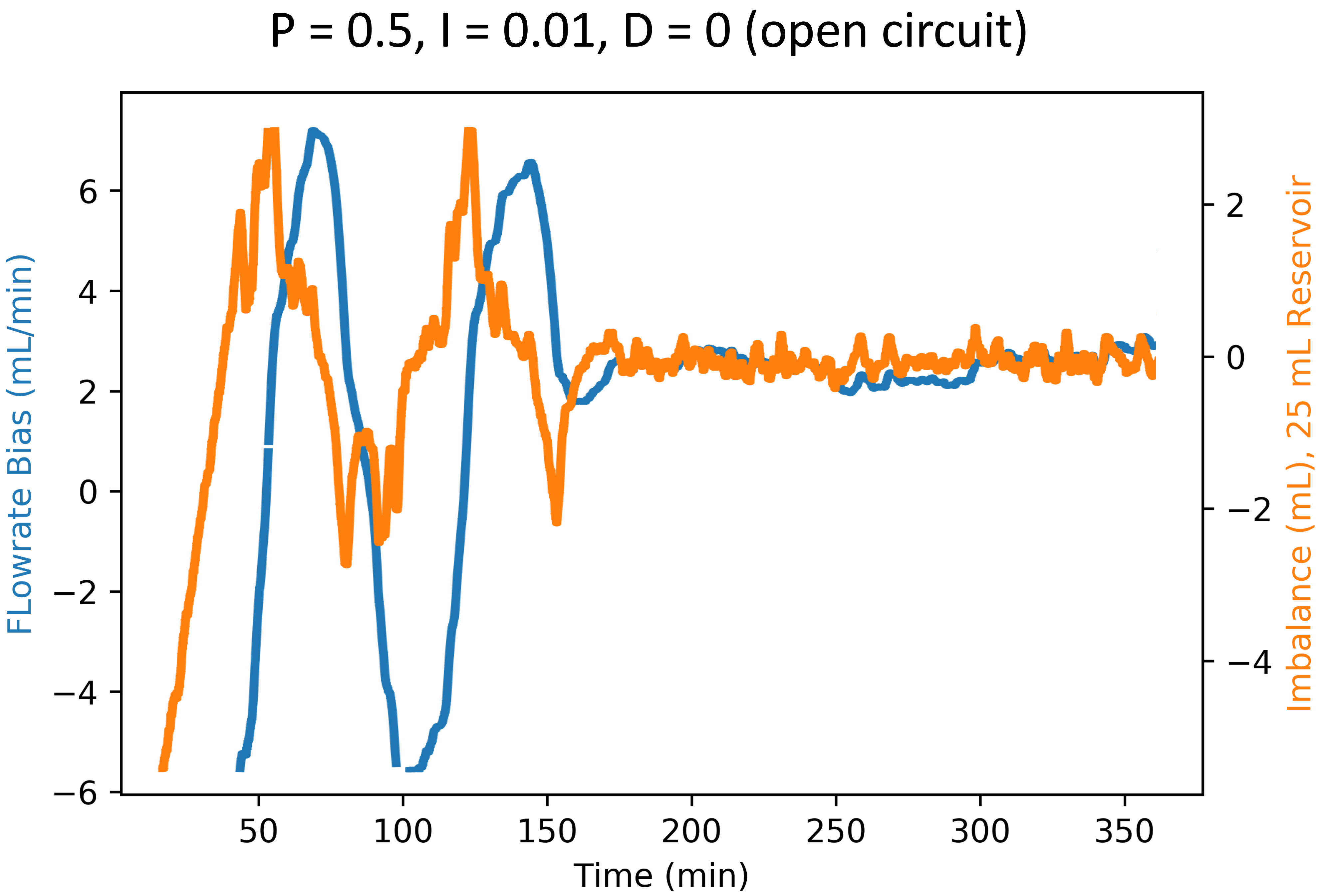
- Mass sensing difficult due to sensitivity requirements, vibration from pumps
- Most submersible level sensors chemically incompatible
- Non-contact sensors (ultrasonic) impractical for small reservoirs

