Performance comparison of four catholyte formulations within a chemically regenerative redox cathode polymer electrolyte fuel cell system

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Outline

- Conventional polymer electrolyte fuel cells (PEFCs)
  - Direct reduction of $O_2$

- Chemically Regenerative Redox Cathode (CRRC) PEFCs
  - In-direct reduction of $O_2$
  - Lower cost and improved durability

- Optimizing the catholyte in CRRC PEFCs
  - Thermodynamic properties
  - Cell performance
  - Regeneration
Conventional PEFCs
Cost and Durability

- **Platinum**
  - $O_2$ reduction is relatively slow and requires large Pt loadings

- **Selectivity**
  - Slight deviations from the 4 e⁻ reduction pathway result in HO• and peroxides that can damage cell components

- **Start up**
  - Air on the cathode vs. a hydrogen | air front on the anode at start up oxidizes the carbon support in the catalyst layer

- **Crossover**
  - $H_2$ crossover to the cathode causes production of peroxides

- **Cooling**
  - PEFCs limited to < 80°C operation
Chemically Regenerative Redox Cathode PEFCs
In-direct Reduction of O\textsubscript{2}

Catholyte ("liquid catalyst") replaces O\textsubscript{2} at the cathode
Advantages

- Carbon cathode
  - Porous carbon cathode material – graphite felt
  - Only Pt required on the anode for hydrogen oxidation

- Air never enters the fuel cell
  - Main pathways for cell degradation avoided
  - 10,000 hours operation on auto test cycle

- Catholyte ensures membrane is always wet
  - No need for gas humidification
  - Can operate above 80°C

- Catholyte is thermodynamically stable
  - Long lifetime
  - 100% recyclable
Catholyte Study
Catholyte (POM)

- The catholyte ("liquid catalyst") plays a key role in determining overall system performance
- Requirements include
  - High redox potential
  - Good ionic conductivity
  - Fast electrode kinetics
  - Fast regeneration kinetics
- Best catholytes discovered to date are V-Mo polyoxometallates (POMs) with the keggin structure
  - $\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_{40}$ (empirical formula)
  - Acidic solutions ($0 < \text{pH} < 2$)

Phosphomolybdic acid
$\text{H}_3\text{PMo}_{12}\text{O}_{40}$
POM Speciation

10 \( H_6PV_3Mo_9O_{40} + 12 H^+ \longrightarrow 9 H_5PV_2Mo_{10}O_{40} + 12 VO_2^+ + H_3PO_4 + 12 H_2O \)

- Dynamic equilibrium present in POM solutions leading to range of species present (\( V_1, V_2, V_3, V_4 \) keggin and free vanadium)

- \(^{31}\)P NMR can identify the different P species present in solution

- Higher acidity leads to less keggin bound vanadium and more free vanadium
Catholyte Reduction and Regeneration

Electrochemical

Keggin: \( V^{5+} + e^- \rightarrow V^{4+} \)
Free Vanadium: \( VO_2^{+} + e^- + 2 H^+ \rightarrow VO^{2+} + H_2O \)

Chemical

Keggin: \( 4 V^{4+} + O_2 + 4 H^+ \rightarrow 4 V^{5+} + 2 H_2O \)

\[
\% \text{Reduction} = \left( \frac{[\text{vanadium(IV)}]}{[\text{vanadium}]} \right) \times 100\%
\]
Catholyte Comparison

- Four catholytes compared (empirical formulas):
  - 0.3 M $\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_{40}$ (HV3)
  - 0.3 M $\text{Na}_3\text{H}_3\text{PV}_3\text{Mo}_9\text{O}_{40}$ (NaV3)
  - 0.3 M $\text{H}_7\text{PV}_4\text{Mo}_8\text{O}_{40}$ (HV4)
  - 0.3 M $\text{Na}_4\text{H}_3\text{PV}_4\text{Mo}_8\text{O}_{40}$ (NaV4)

- Investigate catholyte performance at 80°C
  - Thermodynamic properties
    - POM Reduction curve, pH
  - Cell performance
    - “Standard” fuel cell with graphite felt cathode and 25 cm$^2$ GORE Primea membrane with 0.4 mg cm$^{-2}$ Pt loading on anode only
  - Regeneration reaction
    - Chemical current vs. redox state
  - Steady state performance

Vary the counter ion ($\text{H}^+$ vs. $\text{Na}^+$)
Vary the vanadium content ($\text{V}_3$ vs $\text{V}_4$)
Thermodynamic Properties

- HV3 and HV4 have higher redox potentials than NaV3 and NaV4 for a given level of reduction
  - Suggests better fuel cell performance with HV3 and HV4
Fuel Cell Performance

Cell performance depends on the level of reduction of the catholyte.

Example is for HV4 at different levels of reduction but all the catholytes have similar parallel i-V curves.
- Fuel cell performance of each catholyte at 45% reduction
- HV4 and HV3 have superior performance compared to Na POMs
  - HV4 gives slightly higher maximum power
  - Total vanadium concentration has little effect on $i$-$V$ curve
The rate at which the reduced POM reacts with air can be expressed as a regeneration current, $I_R$:

$$I_R = [\text{POM}] VnF \frac{d\theta}{dt}$$
- HV3 takes much longer to regenerate than the other POMs
- NaV4 and NaV3 capable of much higher regeneration currents at lower levels of reduction
- Regeneration current limits maximum open circuit voltage of system
The system is in a “steady state” when the cell current is equal to the regeneration current.
Summary

- For a given % Reduction, HV4 and HV3 have superior cell performance
  - Higher open circuit potentials due to lower pH
  - Lower pH results in higher conductivity

- For a given % Reduction, NaV4 and NaV3 have superior regeneration rates
  - Higher pH results in POM speciation with more V2, V3 and V4 kegginns and less free vanadium
  - NaV4 has better regeneration rates then NaV3 due to more favourable POM speciation

- Under steady state operation, NaV4 and HV4 have very similar performance, with slightly more power available from NaV4

- Trade-off between cell open circuit potential and regeneration
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