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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

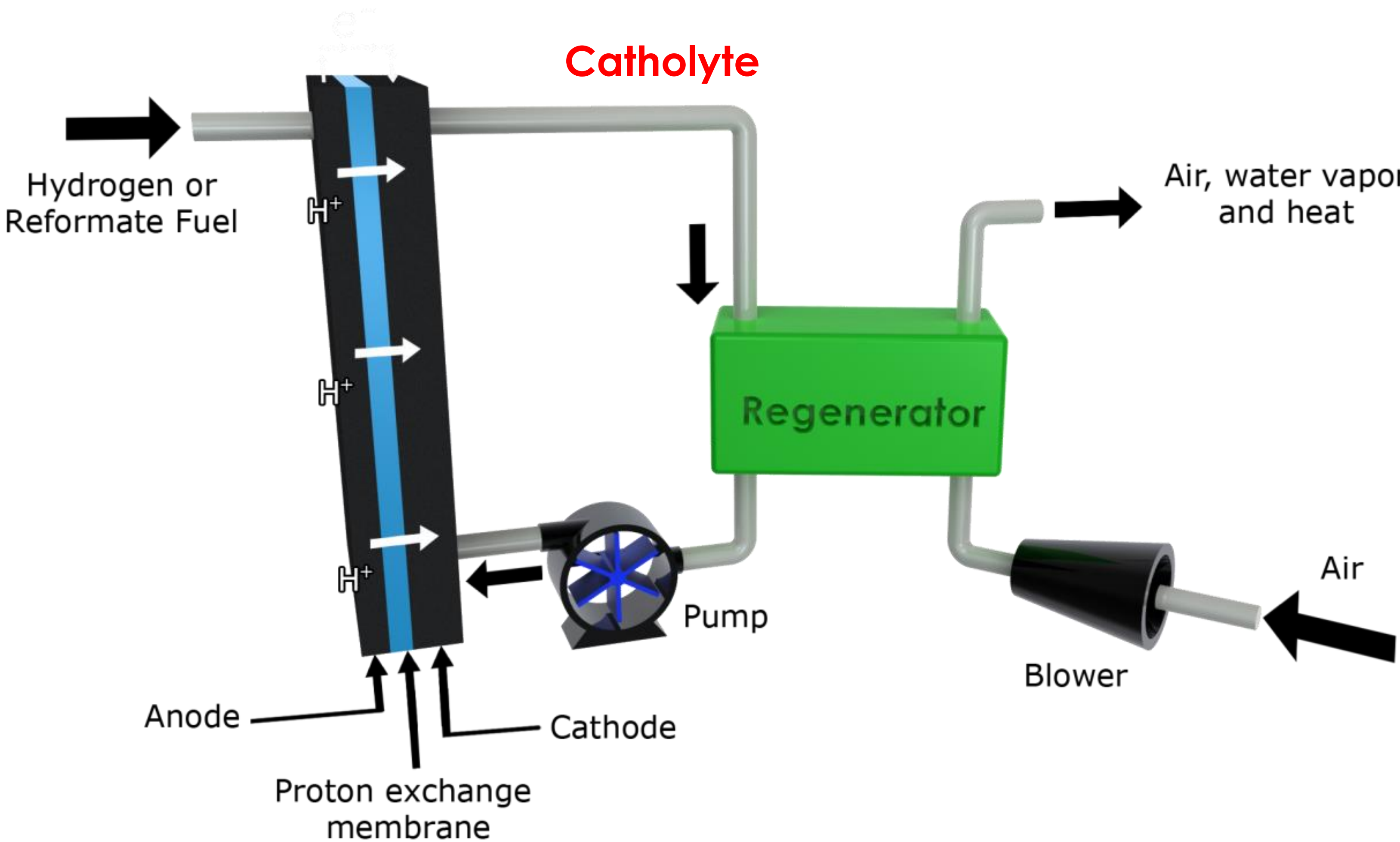
$O_2 + 4\ e^- + 4\ H^+ \rightarrow 2\ H_2O$

- 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_2

Catholyte ("liquid catalyst") replaces O_2 at the cathode



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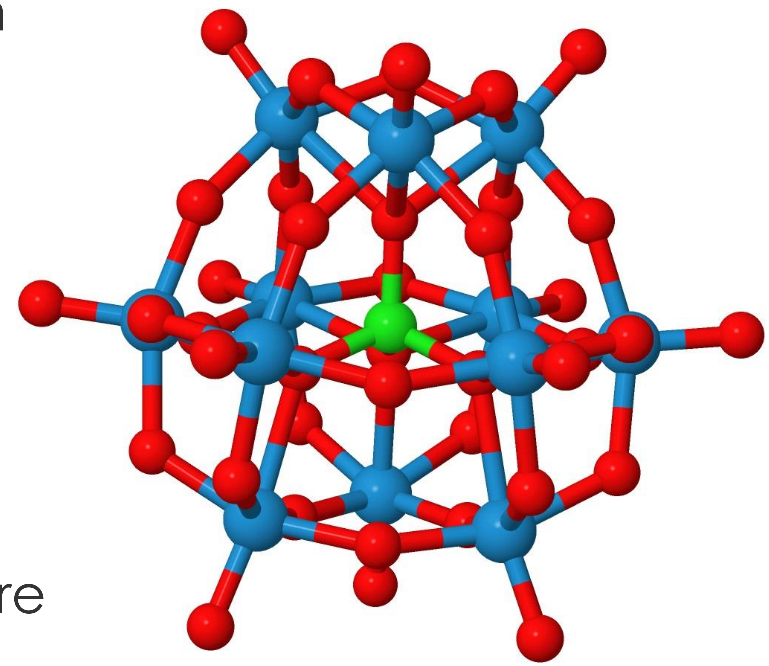
Advantages

- 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
  - $H_6PV_3Mo_9O_{40}$ (empirical formula)
  - Acidic solutions ($0 < pH < 2$)