Camera feed of reservoirs

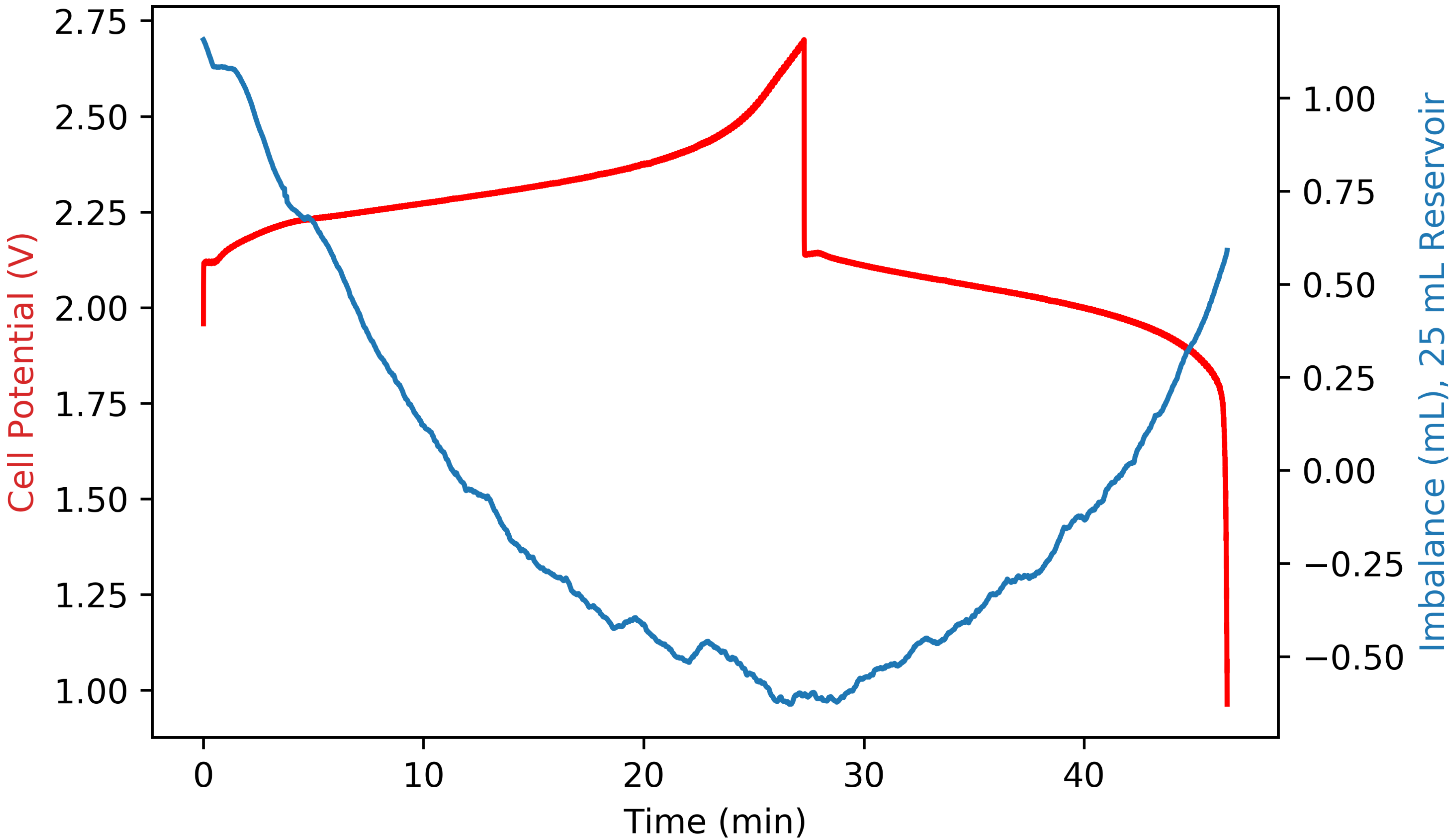
python™

OpenCV

Liquid level height measurements


P = 0.5, I = 0.01, D = 0 (open circuit)
FLowrate Bias (mL/min)
Imbalance (mL), 25 mL Reservoir
Time (min)
6
4
2
0
−2
−4
−6
50
100
150
200
250
300
350
2
0
−2
−4

Inter- and intra-cycle volume imbalance



- Inter-cycle imbalance from pressure difference causes capacity fade
- Intra-cycle imbalance is observable, possibly function of SOC/current

Future work

- Probing intra-cycle imbalance for solvent migration, SOC/current relationship
- Longer term cycling and self-discharge experiments to understand membrane behavior
- Driving development of membranes optimised for disproportionation RFBs
- Operating systems at high active species concentrations

