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Modelling of a Regenerative Hydrogen-Vanadium Fuel Cell

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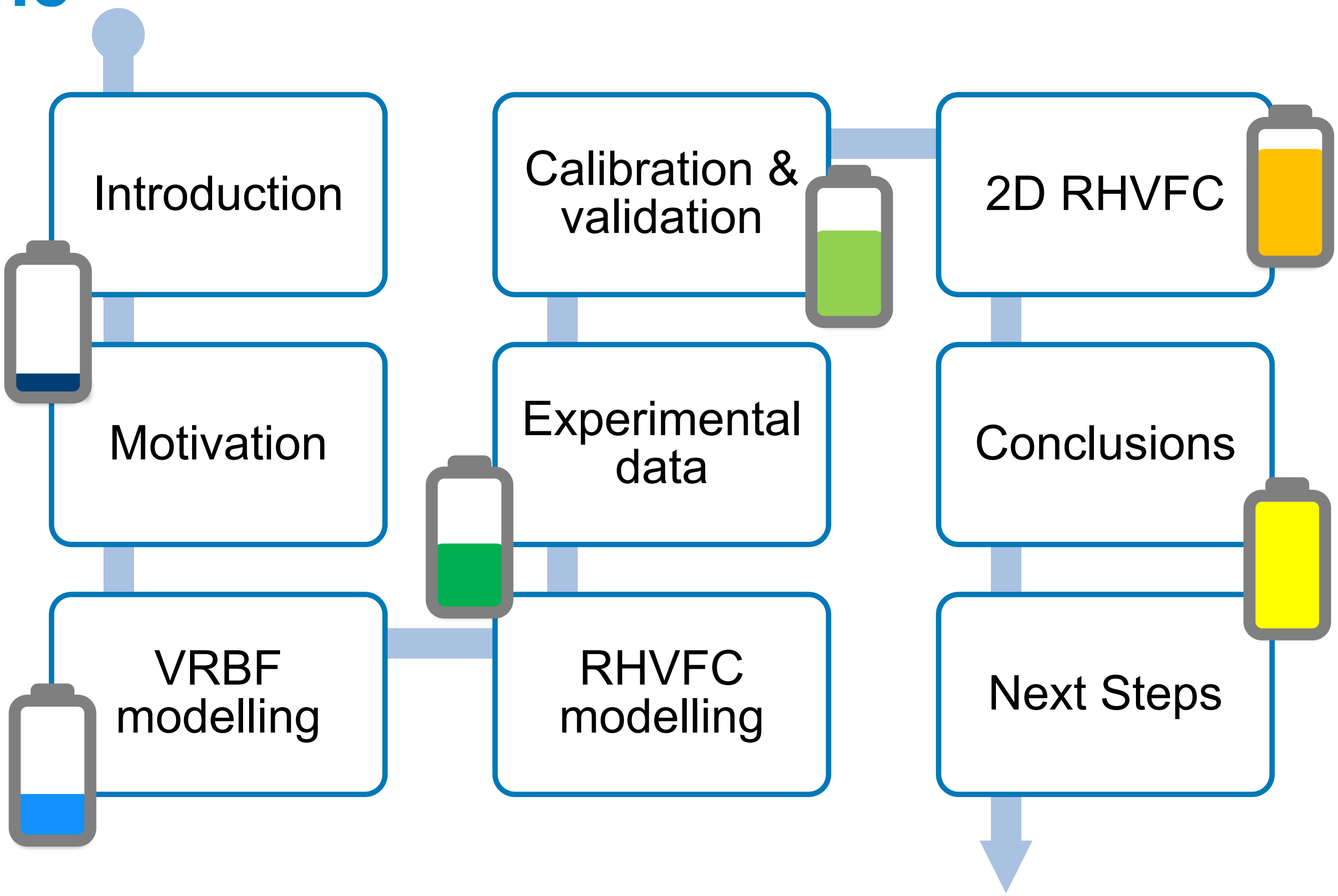
Outline



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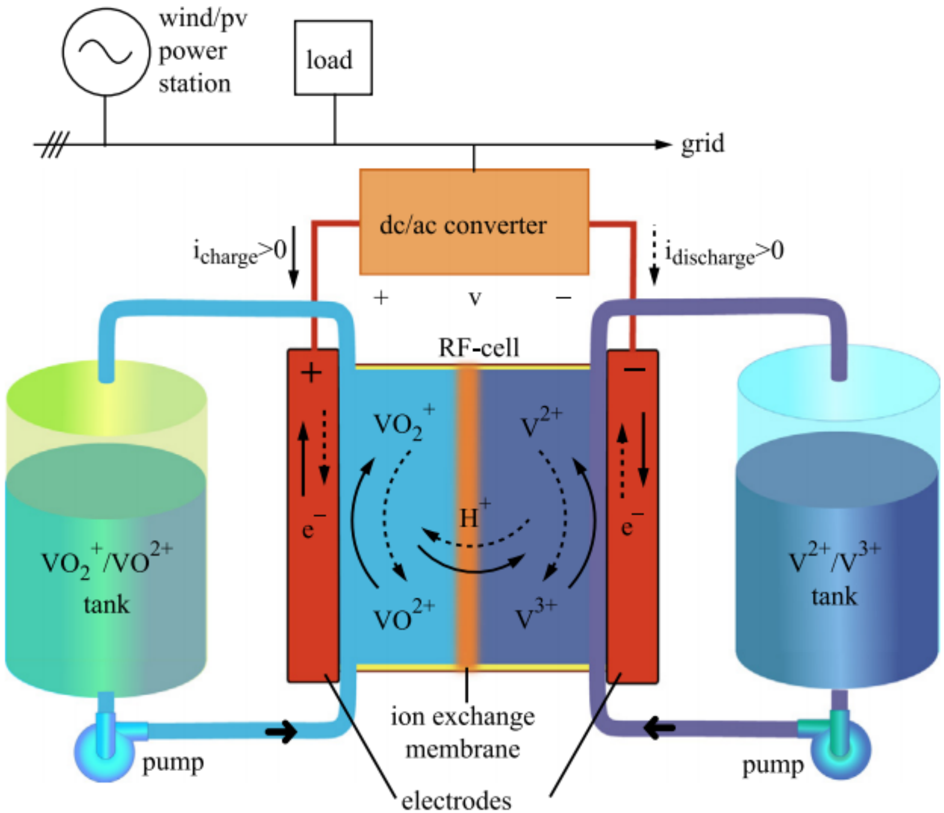
Vanadium Redox Flow Battery (VRFB)

Vanadium based RFB

- *Vanadium / halide*
- *Vanadium / air*

Anolyte V(II) / V(III)



Advantages

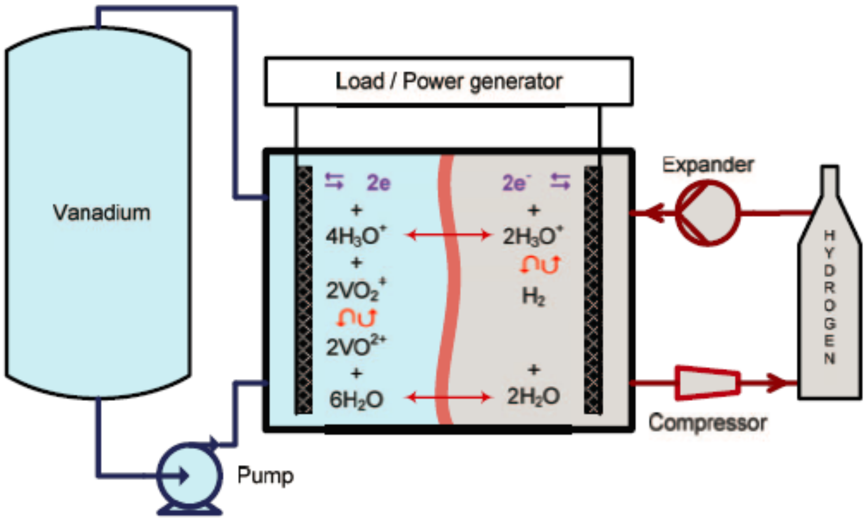
- Scalability and flexibility
- Independent sizing of power and energy
- High round-trip efficiency (>80%)
- Depth of discharge
- Long cycle life (>12000)
- Fast response
- Reduced environmental impact

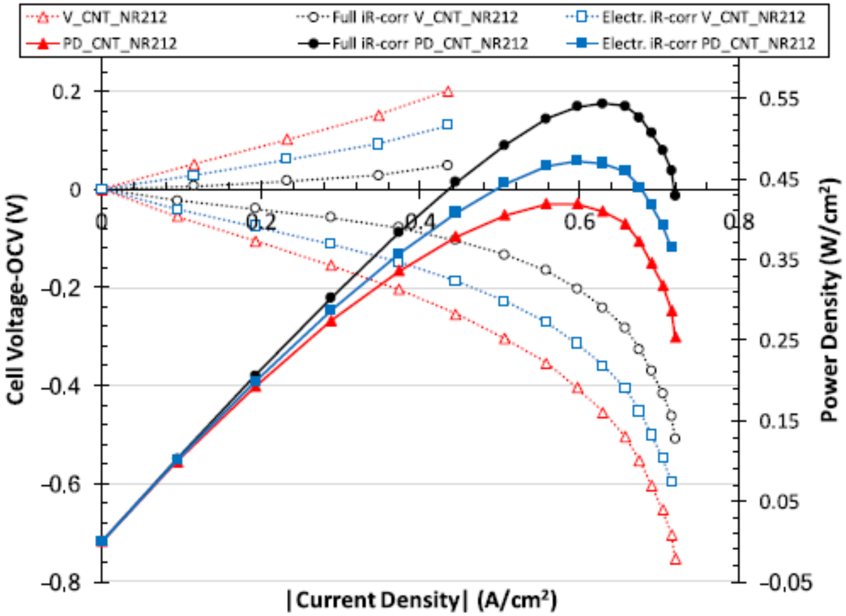
Disadvantages

- Low specific energy density (~30 Wh kg^{-1})
- Limited operating window (10-40 °C below 2 M)
- Electrode and membrane degradation
- Shunt currents
- High capital cost ($150-$1000/kWh)
- Vanadium electrolyte ~40% total cost

Alotto et al., Renewable and Sustainable Energy Reviews, 2014, 29, 325-335; V. Yufit. et al., Journal of The Electrochemical Society, 2013, 160, A856

Regenerative Hydrogen-Vanadium Fuel Cell (RHVFC)





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

- *Carbon nanotube electrode*
- *NR 212*
- *SGL 35 BC GDL, 0.48 mg Pt cm^{-2}*

V. Yufit. et al., Journal of The Electrochemical Society, 2013, 160, A856; Regis P. Dowd Jr., et al, Journal of The Electrochemical Society, 2017, 164, F564.

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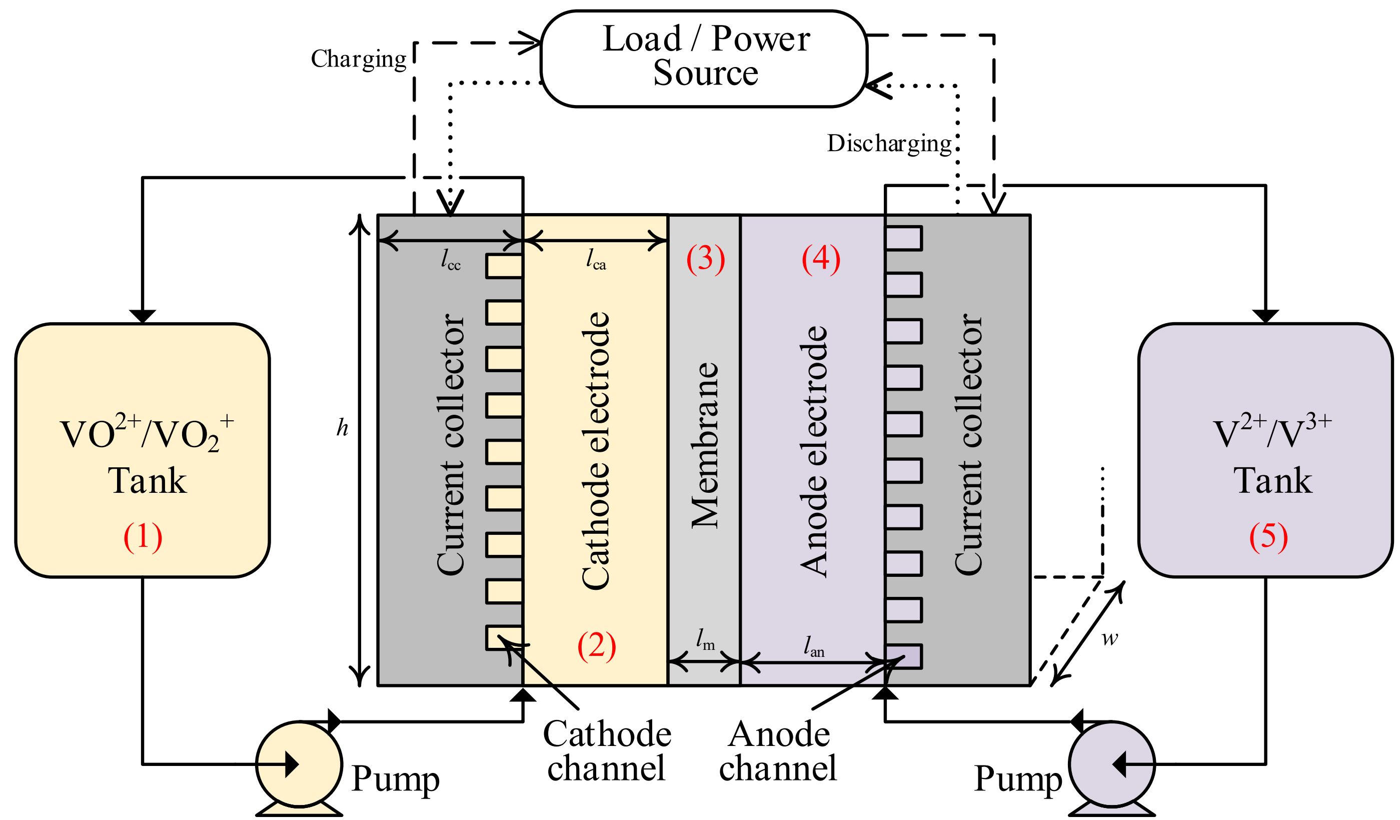
Unit cell model for the VRFB



Cathode:

$$VO_2^+ + 2H_3O^+ + e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} VO^{2+} + 3H_2O, \quad E^0_{ca} = 0.99\,V$$

Anode:

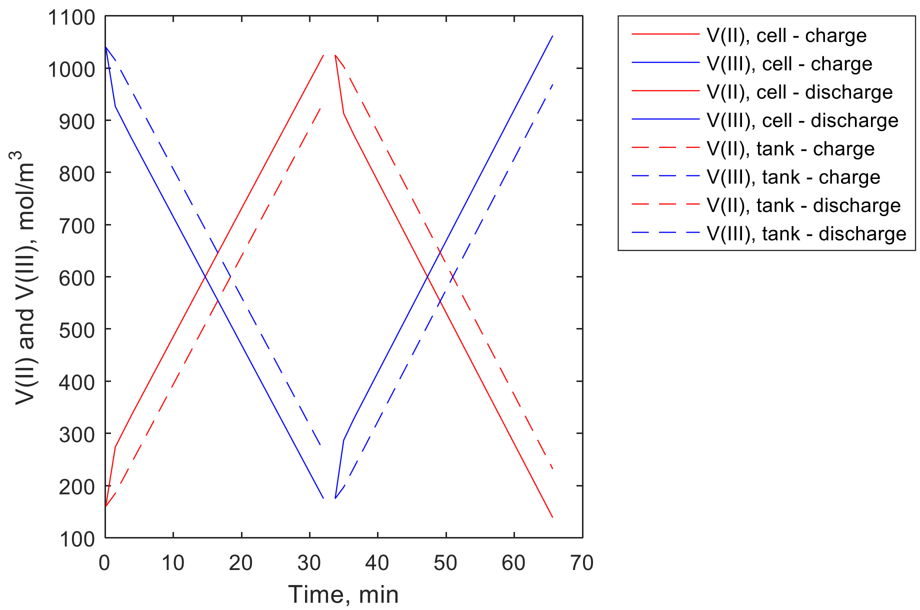
$$V^{2+} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} V^{3+} + e^-, \quad E^0_{an} = -0.26\,V$$

