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Exploring the Scope of Capacitance-Assisted Electrochemical Carbon Dioxide Capture

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Optimisation of a capacitance-assisted electrochemical carbon-capture process is facilitated by the physically separation of the graphite and aluminium anode electrodes. This facilitates graphite electrode recycling and enables high current and increased aluminium surface area experiments which fix carbon at a higher rate and the same cell-voltage. Quantification of the H2 cathode byproduct shows that this process could be a net energy producer if recycled aluminium is used as the sacrificial anode.

How to capture, store or convert CO2 is a challenging problem and there are many potential solutions under investigation ranging from geological CO2 storage1 to amine scrubbing2 and electrochemical methodologies.3-14 Much of the electrochemical CO2 literature focuses on electroreduction, wherein bio-inspired15 or purely synthetic molecular13 and heterogeneous4, 6, 8, 11, 12 (often Cu-based) catalysts are developed for the formation of useful products such as CO,9 C2H4,12 and HCOOH.8 Such technologies could enable a carbon-neutral fuel economy and eliminate our reliance on fossil fuels as the source of hydrocarbon building blocks for the pharmaceutical and chemical industry. However, these technologies are incompatible with large-scale industrial processes such as concrete production and coal-burning fuel stations which require low-energy downstream sequestration solutions.16 Therefore anodic CO2 electrochemical processes are investigated with the aim of achieving the conversion of CO2 into a safe and storable molecule.3, 5, 7, 10, 14 This should be achieved at a scale which could significantly offset current anthropogenic CO2 release rates and with a sustainably low energy input; some studies even describe dual energy producing and carbon-capture processes.3, 7

Via an anodic redox reaction, the oxidation of an Fe or Al electrode captures CO2 through the formation of a mineral-like metal cation-carbonate complex.3, 7 Alternatively, using a carbon-based anode provides a non-redox (non-Faradaic) supercapacitive swing adsorption (SSA) method for pumping CO2 from the gas phase into an aqueous NaCl solution, as reported by Landskron et al.5, 10 Inspired by these two different approaches, we produced a mixed material aluminium-graphite anode which we rationalised should combine Al3+-driven mineralisation of CO2 with the ability of carbon electrodes to concentrate CO2 in solution.14 In Nature, aluminium-carbonate solids are found in the form of Dawsonite (an orthorhombically structured crystalline phase of NaAlCO3(OH)2) and the formation of this material has been linked to carbon capture mechanisms in environmental geochemistry17 and the degradation of manmade aluminium structures.18

In our first publication we focussed on enhancing the green metrics of the electrochemical cell, demonstrating that sea water could be used as the electrolyte, a commercial solar cell could directly power the process, aluminium foil or mild steel could replace an aluminium block at the anode and nickel or iron wires could be used instead of platinum at the H2-producing (proton-reducing) cathode.14 In this paper we present new insight into the scalability of the process, showing we can separate the anode components. This enables us to better probe the chemistry of the carbon capture process. We also probe the aluminium to graphite ratio needed to optimise carbon capture using higher electrical currents and prove that the metal surface area becomes limiting. Overall, these findings enable the design of an electrochemical cell that could consume recycled metal while conserving graphite.

Physically separating the graphite and aluminium anode components

In our original electrochemical cell14 the anode comprised a graphite beaker-shaped liner that fitted snugly into a holder machined from an aluminium block. Holes were drilled into the base of the graphite to facilitate electrolyte solution contact with the aluminium. To enable the exploration of how the



**Fig. 1 (a) Labelled photograph and (b) schematic of the electrochemical cell** mechanistic details are discussed in more detail in the text. As indicated in (a) the new cell design permits the incorporation of up to four different anodes which are distinguished by coloured connectors. The chemical process in (b) illustrates a proposed mechanism for generating an aluminium carbonate containing solid, see text.

anode design impacts upon carbon mineralisation a new electrochemical cell was designed and constructed as shown in Fig. 1 and Fig. S1-3. To quantify how these changes in cell design impacted on cathode-catalysed H2 production levels an in-line gas sensor was also developed (Fig. S4).