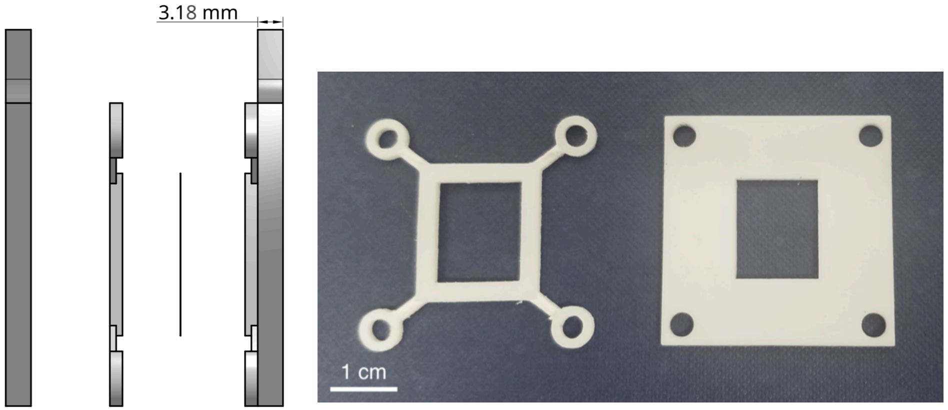
Conclusions

- Nonaqueous RFBs can be operated robustly and offer stable electrochemical performance
- RFBs with porous separators require new models for SOC estimation due to increased crossover
- Engineering solutions can measure, control, and strike balance between transport phenomena
- Balancing these transport phenomena and understanding the self-discharge behavior can enable high energy density disproportionation RFBs

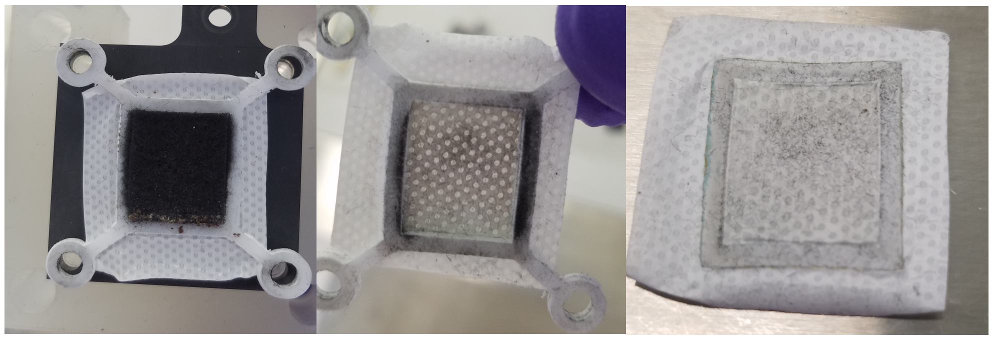
Acknowledgements

- Monroe & Howey Groups
- STFC Batteries Network (ST/R006873/1)

Changed gasket design, connectors for higher sealing pressure

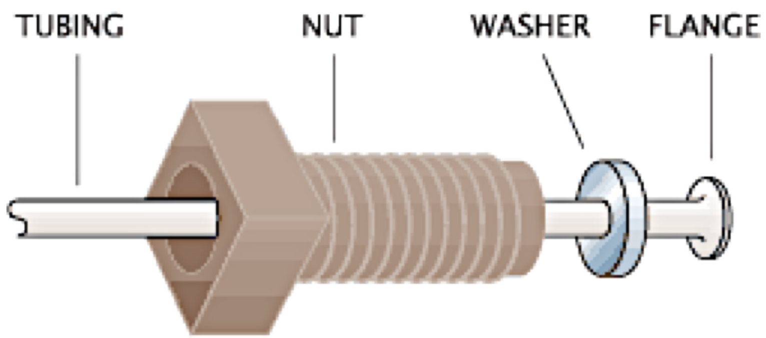


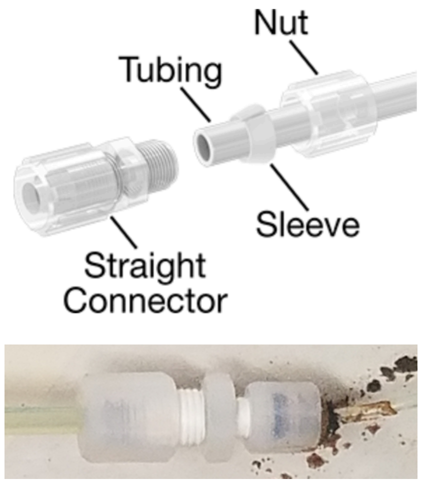
Final gasket design *vs.* original (PTFE, laser cut)



No leaks after over a month

>4x sealing pressure





Cheminert fitting (VICI) *vs.* compression fitting (McMaster-Carr)