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Characterisation of a RHVFC using an experimentally validated unit cell model

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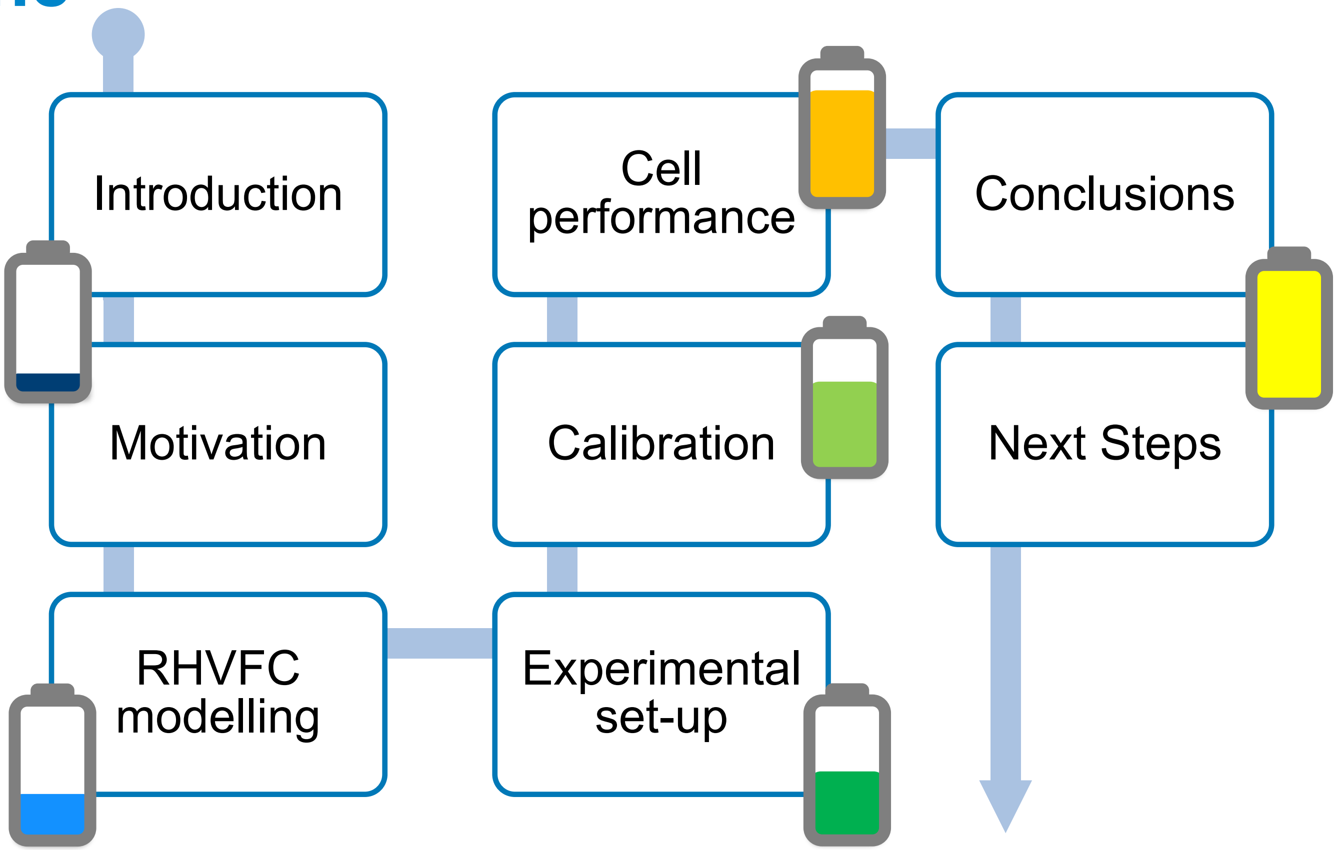
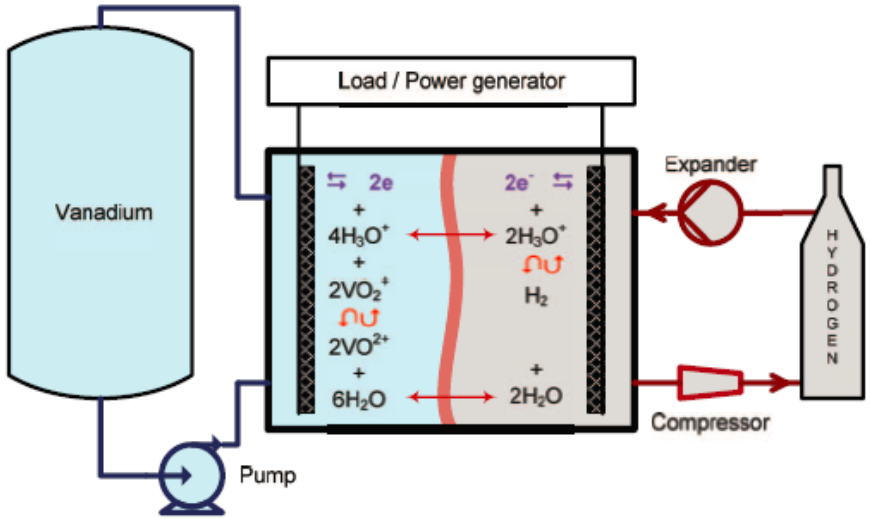
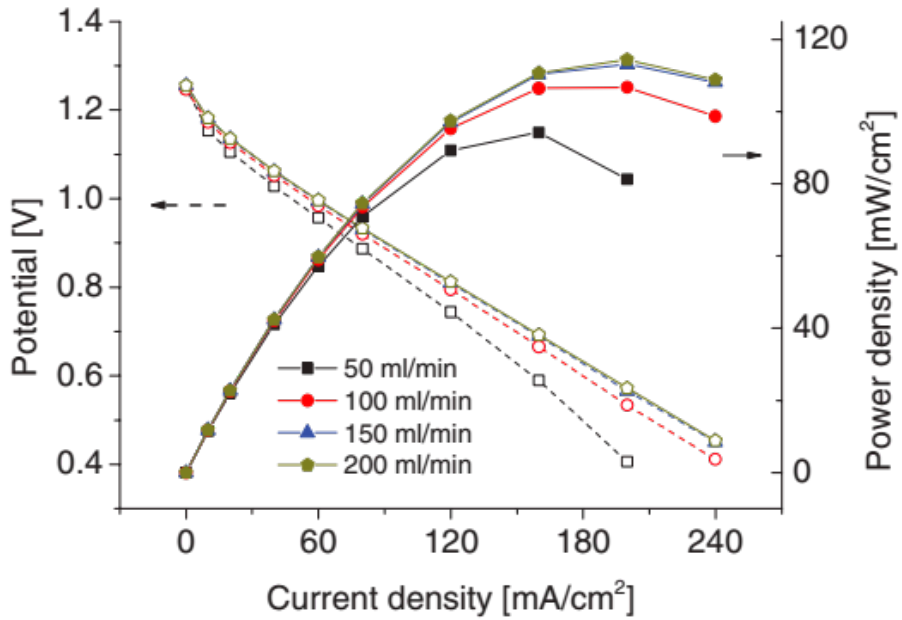
Outline



Regenerative Hydrogen-Vanadium Fuel Cell (RHVFC)





- Fast hydrogen kinetics
- Absence of cross-mixing
- Precious metal catalyst – HOR/HER
- Expertise on PEMFCs

- *Carbon paper electrode SGL 10AA*
- *Nafion 117*
- *SGL GDL, 0.5 mg Pt cm^{-2}*