In our first study,14 we assumed that the close contact between the aluminium and graphite components of the anode was essential. We anticipated that an interaction between bicarbonate ions in the double layer of the graphite electrode and as-generated Al3+ ions was important. However, since we had a cell design which did not permit separation of the anode and graphite components, this hypothesis could not be tested.

A key feature of the new electrochemical cell is that it contains four different anode connection points which can be differentiated by the colours of the connectors on top of the cell lid (Fig. 1 and Fig. S2). As shown in Fig. 2, this has enabled us to vary the configuration of the anode to investigate the voltage, pH and H2 production profiles that result from using either a single 50 x 30 x 2 mm (length x width x depth) aluminium plate submerged in 0.1 M aqueous NaCl electrolyte to a depth of 30 mm as the anode, labelled “Al-only”; a dual-material anode compromising the same sized 50 x 30 x 2 mm graphite plate (18-20% porosity) in physical contact with the aluminium plate and submerged to the same depth, labelled “touching”; or, a dual-material anode made from a graphite plate and an aluminium plate of the same size that were physically separated by a centre-to-centre distance of 21 mm (a solution gap of 18 mm), but electronically connected, labelled “separate”. These first experiments utilised the same electrochemical experimental profile as reported previously,14 with a 10 mA current applied between the anode and cathode for 24 hours (from hour 7 to hour 31).

The similar voltage profiles of the three experiments shown in Fig. 2 indicates that the energy consumption was not substantially impacted by the change in anode composition (total energy (J) = charge (C) x *E*cell (V), where *E*cell = Anode voltage – Cathode voltage). Likewise, the pH and H2-production data of the different experiments are similar. Using the ideal gas



**Fig. 2** **(a) Voltage, (b) pH and (c) %H2 time traces from experiments where either an aluminium-only anode (blue), physically touching and electronically connected graphite and aluminium anode (purple), or physically separated but electronically connected graphite and aluminium anode components (black) were used.** In (a) the solid lines indicate the anode voltage and the dashed lines denote the cathode voltage. Experiments conducted using a 5% CO2 + 95% N2 gas mixture of total flow rate 50 mL min-1. A 10 mA current was applied between the 7 h and 31 h time point (24 h). Cell volume of 600 mL 1 M NaCl(aq) electrolyte, Pt cathode and room temperature.

law and total gas flow rate of 50 mL min-1, the average H2 outlet gas sensor value of 0.15% equates to a total H2 production amount of 4.42 mmol H2 over the 24-hour 10 mA current step. Relative to the total charge passed, this equates to a Faradaic efficiency of 98%, confirming proton reduction (2H+ + 2e-  H2) as the dominant cathodic process catalysed by the platinum wire. Taken together, this data is interpreted as evidence that the redox processes occurring in each experiment are similar, i.e. aluminium oxidation dominates the anodic process and proton reduction dominates the cathodic process regardless of the presence or absence of graphite.

Analysis of the carbon captured in solution and in the solid precipitate (Table 1) suggests that as in our previous study,14 adding a graphite component to the anode increases carbon capture in both the solution (in the form of hydrogen carbonate, see SI) and in the solid (in the form of an amorphous aluminium carbonate, see SI). A new result is that we show that close contact between the graphite and aluminium anode components is not needed for the carbon-capture enhancement effect of the graphite to be observed. The low energy cost of 230 kJ per mol of total captured carbon for the “separated” electrode experiment in Fig. 2 (see Table 1) is similar to the 250 kJ per mol value we reported using the previous cell design where the aluminium was an outer

Table 1. Summary of the carbon captured in the experiments shown in Fig. 2.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Experiment** | **C in**  **solution /**  **mmol** | **C in**  **solid /**  **mmol** | **Total C /**  **mmol** | **Energy**  **costa /**  **kJ molCO2-1** |
| **Al-only anode** | 0.8 | 0.0 | 0.8 | 690 |
| **C+Al anode, touching** | 1.4 | 0.4 | 1.8 | 310 |
| **C+Al anode, separate** | 1.7 | 0.6 | 2.3 | 230 |

a Calculated using current multiplied by integral of voltage difference (anode voltage subtract cathode voltage) over time for the 24-hour cell “on” period to yield energy used.

electrode on a graphite “liner”.14 This suggests that it is not necessary for the Al3+ cations to be generated near the graphitedouble layer. This is further explored below.

