Eliminating the need for anodic gas separation in CO₂ electroreduction systems via liquid-to-liquid anodic upgrading

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Electrochemical reduction of CO₂ to multi-carbon products (C₂+), when powered using renewable electricity, offers a route to valuable chemicals and fuels. In conventional neutral-media CO₂-to-C₂+ devices, as much as 70% of input CO₂ crosses the cell and mixes with oxygen produced at the anode. Recovering CO₂ from this stream adds a significant energy penalty. Here we demonstrate that using a liquid-to-liquid anodic process enables the recovery of crossed-over CO₂ via facile gas-liquid separation without additional energy input: the anode tail gas is directly fed into the cathodic input, along with fresh CO₂ feedstock. We report a system exhibiting a low full-cell voltage of 1.9 V and total carbon efficiency of 48%, enabling 262 GJ/ton ethylene, a 46% reduction in energy intensity compared to state-of-art single-stage CO₂-to-C₂+ devices. The strategy is compatible with today’s highest-efficiency electrolyzers and CO₂ catalysts that function optimally in neutral and alkaline electrolytes.

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The electrochemical conversion of CO₂ (CO₂RR) to multi-carbon (C₂₉) products is a promising approach to reducing net CO₂ emissions. The best existing CO₂RR flow cell systems and zero-gap membrane electrode assembly (MEA) systems achieve C₂ᵉ Faradaic efficiencies (FEs) of 70% and C₂ₓ partial current densities of over 1 A cm⁻² in flow cells and over 100 mA cm⁻² in MEAs. These productivity levels are in a regime of interest with respect to industrial application.

Nevertheless, the total energy required for present-day CO₂-to-C₂ electrolysis is too high—for example, when targeting ethylene, today’s electrosynthesis systems require fully 8x more energy to produce ethylene than is embodied in the product. Major energy costs are incurred in the electrolyser and the downstream separation steps (see Methods: Energy assessment and Supplementary note 1 in SI). Established approaches to reducing the electrolysis energy requirements include increasing the selectivity for the target product and incorporating alternative anode reactions. The major energy and economic penalties associated with downstream separation of CO₂ remain a challenge.

Downstream separation is required to isolate products and recover unconverted CO₂ from the product streams and electrolytes. Recovering CO₂ is particularly costly, requiring 25% and 70% of total energy input in the case of neutral and alkaline media, CO₂-to-C₂ electrolysers, respectively. Present-day CO₂RR catalysts operate with highly alkaline local conditions (pH > 12) to promote C₂⁺ generation at the cathode. However, the carbonate-forming side reaction (CO₂ + OH⁻ → CO₃⁻ or HCO₃⁻) is favored under alkaline conditions, consuming the majority of the CO₂ injected.

Operating with neutral electrolytes (e.g., KHCO₃) in a membrane electrode assembly cell mitigates CO₂ loss. However, a significant amount of input CO₂ (~3x more than the fraction that converted to C₂⁺) crosses the anion exchange membrane (AEM) to the anode as carbonate/bicarbonate, combining with the protons generated from the anodic reaction and is converted back to CO₂ (Fig. 1a).

On the anode side, crossover CO₂ combines with O₂ produced via the oxygen evolution reaction (OER) to produce a gas mixture of 60–80% CO₂ and 20–40% O₂. This mixture cannot be directly recycled into the cathode because oxygen reduction would dominate at the cathode. As a result, separation of CO₂ is required downstream of the anode, incurring an energy penalty of over 100 mA cm⁻² for the electrolyser8. However, prior systems that employed OOR as an alternative anode reaction at the anode. Recent techno-economic analyses have suggested substituting OER with OOR as an opportunity to reduce full-cell voltage and produce salable products from both sides of the cell. Candidate anode reactions include water-to-hydrogen peroxide23,24, chloride-to-hypochlorite25, and a wide range of organic oxidation reactions (OORs)13,26,27. However, previously-published catalysts for hydrogen peroxide and hypochlorite production result in gaseous by-products.

Here we adopt the organic oxidation reaction at the anode. The approach requires an all-liquid-phase anodic process that produces protons (or consumes hydroxides) and operates in near-neutral media. Candidate anode reactions include water-to-hydrogen peroxide23,24, chloride-to-hypochlorite25, and a wide range of organic oxidation reactions (OORs)13,26,27. However, previously-published catalysts for hydrogen peroxide and hypochlorite production result in gaseous by-products. In this work, we couple the CO₂RR with the glucose oxidation reaction (GOR) and demonstrate the liquid-phase anodic process.