V. Yufit. et al., Journal of The Electrochemical Society, 2013, 160, A856

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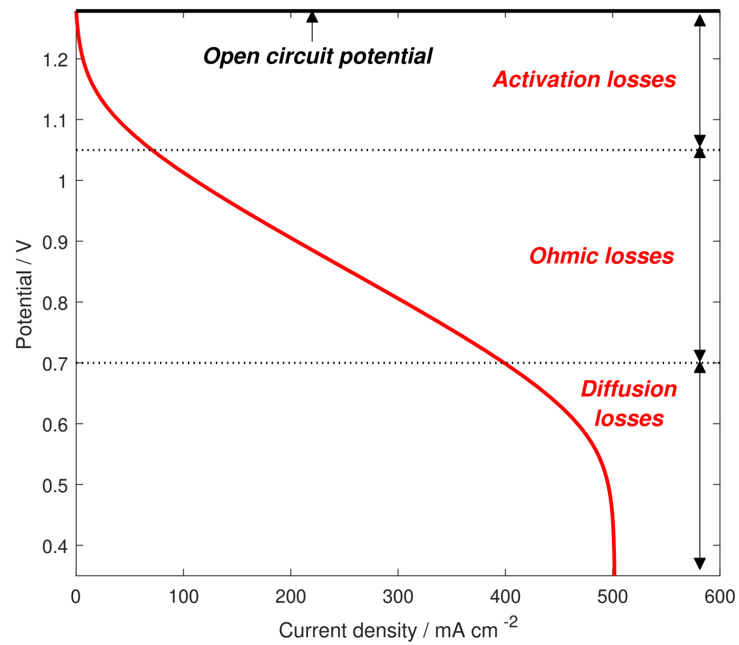
Motivation

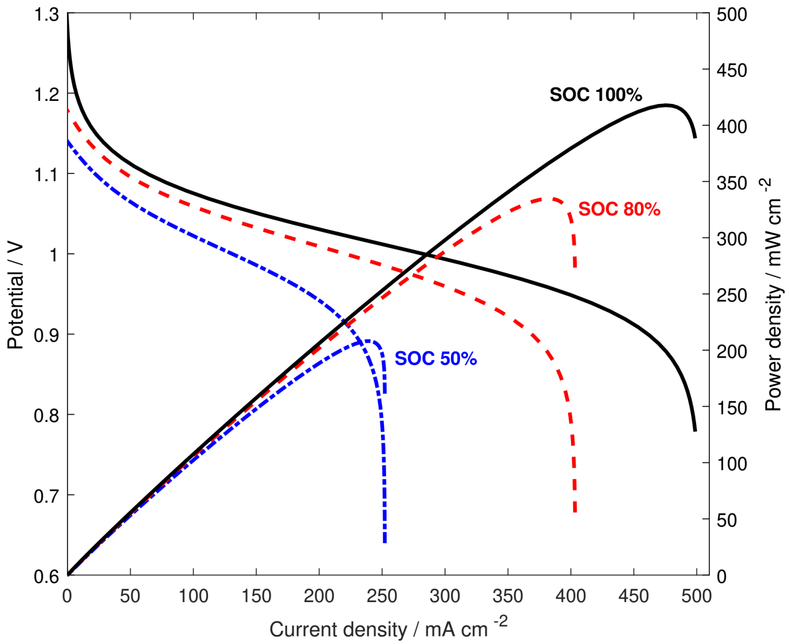
- Unit cell model that can capture the potential dynamics of the cell and allow quick evaluation
- Recognise the dominant processes that affect the cell performance



C. A. Pino-Muñoz, B. K. Chakrabarti, V. Yufit, and N. P. Brandon, Characterisation of a regenerative hydrogen-vanadium fuel cell using an experimentally validated unit cell model, *Journal of The Electrochemical Society* (Submitted)

Motivation

- Unit cell model that can capture the potential dynamics of the cell and allow quick evaluation
- Recognise the dominant processes that affect the cell performance
- Evaluate different operating conditions



C. A. Pino-Muñoz, B. K. Chakrabarti, V. Yufit, and N. P. Brandon, Characterisation of a regenerative hydrogen-vanadium fuel cell using an experimentally validated unit cell model, *Journal of The Electrochemical Society* (Submitted)

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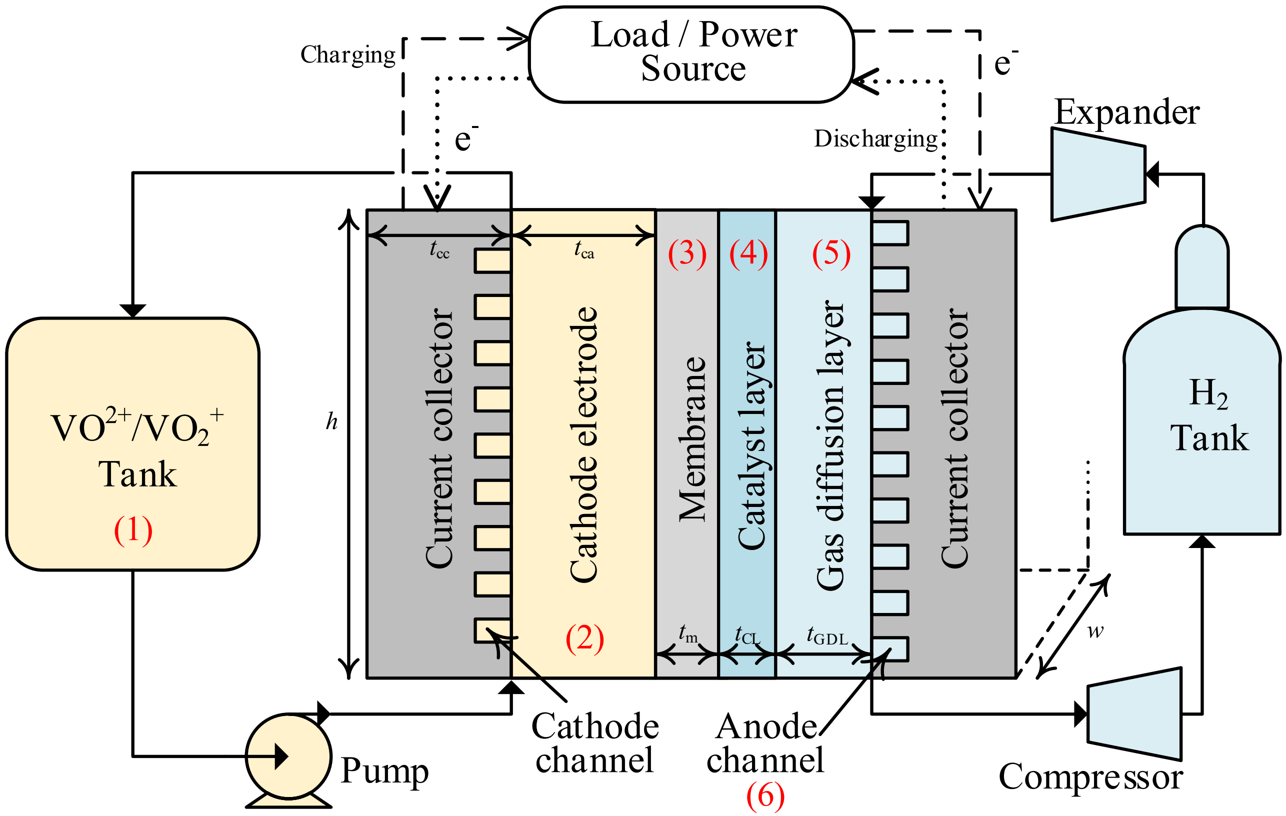
Unit cell model for the RHVFC



Cathode:

$$2VO_2^+ + 4H_3O^+ + 2e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2VO^{2+} + 6H_2O, \quad E^0_{ca} = 0.99\,V$$

Anode:

$$H_2 + 2H_2O \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2H_3O^+ + 2e^-, \quad E^0_{an} = 0\,V$$

