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A unit cell model of a Regenerative Hydrogen-Vanadium Fuel Cell

Catalina Pino, Harini Hewa Dewage, Vladimir Yufit, Nigel Brandon
Department of Earth Science and Engineering, Imperial College London
Email: c.pino15@imperial.ac.uk

October 2nd, 2017

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- Mathematical model
- Experimental tests
- Open circuit potential
- Model calibration and validation
- Conclusions and next steps

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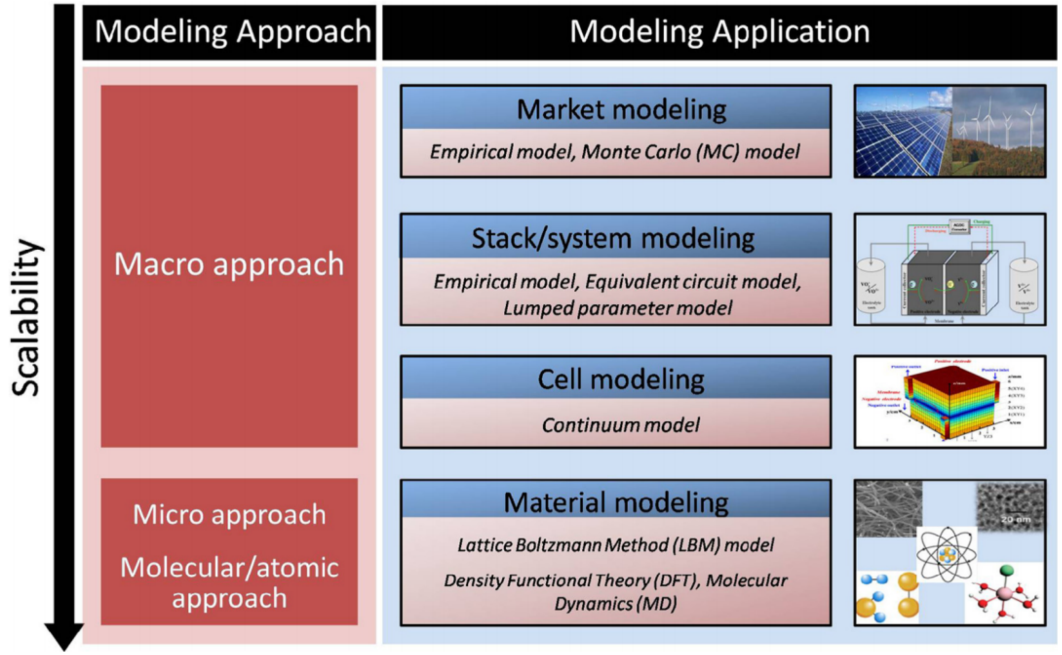
Motivation of the study



To develop a mixed model approach that considers a lumped stack/system and cell continuum models and could better explain how the phenomena influence the flow battery performance.

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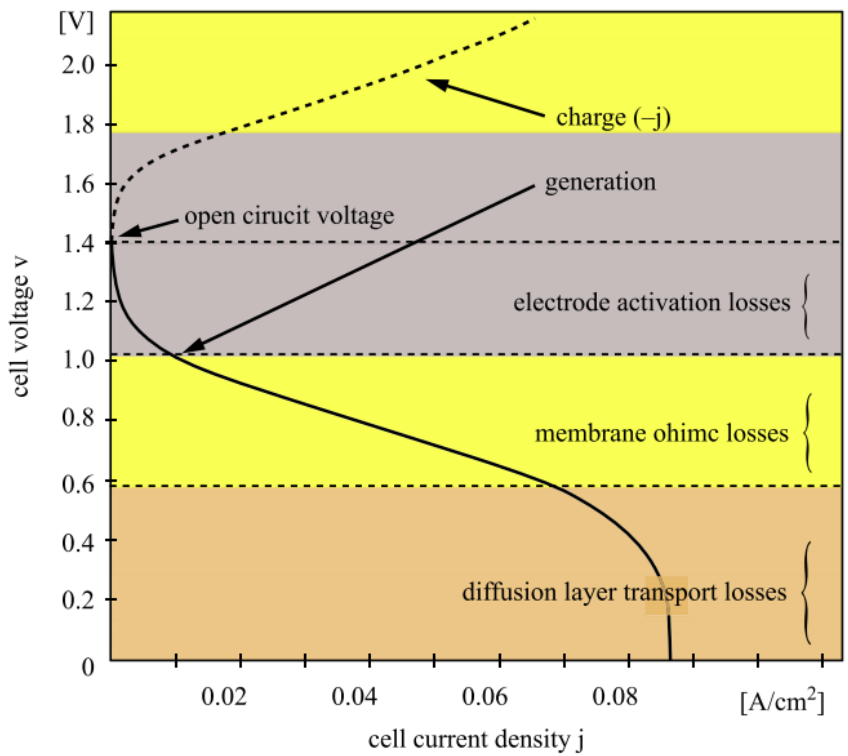
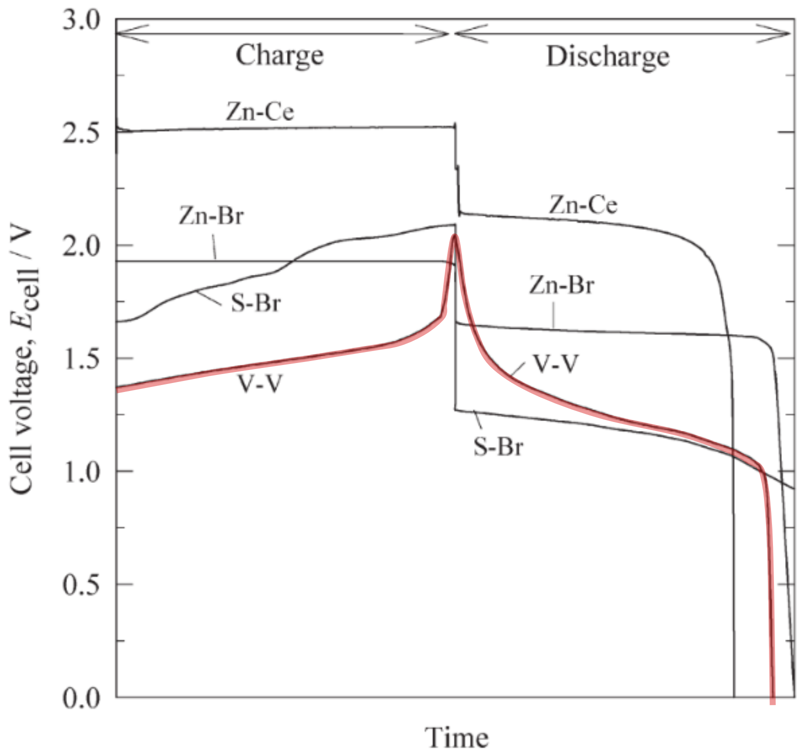
Modeling of RFBs