Glucose is abundant from biomass, with an average market price of $400-500 ton⁻¹, mainly produced from starch. In 2017, over 5 million tons of glucose were produced in the United States (https://www.statista.com/statistics/494685/glucose-production-in-the-us/). Electrochemical oxidation of glucose produces gluconate, glucuronate, and glucarate (Fig. S1)33,34, and these are feedstocks for the production of biopolymers35 and pharmaceuticals36. Gluconic acid commands a market price of $700–1600/ton2,37,38. The projected market size of gluconic acid is ~$80 million39 (2024). Recent techno-economic assessments estimated that renewable energy-powered electrochemical glucose oxidation reaction (GOR) is economically feasible. GOR outcompetes OER at industrially relevant reaction rates in neutral and near-neutral electrolytes. GOR also offers electrolysing energy savings, with a thermodynamic potential of 0.05 V1, significantly lower than that of OER (1.23 V). In this work, we couple the CO₂RR with the glucose oxidation reaction (GOR) and demonstrate the liquid-phase anodic process.

Carbon efficiency (%) = \frac{F₃}{F₁} × 100\%

In an ordinary AEM-based, zero-gap CO₂RR-OER electrolyser (Fig. 1a, b), a large portion of input carbon (F₂, roughly triple to F₄) crosses over from the cathode to the anode and combines with the protons from the anodic process to regenerate gaseous CO₂. Without recirculation, this system shows a carbon efficiency (<30%) close to that of ordinary MEA electrolysers. We noted that if the anodic reaction is designed to be all-liquid in nature—i.e., if it avoids O₂ evolution—then the approach avoids contamination of this CO₂ stream with O₂. The recovered CO₂ is of high purity (>99%), enabling direct recycling to the cathode (Fig. 1d), i.e., F₁ = F₃ + F₄. Such a system breaks the 25% CO₂ utilization limit in AEM-based electrolysers, avoids the full energy penalty associated with anodic gas separation, and does so without incurring penalties to full-cell voltage or selectivity to ethylene.

The approach requires an all-liquid-phase anodic process that produces protons (or consumes hydroxides) and operates in near-neutral media. Candidate anode reactions include water-to-hydrogen peroxide23,24, chloride-to-hypochlorite25, and a wide range of organic oxidation reactions (OORs)13,26,27. However, previously-published catalysts for hydrogen peroxide and hypochlorite production result in gaseous by-products. In this work, we couple the CO₂RR with the glucose oxidation reaction (GOR) and demonstrate the liquid-phase anodic process.
strategy. The system shows a low full-cell voltage of 1.9 V and total carbon efficiency of 48%, enabling 262 GJ/ton ethylene, a 46% reduction in energy intensity compared to state-of-art single-stage CO2-to-C2+ devices.

Results

Catalyst characterization. To perform CO2RR on the cathode, we deposited Cu nanoparticles and perfluorosulfonic acid (PFSA) ionomer on a hydrophobic porous polytetrafluoroethylene (PTFE) gas diffusion electrode. The PTFE gas diffusion electrode was pre-sputtered with 200 nm-thick polycrystalline Cu to improve electrical conductivity (see Methods for details). Scanning and transmission electron microscopy (SEM and TEM, respectively) images reveal a surface morphology composed of Cu nanoparticles bonded by several tens of nm-thick PFSA ionomer films (Fig. 2a). The anode electrode comprised a homogeneous blend of Pt/C nanoparticles and PFSA ionomer on a hydrophilic and highly porous carbon fiber cloth substrate (see Methods for further details). SEM images confirm that the anode is composed of macroporous carbon fibers (Fig. 2b) that are homogeneously covered by Pt/C nanoparticles and PFSA composites (inset in Fig. 2b). TEM images in Fig. 2c show that the diameter of Pt nanoparticles is in the range 5–10 nm. Energy-dispersive X-ray spectroscopy (EDS) elemental mapping reveals that Pt is evenly distributed on the surface of C nanoparticles (Fig. 2e and g).

