The O$_2$-assisted Al/CO$_2$ electrochemical cell: A system for CO$_2$ capture/conversion and electric power generation

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Economical and efficient carbon capture, utilization, and sequestration technologies are a requirement for successful implementation of global action plans to reduce carbon emissions and to mitigate climate change. These technologies are also essential for longer-term use of fossil fuels while reducing the associated carbon footprint. We demonstrate an O$_2$-assisted Al/CO$_2$ electrochemical cell as a new approach to sequester CO$_2$ emissions and, at the same time, to generate substantial amounts of electrical energy. We report on the fundamental principles that guide operations of these cells using multiple intrusive electrochemical and physical analytical methods, including chronopotentiometry, cyclic voltammetry, direct analysis in real-time mass spectrometry, energy-dispersive x-ray spectroscopy, x-ray photoelectron spectroscopy, and coupled thermogravimetric analysis–Fourier transform infrared spectroscopy. On this basis, we demonstrate that an electrochemical cell that uses metallic aluminum as anode and a carbon dioxide/oxygen gas mixture as the active material in the cathode provides a path toward electrochemical generation of a valuable (C$_2$) species and electrical energy. Specifically, we show that the cell first reduces O$_2$ at the cathode to form superoxide intermediates. Chemical reaction of the superoxide with CO$_2$ sequesters the CO$_2$ in the form of aluminum oxalate, Al$_2$(C$_2$O$_4$)$_3$, as the dominant product. On the basis of an analysis of the overall CO$_2$ footprint, which considers emissions associated with the production of the aluminum anode and the CO$_2$ captured/abated by the Al/CO$_2$-O$_2$ electrochemical cell, we conclude that the proposed process offers an important strategy for net reduction of CO$_2$ emissions.

INTRODUCTION

Balancing the increasing world energy demand with the need to economically reduce carbon dioxide emissions is one of the most defining challenges of our time (1). Most world energy forecasts show that fossil fuels will continue to play a major role in meeting worldwide energy demands for the foreseeable future, particularly in the transportation and power generation sectors (2, 3). To capitalize on the exceptional, high energy density of fossil fuels, the incorporation of carbon capture, utilization, and sequestration (CCUS) technologies is essential to reduce global CO$_2$ emissions (4). Large-scale adoption of classical CCUS technologies (for example, absorption, adsorption, and membrane separation) is currently limited by the additional energy requirements associated with CO$_2$ capture, resulting in higher cost of energy and difficulties in transporting and sequestering the captured CO$_2$ (5). Recently, CO$_2$ capture has been demonstrated for mobile sources, capitalizing on the waste energy of combustion engines (6). Conversion of CO$_2$ to useful chemicals and fuels is understood to be a requirement for the commercial success of any CCUS process but has proven to be very difficult because of the thermodynamic and kinetic stability of CO$_2$. Of the catalysts recognized to enable the chemical formation of C–C bonds from CO$_2$, AlCl$_3$ is considered an effective Friedel-Crafts catalyst. Olah et al. (7) reported the carboxylation of benzene with CO$_2$, AlCl$_3$, and Al metal and demonstrated through density functional theory the AlCl$_3$ activation of CO$_2$-forming AlCl$_3$-CO$_2$ complexes, which react with benzene to produce its carboxylate. A similar reaction path has been proposed for the carboxylation of toluene with CO$_2$ and AlCl$_3$ (8). The conversion of CO$_2$ to oxalates (a feedstock to useful chemicals supporting various markets/industries) has been demonstrated electrocatalytically using a copper complex by Angamuthu et al. (9).

The metal/CO$_2$ electrochemical cell has been proposed as a novel approach to capturing CO$_2$ from mixed CO$_2$/O$_2$ gas streams, particularly using metallic Li (10–12), Na (13, 14), and Mg (13) anodes of high-energy densities, while generating electrical energy. An important finding from these studies is that the presence of O$_2$ is important to enable the chemical reduction and thereby capture of CO$_2$. These metal/O$_2$-CO$_2$ electrochemical capture systems may be operated in either secondary (rechargeable) or primary (nonrechargeable) configurations. In a secondary cell, reduced CO$_2$ species react with oxidized metal ions to form the metal carbonate or bicarbonate and electricity during cell discharge. Recharging the cell would ideally reverse the reaction, consuming electrical energy to release the captured CO$_2$ and O$_2$ and regenerate the metal anode. Adoption of these secondary electrochemical systems in a CCUS process would therefore facilitate separation and concentration of CO$_2$, as demonstrated in Fig. 1A. Another configuration of interest is the primary electrochemical cell, where the metal anode is consumed to produce electrical energy and discharge products, which can be harvested (from the electrode, electrolyte, and other cell components) and regenerated to concentrate the CO$_2$ or converted to valuable chemicals if the discharge forms C$_n$ (n ≥ 2) products (Fig. 1B).