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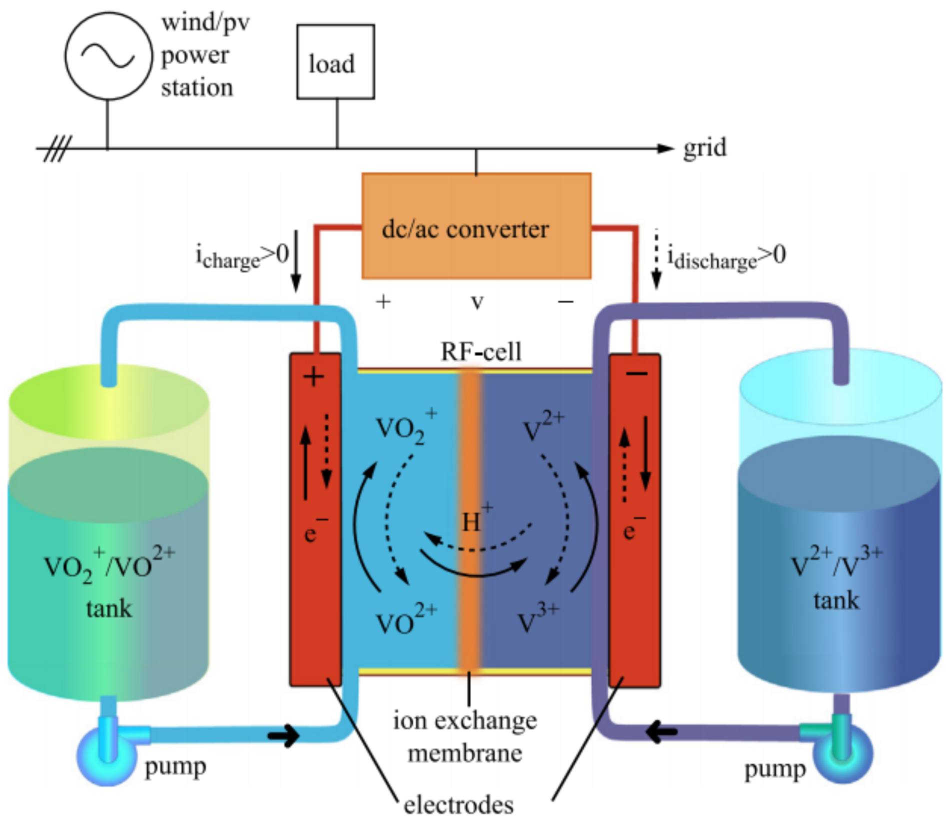
Vanadium redox flow battery

Vanadium based RFB
- *Vanadium / halide*
- *Vanadium / air*

Anolyte V(II) / V(III)

Hydrogen based RFB
- *H_2 / Br_2*
- *H_2 / Fe*
- *H_2 / Ce*



Advantages
- Scalability and flexibility
- Independent sizing of power and energy
- High round-trip efficiency (>80%) and 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) for vanadium concentration 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

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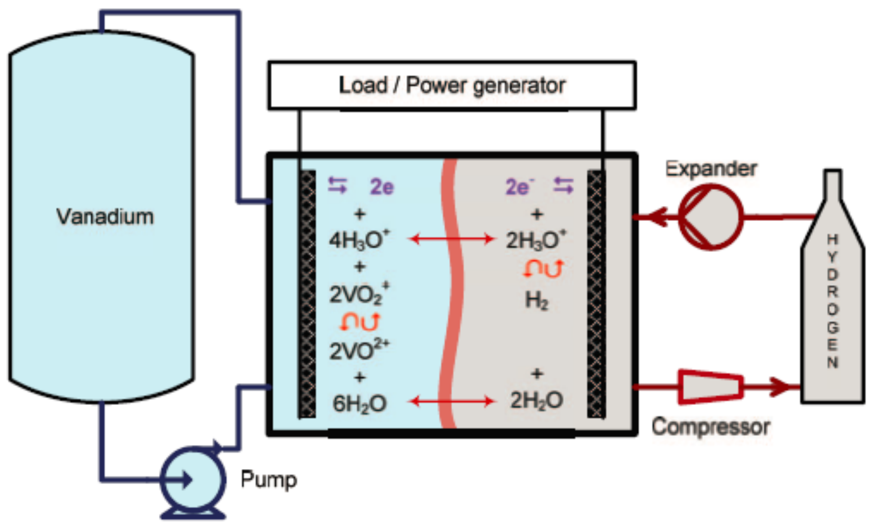
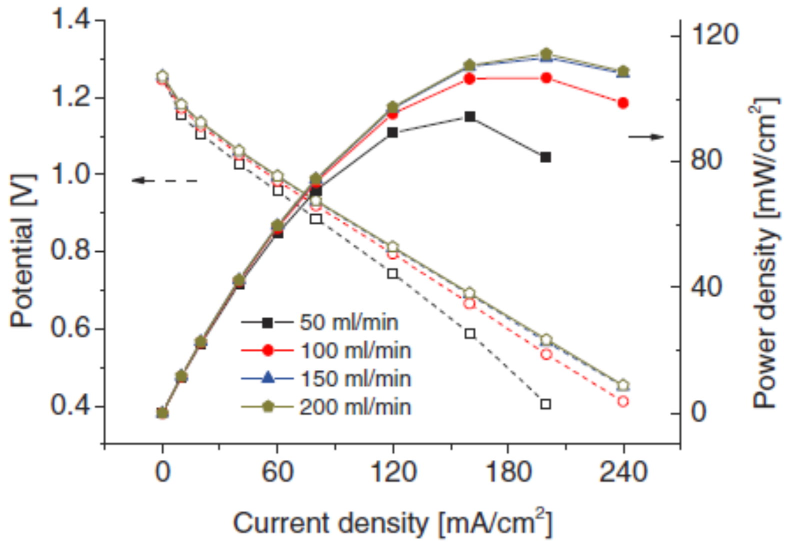
Regenerative Hydrogen-Vanadium Fuel Cell (RHVFC)