Pino-Muñoz et al., Journal of The Electrochemical Society, 2017, 164, F1717

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Model summary

Cell

$$E_{\mathrm{eq}} = E^0_{\mathrm{cell}} + \frac{RT}{F}\ln\left(\frac{c_{\mathrm{V(V)}}c^2_{\mathrm{H^+,ca}}p^{0.5}_{\mathrm{H_2}}}{c_{\mathrm{V(IV)}}c_{\mathrm{H^+,an}}}\frac{c_{\mathrm{H^+,an}}}{c_{\mathrm{H^+,ca}}}\cdot F_\gamma\right)$$

Open circuit potential

Cathode

$$\varepsilon_{ca}V_{\mathrm{ca}}\left(2\frac{dc_{VO^{2+}}}{dt}+\frac{dc_{\mathrm{VO_2^+}}}{dt}+\frac{dc_{\mathrm{H^+}}}{dt}-\frac{dc_{\mathrm{HSO_4^-}}}{dt}-2\frac{dc_{\mathrm{SO_4^{2-}}}}{dt}\right)=0$$

Anode

$$\sum z_i c_i + z_f c_f = 0$$

Charge conservation

Electro-neutrality

UNIT CELL MODEL

$$E_{\mathrm{cell}} = E_{\mathrm{OCP}} \pm |\eta_{\mathrm{ca}}| \pm |\eta_{\mathrm{an}}| \pm \eta_{\mathrm{ohm}}$$

Anode

$$V_{\mathrm{CL}}\varepsilon_{\mathrm{CL}}(1-s_{\mathrm{CL}})\frac{dc_{\mathrm{H_2,CL}}}{dt} = \pm\frac{A_{\mathrm{CL}}j}{2F} - \dot{n}_{\mathrm{H_2,GDL}}$$

Cathode

$$\varepsilon_{\mathrm{ca}}V_{\mathrm{ca}}\frac{dc_{VO^{2+}}}{dt} = Q_{\mathrm{ca}}\left(c_{VO^{2+},T} - c_{VO^{2+}}\right) \mp \frac{A_{\mathrm{ca}}j}{F} - \dot{n}_{VO^{2+},m}$$

Mass balances

Energy balance

Kinetics

Anode

$$\frac{j^{TV}}{k_{des}} = FZ\left(\theta^{TV}_{H_{ad}}\exp\left(\beta f\eta_{an}\right) - B\left(1-\theta^{TV}_{H_{ad}}\right)\exp\left(-(1-\beta)f\eta_{an}\right)\right)$$

Cathode

$$j^{BV} = j^{BV}_{0,ca}\left[\left(\frac{c^s_{VO_2^+}}{c^b_{VO_2^+}}\right)\left(\frac{c^s_{H^+}}{c^b_{H^+}}\right)^2\exp\left(-\alpha f\eta_{ca}\right) - \left(\frac{c^s_{VO^{2+}}}{c^b_{VO^{2+}}}\right)\exp\left((1-\alpha)f\eta_{ca}\right)\right]$$

Pino-Muñoz et al., Journal of The Electrochemical Society, 2017, 164, F1717

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$$N_{\mathrm{i}}^{\mathrm{m}} = -D_{\mathrm{i}}^{\mathrm{m}} \nabla c_{\mathrm{i}}^{\mathrm{m}} - z_{\mathrm{i}} \mu_{\mathrm{i}}^{\mathrm{m}} F \nabla \phi + c_{\mathrm{i}}^{\mathrm{m}} v$$

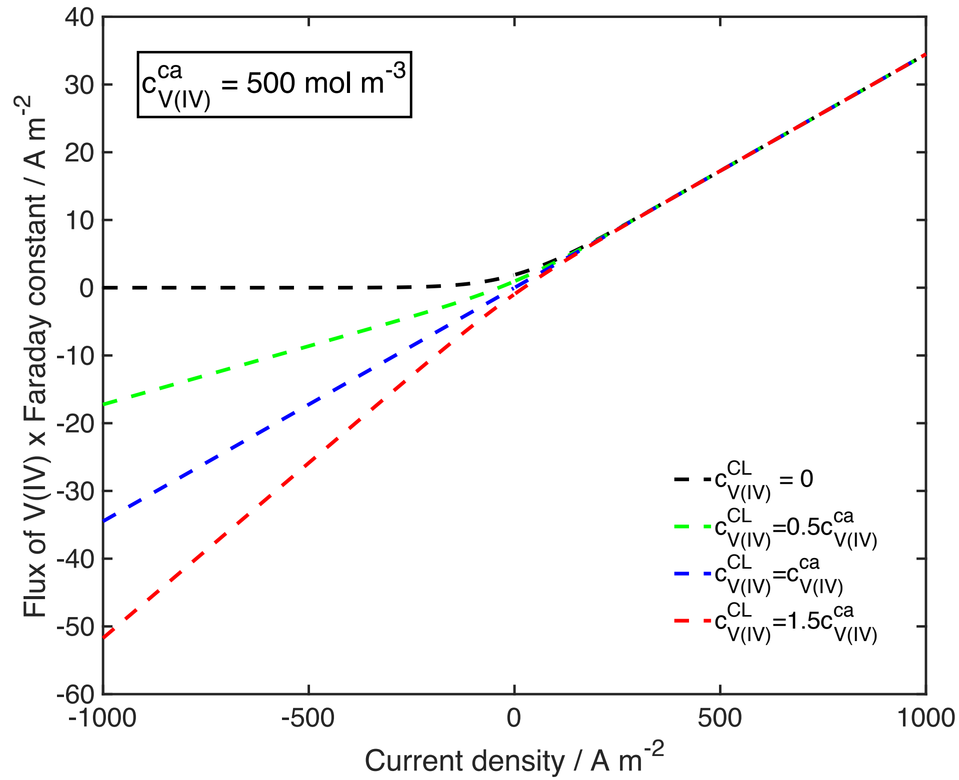
Nernst-Planck equation

Ionic species crossover

$$N_{\mathrm{i,m}}^{\mathrm{m}} = \frac{D_{\mathrm{i}}^{\mathrm{m}} c_{\mathrm{i}}^{\mathrm{m}}}{l_{\mathrm{m}}} \left(\frac{\zeta (\mathrm{e}^{\zeta} - c_{\mathrm{i}}^{\mathrm{CL}} / c_{\mathrm{i}}^{\mathrm{ca}})}{\mathrm{e}^{\zeta} - 1} \right)$$

$$\zeta = \left(\frac{z_{\mathrm{i}} F}{\sigma_{\mathrm{m}} R T} + \frac{\xi_{\mathrm{drag}}}{c_{\mathrm{w}}^{\mathrm{m}} D_{\mathrm{i}}^{\mathrm{m}} F} \right) j l_{\mathrm{m}}$$

$$N_{\mathrm{w}}^{\mathrm{m}} = c_{\mathrm{w}}^{\mathrm{m}} = \frac{\xi_{\mathrm{drag}} j}{F}, \qquad j = -\sigma_{\mathrm{m}} \nabla \phi$$



Darling R. et al., Journal of The Electrochemical Society, 2015, 163(1), A5014

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$$\tilde{\mu}_i = \mu_i + z_i F \phi$$

Electrochemical potential of species i

Equilibrium

$$2\tilde{\mu}^{ca}_{VO_2^+} + 4\tilde{\mu}^{ca}_{H^+} + 2\tilde{\mu}^{CP}_{e^-} = 2\tilde{\mu}^{ca}_{VO^{2+}} + 2\tilde{\mu}^{ca}_{H_2O}$$

Cathode reaction

$$\tilde{\mu}^{an}_{H_2} = 2\tilde{\mu}^{an}_{H^+} + 2\tilde{\mu}^{Pt}_{e^-}$$

Anode reaction

$$F\left(\phi^{M} - \phi^{M'}\right) = \mu^{ca}_{VO_2^+} + 2\mu^{ca}_{H^+} - \mu^{ca}_{VO^{2+}} - \mu^{ca}_{H_2O} - \mu^{an}_{H^+} + \tfrac{1}{2}\mu^{an}_{H_2} + F\left(\phi^{ca} - \phi^{an}\right)$$

