Performance Comparison of Protonic and Sodium Phosphomolybdovanadate Polyoxoanion Catholytes Within a Chemically Regenerative Redox Cathode Polymer Electrolyte Fuel Cell

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Submitted to *the Journal of Power Sources*

Supporting Information

Catholyte Density

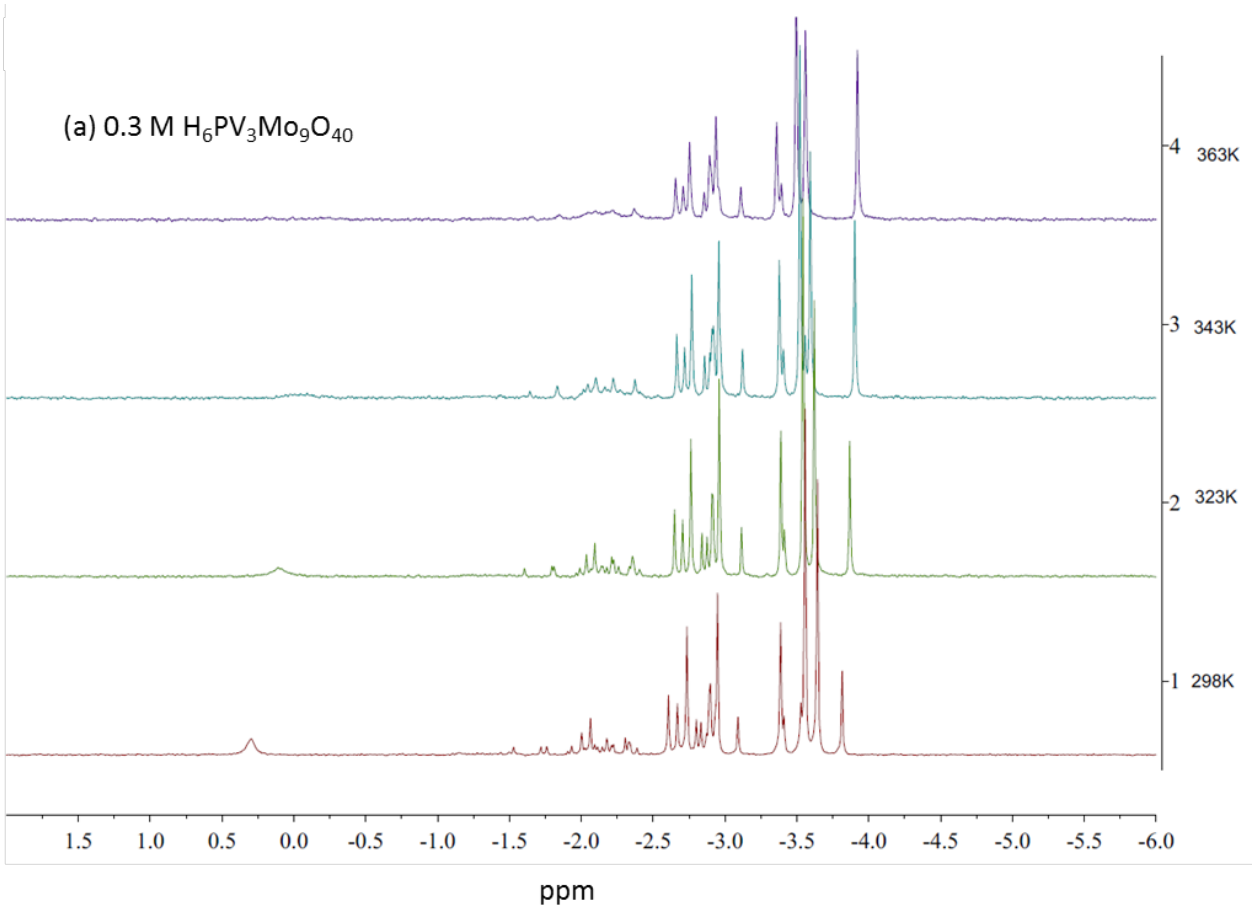
Table S1 lists the densities of the four catholytes used in the main study at a concentration of 0.3 M and temperature of 20°C. The catholytes are $H_6PV_3Mo_9O_{40}$ (HV3), $H_7PV_4Mo_8O_{40}$ (HV4), $Na_3H_3PV_3Mo_9O_{40}$ (NaV3) and 0.3 M $Na_4H_3PV_4Mo_8O_{40}$ (NaV4).