Aluminum is an attractive anode material for electrochemical capture and conversion of CO$_2$ because of its relatively low cost and lower reactivity, in comparison to Li and Na, which makes electrochemical systems involving Al inherently safer and potentially easier to manufacture. As the third most abundant element in Earth’s crust (15), Al is also available in regions all over the world. The material has a high...
specific energy [electrochemical equivalence of 2980 A-hour/kg (16)], which means that its electrochemical conversion by CO₂ may also be used to generate large quantities of electrical energy.

In Al electrochemical systems, room-temperature ionic liquids present attractive alternatives to alkaline and saline (aqueous and non-aqueous) electrolytes, which are associated with parasitic corrosion and hydrogen evolution problems (17–20). The ionic liquid/salt melt of 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl)/aluminum chloride (AlCl₃) is particularly important because of its thermal and electrochemical properties (21). The electrochemically prevalent species can be designated by adjusting the ratio of AlCl₃ to [EMIm]Cl (22, 23). An equimolar mixture will have AlCl₄⁻ as the primary anion. Basic melts, where the molar ratio of [EMIm]Cl is higher than that of AlCl₃, contain Cl⁻ and AlCl₄⁻ anions. Acidic melts with higher AlCl₃-to-[EMIm]Cl ratio have AlCl₅⁻ and Al₂Cl₇⁻ as the prevailing ions and are demonstrated to have higher conductivity (24) and lower viscosity (25). Aluminum batteries based on these electrolytes have recently attracted considerable attention. In aluminum ion batteries, the acidic [EMIm]Cl/AlCl₃ melt has been used in conjunction with sulfur (26), V₂O₅ (27, 28), LiFePO₄ (29), and carbon-based (30) cathodes. Lin et al. (30), for example, demonstrated an ultrafast rechargeable aluminum ion battery based on the intercalation/deintercalation of AlCl₄⁻ in graphitic carbon electrodes. Although the capacity of the battery was limited to about 60 mA-hour/g_{Graphite} the columbic efficiency was maintained at 97% at high applied current density.

Here, we report an Al/CO₂-O₂ electrochemical cell based on an [EMIm]Cl/AlCl₃ electrolyte melt and show that this cell design is effective for both capturing CO₂ and upconverting the captured CO₂ to a C₂ species, an oxalate, without the need for a catalyst or high-temperature cell operation. Al/2O₂ electrochemical cells based on an acidic [EMIm]Cl/AlCl₃ melt have been reported to produce approximately 158 mA-hour/g_{Carbon} of electrical energy during cell discharge at around 0.7 V under a current density of 0.2 mA/g_{Carbon} (24). More recently, Gelman et al. (31) demonstrated an Al/2O₂ battery based on 1-ethyl-3-methylimidazolium oligo-fluoro-hydrogenate [EMIm(HF)ₓ₂₃F] electrolyte producing substantially higher discharge capacity (7450 mA-hour/g_{Carbon}) at around 1.0 V under current density of about 79 mA/g_{Carbon}. Here, we show that in addition to providing a process for CO₂ capture and conversion, an Al/CO₂-O₂ cell based on [EMIm]Cl/AlCl₃ can deliver very high discharge capacities (as high as 13,000 mA-hour/g_{Carbon}) at a discharge voltage of around 1.4 V when discharged at a fixed rate of 70 mA/g_{Carbon}.

RESULTS

Using aluminum as an anode in the electrochemical cell enabled the production of electrical energy when the cell is galvanostatically discharged in an atmosphere of specific gases, which are allowed to diffuse in the electrolyte through the porous, electrically conductive cathode. Under constant current, oxidation of the aluminum anode and reduction of the diffused gases on the cathode produced a potential plateau indicative of the electrochemical reaction taking place. Postmortem analysis of the discharged cells was carried out using different techniques to identify the reaction products and showed congruence in the results. Direct analysis in real-time mass spectrometry (DART-MS) was used to identify the main reaction products from the ionized fragments. Energy-dispersive x-ray spectroscopy (EDXS) and wide-scan x-ray photoelectron spectroscopy (XPS) were used to compare the atomic ratios of aluminum, oxygen, and carbon, and high-resolution XPS was used to identify the bonds formed by these atoms. Coupled thermogravimetric analysis (TGA)–Fourier transform infrared (FTIR) spectroscopy was used to compare the discharged cathodes with the expected spectra for the primary reaction product as deduced from the EDXS and XPS analyses.

