Direct CO2 Electroreduction from Carbonate

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The process of CO2 valorization – all the way from capture/concentration of CO2 to its electrochemical upgrade - requires significant inputs in each of the capture, upgrade, and separation steps. The gas-phase CO2 feed following the capture-and-release stage and into the CO2 electroreduction stage produce a large waste of CO2 (between 80 and 95% of CO2 is wasted due to carbonate formation or electrolyte crossover) that adds cost and energy consumption to the CO2 management aspect of the system. Here we report an electrolyzer that instead directly upgrades carbonate electrolyte from CO2 capture solution to syngas, achieving 100% carbon utilization across the system. A bipolar membrane is used to produce proton in situ, under applied potential, which facilitates CO2 releasing at the membrane:catalyst interface from the carbonate solution. Using an Ag catalyst, we generate pure syngas at a 3:1 H2:CO ratio, with no CO2 dilution at the gas outlet, at a current density of 150 mA/cm2, and achieve a full cell energy efficiency of 35%. The direct carbonate cell was stable under a continuous 145 h of catalytic operation at ca. 180 mA/cm2. The work demonstrates that coupling CO2 electrolysis directly with a CO2 capture system can accelerate the path towards viable CO2 conversion technologies.
Direct CO₂ Electrocatalysis from Carbonate

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The process of CO₂ valorization – all the way from capture/concentration of CO₂ to its electrochemical upgrade - requires significant inputs in each of the capture, upgrade, and separation steps. The gas-phase CO₂ feed following the capture-and-release stage and into the CO₂ electroreduction stage produce a large waste of CO₂ (between 80 and 95% of CO₂ is wasted due to carbonate formation or electrolyte crossover) that adds cost and energy consumption to the CO₂ management aspect of the system. Here we report an electrolyzer that instead directly upgrades carbonate electrolyte from CO₂ capture solution to syngas, achieving 100% carbon utilization across the system. A bipolar membrane is used to produce proton in situ, under applied potential, which facilitates CO₂ releasing at the membrane:catalyst interface from the carbonate solution. Using an Ag catalyst, we generate pure syngas at a 3:1 H₂:CO ratio, with no CO₂ dilution at the gas outlet, at a current density of 150 mA/cm², and achieve a full cell energy efficiency of 35%. The direct carbonate cell was stable under a continuous 145 h of catalytic operation at ca. 180 mA/cm². The work demonstrates that coupling CO₂ electrolysis directly with a CO₂ capture system can accelerate the path towards viable CO₂ conversion technologies.

TOC GRAPHICS
CO₂ capture systems often use alkali hydroxide solution to form alkali carbonate, and this requires additional energetic steps to dry and calcite the carbonate salt to generate a pure gas-phase CO₂ stream for the subsequent electrolysis reaction.¹⁻² Direct electrochemical reduction of carbonate from the CO₂ capture solution could bypass the energy-intensive calcination step and significantly reduce the carbon footprint of the CO₂-to-products process.

This also addresses several limitations in the state-of-the-art CO₂RR systems: CO₂ waste arising due to the conversion of CO₂ gas into carbonate anions, especially in alkaline solutions.³⁻⁴ Carbonate anions travel through an anion exchange membrane (AEM), along with some CO₂RR products, and be oxidized at the anode.⁵ Additionally, as much as 80% of the input CO₂ gas may simply exit the electrolysis cell unreacted: many systems exhibit low single-pass utilizations even along the input-to-output gas channel.⁶ As illustrated in Figure 1a, with the loss of CO₂ through carbonate formation, electrolyte crossover, and low single pass conversion efficiency, the utilization of carbon is low in many present-day CO₂RR electrolyzer designs.

