Towards Scalable Electrochemical Reduction Cells for Hexavalent Chromium

Authors: Collin Dunn, Alan Rassoolkhani, Cameron Lippert, James Landon

ElectraMet, 749 W. Short St., Lexington, KY 40508

Linear Sweep Voltammograms with Graphite Felt

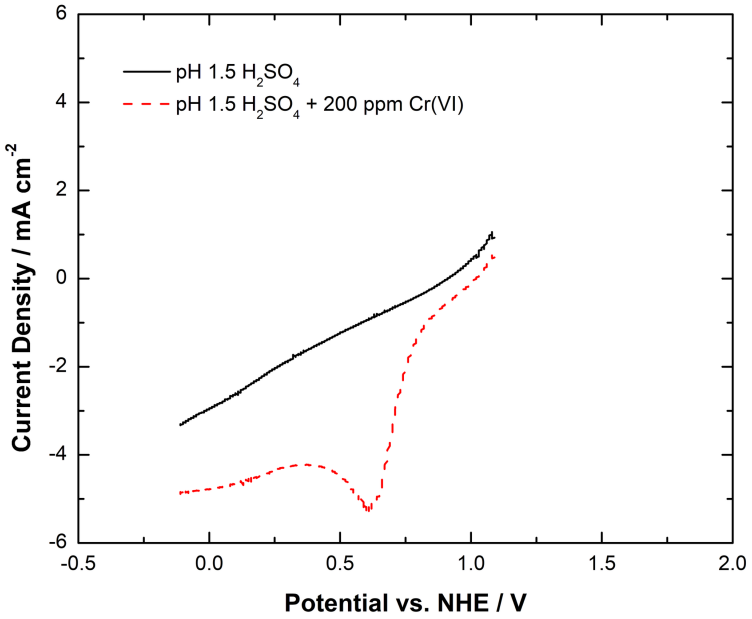

Figure S1: LSV at 10 mV/s in pH 1.5 sulfuric acid for graphitic carbon felt (black line) and pH 1.5 sulfuric acid with 200 ppm Cr(VI) for graphitic carbon felt (red dash).

Charge and current data from pH variation and effluent Cr(VI) studies.

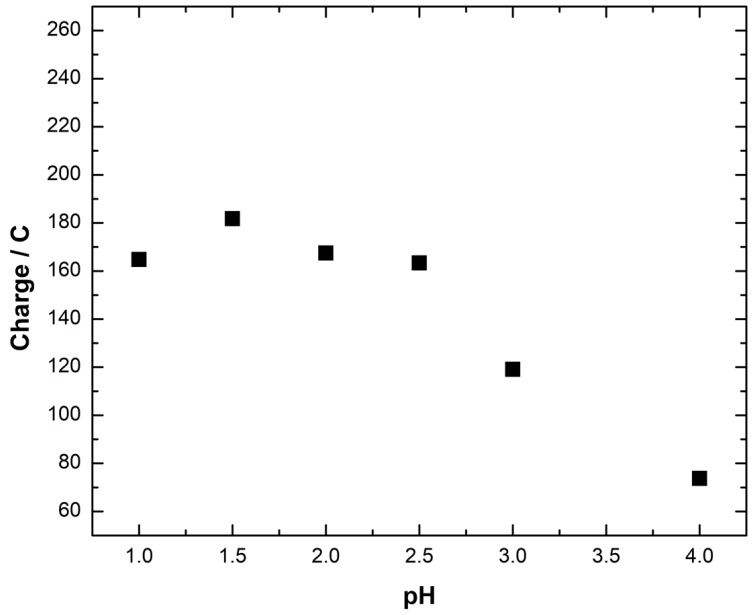

Figure S2: Charge passed over 20 minutes while applying 1.5 V at various pH values.

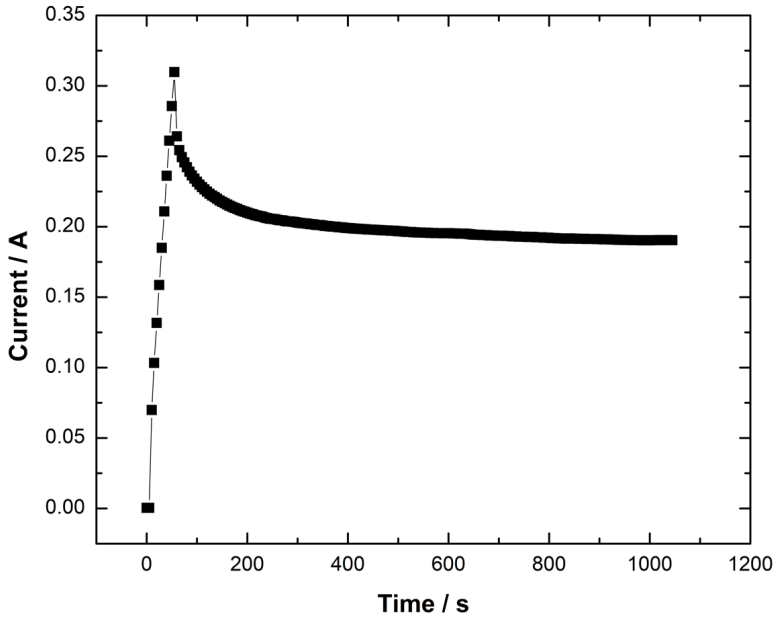

Figure S3: Current transient applying 1.5 V at pH 1.5.

