Investigation of a Chemically Regenerative Redox Cathode Polymer Electrolyte Fuel Cell using a Phosphomolybdovanadate Polyoxoanion Catholyte

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Supporting Information

Figure S1 illustrates the chemically regenerative redox cathode (CRRC) proton electrolyte membrane (PEM) fuel cell test stand used throughout this investigation in the form of a Process and Instrumentation Diagram (P&ID). Figure S2 shows a photograph of the same apparatus. An expanded diagram of cell build components is given in Figure S3.

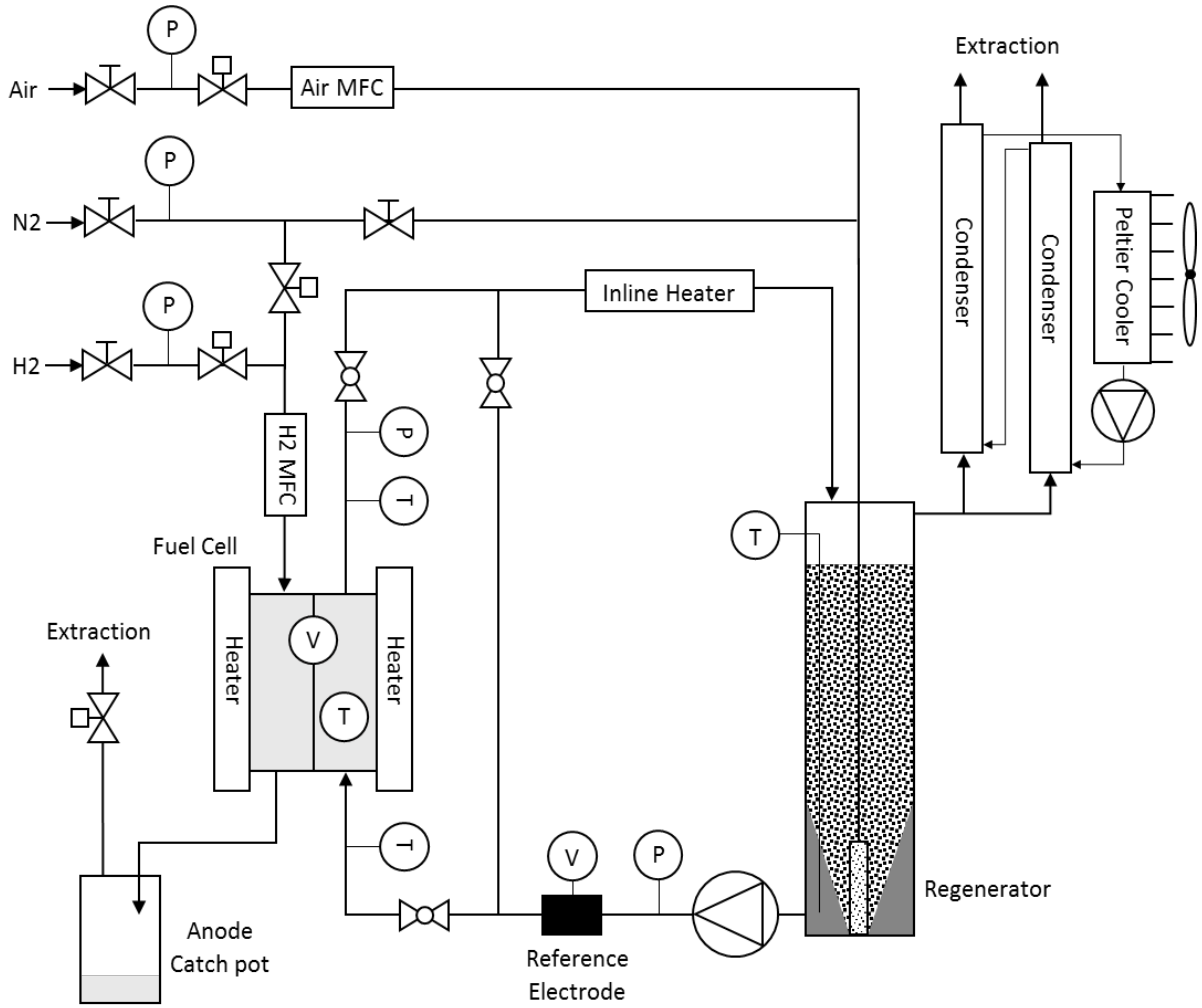

Figure S1. Simplified P&ID illustrating the CRRC PEM fuel cell test stand apparatus used throughout this investigation.