We focused herein on carrying out CO₂RR electrolysis using carbonate solution directly as the carbon supply. We document 100% carbon utilization of input-carbon-to-products, evidenced by the lack of gaseous CO₂ at the reactor outlet. We do so by leveraging the facile acid/base reaction between proton and carbonate anion. We design an electrolysis system that generates CO₂ in situ from carbonate to initiate CO₂RR. Figure 1b shows the conventional/prior catalyst-membrane approach that uses a membrane-electrode-assembly (MEA) design. Here we instead use a bipolar membrane (BPM) which dissociates water to generate proton and hydroxide and directs them to the cathode and anode respectively.⁷⁻⁹ Carbonate electrolyte circulates to the cathode via a peristaltic pump. Under applied potential conditions, the BPM proton reacts with carbonate to generate CO₂ near the membrane:cathode interface (Figure 1b and Video S1) which
is reduced to value-added products via normal CO$_2$RR. The chemical balance of the full system is presented in Figure 1c.

![Diagram of CO$_2$ electrolysis cell](image)

**Figure 1.** (a) Carbon loss mechanisms in a CO$_2$ electrolysis cell with gas-fed CO$_2$. (b) Illustration of the bipolar membrane generating CO$_2$ *in situ* via the acid/base reaction of proton and carbonate ion. (c) Full chemical balance of the direct carbonate electrolysis cell with BPM.

We evaluated performance using Ag electrocatalysts (Figure S1) and Cu electrocatalysts (Figure S2) in 1 M K$_2$CO$_3$ electrolyte. The catholyte in Figure 2a-c was purged with N$_2$ to ensure that there is no dissolved CO$_2$. Ni foam was used as the anode with 1 M KOH electrolyte, a non-precious catalyst in an alkaline condition, favorable for the oxygen evolution reaction. All studies herein report the full cell voltage - which includes the series resistance, transport and kinetic overpotentials, from the cathode, anode and membrane – as seen for example in Figure 2a. The onset full-cell potentials for both Ag and Cu catalysts were observed at ca. 2.2 V, with Ag showing faster kinetics at higher applied potentials. For the Ag catalyst (Figure 2b), the CO Faradaic
Efficiency (FE) ranges from 28% to 12% at the applied current densities of 100 mA/cm² to 300 mA/cm², with the remainder of the FE being hydrogen. This yields a syngas ratio (H₂:CO) from ca. 2.5 to 7, suitable as feedstock to the Fischer-Tropsch (FT) reaction. Since the source of carbon in this reaction is carbonate - a liquid phase reactant - the gas product exiting the electrolysis cell is pure syngas with small amount of moisture. Gas chromatography confirms no CO₂ is detected from the gas outlet stream. The full cell energy efficiency (EE) is 35% at 150 mA/cm², where we have included the contributions of both CO and H₂.

Figure 2. Performance of the direct carbonate electrolysis cell. (a) Full cell j-V curve with Ag and Cu catalyst. (b) Product distribution for the Ag catalyst. H₂ and CO are the major products, summing up to ~100% of the total FE. (c) Product distribution for the Cu catalyst. Propanol, formate and acetate are detected as well in a small amount. Figure (a) – (c) are conducted in 1 M K₂CO₃ catholyte with nitrogen purging as controls to demonstrate the concept of in situ CO₂ generations. 1 M KOH and Ni foam were used at the anode. (d) The product distribution of an Ag catalyst under different applied current density (1st x-axis, mA/cm²) in different concentration of KOH electrolyte (2nd x-axis) purged with CO₂ prior to reaction, simulating the product of a CO₂ capture solution.
With a Cu catalyst, ca. 10% FE of ethylene is detected, as well as a small amount of ethanol and methane. In total, 17% CO$_2$RR to hydrocarbon products was achieved. The full product distribution is available in Table S1.

The BPM also offers the benefit of mitigating product crossover as a result of the electro-osmotic drag of the proton emerging from the membrane, opposing the direction of products migration from cathode to anode.\textsuperscript{5,11} Anolytes from the Cu catalyst experiments were checked, and no liquid products were detected on the anode side. With this system design, the carbon loss mechanisms in a typical flow cell are overcome: CO$_2$ reaction with electrolyte to form carbonate; product crossover in the AEM system; and low single pass CO$_2$ utilization.

