

**Effect of Temperature and Catholyte Concentration on the Performance of a  
Chemically Regenerative Fuel Cell  
Supplementary Information**

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## **1. Experimental Details**

### ***1.1 Catholyte Synthesis***

Catholyte synthesis was carried out as per the “Metallomax” procedure using the following reagents (1): deionised water (with a resistivity of 18.2 MΩ cm), V<sub>2</sub>O<sub>5</sub> powder (99.2%, Alfa Aesar, UK), Mo powder (99.9%, Alfa Aesar, UK), H<sub>3</sub>PO<sub>4</sub> (85.0%, Sigma Aldrich, UK) and MoO<sub>3</sub> (99.5%, Alfa Aesar, UK). Final conversion of protonic H<sub>7</sub>PV<sub>4</sub>Mo<sub>8</sub>O<sub>40</sub> (HV4), to the sodium baring Na<sub>4</sub>H<sub>3</sub>PV<sub>4</sub>Mo<sub>8</sub>O<sub>40</sub> (NaV4), was achieved by the addition of NaOH (98%, Alfa Aesar, UK).

HV4 and NaV4 stock solutions were produced in 3 L batches at 0.45 M concentration. Each was then oxidised so that <1% of the vanadium present was available in the +4 state. This was achieved by a combination of chemical (i.e. air bubbling) and electrochemical oxidation (i.e. a sacrificial, non-test, cell operated in reverse). Stock solutions were then stored in sealed glass bottles for dilution and use as required.

Catholyte concentration was determined gravimetrically using 25 mL glass density jars and pre-determined density vs. concentration calibration curves. Adjustment was achieved by either deionised water addition or heating and evaporation as required.

### ***1.2 Fuel Cell Test System***

The CRRC test stand used in this study was that reported previously by Gunn et al. (2). This consisted of a catholyte flow circuit involving a gear pump (Micropump, UK), ¼ inch PFA tubing and fittings (Swagelok, UK), a 25 µm stainless steel filter (Swagelok, UK), CAST-X 300 inline heater (Cast Aluminum Solutions, USA), CRRC fuel cell (see below) and regenerator. The regenerator consisted of a cylindrical gas vessel (55 mm diameter, 205 mm height), fitted with a sintered POR4 glass ‘candle’ sparge (ROBU® Glasfilter-Geraete GmbH, Germany) at its base. As such, the regenerator was operated in a manner similar to a bubble column reactor. Exhaust material, released from bubbles breaking at the gassed liquid surface, were extracted via twin, parallel glass coil reflux condensers. The purpose of the condensers was to capture and return any moisture and/or aerosols attempting to exit the system. Throughout all tests, catholyte concentration was maintained to within ±5% of the target value.

Table S1, gives general operating conditions employed throughout all tests. Fuel cell and regenerator temperatures were maintained to within ±2°C of target values. The cell anode was operated in a ‘dead ended’ mode and purged for 1 s every 2 minutes, (suspended for cell performance and impedance tests). An HCP-803 potentiostat (Bio-Logic, France) was used to control and monitor current load and cell voltage. All other system monitoring and control was achieved using LabVIEW software (National Instruments, USA) via an

on-board programmable logic controller (PLC). All sensor outputs were recorded at a logging rate of 1 s<sup>-1</sup>.

**Table S1.** General test rig operating conditions.

Parameter	Value
Catholyte volume	300±2 mL
Anode hydrogen pressure	1000±10 mbar
Cathode Inlet pressure <sup>a</sup>	580 – 980 mbar
Regenerator air flow	1000±20 mL min <sup>-1</sup>
Catholyte flow rate	140±5 mL min <sup>-1</sup>

<sup>a</sup> Varied with temperature, concentration and reduction level.

Catholyte redox potential was monitored using an in-line reference electrode identical to that described previously (2). This consisted of a mercurous sulphate reference electrode (Cambria Scientific, UK) immersed in a 0.1 M sulphuric acid solution and separated from a catholyte/JP945 carbon electrode (Merson UK, UK) via a Nafion® salt bridge.