Cell

Donnan potential across both interfaces (dialysis potential)

$$FE^{m}_{Don} = F\left(\phi^{ca} - \phi^{an}\right) = \mu^{an}_{H^+} - \mu^{ca}_{H^+}$$

Complete Nernst Equation

$$\mu_i = \mu_i^o + RT\ln(a_i)$$

$$a_i = \gamma_i c_i$$

Chemical potential of species i

Nernst equation

F_γ

$$E_{OCP} = E^0_{cell} + \frac{RT}{F}\ln\left(\frac{c^{ca}_{VO_2^+}\left(c^{ca}_{H^+}\right)^2\left(p^g_{H_2}\right)^{0.5}}{c^{ca}_{VO^{2+}}c^{an}_{H^+}} \times \frac{c^{an}_{H^+}}{c^{ca}_{H^+}} \times \frac{\gamma^{ca}_{VO_2^+}\gamma^{ca}_{H^+}}{\gamma^{ca}_{VO^{2+}}}\right)$$

Thermodynamic derivation

Potential difference between electrolytes

$$\phi^{ca} - \phi^{an} = \frac{RT}{F}\ln\left(\frac{c^{an}_{H^+}}{c^{ca}_{H^+}}\right)$$

Pino-Muñoz et al., Journal of The Electrochemical Society, 2017, 164, F1717

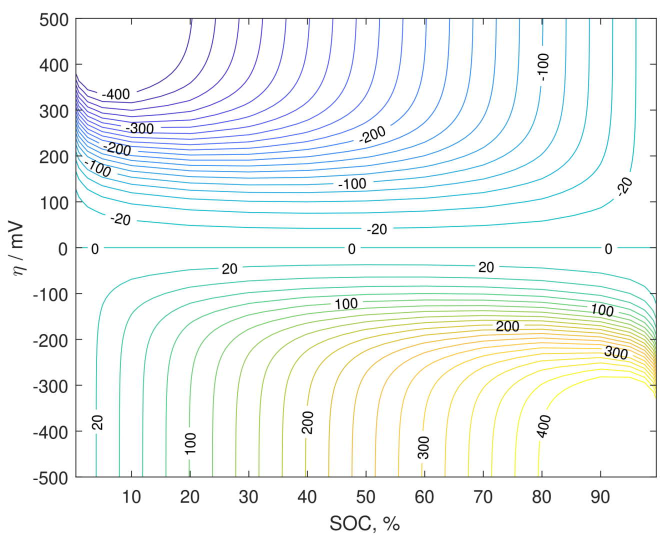
All ionic species in reaction

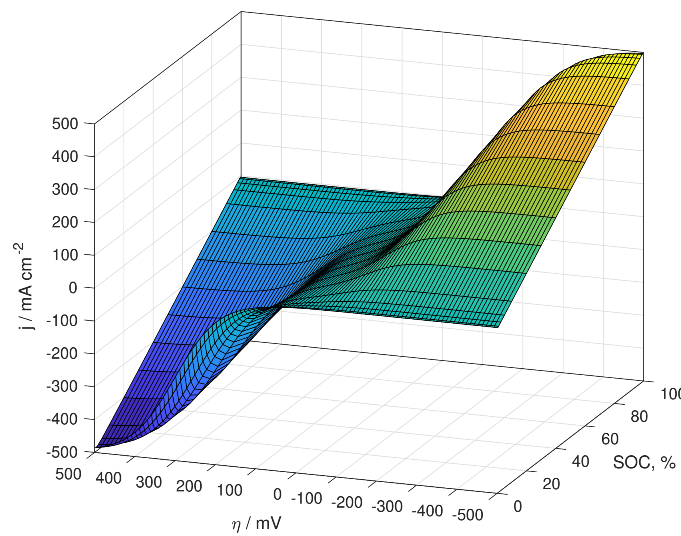
Complete Butler-Volmer equation for cathode

$$j^{BV} = j_{0,ca}^{BV}\left[\left(\frac{c_{VO^{2+}}^{s}}{c_{VO^{2+}}^{b}}\right)\exp\left(\frac{\alpha_a F\eta_{ca}}{RT}\right) - \left(\frac{c_{VO_2^+}^{s}}{c_{VO_2^+}^{b}}\right)\left(\frac{c_{H^+}^{s}}{c_{H^+}^{b}}\right)^2\exp\left(\frac{-\alpha_c F\eta_{ca}}{RT}\right)\right]$$

$$j_{0,ca}^{BV} = Fk_{ca}\left(c_{VO^{2+}}^{b}\right)^{\alpha_c}\left(c_{VO_2^+}^{b}\right)^{\alpha_a}\left(c_{H^+}^{b}\right)^{2\alpha_a}$$

Concentration of protons





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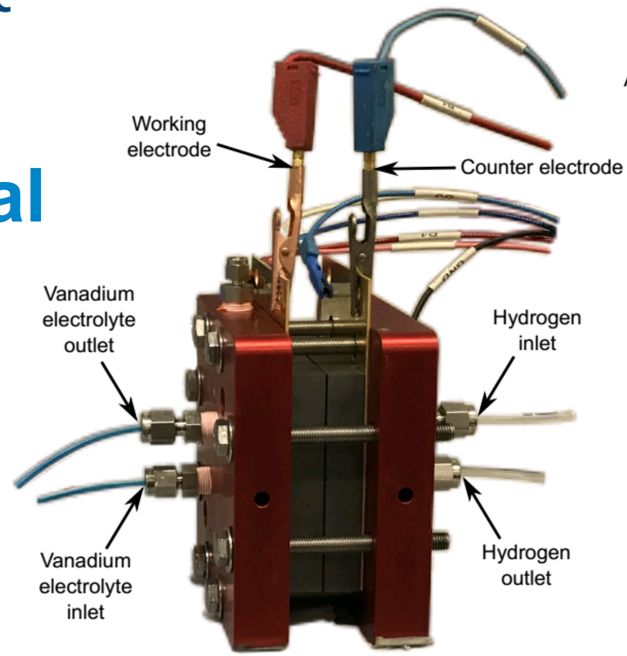
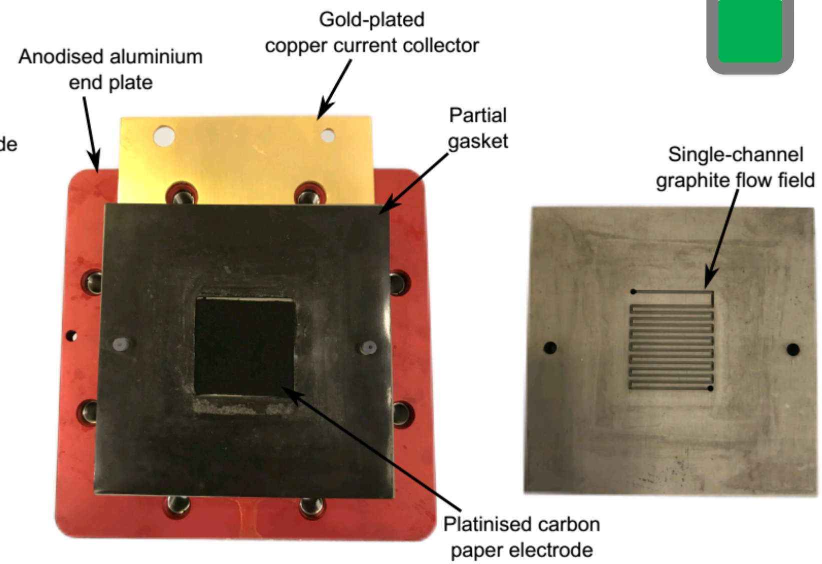
Experimental data RHVFC





(Scribner Associates)