Model summary

Mass conservation

Equilibrium potential

Electrochemical kinetics



Anode

$$j_{\mathrm{an}}^{\mathrm{BV}} = j_{0,\mathrm{an}}^{\mathrm{BV}}\left[\left(\frac{c_{\mathrm{V^{2+}}}^{\mathrm{s}}}{c_{\mathrm{V^{2+}}}^{\mathrm{b}}}\right)\exp\left(\frac{-\alpha F\eta_{\mathrm{an}}}{RT}\right)-\left(\frac{c_{\mathrm{V^{3+}}}^{\mathrm{s}}}{c_{\mathrm{V^{3+}}}^{\mathrm{b}}}\right)\exp\left(\frac{(1-\alpha)F\eta_{\mathrm{ca}}}{RT}\right)\right]$$

Cathode

$$j_{\mathrm{ca}}^{\mathrm{BV}} = j_{0,ca}^{BV}\left[\left(\frac{c_{VO_2^+}^{s}}{c_{VO_2^+}^{b}}\right)\boxed{\left(\frac{c_{H^+}^{s}}{c_{H^+}^{b}}\right)^2}\exp\left(\frac{-\alpha F\eta_{ca}}{RT}\right)-\left(\frac{c_{VO^{2+}}^{s}}{c_{VO^{2+}}^{b}}\right)\exp\left(\frac{(1-\alpha)F\eta_{ca}}{RT}\right)\right]$$

Cell

$$E_{\mathrm{eq}} = E_{\mathrm{cell}}^{0} + \frac{RT}{F}\ln\left(\frac{c_{\mathrm{VO_2^+}}^{\mathrm{ca}}\left(c_{\mathrm{H^+}}^{\mathrm{ca}}\right)^2 c_{\mathrm{V^{2+}}}^{\mathrm{an}}}{c_{\mathrm{VO^{2+}}}^{\mathrm{ca}}\, c_{\mathrm{V^{3+}}}^{\mathrm{an}}}\,\boxed{\frac{c_{\mathrm{H^+}}^{\mathrm{an}}}{c_{\mathrm{H^+}}^{\mathrm{ca}}}}\cdot F_{\gamma}\right)$$

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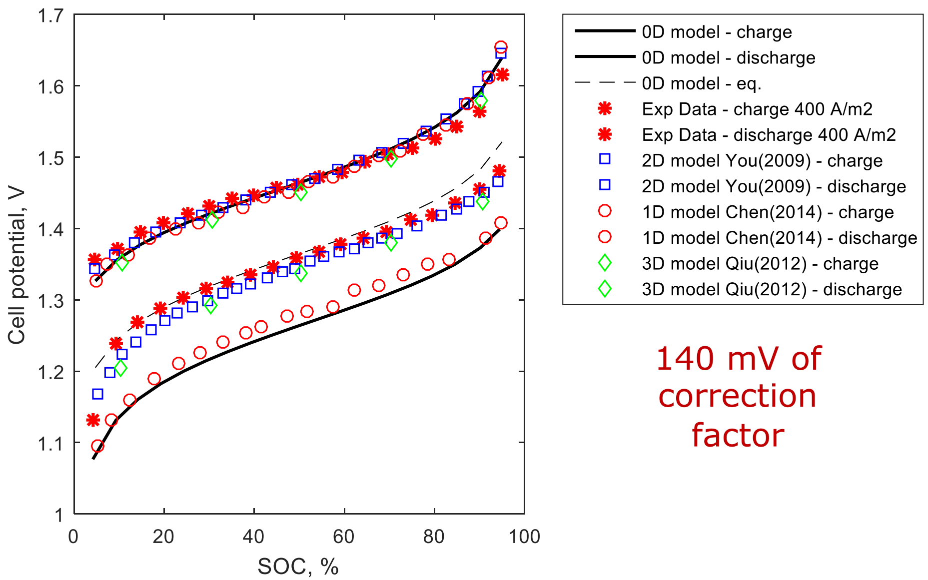
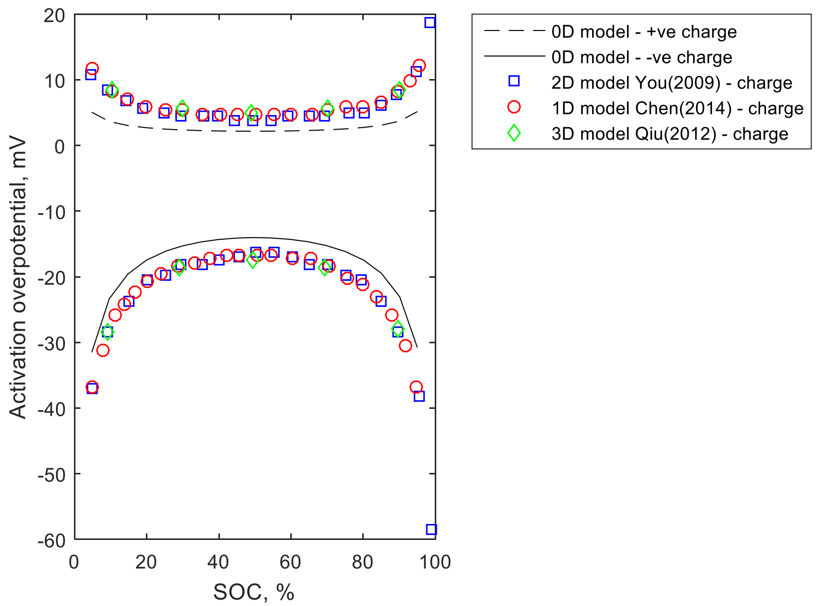
Model validation with literature data

Charge – discharge potential

Overpotential



140 mV of correction factor



c_V=1500 mol m-3, c_{acid}= 5000 mol m^{-3}, V=30 mL, j= 400 A m^{-2}, Q_V=60 mL min^{-1}

D. You, et al. Electrochimica Acta, 2009, 54, 6827; C. Chen et al. Electrochimica Acta, 2014, 120, 167; G. Qiu et al. Electrochimica Acta, 64, 2012, 46.

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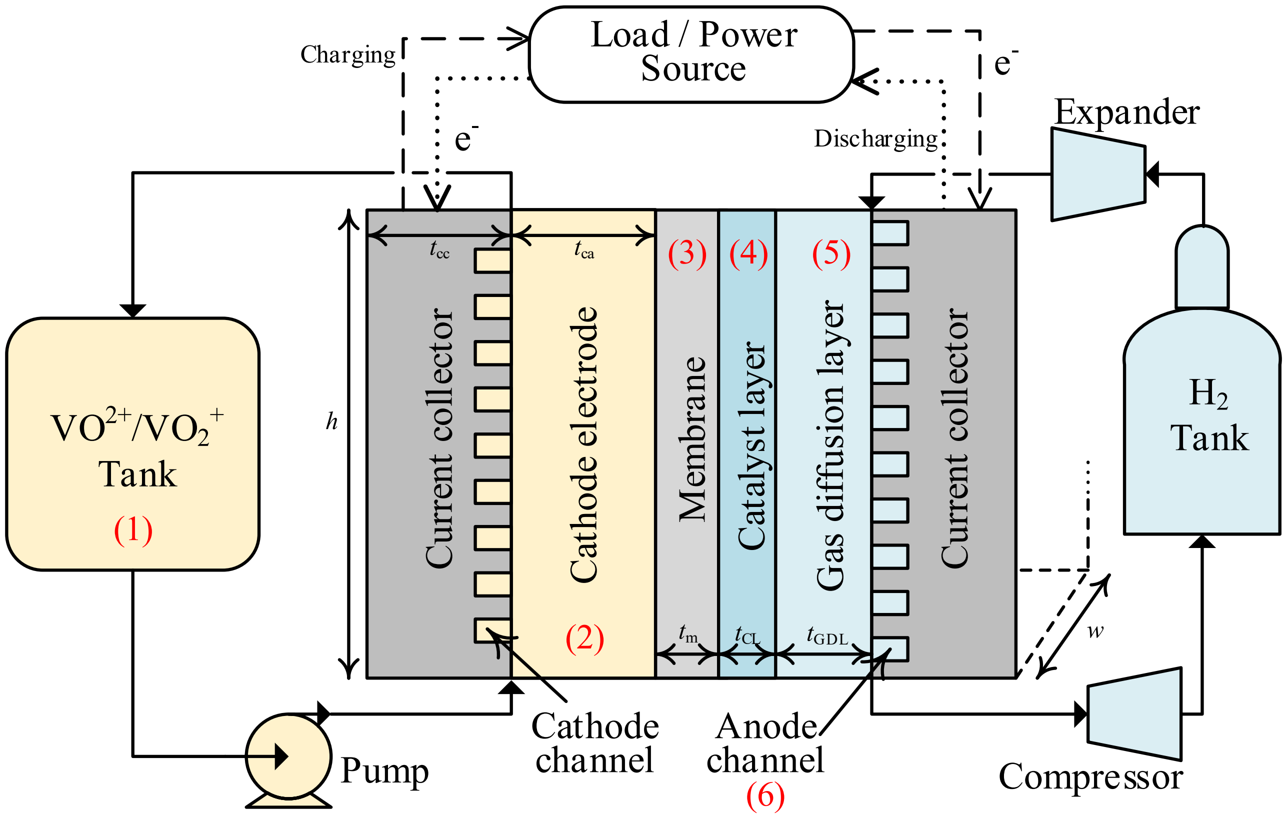
Unit cell model for the RHVFC



Cathode:

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

Anode:

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

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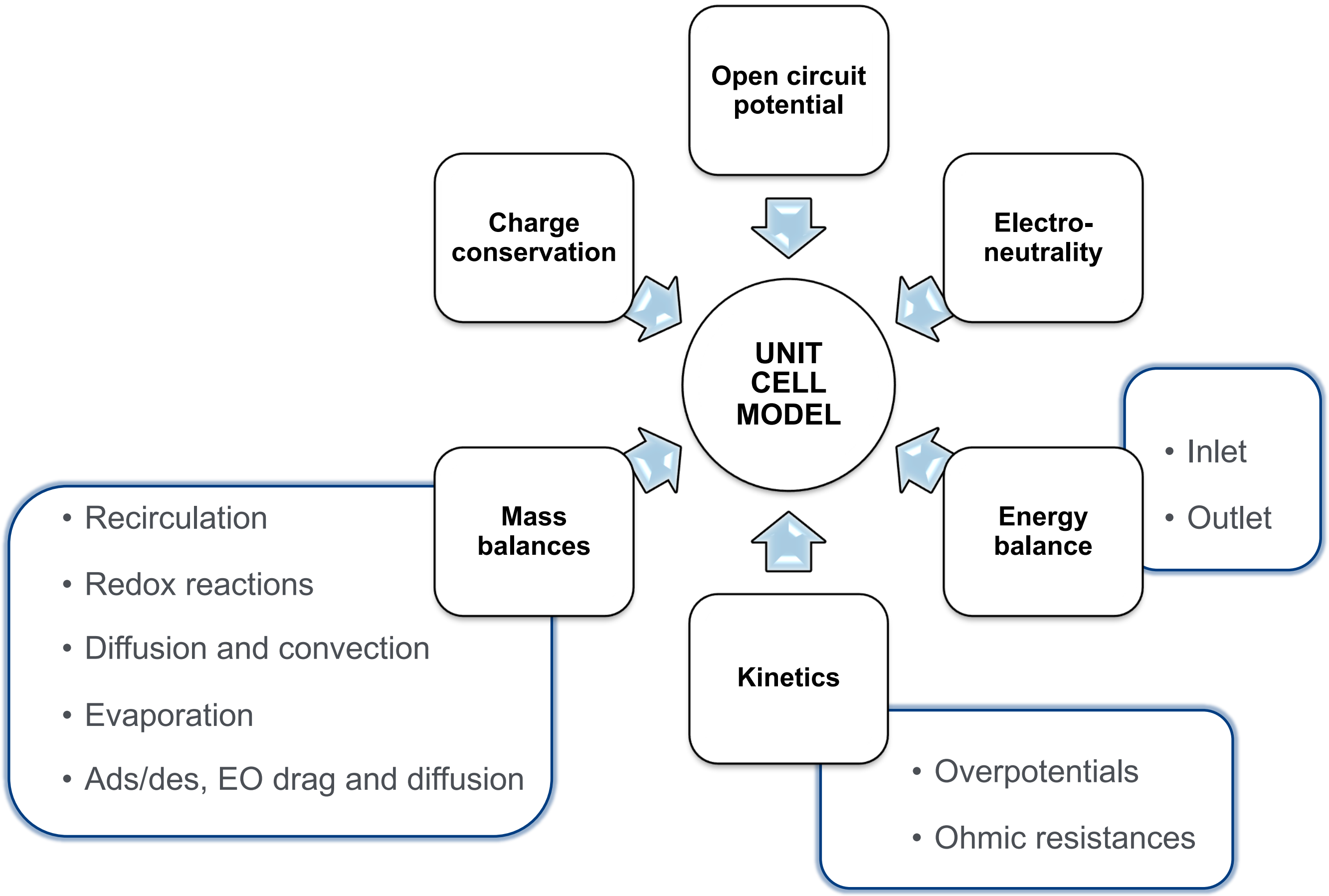
Model summary



Assumptions

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Model summary

Cell

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

Open circuit potential

Cathode

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

Anode

$$c_{H^+}+z_f c_f = 0$$

Charge conservation

Electro-neutrality

UNIT CELL MODEL

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

Anode

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

Cathode

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

Mass balances

Energy balance

Kinetics

Anode

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

Cathode

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

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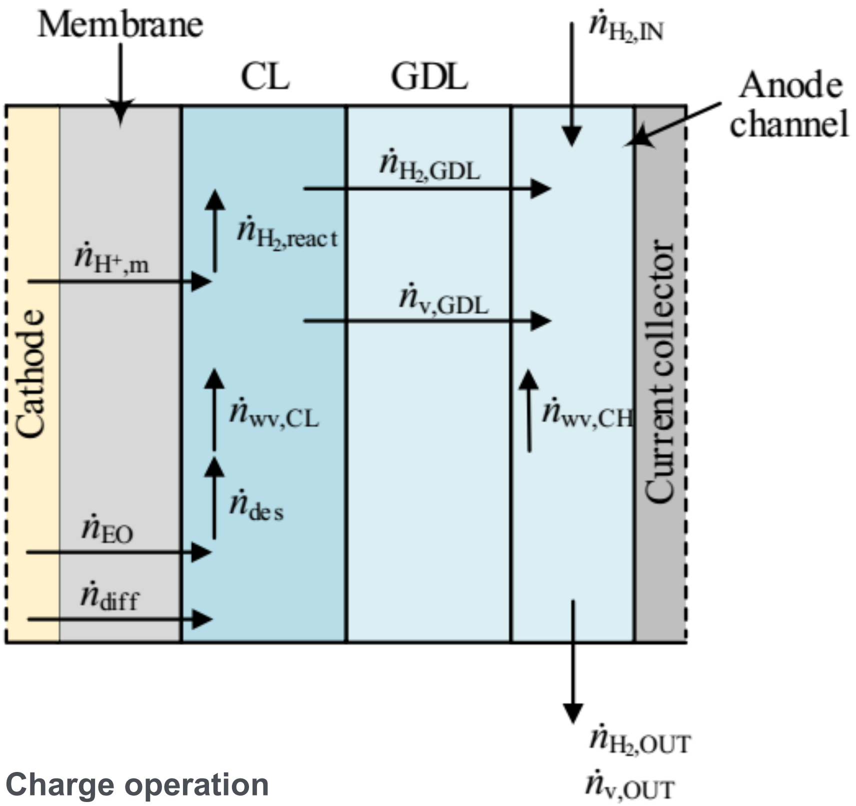
Hydrogen side