### **1.3 Cell Build**

Apart from the choice of MEA, cell construction was identical to that previously reported by Gunn et al. (2). A brief description is given here. NR212 (Ion Power, EU online store) MEAs were used throughout this investigation. These possessed an anode platinum loading of 0.3 mg.cm<sup>-2</sup> over a 25 cm<sup>2</sup> active area (5 × 5 cm). The MEA anode surface was positioned adjacent to an anode gas diffusion layer of 34BC (SGL Group GmbH, Germany) followed by JP945 graphite plate with machined serpentine flow channels (Mersen, UK). The naked cathode MEA face was set against a GFD 2.5EA carbon

felt (SGL Carbon GmbH, Germany), held within a 1 mm deep catholyte flow well machined in an opposing JP945 graphite plate (Mersen, UK). Gold plated copper current collectors were placed against the outer surface of each opposing carbon plate and the whole array was compressed and sealed between two stainless steel end plates – producing 3.5-4 bar compression on the active area. To ensure target cell temperatures could be maintained, additional heating was provided using fire rods (Watlow Ltd, UK) mounted within the steel end plates.

#### ***1.4 Catholyte Redox Reduction Curves***

Knowledge of the catholyte reduction level is key when operating a CRRC system as it has a strong and direct bearing on both cell performance (i.e. voltage) and regeneration rate (i.e. sustainable current load) (2). The reduction level,  $\theta$ , can be quantified as the fraction of total vanadium in the 4+ oxidation state:

$$\theta = \frac{[\text{vanadium(IV)}]}{[\text{vanadium}]} \quad (\text{eq. S1})$$

Using the temperatures and concentrations matrix given in Table S2, the relationship between  $\theta$  and cell open circuit voltage (OCV) was examined for each catholyte under each combination of conditions. Each test involved the gentle and incremental reduction of stock solution catholyte. Solutions were prior diluted (using deionised water) to required concentrations before being circulated and heated to target temperatures within the CRRC test rig. During this process, any counter oxidation was prevented by the supply of pure nitrogen to the regenerator. Assuming 100% efficiency,

OCV vs.  $\theta$  curves were generated. These were then employed in all subsequent tests to achieve target reduction levels.

**Table S2.** Temperature and concentration condition test matrix used throughout this investigation.

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

### ***1.5 Cell Performance at Various Catholyte Reduction States***

Cell performance was evaluated for each catholyte at each condition in Table S2. At each point, current-voltage (*I-V*) curves were generated over a range of catholyte reduction levels (i.e.  $\theta = 0.05, 0.25, 0.45, 0.65$  and  $0.85$ ). Electrochemical impedance spectrometry was performed under 8.75, 15 and 25 A loads, corresponding to current densities of 0.35, 0.6 and 1 A cm<sup>-2</sup>. For consistency, and to maintain a sufficient and sustainable cell voltage under load, all impedance testing was conducted at a catholyte reduction level corresponding to an OCV of 800±25 mV (i.e.  $\theta \approx 0.2$  for NaV4 and  $\theta \approx 0.5$  for HV4). To maintain target reduction levels during cell performance tests, the air to the regenerator was turned on/off as required. To demonstrate consistency over the investigative period (i.e. no performance drift), *I-V* curves were generated under standard conditions (i.e. 0.3 M, 80°C and  $\theta = 0.65$  for HV4 and  $\theta = 0.45$  for NaV4) before and after

each complete set of catholyte tests. All tests were carried out in duplicate with an anode air purge performed before each test. The air purge involved flooding the anode with air whilst the cell was at open circuit. This has been found to completely reverse a suspected anode poisoning, caused by crossover of catholyte species to the anode, similar to the platinum poisoning found in hydrogen/bromine flow batteries (3). The exact nature of the anode deactivation is currently under investigation and will be reported in a subsequent research article.