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

- *Untreated carbon paper*
- *Nafion 117*
- *GDL, 0.5 mg Pt cm^{-2}*

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

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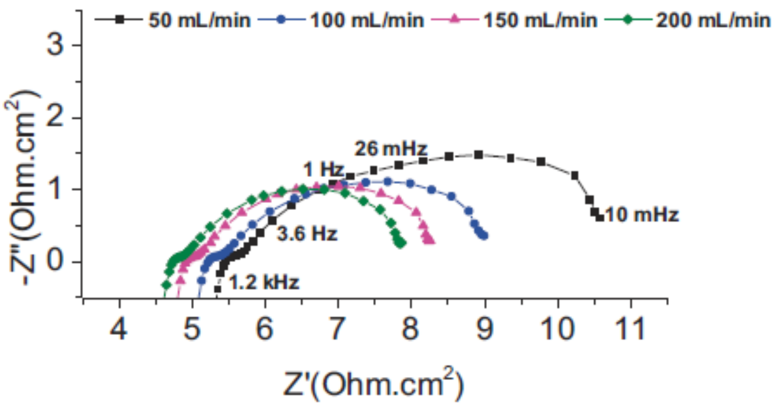
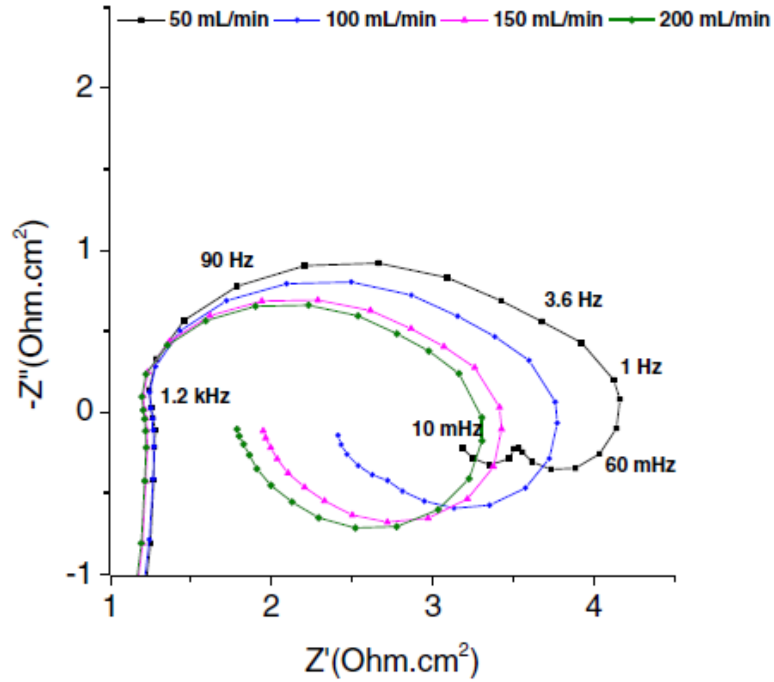
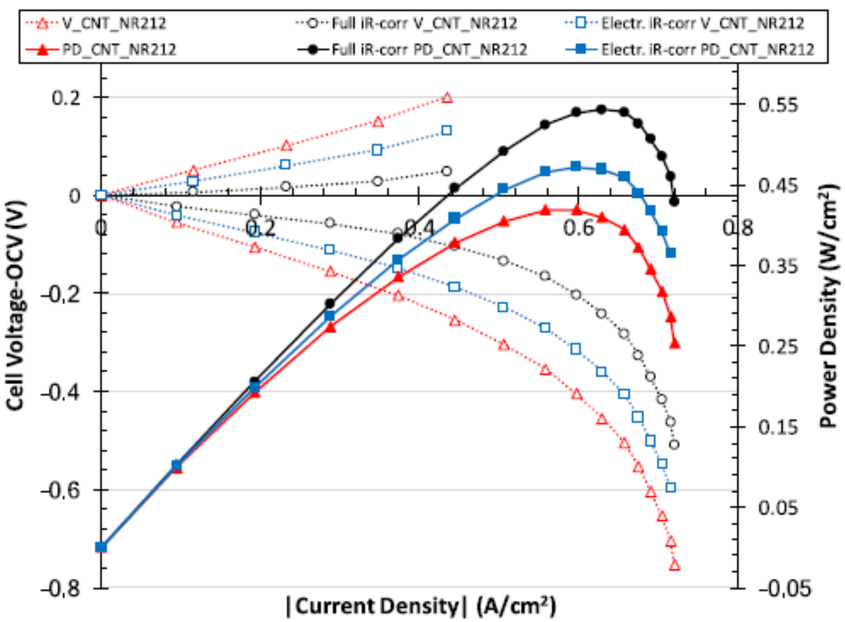




- *Untreated carbon paper*
- *Nafion 117*
- *GDL, 0.5 mg Pt cm^{-2}*



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

H. Hewa Dewage et al., Journal of The Electrochemical Society, 2016, 163(1), A5236 (2016); Regis P. Dowd Jr., et al, Journal of The Electrochemical Society, 2017, 164, F564.

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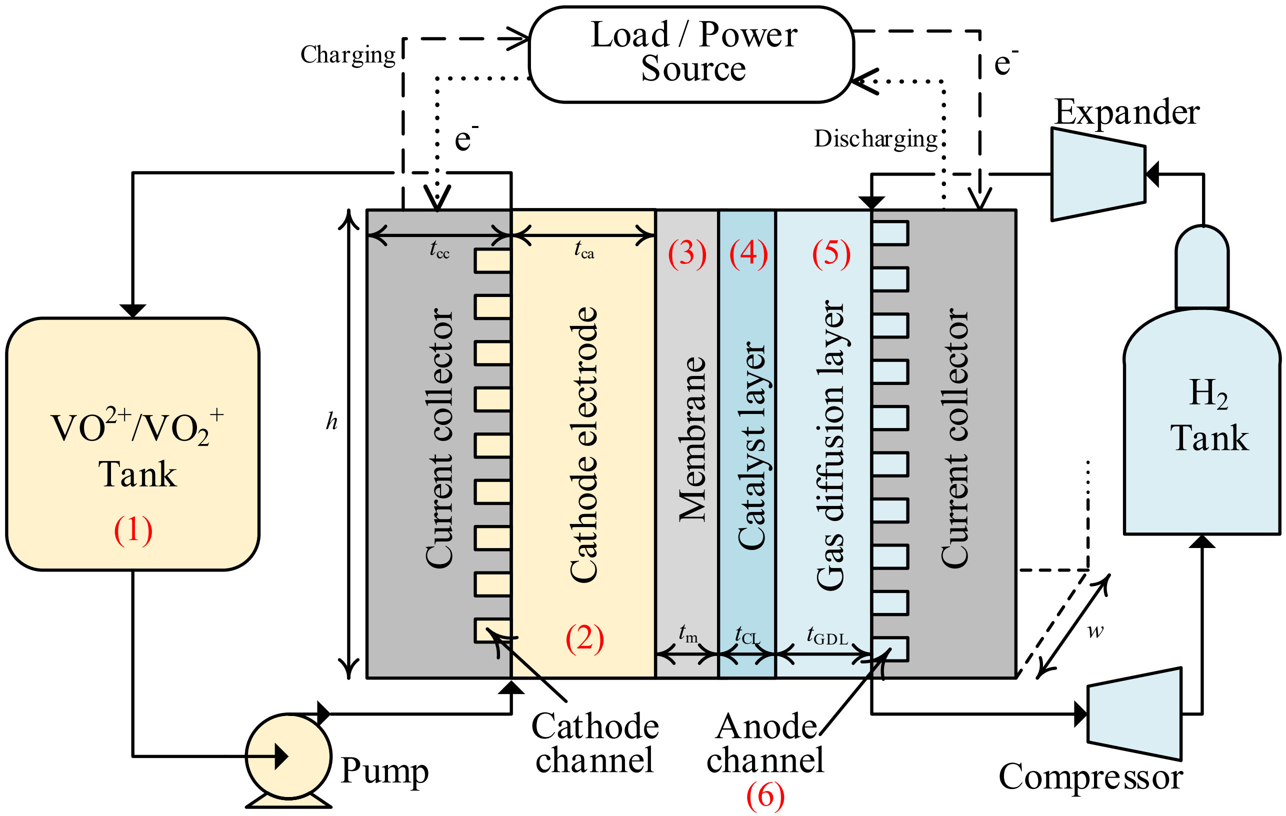
Unit cell model for the RHVFC



Cathode:

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

Anode:

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

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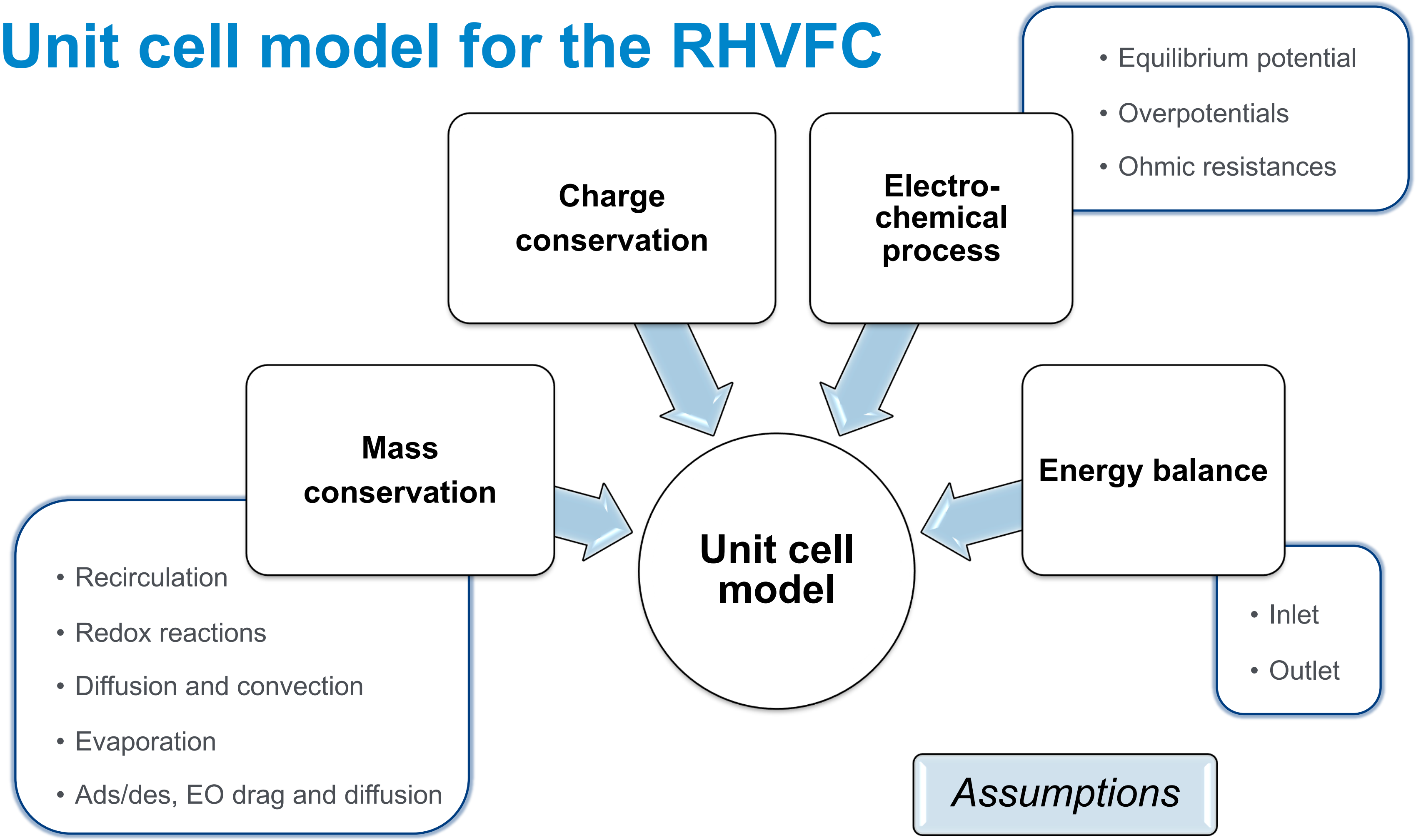
Unit cell model for the RHVFC



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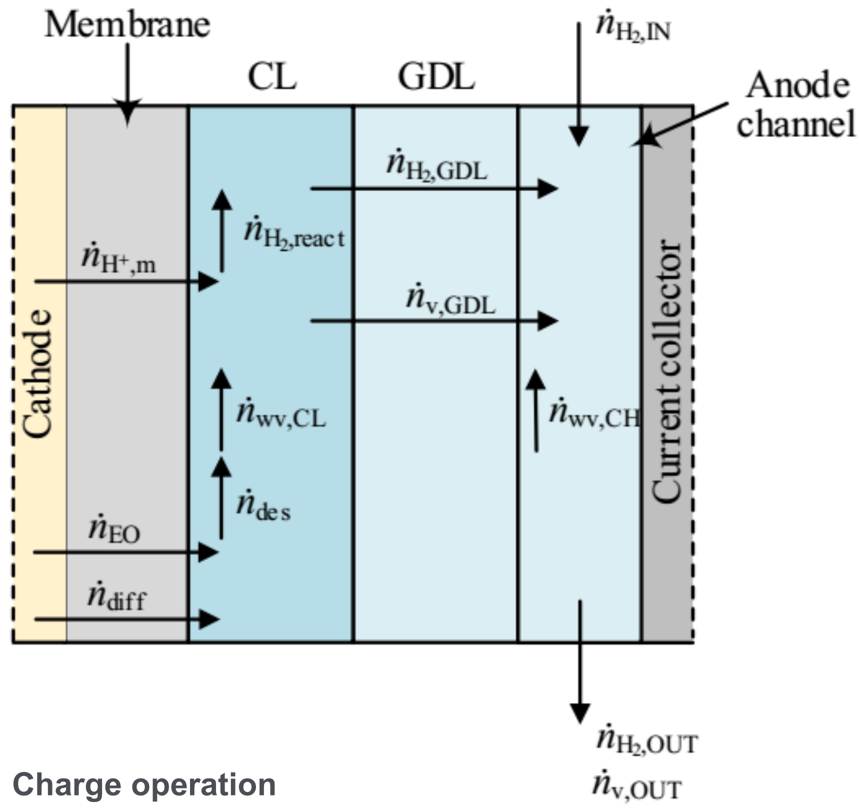
Hydrogen side

Dissolved water transport

Dusty Gas Model

Evaporation/condensation



Charge operation

→ +ve transport
↑ +ve generation

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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