Dissolved water transport

Dusty Gas Model

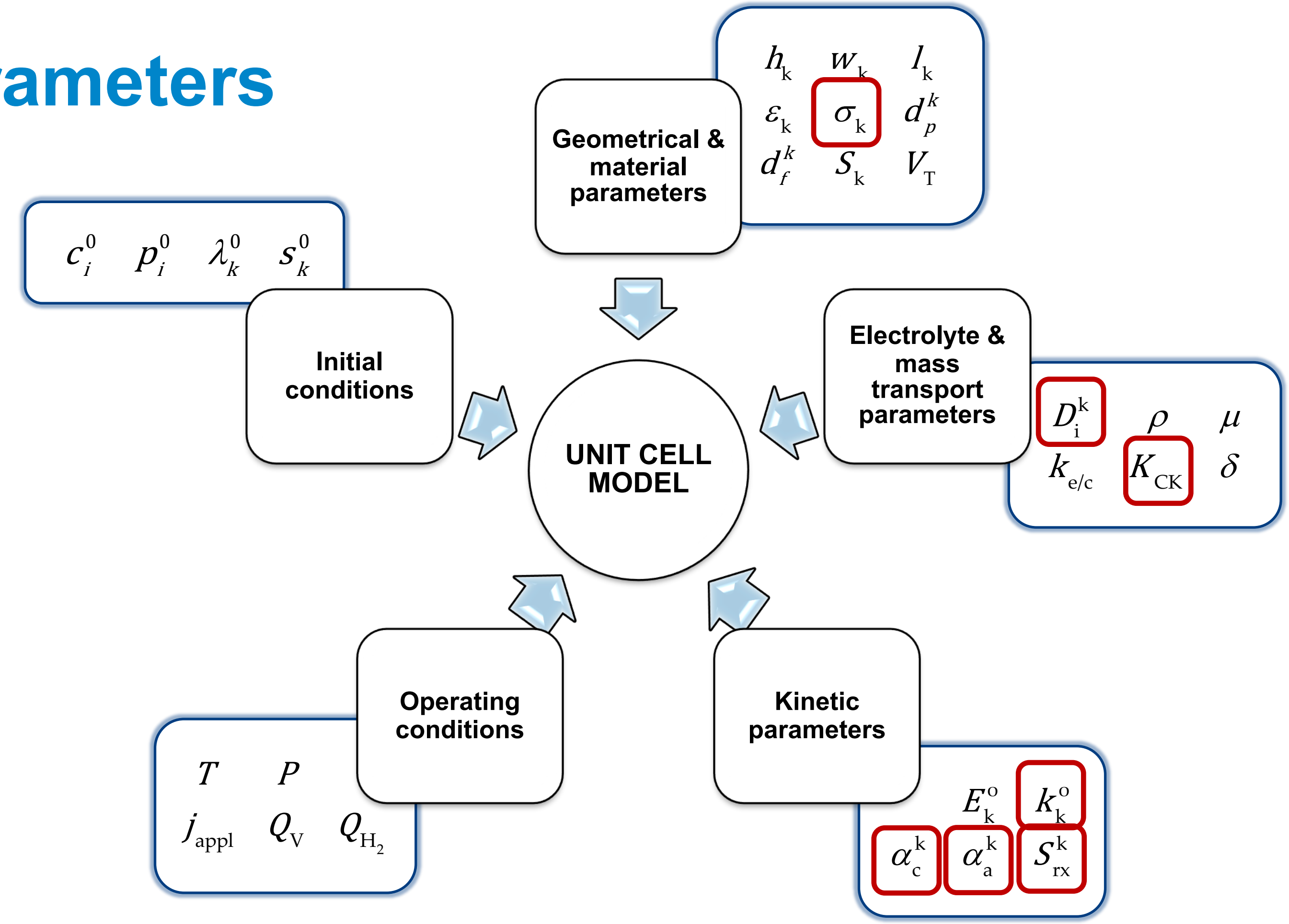
Evaporation/condensation



Charge operation

→ +ve transport
↑ +ve generation

Parameters


UNIT CELL MODEL
Geometrical & material parameters
h_k w_k l_k
ε_k σ_k d_p^k
d_f^k S_k V_T
Initial conditions
c_i^0 p_i^0 λ_k^0 s_k^0
Electrolyte & mass transport parameters
D_i^k ρ μ
$k_{e/c}$ K_{CK} δ
Operating conditions
T P
j_{appl} Q_V Q_{H_2}
Kinetic parameters
E_k^o k_k^o
α_c^k α_a^k S_{rx}^k

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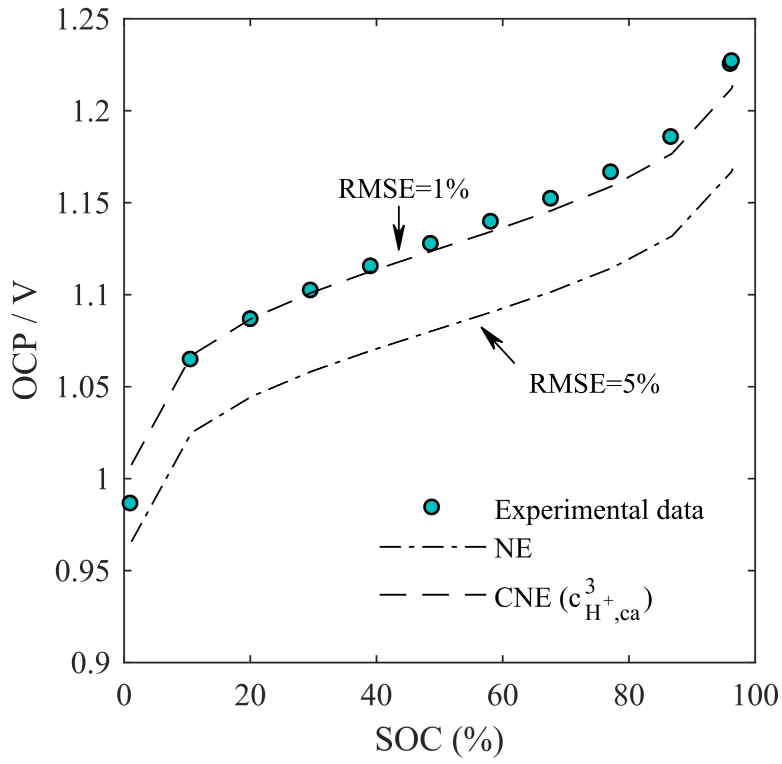
Open Circuit Potential



Nernst Equation (NE)

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

Complete Nernst Equation (CNE)

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

Donnan potential across the membrane (dialysis potential)

$$E_m = \frac{RT}{F}\ln\left(\frac{c_{H^+,ca}}{c_{H^+,an}}\right)$$

Inconsistent with thermodynamics

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$$\tilde{\mu}_{\mathrm{i}} = \mu_{\mathrm{i}} + z_{\mathrm{i}} F \phi$$

Electrochemical potential of species i

Equilibrium

$$2\tilde{\mu}^{\mathrm{ca}}_{\mathrm{VO}_2^+} + 4\tilde{\mu}^{\mathrm{ca}}_{\mathrm{H}^+} + 2\tilde{\mu}^{\mathrm{CP}}_{\mathrm{e}^-} = 2\tilde{\mu}^{\mathrm{ca}}_{\mathrm{VO}^{2+}} + 2\tilde{\mu}^{\mathrm{ca}}_{\mathrm{H_2O}}$$

Cathode reaction

$$\tilde{\mu}^{\mathrm{an}}_{\mathrm{H}_2} = 2\tilde{\mu}^{\mathrm{an}}_{\mathrm{H}^+} + 2\tilde{\mu}^{\mathrm{Pt}}_{\mathrm{e}^-}$$

Anode reaction

$$F\left(\phi^{\mathrm{M}} - \phi^{\mathrm{M'}}\right) = \mu^{\mathrm{ca}}_{\mathrm{VO}_2^+} + 2\mu^{\mathrm{ca}}_{\mathrm{H}^+} - \mu^{\mathrm{ca}}_{\mathrm{VO}^{2+}} - \mu^{\mathrm{ca}}_{\mathrm{H_2O}} - \mu^{\mathrm{an}}_{\mathrm{H}^+} + \tfrac{1}{2}\mu^{\mathrm{an}}_{\mathrm{H}_2} + \boxed{F\left(\phi^{\mathrm{ca}} - \phi^{\mathrm{an}}\right)}$$

Cell

Donnan potential across both interfaces (dialysis potential)

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

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Equilibrium

$$\mu_i = \mu_i^0 + RT\ln\left(a_i\right)$$

$$a_i = \gamma_i c_i$$

Chemical potential of species i

$$E_{OCP} = E_{\text{cell}}^0 + \frac{RT}{F}\ln\left(\frac{a_{\text{VO}_2^+}^{\text{ca}}\left(a_{\text{H}^+}^{\text{ca}}\right)^2\left(a_{\text{H}_2}^{\text{an}}\right)^{0.5}}{a_{\text{VO}^{2+}}^{\text{ca}}a_{\text{H}_2\text{O}}^{\text{ca}}a_{\text{H}^+}^{\text{an}}}\times\frac{a_{\text{H}^+}^{\text{an}}}{a_{\text{H}^+}^{\text{ca}}}\right)$$

Potential difference between electrolytes

Thermodynamic derivation

Complete Nernst Equation

Nernst equation

$$F_\gamma$$

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

Thermodynamic derivation

Potential difference between electrolytes

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

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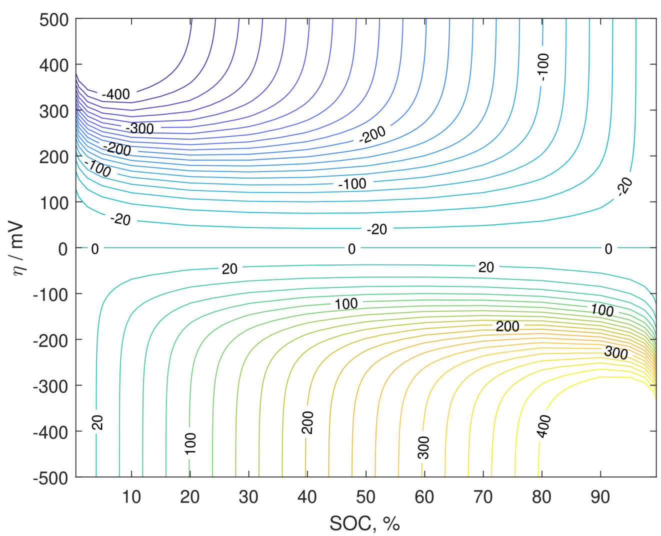
All ionic species in reaction

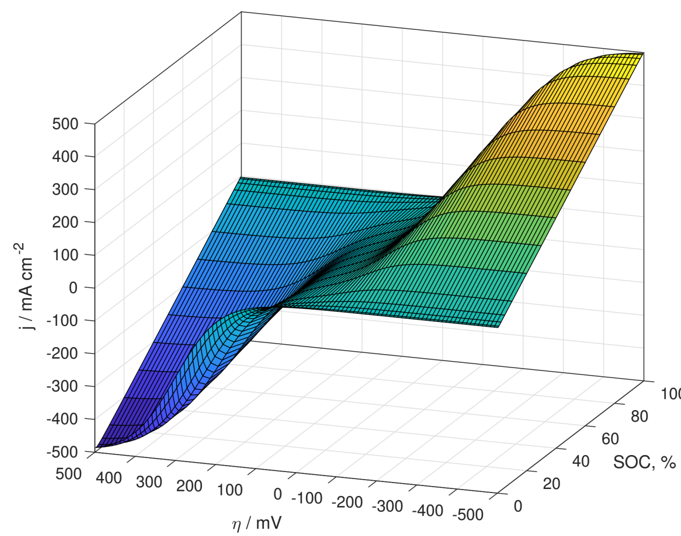
Complete Butler-Volmer equation for cathode

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

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

Protons concentration





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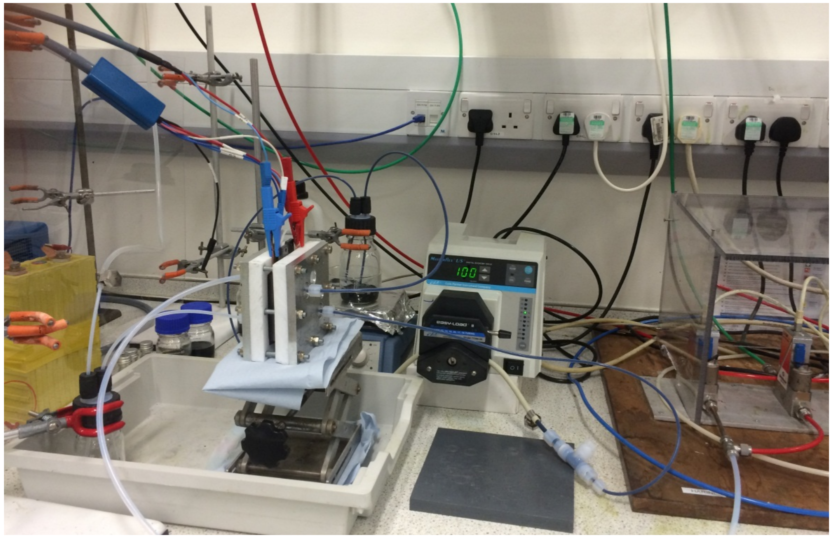
Experimental data RHVFC



Cell	1	2	3
Area	25 cm^2	5 cm^2	5 cm^2
Cathode	SGL 10AA, 400 μm, untreated	SGL 10AA, 400 μm, untreated	Freudenberg H23, 210 μm, heat treated (500 °C, 6 h)
Anode	Alfa Aesar, 200 μm, 0.5 mg cm^{-2} Pt	SGL 25BC, 235 μm, 0.2 mg cm^{-2} Pt	SGL 29BC, 235 μm, 0.3 mg cm^{-2} Pt
Membrane	Nafion 117, 183 μm	Nafion 117, 183 μm	Nafion 115, 127 μm
Flow channel	Multi-channel serpentine	Single-channel serpentine	Single-channel serpentine
Catholyte	1M $VOSO_4$ in 60 mL 5M H_2SO_4	1M $VOSO_4$ in 60 mL 5M H_2SO_4	0.75M $VOSO_4$ in 60 mL 5M H_2SO_4
Current density	50 – 600 A m^{-2}	1000 & 2000 A m^{-2}	500 – 1500 A m^{-2}
Catholyte flow rate	100 & 150 mL min^{-1}	77 mL min^{-1}	50 & 100 mL min^{-1}
Hydrogen flow rate	50 & 100 mL min^{-1}	100 mL min^{-1}	100 mL min^{-1}
Tests	OCP, ch-dch, polarization	dch, polarization, RE	OCP, ch-dch, polarization

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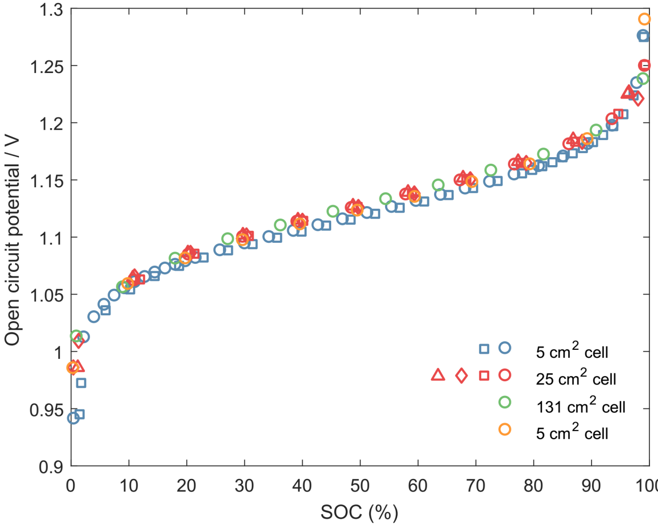
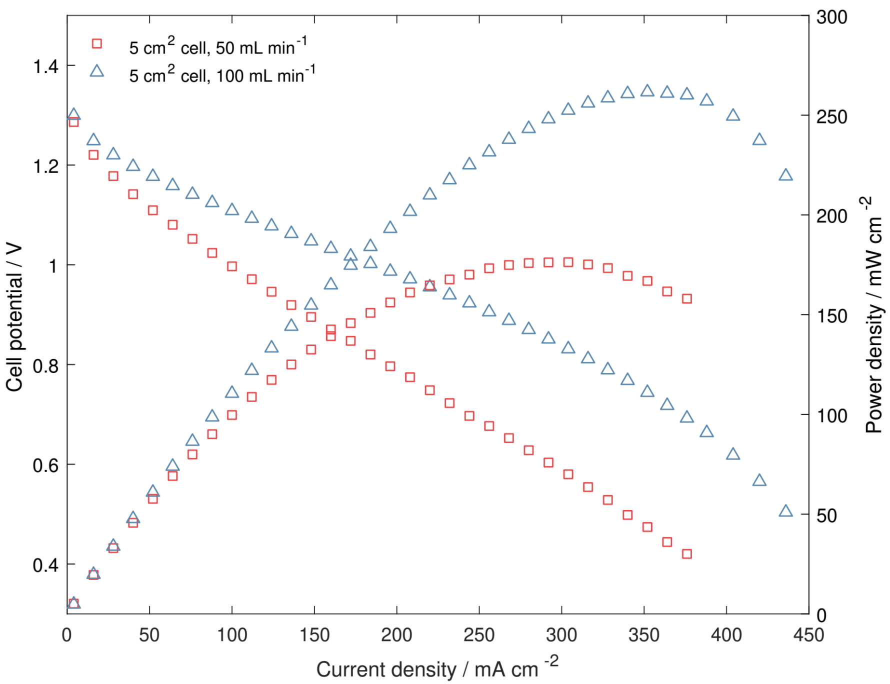
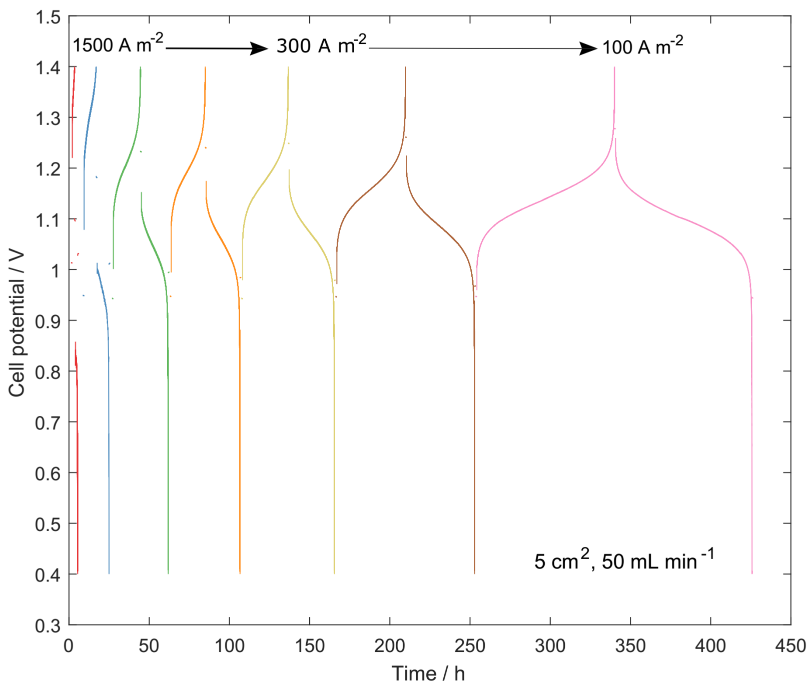
Experimental data RHVFC