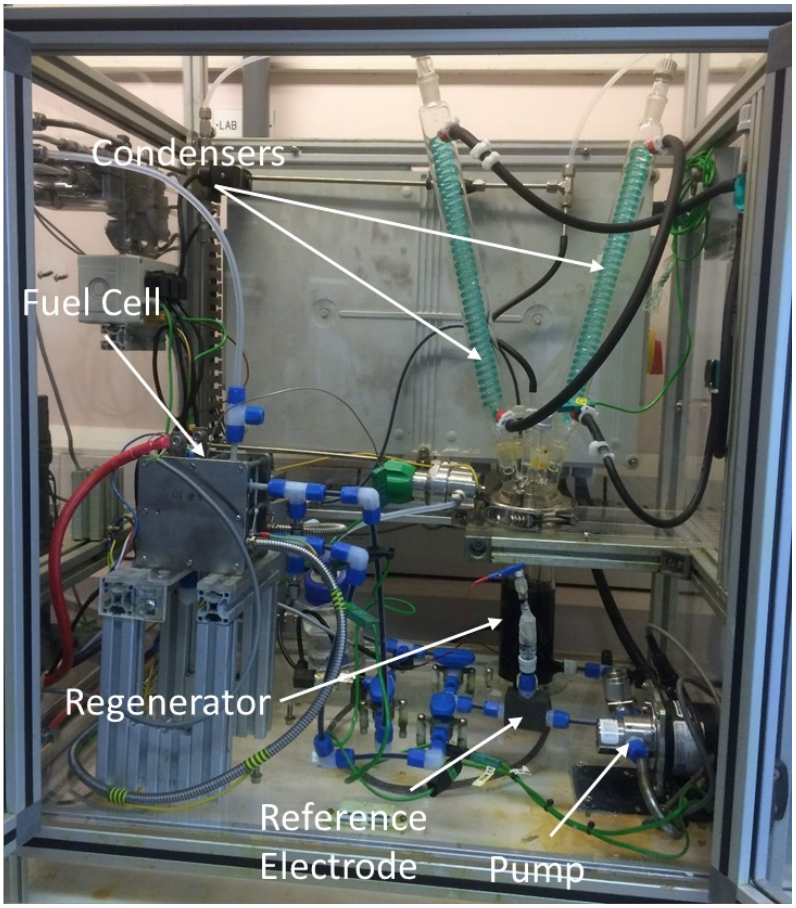

Figure S2. Photograph showing CRRC PEM fuel cell test rig apparatus used throughout this investigation.

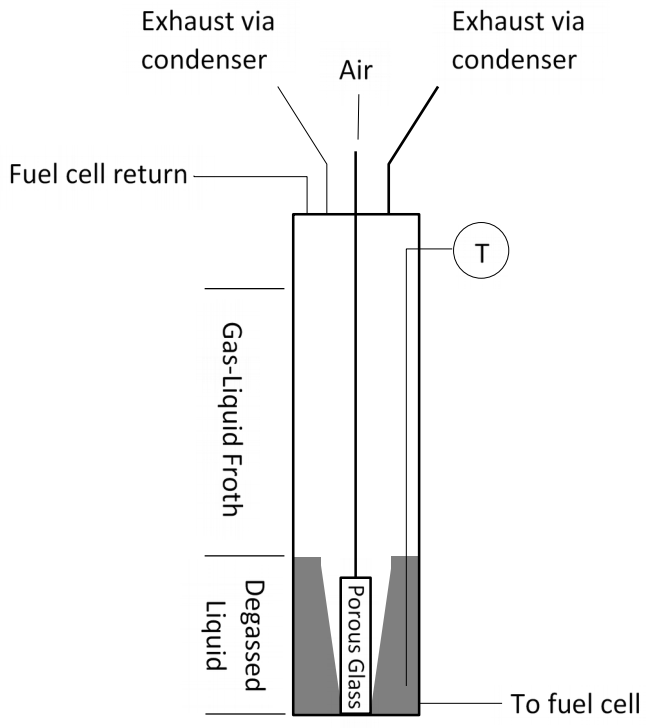

Figure S3. Basic concept design of the regenerator oxidation reactor.