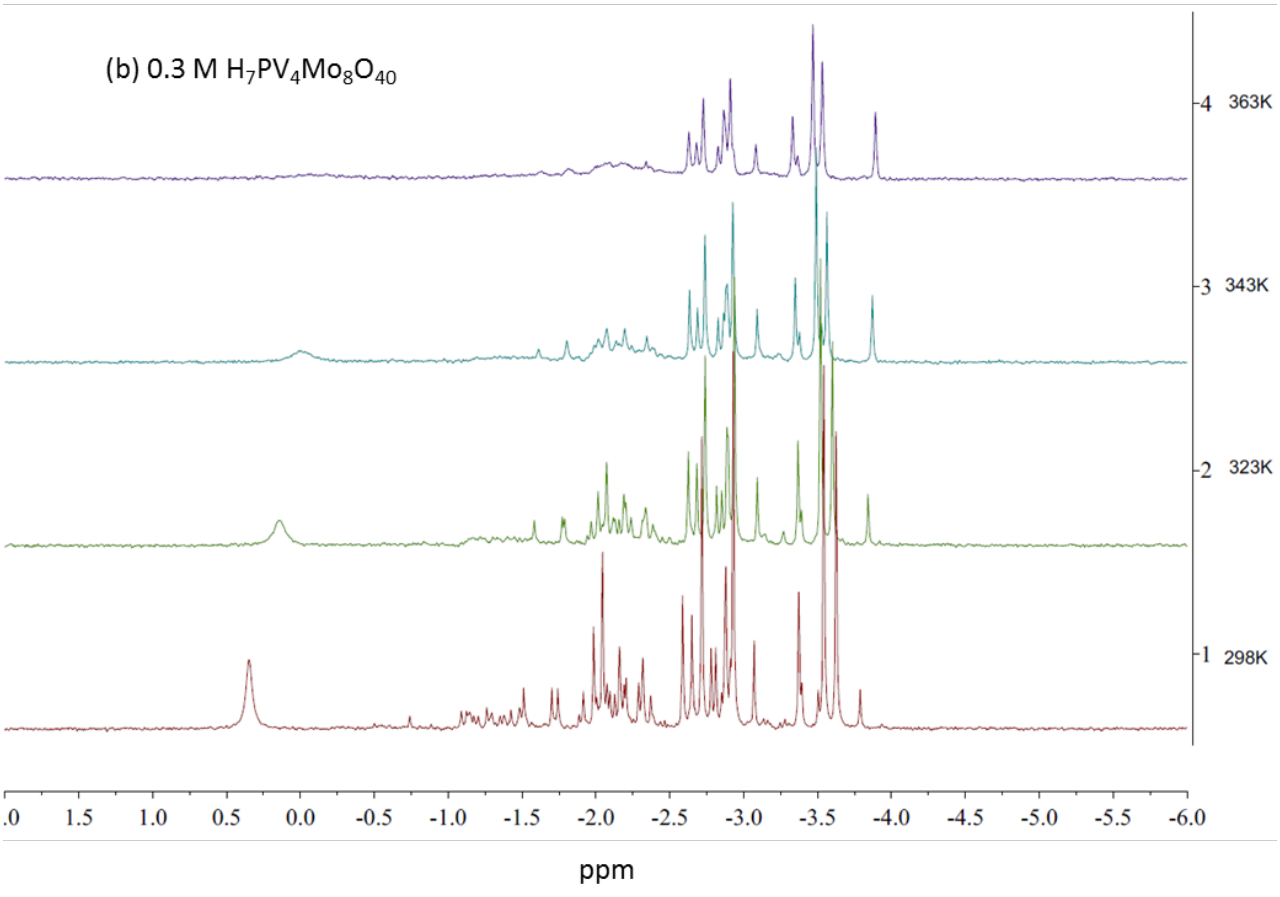
Table S1: Catholyte density at 0.3M and 20°C.