Phosphomolybdic acid
$H_3PMo_{12}O_{40}$

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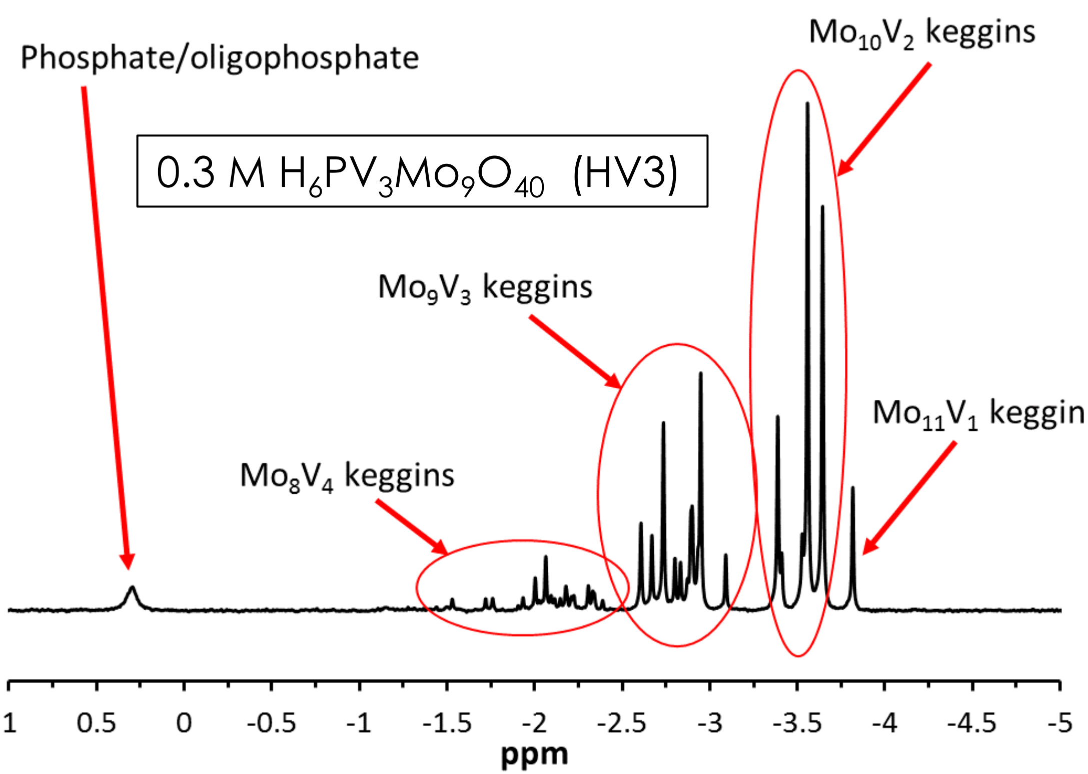
POM Speciation

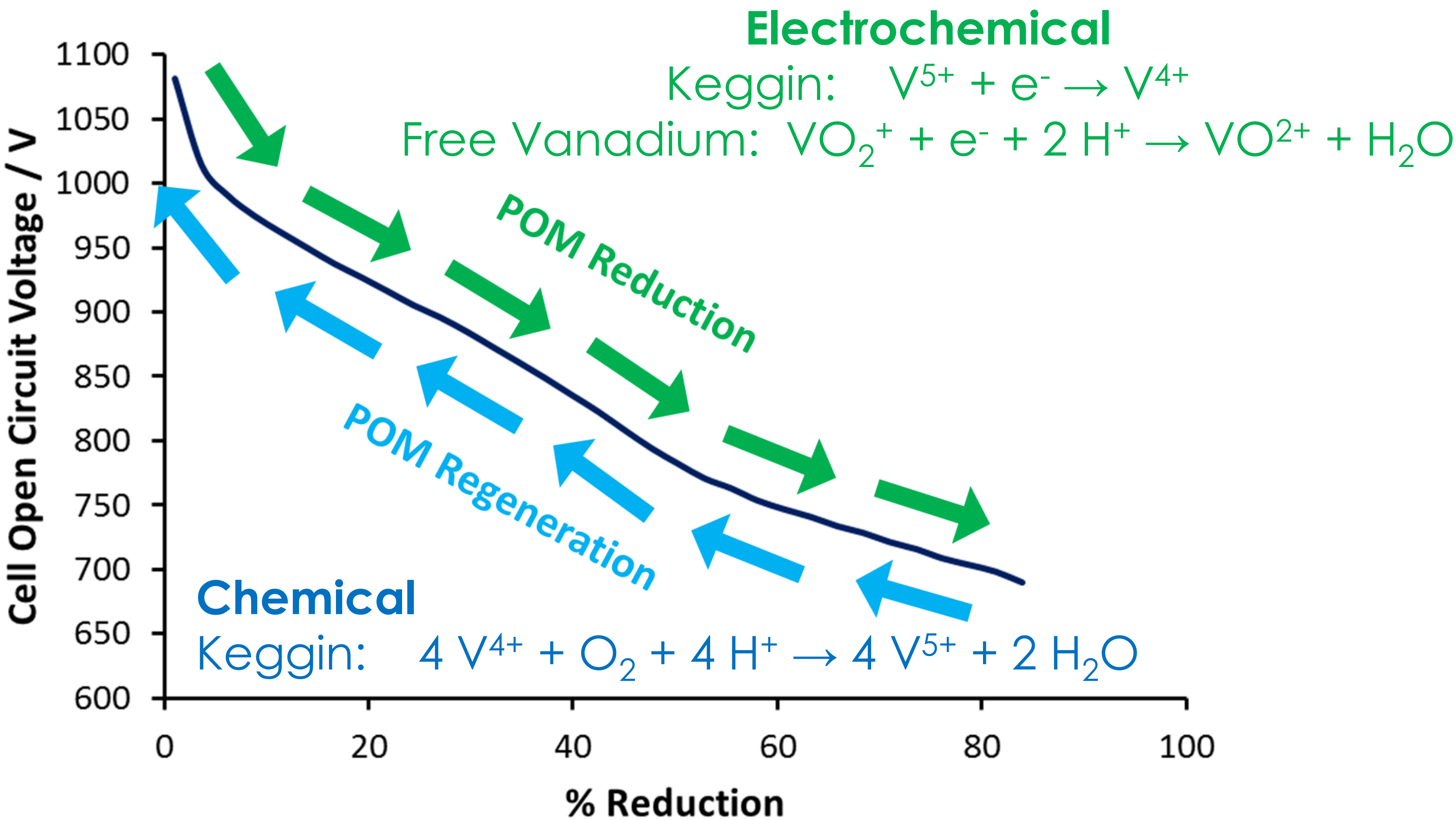
$$10\ H_6PV_3Mo_9O_{40} + 12\ H^+ \rightleftharpoons 9\ H_5PV_2Mo_{10}O_{40} + 12\ VO_2^+ + H_3PO_4 + 12\ H_2O$$