We examined the compatibility of the direct carbonate electrolysis cell in different CO$_2$ capture solutions directly. CO$_2$ gas was bubbled into 0.1 to 2 M of KOH solutions, simulating an industrial CO$_2$ capture process, and the CO$_2$ purged electrolyte was tested for carbonate electrolysis, showed in Figure 2d. The pH of the capture solution after CO$_2$ purging was approximately 11, which indicates that carbonate is the primary carbon species after CO$_2$ capture. With an Ag catalyst, the CO FE performance was observed to increase directly with respect to the concentration of the KOH electrolyte. This is likely due to the increase of the capture-generated K$_2$CO$_3$ concentration. The best performance of the KOH-CO$_2$ capture electrolyte shows a few percentage improvements compared to the pure K$_2$CO$_3$ electrolyte (Figure 2b). This is likely due to the small amount of bicarbonate salt present in the solution, generating small amount CO$_2$ via chemical equilibrium, and also a small amount of dissolved CO$_2$, both giving additional sources of reactant.\textsuperscript{12-13}

In the full system chemical balance provided in Figure 1c, carbonate is consumed as the source of carbon in the cathodic reaction, and hydroxide is generated: this has the effect of
regenerating the CO₂ capture solution. A capture-and-electrolysis system design can therefore operate continuously: the KOH capture solution removes CO₂ from the air or flue gas, forming carbonate; the carbonate electrolyte is then reduced to form value-added products via electrolysis with high carbon utilization; and the capture solution is thereby regenerated to restart the cycle.

**Figure 3.** Stability evaluation of the direct carbonate electrolysis cell. CO₂ gas was first captured with KOH solution and transferred to an electrolysis bottle with no gas purging. The amount of gas produced from the electrolysis was measured with a mass flow meter and the ratio of H₂ and CO was monitored with GC injection. 1 M KOH and Ni foam were used at the anode. The cell was held at a constant potential of 3.8V.

We demonstrate a capture-electrolysis system in continuous operation for 145 hours with an Ag catalyst (in Figure 3). Two electrolyte bottles were used – one for capturing CO₂ gas directly with KOH electrolyte, and a second one for electrolysis. The carbonate capture solution and the electrolysis electrolyte are exchanged with a peristaltic pump (Figure S5). The electrolyte in the electrolysis bottle is pumped to the direct carbonate cell with no gas purging. Syngas generated from the reaction exits the bottle to a mass flow meter. The flow rate of gas products was recorded to calculate the total gas produced. During the 145 hours of electrolysis, the current density was
stable at ca. 180 mA/cm² due to the pH balance and crossover prevention benefits offered by the BPM. The H₂:CO ratio also remains stable at between 2 and 3. Approximately 10 L of syngas were collected.

To assess the economics of the direct carbonate reduction, we calculated the energy cost per product molecule, considering the full process all the way from CO₂ capture and electrolysis to separation processes. We evaluated:

- alkaline flow cell
- MEA cell with gas-fed CO₂
- direct carbonate cell explored herein.

Table 1 shows the summarises the results (detailed calculations available in the SI). The total energy required to generate 1 mole of products is 4 times higher in the MEA cell with gas-fed CO₂ and 20 times higher for the alkaline flow cell. Figure 4 shows the energy capital per product molecule as a function of the CO₂ capture cost and the separation cost. Even in the best-case scenario (low capture cost and low separation cost), the energy cost for CO₂RR in today’s gas-fed CO₂ MEA cells is about two times higher than in the direct carbonate cell. Regeneration costs associated with removing carbonate from the electrolyte and from the anodic side add further to the expense of producing fuels and feedstocks in the gas-fed CO₂ MEA cell.