Electrochemical characterization of the CO2RR-GOR system. We conducted linear scan voltammetry (LSV) measurements to investigate the electrochemical response of the CO2RR-GOR system with a cathode Cu loading of 0.5 mg cm−2 and an anode Pt loading of 2 mg cm−2 (Fig. 3a and b). When we did not add glucose to the anolyte (CO2RR-OER), the electrolyzer delivered a current density of 94 mA cm−2 at a full-cell voltage of 3 V. At 100 mA cm−2, when we introduced glucose, increasing its concentration in the anolyte from 0.1 to 0.5 M and 1 M, the full-cell voltage decreased from 2.90 to 2.18 V and 2.23 V. The full-cell
We thus adopted 1 M glucose for the performance investigations. An increase in the glucose concentration to 2 M enabled further reduction in the cell voltage. A further increase in the glucose concentration to 1 M does not enable further reduction in the cell voltage to <2.4 V (Fig. S5a) and consequently the O2 FE to <1% (Fig. S5d) with the full-cell voltage of 3.23 V and O2 FE of 7% (Fig. S5a, b). This is not overcome by further increasing Pt loading (Fig. S5a, b), attributed to accelerated electrochemical kinetics. A similar degradation of selectivity of GOR over OER, leading to an anodic efficiency of >8% (Fig. S5b), attributable to accelerated electrochemical kinetics. A similar degradation of selectivity of GOR over OER, leading to an anodic efficiency of >8% (Fig. S5b), attributed to accelerated electrochemical kinetics. A similar degradation of selectivity of GOR over OER, leading to an anodic efficiency of >8% (Fig. S5b), attributed to accelerated electrochemical kinetics.

Performing LSV and chronopotentiometry measurements, we investigated the voltage-current density dependence at various temperatures (Fig. 3b and c). Elevating the operating temperature from 20 to 35 °C lowers the full-cell voltage by 0.1–0.3 V in a wide range of current densities from 80 to 160 mA cm−2 (Fig. 3b and c), attributed to accelerated electrochemical kinetics. A similar full-cell voltage reduction was observed as the operating temperature increased from 35 to 50 ºC.

Table 1 Energy assessment comparison between the state-of-art CO2-to-ethylene CO2RR devices.

| Metrics                                      | Neutral-MEA4 | Acidic flow cell14 | Acidic MEA21 | This work (max carbon efficiency) | This work (max FE) | This work (min energy) |
|----------------------------------------------|--------------|--------------------|--------------|-----------------------------------|--------------------|------------------------|
| Reaction pair                                | CO2R-OER     | CO2R-OER           | CO2R-OER     | CO2R-GOR                          | CO2R-GOR           | CO2R-GOR               |
| Cell type                                     | MEA          | Flow cell          | MEA          | MEA                               | MEA                | MEA                    |
| Electrolyte                                   | Neutral      | Acidic             | Acidic       | Neutral                           | Neutral            | Neutral                |
| Full-cell voltage (V)                         | 3.75         | 4.20               | 3.80         | 1.90                              | 1.80               | 1.90                   |
| Ethylene FE (%)                               | 45           | 28                 | 34           | 26                                | 45                 | 32                     |
| Anode O2 FE (%)                               | 100          | 100                | 100          | —                                 | 0.6                | —                      |
| Anode GOR FE (%)                              | 0            | 0                  | 0            | —                                 | 94e                | —                      |
| Current density (mA cm−2)                     | 120          | 1200               | 100          | 100                               | 100                | 100                    |
| Input CO2 flow rate (sccm cm−2)               | 10           | 3                  | 0.8          | 0.18                              | 10                 | 0.36                   |
| CO2 carbon efficiency (%)                    | 3.6          | 78                 | 31           | 78                                | N/A                | 48                     |
| CO2-to-ethylene carbon efficiency (%)         | 1.2          | 28.4               | 10.5         | 36                                | 1.1                | 23                     |
| Demonstrated stability (h)                   | 100b         | 14c                | 8d           | —                                 | —                  | 80b                    |
| Energy distributions (GJ per ton ethylene)    |              |                    |              |                                   |                    |                        |
| Electrolyser electricity                     | 345          | 620                | 462          | 302                               | 165                | 246                    |
| Cathode gas separation                       | 38           | 17                 | 23           | 17                                | 147                | 16                     |
| Anode gas separation                         | 71           | 0                  | 0            | 0                                 | 0                  | 0                      |
| Overall energy                               | 499          | 637                | 485          | 319                               | 312                | 262                    |

*aAll the data sets from references are the ones that consume the least overall energy for producing one ton of ethylene.
*bRecorded with the CO2 carbon efficiency indicated in the same column above.
*cRecorded with a CO2 carbon efficiency of 20%.
*dRecorded with a CO2 carbon efficiency of 1.8%.
*eThe sum of the GOR product FEs obtained from NMR (Fig.3e) and HPLC (Fig. S13).
*fThe comparison between CO2RR-OER and CO2RR-GOR systems can be found in Table S14 of SI.

Fig. 2 Electron microscopy characterization of MEA electrolysers. a Scanning electron microscopy (SEM) and transmission electron microscopy (TEM, inset) images of the cathodic catalyst: Cu nanoparticles/PFSA composite. b SEM images of the anodic catalyst: Pt/C loaded on hydrophilic carbon fibers. c SEM images of the Pt/C catalyst. d-g The scanning transmission electron microscope image (d) and corresponding Energy-dispersive X-ray spectroscopy (EDS) elemental mappings of carbon (e), platinum (f), and overlap (g) for Pt/C catalyst.