- Dynamic equilibrium present in POM solutions leading to range of species present (V_1, V_2, V_3, V_4 keggins 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



$$\%\text{Reduction} = \frac{[\text{vanadium(IV)}]}{[\text{vanadium}]} \times 100\%$$

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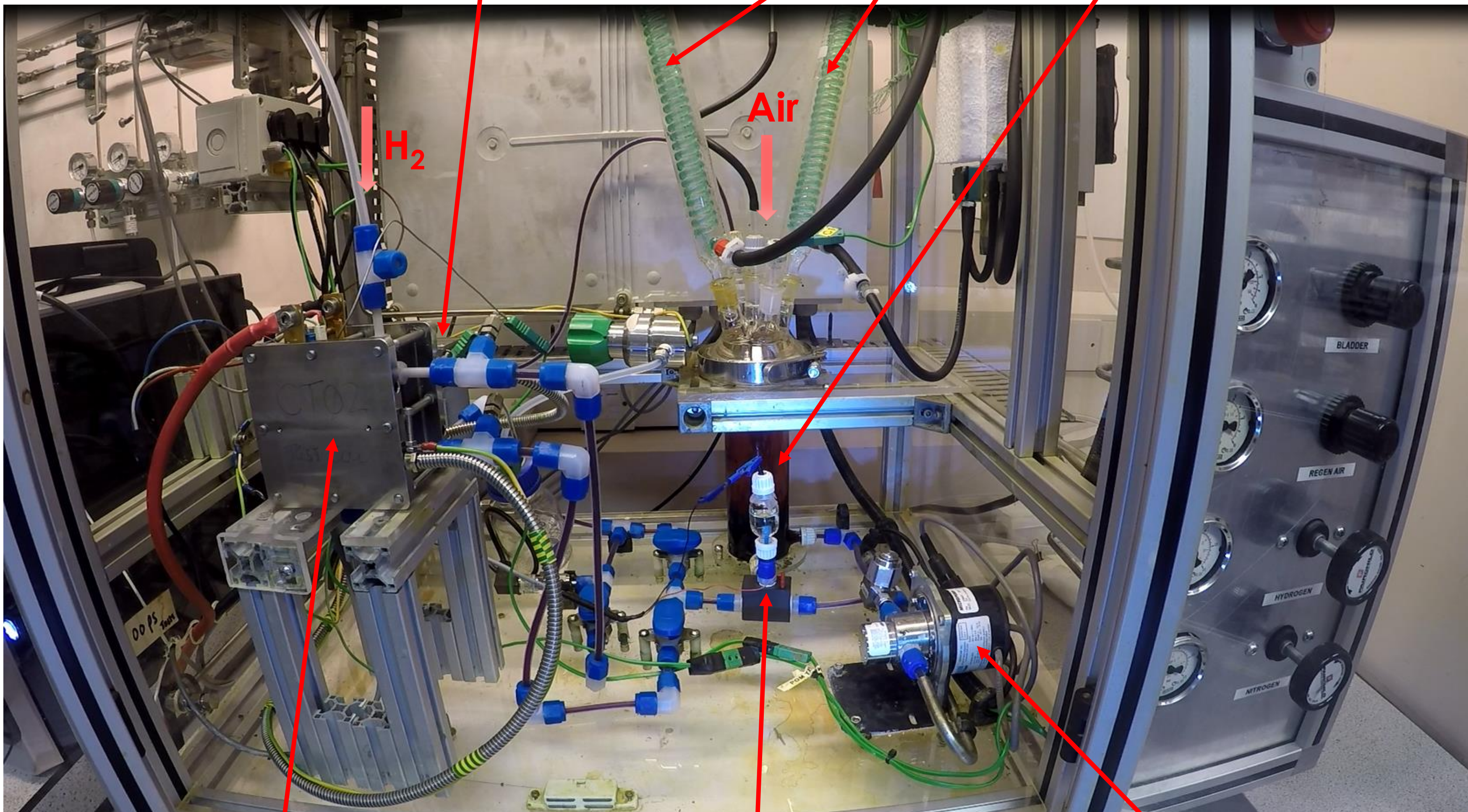

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Catholyte Comparison

- Four catholytes compared (empirical formulas):
  - 0.3 M $H_6PV_3Mo_9O_{40}$ (HV3)
  - 0.3 M $Na_3H_3PV_3Mo_9O_{40}$ (NaV3)
  - 0.3 M $H_7PV_4Mo_8O_{40}$ (HV4)
  - 0.3 M $Na_4H_3PV_4Mo_8O_{40}$ (NaV4)

Vary the counter ion (H^+ vs. Na^+)

Vary the vanadium content (V_3 vs V_4)