![Energy/Product graph](image)
Figure 4. Technoeconomic analysis of the MEA cell with gas-fed CO$_2$ with different energy costs for CO$_2$ capture and different energy cost for products separation.

Table 1. The energy cost for the alkaline flow cell, CO$_2$ gas-fed MEA cell and direction carbonate cell. The cost of CO$_2$ capture was taken to be 178 kJ/mol$^1$ and the energy cost of separation is 500 kJ/mol.$^{15-16}$

| Energy Capital                  | Flow Cell | MEA   | Direct CO$_2$  |
|--------------------------------|-----------|-------|---------------|
| CO$_2$ Utilization             | 3         | 20    | 100           |
| carbonate formation (%)        | 45        | 0     | 0             |
| crossover (%)                  | 2         | 30    | 0             |
| Exit CO$_2$ (%)                | 50        | 50    | 0             |
| CO$_2$ capture (kJ/mol of product) | 5943     | 892   | 0             |
| CO$_2$ required (mol)           | 33        | 5     | 1             |
| CO$_2$ Electrolysis (kJ/mol of product) | 476      | 733   | 733           |
| EE (%)                         | 54        | 35    | 35            |
| Separation (kJ/mol)            | 8333      | 1250  | 0             |
| Energy/Product (kJ/mol of product) | 14753    | 2874  | 733           |

A number of topics require further study and progress in the direct carbonate cell. The thermodynamic onset potential for CO$_2$ reduction to syngas is approximately 1.34 V, and the experimental onset potential is ca. 2.2 V. The overpotential is large compared to a water electrolyzer, which obtains 1 A/cm$^2$ using less than 1 V of full cell overpotential.$^{18}$ The optimization of each cell components will be required to increase the full cell EE further and thereby lower the energy consumption for CO$_2$RR. While the gas products generated in the direct carbonate electrolysis cell do not contain CO$_2$, moisture is present in the exit stream, and requires separation before the syngas is utilized. There are also several competing reactions on the cathodic side. When a proton is generated from the BPM, it can be reduced directly on the cathode, leading to HER; when CO$_2$ is generated from carbonate, it can react with KOH, forming carbonate again, instead of being reduced in CO$_2$RR; and the proton from the BPM can also simply react with KOH in the electrolyte to form water. The penalties for these side reactions are reflected in less-than-
100% total Faradaic efficiencies seen herein. The study of syngas in this report benefits from an industrially chosen preference of 30% CO₂-to-CO mixed with H₂, thus fits well with the finite FE to CO;¹⁹ but future studies of carbonate-to-products will benefit from further insights, progress, and innovation to other higher value products in better conversion efficiency.

The system design herein achieves direct carbonate conversion via the acid/base reaction of proton and carbonate, which generates an in-situ source of CO₂, enabled by the use of a bipolar membrane. The device operated continuously for 145 hours and generated pure syngas in an optimal ratio suited for subsequent FT reaction. A faradaic efficiency of 17% of total carbonate-to-hydrocarbon products was also achieved with a Cu catalyst. This study demonstrates the direct implementation of carbonate to CO₂RR products from a CO₂ capture solution as input and a gas product suitable for the FT reaction as output. It enables direct CO₂ utilization from air or flue gas capture to hydrocarbon products.
ASSOCIATED CONTENT

**Supporting Information.** The Supporting Information is available free of charge on the ACS Publications web site at DOI:XXX

Experimental details and supplementary Figures S1-5

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**Notes**

The authors declare no competing financial interest.