Electrochemical methods

Voltage profiles from galvanostatic discharge of Al electrochemical cells operated under Ar, O₂, CO₂, and mixtures of CO₂/O₂ are reported in Fig. 2. Discharging the Al cell under pure O₂ (denoted 100% O₂) produced considerable electrical energy (about 890 mA-hour/g_{Carbon}) at about 1.4 V. The capacity increased about 15-fold when CO₂ was introduced at a molar ratio of 80:20 compared to O₂ (denoted 80% CO₂). Discharging Al under pure CO₂ or Ar produced no/negligible electrical energy, with the only noticeable discharge voltage plateau at lower potential of about 0.3 V. Cyclic voltammetry (CV) (Fig. 2, inset) revealed a matching reduction peak around 1.5 V for Al/100% O₂ and Al/80% CO₂ systems, corresponding to the discharge potential. However, no corresponding oxidation peak was detected at the reduction peak of 1.5 V. The redox couple peaks at 0.45 to 0.55 V correspond to the lower discharge potential (0.3 V), which was noticed regardless of the
Gas environment, and probably arise from intercalation/deintercalation processes similar to those reported by Lin et al. (30).

Direct analysis in real-time mass spectrometry
The main negative and positive ion mode fragments/ionized species detected in pristine cathodes and cathodes discharged under 100% O₂ and 80% CO₂ were identified (table S1). As expected considering their abundance, the strongest signals were produced by fragmentation/ionization of the ionic liquid and salt. Table S2 lists the negative and positive ion mode species detected by DART-MS and their corresponding theoretical signatures. Cl₂⁻ and HCl₂⁻ produced the strongest signals. AlCl₄⁻ was detected, but not Al₂Cl₃⁻, which we believe to have been fragmented. Fragments of the salt complexed with moisture in the air and produced the species AlCl₃(OH)⁺, AlCl₃(OH)₂⁺, and AlCl₃(OH)₃⁺. Fragmentation of [EMIm]Cl produced C₆H₁₁N₂Cl⁺, C₆H₁₃N₂⁺, C₄H₇N₂⁺, and C₃H₆N₂⁺, indicating the loss of chlorine, methyl, and ethyl groups. The C₆H₁₁N₂Cl₂⁻ species were detected from the ionization of [EMIm]Cl with an additional chlorine. Those species were produced similarly from undischarged cathodes and cathodes discharged under 100% O₂ and 80% CO₂. The same fragments/species were reported for the [EMIm]Cl/AlCl₃ melt using other MS techniques, including fast atom bombardment (32), secondary ion (33), collision-induced dissociation (34), and pyrolysis gas chromatography (35) MS.

Remarkably, what sets cathodes discharged under 80% CO₂ apart is the detection of Al₃(C₂O₄)Cl₃, fragments and ionized species with the electrolyte melt. Aluminum oxalate fragments to produce Al(C₂O₄)₃⁺, Al(C₂O₄)₂⁻, Al(C₂O₄)Al(C₂O₄), and Al(C₂O₄)²⁺ as demonstrated in tables S1 and S2. It also ionizes and complexes with AlCl₃ and [EMIm]Cl to produce AlCl₃(C₂O₄), C₆H₁₂N₂(C₂O₄)⁺, (C₆H₁₁N₂)₂(C₂O₄)⁺, and (C₆H₁₁N₂)₃(C₂O₄)Cl⁻. The intensity of the oxalate fragments was much lower than that of electrolyte species, where only the main peaks were detectable.

Scanning electron microscopy–EDXS
Distinct differences were noted between cathodes discharged under 80% CO₂ and 100% O₂ (Table 1). Reaction products formed rugged micrometer-size particles on the stainless steel mesh cathodes discharged under 80% CO₂. On the other hand, cathodes discharged under 100% O₂ showed submicron bead-like structures. The reaction products seemed to be distributed throughout the electrodes, though not completely covering them. It is not clear whether the acetonitrile wash removed part of the reaction products from the electrodes. Even after the acetonitrile wash, weak N and Cl signals are observed in the discharged and undischarged stainless steel cathodes by EDXS (table S3), most likely from the remaining electrolyte. Whereas the Al atomic percentage in discharged cathodes was close to 10%, the undischarged cathode revealed values close to 1%. In the case of discharged cathodes, the atomic percentage of Al exceeded the stoichiometric values expected in the electrolyte when comparing to Cl atomic percentage, suggesting that Al is part of the reaction product depositing on the electrode. To discount the Al signal from the remaining electrolyte, the Al atomic percentage was adjusted on the basis of the Cl signal and electrolyte stoichiometric value. Similarly, C was discounted on the basis of the detected N and the corresponding electrolyte stoichiometry. The O-to-Al, C-to-Al, and C-to-O atomic ratios are larger for the cathodes discharged under 80% CO₂ (Table 1) and close to the stoichiometric values of aluminum oxalate (6, 3, and 0.5, respectively). For the cathodes discharged under 100% O₂, the measured ratios are as expected, consistent with the stoichiometric values for aluminum oxide (3, 0, and 0, respectively). In contrast, for the undischarged cathodes, the ratios are close to the stoichiometric values for aluminum hydroxide (3, 0, and 0, respectively), suggesting that part of the remaining aluminum chloride reacts with moisture in the air during the short sample transfer. Both carbon and oxygen were detected in pristine stainless steel electrodes (not soaked in the electrolyte), which could explain the slightly higher ratios compared to that of aluminum in discharged cathodes.

