Characterisation of a RHVFC using an experimentally validated unit cell model

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March 12th, 2019
Outline

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2. Motivation
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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


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

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

Unit cell model for the RHVFC

Cathode:
\[ 2\text{VO}^{2+} + 4\text{H}_3\text{O}^+ + 2e^- \xrightarrow{\text{charge}} 2\text{VO}^{2+} + 6\text{H}_2\text{O}, \quad E^0_{\text{ca}} = 0.99\text{V} \]

Anode:
\[ \text{H}_2 + 2\text{H}_2\text{O} \xrightarrow{\text{charge}} 2\text{H}_3\text{O}^+ + 2e^-, \quad E^0_{\text{an}} = 0\text{V} \]
**Model summary**

Cell

\[
E_{\text{eq}} = E_{\text{cell}}^0 + \frac{RT}{F} \ln \left( \frac{c_{V(V)}^2 c_{H^+,\text{ca}}^2 P_{H_2}^{0.5} c_{H^+,\text{an}}^{0.5} F}{c_{V(IV)}^2 c_{H^+,\text{an}}^2 c_{H^+,\text{ca}}^2} \right)
\]

Open circuit potential

Charge conservation

Electro-neutrality

Mass balances

Anode

\[
V_{\text{cl}} e_{\text{cl}} (1 - s_{\text{cl}}) \frac{dc_{H_2,\text{cl}}}{dt} = \pm \frac{A_{\text{cl}} j}{2F} - \dot{n}_{H_2,GDL}
\]

Cathode

\[
E_{\text{ca}} V_{\text{ca}} \frac{dc_{V_2^{2+}}}{dt} = Q_{\text{ca}} \left( c_{V_2^{2+},\text{r}} - c_{V_2^{2+},\text{i}} \right) + \frac{A_{\text{ca}} j}{F} - \dot{n}_{V_2^{2+},\text{m}}
\]

Energy balance

Kinetics

Anode

\[
\frac{j^V}{k_{\text{des}}} = FZ \left( \theta_{H_2}^{\text{PV}} \exp(\beta f \eta_{\text{an}}) - B \left( 1 - \theta_{H_2}^{\text{PV}} \right) \exp(- (1 - \beta) f \eta_{\text{an}}) \right)
\]

Cathode

\[
j^V = j_{\text{ca}}^{BV} \left[ \frac{c_{V_2^{2+}}^{s}}{c_{V_2^{2+}}^{b}} \left( \frac{c_{H^+}^{s}}{c_{H^+}^{b}} \right)^2 \exp(- \alpha f \eta_{ca}) - \frac{c_{V_2^{2+}}^{s}}{c_{V_2^{2+}}^{b}} \exp((1 - \alpha) f \eta_{ca}) \right]
\]

Cell OCP

\[
E_{\text{cell}} = E_{\text{OCP}} \pm |\eta_{\text{ca}}| \pm |\eta_{\text{an}}| \pm |\eta_{\text{ohm}}|
\]

Ionic species crossover

\[
N_{i,m}^m = \frac{D_i^m c_i^m}{l_m} \left( \zeta \left( e^\zeta - \frac{c_i^{CL}}{c_i^{ca}} \right) \right)
\]

\[
\zeta = \left( \frac{z_i F}{\sigma_m RT} + \frac{\xi_{\text{drag}}}{c_w^m D_i^m F} \right) j l_m
\]

\[
N_w^m = c_w^m = \frac{\xi_{\text{drag}} j}{F}, \quad j = -\sigma_m \nabla \phi
\]

\[
N_i^m = -D_i^m \nabla c_i^m - z_i \mu_i^m F \nabla \phi + c_i^m v
\]

Nernst-Planck equation

\[c_{V(IV)}^{ca} = 500 \text{ mol m}^{-3}\]
Equilibrium

\[ 2 \tilde{\mu}^{ca}_{\text{VO}_2^+} + 4 \tilde{\mu}^{ca}_{\text{H}^+} + 2 \tilde{\mu}^{\text{CP}}_{e^-} = 2 \tilde{\mu}^{ca}_{\text{VO}^{2+}} + 2 \tilde{\mu}^{ca}_{\text{H}_2\text{O}} \]

**Cathode reaction**

\[ \tilde{\mu}^{\text{an}}_{\text{H}_2} = 2 \tilde{\mu}^{\text{an}}_{\text{H}^+} + 2 \tilde{\mu}^{\text{Pt}}_{e^-} \]

**Anode reaction**

\[ F(\phi^M - \phi^{M'}) = \mu^{ca}_{\text{VO}_2^+} + 2 \mu^{ca}_{\text{H}^+} - \mu^{ca}_{\text{VO}^{2+}} - \mu^{ca}_{\text{H}_2\text{O}} - \mu^{\text{an}}_{\text{H}^+} + \frac{1}{2} \mu^{\text{an}}_{\text{H}_2} + F(\phi^{ca} - \phi^{\text{an}}) \]

**Cell**

\[ FE_{\text{Don}}^m = F(\phi^{ca} - \phi^{\text{an}}) = \mu^{\text{an}}_{\text{H}^+} - \mu^{ca}_{\text{H}^+} \]