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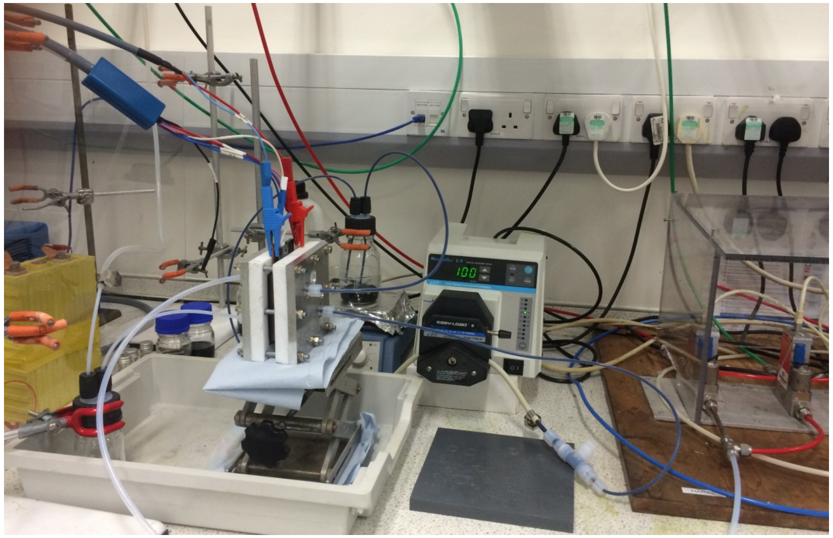
Experimental data
RHVFC

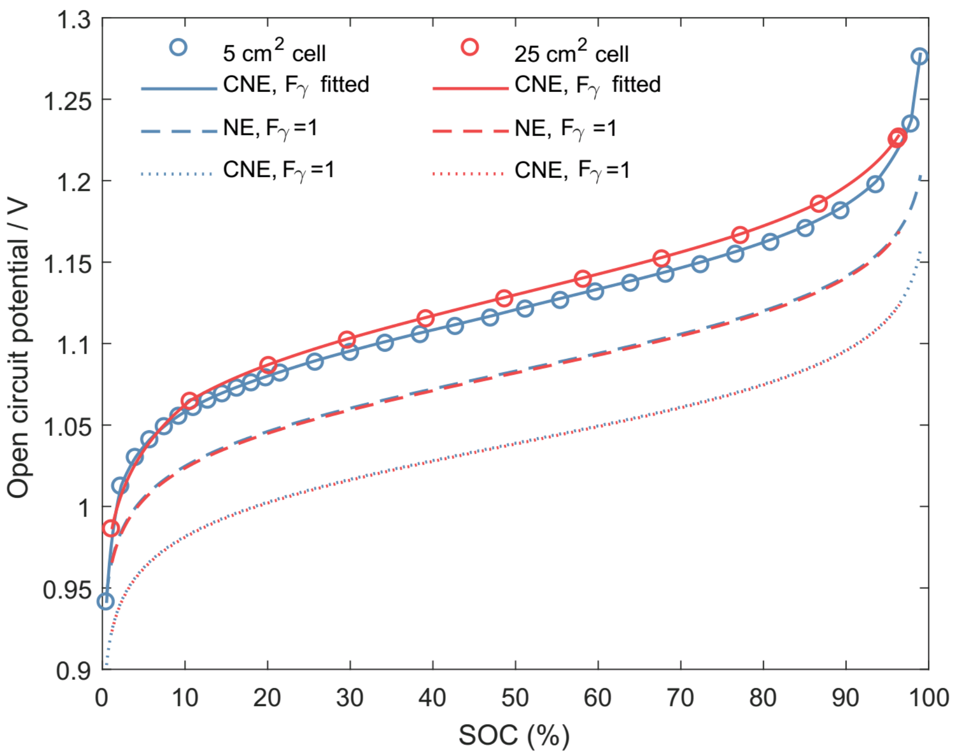


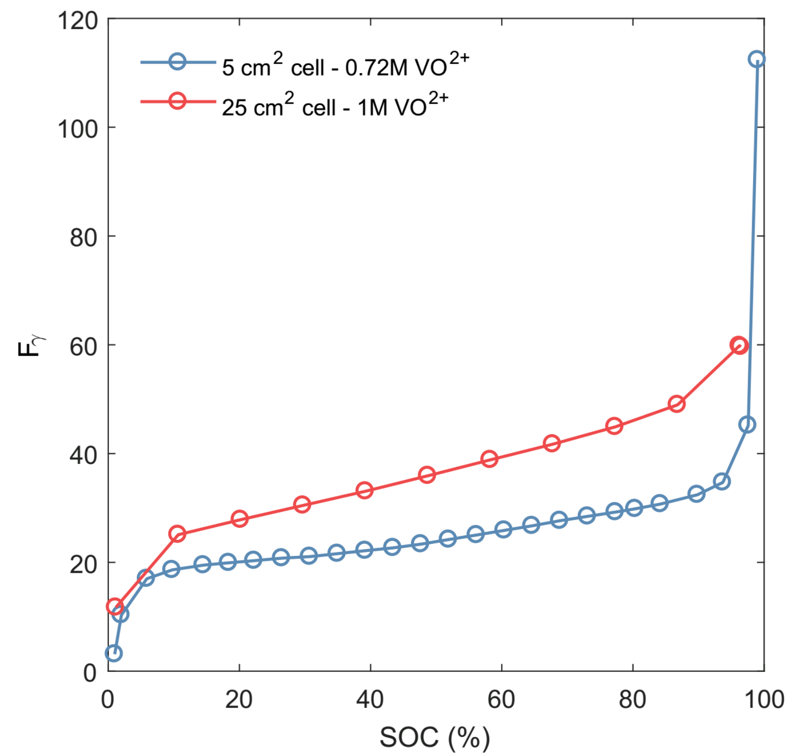
Cell 3	AVIZO	TauFactor
Area	5 cm^2	
Cathode	Freudenberg H23, 210 µm, heat treated (500 °C, 6 h)	
Porosity	0.848	0.850
Specific surface area	68.9 $\mu m^2\ \mu m^{-3}$	73.8 $\mu m^2\ \mu m^{-3}$
Mean pore diameter	31.77 µm	---
Mean fibre diameter	13.50 µm	---

Open Circuit Potential

Thermodynamic derivation of CNE

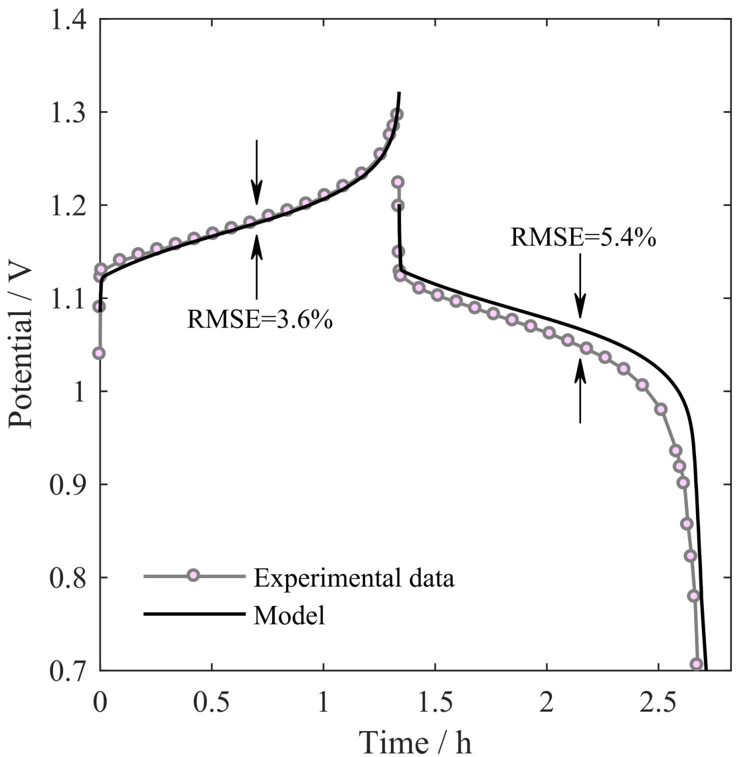
$$E_{OCP} = E^{0}_{\mathrm{cell}} + \frac{RT}{F}\ln\left(\frac{c^{\mathrm{ca}}_{\mathrm{VO}_2^+}\left(c^{\mathrm{ca}}_{\mathrm{H}^+}\right)^2\left(p^{\mathrm{g}}_{\mathrm{H}_2}\right)^{0.5}}{c^{\mathrm{ca}}_{\mathrm{VO}^{2+}}\,c^{\mathrm{an}}_{\mathrm{H}^+}} \times \frac{c^{\mathrm{an}}_{\mathrm{H}^+}}{c^{\mathrm{ca}}_{\mathrm{H}^+}}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





Pino Muñoz et al, Journal of The Electrochemical Society, 164 (14) F1717-F1732 (2017)

Model calibration



Cell 1: 25 cm^2, j= 400 A m^{-2}, Q_V=Q_{H2}=100 mL min^{-1}

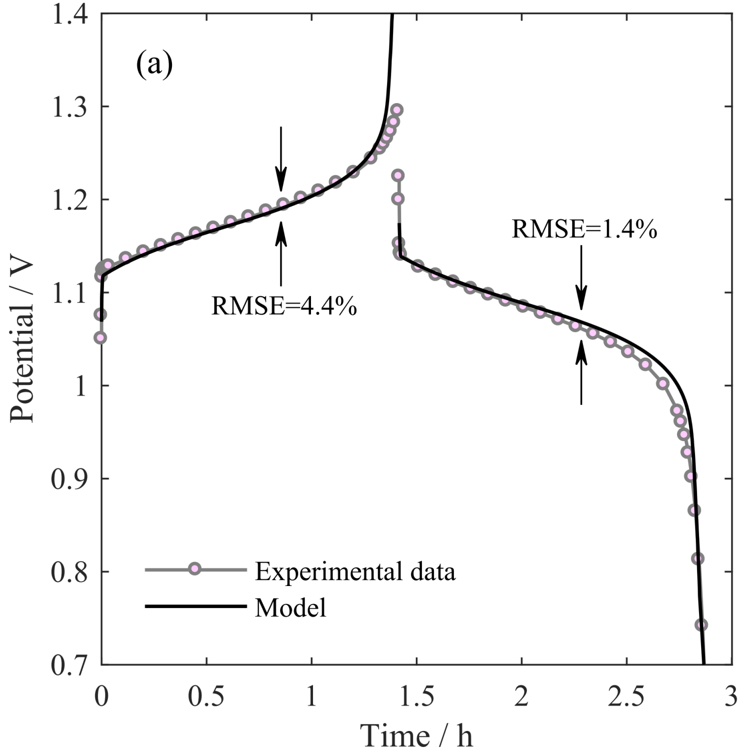
Model implementation

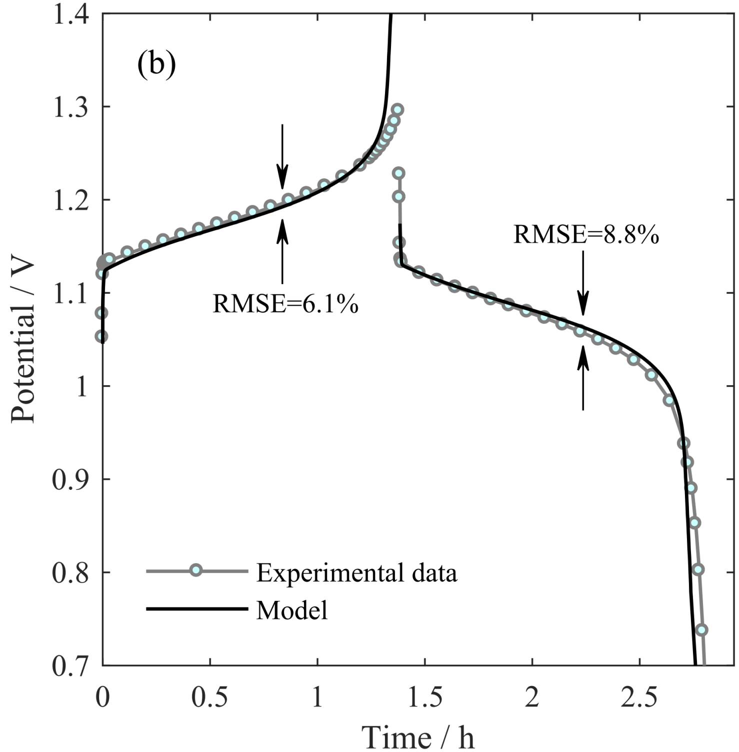
- *MATLAB*
- ode15s → solve ODE problem
- lsqcurvefit → curve fitting, lb & ub

Fitting parameters

- Standard rate constant of cathode → k^{o}_{ca}
- Nernst diffusion layer thickness → δ
- Additional Ohmic resistance (contact) → R_C

Charge-discharge: vary flow rate





Cell 1: j= 400 A m^{-2}, Q_V=150 mL min^{-1}, Q_{H2}=100 mL min^{-1}

Cell 1: j= 400 A m^{-2}, Q_V=100 mL min^{-1}, Q_{H2}=50 mL min^{-1}

Pino Muñoz et al., Journal of The Electrochemical Society, 164 (14) F1717-F1732 (2017)