X-ray photoelectron spectroscopy
Wide survey scans (table S4) were performed to estimate surface atomic ratios, and high-resolution scans were conducted for Al 2p, O 1s, and C 1s to determine more precise chemical bonding information. Table 2 reports...
the high-resolution spectra and bonds assigned to the deconvoluted peaks; multiple bonds were assigned to some peaks. Two doublet Al 2p (2p3/2 and 2p1/2) peaks were detected in discharged and pristine electrodes at 74 eV, which could be assigned to chloride (36) and hydroxide (37) compounds, and at 77 eV, which could be assigned to oxide (38) and oxalate (39) compounds. Two peaks at 531 and 534 eV were detected for O 1s and are attributed to hydroxides (40), oxides (41), and the two oxygen bonds (Al–O–C and C=O) in oxalate (39, 41). Seven different carbon bonds can be attributed to the three C 1s peaks at 284, 286, and 288 eV originating from the ionic liquid (42–44), remaining acetonitrile (45), and oxalate (39).

Our findings are similar to those reported by Young and Williams (39) from their XPS analysis of aluminum oxalate tetrahydrate, with the exception that binding energies are consistently around 2 eV higher than those observed in our study. We suspect that the difference in binding energies originates from differences in referencing of the spectra, which is particularly important for nonconductive materials. The study by Young and Williams indicated that XPS degrades aluminum oxalate to form aluminum oxides. We conducted XPS on chemically synthesized aluminum oxalate samples purchased from Alfa Aesar to compare with the results from electrochemically created material. These results are also included in Table 2. It is apparent that the C 1s spectra did not show the 288-eV peak, but rather displays a peak at 291 eV, which could be attributed to surface-adsorbed CO₂ and CO (39). The C 1s 284 eV peak is attributed to the remaining adventitious carbon because it is difficult to sputter powders.

The high-resolution peak contributions were used in conjunction with atomic ratios from wide surveys to predict discharge compounds. Table 2 shows the atomic ratios of oxygen to aluminum, carbon to aluminum, and carbon to oxygen for specific bonds. The O₅₃₄ eV-to-Al₇₇ eV ratio can be used to evaluate the presence of aluminum oxalate because the peaks associated with those binding energies are linked to the Al–O–C bond. The ratios are higher for the cathode discharged under 80% CO₂ compared to those for the cathode discharged under 100% O₂ or undischarged electrode. The ratio for the cathode discharged under 80% CO₂ is higher than the stoichiometric value of 3.0 and can be attributed to the presence of aluminum-oxygen complexes (notorious of this electrolyte melt in the presence of O₂ gas (32)), which are linked to the same oxygen and aluminum peaks. Comparing the C₂₈₆ eV peak (associated with oxalate) to Al₇₇ eV and O₅₃₄ eV peaks demonstrates higher ratios of carbon for the cathode discharged under 80% CO₂ compared to 100% O₂ and undischarged electrode. The C₂₈₆ eV-to-Al₇₇ eV ratio higher than the stoichiometric value of 3.0 in aluminum oxalate could be attributed to the presence of the remaining ionic liquid on the surface because the same carbon peak is attributed to the methyl and ethyl groups in the

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<th>SEM</th>
<th>O/Al</th>
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<tr>
<td>Al/80% CO₂ cathode</td>
<td>7.11</td>
<td>4.04</td>
<td>0.57</td>
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<tr>
<td>Al/100% O₂ cathode</td>
<td>2.58</td>
<td>0.77</td>
<td>0.30</td>
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<td>Undischarged cathode</td>
<td>3.59</td>
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ionic liquid. The $C_{286\, \text{eV}}$-$O_{534\, \text{eV}}$ ratio is lower than the stoichiometric value of 1.0 for oxalate and can be explained by the presence of oxides attributed to the same oxygen peak. Comparing the contribution of the same peaks for chemically synthesized aluminum oxalate, the $O_{534\, \text{eV}}$-$Al_{77\, \text{eV}}$ and $C_{286\, \text{eV}}$-$Al_{77\, \text{eV}}$ ratios are close to the stoichiometric values. The $C_{286\, \text{eV}}$-$O_{534\, \text{eV}}$ ratio is slightly lower than the stoichiometric value and could be explained by the presence of aluminum oxide, as reported by Young and Williams (39).