The most significant difference between the voltage and pH data in Fig. 2 and our previous work14 is that a maximum pH of 6 is achieved in the experiments in Fig. 2, while in the first cell a pH change from 4.5 to 8.5 was achieved.14 This can be somewhat rationalised by accounting for changes in electrochemical cell volume. In the first cell model, 60 mL of electrolyte was used and 1.9 µmol of protons were consumed. If the same number of protons were to be lost from the 600 mL cell volume of the new set-up used in Fig. 2 a pH change from 5 to 5.4 would be observed.

Anode component separation distance

In experiments conducted to further probe the impact of the anode-component separation, we show that extending the aluminium-to-graphite distance from 21 mm to 64 mm does not change the energetics of carbon capture (Fig. S7 and Table S2). We also show that moving from full size plates (50 (h) x 30 (w) x 2 (d) mm) to half width plates (15 mm wide) does not impact on the energetics of carbon capture in these 5 mA experiments.

The fact that we can physically separate the aluminium and graphite components of the anode and see the same carbon capture profile means that we can extend the mechanistic hypothesis presented in our first study.14 The graphite-to-aluminium separation distances that we have probed are too long to suggest that the as-generated Al3+ ions immediately encounter CO2-derived anions in the double layer of the graphite electrode. A molecular dynamics simulation study examining the approach of ethylene carbonate towards a graphite electrode at positive voltages shows the first layer of carbonate ions are approximately 0.6 nm from the surface.19 In calculations on how ion density profiles change with distance from planar electrodes, 3 nm is generally far enough to see levels return to bulk values.20 We therefore propose that the Al3+ cations instead interact with hydrogen carbonate ions in the bulk solution. It is suggested that the carbon-capture experiments are envisaged as a two-step process. First, before application of the current, the CO2 in the gas feedstock equilibrates with the aqueous NaCl solution, resulting in an acidic shift in pH (reaction A):

Rxn A:

When a current is applied, the electrochemical process of aluminium oxidation at the anode is countered by proton reduction at the cathode, yielding the overall redox processes shown by Reactions B-D, which differ in whether the Al3+ either combines with hydrogen carbonate (Reaction B), or not (Reactions C and D). To simplify these processes, the role of NaCl is ignored. This correlates with the TGA-IR and 13C NMR profiles of the solid which are similar to commercial basic aluminium carbonate, Al(CO3)(HCO3).14

Rxn B:

Rxn C:

Rxn D:

The aluminium oxide species generated in Reaction D is amphoteric21 and we suggest the formation of this material to account for the pH increase which occurs during the application of electrical current (Reaction E).

Rxn E:

The ratio between the competing carbon-capture and non-carbon capture redox reactions, B-D, would be expected to depend on the solution concentration of carbon species. The increased carbon capture in experiments which include a graphite anode component is therefore attributed to the supercapacitive swing adsorption effect of the graphite electrodes increasing the bulk concentration of carbon species in solution, and therefore increasing the amount of process B.

Increasing the electrical current

Ultimately, the aim of any CO2 capture technology is to generate a carbon-free gas output, in this case a mixture of H2 and N2. The gas flow rate of 50 mL min-1 applied throughout the 24-hour, 10 mA current step in the experiments in Fig. 2 equates to a total input of 150 mmol CO2. Thus, a total carbon capture value of approximately 2 mmol in the dual anode experiments of Fig. 2 yields a capture-efficiency of only 1.4%. Experiments were therefore carried out at higher currents to try and increase the rate of carbon capture. To decrease experimental run times, the current was only applied for 18 hours and a smaller electrolyte volume of 250 mL is used (see Fig. S3).