### ***1.6 Catholyte Regeneration Performance Tests***

Catholyte regeneration performance was assessed under each of the condition combinations given in Table S2. This was determined in triplicate using the ‘sweep’ method described in by Gunn et al (2). First, catholyte was electrochemically reduced to a level of  $\theta \approx 0.8$  under nitrogen. On achieving this, the regenerator gas supply was switched to air and, in the presence of atmospheric oxygen, the oxidation reaction was allowed to progress, whilst flowing catholyte around the system, via the cell under zero load. The cell OCV was monitored throughout and, by applying the appropriate catholyte reduction curves, used to develop plots of  $\theta$  vs. time, the gradient of which represents the quantity of electrons lost by the constituent vanadium(IV) centres per unit time. Hence, for each value of  $\theta$ , a regeneration current ( $I_R$ ) can be determined using (2):

$$I_R = V[\text{POM}]nF \frac{d\theta}{dt} \quad (\text{eq. S2})$$

In the above equation,  $t$  is time,  $V$  is the catholyte volume, [POM] is the concentration of the catholyte (i.e. concentration of the empirical formula),  $n$  is the number of vanadium centres in the catholyte empirical formula (i.e. 4) and  $F$  is the Faraday

constant. When a CRRC system is at steady state, regeneration current will equal cell load ( $I$ ) and hence, a plot of  $I_R$  vs.  $\theta$  can be used to predict the reduction level of a catholyte at a given steady state current load.

### ***1.7 Steady State Tests***

For each combination of conditions given in Table S2, steady state system performance was examined for HV4 and NaV4 under a 25 A load (i.e. 1 A cm<sup>-2</sup>). In order to allow the true point of steady state operation to be achieved, the system was allowed to run under the applied conditions for at least 10 minutes or until cell potential appeared sufficiently stable (i.e. <1 mV drift per minute). Once achieved, both cell load and air supply to the regenerator were simultaneously withdrawn and an anode recovery procedure performed in order to ensure comparability of results. Cell load and air supply were then simultaneously re-applied and the system allowed to re-equilibrate before final cell voltage and catholyte reduction level were recorded.

### ***1.8 Ex-situ Conductivity, pH and NMR Analysis***

Using the CRRC test system, stock solutions of both catholytes were electrochemically reduced to allow the collection of sub-samples at  $\theta=0.05, 0.25, 0.45, 0.65$  and  $0.85$ . Each sub-sample was then split and diluted to form individual 10 mL quantities at 0.2, 0.3, 0.4 and 0.45 M concentration (stored in sealed glass vials). Using a water bath, quantities were then heated to 40, 50, 60, 70, 80 and 90±2°C. At each temperature point, the diluted sub-samples were subjected to conductivity, pH and redox potential analysis using a pHenomenal CO1300L conductivity meter (VWR International,

UK) and 827 pH Lab pH meter (Metrohm, UK). Redox potential was measured using a 117 True RMS Multimeter (Hanna Instruments, UK) between a mercurous sulphate reference electrode and a JP945 graphite rod (Merson UK).