Table 2. High-resolution XPS spectra and atomic ratios associated with aluminum oxalate. High-resolution spectra (versus number of counts) for Al 2p, O 1s, and C 1s. Red dotted lines and solid lines represent the experimental data and the fitted curves, respectively. Numbers are assigned to the different bonds and corresponding XPS peaks. Atomic ratios of specific bonds associated with aluminum oxalate, derived from coupling overall atomic ratios (from wide survey scans) with contributions of specific binding energies (from high-resolution scans).
Coupled TGA-FTIR spectroscopy
Cathodes discharged under 80% CO₂ and 100% O₂ and the undischarged cathode exhibited similar TGA profiles, with a significant mass loss occurring around 530°C (Fig. 3). This mass loss is attributed to the thermal decomposition of the ionic liquid (46). Only the cathode discharged under 80% CO₂ featured an additional defined dip at around 280°C. The TGA was coupled with FTIR to analyze the composition of the thermally degraded products, as demonstrated in Fig. 3. All cathodes showed the evolution of CO₂ and H₂O throughout the TGA experiment, from sample-adsorbed CO₂ and H₂O during sample loading as well as from degraded species. Focusing on the region of asymmetric stretch of CO₂ (2349 cm⁻¹), both the undischarged cathode and the cathode discharged under 100% O₂ show that CO₂ is evolved and that the evolution plateaus up to 600°C. The cathode discharged under 80% CO₂ also shows the evolution of CO₂ reaching a plateau and then a spike that is associated with the 280°C TGA drop, which is hypothesized to result from degradation of discharge-deposited aluminum oxalate. The TGA-FTIR experiment was duplicated for the chemically synthesized aluminum oxalate to test this hypothesis. Significantly, the results show a similar thermal profile, including the spike, confirming a significant release of CO₂. However, the TGA results show the weight drop occurring around 350°C. The higher weight-loss temperature for the chemically synthesized aluminum oxalate could be attributed to the larger particles (>10 μm by scanning electron microscopy (SEM)] compared to the aluminum oxalate deposited in Al/80% CO₂ electrochemical cell (~1 μm by SEM). Decreasing the TGA ramp-up rate provides a simple strategy for accommodating mass transfer differences between smaller and larger sample aggregate sizes. This expectation was confirmed by reducing the scan rate to 0.05°C/min, whereupon the weight drop was seen to shift to 280°C. Young and Williams (39) reported the decomposition of aluminum oxalate tetrahydrate between 300° and 320°C, with a ramp-up rate of 10°C/min. The chemically synthesized aluminum oxalate sample also showed the evolution of CO (2099 cm⁻¹) at very low intensity compared to that of CO₂.

Preliminary system analysis
When recharging Al/80% CO₂ or Al/100% O₂ electrochemical cells using stainless steel cathodes, the recharge potential exhibits a shuttling-like behavior where it reaches a plateau and fluctuates radically. Similar behavior is well known for Li/S (47) and Na/S (48) batteries, where current is continuously consumed in a parasitic redox loop involving interconversion of metal polysulfide species of different orders dissolved in the electrolyte. In the case of Al/80% CO₂ and Al/100% O₂, shuttling is tentatively attributed to a similar loop involving interconversion of different aluminum chloride species present in the electrolyte. These behaviors can be contrasted with what is seen when the cathode is replaced by Ketjenblack-casted carbons, where the Al electrochemical cell showed good cyclability achieving and maintaining about 200 mA-hour/g_carbon for more than 50 cycles. However, as noted previously, the cell rechargeability corresponds to an intercalation/deintercalation process and was seen under CO₂, O₂, CO₂/O₂, and Ar.

On the basis of these results, we conclude that a CO₂ capture/conversion system based on an Al/80% CO₂ electrochemical cell may be most easily operated in a primary mode in which the Al anode is continuously fed to the cell (Fig. 1B) and oxidized/consumed to form aluminum oxalate. Oxalic acid is used as a bleaching agent in the pharmaceutical and fiber industries, as a cleaning agent, and as a precipitant in metal smelters. Demand for oxalic acid in these applications has been increasing in recent years to support different sectors with an estimated worldwide demand of 230,000 metric tons in 1998 (49). Oxalic acid can also be used as a feedstock to the production of dimethyl oxalate (9) and eventually ethylene glycol, where the global production was estimated at 20 million metric tons in 2010 (50).

To evaluate the effectiveness of the proposed primary Al/80% CO₂ electrochemical cell as a CO₂ sequestration technology, life cycle assessment (LCA) may be used. LCA presents a structured approach to evaluating environmental impacts throughout a product’s life cycle (from raw material, production, waste management, etc.) (51). It enables balancing CO₂ emissions associated with the Al anode production to abated CO₂ emissions.