As shown in Table 2, the application of a 20 mA current to an electrochemical cell containing a dual-material anode made from a single graphite plate and a single aluminium plate that were physically separated but electronically connected traps approximately double the amount of carbon in the solid relative to a comparable 10 mA experiment (1 mmol versus 0.4 mmol). Therefore, a scalar increase in the rate of solid-carbon fixation can be induced via a scalar increase in electrical current. Unfortunately, in the one-graphite + one-aluminium anode experiment the application of 20 mA current also resulted in a consistently high anode voltage of over 0 V vs SHE (Fig. 3). Such positive anode voltages translate into very high energy costs of 870 kJ per mol of total captured carbon (Table 2). As shown in Fig. 3, a range of different anode configurations were therefore explored using a 20 mA current setting. The addition of a second aluminium anode of half the width of the first (1C+1½Al) has a significant impact on decreasing the energy cost of carbon capture, without the addition of a second graphite anode (Table 2), suggesting that it is the aluminium surface area that limits the anode voltage in 20 mA experiments. Upon changing to a set up with two full-size Al plates and one graphite (1C+2Al),



**Fig. 3 (a) Current, (b) voltage, (c) pH and (d) %H2 time traces from experiments using different anode configurations, as indicated by the legends.** Experiments were conducted with an applied current of (i) 5, (ii) 10, (iii) 20 and (iv) 40 mA. In (b) the solid lines indicate the anode voltage and the dashed lines denote the cathode voltage. The current was applied between the 4 h and 22 h time points (18 h) across a Pt cathode and an anode comprising 1 or 2 aluminium plates and 1 or 2 or 3 graphite plates that were physically separated but electronically connected. All experiments conducted using a 5% CO2 + 95% N2 gas mixture of total flow rate 50 mL min-1 and a cell volume of 250 mL 1 M NaCl(aq) electrolyte at room temperature.

the Al voltage remains at a similar level, yielding a correspondingly similar total energy use of approx. 900 J in both cases. This contrasts with the aforementioned 5 mA electrode separation experiments and 10 mA experiments where increasing either electrode surface area has little effect on the energy of carbon capture.

Using the two-graphite and two-aluminium anode set-up it is possible to run 10, 20 and 40 mA experiments which all have essentially the same anode voltages as one another and as one-graphite and one-aluminium 5 and 10 mA experiments (Fig. 3). As is visually represented by the photographs in Fig. 4, increasing the current from 10 to 20 to 40 mA has a linear effect on the total amount of solid. Assuming a 100% Faradaic efficiency for the oxidation of Al to Al3+ indicates that the ratio of C:Al3+ in the solid is approximately constant at about 1:7 (Table 2). This ratio was not impacted by increasing the number of graphite anodes in 10 mA experiments (Table 2). The amorphous nature of the solid makes it difficult to probe the material chemistry of the precipitate.14

Because the amount of carbon in solution levels off at a maximum of approximately 2 mmol, the energy cost of total carbon capture increases with increasing current, despite the increased solid fixation. This can be somewhat offset by considering that H2 production approximately doubles upon increasing the current from 5 to 10 to 20 mA, indicating that proton reduction is still the dominant process at the platinum cathode even at higher currents. No data is shown for H2 production at 40 mA because the maximum detection limit of the H2-sensor (0.5%) was reached. This increased fuel production can be used to counteract the increasing energy cost of CO2 capture at higher currents, as shown in the “Energy in – H2 out” column of Table 2 which shows that extraction of the H2 product could make this a net energy generating process.

To try and increase the solution carbon capture we have conducted experiments in which we have increased the surface area of the graphite anode component. This has an inconsistent impact on the amount of carbon in solution, see Table 2. In 10 mA experiments, changing from a single-graphite plus single-aluminium “1C+1Al” anode configuration to a two-graphite plus one-aluminium “2C+1Al” set-up has a very small effect on the amount of carbon trapped in solution (1.2 and 1.3 mmol, respectively). Conversely, in 20 mA experiments with 1 Al electrode, adding in a second graphite component more than doubles the carbon in solution (1C+1Al = 1.0 mmol versus 2C+1Al = 2.3 mmol), but this does not happen when 2