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

Anode

$$c_{\mathrm{H^+}}+z_{\mathrm{f}}c_{\mathrm{f}}=0$$

Cathode

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

Mass balances

Electro-neutrality

Open circuit potential

Kinetics

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

Cell

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

Anode

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

Cathode

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

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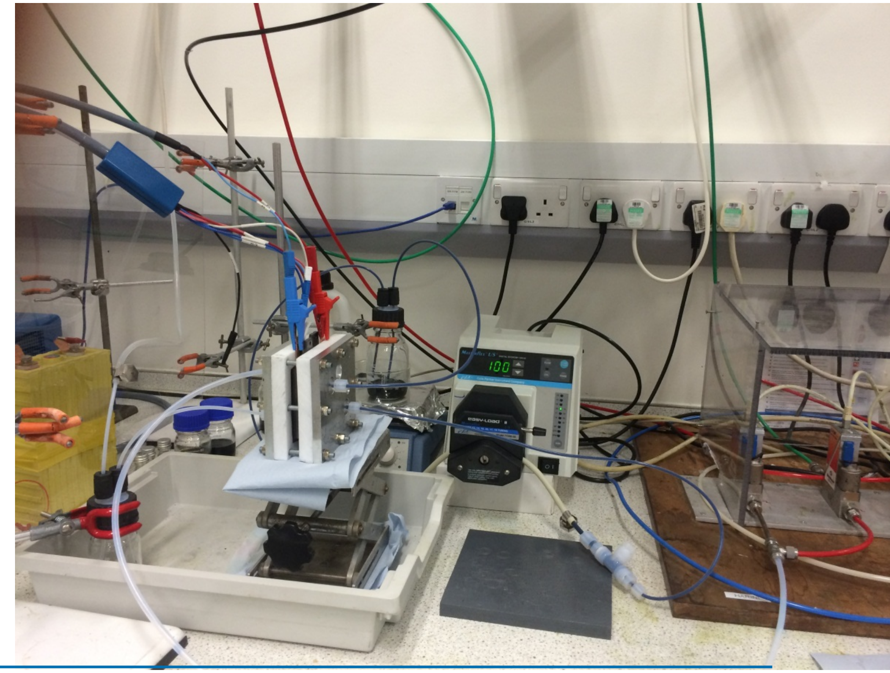

Experimental tests

- *1M $VOSO_4$*
- *60 mL, 5M H_2SO_4*

N°	Test	Current density A m^{-2}	Catholyte flow rate mL min^{-1}	Hydrogen flow rate mL min^{-1}	Cu current collector Yes or No
1	OCP	0	100	100	No
2	Charge-discharge	50	100	100	No
3	Charge-discharge	100	100	100	No
4	Charge-discharge	80	100	100	Yes
5	Charge-discharge	400	100	100	Yes
6	Charge-discharge	400	100	50	Yes
7	Charge-discharge	400	150	100	Yes
8	Charge-discharge	600	100	100	Yes

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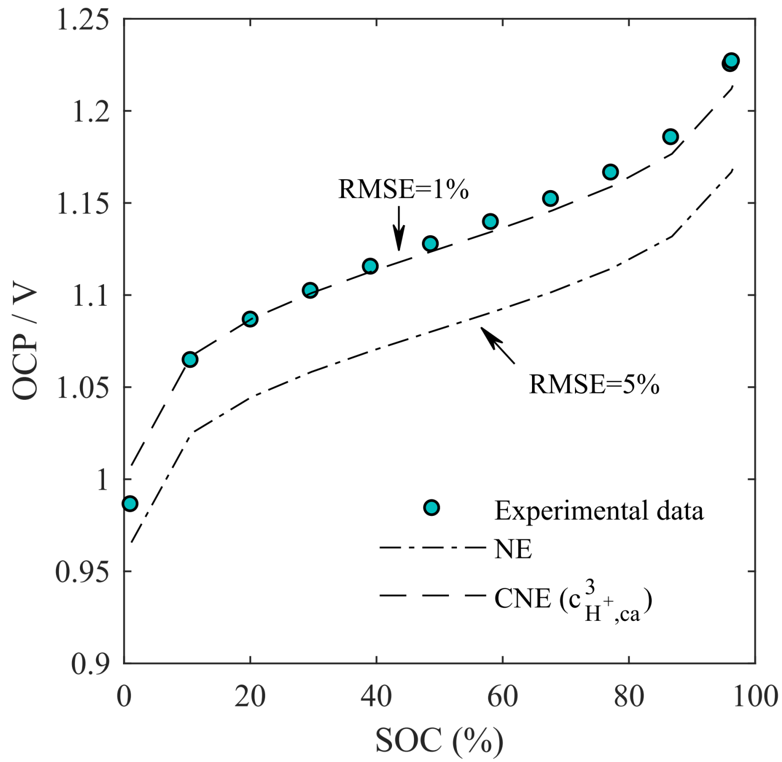
Open Circuit Potential



Nernst Equation (NE)

$$E_{OCP} = E^0_{\text{cell}} + \frac{RT}{F}\ln\left(\frac{c_{\text{V(V)}}c^2_{\text{H}^+,\text{ca}}p^{0.5}_{\text{H}_2}}{c_{\text{V(IV)}}c_{\text{H}^+,\text{an}}}\right)$$

Complete Nernst Equation (CNE)

$$E_{OCP} = E^0_{\text{cell}} + \frac{RT}{F}\ln\left(\frac{c_{\text{V(V)}}c^2_{\text{H}^+,\text{ca}}p^{0.5}_{\text{H}_2}}{c_{\text{V(IV)}}c_{\text{H}^+,\text{an}}}\frac{c_{\text{H}^+,\text{ca}}}{c_{\text{H}^+,\text{an}}}\right)$$

Knehr & Kumbur, Electrochemistry Communications, 13 (2011) 342-345

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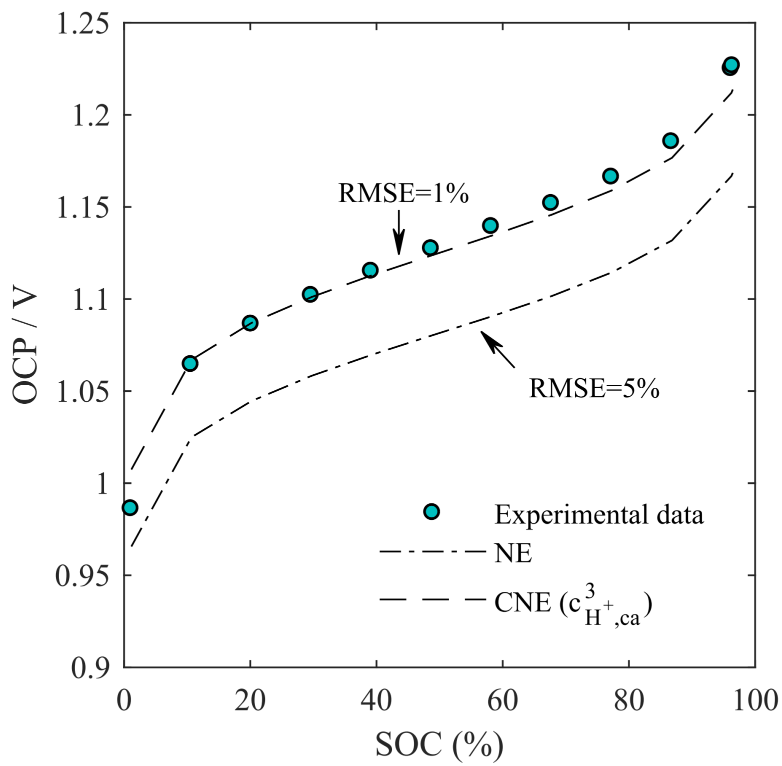
Open Circuit Potential



Nernst Equation (NE)

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

Complete Nernst Equation (CNE)

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

Donnan potential across the membrane

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

Inconsistent with thermodynamics

Knehr & Kumbur, Electrochemistry Communications, 13 (2011) 342-345, Pavelka et al., Journal of Power Sources, 2015, 293, 400

