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SI for "Exploring the Scope of Capacitance-Assisted Electrochemical Carbon Dioxide Capture"

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1. Experimental methods

1.1. Cell design

The electrochemical cell was designed and constructed in-house. Shown in Figure S1 are technical drawings of the cell lid design which could hold up to four physically separated plate electrodes.





Figure S1. Technical drawings of the cell lid design.

The photographs in Figure S2 further clarify how the different anode electrode configurations used to collect the data reported in the paper were achieved. Experiments at 10 mA with 1 aluminium plate and 1, 2 and 3 graphite anodes were all run with an aluminium plate attached to the red connector and either 1 graphite plate attached to the blue connector, or 2 graphite plates attached to the blue and black connectors or 3 graphite plates attached to the blue, black and green connectors. In experiments at 20 mA with different anode configurations there was always an aluminium plate connected to the red connector and a graphite plate attached to the blue connector, the additional aluminium was added to the green connector and additional graphite to the black connector.

(i) C+Al anode, touching (graphite and aluminium plate attached to blue connector)



(ii) **C+Al anode, separate** (graphite plate attached to blue connector and aluminium plate attached to red connector)



(iii) **2C+2AI anode, separate** (graphite plates attached to blue and black connectors and aluminium plate attached to red and green connectors)



Figure S2. Photographs of the different anode electrode configurations.

A glass lining was placed inside the electrochemical cell to enable the electrolyte cell volume to be reduced from 600 mL (used in experiments reported in Figure 2 of the paper) to 250 mL (used in experiments in Figure 3). Figure S3 shows a photograph of this inner glass liner in place in the cell base.



Figure S3. Photograph of the inner glass cell lining used to reduce the electrolyte solution volume from 600 mL to 250 mL.

1.2. Electrochemical methodology

As shown in Figure S2, the electrodes were held in place by the cell lid and a glass liner (Figure S3) was used to ensure that either an electrolyte volume of 600 or 250 mL would result in an anode electrode submersion depth of 30 mm. The aluminium anode components (plates measuring height 50 mm by width 30 or 15 mm by depth 2 mm) were cut in-house from a sheet purchased from Alaco (Grade 6082, Temper T6), with an aluminium content of 95-98%. The used to make anode electrodes was purchased from OLMEC, graphite grade MCCA, see http://www.olmec.co.uk/technical data downloads/Technical Data medium grained Graphite.pdf and was likewise cut in-house to plates of dimension height 50 mm by width 30 or 15 mm by depth 2 mm. The cathode was a platinum wire (Advent, >99.95%, 1.5 mm diameter) and electrode voltages were monitored relative to a Ag/AgCl (3 M KCl_(ag), BASi) reference electrode (see 1.2). A pre-calibrated pH probe (see 1.3) was also used to follow reaction progress.

The constant-current chronopotentiometric method used in this study is analogous to that of our previous paper.¹ Electrolyte solution of 1 M NaCl_(aq) (250 or 600 mL) was added to the electrochemical cell, it was charged with a 2 cm stirrer bar and an o-ring was placed into the recessed space in the cell base (see Figure S3). The cell lid (see Fig. 1, main paper and Figure S2) containing the electrode components was screwed down to give a gas tight seal onto the o-ring and the cell was then placed under a 5% CO₂/95% N₂ atmosphere at a flow rate of 50 mL min⁻¹ and room temperature for an equilibration time of 4 or 7 h, with a solution stir rate of 500 rpm. Following this equilibration stage, using a Voltalab 50 potentiostat with VoltaMaster software a current (5-40 mA) was passed for 18 or 24 h and the cell was held at open circuit potential (OCP) for a further 2 or 7 h post-electrolysis.

1.3. H₂ detector calibration

An in-line gas detection instrument containing an AlphaSense H2-BF sensor was constructed in-house. This is capable of detecting hydrogen between 0-5000 ppm. The instrument was calibrated by dilution of a 5% H_2 / 95% N_2 gas stream with a pure N_2 gas stream by mass flow controllers to generate the plot shown in Figure S4.



Figure S4. Plot of H₂ detector calibration curve.

1.4. Reference electrode calibration

The Ag/AgCl (3 M KCl_(aq)) reference electrode was calibrated using the potassium ferricyanide redox couple. Cyclic voltammetry assessed the average redox potential (E_{χ}) and this was related to a literature value.



