



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

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Outline of Presentation

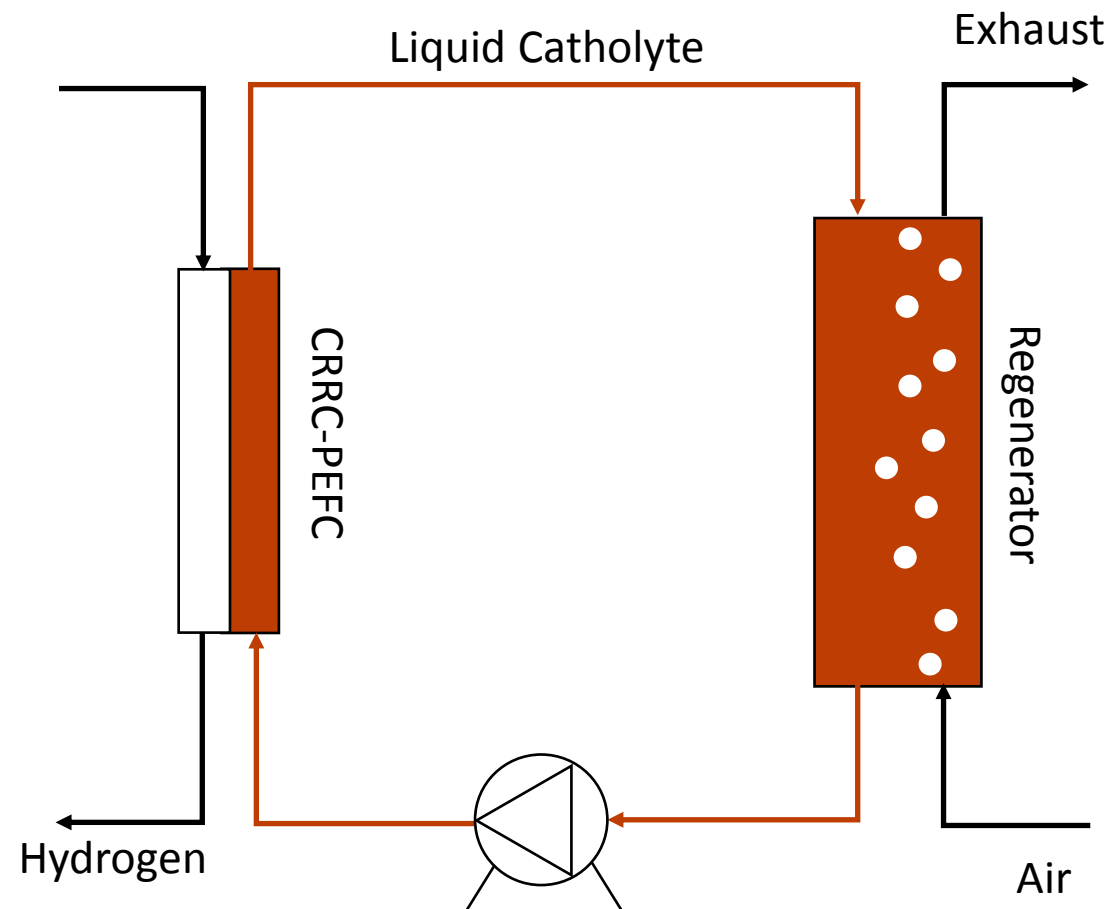
- Background
 - What is a **Chemically Regenerative Redox Cathode (CRRC) Polymer Electrolyte Fuel Cell (PEFC)** system?
 - What are the advantages over conventional PEFC systems?
- Investigation objectives
- Methodology and operating condition
 - How is CRRC-PEFC performance measured?
- Results
- Conclusions
- Future Investigation

Background

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

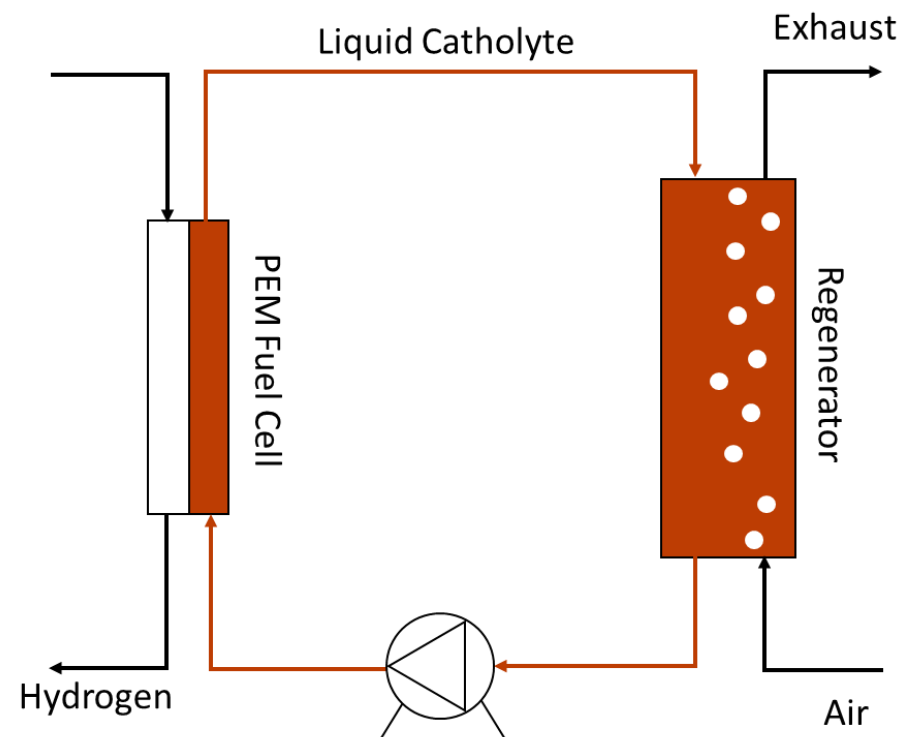
What is a CRRC-PEFC System?