Catholyte	Density / g.cm^{-3} (0.3 M & 20°C)
HV3	1.369
HV4	1.384
NaV3	1.388
NaV4	1.410

NMR Analysis of $H_6PV_3Mo_9O_{40}$, $H_7PV_4Mo_8O_{40}$, $Na_3H_3PV_3Mo_9O_{40}$ and $Na_4H_3PV_4Mo_8O_{40}$

Figure S1 illustrates the ^{31}P NMR spectra recorded from fully oxidised samples of 0.3 M $H_6PV_3Mo_9O_{40}$, 0.3 M $H_7PV_4Mo_8O_{40}$, 0.3 M $Na_3H_3PV_3Mo_9O_{40}$ and 0.3 M $Na_4H_3PV_4Mo_8O_{40}$ at a range of temperatures. ^{31}P{1H} 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 D_2O and the ^{31}P was referenced to H_3PO_4.


(a) 0.3 M $H_6PV_3Mo_9O_{40}$
4 363K
3 343K
2 323K
1 298K
1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5 -3.0 -3.5 -4.0 -4.5 -5.0 -5.5 -6.0
ppm


(b) 0.3 M $H_7PV_4Mo_8O_{40}$
4 363K
3 343K
2 323K
1 298K
.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5 -3.0 -3.5 -4.0 -4.5 -5.0 -5.5 -6.0
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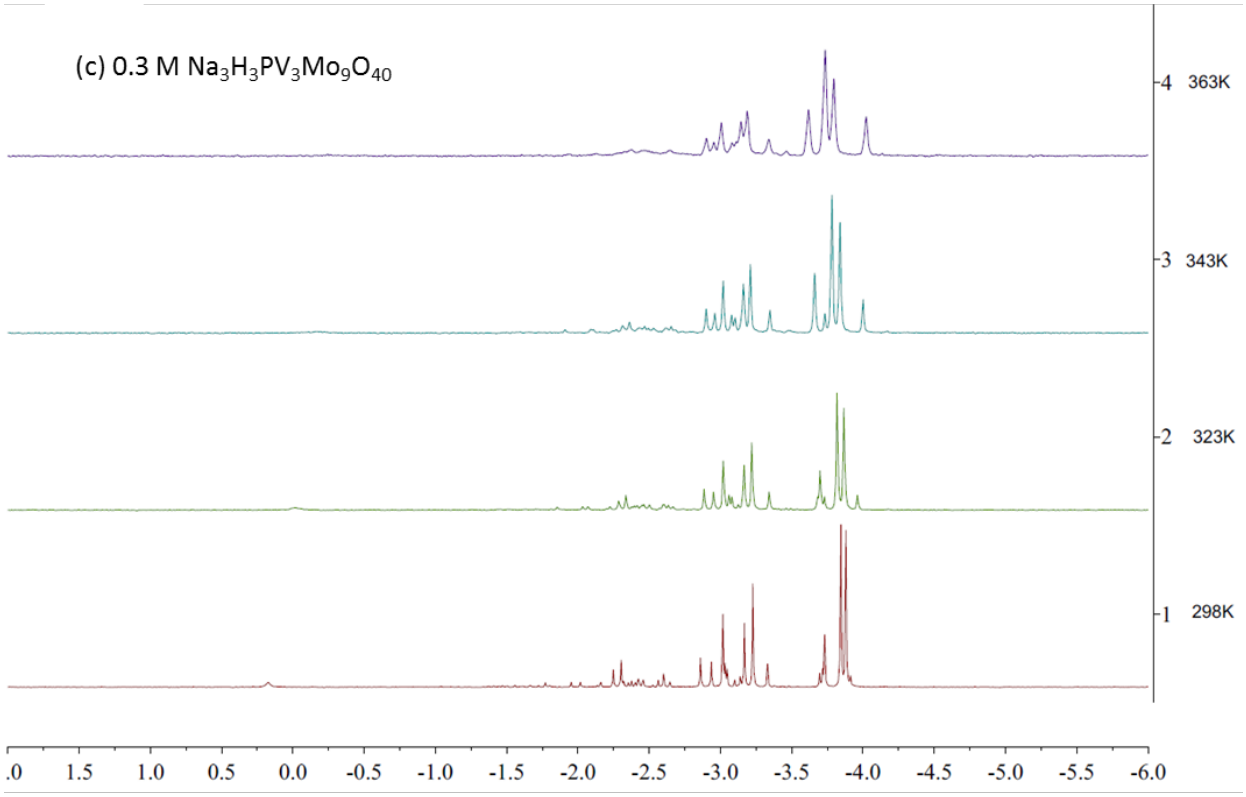