**Donnan potential across both interfaces (dialysis potential)**

\[ \tilde{\mu}_{i} = \mu_{i} + z_{i}F\phi \]

**Electrochemical potential of species** \( i \)
Potential difference between electrolytes

\[ E_{OCP} = E_{cell}^0 + \frac{RT}{F} \ln \left( \frac{c_{V_{O_2}^+}^{ca} \left( c_{H^+}^{ca} \right)^2 \left( p_{H_2}^g \right)^{0.5}}{c_{V_{O_2}^{2+}}^{ca} c_{H^+}^{an}} \times \frac{c_{H^+}^{an}}{c_{H^+}^{ca}} \times \frac{c_{V_{O_2}^+}^{ca} c_{H^+}^{an}}{c_{V_{O_2}^{2+}}^{ca} c_{H^+}^{an}} \right) \]

Thermodynamic derivation

Chemical potential of species \( i \)

\[ \mu_i = \mu_i^0 + RT \ln(a_i) \]

\[ a_i = \gamma_i c_i \]
Complete Butler-Volmer equation for cathode

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

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

Concentration of protons

Experimental data RHVFC

**Experimental set-up 5 cm² area cell**

<table>
<thead>
<tr>
<th>Component</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>Freudenberg H23, 210 µm, heat treated (500 °C, 6 h)</td>
</tr>
<tr>
<td>Anode</td>
<td>SGL 29BC, 235 µm, 0.3 mg cm⁻² Pt</td>
</tr>
<tr>
<td>Membrane</td>
<td>Nafion 115, 127 µm</td>
</tr>
<tr>
<td>Flow channel</td>
<td>Single-channel serpentine</td>
</tr>
<tr>
<td>Catholyte</td>
<td>0.8M VOSO₄ in 60 mL 5M H₂SO₄</td>
</tr>
<tr>
<td>Current density</td>
<td>500 – 1500 A m⁻²</td>
</tr>
<tr>
<td>Catholyte / hydrogen flow rate</td>
<td>50 &amp; 100 mL min⁻¹ / 100 mL min⁻¹</td>
</tr>
</tbody>
</table>

Tests:
- Open circuit potential (2 sets)
- Single-cycle charge-discharge (14 sets)
- Polarization curves (2 sets)
- Cycling test (1 set)
## Experimental data RHVFC

<table>
<thead>
<tr>
<th>Cell</th>
<th>AVIZO</th>
<th>TauFactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area</td>
<td>5 cm$^2$</td>
<td></td>
</tr>
<tr>
<td>Cathode</td>
<td>Freudenberg H23, 210 µm, heat treated (500 °C, 6 h)</td>
<td></td>
</tr>
<tr>
<td>Porosity</td>
<td>0.79</td>
<td>0.79</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>0.429 µm$^2$ µm$^{-3}$</td>
<td>0.144 µm$^2$ µm$^{-3}$</td>
</tr>
<tr>
<td>Mean pore diameter</td>
<td>21.01 µm</td>
<td>---</td>
</tr>
<tr>
<td>Mean fibre diameter</td>
<td>7.92 µm</td>
<td>---</td>
</tr>
</tbody>
</table>
Model calibration: Open Circuit Potential

Thermodynamic derivation of CNE

$$E_{OCP} = E_{cell}^0 + \frac{RT}{F} \ln \left( \frac{c_{VO_2}^{ca} (c_{H^+}^{ca})^{2} (p_{H_2}^g)^{0.5}}{c_{VO_2^2}^{ca} c_{H^+}^{an}} \times \frac{c_{H^+}^{an}}{c_{H^+}^{ca}} \times F \right)$$
EIS data
Model calibration: cell potential

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

**Fitting parameters**
- Cathodic reaction → $K_{ca} = S_{ca} k_{ca}^0$
- Nernst diffusion layer thickness → $\delta_{ca}$
- Anodic reaction → $k_{des}^0$

$j = 500 \text{ A m}^{-2}$
Charge-discharge: vary current density

\[ Q_v = 100 \text{ mL min}^{-1} \]
Cycling and polarization curve

\[ j = 700 \text{ A m}^{-2}, Q_v = 50 \text{ mL min}^{-1}, Q_{H_2} = 30 \text{ mL min}^{-1} \]
Cycling performance

\[ j = 700 \text{ A m}^{-2}, \quad Q_V = 50 \text{ mL min}^{-1}, \quad Q_{H_2} = 30 \text{ mL min}^{-1} \]
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.

\[
E_{OCP} = E_{cell}^0 + \frac{RT}{F} \ln \left( \frac{C_{H^+}^{ca} \left( C_{H^+}^{ca} \right)^2 \left( P_{H_2}^2 \right)^{0.5}}{C_{V_0}^{ca} C_{H^+}^{ca} C_{H^+}^{an}} \times \frac{C_{H^+}^{an} \times F}{C_{H^+}^{ca}} \right)
\]
Next steps

- Detailed crossover model vanadium and sulphuric acid species and water in a hybrid H₂-based redox flow battery
- Study possible side reaction of vanadium ionic species at anode catalyst layer to correctly simulate the evolution of concentration.
Thank you!

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March 12th, 2019