- 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

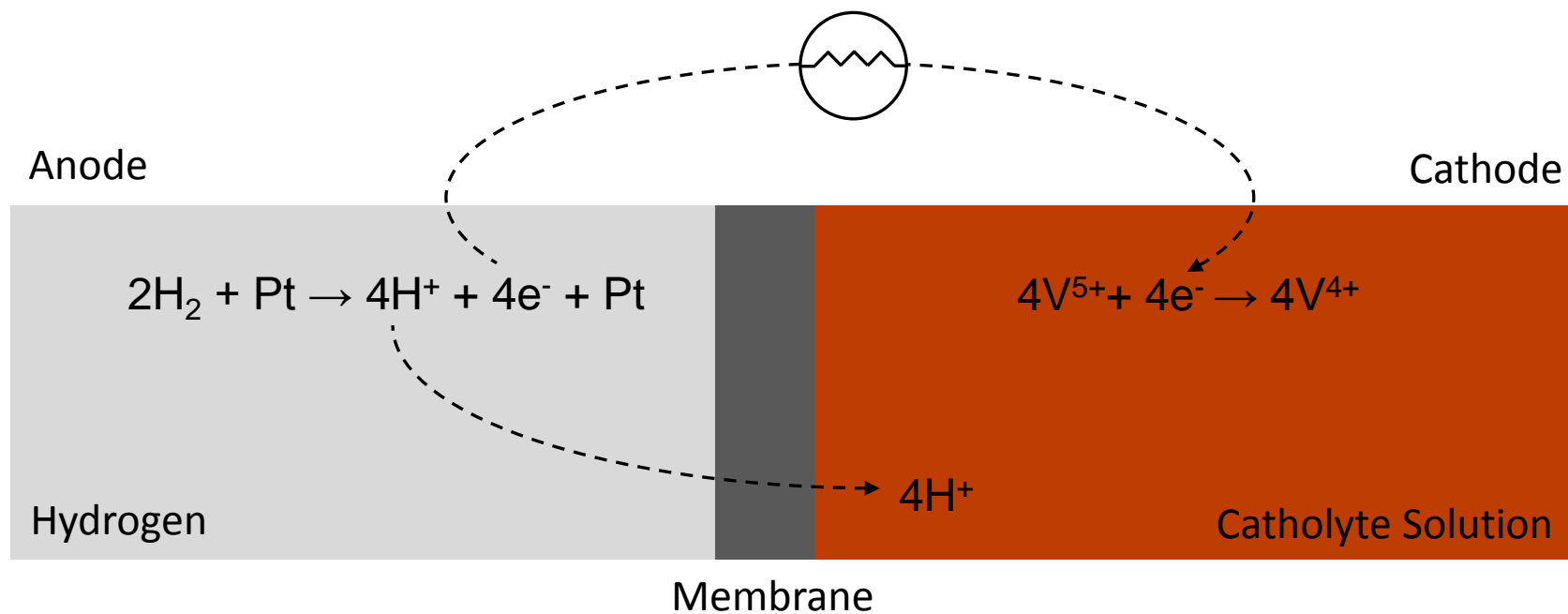


Advantages over conventional PEFCs

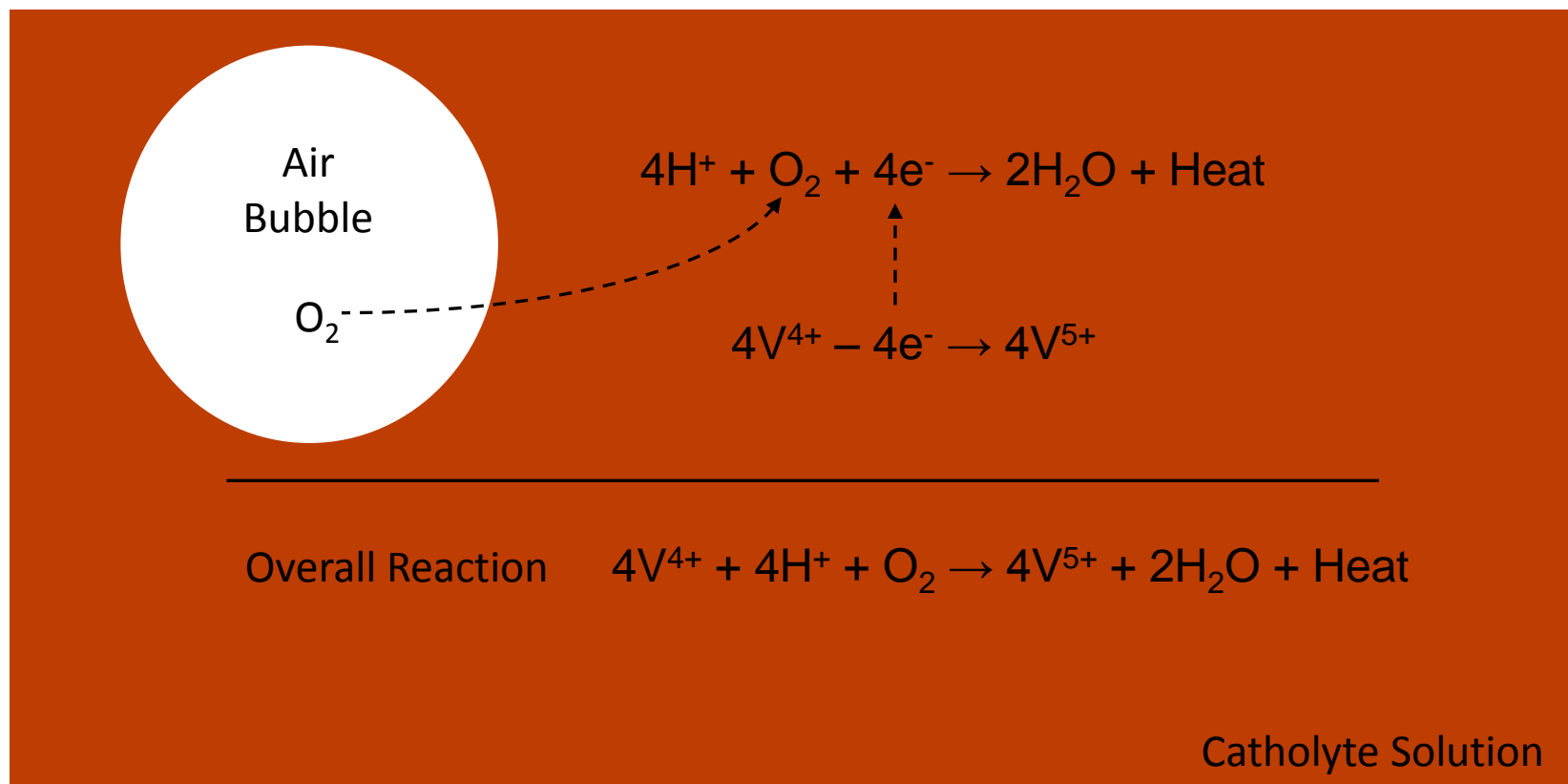
- Eliminates need for Pt on the cathode
 - Pt reduced by as much as 80%
 - Significant cost saving
 - Performance less vulnerable Pt loss
- Indirect reduction of oxygen
 - Degradation via by-products avoided (e.g. H_2O_2)
- Liquid cathode
 - Avoids damage via internal conflagrations (hot spots)
 - Maintains 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?