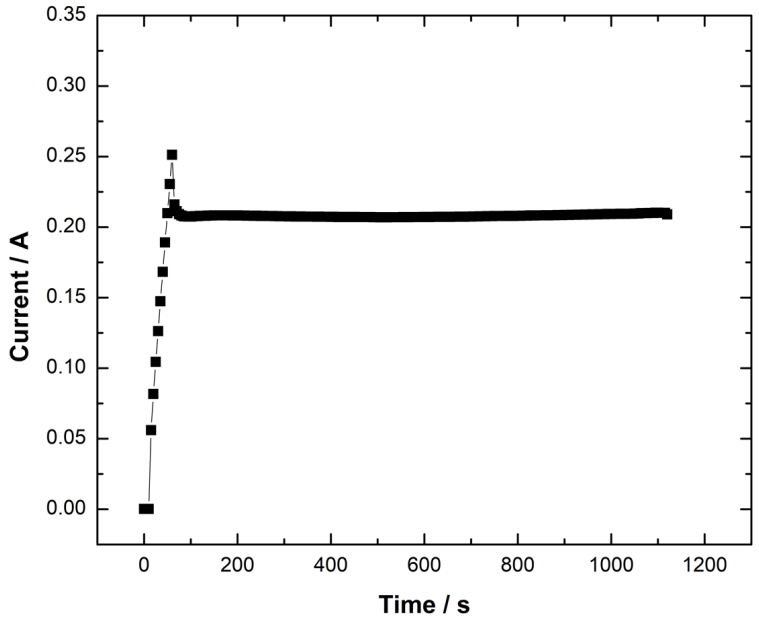

Figure S4: Current transient applying 1.5 V at pH 2.

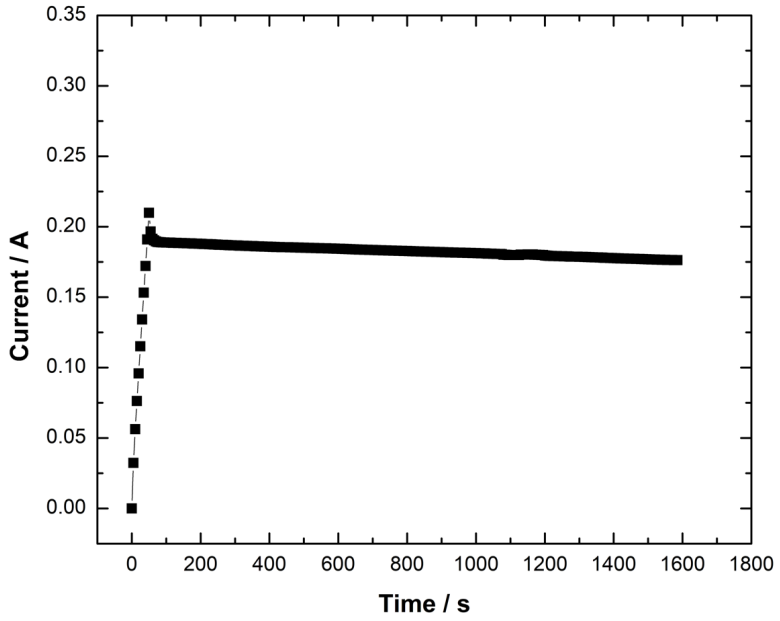

Figure S5: Current transient applying 1.5 V at pH 2.5.

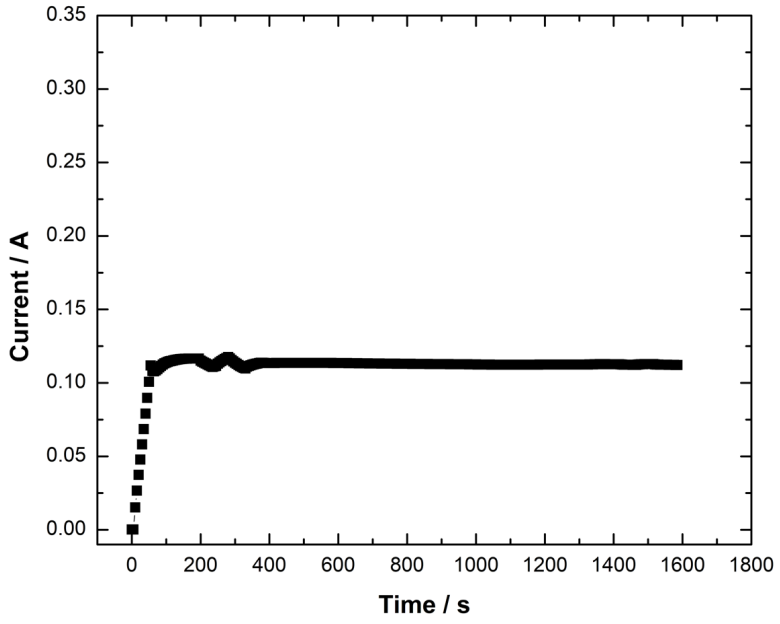

Figure S6: Current transient applying 1.5 V at pH 3.

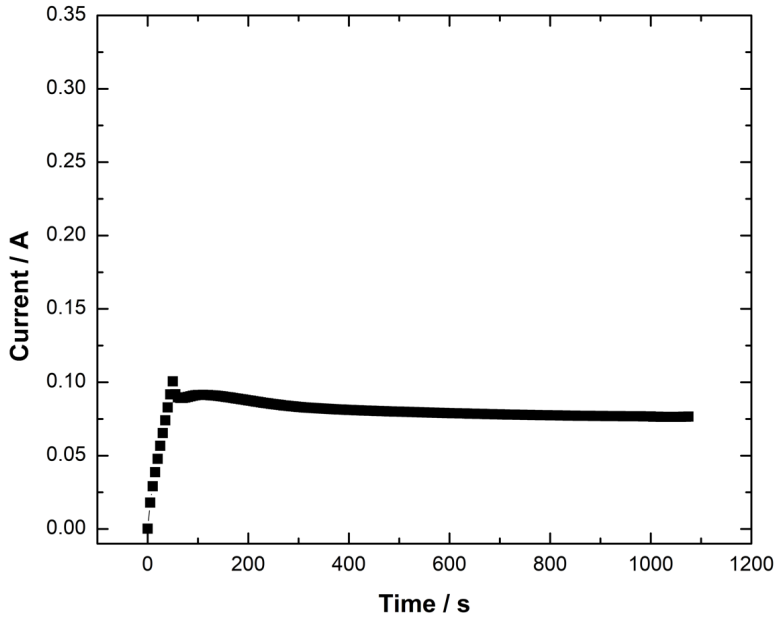

Figure S7: Current transient applying 1.5 V at pH 4.