Fig. 3. Coupled TGA-FTIR spectra. TGA curves and coupled time-resolved FTIR spectra for discharged cathodes (under 80% CO₂ and 100% O₂), undischarged cathode, and chemically synthesized aluminum oxalate. Ramp-up rates for solid and dashed lines are 5°C/min and 0.05°C/min, respectively.
converted by the electrochemical cell from flue streams. Here, we extend an LCA for aluminum metal production to act as a preliminary LCA for the Al/80% CO₂ electrochemical cell. Aspects related to efficiencies, electrolyte production/replacement, flue gas pretreatment, and other features are not considered. An LCA study that was conducted by The Aluminum Association, in line with ISO 1404/14044, estimated the average genetic CO₂ emission values for North American aluminum industry based on input from 25 companies (52). The study accounted for CO₂ emissions from the four main process steps for Al metal production: bauxite mining, alumina refining, aluminum electrolysis, and primary aluminum production. An average of 7.88 kg CO₂/kg Al was estimated for the combined steps of aluminum production and associated processes (Fig. 4).

Integrating the Al/80% CO₂ electrochemical cell in a flue gas stream, we estimate a total of 9.31 kg CO₂/kg Al to be captured and abated (Fig. 4). We calculate 4.89 kg CO₂/kg Al to be separated on the basis of the proposed discharge reaction. Generated electric power from the battery replacing other energy sources results in overall reduction of CO₂ emissions. If the battery replaces natural gas sources, reduction of 1.97 kg CO₂/kg Al can be credited to the system, on the basis of a theoretical energy of 3.58 kWh/kg Al and CO₂ emissions of 0.55 kg CO₂/kWh associated with natural gas (53). We propose that the main discharge product of the battery can be converted to oxalic acid. Fischer et al. (54) demonstrated the relatively simple production of H₂C₂O₄ from ZnC₂O₄. We propose that Al₂(C₂O₄)₃ can be converted to H₂C₂O₄ and Al₂O₃, reducing CO₂ emissions associated with oxalic acid produced commercially through classical methods. One of the established commercial methods for producing oxalic acid is through the oxidation of propene with nitric acid, where CO₂ is produced in equimolar quantities to the oxalic acid (55). If Al/80% CO₂ electrochemical cell is used to produce H₂C₂O₄ instead of propene oxidation, CO₂ abatement can be estimated at 2.45 kg CO₂/kg Al. The overall balance of CO₂ shows that the primary Al/80% CO₂ electrochemical system reduces emissions from flue streams after accounting for emissions from Al metal production (Fig. 4A). If Al₂O₃ produced from Al₂(C₂O₄)₃ conversion to H₂C₂O₄ is recycled back to the Al production facility, aluminum can be produced, considerably reducing CO₂ emissions associated with the bauxite mining and alumina refining steps. This results in even higher CO₂ reduction (3.52 kg CO₂/kg Al) of the overall system, as demonstrated in Fig. 4B. This outlines a preliminary LCA, and a rigorous study is to be conducted to account for emissions associated with electrolyte replacement (depending on degradation rate), moisture removal from flue gases, oxalic acid production from aluminum oxalate, and other aspects.

Fig. 4. Preliminary system analysis. (A) Overall balance of CO₂ emissions captured/abated by the primary Al/80% CO₂ electrochemical system contrasted with emissions of aluminum metal production. (B) Overall balance of CO₂ emissions, allowing the recycling of Al₂O₃ for production of aluminum metal.
**DISCUSSION**

The galvanostatic discharge at relatively high potential (1.4 V) and the CV experiments suggest that O₂ reduction is the main electrochemical process in the Al/CO₂-O₂ cell. Similar potential plateaus for Al discharged under pure O₂ or CO₂/O₂ mixture lend support to the fact that the main electrochemical process involves the reduction of O₂, expectedly forming superoxide species (O₂⁻). Electrochemical reduction of CO₂ does not take place directly but rather through the chemical reduction by the superoxide species.

Similar results have been reported previously when incorporating CO₂ to Li/O₂ and Na/O₂ batteries, demonstrating an increase in discharge capacity while maintaining the same discharge potential. In ethylene carbonate/diethyl carbonate electrolyte, the incorporation of 50% CO₂ into Li/O₂ batteries increased the discharge capacity threefold while maintaining the same discharge potential (10). The proposed discharge mechanism involves the reduction of O₂ to form the superoxide radical that in turn chemically reduces CO₂ to form CO₃²⁻ and then C₂O₆²⁻ radicals, resulting in the formation of Li₂CO₃ as the main discharge product (36). In tetraethyl glycol dimethyl ether (tetruglyme), Li/CO₂-O₂ (2:1 ratio) was demonstrated to be rechargeable over a limited number of cycles, forming Li₂CO₃ as the main discharge product (11). In Na/O₂ batteries, the introduction of CO₂ in ratios between 40 and 60% compared to O₂ increased the capacity two- to threefold, depending on the electrolyte system (13). Na₂CO₃ and Na₂C₂O₄ were reported as the main discharge products in tetraglyme and ionic liquid electrolytes, respectively. Rechargeability was demonstrated when stabilizing the propylene carbonate electrolyte with ionic liquid–tethered silica nanoparticles, where NaHCO₃ was the main discharge product (14).