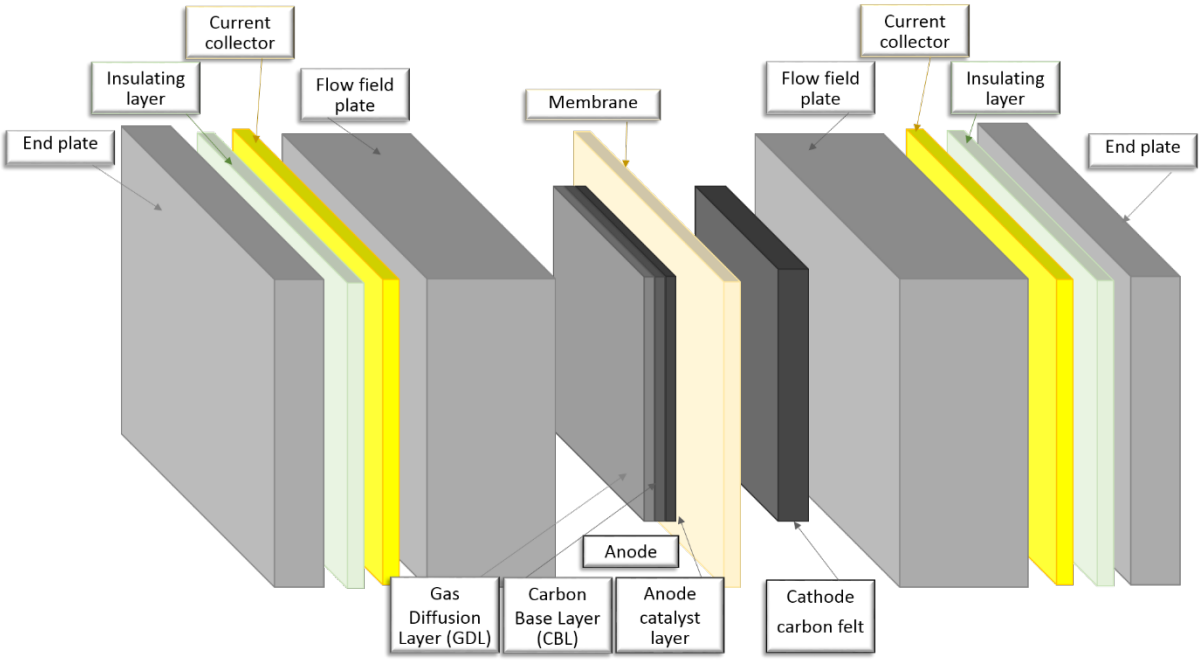

Figure S4. Expanded diagram of the cell build used throughout all experiments.

NMR Analysis of $H_6PV_3Mo_9O_{40}$

Figure S5 illustrates the ^{31}P NMR spectrum recorded from a fully oxidised sample of 0.3 M $H_6PV_3Mo_9O_{40}$ at 298 K. $^{31}P\{1H\}$ 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. The peak assignments are also shown in Figure S4, where V1 keggin represents (partially) protonated $[PV_1Mo_{11}O_{40}]^{4-}$, V2 keggin is (partially) protonated $[PV_2Mo_{10}O_{40}]^{5-}$, V3 keggin is (partially) protonated $[PV_3Mo_9O_{40}]^{6-}$, V4 keggin is (partially) protonated $[PV_4Mo_8O_{40}]^{7-}$ and Phosphate is (partially) protonated $[PO_4]^{3-}$.