Carbon electrode material specifications:

Graphitic felt electrodes were purchased with an initial, nominal thickness of 2.5 mm and a compressibility of approximately 15%. This material has a listed resistivity of less than 5 Ωmm. Specific surface area was also noted to be < 5 m^2/g. The activated carbon film anodes have a listed resistivity of less than 2 Ωcm and a thickness of around 150 microns. Specific surface areas were measured to be approximately 1,100 m^2/g with areal densities of approximately 32 mg/cm^2.

Carbon cathodes from pH adjustment studies.

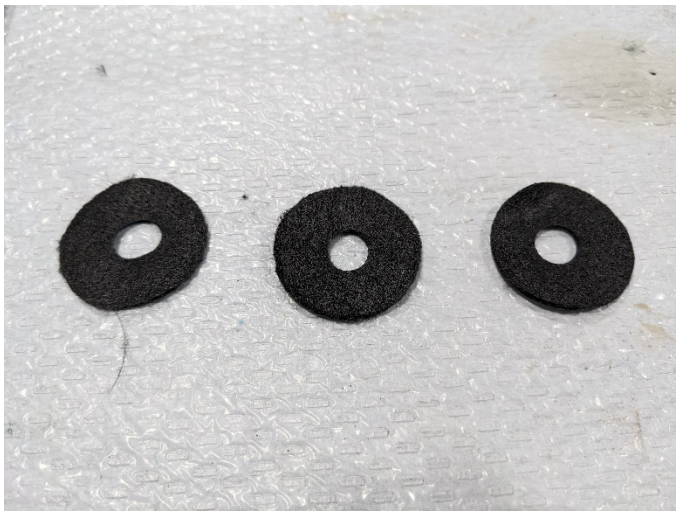

Figure S8: Used carbon cathodes from a deconstructed electrochemical cell used to reduce Cr(VI) in a pH 1.5 feed and an applied potential of 1.5 V.

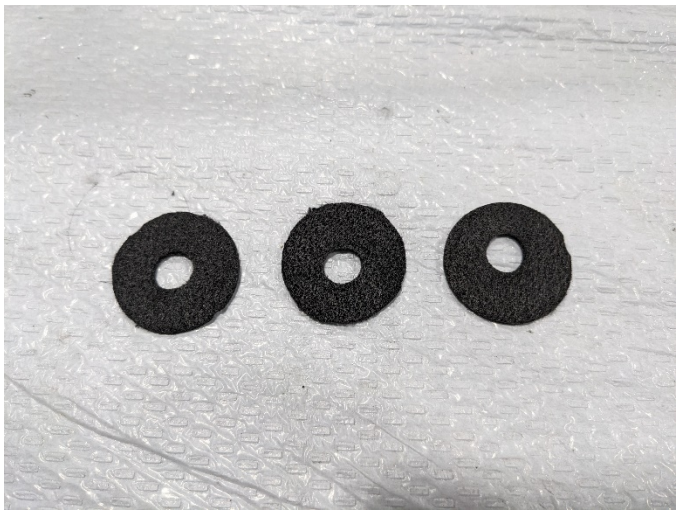

Figure S9: Used carbon cathodes from a deconstructed electrochemical cell used to reduce Cr(VI) in a pH 2 feed and an applied potential of 1.5 V.

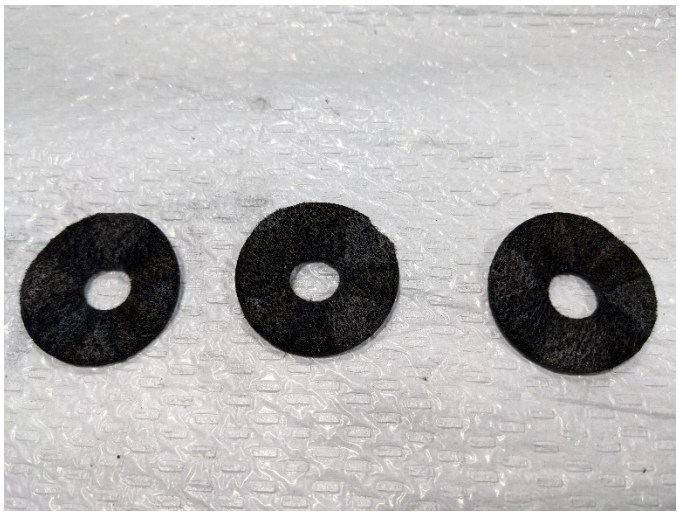

Figure S10: Used carbon cathodes from a deconstructed electrochemical cell used to reduce Cr(VI) in a pH 2.5 feed and an applied potential of 1.5 V.