- 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

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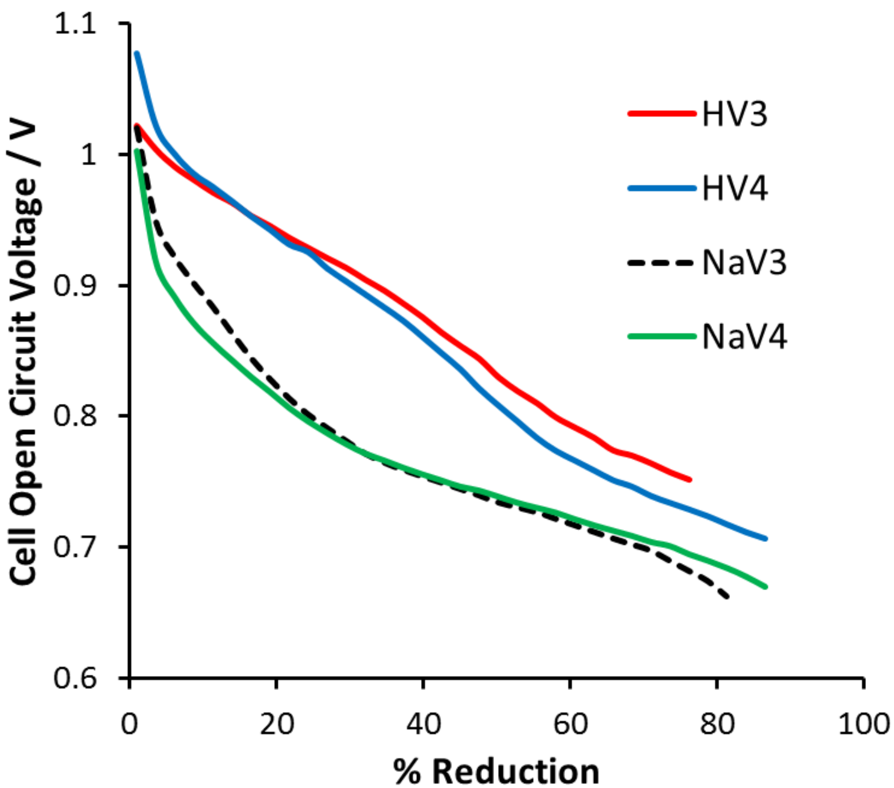
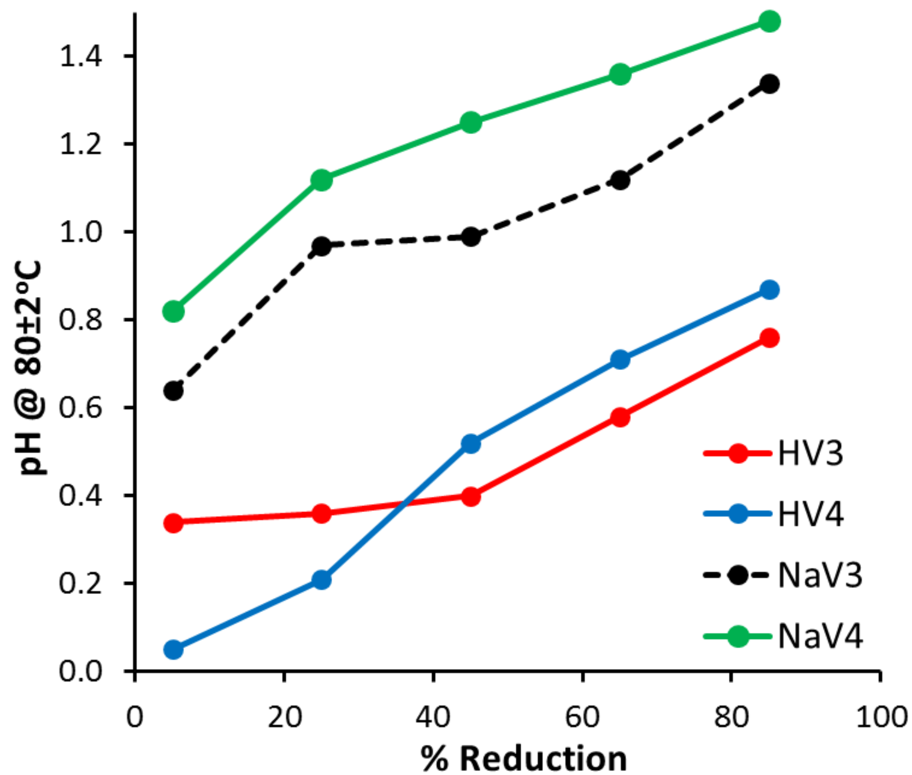
Thermodynamic Properties

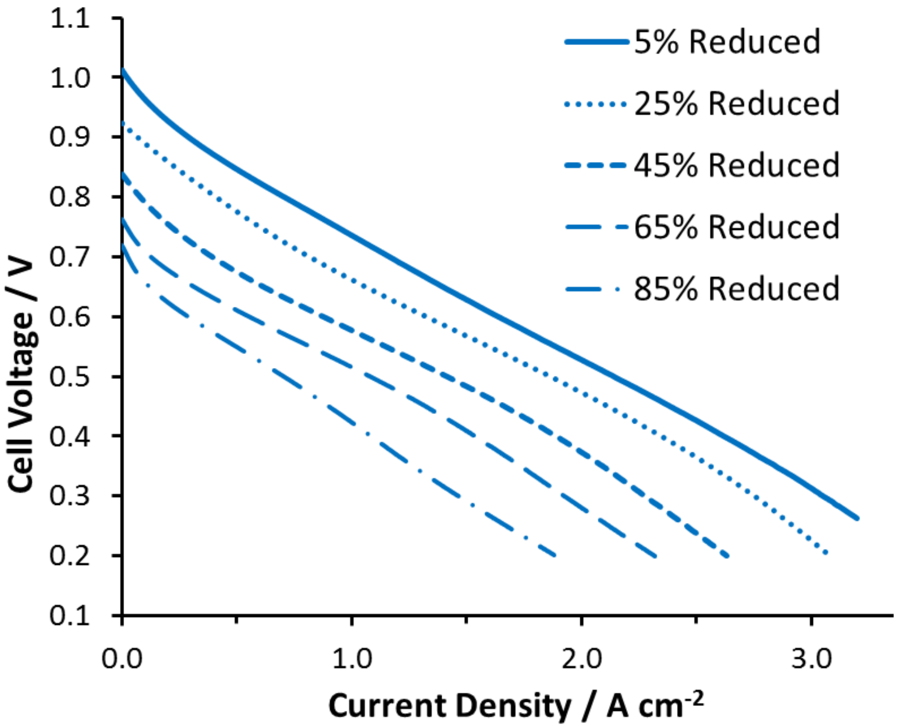
- HV3 and HV4 have higher redox potentials than NaV3 and NaV4 for a given level of reduction
  - Suggests better fuel cell performance with HV3 and HV4