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Supplementary Information for

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**Experimental Methods**

**Catalysts synthesis.** All reagents used in this work were purchased from Sigma Aldrich without further purification. Ag catalysts were prepared by spray coating Ag nanoparticle ink onto a sputtered Ag film. For the Ag film, Ag was first sputtered on a carbon paper (AvCarb MGL190, Fuel Cell Store) using an Ag target at the sputtering rate of ~1 Ås⁻¹ in order to fabricate a 300 nm thick Ag film. 200 mg of Ag nanoparticles were then dispersed in a mixture of 10mL of methanol, 125 uL of Nafion and 50 mg of carbon black (Super P® Conductive, Alfa Aesar) and then sonicated for 1hr. On the top of the Ag film, the Ag nanoparticle ink was spray coated with a loading of ~2 mg/cm² and dried under atmospheric conditions. Cu catalysts were prepared by spray coating Cu nanoparticles ink onto a Cu film. For the Cu film, Cu was first sputtered on a carbon paper (AvCarb MGL190, Fuel Cell Store) using a Cu target at a sputtering rate of ~1 Ås⁻¹ in order to fabricate a 300 nm thick Cu film. 200 mg of Cu nanoparticles were then dispersed in a mixture of 10 mL of methanol and 400 uL of Alkaline inomer (Sustainion® XA-9, Dioxide Materials), and then sonicated for 1hr. On the top of the Cu film, the Cu nanoparticles ink was spray coated with a loading of ~2 mg/cm² and dried under atmospheric conditions.

**Materials characterizations.** The Ag and Cu catalysts were characterized by field emission scanning electron microscopy (Hitachi, SU5000), showing uniform coating over the entire carbon paper and porous structure down to the 100s of nm scale. X-ray diffraction (MiniFlex600) data was collected with Cu Kα as the radiation source.

**Electrochemical characterizations.** Electrochemical characterization was performed using an electrochemical station (PGSTAT204) with a commercial membrane electrode assembly (MEA) cell (Dioxide Materials). The as-synthesized Ag or Cu catalyst was used as the cathode catalyst and Ni foam was used as the anode catalyst. A bipolar membrane (Fumasep FBM, Fuel Cell Store) was used as the separator in accordance with the manuscript. The catholyte (40ml) was either 1 M K₂CO₃ or CO₂ saturated KOH and it is circulated using a peristaltic pump. The anolyte (40ml) is 1 M KOH and it is circulated to using a peristaltic pump. The j-V polarization curve was obtained by applying constant currents to the cell for three minutes and averaging the stable voltages from the last minute.

The gas phase products are analyzed using a gas chromatography (Clarus® 580) coupled with a thermal conductivity detector (TCD) and a flame ionization detector (FID), with Ar as the carrier gas. The liquid phase products are characterized by high performance liquid chromatography (UltiMate 3000). Typically, 1 ml of liquid sample was injected into the HPLC after 20 min of operation. All Faradaic efficiency (FE) measurements were repeated three times for average and error bar.

The syngas full cell energy efficiency (EE) with the Ag catalyst is calculated according to the equation below:

\[
\text{Energy Efficiency} = \frac{E_{CO}}{\text{Applied potential}} \times FE_{CO} + \frac{E_{H2}}{\text{Applied potential}} \times FE_{H2}
\]

Where the \(E_{CO}\) (1.34 V) and \(E_{H2}\) (1.23 V) are the thermodynamic onset voltage for CO and hydrogen generation respectively.
**Long term stability test.** The stability test was operated in a capture-electrolysis configuration (Figure S5). CO$_2$ was first captured using a 2 M KOH solution generating carbonate and simulating the industrial capture process; the carbonate saturated solution is delivered to a 2nd bottle with a peristaltic pump with no gas purging. Total electrolyte between the capture bottle and the electrolysis bottle is about 1.5 L. The carbonate saturated electrolyte is then pumped to the carbonate cell with an Ag catalyst, Ni foam and BPM as the cathode, anode and separation membrane respectively. 1 M KOH was used as the anolyte and circulated to the anode in a similar fashion to the cathode. The cell was held at a constant potential of -3.8 V for the whole duration of the test. The gas products exit the reaction is measured with a mass flow meter to determine the total volume generated. The gas contents were collected and monitored by gas chromatography periodically during the stability test in order to confirm the H$_2$:CO ratio.
**Technoeconomic Analysis**