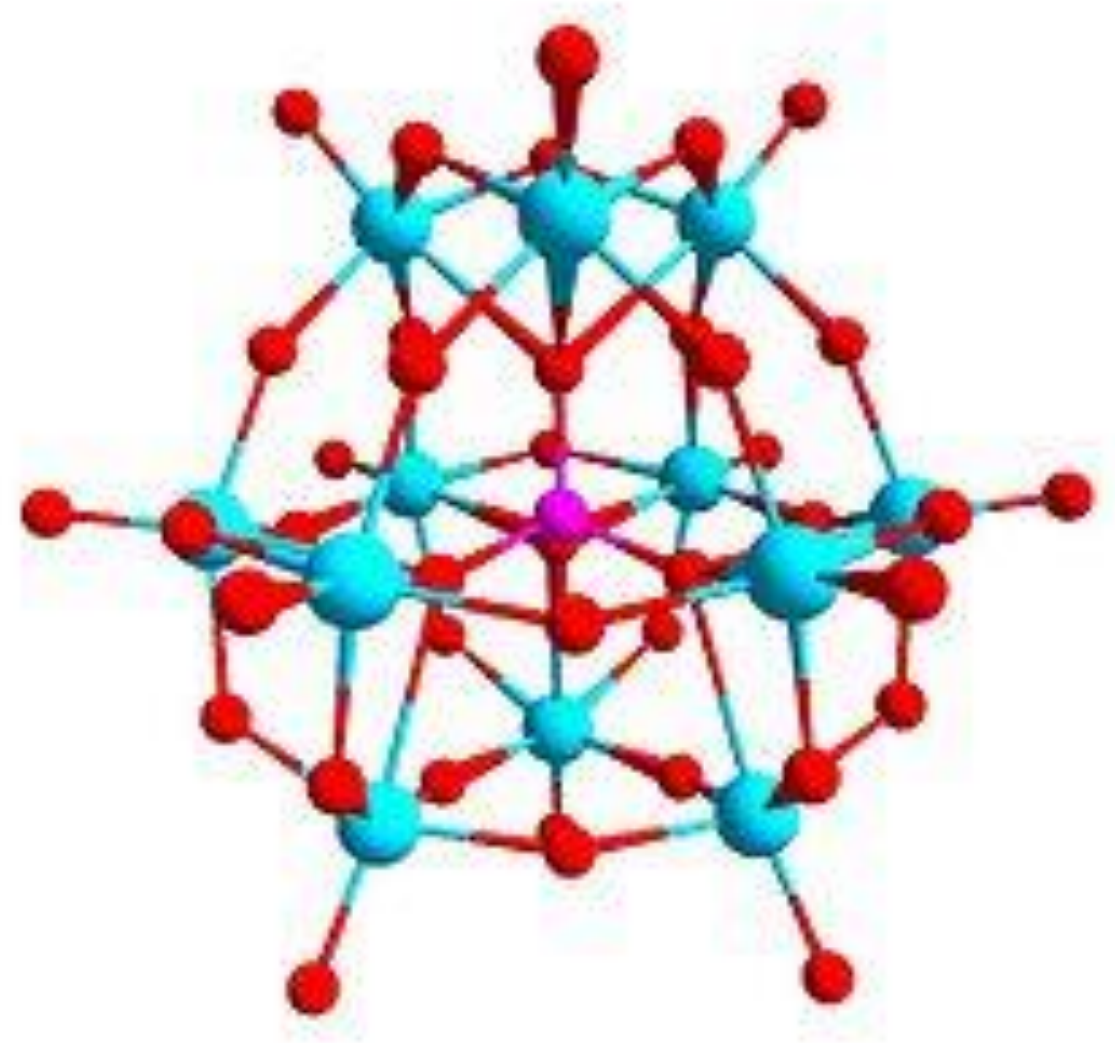


What happens within the Regenerator?



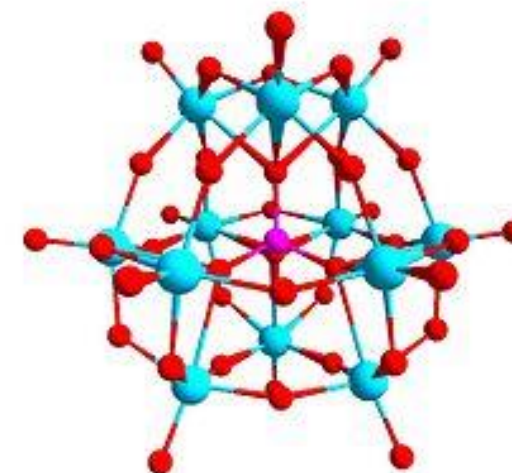
What is the catholyte?

- Empirical formula $\text{H}_7\text{PV}_4\text{Mo}_8\text{O}_{40}$ (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 ($\text{H}_7\text{PV}_4\text{Mo}_8\text{O}_{40}$)
 - Previously reported results relevant to **80°C and 0.3M¹**
- Examine with performance with respect to...
 - Cell performance (I-V curves)
 - Regenerator oxidation kinetics (sustainable current)
 - Combined system performance (sustainable power)



1. David B.Ward, Natasha L.O.Gunn, NadineUwigena and Trevor J.Davies. "Performance comparison of protonic and sodium phosphomolybdovanadate polyoxoanion catholytes within a chemically regenerative redox cathode polymer electrolyte fuel cell", *Journal of Power Sources*, 375 (2018), 68-76.