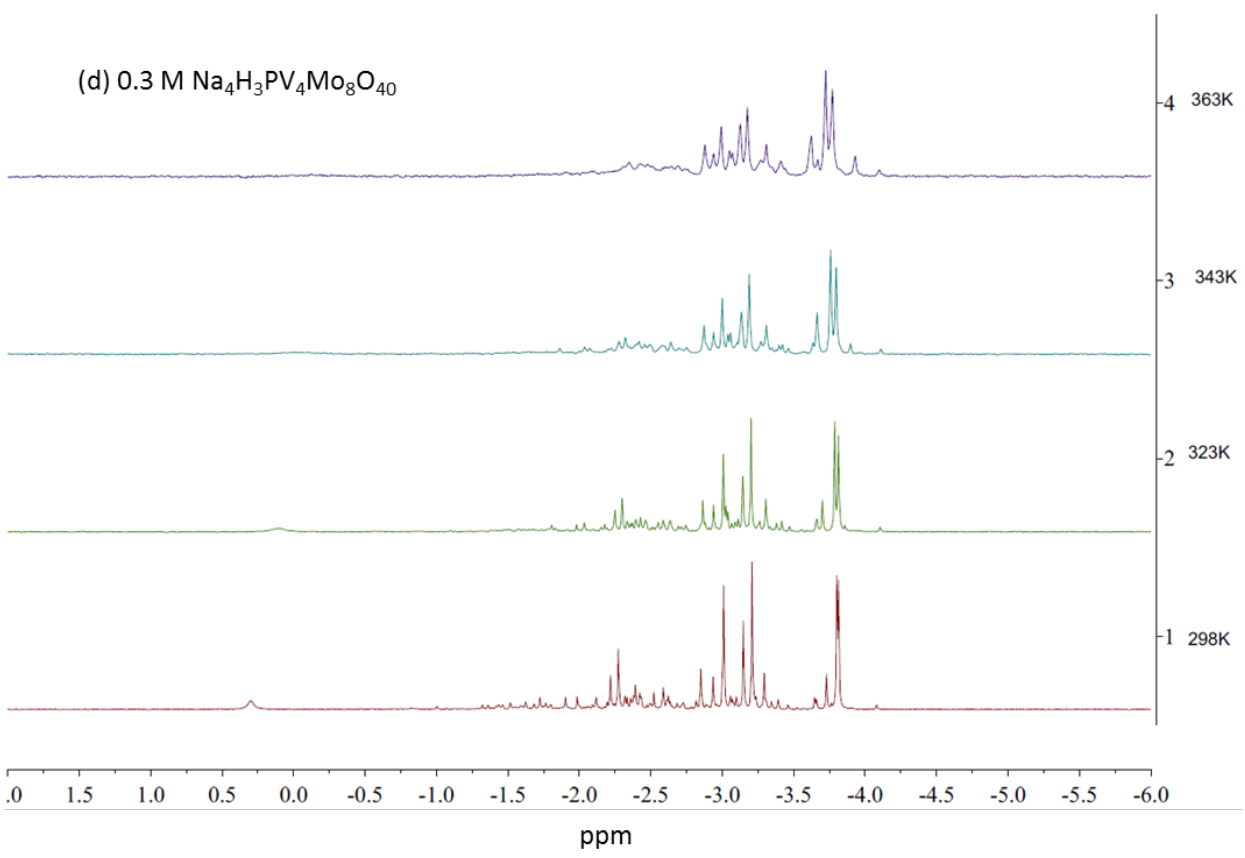

Figure S1: ^{31}P NMR spectra of the four POM catholytes at 298, 323, 343 and 363 K: (a) $H_6PV_3Mo_9O_{40}$; (b) $H_7PV_4Mo_8O_{40}$; (c) $Na_3H_3PV_3Mo_9O_{40}$; and (d) $Na_4H_3PV_4Mo_8O_{40}$.