Analytically, using DART-MS, SEM-EDXS, XPS, and TGA-FTIR, we show that the principal discharge product of the Al/CO₂-O₂ cells is aluminum oxalate [Al₂(C₂O₄)₃]. Accordingly, building on the hypothesized reaction mechanisms for Li/CO₂-O₂ and Na/CO₂-O₂ batteries, we propose the following reaction mechanism for the Al/CO₂-O₂ electrochemical cell:

\[
2 \text{Al} \leftrightarrow 2 \text{Al}^{3+} + 6 e^- \\
6 \text{O}_2 + 6 e^- \leftrightarrow 6 \text{O}_2^{2-} \\
3 \text{CO}_2 + 3 \text{O}_2^{2-} \leftrightarrow 3 \text{CO}_3^{2-} \\
3 \text{CO}_3^{2-} + 3 \text{O}_2^{2-} \leftrightarrow 3 \text{CO}_4^{2-} + 3 \text{O}_2 \\
3 \text{CO}_4^{2-} + 3 \text{C}_2 \text{O}_4^{2-} \leftrightarrow 3 \text{C}_2 \text{O}_4^{2-} + 3 \text{O}_2 \\
2 \text{Al}^{3+} + 3 \text{C}_2 \text{O}_4^{2-} \leftrightarrow \text{Al}_2(\text{C}_2\text{O}_4)_3 \\
\text{Overall reaction: } 2 \text{Al} + 6 \text{CO}_2 \leftrightarrow \text{Al}_2(\text{C}_2\text{O}_4)_3
\]

Protonic impurities could present a challenge when using [EMIm]Cl/AlCl₃ as an electrolyte because the electrochemically generated superoxide (O₂⁻) could react with impurities in the electrolyte melt (57). A strong nucleophilic reagent such as O₂⁻ is reported to react with and degrade the EMIm⁺ cation (58, 59). Despite these possible side reactions, the introduction of CO₂ in higher ratios compared to O₂ demonstrated that O₂⁻ reduces CO₂ to produce oxalates. We believe that the CO₂ complexing with AlCl₃ in the electrolyte facilitates the chemical reduction of CO₂ by the superoxide and the eventual formation of oxalate.

The proposed O₂-assisted Al/CO₂ electrochemical cell demonstrates a new approach for converting CO₂ from flue gas streams to useful products while producing considerable electrical energy. The preliminary LCA, which compares the captured/abated CO₂ by the proposed primary Al/CO₂-O₂ system to emissions associated with the production of the Al anode, showed a net reduction of CO₂ emissions. Future work is planned to better understand the rate performance/kinetics of the system (enabling comparison with classical CO₂ capture/conversion techniques) and to study different electrolytes (the most sensitive part of the system, particularly to water) and other metal anodes.

**MATERIALS AND METHODS**

**Electrolyte preparation and material handling**

The electrolyte was prepared by slowly mixing 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) (>95%; Sigma-Aldrich) with aluminum chloride (AlCl₃) (99.99%; Sigma-Aldrich). Acidic electrolyte melt (1:2 [EMIm]Cl/AlCl₃) was primarily used in this study. No major differences in electrochemical performance were noticed for electrolyte melts between ratios 1:2.1 and 1:1.5 ([EMIm]Cl/AlCl₃). The electrolyte was vacuum-heated at 130°C for 15 min to remove/reduce water and oxygen complexes before it was applied to the battery. Chemically synthesized aluminum oxide hydrate (99%; Alfa Aesar) was vacuum-heated overnight at 120°C to drive out hydrates. All materials used in the study were stored/prepared in an Ar-filled glove box (MBRAUN, LABmaster). Electrochemical cells were also assembled in an Ar-filled glove box. Electrode and electrolyte samples for postmortem analysis were obtained after disassembling cells inside the glove box and transferring using Ar-filled vials for analysis outside the glove box.