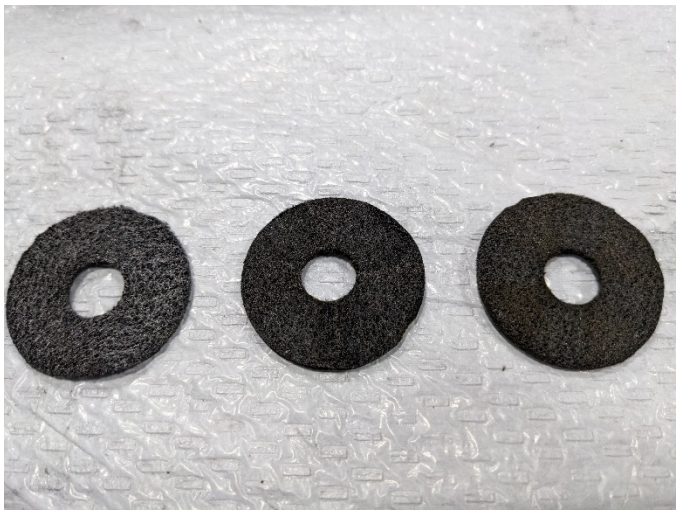

Figure S11: Used carbon cathodes from a deconstructed electrochemical cell used to reduce Cr(VI) in a pH 3 feed and an applied potential of 1.5 V.

Figure S12: Used carbon cathodes from a deconstructed electrochemical cell used to reduce Cr(VI) in a pH 4 feed and an applied potential of 1.5 V.

Long term chromium reduction experiment samples.

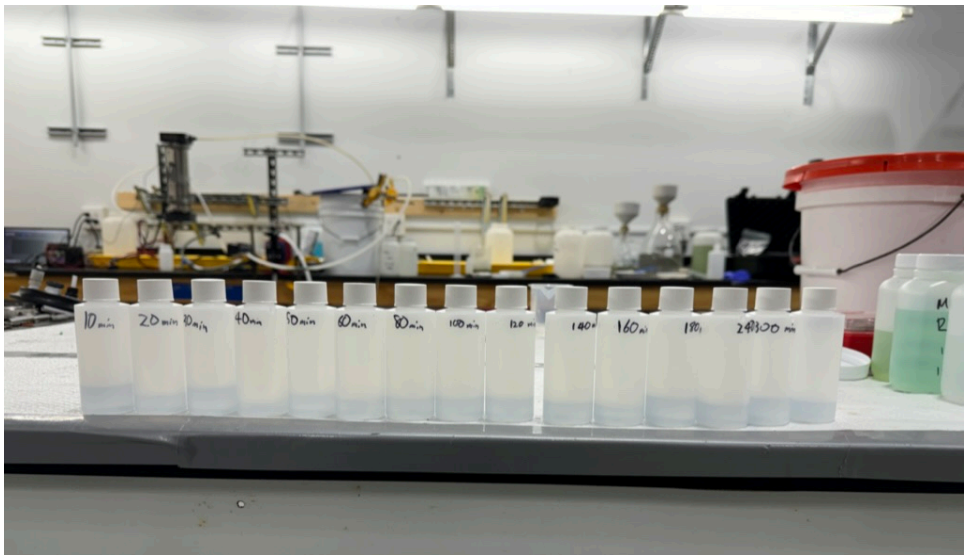

Figure S13: A series of hexavalent chromium samples taken over the course of a 6-hour reduction experiment using mixed-metal oxide anodes.

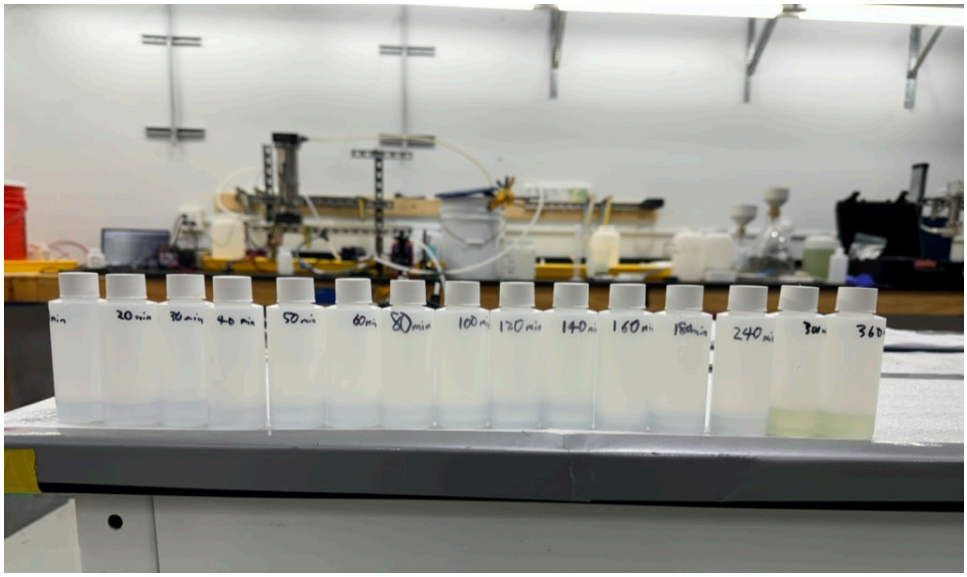

Figure S14: A series of hexavalent chromium samples taken over the course of a 6-hour reduction experiment using carbon-based anodes.

Long term chromium reduction experiment current data.