Catholyte Redox Potential

Figure S2 illustrates reduction curves recorded using the in-line redox probe for the four catholytes (HV3, HV4, NaV3 and NaV4) in the CRRC test rig at 80°. Apart from a shift in voltage of approximately 700 mV, Figure S2 is almost identical to Figure 3a in the main text, suggesting the potential of the hydrogen anode is constant for all four catholytes.

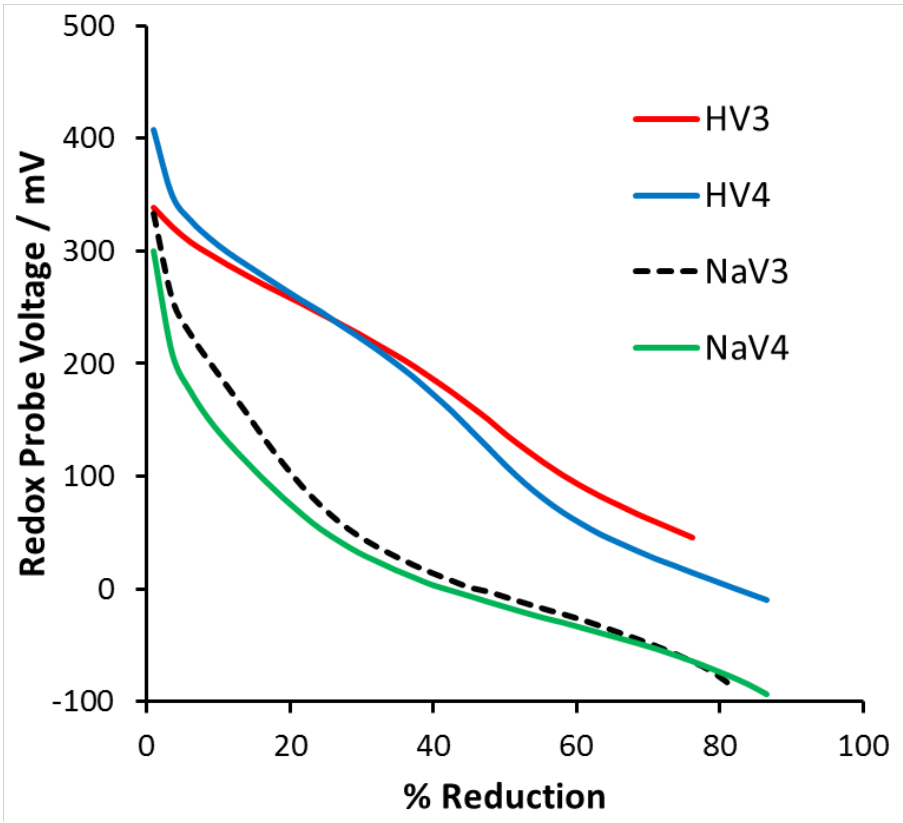

Figure S2. In-line redox probe voltage obtained with various catholytes over a range of reduction levels at 80°C.

Cell Performance

Figure S3 illustrates fuel cell performance curves for the HV3, NaV3 and NaV4 catholytes (all 0.3 M concentration) at a range of reduction levels.