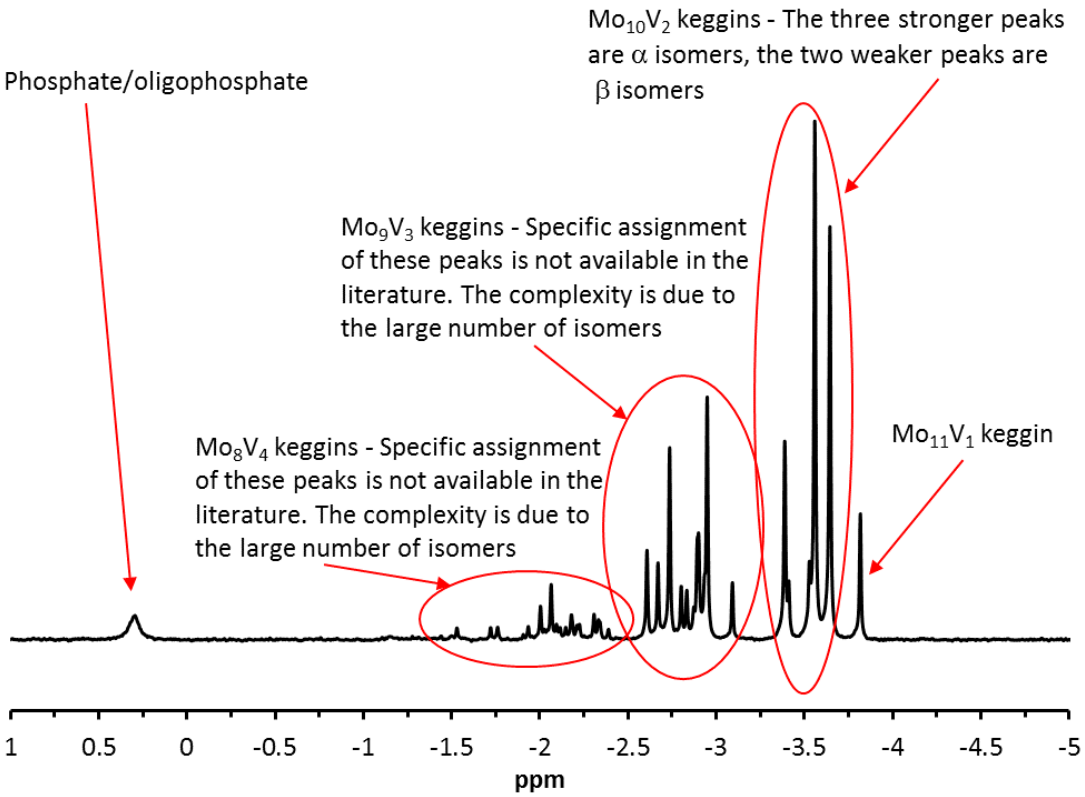

Figure S5. ^{31}P spectrum for a fully oxidised (i.e. 100% vanadium(V)) sample of 0.3 M $H_6PV_3Mo_9O_{40}$ at 298 K.

Figure 3 and the Nernst equation

Although the curves in Figure 3 (in the main article) suggest a Nernstian behaviour (as expected), it proved too difficult to fit a Nernst-type equation to the experimental data. There are at least 11 individual redox couples corresponding to the different vanadium species that contribute to the measured potential, each with their own standard redox potential, E^o:

Free vanadium:

$$VO_2^+ + e^- + 2H^+ \leftrightarrow VO^{2+} + H_2O \quad (1)$$

V1-Keggin:

$$\left[PV^{V}Mo_{11}O_{40}\right]^{4-} + e^- + H^+ \leftrightarrow \left[HPV_1^{IV}Mo_{11}O_{40}\right]^{4-} \quad (2)$$

V2-Keggin:

$$\left[HPV_2^{V}Mo_{10}O_{40}\right]^{4-} + e^- + H^+ \leftrightarrow \left[H_2PV^{IV}V^{V}Mo_{10}O_{40}\right]^{4-} \quad (3)$$

$$\left[H_2PV^{IV}V^{V}Mo_{10}O_{40}\right]^{4-} + e^- + H^+ \leftrightarrow \left[H_3PV_2^{IV}Mo_{10}O_{40}\right]^{4-} \quad (4)$$

V3-Keggin:

$$\left[H_2PV_3^{V}Mo_9O_{40}\right]^{4-} + e^- + H^+ \leftrightarrow \left[H_3PV_1^{IV}V_2^{V}Mo_9O_{40}\right]^{4-} \quad (5)$$

$$\left[H_3PV_1^{IV}V_2^{V}Mo_9O_{40}\right]^{4-} + e^- + H^+ \leftrightarrow \left[H_4PV_2^{IV}V_1^{V}Mo_9O_{40}\right]^{4-} \quad (6)$$

$$\left[H_4PV_2^{IV}V_1^{V}Mo_9O_{40}\right]^{4-} + e^- + H^+ \leftrightarrow \left[H_5PV_3^{IV}Mo_9O_{40}\right]^{4-} \quad (7)$$