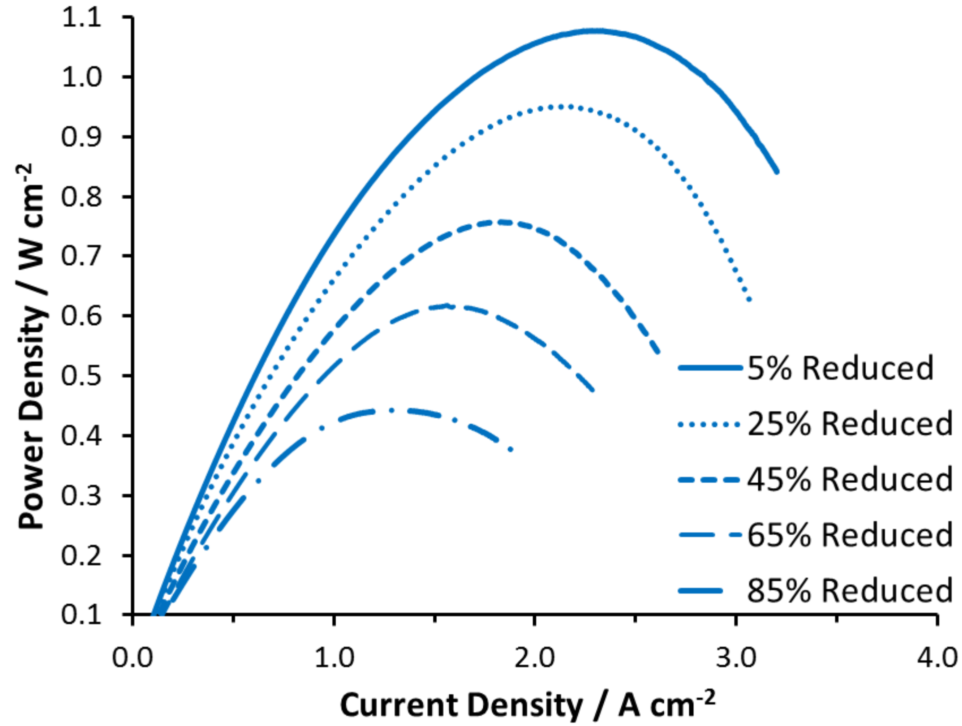




Fuel Cell Performance

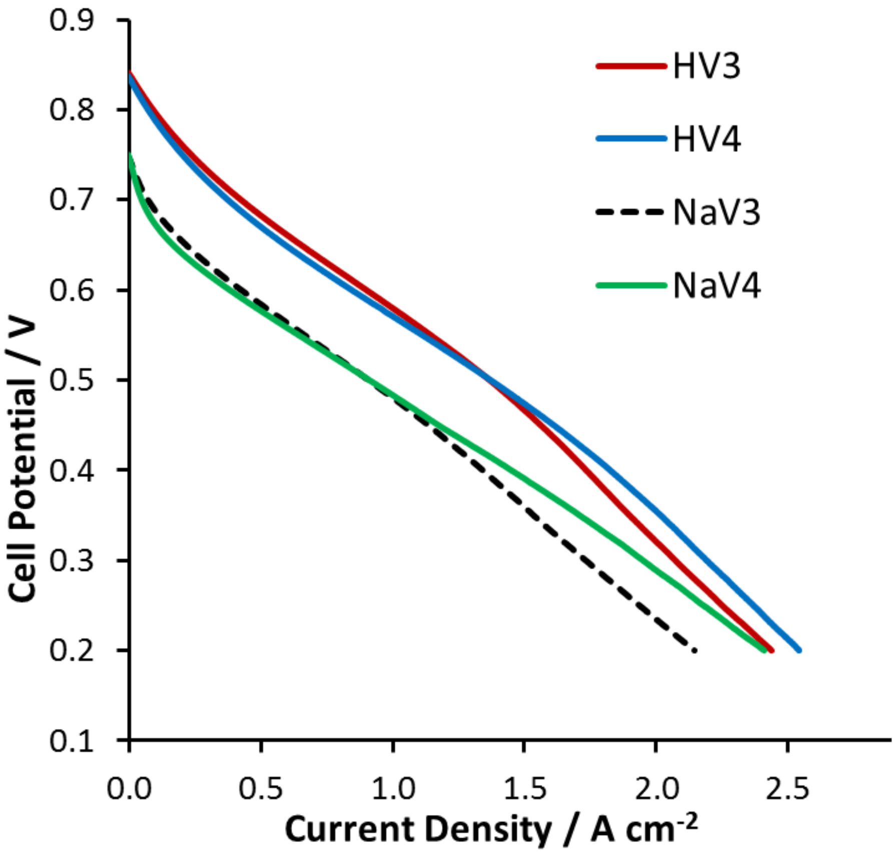
0.3 M $H_7PV_4Mo_8O_{40}$ (HV4)