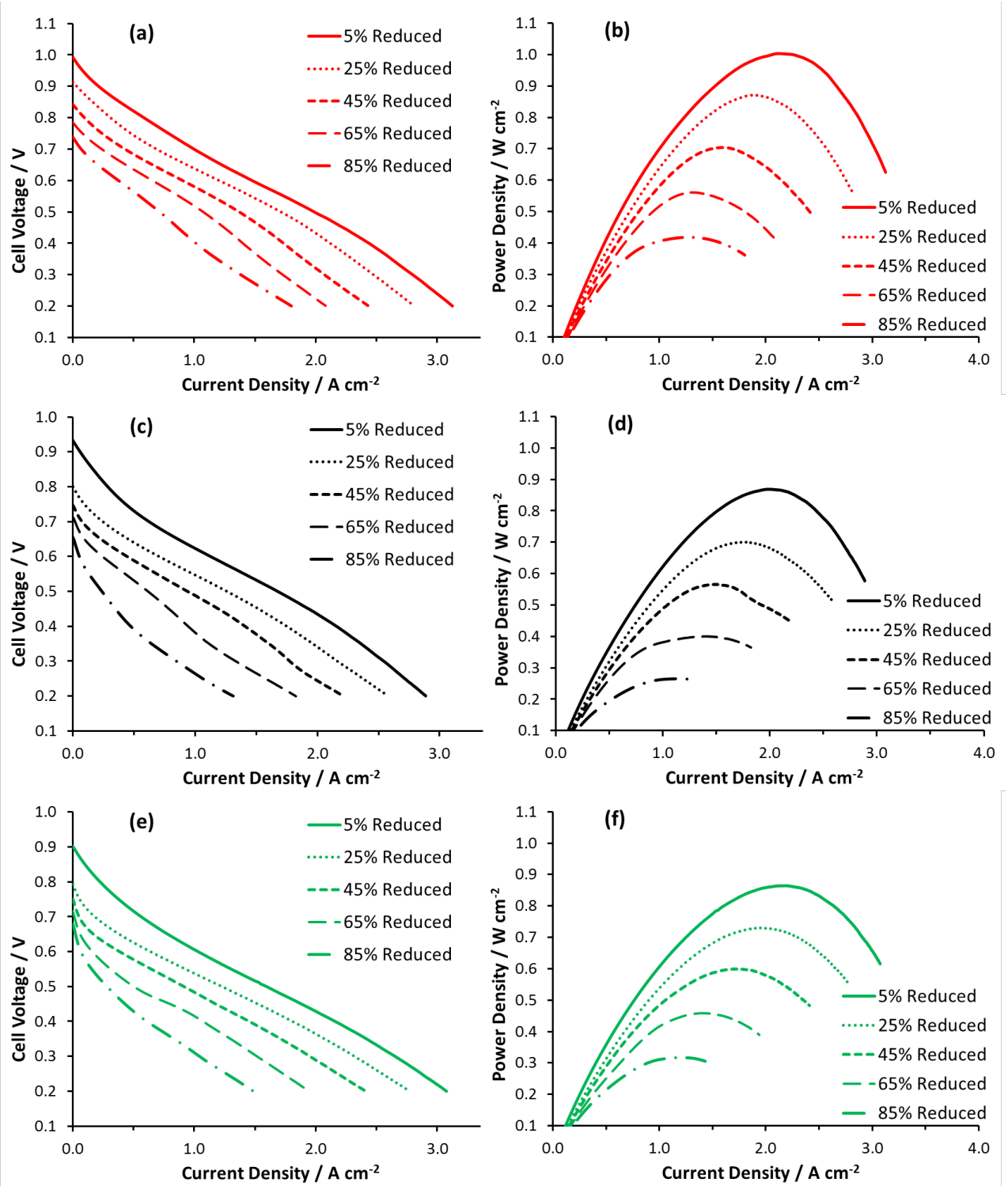

Figure S3. (a) *i-V* and (b) corresponding power density curves generated with 0.3 M HV3 at varying levels of reduction. (c) *i-V* and (d) corresponding power density curves generated with 0.3 M NaV3 at varying levels of reduction. (e) *i-V* and (f) corresponding power density curves generated with 0.3 M NaV4 at varying levels of reduction.