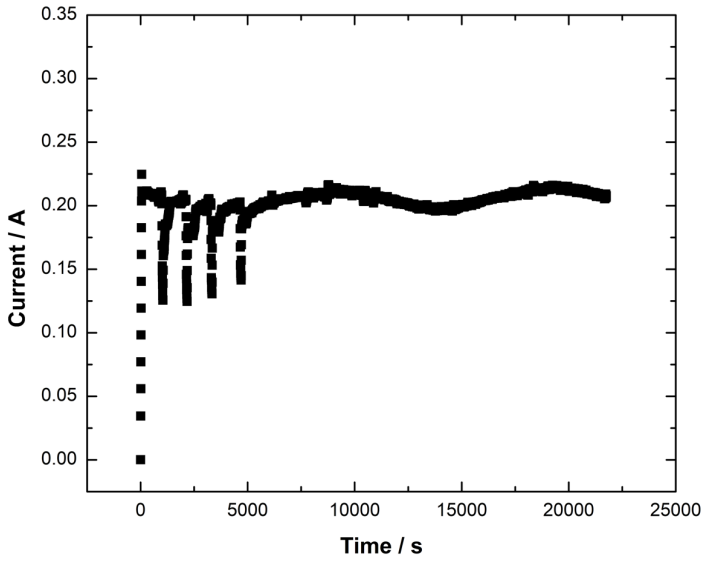

Figure S15: Current transient of a 6-hour reduction experiment using mixed-metal oxide anodes.

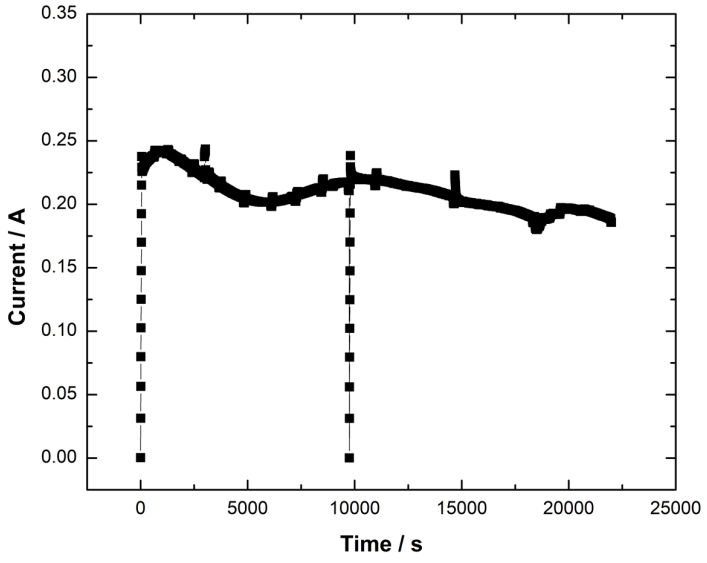

Figure S16: Current transient of a 6-hour reduction experiment using carbon-based anodes.

Repeat long term chromium reduction experiment samples.

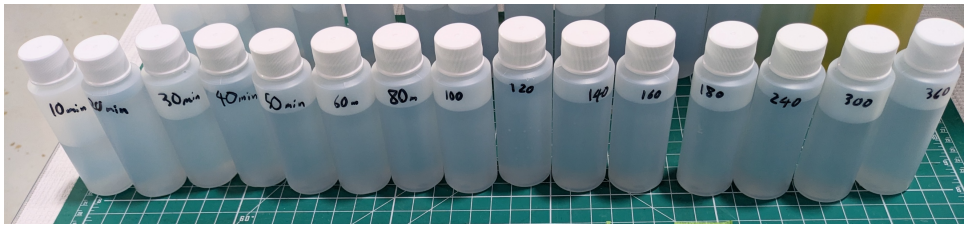

Figure S17: A series of hexavalent chromium samples taken over the course of a repeat 6-hour reduction experiment using mixed-metal oxide anodes.

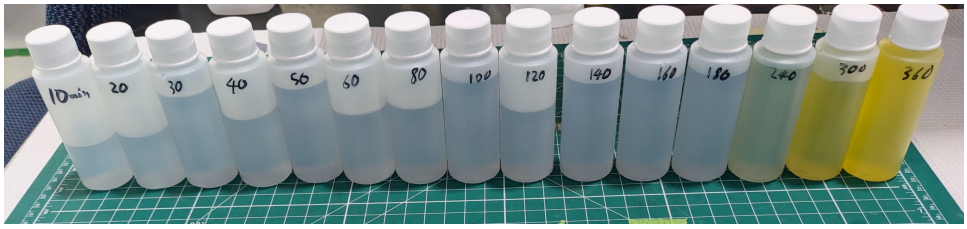

Figure S18: A series of hexavalent chromium samples taken over the course of a repeat 6-hour reduction experiment using carbon-based anodes.

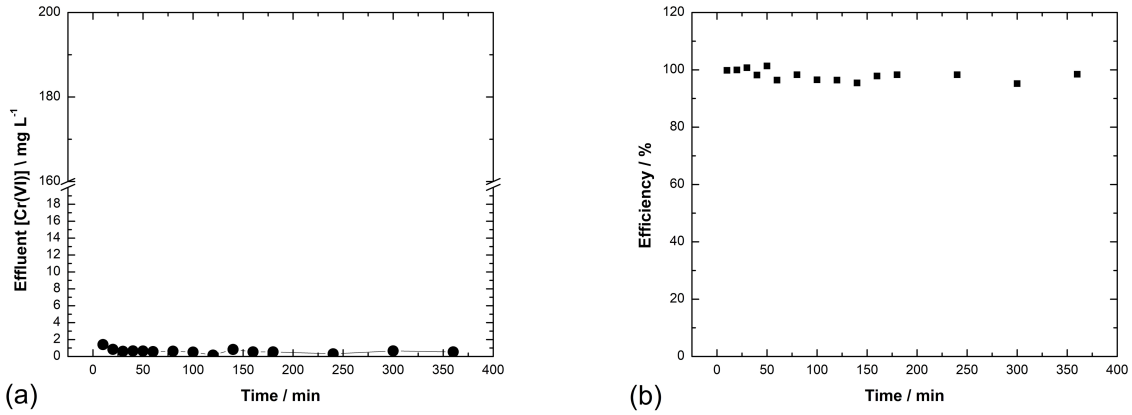

Figure S19: Repeat long term removal results with mixed-metal oxide showing complete reduction of Cr(VI) for six hours of operation. (a) Effluent [Cr(VI)] versus time and (b) charge

efficiency of the process. Applied potential was 1.5 V with a 200 ppm Cr(VI) feed solution at pH 1.5 and flow rate of 12 ml/min..