Experimental set-up 5 cm² area cell	
Cathode	Freudenberg H23, 210 µm, heat treated (500 °C, 6 h)
Anode	SGL 29BC, 235 µm, 0.3 mg cm^{-2} Pt
Membrane	Nafion 115, 127 µm
Flow channel	Single-channel serpentine
Catholyte	0.8M $VOSO_4$ in 60 mL 5M H_2SO_4
Current density	500 – 1500 A m^{-2}
Catholyte / hydrogen flow rate	50 & 100 mL min^{-1} / 100 mL min^{-1}

Tests:

- Open circuit potential (2 sets)
- Single-cycle charge-discharge (14 sets)
- Polarization curves (2 sets)
- Cycling test (1 set)

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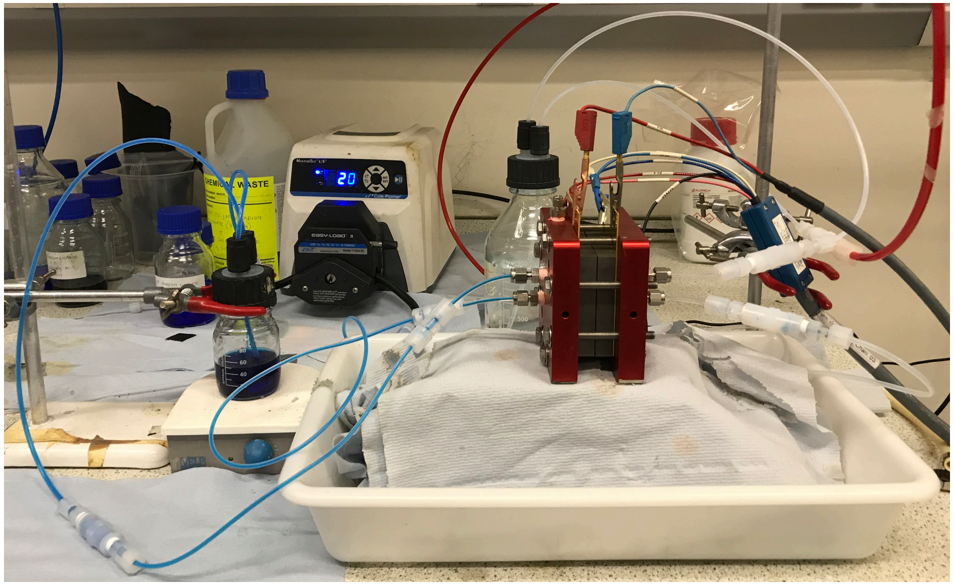
Experimental data RHVFC



Cell	AVIZO	TauFactor
Area	5 cm^2	
Cathode	Freudenberg H23, 210 μm, heat treated (500 °C, 6 h)	
Porosity	0.79	0.79
Specific surface area	0.429 $\mu m^2\ \mu m^{-3}$	0.144 $\mu m^2\ \mu m^{-3}$
Mean pore diameter	21.01 μm	---
Mean fibre diameter	7.92 μm	---

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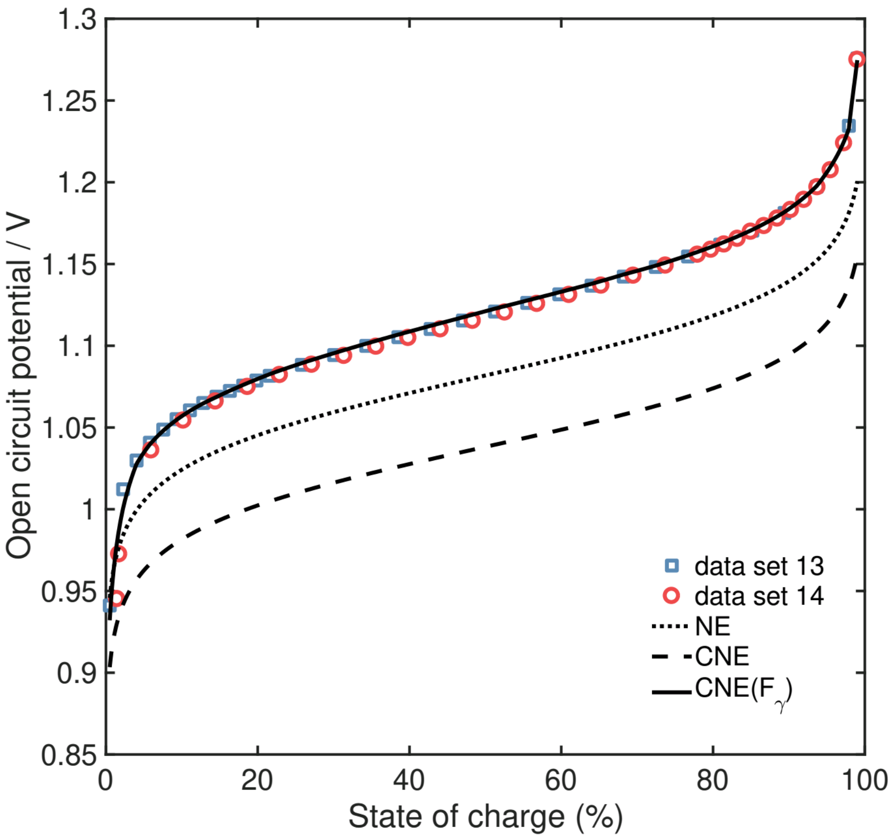
Model calibration: Open Circuit Potential

Thermodynamic derivation of CNE

$$E_{OCP} = E^0_{\text{cell}} + \frac{RT}{F}\ln\left(\frac{c^{\text{ca}}_{\text{VO}_2^+}\left(c^{\text{ca}}_{\text{H}^+}\right)^2\left(p^{\text{g}}_{\text{H}_2}\right)^{0.5}}{c^{\text{ca}}_{\text{VO}^{2+}}c^{\text{an}}_{\text{H}^+}}\times\frac{c^{\text{an}}_{\text{H}^+}}{c^{\text{ca}}_{\text{H}^+}}\times F_\gamma\right)$$