Durability Testing

A continuous 200-hour durability test was performed with 0.3 M $Na_4H_3PV_4Mo_8O_{40}$ (NaV4 - the most promising catholyte from the steady state performance tests) in a similar test rig to that described in

the main article. The cell build was identical to that used for performance testing apart from the electrode well depth was approximately 1.2 mm (as opposed to 1 mm for performance tests). This slightly larger well depth was used to reduce the pumping pressure and minimize the risks of leaks during long periods of unmanned operation. The cell and regenerator temperatures were held at 70 ± 3°C, the catholyte flow rate was 150 mL min^{-1}, air flow to the regenerator was 1 L min^{-1} and hydrogen pressure on the anode was 0.5 barg. During long periods of operation, the single cell system gradually loses water – the rate of evaporative losses (due to air bubbling) exceeds the rate of water production via oxygen reduction. For unmanned operation, an automated water top-up system was used to maintain the catholyte concentration at 0.3 M ± 10%. This consisted of a level detector on the sidearm of the regenerator vessel in communication with a water pump. As the concentration of the NaV4 POM decreased, the catholyte level dropped, triggering the pump to squirt a small quantity of ultrapure water into the regeneration vessel. During the durability test the cell was held at a constant load of 0.4 A cm^{-2}, with the cell voltage recorded every second. Every 5 hours, the cell returned to open circuit for 30 minutes. Throughout the 200-hour test, the anode was operated "dead-ended" (i.e. zero hydrogen flow) with a hydrogen purge (i.e. open and close the anode exhaust valve) every 5 minutes. The hydrogen purge eliminated water build up on the anode catalyst layer.

Figure S4a illustrates the cell operating voltage over the period of the 200-hour durability test. The large spikes above 0.8 V correspond to the times when the cell returned to open circuit. The thick wedge between 0.5 and 0.55 V is the cell voltage under current (0.4 A cm^{-2}) combined with downward spikes from the anode purge events. Figure S4b illustrates a 1-hour section of the same data. The anode purge events are now well separated and the cell operating voltage appears to have a sinusoidal pattern. The latter was caused by the control software for the cell temperature, which oscillated between 67°C and 73°C at the same frequency. Once the cell voltage settled after the initial start-up, no loss in performance was evident over the 200-hour period, indicating minimal cell degradation and good catholyte stability.

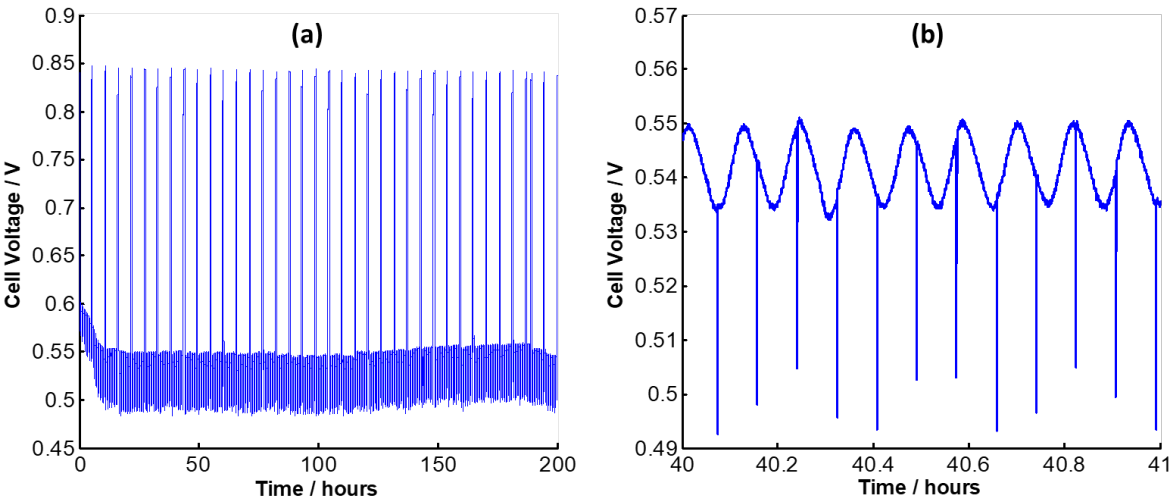

Figure S4. Plots of cell operating voltage vs. time over (a) 200 hours and (b) a 1-hour section of the 200-hour test.