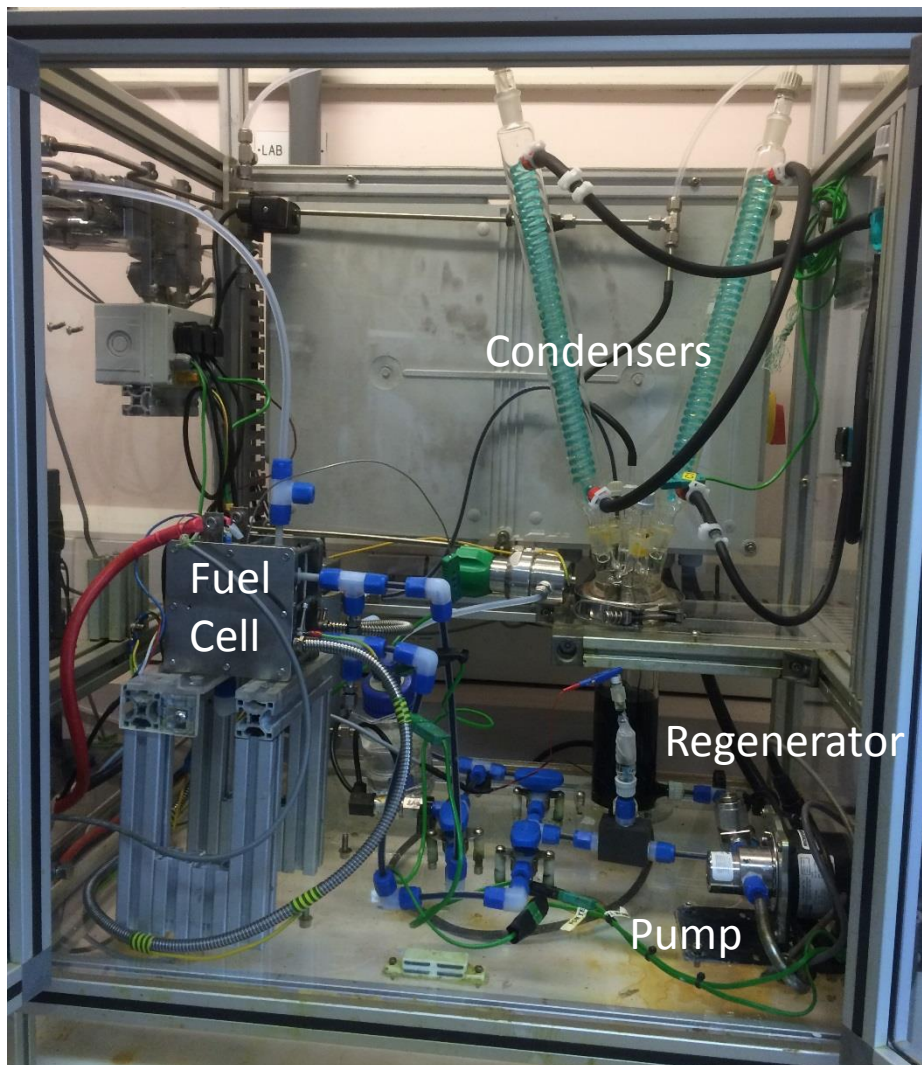


Method:

How to quantify **CRRC-PEFC** Performance?

Apparatus and Operating Conditions

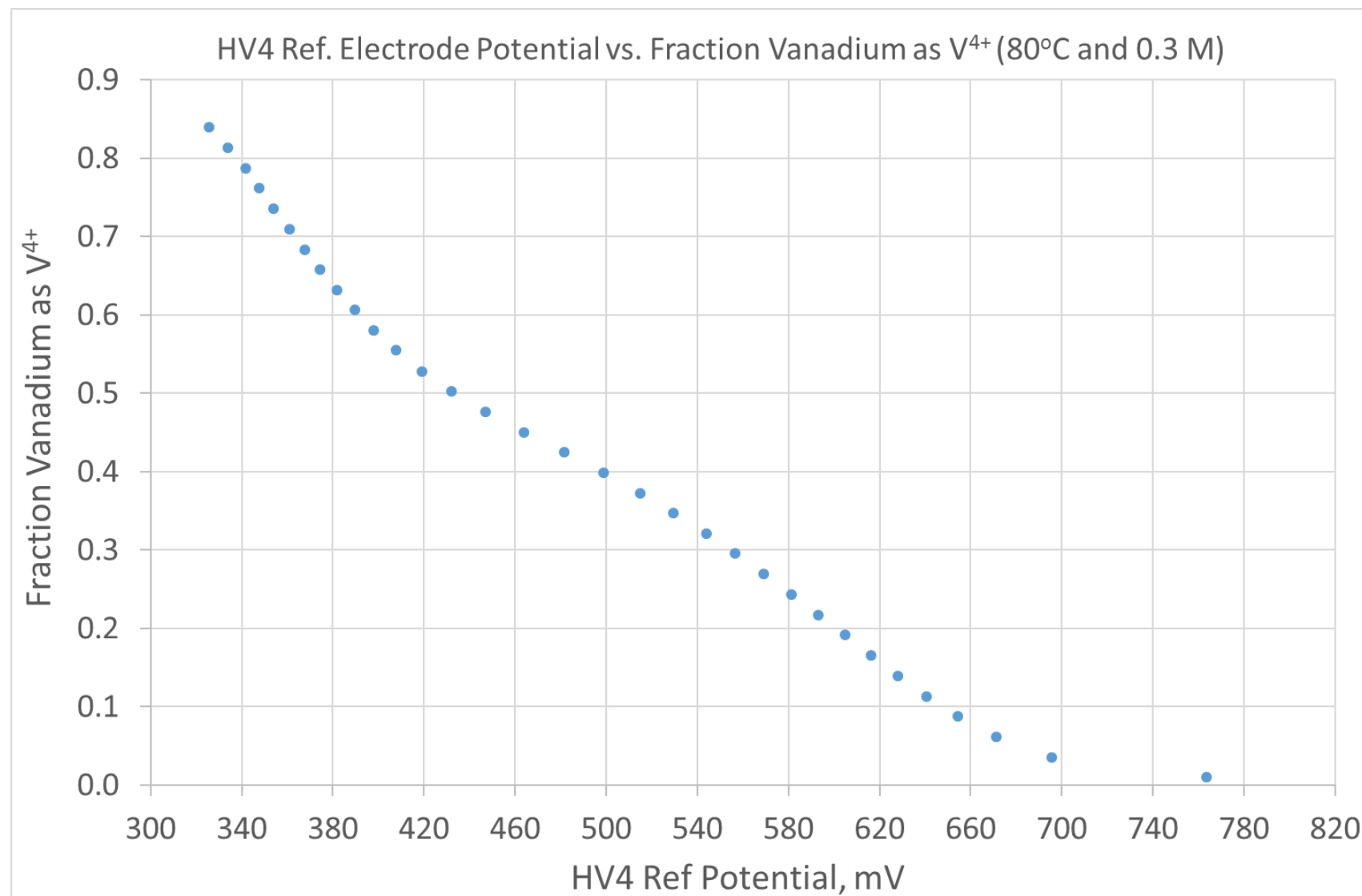
- Anode membrane assembly:
 - 25 cm² active area
 - Ion Power NR212
- Anode:
 - ~600 mbar hydrogen
 - Dead ended
- Catholyte:
 - 0.2, 0.3, 0.4 and 0.45 M
 - 0.3 L system volume
 - ~140 mL/min recirculation rate
- Regenerator:
 - 1 L/min air flow
 - 500 mL bubble column with sintered glass sparge
- System operating temperature, 40, 50, 60, 80 & 90°C