To assess the economic value of the direct carbonate cell, we compared it with well-known \( \text{CO}_2 \text{RR} \) systems - alkaline flow cell\(^3\) and gas-fed MEA cell. The energy capital for the overall \( \text{CO}_2 \) reduction is divided into three steps – \( \text{CO}_2 \) capture, electrolysis and products separation. We fully noted that the economic performance of each system depends on the targeted products, reaction conditions, operation scale and many more other factors. This exercise provides a first-degree estimation of the basic energy cost only.

**CO\(_2\) Capture.** The energy consumption for the \( \text{CO}_2 \) capture step, based on the generation of 1 mole of product, is calculated using the \( \text{CO}_2 \) utilization rate and the \( \text{CO}_2 \) capture energy cost. The \( \text{CO}_2 \) capture energy cost in Table 1 was given a value of 178.3 kJ/mol based on air capture.\(^2\) We should note that the \( \text{CO}_2 \) capture step with hydroxide solution is thermodynamically downhill, this energy cost is required for the \( \text{CO}_2 \) release from carbonate step. This number could vary based on the capture technology and Figure 4 in the main manuscript explores the effect of this value from 50 to 178 kJ/mol.

The existing \( \text{CO}_2 \text{RR} \) systems suffer from carbonate formation, crossover and low single pass conversion. Thus, to generate 1 mole of product, a higher amount of input \( \text{CO}_2 \) is required. In the case of the alkaline flow cell, we estimate 45% of \( \text{CO}_2 \) loss to carbonate formation, 2% loss to crossover and 50% loss to unreacted exit.\(^3\) This leaves us with a 3% \( \text{CO}_2 \) utilization, which in turn requires 33 moles of \( \text{CO}_2 \) for 1 mole of product. The total energy cost for \( \text{CO}_2 \) capture is then calculated as 5943 kJ/mol product for the alkaline flow cell. In the gas-fed MEA cell, the catholyte of the MEA system is humidified \( \text{CO}_2 \), therefore, the system is free from carbonate formation. However, humidified \( \text{CO}_2 \) forms bicarbonate ions with water moisture; and under the applied potential condition with an AEM membrane, bicarbonate is the only anion available for transport across the membrane.\(^5\) We estimate a 30% \( \text{CO}_2 \) loss due to crossover from our own experimental observations running MEA system. We also assume a 50% \( \text{CO}_2 \) loss to unreacted \( \text{CO}_2 \) similar to the alkaline flow cell system. The \( \text{CO}_2 \) capture energy requirement for the gas-fed MEA cell is then 892 kJ/mole of product. In comparison to the two existing systems, the direct carbonate reduction system is able to convert 1 mole of carbonate to 1 mole product directly. The system reaches 100% of \( \text{CO}_2 \) utilization and the capture energy is 0.

\[
\text{Energy Cost for Capturing} = \text{Capture energy (kmol of CO}_2\text{) × 1 mol of product} \div \text{CO}_2\text{ Utilization (\%)}
\]

| Energy Capital          | Flow Cell | MEA   | Direct CO\(_2\)\(^2\) |
|-------------------------|-----------|-------|-----------------------|
| carbonate formation (%) | 45        | 0     | 0                     |
| crossover (%)           | 2         | 30    | 0                     |
| Exit CO\(_2\) (%)       | 50        | 50    | 0                     |
| \( \text{CO}_2 \text{ capture (kJ/mol Prod.)} \) | 5943      | 892   | 0                     |