**Table 2 Summary of the carbon captured in the experiments shown in Fig. 3.** All experiments involve the application of the current indicated for 18 hours.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Experiment** | **C in solution**  **/ mmol** | **C in solid**  **/ mmol** | **Total C**  **/ mmol** | **Energy costa**  **/ kJ molCO2-1** | **Calculated Al3+ b**  **/ mmol** | **Ratio Al3+:Csolid** | **Calculated H2c**  **/ mmol** | **Energy in – H2 outd**  **/ Kj** |
| **5 mA, 1C+1Al** | 0.5 | 0.1 | 0.6 | 200 | 1.1 | 11:1 | 1.7 | -0.4 |
| **10 mA, 1C+1Al** | 1.2 | 0.4 | 1.6 | 190 | 2.2 | 6:1 | 3.4 | -0.7 |
| **10 mA, 2C+1Al** | 1.3 | 0.2 | 1.5 | 220 | 2.2 | 11:1 | 3.4 | -0.6 |
| **10 mA, 3C+1Al** | 1.3 | 0.3 | 1.6 | 190 | 2.2 | 7:1 | 3.4 | -0.7 |
| **10 mA, 2C+2Al** | 1.7 | 0.3 | 2.0 | 170 | 2.2 | 7:1 | 3.4 | -0.6 |
| **20 mA, 1C+1Al** | 1.0 | 1.0 | 2.0 | 870 | 4.5 | 5:1 | 6.7 | -0.2 |
| **20 mA, 2C+1Al** | 2.3 | 0.6 | 2.9 | 590e | 4.5 | 8:1 | 6.7 | -0.2 |
| **20 mA, 1C+1½Al** | 1.3 | 0.6 | 1.9 | 500 | 4.5 | 8:1 | 6.7 | -1.0 |
| **20 mA, 1C+2Al** | 1.9 | 1.0 | 2.9 | 300 | 4.5 | 5:1 | 6.7 | -1.1 |
| **20 mA, 2C+2Al** | 1.9 | 0.8 | 2.7 | 290 | 4.5 | 6:1 | 6.7 | -1.1 |
| **40 mA, 1C+1Al** | 2.1 | 1.5 | 3.6 | 1330 | 9.0 | 6:1 | 13.4 | 0.9 |
| **40 mA, 2C+2Al** | 1.9 | 1.6 | 3.5 | 610 | 9.0 | 6:1 | 13.4 | -1.7 |

a Calculated as in Table 1. b Assuming a 100% Faradaic efficiency for Al Al3+ + 3e-

c Assuming a 100% Faradaic efficiency for 2H+ + 2e- H2 d Calculated using a value of -286 kJ mol-1 for the enthalpy of combustion for H2

e Calculated based on the integral of voltage-time data from 20 mA, 1C+1Al

aluminium anodes are used (1C+2Al = 1.9 mmol versus 2C+2Al = 1.9 mmol). Based on the SSA effect, we would expect that the larger the anodic capacitance the larger the amount of carbon in solution. As shown in the EIS experiments reported in our previous paper,14 the capacitance of the graphite anode changes as a function of potential, and it may therefore be that in high current experiments increasing the amount of graphite has a greater effect when there are high anode voltages, i.e. in 20 mA one-aluminium experiments, but not 20 mA two-aluminium experiments. However, this does not seem to hold true for the 40 mA data, indicating that the amount of solid generated may also need to be factored in. We therefore highlight that fully understanding the limiting effects of the graphite electrode surface area on solution carbon capture will require more work.

Conclusions

To conclude, the graphite and aluminium components of a dual- material anode can be physically separated to yield an electrochemical cell design which still demonstrates low energy carbon capture. The ratio of 1:7 carbon-to-aluminium in the solid is not as good as the 1:4 ratio in the first cell, suggesting that lining the aluminium with graphite maximised carbon mineralisation, but the more flexible, separated anodes enabled us to optimise high current experiments. The amount of carbon in the solid scales linearly with applied current and the scalar increases in energy cost of total carbon capture could be offset by the proportionate increase in H2 production. This paper therefore directs future work towards trying to match the rate of CO2 delivery into the cell with the rate of CO2 removal, with potentially air as the input gas stream.

This new electrochemical cell design is a significant step forward in facilitating the development of experiments using composite Al materials. Having an integrated graphite-aluminium component presents the problem that once the metal portion is depleted the graphite electrode would also have to be scrapped. The separation of the two anode materials therefore now sets up future work that can look at using plastic-coated and other waste aluminium, which is less suitable for conventional recycling, at the anode.



**Fig. 4 Photographs to illustrate how the amount of solid scales with the electrical current.**

As well as CO2 capture, the supercapacitive properties of graphite also have great utility in electronic material development22 and water deionisation and hopefully material optimisation applied in these fields could be used to boost the efficiency of the process shown here.23

Conflicts of interest

There are no conflicts to declare.

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