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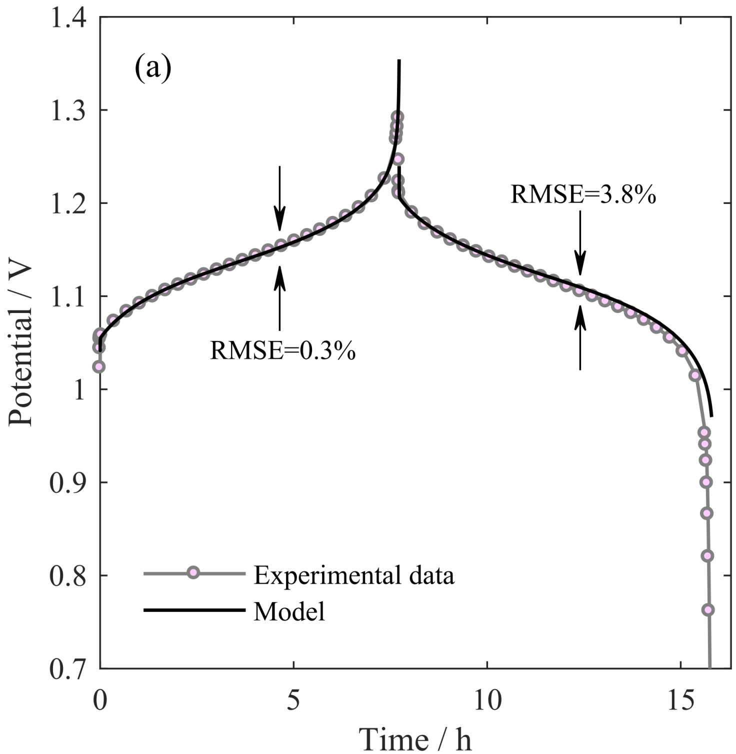
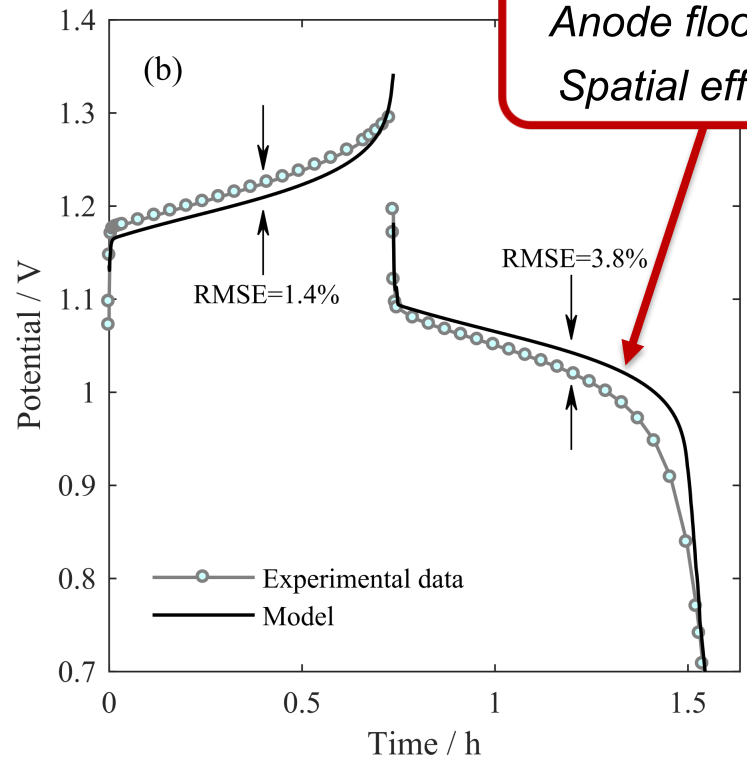
Charge-discharge: vary current density

Bulk diffusion
Crossover
Anode flooding
Spatial effects



Cell 1: 25 cm^2, j= 80 A m^{-2}, Q_V=Q_{H2}=100 mL min^{-1}



Cell 1: 25 cm^2, j= 600 A m^{-2}, Q_V=Q_{H2}=100 mL min^{-1}

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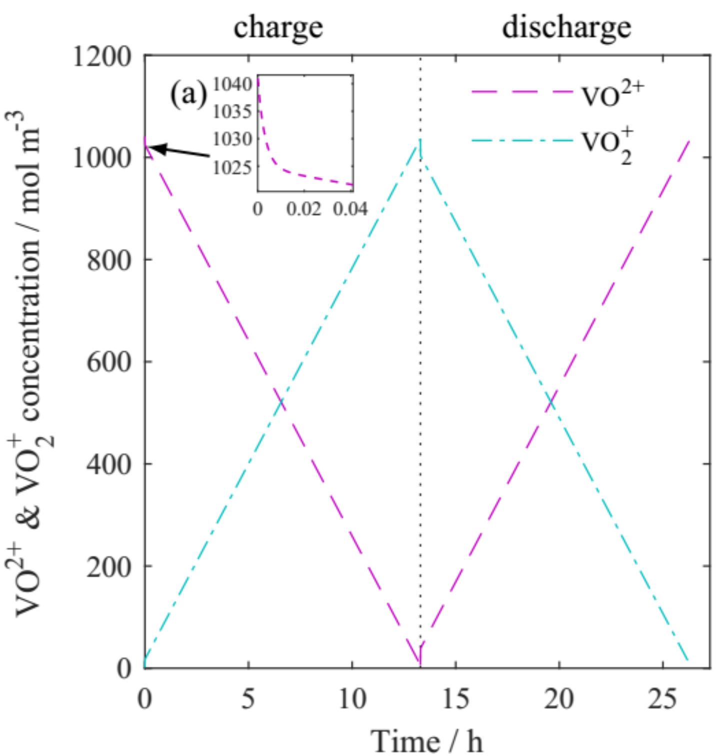
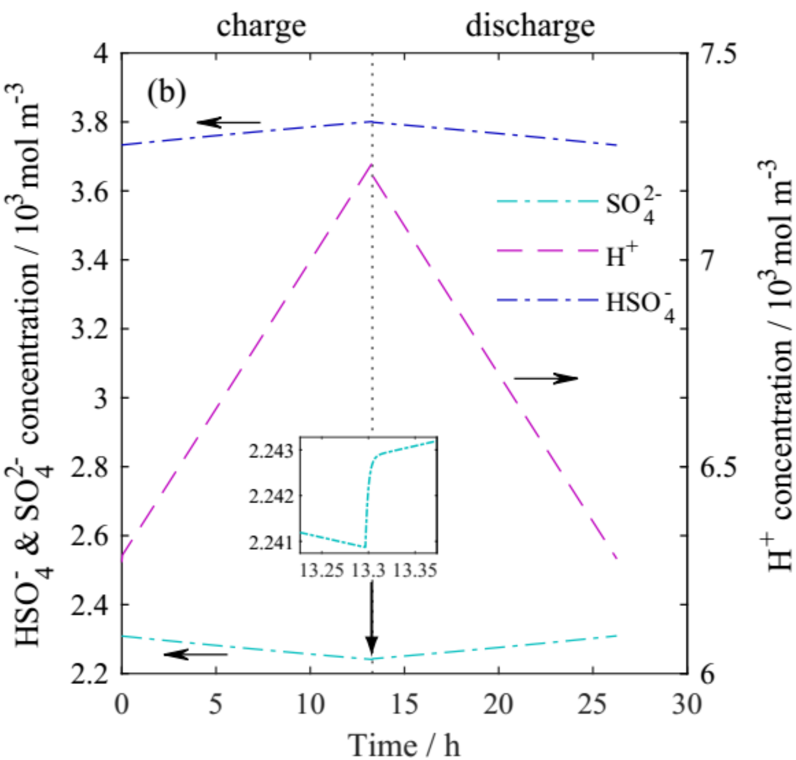
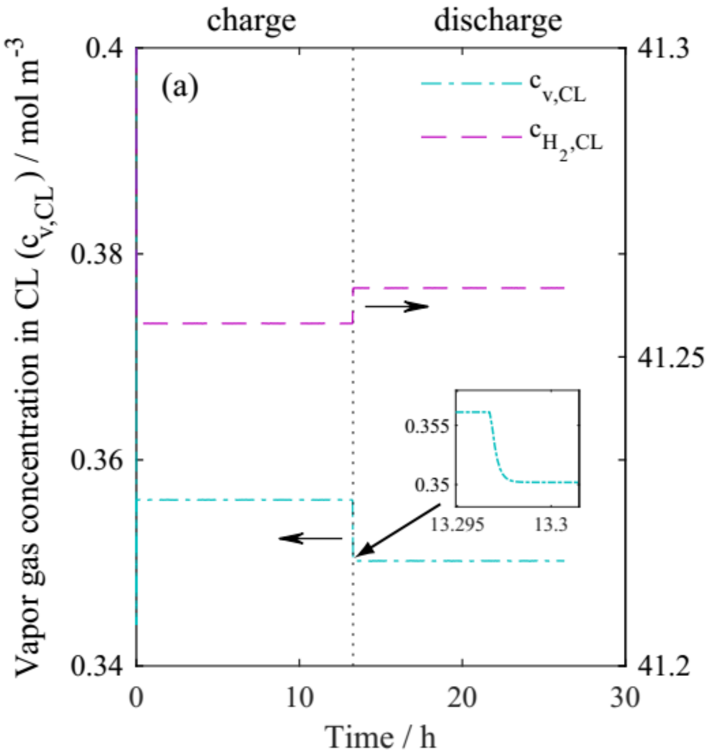
Species evolution in cathode

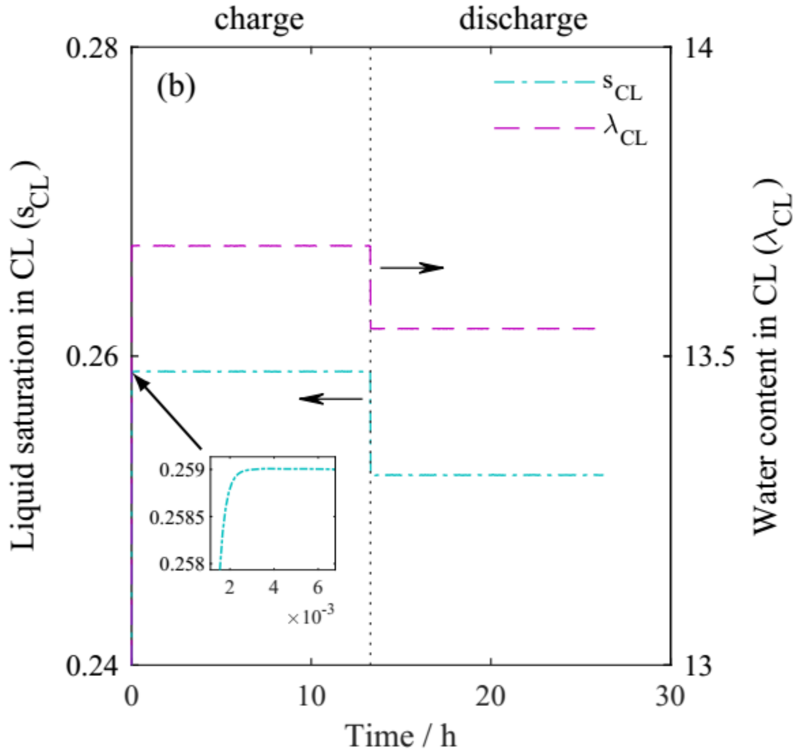




Cell 1: j= 50 A m^{-2}, Q_V=Q_{H2}=100 mL min^{-1}

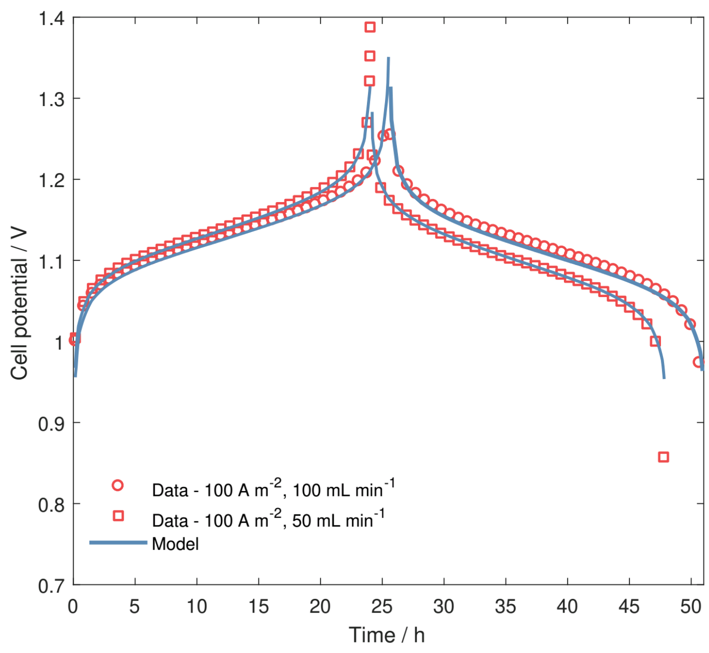
Species evolution in anode





Cell 1: j= 50 A m^{-2}, Q_V=Q_{H2}=100 mL min^{-1}

Charge-discharge

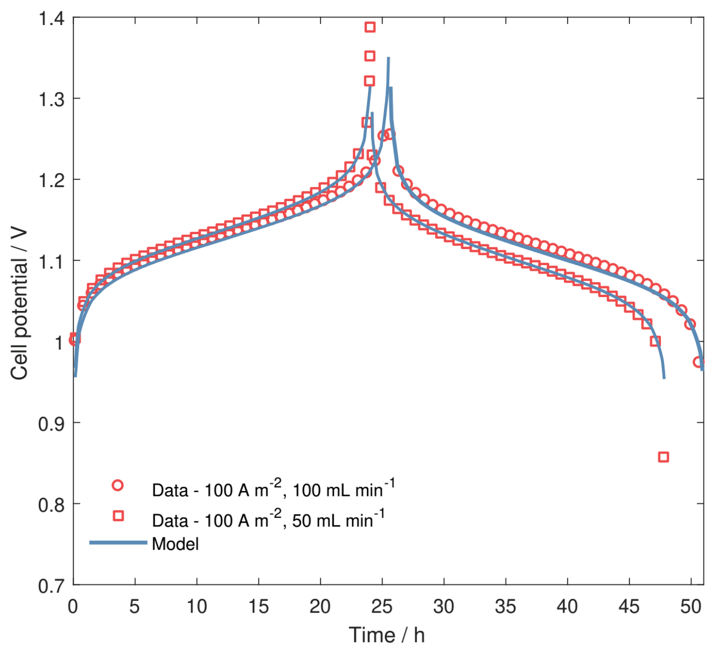


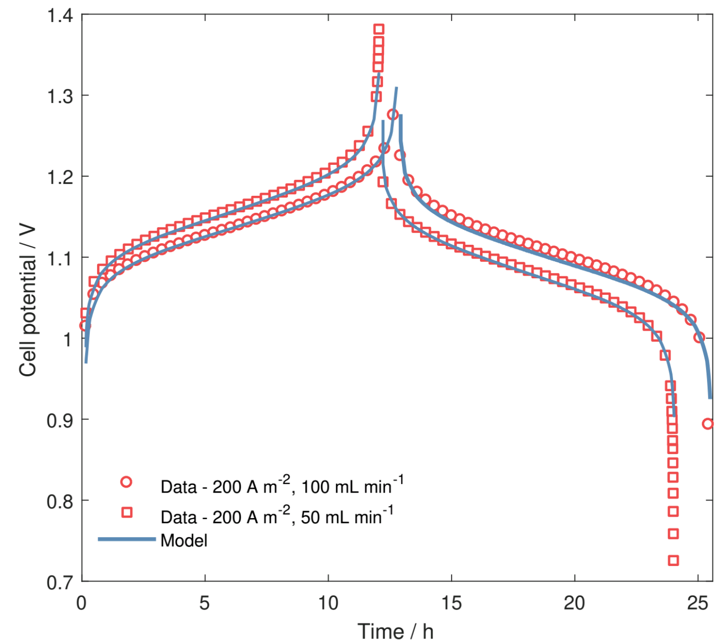
Cell 3: Q_V=50 & 100 mL min^{-1}, Q_{H2}=100 mL min^{-1}

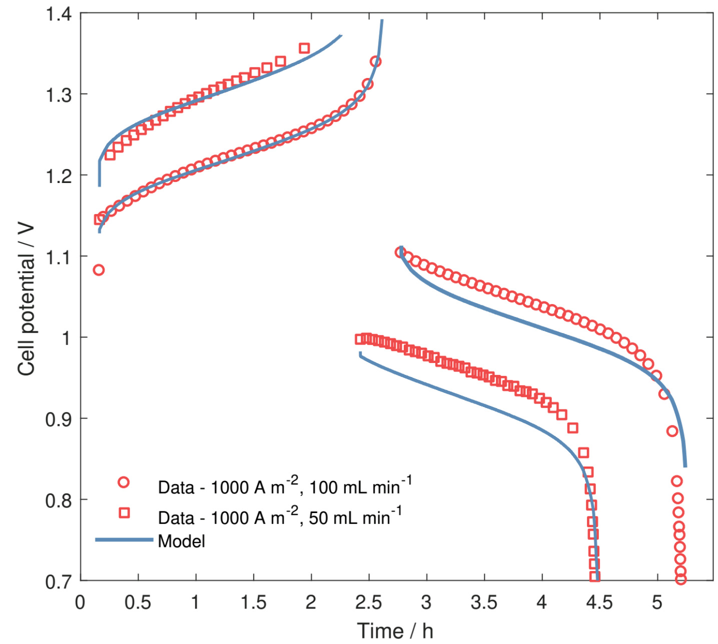
Fitting parameters

- Standard rate constant of cathode → $k^{\mathrm{o}}_{\mathrm{ca}}$
- Specific surface (active) area of cathode → $S^{\mathrm{ca}}_{\mathrm{rx}}$
- Standard desorption rate constant of anode → $k^{\mathrm{o}}_{\mathrm{des}}$
- Electronic conductivity of current collectors → σ^{cc}