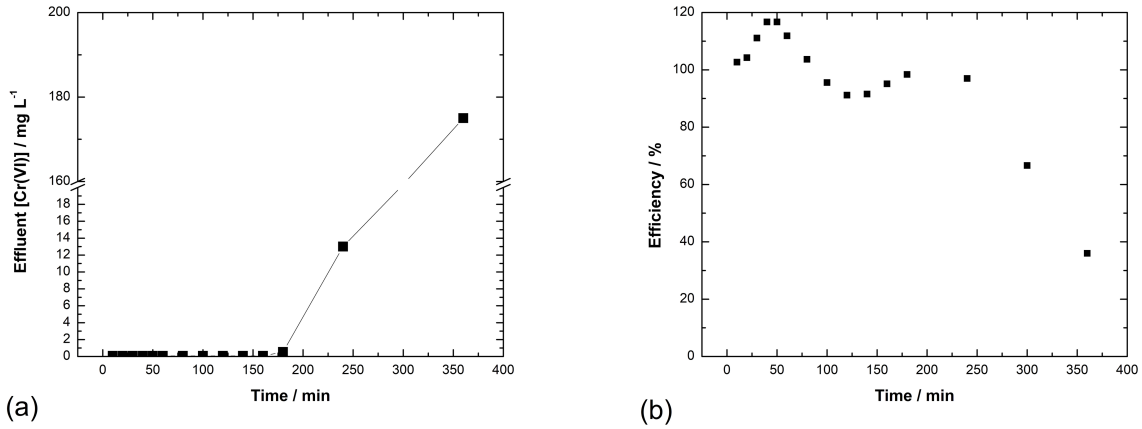

Figure S20: Repeat long term removal results with carbon anodes showing breakthrough of Cr(VI) into the cell effluent after 6 hours of operation. (a) Effluent [Cr(VI)] versus time and (b) charge efficiency of the process. Applied potential was 1.5 V with a 200 ppm Cr(VI) feed solution at pH 1.5 and flow rate of 12 ml/min.

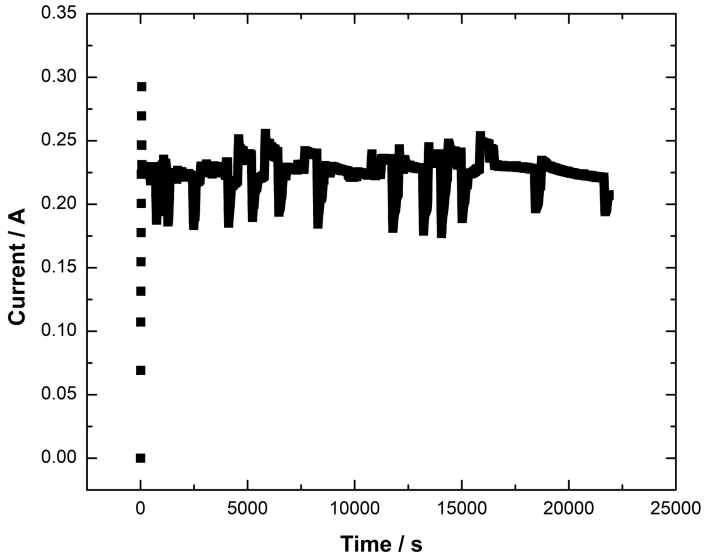

Figure S21: Current transient of a repeat 6-hour reduction experiment using mixed-metal oxide anodes.

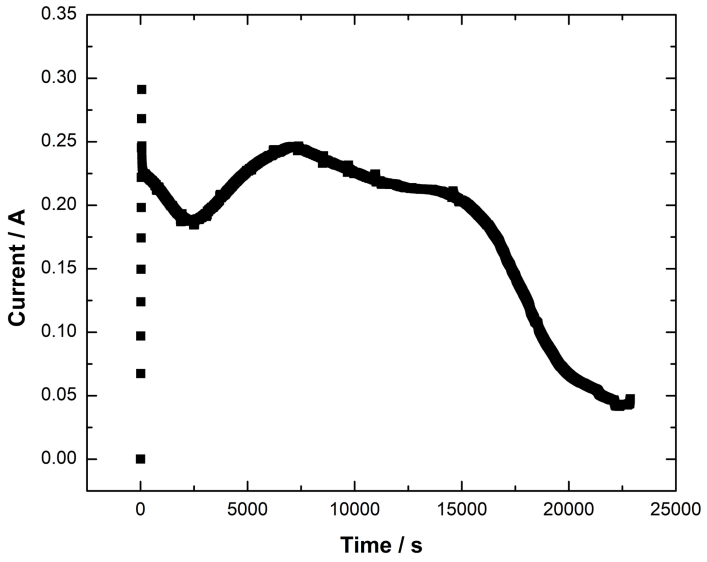

Figure S22: Current transient of a repeat 6-hour reduction experiment using carbon-based anodes.

Table S1: pH measurements of effluent from long term LiCAP and MMO anode studies.