Redox Potential vs. Fraction V Reduced

V^{4+}
Reduced

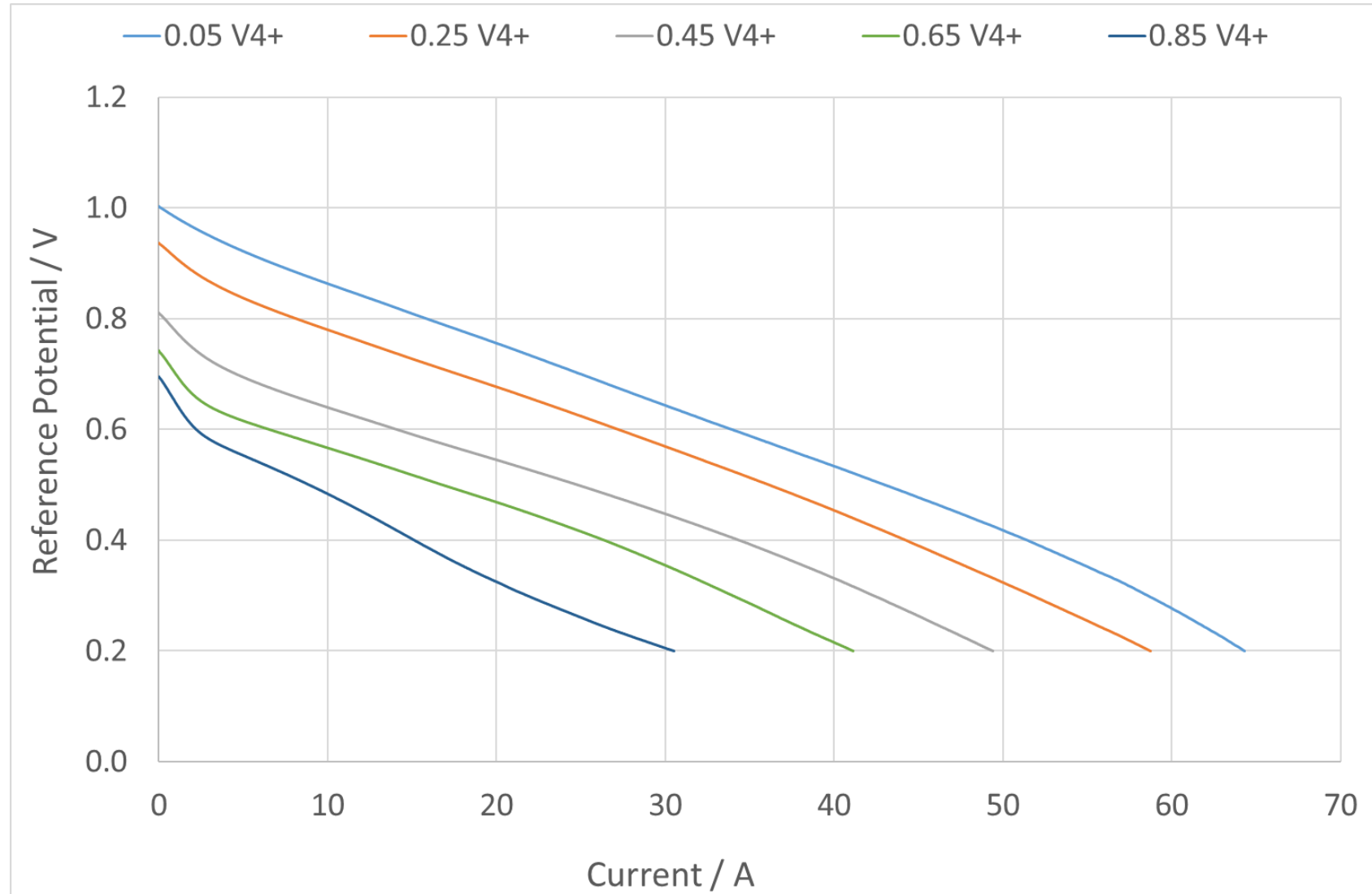
V^{5+}
Oxidised



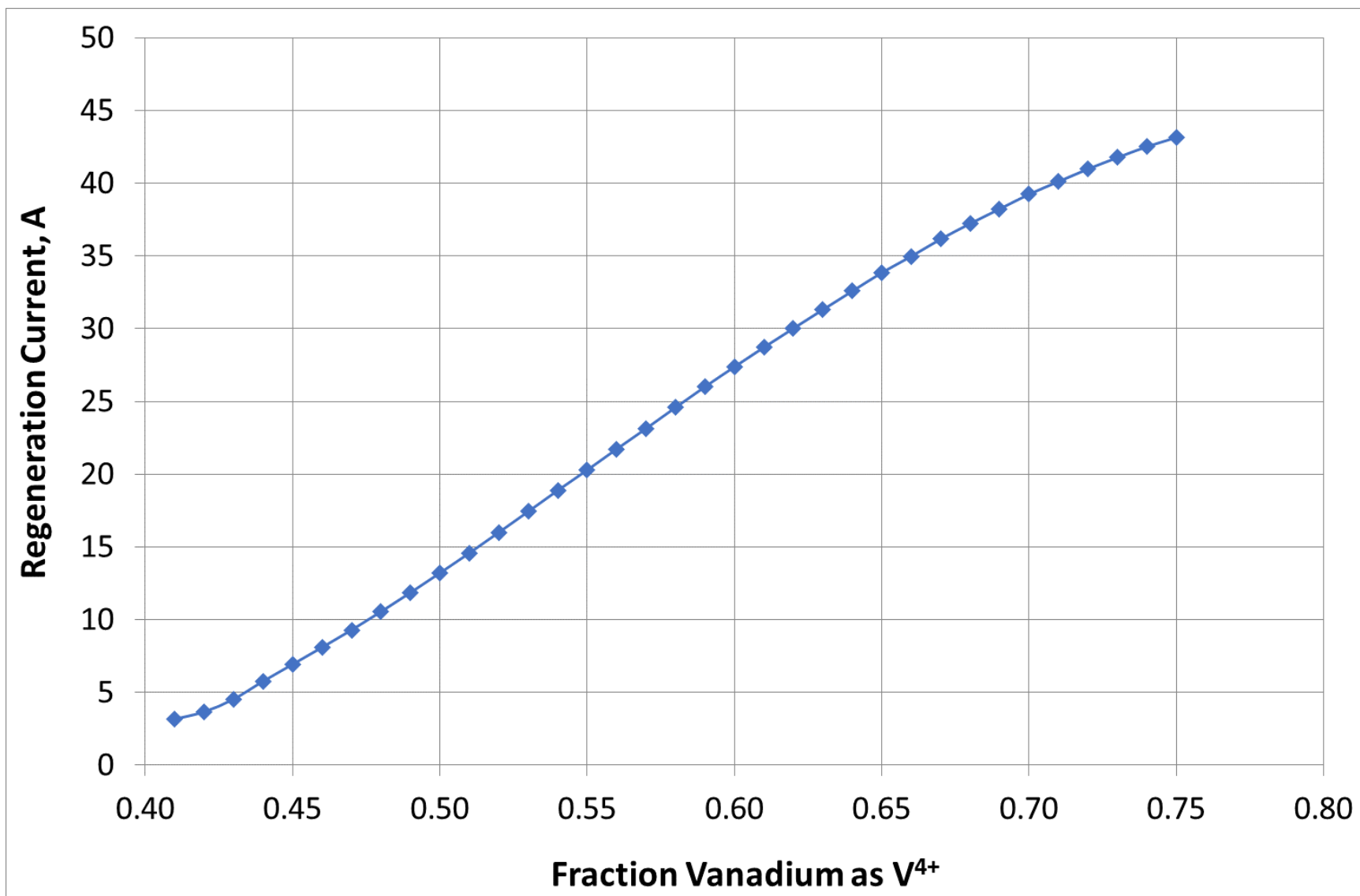
I-V curves at varying states of vanadium reduction (0.3 M HV4 catholyte at 80°C)

V^{5+}
Oxidised

V^{4+}
Reduced