Complete Nernst Equation

Nernst equation

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

Thermodynamic derivation

Potential difference between electrolytes

$$\tilde{\mu}^{\alpha}_{\mathrm{i}} = \mu^{\alpha}_{\mathrm{i}} + z_{\mathrm{i}} F \phi^{\alpha}, \quad \tilde{\mu}^{\mathrm{e}}_{\mathrm{H^+}} = \tilde{\mu}^{\mathrm{m}}_{\mathrm{H^+}}, \quad \rightarrow \quad \phi^{\mathrm{ca}} - \phi^{\mathrm{an}} = \frac{RT}{F}\ln\left(\frac{c_{\mathrm{H^+,an}}}{c_{\mathrm{H^+,ca}}} \right)$$

Donnan potential across both interfaces

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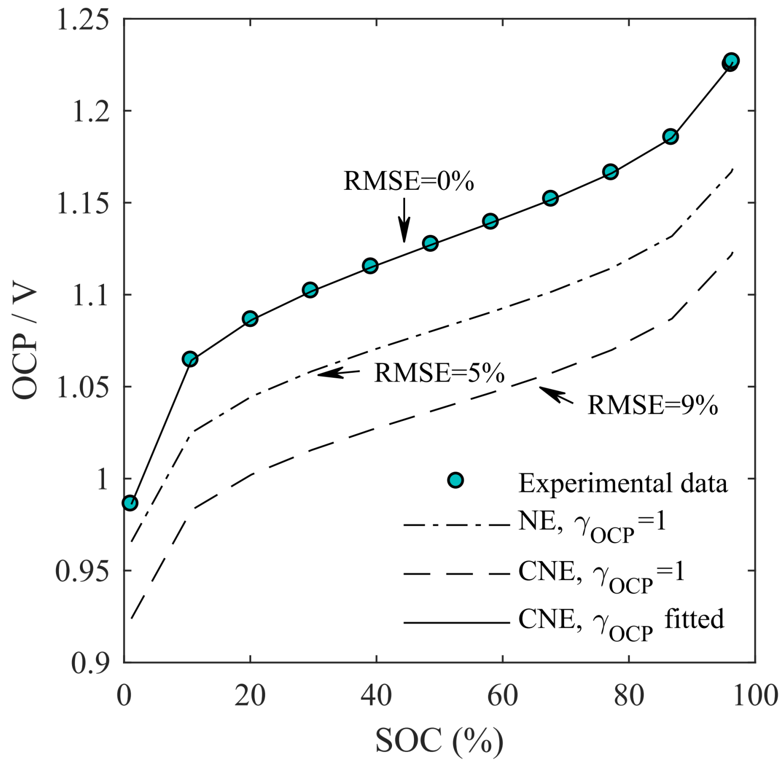
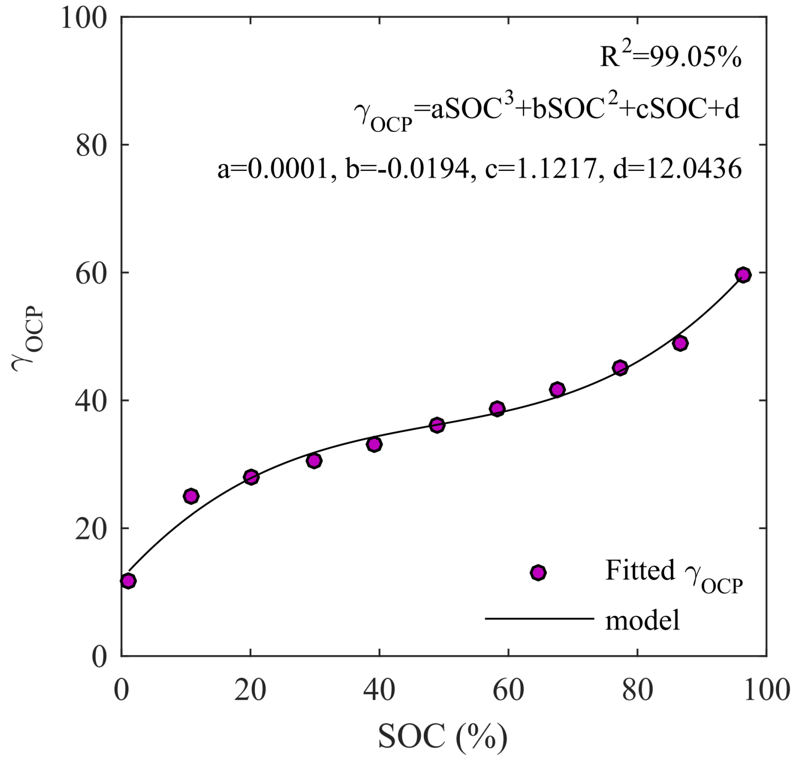
Open Circuit Potential

Thermodynamic derivation of CNE

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





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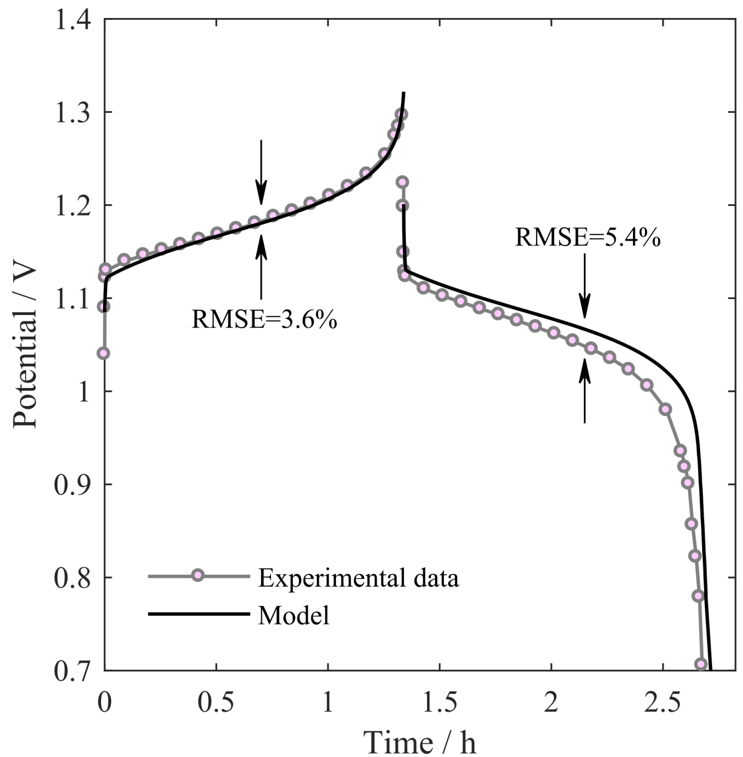
Model calibration