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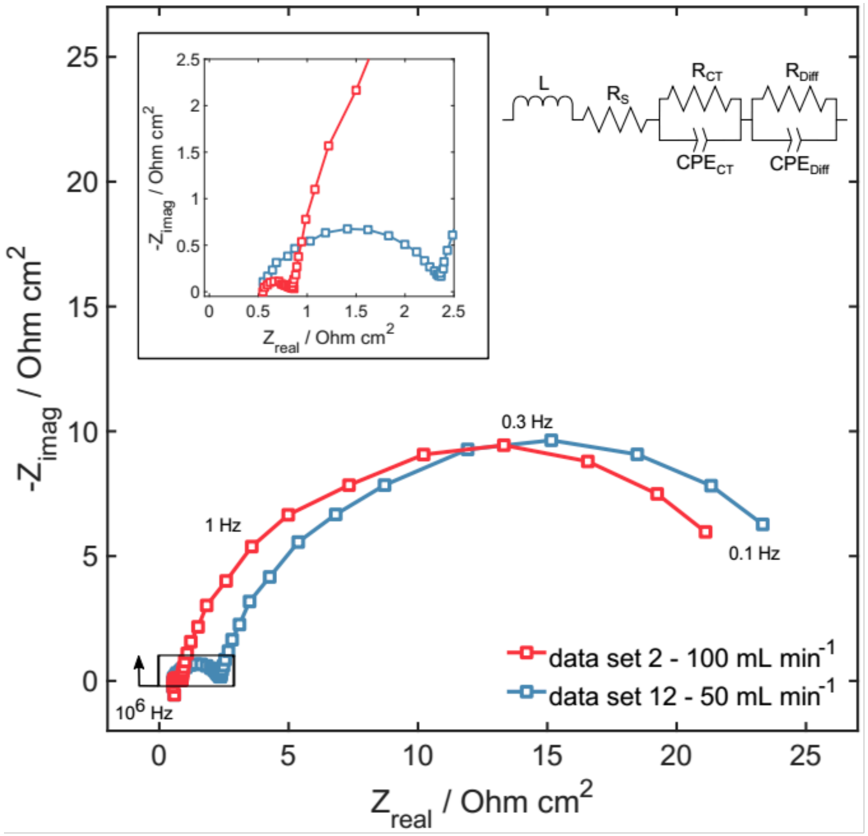
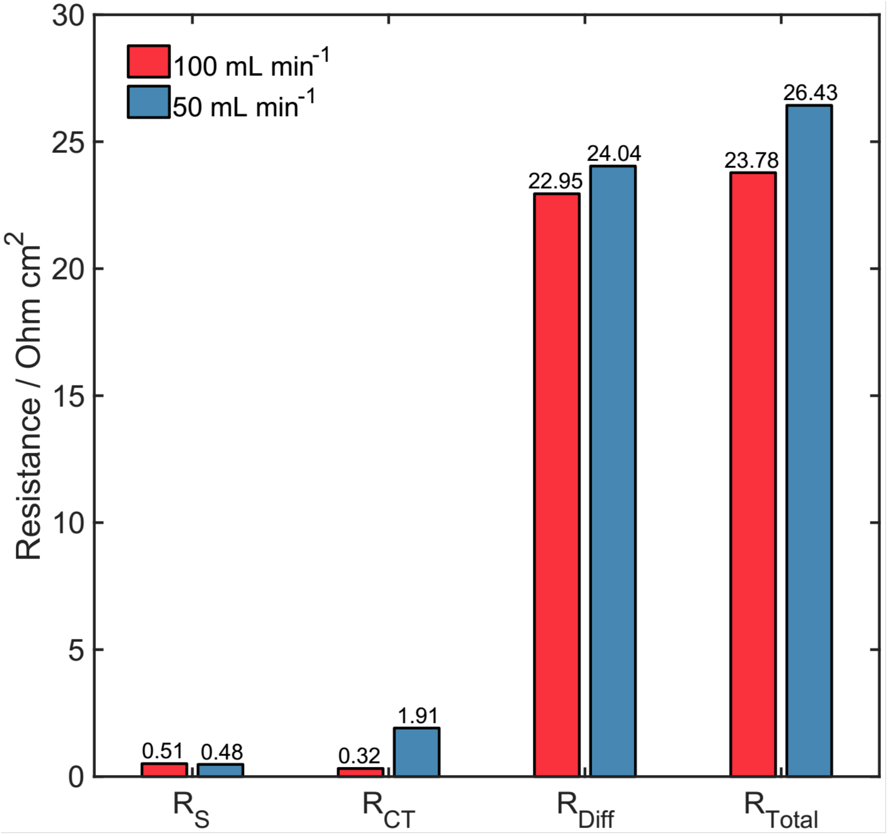
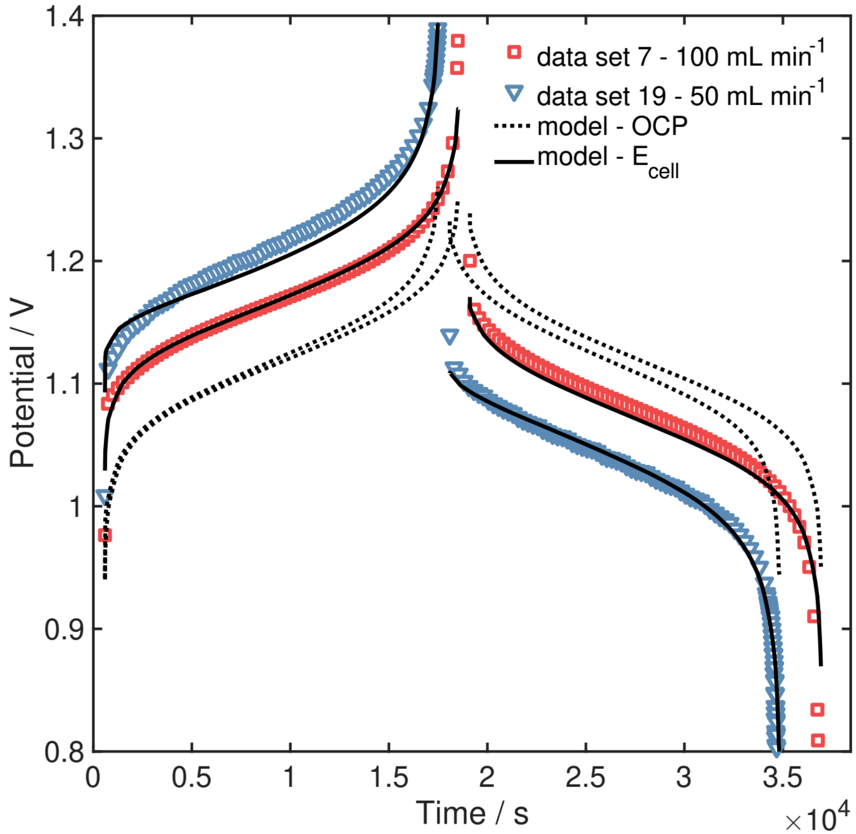
EIS data





Model calibration: cell potential



Model implementation

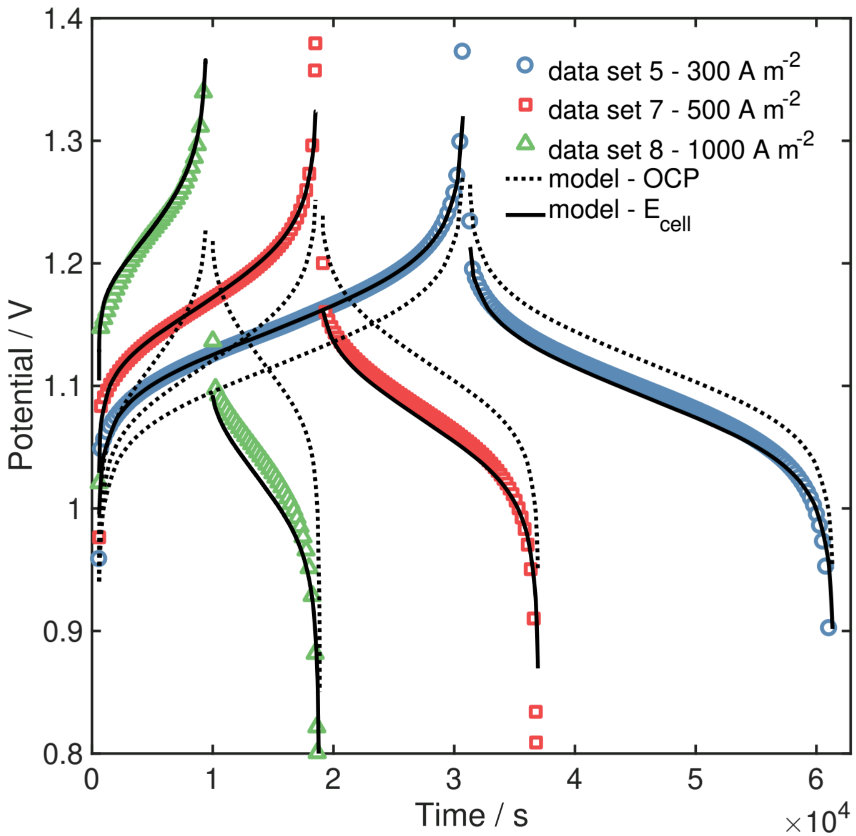
- *MATLAB R2017a*
- ode15s → solve ODE system
- lsqcurvefit → curve fitting, lb & ub