Regeneration Current vs. fraction vanadium reduced



CRRC-PEFC at Steady State Operation

Electrons Transferred in Cell

=

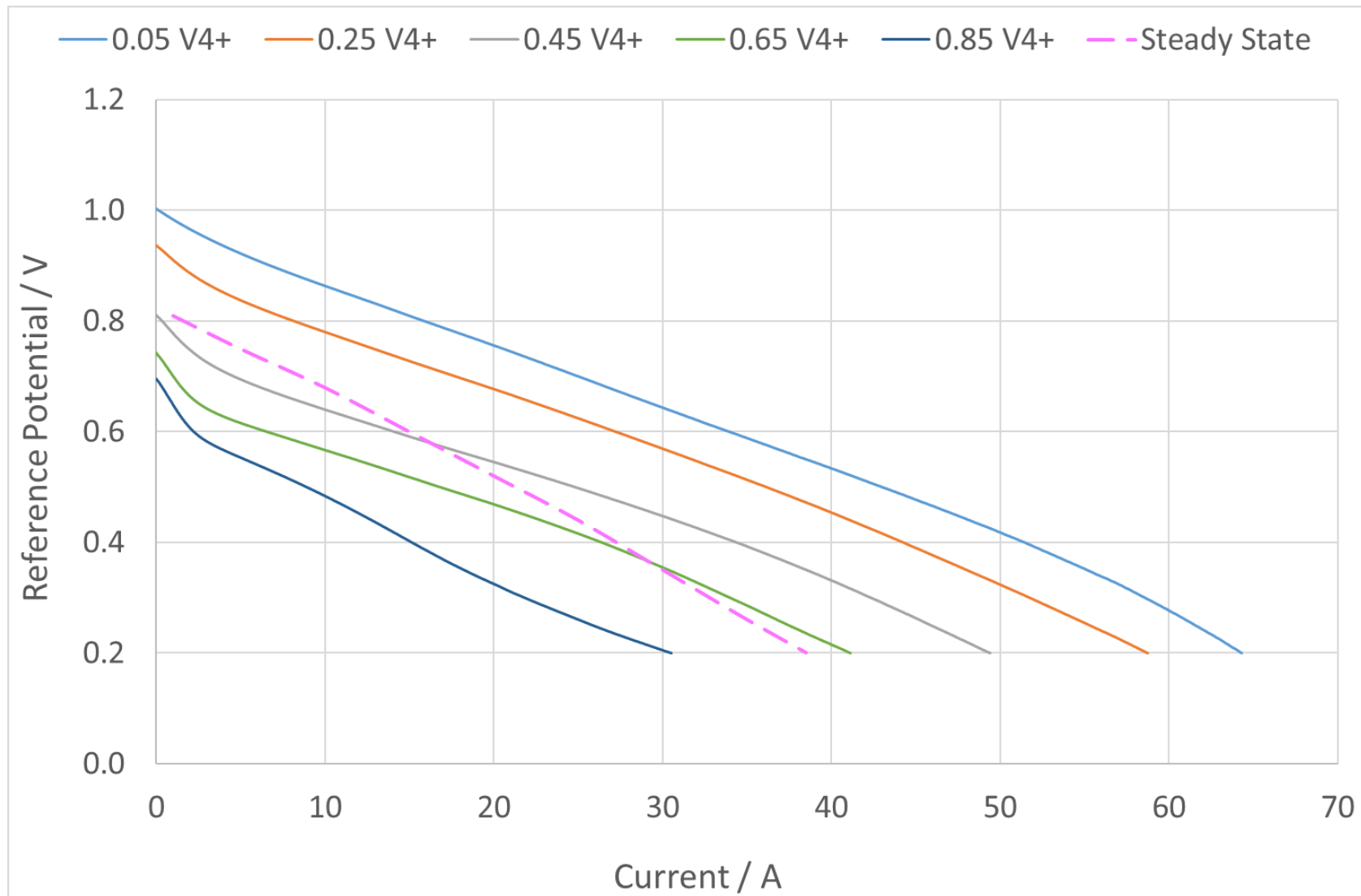
Electrons Transferred in Regenerator

Hence, sustainable current determined by rate of regeneration

Sustainable I-V curve (0.3 M HV4 catholyte at 80°C)