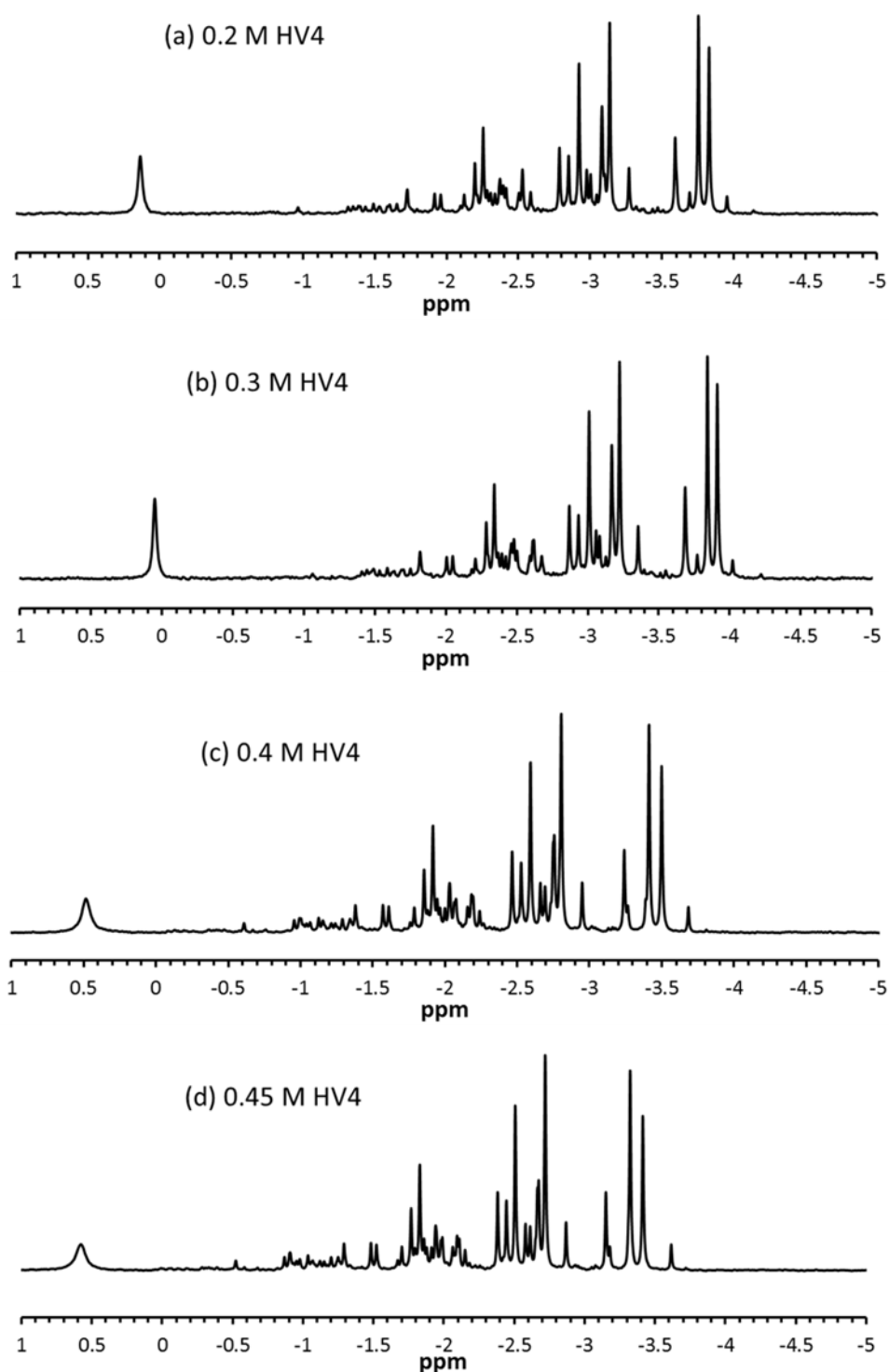
In order to avoid re-oxidation due to atmospheric oxygen exposure, all samples and sub-samples were generated, collected, diluted, stored, heated and analysed under nitrogen. In addition, deionised dilution water was boiled, cooled to room temperature and stored under nitrogen before use.

Fully oxidised samples of HV4 and NaV4 were submitted for NMR analysis at 0.2, 0.3, 0.4 and 0.45 M concentrations (oxidation by electrochemical oxidation using fuel cell in reverse). Figures S1 and S2 illustrate the corresponding  $^{31}\text{P}$  NMR spectra recorded at 298 K.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were obtained on a 500 MHz Bruker Avance III HD NMR spectrometer operating at 202.46 MHz. The spectra were run with 48 scans, no nOe enhancement and the relaxation delay was 30 s. Spectra were locked to  $\text{D}_2\text{O}$  and the  $^{31}\text{P}$  was referenced to  $\text{H}_3\text{PO}_4$ .