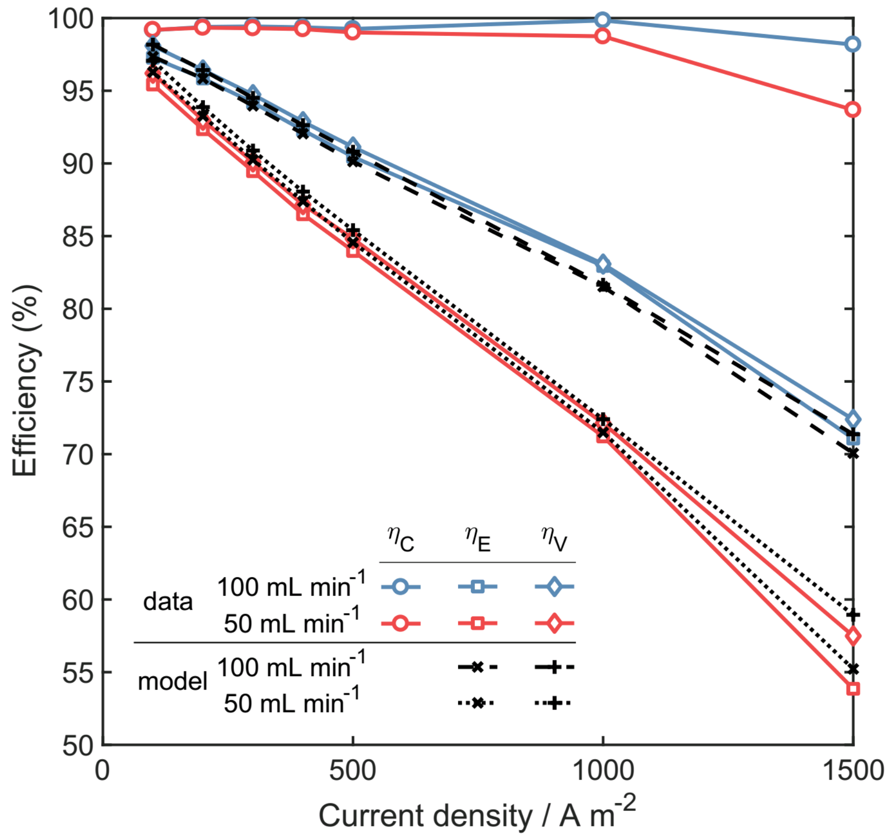
Fitting parameters

- Cathodic reaction → $K_{ca} = S_{ca}^{ac} k_{\mathrm{ca}}^{\mathrm{o}}$
- Nernst diffusion layer thickness → δ_{ca}
- Anodic reaction → $k_{des}^{\emptyset}$