V^{5+}
Oxidised

V^{4+}
Reduced



Experimental Design

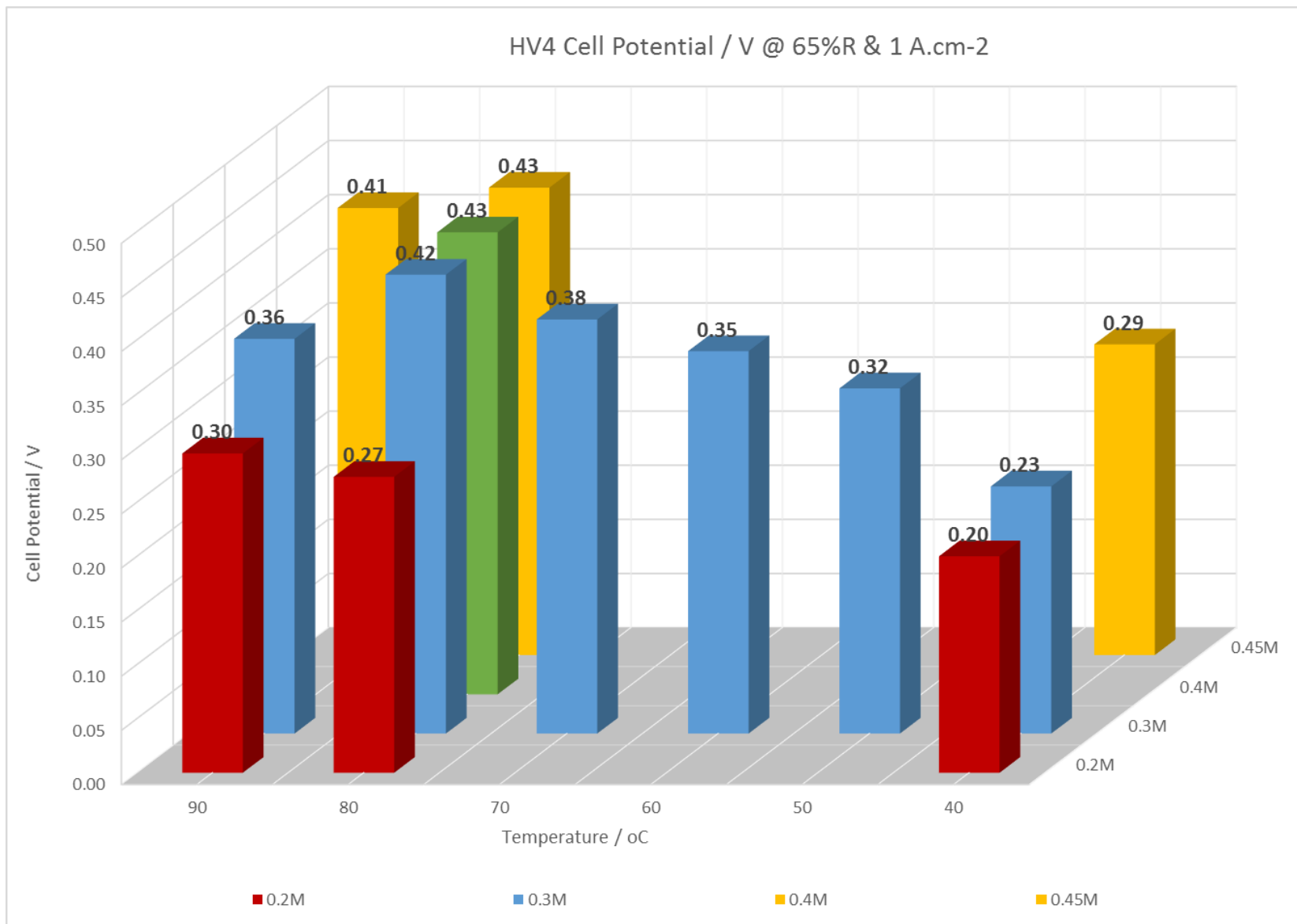
Temperature / °C	Catholyte Concentration / M			
	0.2	0.3	0.4	0.45
40	X	X		X
50		X		
60		X		
70		X		
80	X	X	X	X
90	X	X		X



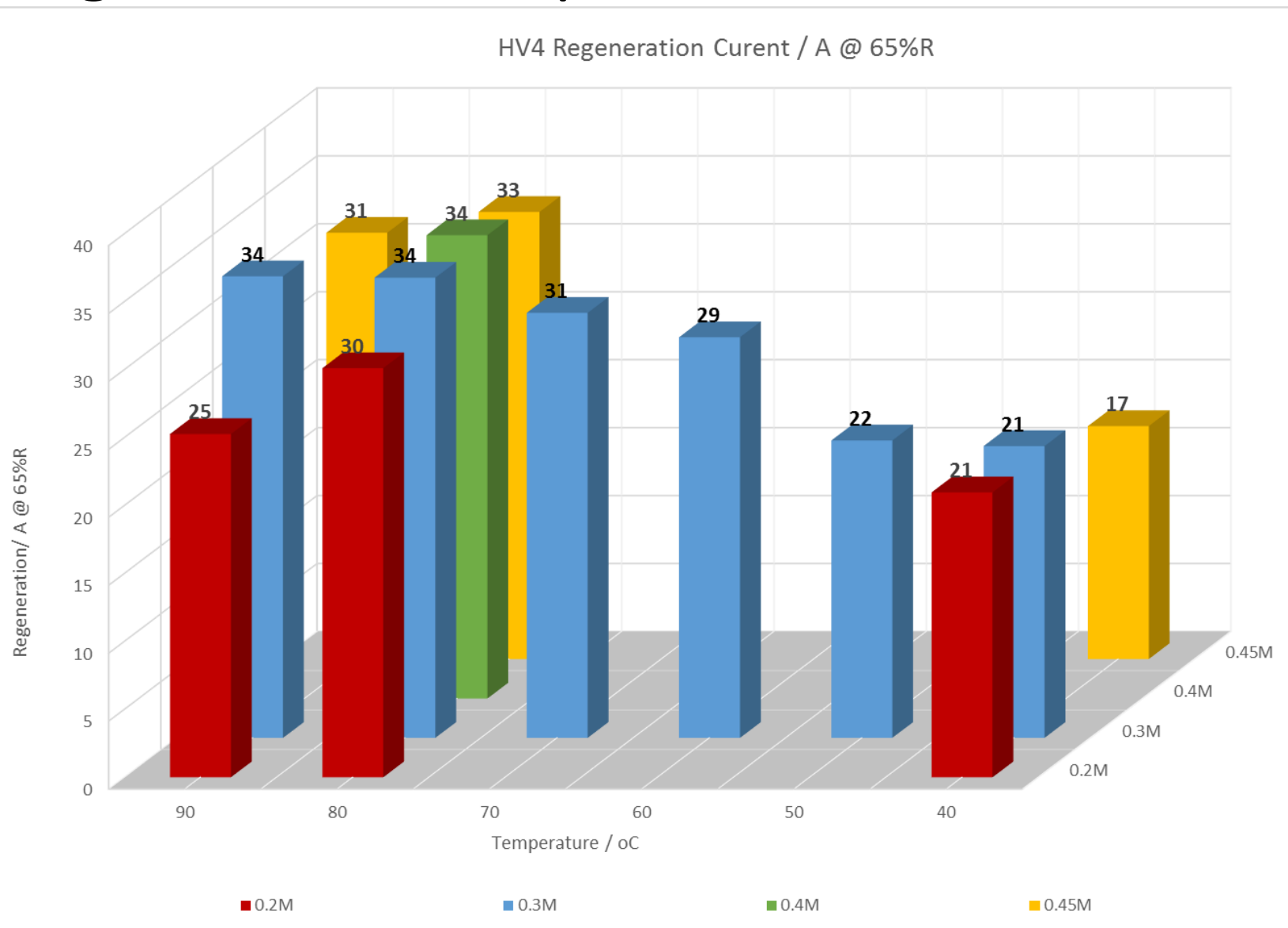
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Results