Figure S5. Example cyclic voltammogram of 10 mM ferricyanide in 0.1 M pH7 phosphate buffer between -0.4 and 0.8 V vs Ag/AgCl for the calibration relative to SHE. Experimental conditions: starting potential: 0.2 V vs Ag/AgCl; scan rate: 50 mV s⁻¹; total number of scans: 8; equilibration time: 10 s.

Table S1. Calculating the reference electrode conversion factor.

Run	<i>E_{p,a}</i> (V vs Ag/AgCl)	<i>E_{p,c}</i> (V vs Ag/AgCl)	E _{1/2} (V vs Ag/AgCl)	Reported E _{1/2} (V vs SHE) ²	Conversion factor for V vs Ag/AgCl to V vs SHE (V)
1	0.275	0.185	0.230		
2	0.285	0.180	0.233	0.425	0.194
3	0.285	0.175	0.230		
		Average	0.231 ± 0.0014		

1.5. pH probe calibration

The VWR double junction Pellon pH probe was connected to a DT-4000ZC voltmeter and the output was calibrated against a range of pH buffered solutions (Fisher Scientific) prior to each electrochemical experiment.



Figure S6. A sample pH probe calibration curve.

1.6. Quantifying carbon in the solid via TGA-IR

To obtain solid samples for analysis, post-electrochemistry the electrolyte was filtered and the precipitate dried *in vacuo*. To quantify the carbon-content in such a dried sample, an aliquot (*ca* 40 mg) was placed into a pre-calcined alumina cup inserted into Netzsch 409 STA for thermogravimetric analysis (TGA). The atmosphere was placed under a vacuum then nitrogen-purge cycle three time. The sample was then purged under a continuous nitrogen flow of 100 mL min⁻¹ for 10 minutes before heating began from 25 °C to either 500 or 1300 °C at a ramp rate of 10 °C min⁻¹ under the same flow of nitrogen. Throughout this experiment the exit gas was transferred through a 200 °C transfer pipe to a Bruker Equinox 55 FT-IR instrument for gas analysis. IR spectra were recorded every 34 seconds in the range 4000 – 500 cm⁻¹ with a resolution of 4 cm⁻¹ with 64 scans per spectrum. Spectra were recorded relative to a nitrogen background. To relate the integration of the CO₂ IR peak area to the amount of CO₂ obtained, a calibration curve using CaCO₃ (Sigma Aldrich, \geq 99%) was obtained, using the method described previously.¹

1.7. Solution titration analysis

Using the method outlined in Vogel's titration method,³ an aliquot (4 mL) of filtered electrolyte solution was taken for analysis. 0.01 M NaOH_(aq) (16 mL) was added to the sample solution. Added to this was three drops of phenolphthalein and 10_{wt} % BaCl_{2 (aq)} (20 mL). This was titrated against 0.01 M HCl_(aq) until the solution turned from pink to colourless.

2. Varying the Al size and Al-to-C separation

Graphite and aluminium plates of dimension either height 50 mm by width 15 mm by depth 2 mm ("21 mm, small" and "64 mm" experiments) or height 50 mm by width 30 or 15 mm by depth 2 mm ("21 mm, large" experiment) were arranged in separate slots in the electrochemical cell lid to investigate the impact of separation distance on the carbon capture chemistry using 5 mA current runs, as summarised in Figure S7 and Table S2. The separation distances quoted are measured from the centre point of each plate, as illustrated in Figure S7.



Figure S7. (a) Illustration of how the separation distance between the aluminium and graphite components was varied and (b) voltage time traces. In (b) the solid lines indicate the anode voltage and the dashed lines denote the cathode voltage. Experiments conducted using a 5% CO_2 + 95% N_2 gas mixture of total flow rate 50 mL min⁻¹. A 5 mA current was applied between the 4 h and 22 h time point (18 h). Cell volume of 250 mL 1 M NaCl_(aq) electrolyte, Pt cathode and room temperature.

C-Al separation	C in solution /	C in solid /	Total C /	Energy cost ^a /
	mmol	mmol	mmol	kJ mol _{co2} -1
21 mm, small	0.7	0.1	0.8	180
21 mm, large	0.5	0.1	0.6	200
64 mm	0.7	0.1	0.8	160

Table S2. Summary of the carbon captured in the experiments shown in Figure S7.

^a Calculated using current multiplied by integral of voltage difference (anode voltage subtract cathode voltage) over time for the cell "on" period to yield energy used.

3. References

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