**Electrolysis.** The electrolysis energy required for the \( \text{CO}_2 \) reduction is based on the theoretical Gibb’s free energy of reaction for \( \text{CO}_2\)-to-CO divided by the full cell energy efficiency. The energy efficiency of each system is obtained from literature and this work. The best record of energy efficiency for the flow cell system is 54%.\(^3\) The EE for the direct carbonate reduction system in this study is 35% and we assume a similar performance can be achieved in gas-fed MEA system.
The energy costs are then 476 kJ/mole for the alkaline flow cell system, 733 kJ/mole for the MEA system and the direct carbonate system.

\[
\text{Energy cost for electrolysis} = \Delta G_{CO} \left( \frac{\text{kJ}}{\text{mole of CO}} \right) / \text{Energy efficiency (\%)}
\]

Where \( \Delta G_{CO} = 257.2 \text{ kJ/mol} \)

| Energy Capital    | Flow Cell | MEA | Direct CO\(_2\)-CO\(_2\) RR (kJ/mol Prod.) |
|-------------------|-----------|-----|------------------------------------------|
| CO\(_2\)RR (kJ/mol Prod.) | 476       | 733 | 733                                      |
| EE (%)            | 54        | 35  | 35                                       |

**Products separation.** In this work, we assume a fixed cost of 500 kJ/mol for products separation.\(^6\) We note that this number has considerable variation and we explored value from 100 kJ/mol up to 900 kJ/mol in Figure 4 in the main manuscript.

\[
\text{Separation energy} = \text{Fix cost} \left( \frac{\text{kJ}}{\text{mole of gas}} \right) \times \text{gas emission at outlet (mol)}
\]

The gas emission at the outlet is defined as the unreacted CO\(_2\), along with products, exiting the electrolyzer after the capture and electrolysis steps. We note that syngas was the targeted product in this study and we have 0 energy cost for separation. However, if a different targeted product from CO\(_2\)RR is required, such as ethylene, the separation cost of ethylene from hydrogen is still required.

| Energy Capital  | Flow Cell | MEA | Direct CO\(_2\)-CO\(_2\) RR (kJ/mol) |
|-----------------|-----------|-----|-------------------------------------|
| Separation (kJ/mol) | 8333      | 1250| 0                                   |

In conclusion, the total energy required for the overall CO\(_2\) conversion is then the sum of the individual energy requirements from the capture, electrolysis and separation steps.
Figure S1. SEM images of the as-synthesized Ag catalyst.
Figure S2. SEM images of the as-synthesized Cu catalyst.
Figure S3. XRD diffraction pattern of the Ag catalyst. The reflection labelled with “*” is contributed from the carbon substrate.
**Figure S4.** XRD diffraction pattern of the Cu catalyst. The reflection labelled with “*” is contributed from the carbon substrate.
**Figure S5.** Experimental setup of the long-term stability test. CO₂ was captured (1) in 2 M KOH to generate carbonate. The saturated carbonate is then pumped to a new bottle (2) and reduced in a direct carbonate cell (3). The gas products generated exit the reaction and were measured by a mass flow meter (4) to determine total volume.
Table S1. Product distribution of the Cu catalyst in the direct carbonate cell under different applied current density. “tr” indicates the FE is lower than 1%.

| j (mA/cm²) | CO (%) | H₂ (%) | CH₄ (%) | C₂H₄ (%) | C₂H₅OH (%) | HCOO⁻ (%) | C₃H₇OH (%) | Total (%) |
|------------|--------|--------|---------|----------|-------------|-----------|------------|-----------|
| 150        | tr     | 75.3   | 1.3     | 6        | 3.6         | 2.2       | tr         | 89.5      |
| 200        | tr     | 73.8   | 2.5     | 8.3      | 3.3         | 2         | tr         | 91.1      |
| 250        | tr     | 84.7   | 3.2     | 10.1     | 4.3         | 2.1       | tr         | 104.4     |
| 300        | tr     | 83.7   | 3.2     | 7.1      | 4.1         | 1.2       | 1.5        | 100.8     |
| 350        | tr     | 86.5   | 3.2     | 6.3      | 4.4         | tr        | 1.8        | 102.2     |
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