Charge-discharge







Cell 3: Q_V=50 & 100 mL min^{-1}, Q_{H2}=100 mL min^{-1}

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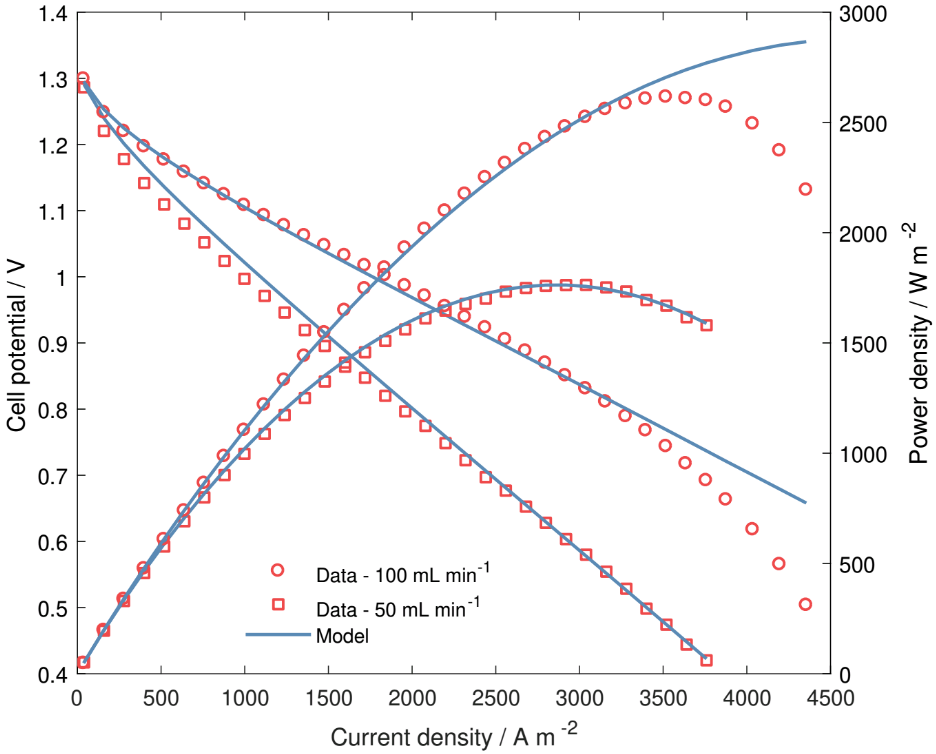
Polarization curve



Cell 3: 100% SOC, Q_V=50 & 100 mL min^{-1}, Q_{H2}=100 mL min^{-1}

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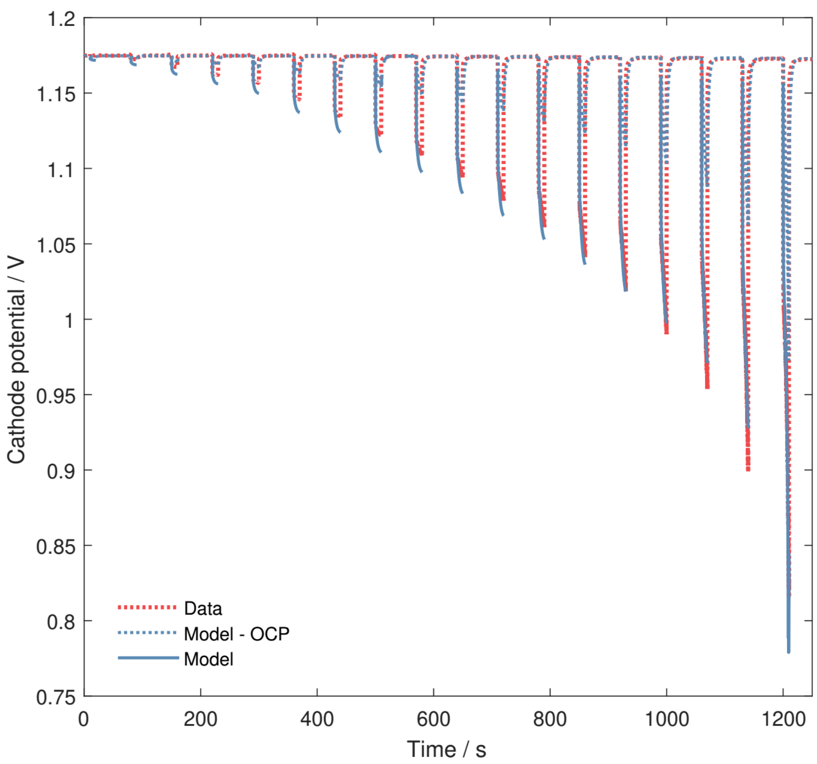
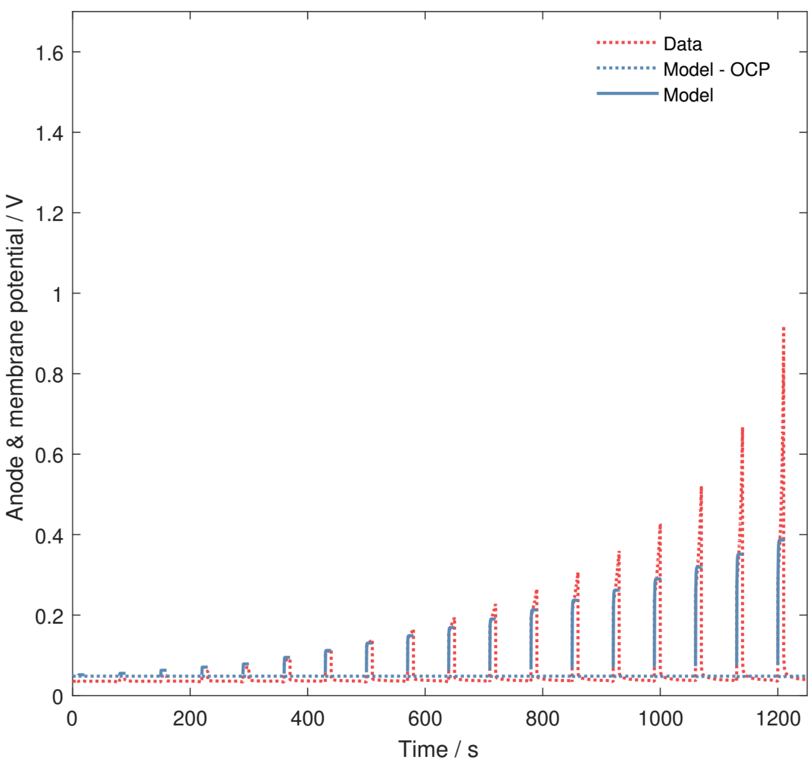
Polarization curves – reference electrodes





Cell 2: 50% SOC, Q_V=77 mL min^{-1}, Q_{H2}=100 mL min^{-1}

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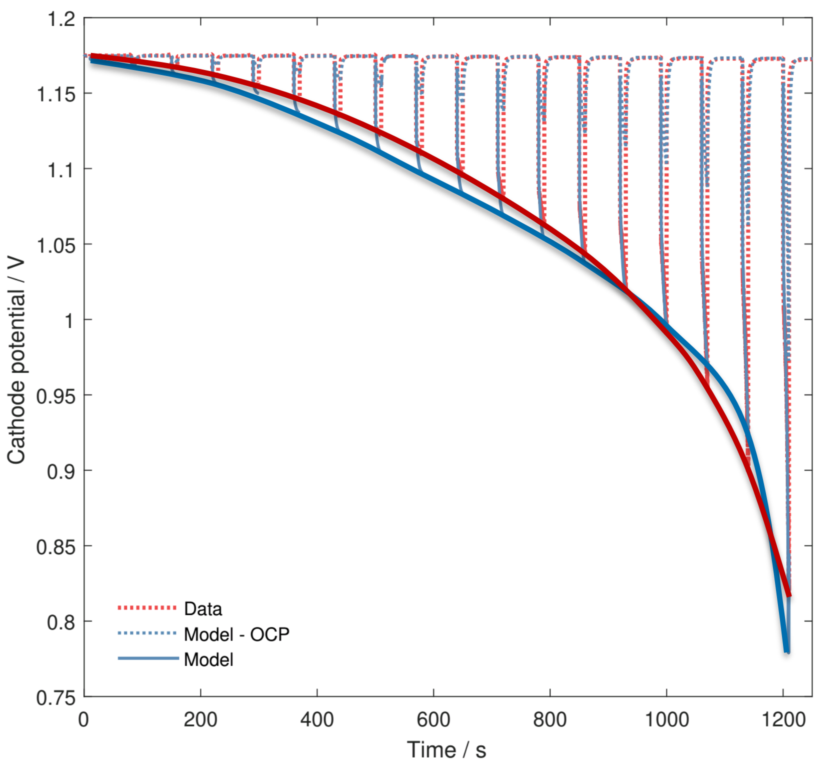
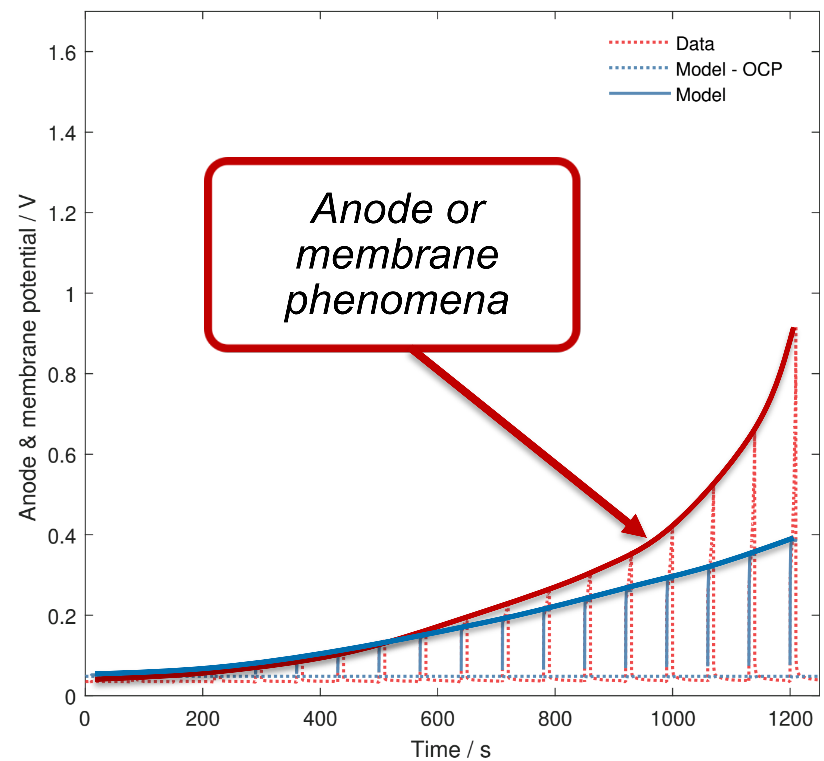
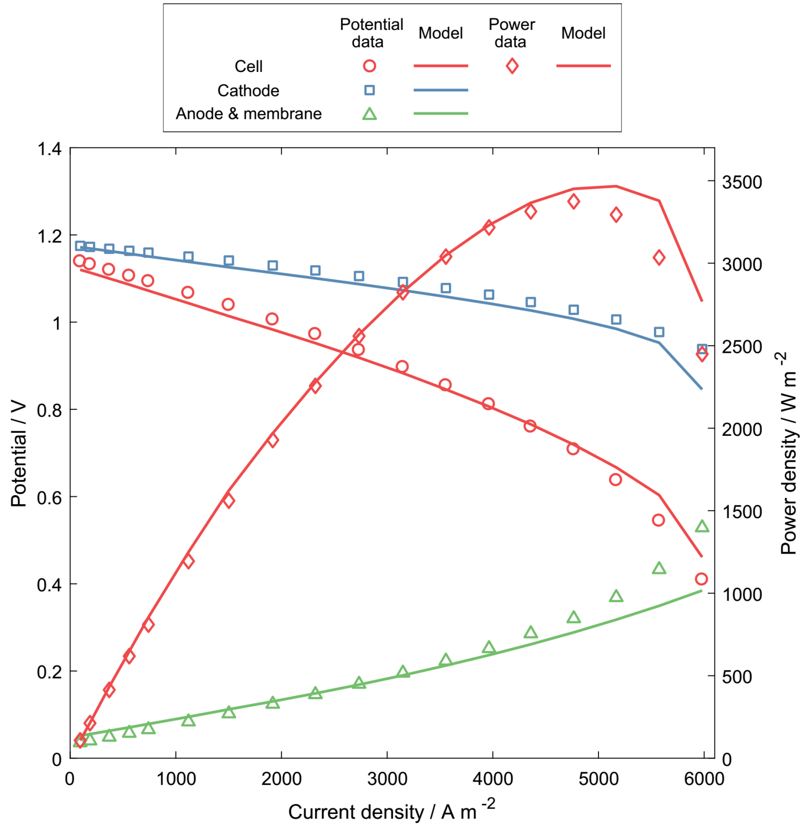
Polarization curves – reference electrodes