Time (min)	LiCAP Effluent pH	MMO Effluent pH
10	1.55	1.56
20	1.63	1.56
30	1.54	1.58
40	1.51	1.54
50	1.55	1.52
60	1.52	1.52
80	1.56	1.51
100	1.55	1.54
120	1.51	1.54
140	1.6	1.51
160	1.52	1.53
180	1.56	1.54
240	1.54	1.55
300	1.45	1.54
360	1.42	1.56

Resistivity of anodes:

Two pieces of each carbon anode from the long-term reduction experiment were cut into 1 cm wide strips. Samples from an unused carbon anode were also cut to this shape. Due to the small size of the anodes, only 2 pieces could be produced from each electrode. The thicknesses of all pieces were measured as 365 microns by a digital micrometer. The leads of a multimeter were placed in the center of a strip of anode 3.5 cm from one another, and the resistance value was read from the multimeter. Based on the cross-sectional area of the pieces and the 3.5 cm path length, resistivity values were calculated for each piece and are presented in Table S1.

Table S2: Resistance and resistivity measurements of carbon anodes.

Sample	R (kΩ)	ρ (Ω·cm)	Mean ρ (Ω·cm)
Unused carbon anode - sample 1	2.519	26.27	26.92
Unused carbon anode - sample 2	2.644	27.57	
Carbon anode 1 - sample 1	3.944	20.57	36.72
Carbon anode 1 - sample 2	5.07	52.87	
Carbon anode 2 - sample 1	100.6	1049	2980
Carbon anode 2 - sample 2	471.0	4911	
Carbon anode 3 - sample 1	68.4	713.3	929.2
Carbon anode 3 - sample 2	109.8	1145	

There is a large increase in resistivity in the used anodes compared to the fresh material. Additionally, different anodes, at different positions in the electrochemical cell show very different resistivities. This is consistent with previous experience using cell geometries of this type, where minor differences in flow path can lead to uneven electrical load on the anode-cathode pairs. The increase in resistivity is consistent with oxidation of the carbon anodes and with the loss of cell efficiency seen at the end of the long-term reduction experiment.

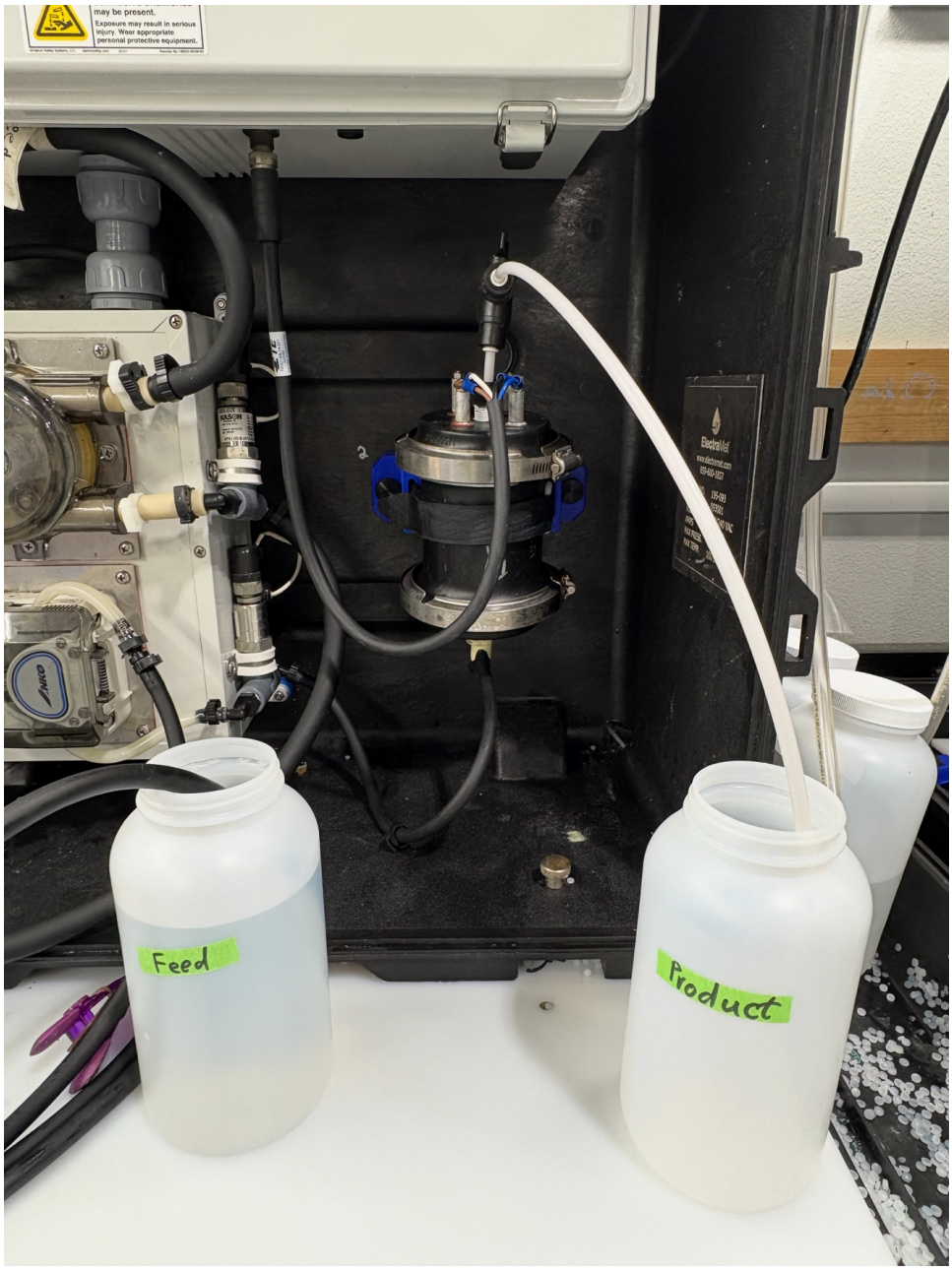

Figure S23: Electrochemical cell used for Cr(VI) reduction studies.