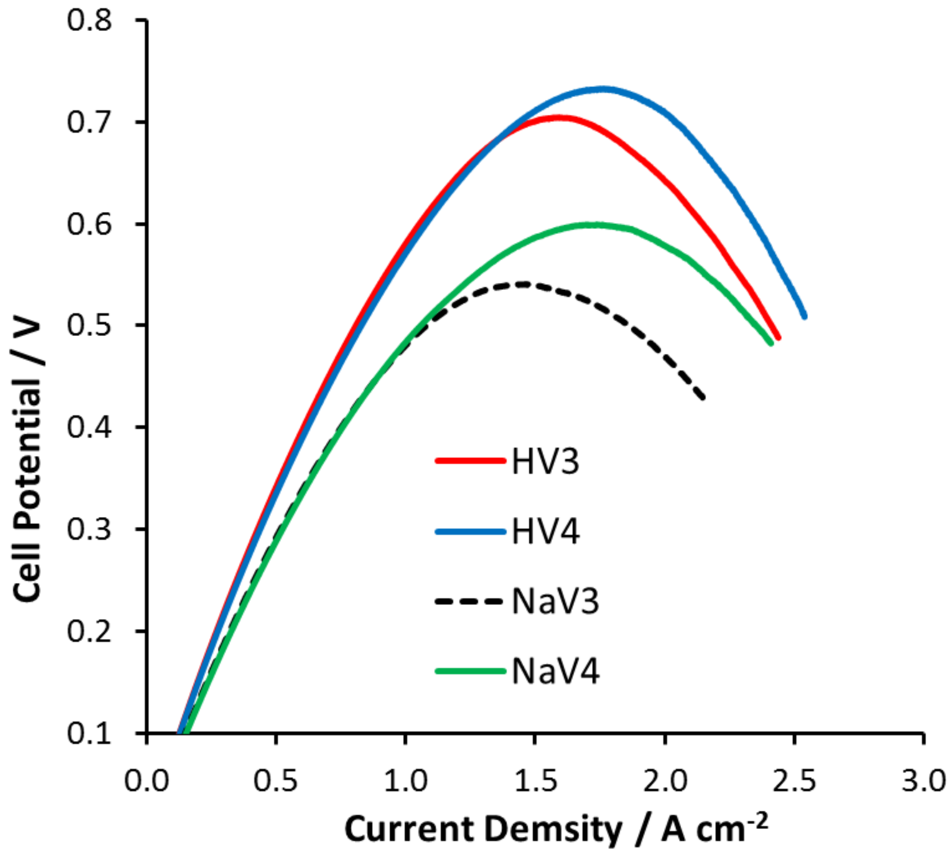




- Cell performance depends on the level of reduction of the catholyte
- Example is for HV4 at different levels of reduction but all the catholytes have similar parallel *i-V* curves