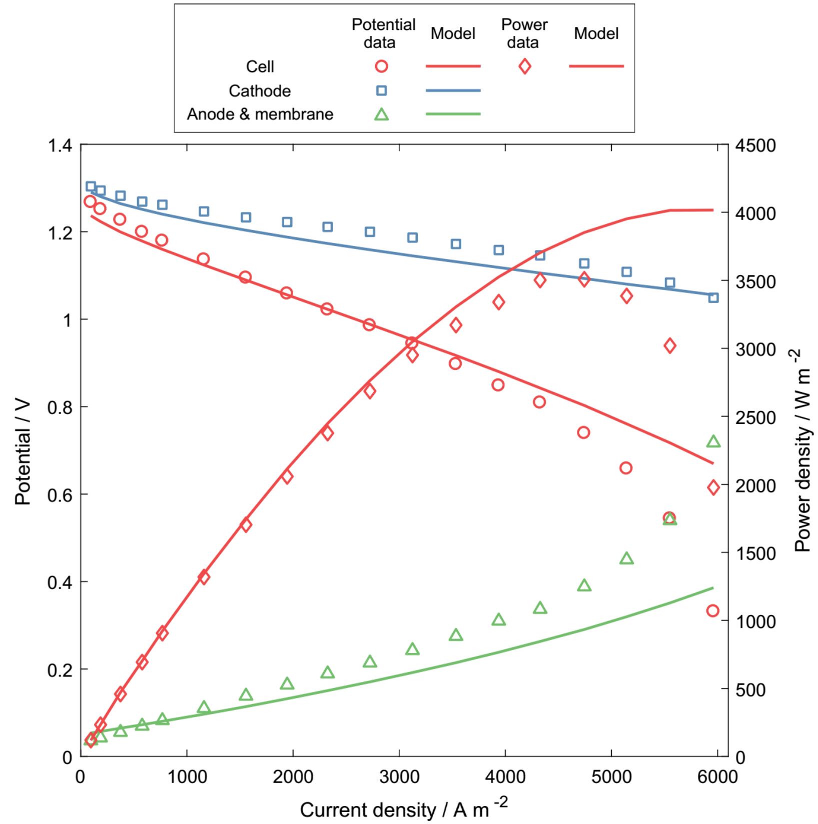


Cell 2: 50% SOC, Q_V=77 mL min^{-1}, Q_{H2}=100 mL min^{-1}

Polarization curves – reference electrodes

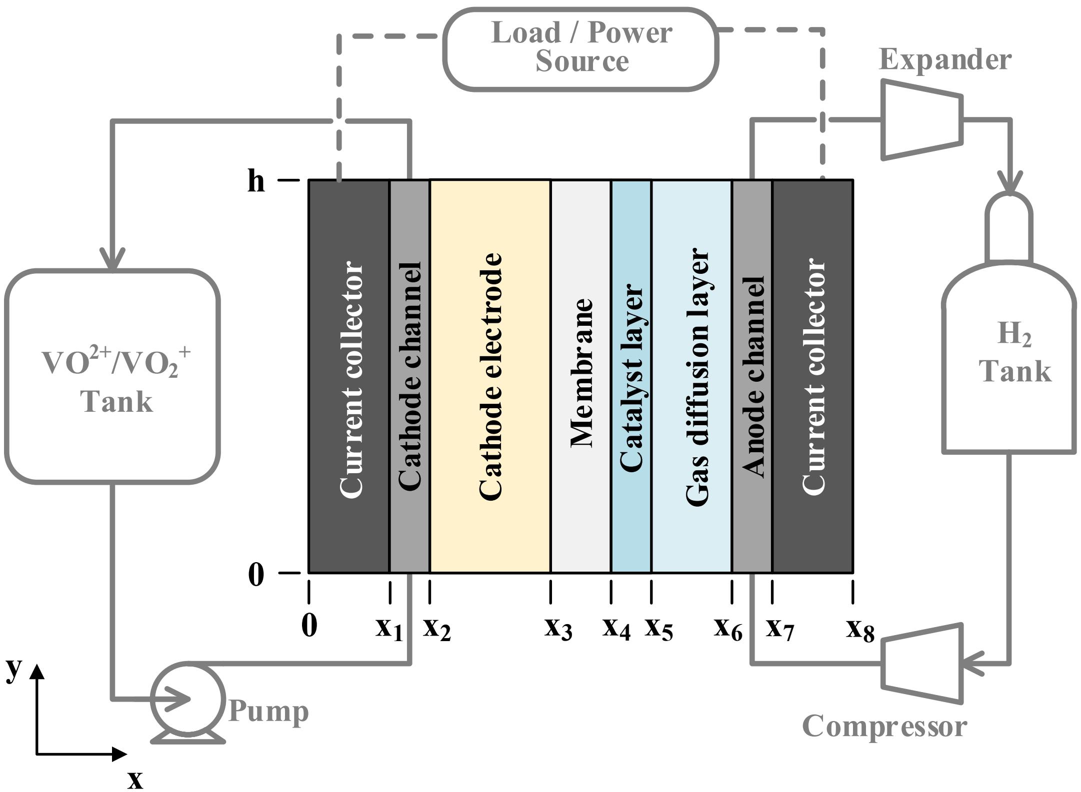


Cell 2: 50% SOC, Q_V=77 mL min^{-1}, Q_{H2}=100 mL min^{-1}

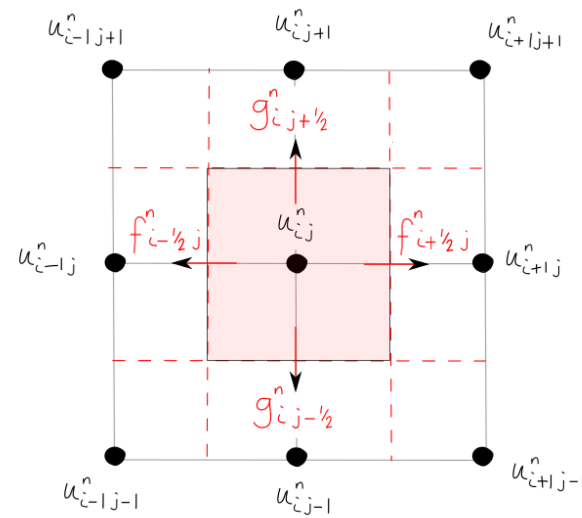


Cell 2: 100% SOC, Q_V=77 mL min^{-1}, Q_{H2}=100 mL min^{-1}

2D continuum model



- Finite volume method



$$\frac{\partial u}{\partial t} + \nabla \cdot F = q$$

$$\frac{\partial}{\partial t}\frac{1}{h^2}\int_{I_{ij}} u\mathrm{dxdy} + \frac{1}{h^2}\oint_{I_{ij}} (F \cdot \mathrm{n})\mathrm{dS} = \frac{1}{h^2}\int_{I_{ij}} u\mathrm{dxdy}$$

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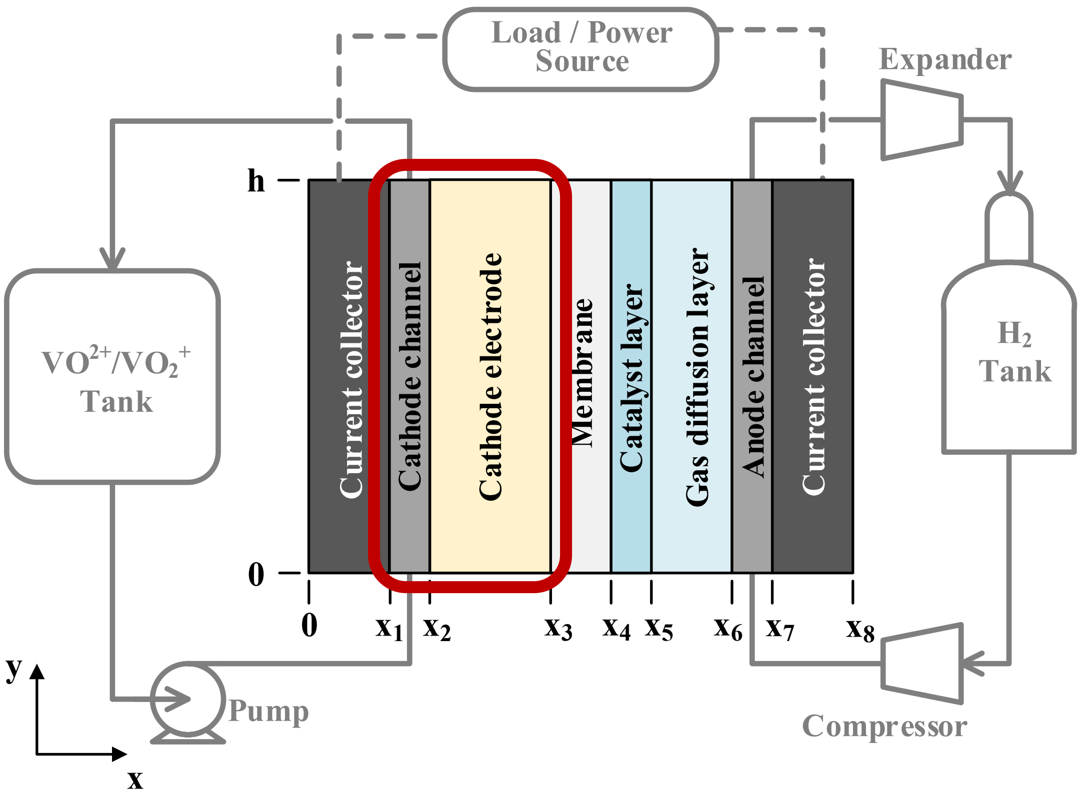
2D continuum model



Model implementation

- *Visual Studio C++*
- Semi-implicit FVM
- CGM optimization

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Model summary

CATHODE MODEL

Redox kinetics

$$j^{\mathrm{BV}} = j_0^{\mathrm{BV}}\left[\left(\frac{c^{\mathrm{s}}_{\mathrm{VO^{2+}}}}{c_{\mathrm{VO^{2+}}}}\right)\exp\left(\frac{\alpha_{\mathrm{a}} F \eta_{\mathrm{ca}}}{RT}\right) - \left(\frac{c^{\mathrm{s}}_{\mathrm{VO_2^+}}}{c_{\mathrm{VO_2^+}}}\right)\left(\frac{c^{\mathrm{s}}_{\mathrm{H^+}}}{c_{\mathrm{H^+}}}\right)^2\exp\left(\frac{-\alpha_{\mathrm{c}} F \eta_{\mathrm{ca}}}{RT}\right)\right]$$

$$j_0^{\mathrm{BV}} = F k_{\mathrm{ca}} c_{\mathrm{VO^{2+}}}^{\alpha_{\mathrm{c}}}\left(c_{\mathrm{VO_2^+}} c_{\mathrm{H^+}}^2\right)^{\alpha_{\mathrm{a}}} \qquad \eta_{\mathrm{ca}} = \phi_{\mathrm{s}} - \phi_{\mathrm{e}} - E_{\mathrm{ca}}$$

Continuity & Momentum conservation

$$\nabla \cdot v = 0$$

$$v = -\frac{d_{\mathrm{f}}^2}{K_{\mathrm{CK}}\mu}\frac{\varepsilon^3}{(1-\varepsilon)^2}\nabla p$$

Redox equilibrium

$$E_{\mathrm{ca}} = E^0_{\mathrm{ca}} + \frac{RT}{F}\ln\left(\frac{c_{\mathrm{V(V)}}c^2_{\mathrm{H^+,ca}}}{c_{\mathrm{V(IV)}}}\cdot F^*_{\gamma}\right)$$

Electro-neutrality

$$\sum z_{\mathrm{k}} c_{\mathrm{k}} = 0$$

$$\mathrm{k} = [\mathrm{VO^{2+}},\ \mathrm{VO_2^+},\ \mathrm{H^+},\ \mathrm{SO_4^{2-}},\ \mathrm{HSO_4^-}]$$

Species conservation

$$\frac{\partial \varepsilon c_{\mathrm{k}}}{\partial t} + \nabla \cdot N_{\mathrm{k}} = -S_{\mathrm{k}}$$

$$\mathrm{k} = [\mathrm{VO^{2+}},\ \mathrm{VO_2^+},\ \mathrm{H^+},\ \mathrm{SO_4^{2-}},\ \mathrm{HSO_4^-}]$$

Charge conservation

$$\nabla \cdot i_{\mathrm{e}} + \nabla \cdot i_{\mathrm{s}} = 0$$

$$i_{\mathrm{e}} = F\sum z_{\mathrm{k}} N_{\mathrm{k}}, \quad i_{\mathrm{s}} = -\sigma_{\mathrm{s}}^{\mathrm{eff}}\nabla\phi_{\mathrm{s}}$$

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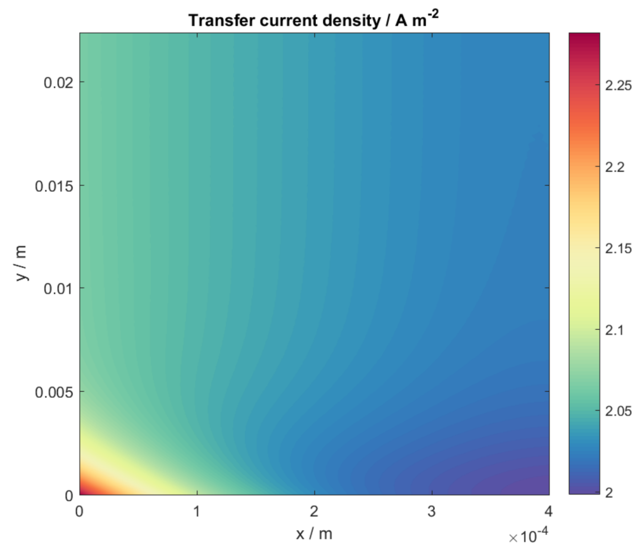
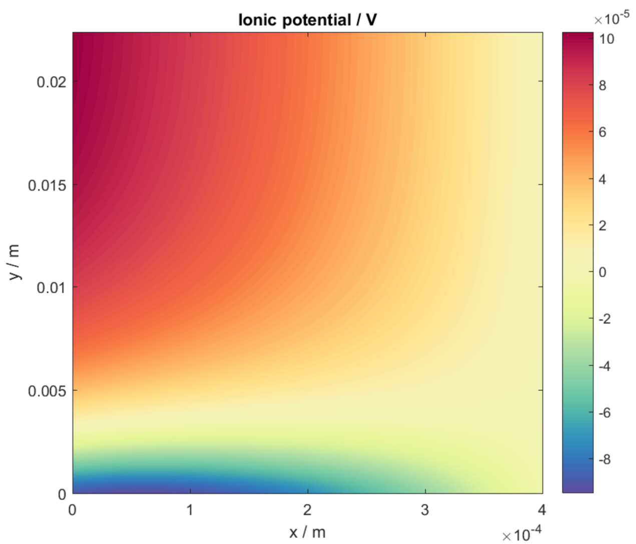
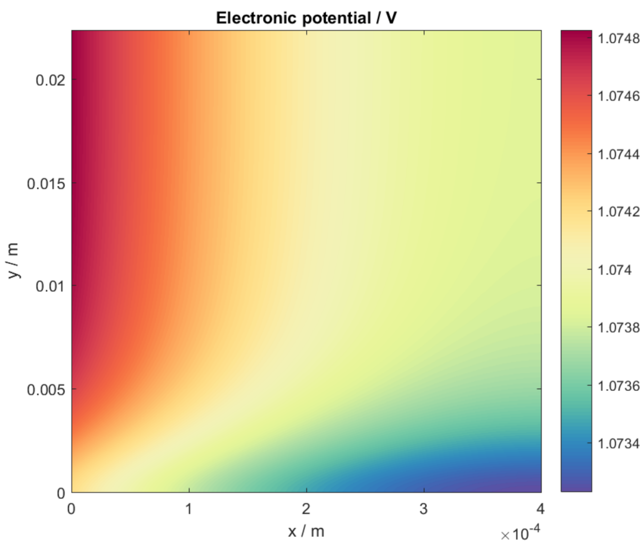
Preliminary results







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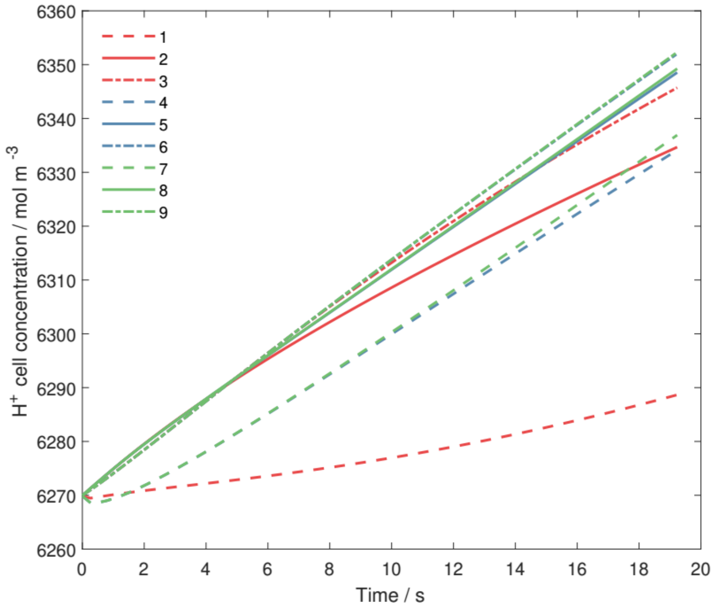
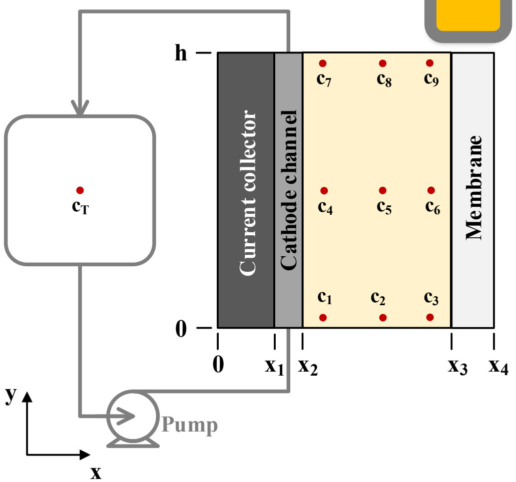
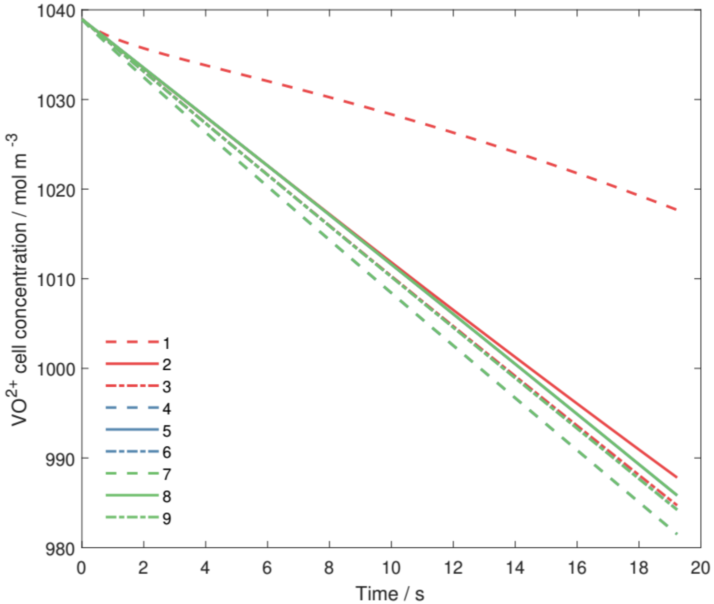
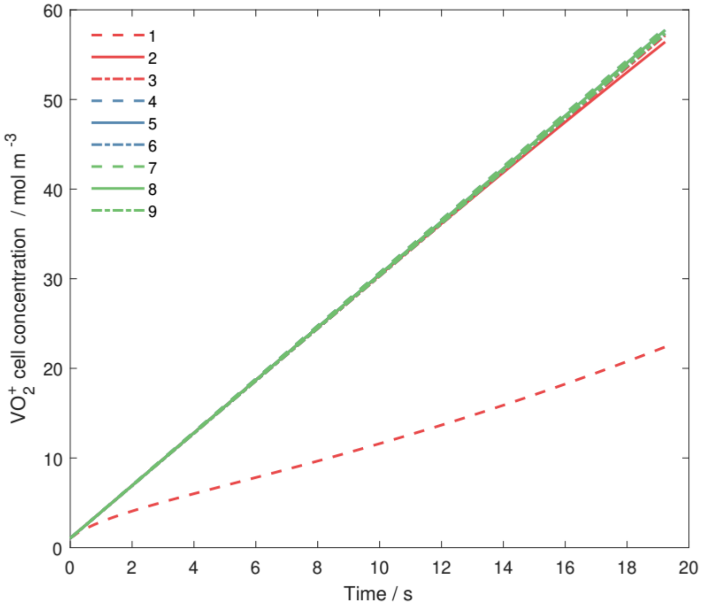
Species concentration