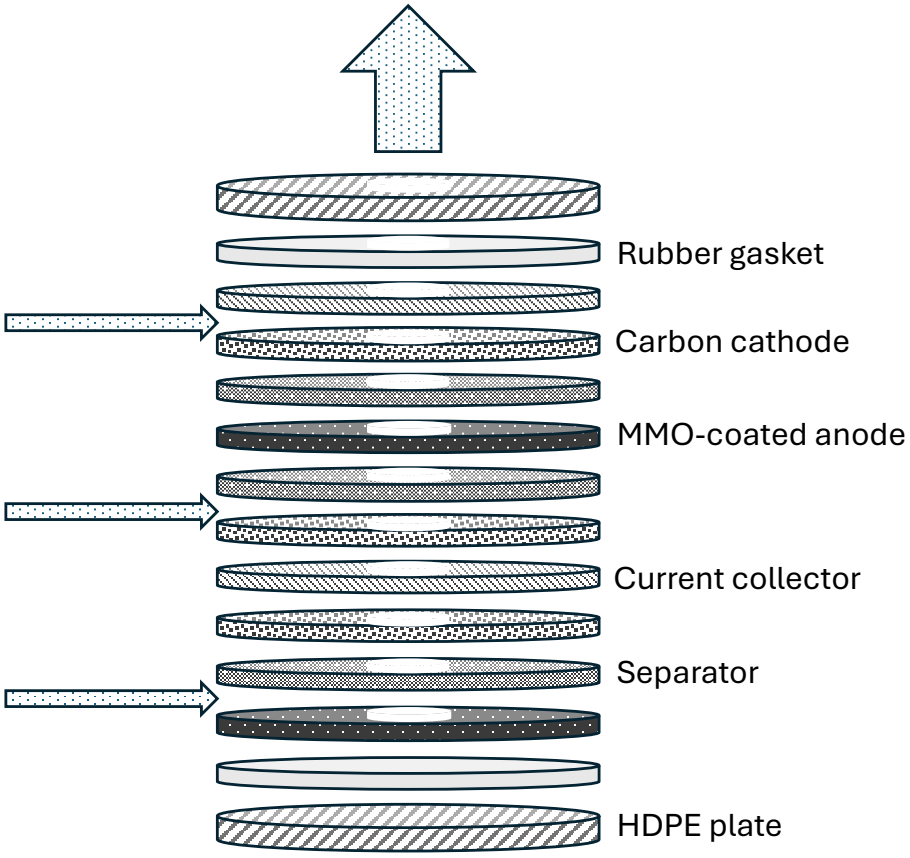

Figure S24: Electrochemical cell stack components used for Cr(VI) reduction studies. The MMO-coated anode is replaced with the LiCAP carbon film anode for the all-carbon cell studies.

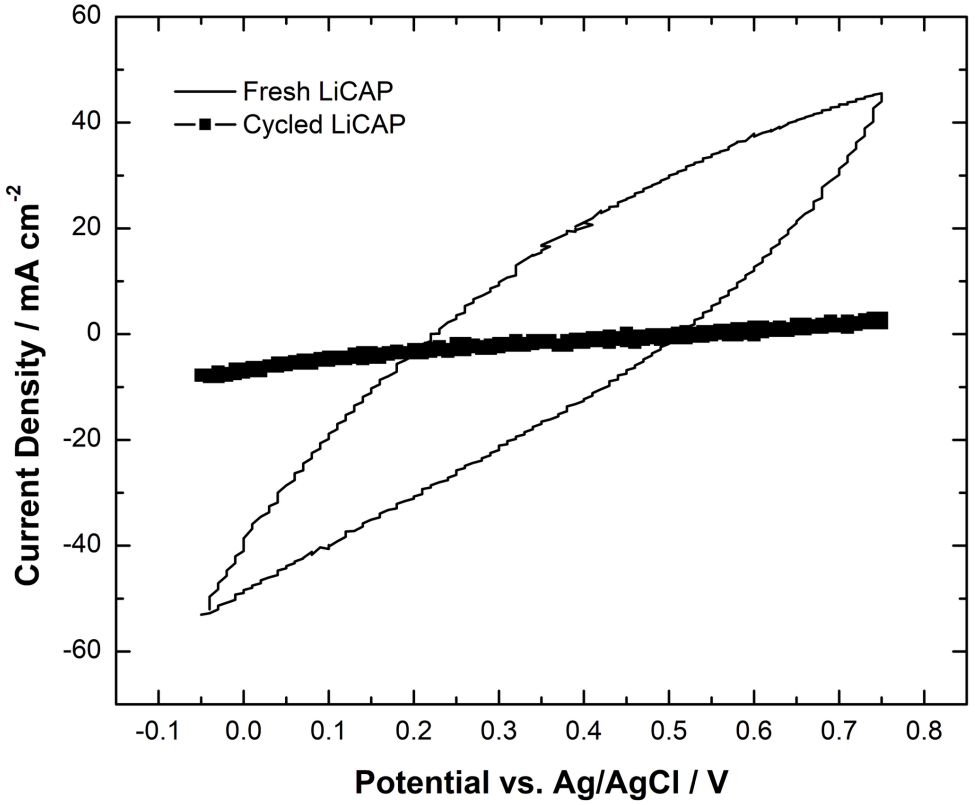

Figure S25: Cyclic voltammograms (CV) at 10 mV/s for fresh (line) and cycled (square) LiCAP carbon film anodes in 0.1 M H_2SO_4.