- 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

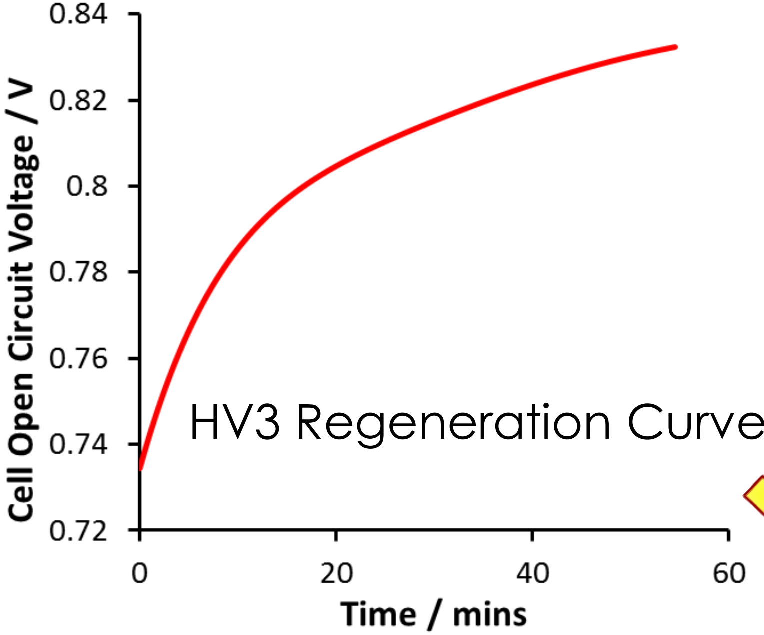


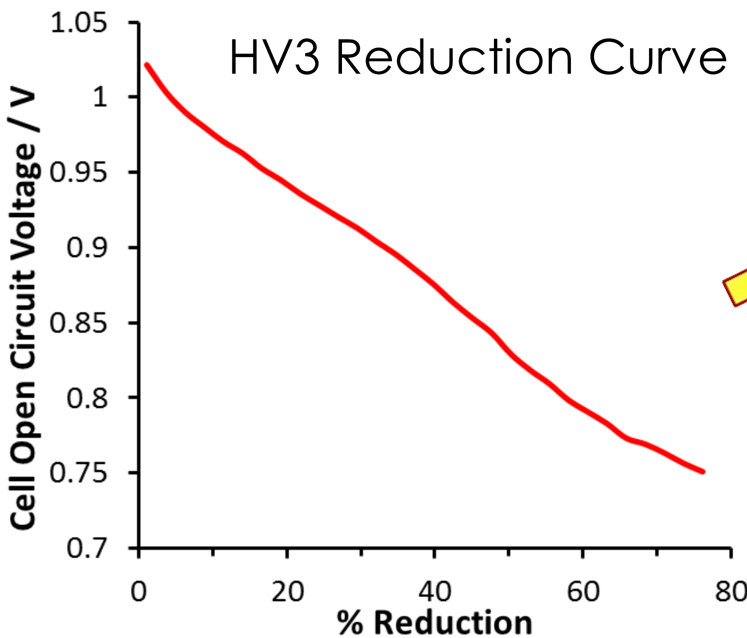


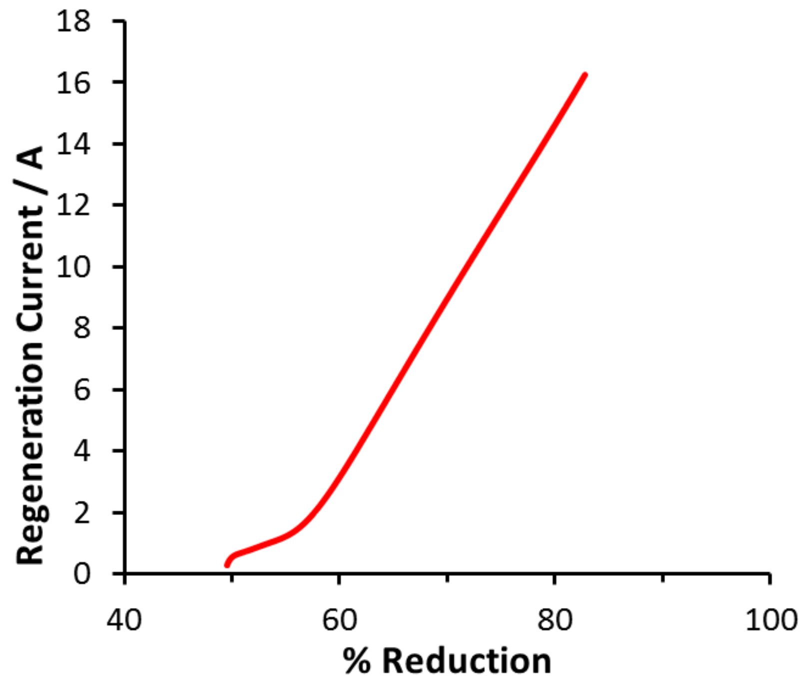
Regenerator Performance

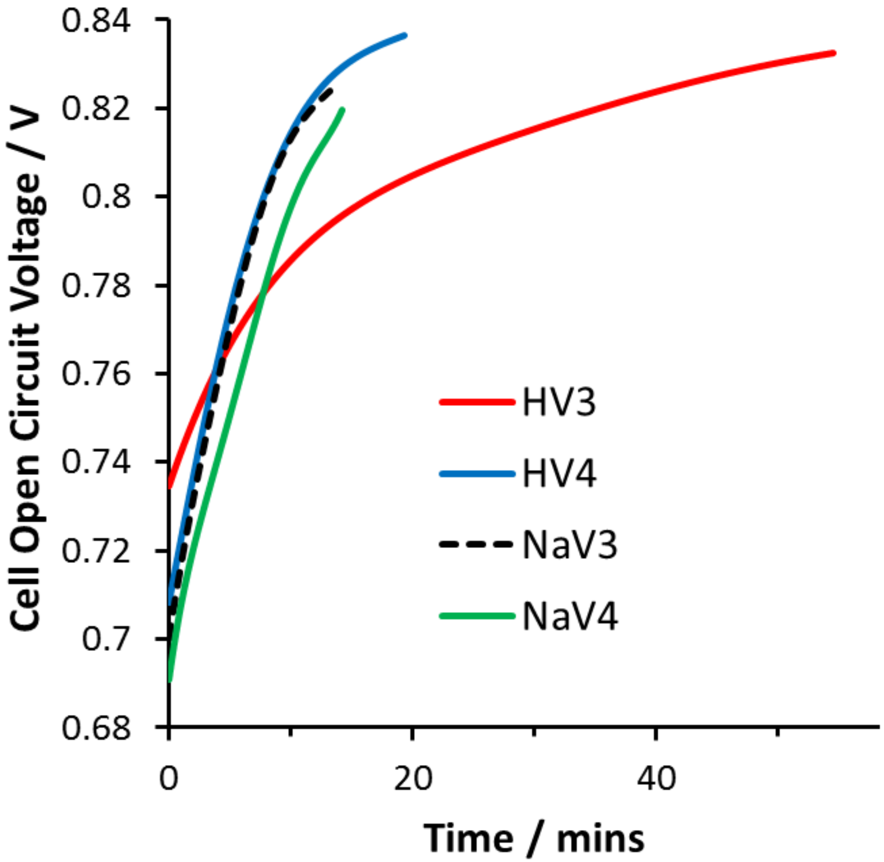
- The rate at which the reduced POM reacts with air can be expressed as a regeneration current, I_R:

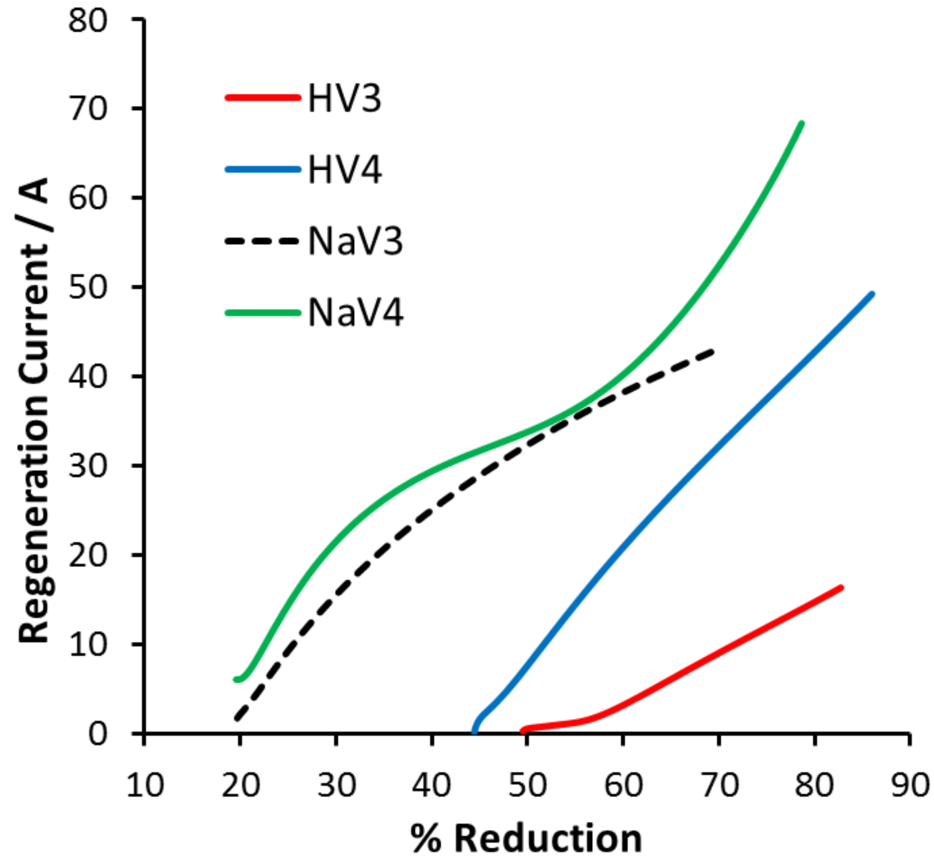
$$I_R = [\text{POM}] V n F \frac{d\theta}{dt}$$