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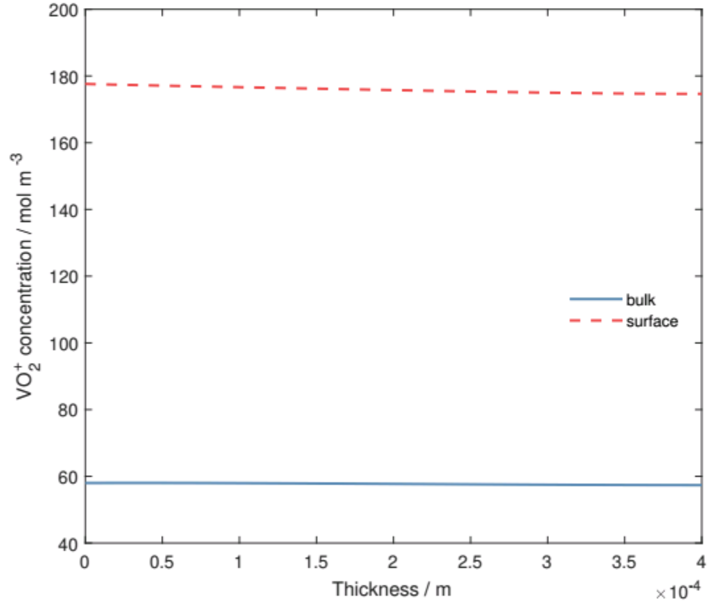
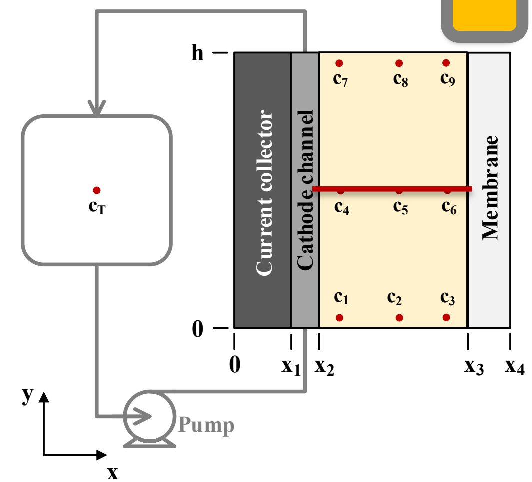
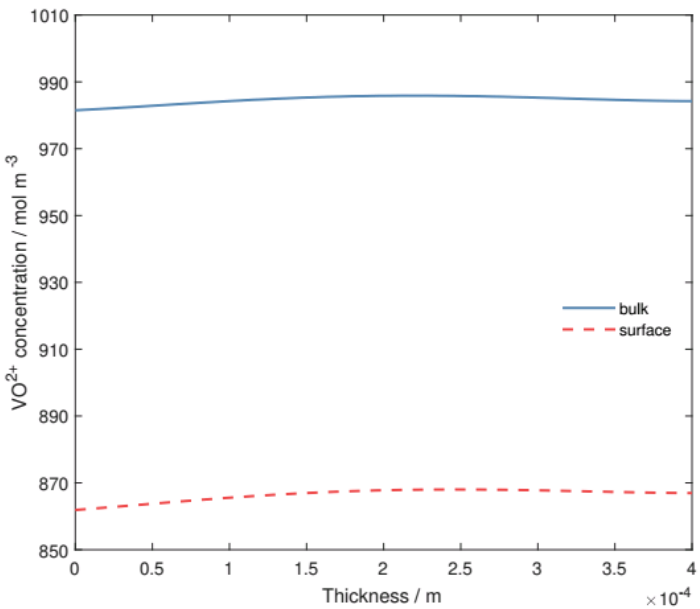
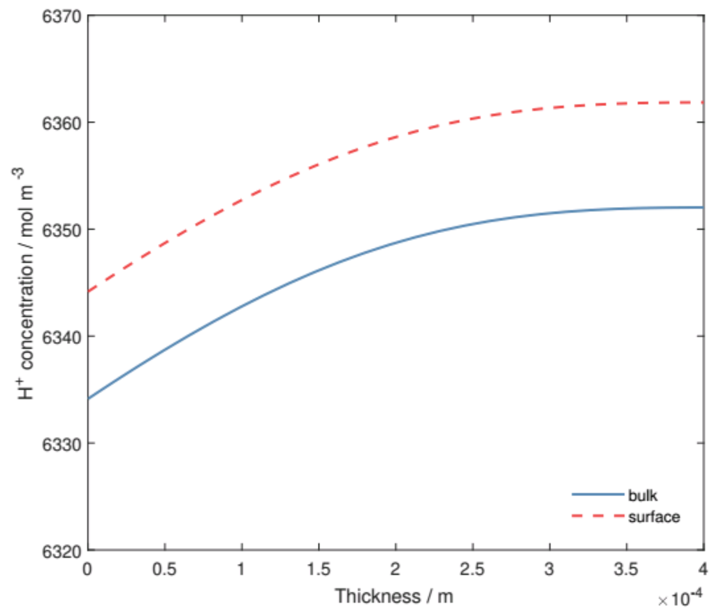
Species concentration







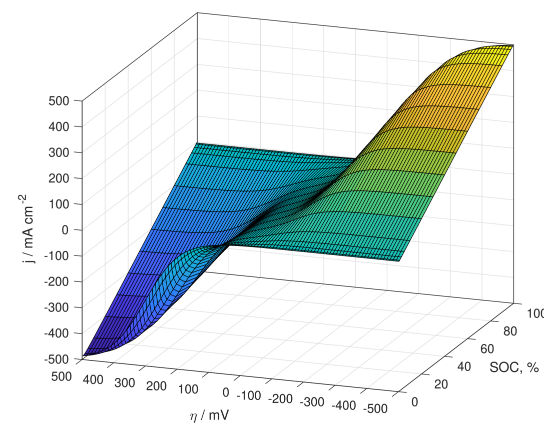


Conclusions

- A unit cell model for a VRFB was validated against literature data.
- A complete Nernst equation based on thermodynamic principles was proposed and fit to the OCP data.
- A complete Butler-Volmer kinetic equation was proposed for the cathode, considering the effect of protons concentration.

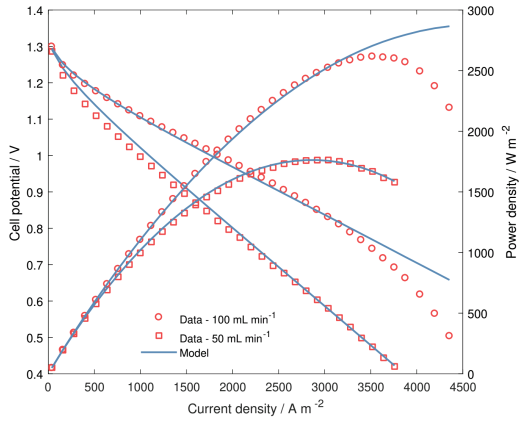
Thermodynamic derivation of CNE

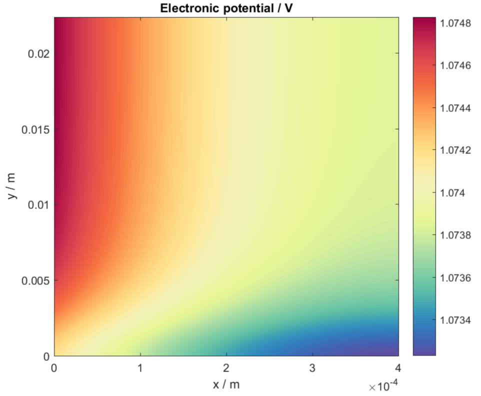
$$E_{OCP} = E^0_{\mathrm{cell}} + \frac{RT}{F}\ln\left(\frac{c^{\mathrm{ca}}_{\mathrm{VO_2^+}}\left(c^{\mathrm{ca}}_{\mathrm{H^+}}\right)^2\left(p^{\mathrm{g}}_{\mathrm{H_2}}\right)^{0.5}}{c^{\mathrm{ca}}_{\mathrm{VO^{2+}}}\,c^{\mathrm{an}}_{\mathrm{H^+}}} \times \frac{c^{\mathrm{an}}_{\mathrm{H^+}}}{c^{\mathrm{ca}}_{\mathrm{H^+}}}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



Conclusions

- A unit cell model for a RHVFC was introduced and calibrated against experimental data from 3 different devices.
- Well fitted polarization curves for the range of current density validated.
- An initial 2D model of the cathode was introduced.





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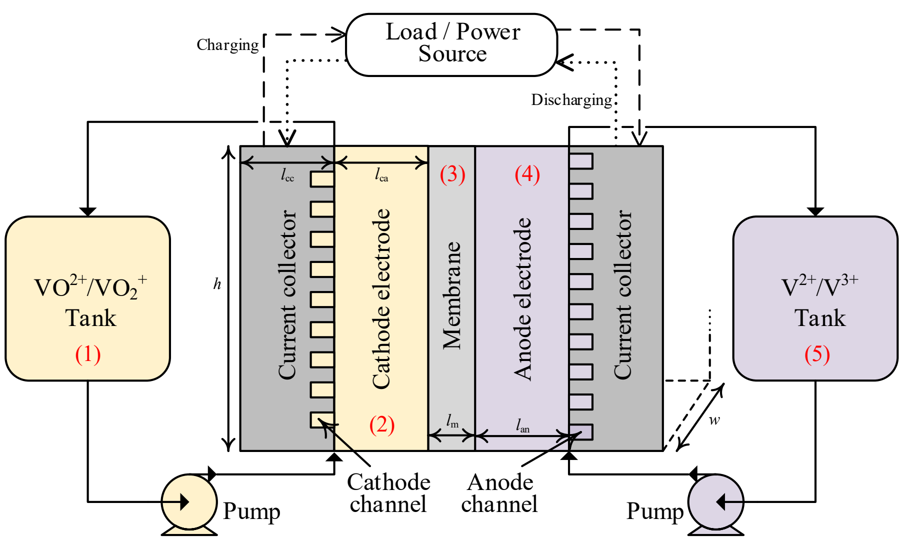
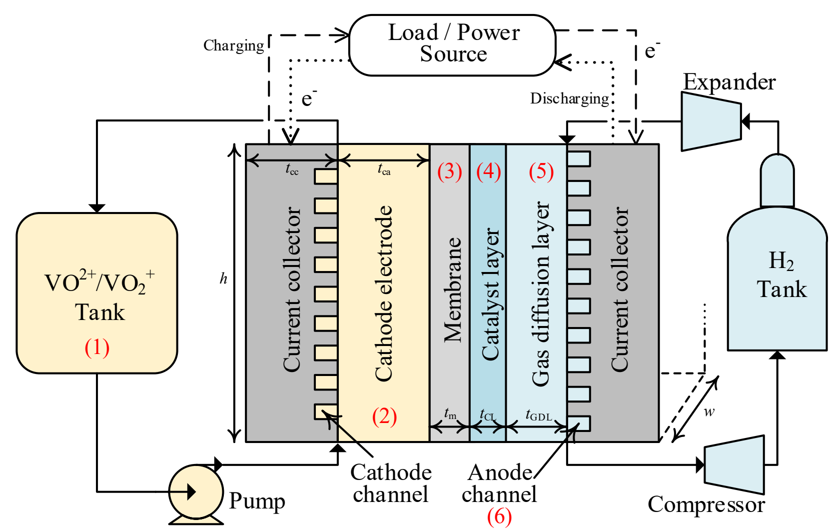
Next steps – unit cell models

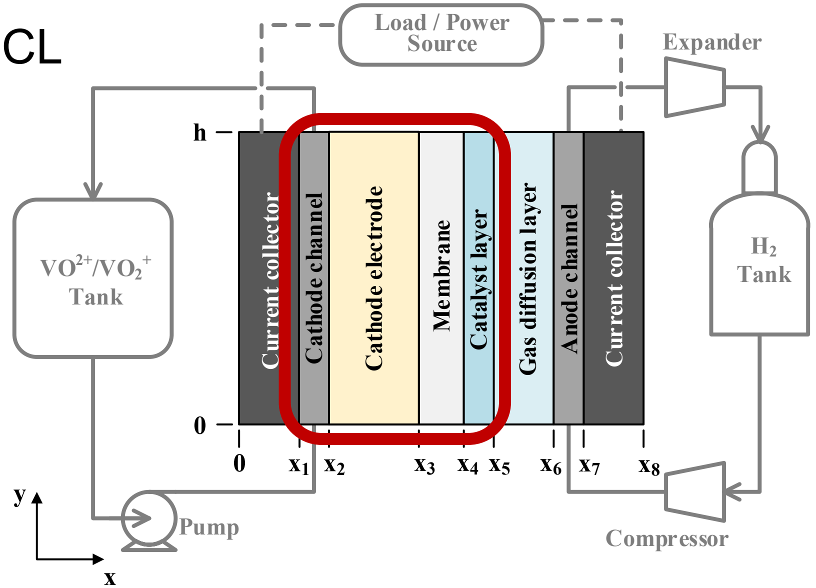
- To better validate (anode + membrane) potential from reference electrodes
- Performance comparison of VRFB and RHVFC
- Parameter sensitivity studies





Next steps – 2D continuum model

- Distributed model for the Membrane and CL
- Cross-over of ionic species
- Dominant transport phenomena
- Overpotential contributions



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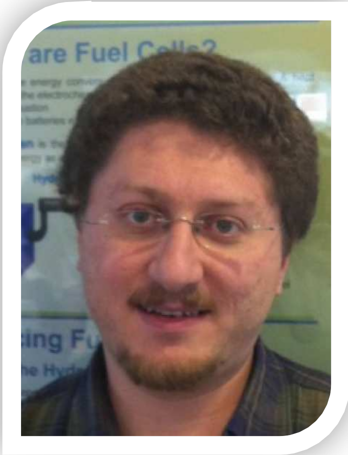
Acknowledgements



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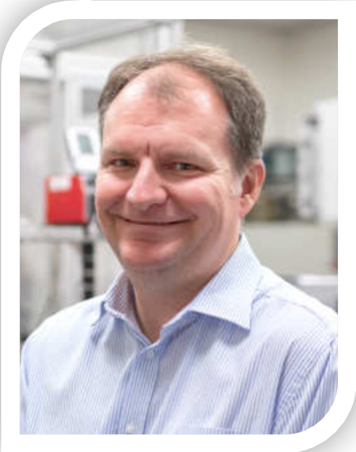

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BECAS CHILE

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Thank you!

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