Impact of temperature and concentration within a chemically regenerative redox cathode polymer electrolyte fuel cell system using phosphomolybdovanadium polyoxoanion catholyte

David Ward, Bob Smith and Trevor Davies

University of Chester, UK
Faculty of Science & Engineering

14th March 2018
Outline of Presentation

• Background
  • What is a Chemically Regenerative Redox Cathode (CRRC) Polymer Electrolyte Fuel Cell (PEFC) system?
  • What are the advantages over conventional PEFC systems?

• Investigation objectives

• Methodology and operating condition
  • How is CRRC-PEFC performance measured?

• Results

• Conclusions

• Future Investigation
Background

What is a CRRC-PEFC System?
What is a CRRC-PEFC System?

- Fuel cell / flow battery hybrid
  - Conventional PEFC fuel cell anode
  - Redox flow battery cathode
- Circulates a liquid mediator/catalyst solution through the cathode
- Can be likened to the cardiovascular system
- Technology developed by Acal Energy Ltd but now IP owned of UoC
Advantages over conventional PEFCs

- Eliminates need for Pt on the cathode
  - Pt reduced by as much as 80%
  - Significant cost saving
  - Performance less vulnerable Pt loss

- Indirect reduction of oxygen
  - Degradation via by-products avoided (e.g. $\text{H}_2\text{O}_2$)

- Liquid cathode
  - Avoids damage via internal conflagrations (hot spots)
  - Maintains membrane hydration (no need to humidify gas supply)

- Ease of heat management
  - Heat absorbed and distributed by flow of catholyte (high SHC)
  - Exothermic reaction occurs in Regenerator not cell
  - Eliminates need for complex cell stack cooling channels
  - Heat can be removed via a simple inline heat exchanger
What happens within the cell?

Anode

2H₂ + Pt → 4H⁺ + 4e⁻ + Pt

Cathode

4V⁵⁺ + 4e⁻ → 4V⁴⁺
What happens within the Regenerator?

Air Bubble

O₂

4H⁺ + O₂ + 4e⁻ → 2H₂O + Heat

4V⁴⁺ – 4e⁻ → 4V⁵⁺

Overall Reaction: 4V⁴⁺ + 4H⁺ + O₂ → 4V⁵⁺ + 2H₂O + Heat

Catholyte Solution
What is the catholyte?

- Empirical formula $H_7PV_4Mo_8O_{40}$ (HV4)
- Polyoxometalate Keggin Structure
- Single atom of phosphorus at core
- Surrounded by $x4$ vanadium atoms
- Surrounded by molybdenum and oxygen atoms
Objectives of this Investigation

- Examine system performance over a range of operating temperatures and concentrations
  - With respect to HV4 polyoxometalate catholyte ($H_7PV_4Mo_8O_{40}$)
  - Previously reported results relevant to 80°C and 0.3M

- Examine with performance with respect to...
  - Cell performance (I-V curves)
  - Regenerator oxidation kinetics (sustainable current)
  - Combined system performance (sustainable power)

Method:

How to quantify CRRC-PEFC Performance?
Apparatus and Operating Conditions

- **Anode membrane assembly:**
  - 25 cm$^2$ active area
  - Ion Power NR212

- **Anode:**
  - ~600 mbar hydrogen
  - Dead ended

- **Catholyte:**
  - 0.2, 0.3, 0.4 and 0.45 M
  - 0.3 L system volume
  - ~140 mL/min recirculation rate

- **Regenerator:**
  - 1 L/min air flow
  - 500 mL bubble column with sintered glass sparge

- **System operating temperature, 40, 50, 60, 80 & 90°C**
Redox Potential vs. Fraction V Reduced

V⁴⁺ Reduced

V⁵⁺ Oxidised

HV4 Ref. Electrode Potential vs. Fraction Vanadium as V⁴⁺ (80°C and 0.3 M)
I-V curves at varying states of vanadium reduction (0.3 M HV4 catholyte at 80°C)
Regeneration Current vs. fraction vanadium reduced
Electrons Transferred in Cell = Electrons Transferred in Regenerator

Hence, sustainable current determined by rate of regeneration
Sustainable I-V curve (0.3 M HV4 catholyte at 80°C)
## Experimental Design

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>Catholyte Concentration / M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>40</td>
<td>X</td>
</tr>
<tr>
<td>50</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>X</td>
</tr>
<tr>
<td>90</td>
<td>X</td>
</tr>
</tbody>
</table>
Results
Cell voltage comparison @ 65%R & 1 A.cm\(^{-2}\)
Regeneration Comparison @ 65%R
Sustainable power comparison @ 1 A.cm\(^{-2}\)
Conclusions

• **80ºC** demonstrated to give *optimum* cell, regenerator and therefore, overall system performance

• **0.3 – 0.45M** range demonstrated to give *comparable* cell, regenerator and therefore, overall system performance
  - Significant performance *decline* demonstrated at **0.2M**

• Therefore, *considering material costs*, **80ºC and 0.3M** suggested to be *optimal* operating point
Future Investigation

• Impact of temperature and concentration with respect to other catholyte formulations
  • e.g. $\text{Na}_4\text{H}_3\text{PV}_4\text{Mo}_8\text{O}_{40}$ (pH adjusted using NaOH)$^2$

• Varying the proportion of NaOH added$^3$

• Addition of other salts (e.g. KHO)

• Alternative membranes

2. David B. Ward & Trevor J. Davies, “Effect of Temperature and Catholyte Concentration on the Performance of a Chemically Regenerative Fuel Cell”, Accepted for publication by Johnson Matthey Technology Review.

Thank you for listening

• Any questions?

• Email contact: dward@chester.ac.uk

• Acknowledgements:
  • Dr. Natasha L. O. Gunn
  • Mr. Constantinos Menelaou
  • Dr. Matthew Herbert