j= 400 A m^{-2}, Q$_V$=Q$_{H2}$=100 mL min^{-1}

Model implementation

- *MATLAB*
- ode15s → solve ODE problem
- lsqcurvefit → curve fitting

Fitting parameters

- $k_{ca,ref}$ = 1.2 x 10^{-7} m s^{-1}
- δ= 84.8 x 10^{-6} m
- R_C= 0.3 Ω cm^2

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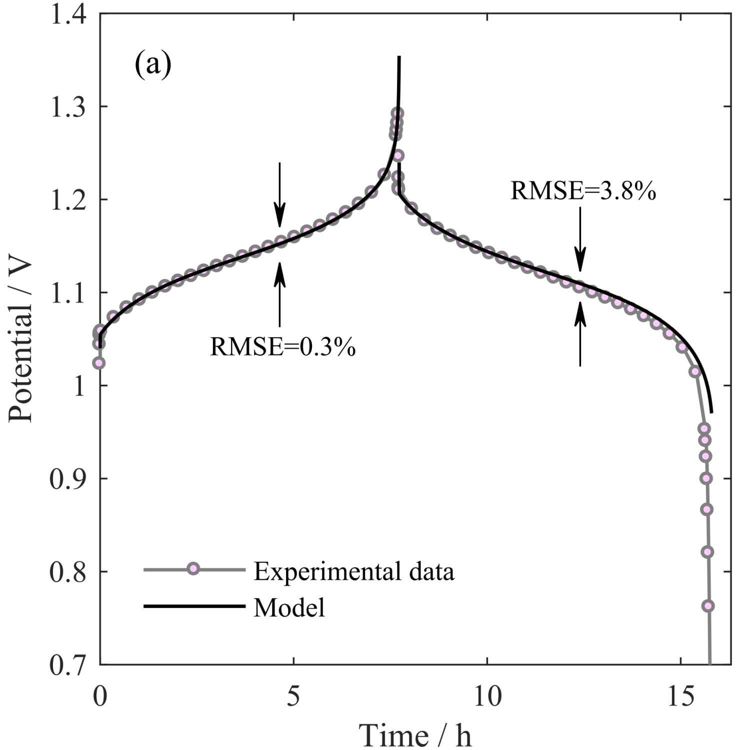
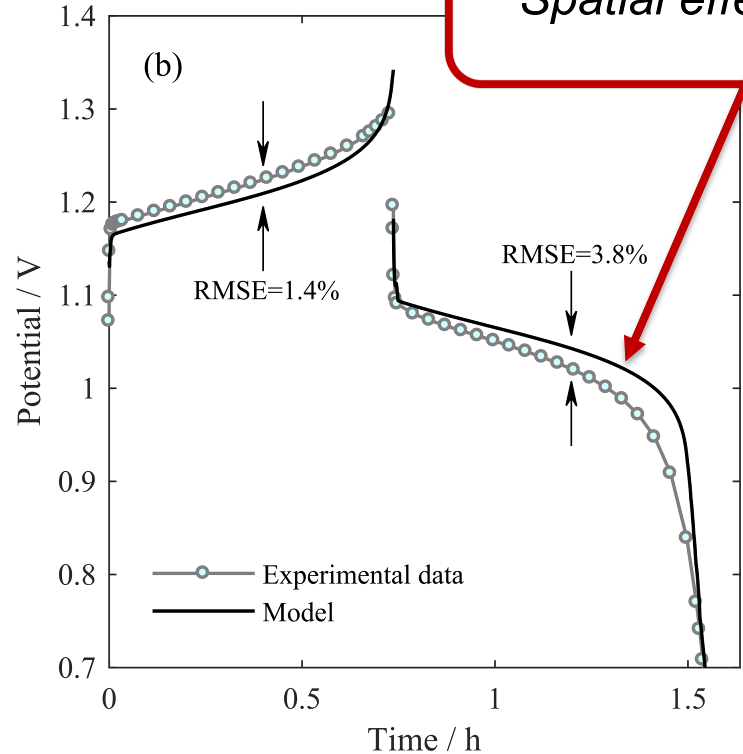
Model validation: vary current density

Crossover
Anode flooding
Spatial effects



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



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

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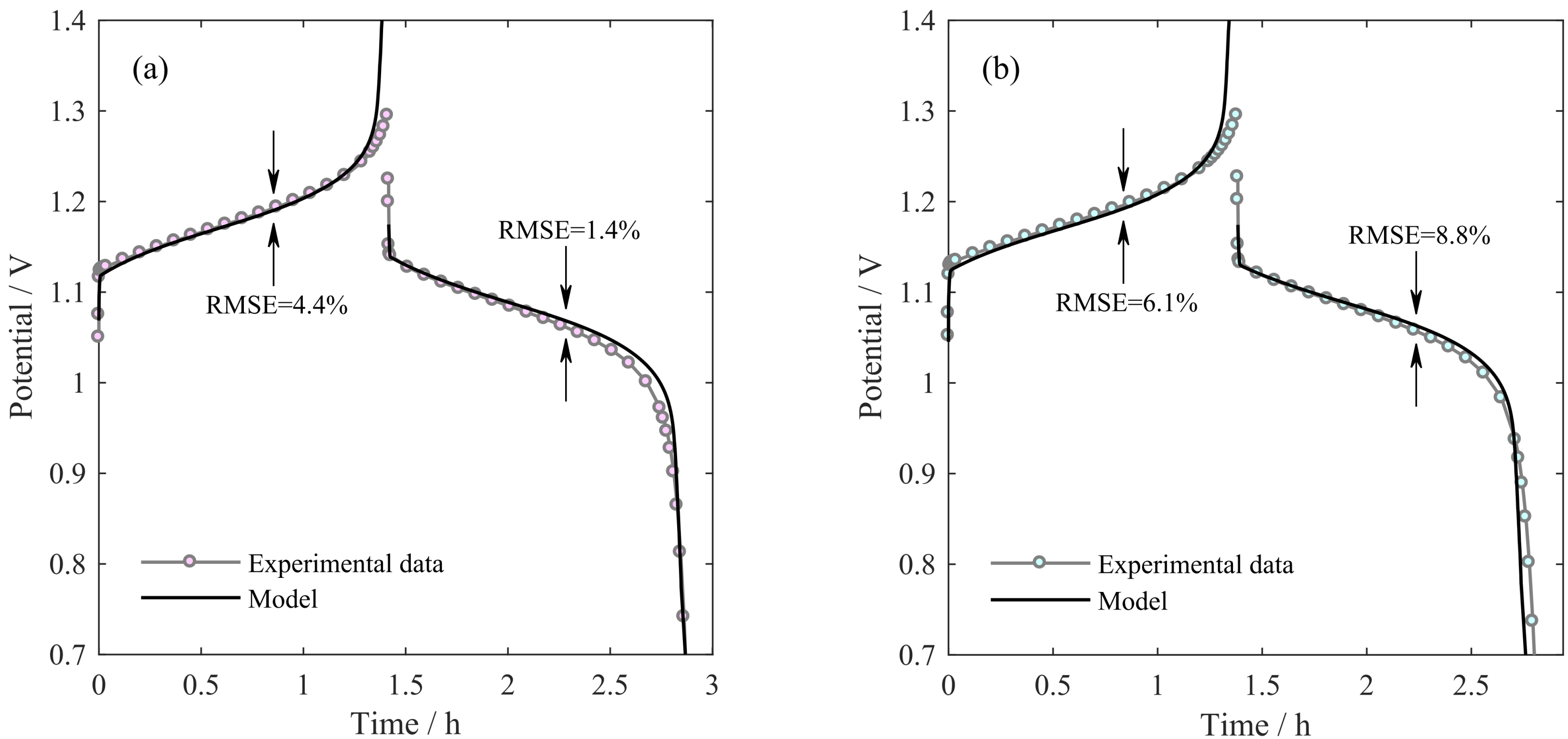
Model validation: vary flow rate