j= 500 A m^{-2}

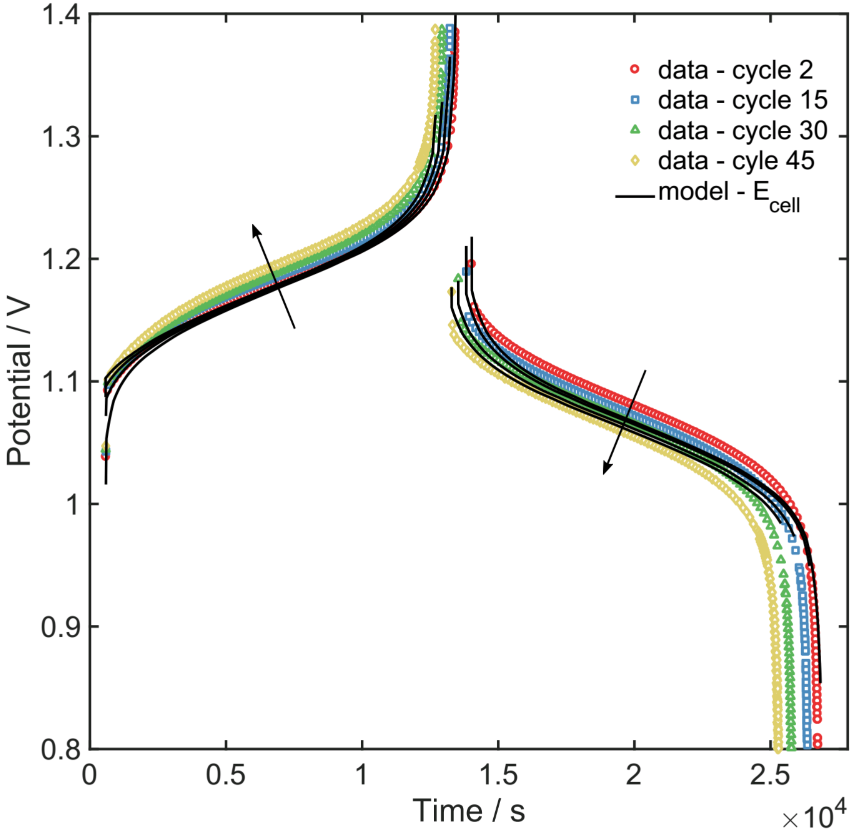
Charge-discharge: vary current density

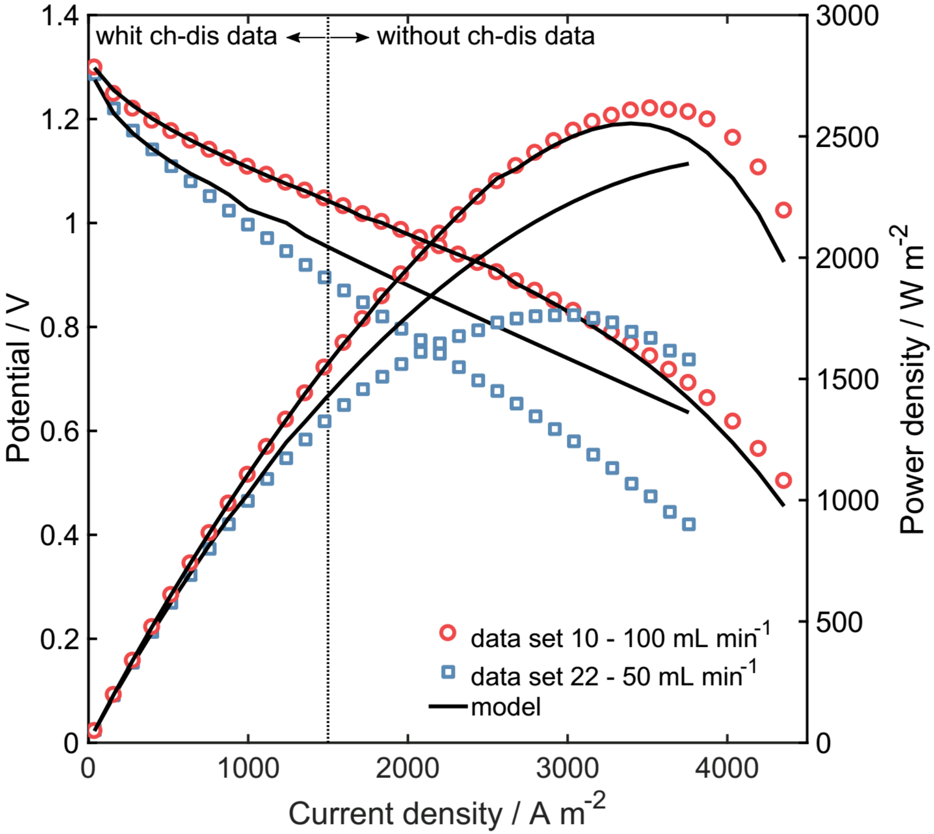




Q_V= 100 mL min^{-1}

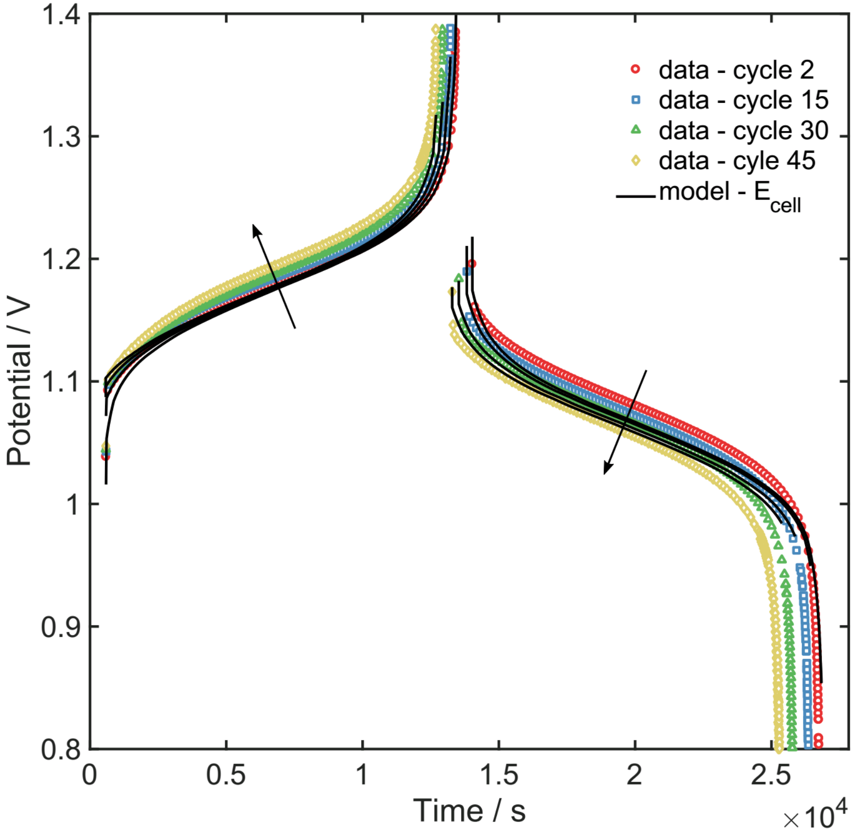
Cycling and polarization curve



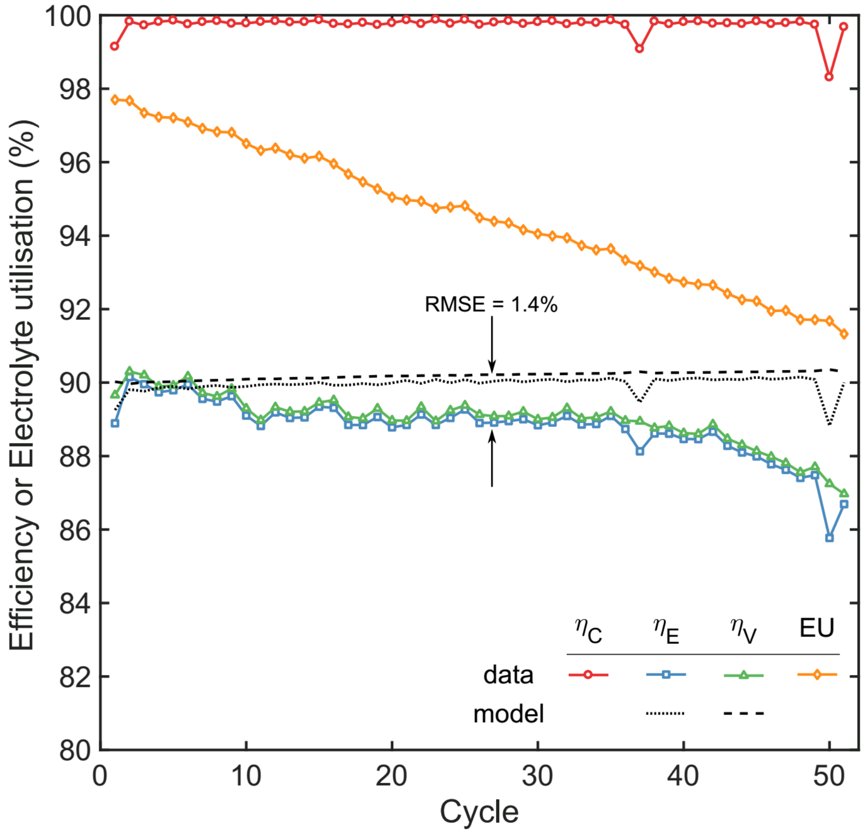


j = 700 A m^{-2}, Q_V= 50 mL min^{-1}, Q_{H2}= 30 mL min^{-1}

Cycling performance



j = 700 A m^{-2}, Q_V= 50 mL min^{-1}, Q_{H2}= 30 mL min^{-1}



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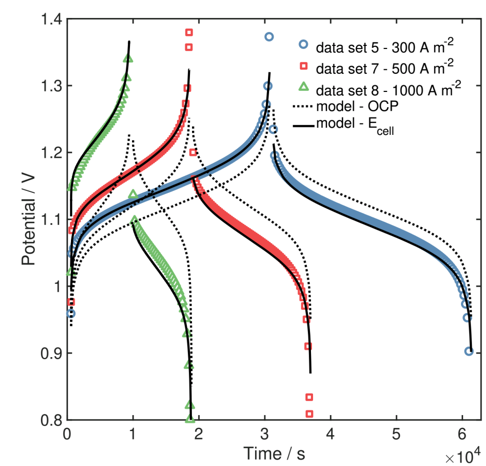
Conclusions

- The unit cell model was able to reasonably describe the cell potential dynamics at different operating conditions
- The unit cell model reproduced the cell performance for a wide range of experimental data, including power curves and cycling test
- A complete Nernst equation based on thermodynamic principles was used and fit to the OCP data
- A complete Butler-Volmer kinetic equation, considering the effect of protons concentration, was used for the cathode
- This model is a fast mathematical approach to simulate cell performance.

Thermodynamic derivation of CNE

$$E_{OCP} = E^{0}_{\mathrm{cell}} + \frac{RT}{F}\ln\left(\frac{c^{\mathrm{ca}}_{\mathrm{VO}_2^+}\left(c^{\mathrm{ca}}_{\mathrm{H}^+}\right)^2\left(p^{\mathrm{g}}_{\mathrm{H}_2}\right)^{0.5}}{c^{\mathrm{ca}}_{\mathrm{VO}^{2+}}\,c^{\mathrm{an}}_{\mathrm{H}^+}}\times\frac{c^{\mathrm{an}}_{\mathrm{H}^+}}{c^{\mathrm{ca}}_{\mathrm{H}^+}}\times F_{\gamma}\right)$$



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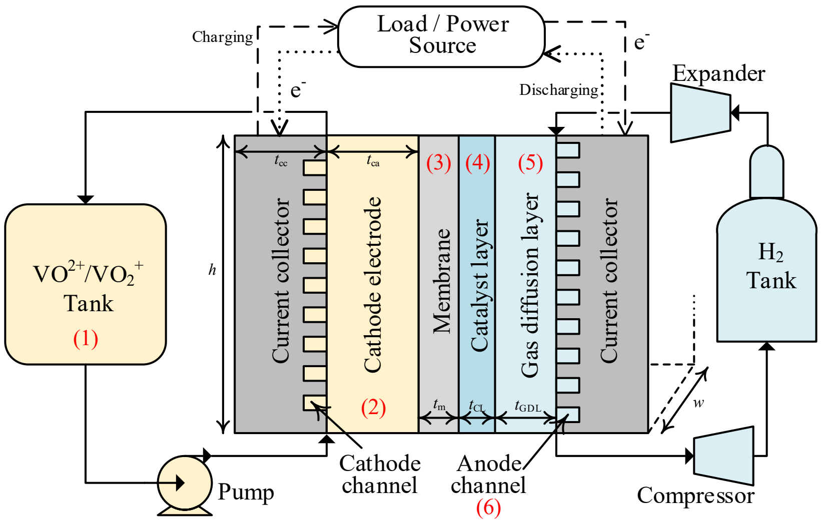
Next steps

- Detailed crossover model vanadium and sulphuric acid species and water in a hybrid H_2-based redox flow battery
- Study possible side reaction of vanadium ionic species at anode catalyst layer to correctly simulate the evolution of concentration.



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Thank you!

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