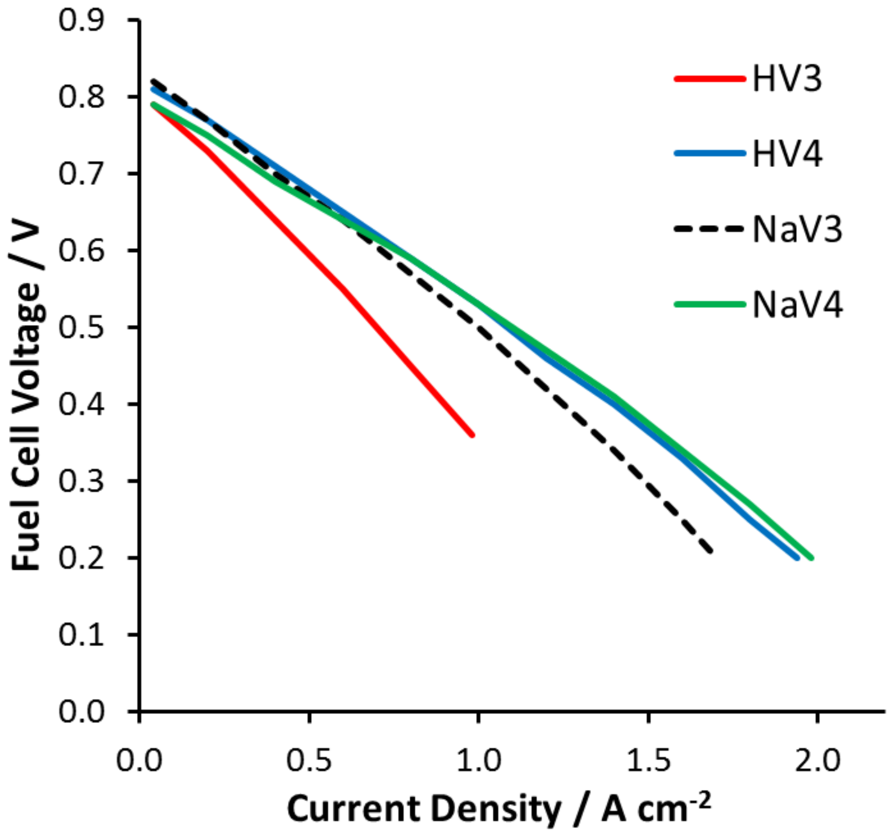


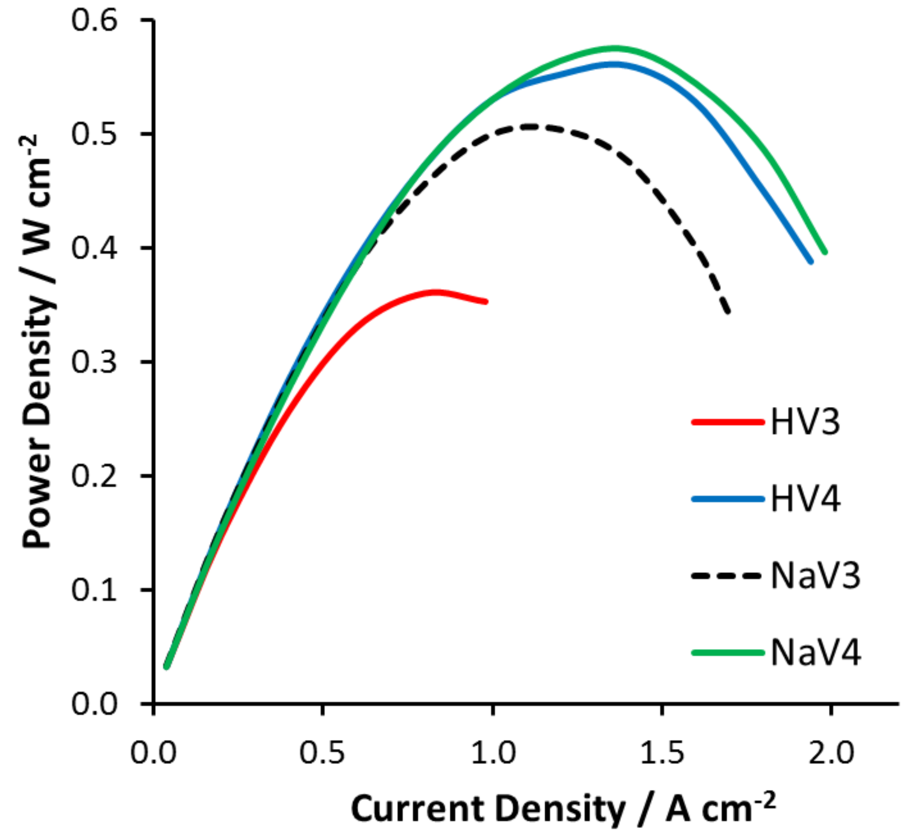




- HV3 takes much longer to regenerate than the other POMs
- NaV4 and NaV3 capable of much higher regeneration currents at lower levels of reduction
- Regeneration current limits maximum open circuit voltage of system

Steady State Fuel Cell Performance





- 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 keggins 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

Thank you

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