V4-Keggin:

$$\left[H_3PV_4^{V}Mo_8O_{40}\right]^{4-} + e^- + H^+ \leftrightarrow \left[H_4PV_1^{IV}V_3^{V}Mo_8O_{40}\right]^{4-} \quad (8)$$

$$\left[H_4PV_1^{IV}V_3^{V}Mo_8O_{40}\right]^{4-} + e^- + H^+ \leftrightarrow \left[H_5PV_2^{IV}V_2^{V}Mo_8O_{40}\right]^{4-} \quad (9)$$

$$\left[H_5PV_2^{IV}V_2^{V}Mo_8O_{40}\right]^{4-} + e^- + H^+ \leftrightarrow \left[H_6PV_3^{IV}V_1^{V}Mo_8O_{40}\right]^{4-} \quad (10)$$

$$\left[H_6PV_3^{IV}V_1^{V}Mo_8O_{40}\right]^{4-} + e^- + H^+ \leftrightarrow \left[H_7PV_4^{IV}Mo_8O_{40}\right]^{4-} \quad (11)$$

Note, this assumes the keggins are in the "-4" anionic state and undergo 1-electron/1-proton redox reactions, both of which may be incorrect. However, given that there are at least 11 different standard redox potentials that are all probably pH dependent (some more than others) and the pH of the catholyte varies with reduction level, deriving the Nernst equation for the system is very challenging. For the purposes of the data analysis in this study, it is far easier to fit a polynomial equation to the data in Figure 3.

Table S1 gives initial and final vanadium(IV) fractions recorded before and after the *I-V* curves in Figure 5a. Where regeneration rates were slow (i.e. < 0.5 vanadium(IV) fraction), values were observed to drift significantly away from the initial target value despite the action of the regenerator.

Table S1. V3-POM vanadium(IV) fractions and corresponding open circuit voltage (OCV) values before and after *I-V* tests.

Initial Inlet V(IV) fraction	Initial OCV / mV	Final V(IV) fraction post *I-V* test	Final OCV / mV
0.05	996	0.27	924
0.25	926	0.46	848
0.45	854	0.59	796
0.65	778	0.67	786
0.85	730	0.80	742

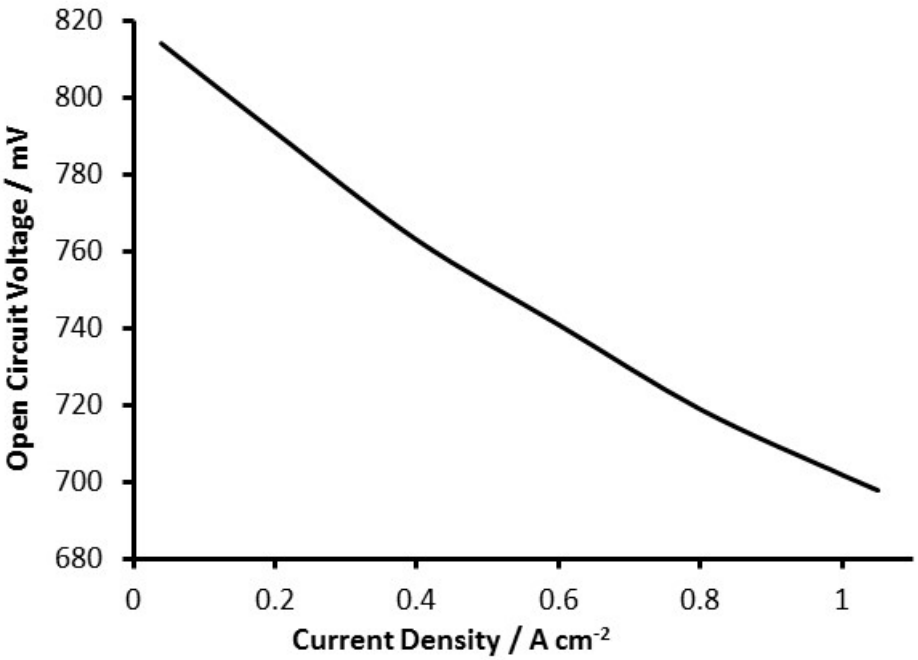

Figure S6. Predicted inlet catholyte potential (as a cell open circuit voltage) for the steady state *I-V* curve in Figure 5(a).