**Electrochemical cell assembly**

Al/CO₂-O₂ cells were assembled with CR2032 coin-type cells that were perforated on the cathode side (15.8-mm diameter). Ketjenblack (AkzoNobel EC-600JD) was dissolved with polyvinylidene fluoride binder (8:2 carbon/binder ratio) in N-methyl-2-pyrrolidone solvent, ball-milled, and cast on carbon paper (Toray TGP-H-030). The cathodes were dried in a vacuum oven overnight at 100°C. Typical loading of cathodes was 0.5 to 1.0 mg carbon/cm². For comparison, other electrodes such as carbon paper, stainless steel mesh, and nickel foam were tested with or without the porous carbon with comparable electrochemical performance. However, the use of porous carbon (providing extensive surface area for the reduction reaction) was essential to reduce the overpotential in the system during discharge and to obtain a high potential plateau. Al foil (99.99%, 0.1 mm thick; Alfa Aesar) was used as the anode after mechanical cleaning with silicon carbide sandpaper and washing with acetonitrile. Whatman GF/D glass fiber was used as separator and was soaked with 100-μl electrolyte. Custom-designed chambers were used to place battery cells, exposing them to premixed gases at 1 atm. Cuvette-type cells were used to conduct CV and allow harnessing of the electrolyte (1 ml) after discharge for postmortem analysis.

**Electrochemical experiments**

Galvanostatic discharge experiments were conducted using Neware CT-3008 battery testers at a fixed current density of 70 mA/g Carbon. CV was performed using Solartron Frequency Response Analyzer (model 1252) with a three-electrode configuration and a fixed scan rate of 0.1 mV/s. Ketjenblack on carbon paper was used as the working electrode. The counter electrode used was Tn wire (99.99%, 1.0-mm diameter; Alfa Aesar), whereas the reference electrode constituted an Al wire (99.999%, 2.0-mm diameter; Alfa Aesar) immersed in the same electrolyte. Counter and reference electrodes were mechanically cleaned with silicon carbide sandpaper and washed with acetonitrile.
Direct analysis in real-time mass spectrometry
High-resolution MS analyses were carried out on a Thermo Scientific Exactive Orbitrap MS system equipped with an Ionsense DART ion source. MestReNova software was used to analyze the MS results and to compare them to the predicted spectra. DART-MS enables the analysis of products on discharged cathodes in their native states without the need for sample preparation. Exposing cathodes to the ion source fragments/ionizes the different species.

SEM and EDXS
SEM (Keck SEM) was conducted using Zeiss 1550 Field Emission (Schottky field emitter). EDXS was carried out with Bruker QUANTAX 200 and with XFlash 6 SDD and an energy resolution of <126 eV at Mn-Kα line. For SEM-EDXS postmortem analysis, batteries were discharged using stainless steel mesh cathodes to enable differentiation of the reaction products from porous carbon electrodes. Discharged cathodes were washed with acetonitrile inside the Ar glove box to remove excess electrolyte.

X-ray photoelectron spectroscopy
Samples were analyzed using a Surface Science Instruments SSX-100 with operating pressure of ~2 x 10⁻⁷ torr. Monochromatic Al Kα x-rays (1486.6 eV) with beam diameter of 1 mm were used. Photoelectrons were collected at an emission angle of 55°. A hemispherical analyzer determined electron kinetic energy, using a pass energy of 150 V for wide/survey scans and 50 V for high-resolution scans. Samples were ion-etched using 4-kV Ar ions, which were rastered over an area of 2.25 x 4 mm with total ion beam current of 2 μA, to remove adventitious carbon. Spectra were referenced to adventitious C 1s at 284.5 eV. CasaXPS software was used for XPS data analysis with Shelby backgrounds. C 1s and O 1s were assigned to single peaks for each bond, whereas Al 2p was assigned to double peaks (2p½ and 2p½) for each bond with 0.44-eV separation. Residual SD was maintained close to 1.0 for the calculated fits. For XPS postmortem analysis, batteries were discharged using stainless steel mesh cathodes to enable differentiation of reaction products from carbon electrodes. Discharged cathodes were washed with acetonitrile inside the Ar glove box to remove excess electrolyte.

Coupled TGA-FTIR spectroscopy
TGA was carried out using TA Instruments TGA Q500 up to 600°C at 5°C/min, unless otherwise stated. The FTIR spectrum was obtained by Thermo Scientific Nicolet iZ10 spectrometer with a TGA sampling accessory. Evolved gases were flushed through the TGA-FTIR chambers with N2 (10 ml/min with VWR peristaltic pump terminating at a liquid seal). OMNIC software was used to construct three-dimensional (absorbance and wave number versus time) plots of FTIR spectra. TGA-FTIR was conducted on Ketjenblack-based cathodes that were washed with acetonitrile to remove excess electrolyte.

Base case tests
Considering the sensitivity of the electrolyte system and to account for any interaction with air, moisture, and impurities, the DART-MS, SEM-EDXS, XPS, and TGA-FTIR experiments of discharged cathodes were compared with those of undischarged cathodes (base case). The undischarged cathodes were assembled in exactly the same way as the discharged cathodes, soaked in the electrolyte system, and exposed to a mixture of CO2 and O2 before they were washed with acetonitrile.

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/2/7/e1600968/DC1

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