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

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

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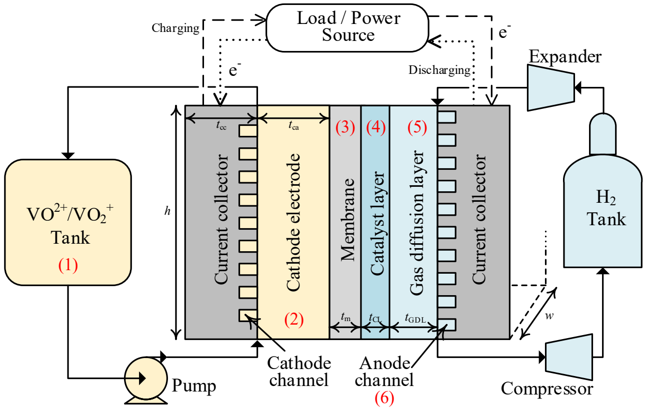
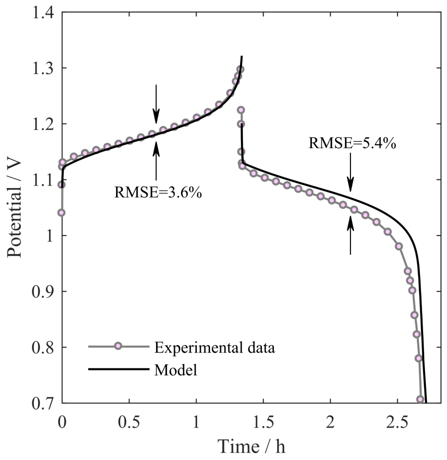
Conclusions

- A unit cell model for a RHVFC was introduced and calibrated against experimental data.
- Model validation at different current densities and flow rates.
- A CNE based on thermodynamic principles was proposed and fit to the OCP data, enabling a global activity coefficient to be obtained.





Thermodynamic derivation

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

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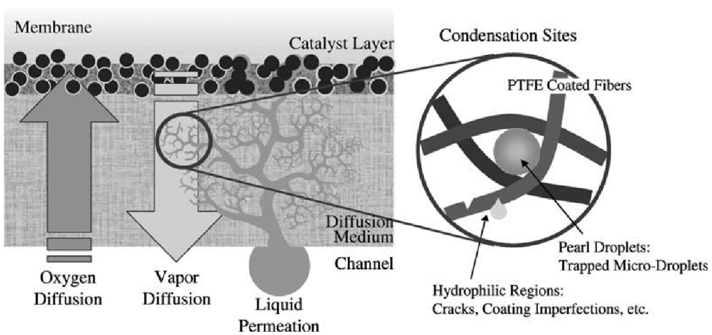
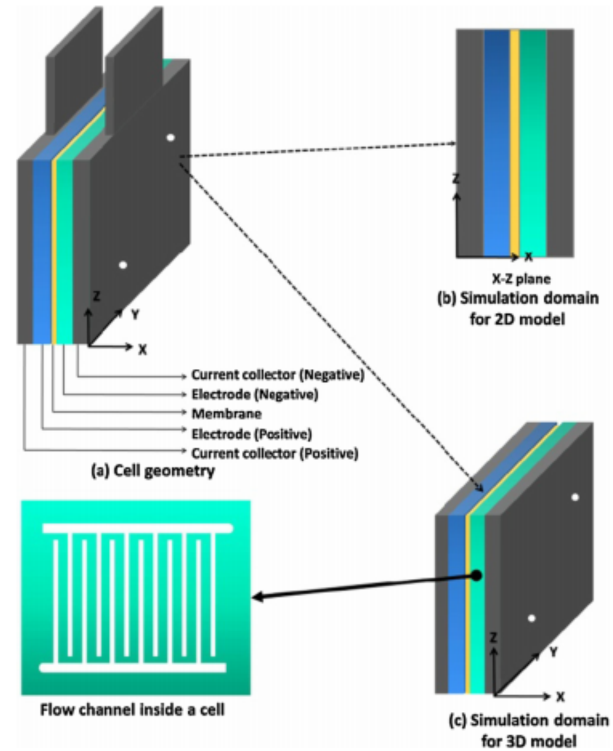
Next steps

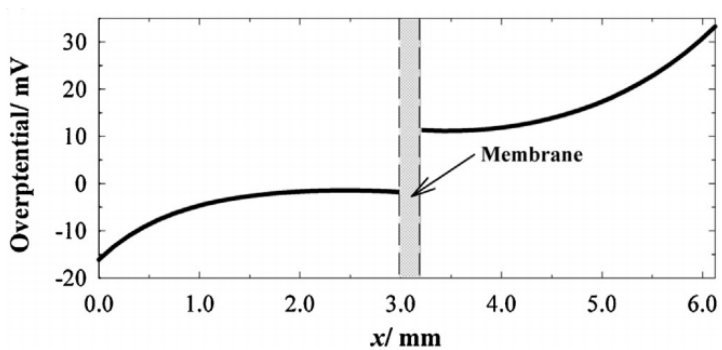
- Water transport in GDL



- Cross-over of ionic species
- Experimental data for the RHVFC

- Continuum model (1-2D).





Zheng et al., Applied Energy, 2014,132, 254; Chen et al., Electrochimica Acta, 2014, 120, 167; Nam & Kaviany, International Journal of Heat and Mass Transfer, 2003, 46, 4595.

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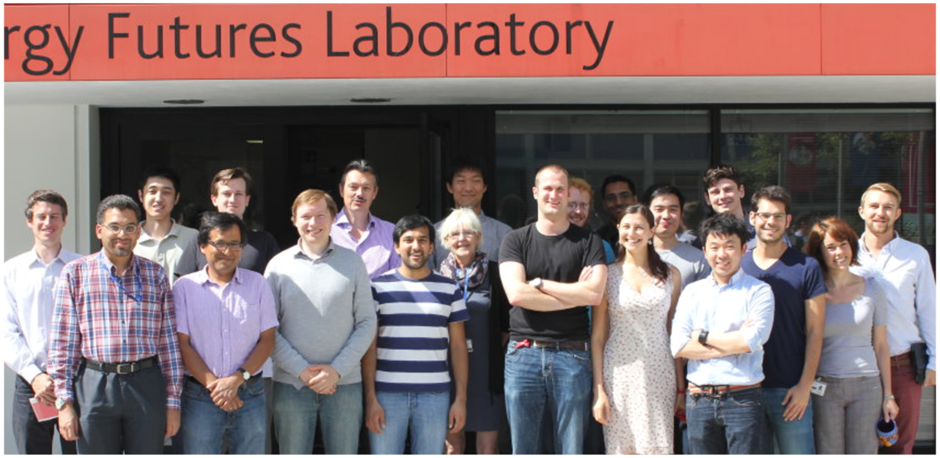
Acknowledgements

Professor Nigel Brandon



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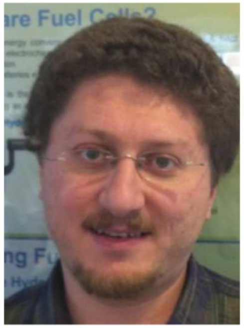

Dr Vladimir Yufit.

Dr. Harini Hewa Dewage

Dr. Antonio Bertei

- **Travel funding:**
  - Imperial College Trust, ICL
  - Old Centralians' Trust, ICL

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