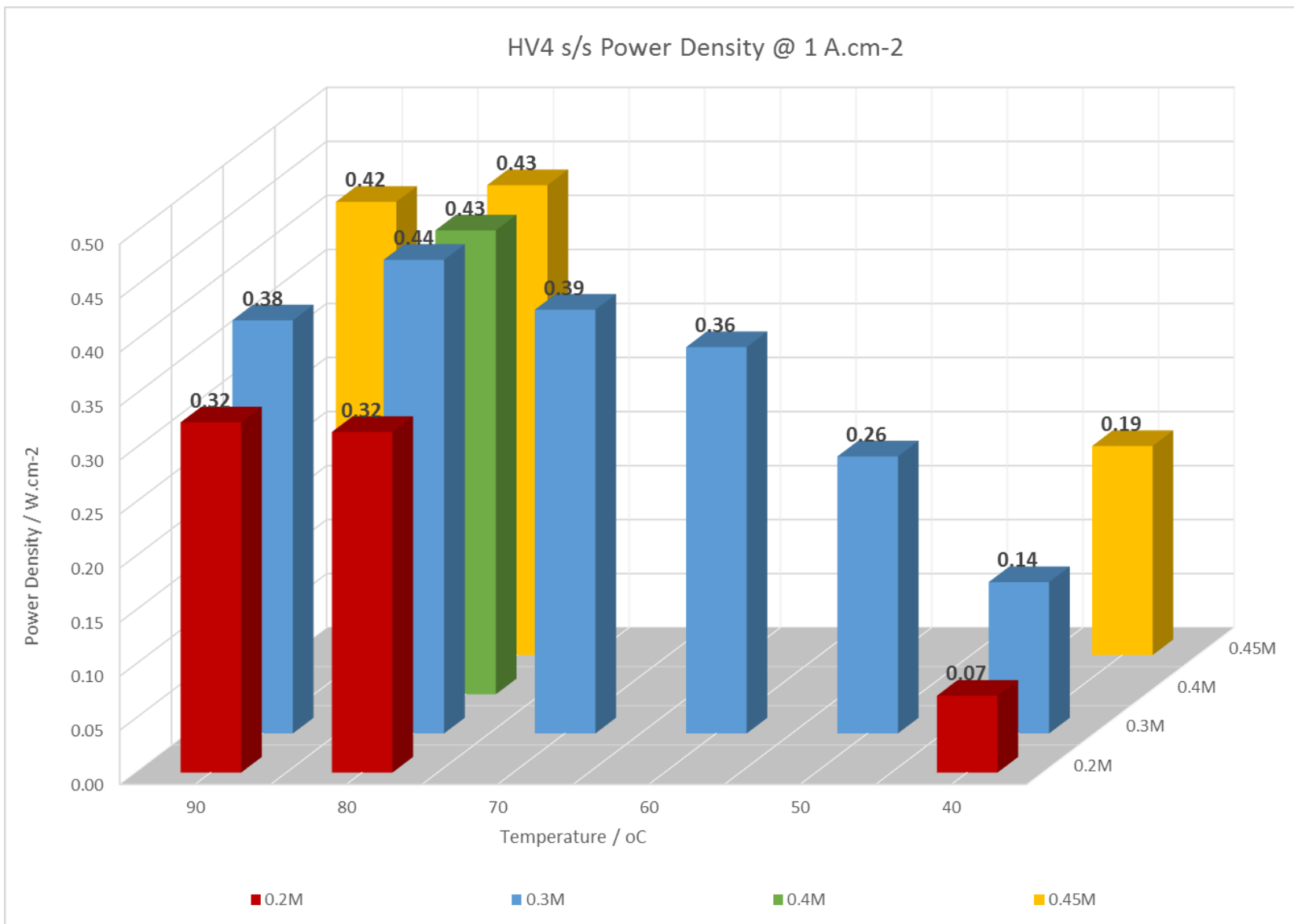
Cell voltage comparison @ 65%R & 1 A.cm⁻²



Regeneration Comparison @ 65%R



Sustainable power comparison @ 1 A.cm⁻²



Conclusions

- **80°C** 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, **80°C 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 added³
- 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.
3. David Ward, Bob Smith & Trevor Davies, "Impact of Incrementally Adding NaOH to Catholyte used in a Chemically Regenerative Redox Cathode Polymer Electrolyte Fuel Cell", **Poster Presentation, Fuel Cell & Hydrogen Technical Conference 2018.**

Thank you for listening

- Any questions?
- Email contact: dward@chester.ac.uk
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