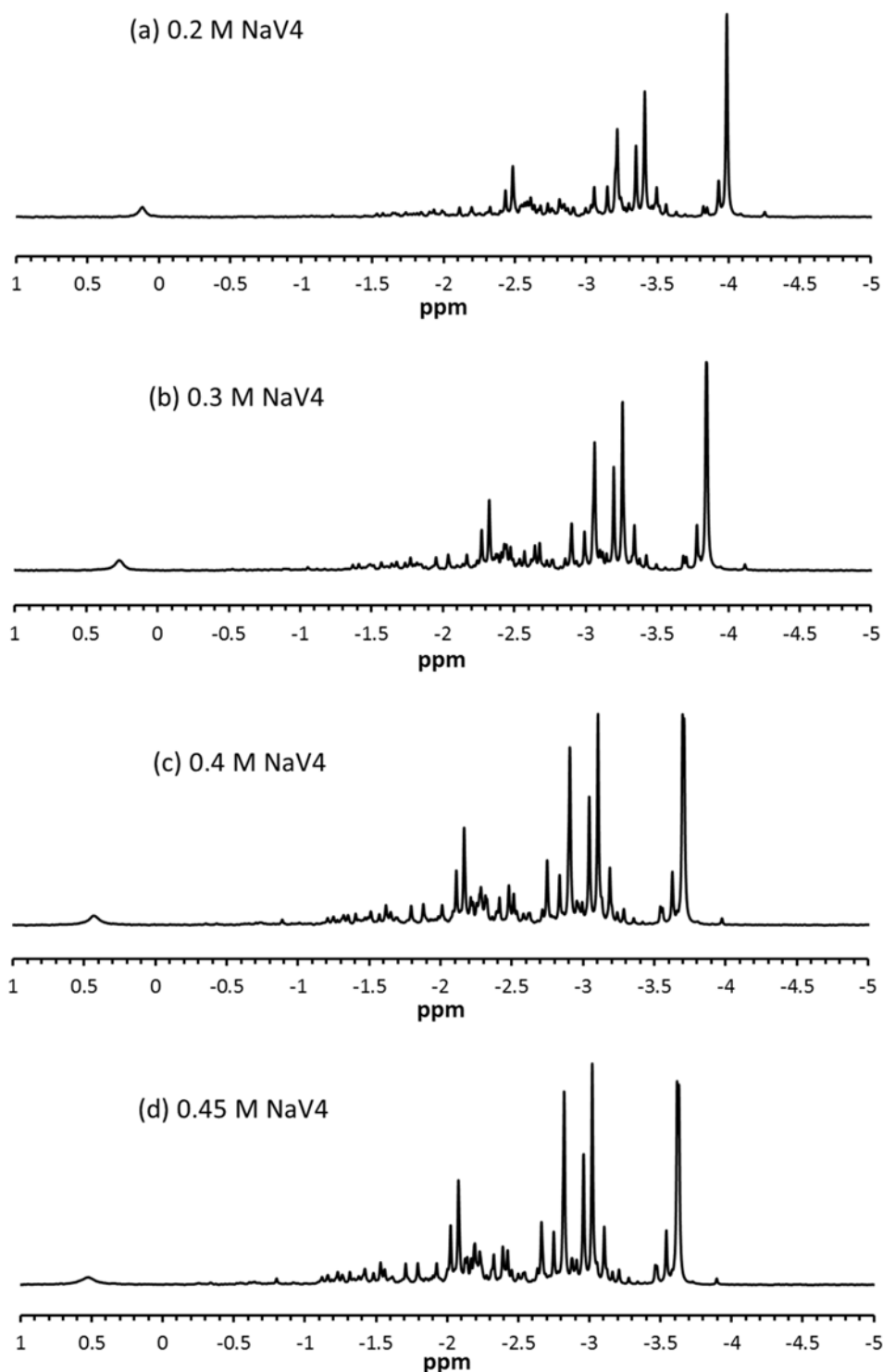
## References

1. N. Martin and M. Herbert, Synthesis of Polyoxometalates, WO2015/097459 A1
2. N. L. O. Gunn, D. B. Ward, C. Menelaou, M. A. Herbert and T. J. Davies, *Journal of Power Sources*, 2017, **348**, 107
3. H. Kreutzer, V. Yarlagadda and T. Van Nguyen, *Journal of The Electrochemical Society*, 2012, **159**, F331





**Figure S1:**  $^{31}\text{P}$  NMR spectra of aqueous solutions of  $\text{H}_7\text{PV}_4\text{Mo}_8\text{O}_{40}$  at 298 K and four concentrations: (a) 0.2 M; (b) 0.3 M; (c) 0.4 M; and (d) 0.45 M.



**Figure S2:**  $^{31}\text{P}$  NMR spectra of aqueous solutions of  $\text{Na}_4\text{H}_3\text{PV}_4\text{Mo}_8\text{O}_{40}$  at 298 K and four concentrations: (a) 0.2 M; (b) 0.3 M; (c) 0.4 M; and (d) 0.45 M.