Achieving high ethylene FE and low oxygen FE simultaneously. Maintaining a low OER FE is critical to ensure high GOR efficiency and sufficient purity of the recovered CO2. In the present CO2RR-GOR system, we found that the cathodic and anodic catalysts needed to be carefully engineered to enable the CO2 recovery strategy.

In prior studies, typical mass loadings of the cathode Cu (CO2RR) and anode Pt (GOR) were 1 mg cm−2,6,44 and 0.5 mg cm−2,8. When we used these configurations in our CO2RR-GOR system, we obtained high full-cell voltages of >3.4 V when seeking to operate above 100 mA cm−2, Fig. S5a, showing little advantage over CO2RR-OER systems (Fig. S3). The high full-cell voltage degraded the selectivity of GOR over OER, leading to an anodic O2 FE of >8% (Fig. S5b).

Reexamining Pt loading was essential to reduce the full-cell voltage to <2.4 V (Fig. S5a), and consequently the O2 FE to <1% (Fig. S5b) at the current density of 120 mA cm−2. However, operating at this current density, the CO2RR selectivity toward ethylene is ~30% (Fig. S5c, d), significantly lower than the 40–45% benchmark for Cu6,8. To achieve this benchmark, the system must run at 200 mA cm−2 (Fig. S5d) with the full-cell voltage of 3.23 V and O2 FE of 7% (Fig. S5a, b). This is not overcome by further increasing Pt loading (Fig. S5a), as discussed in Fig. S5. Tuning the Cu loading changes the current density required to maximize the ethylene FE. We, therefore, pair a 0.5 mg cm−2 Cu cathode with a 2 mg cm−2 Pt anode to achieve...
Detected anodic CO$_2$ flow

Acetate

Recovery efficiency detected from cathodic CO$_2$ electricity demand (Table 1). At 100 mA cm$^{-2}$ toward GOR. Such a low full-cell potential significantly reduces electrictiy demand (Table 1). At 100 mA cm$^{-2}$, the system delivers ethylene FEs of 42%, 48%, and 44% at 2 °C, 35 °C, and 50 °C (Figs. S7, 3d, Tables S5, S6 and S8). The Cu-sputtered on the PTFE GDE is unlikely to participate in CO$_2$RR: we observed similar performance when spraying Cu nanoparticles onto a hydrophobic carbon paper (Fig. S4).

We investigated the selectivity of the GOR in a wide range of current densities (from 80 to 160 mA cm$^{-2}$) and operating temperatures (Fig. 3e, Tables S7 and S9). With the temperature increasing from 20 to 50 °C, we detected a slight increase in anolyte pH (from pH 7.9 to 8.3, Fig. S10), attributable to the lower solubility of CO$_2$ in warmer anolyte. We detected glucuronate as the major GOR product (>49% FE), achieving a plateau of 58% at 140 mA cm$^{-2}$. The full analysis of GOR products is shown in Figs. S12 and S13. The FEs toward oxygen remained <3% at current densities from 80 and 160 mA cm$^{-2}$ (<1% at 100 mA cm$^{-2}$ and a full-cell voltage of 1.80 V) owing to the sluggish kinetics of OER (Fig. 3a).

Recovering CO$_2$. The CO$_2$ recycling strategy requires a high CO$_2$ recovery efficiency, in this work defined as:

\[
\text{Recovery efficiency} = \frac{\text{Detected anodic CO}_2\text{ flow (mol s}^{-1})}{\text{Theoretical CO}_2\text{ crossover (mol s}^{-1})} \times 100\%
\]  

Fig. 3 Performance of the CO$_2$RR-GOR electrolysis system. The mass loadings on the cathode and anode are Cu: 0.5 mg cm$^{-2}$ and Pt: 2 mg cm$^{-2}$. a, b The linear scan voltammetry (LSV) of the CO$_2$RR-GOR electrolysis system with various glucose concentrations (0 M refers to CO$_2$RR-OER on a high-surface-area IrO$_2$-Ti catalyst) at 20 °C (a) and (b) with 1M glucose at various temperatures. All the profiles were recorded at a scanning rate of 5 mV s$^{-1}$ immediately after three cycles of voltammetry scanning. c The full-cell potentials of the CO$_2$RR-GOR at various temperatures which are measured by applying constant currents. d CO$_2$RR FE distributions at 50 °C and a number of different current densities. The liquid FEs are based on the sum of products detected from cathodic anolyte outlets. e FE distributions of liquid products (measured by NMR and GC) of GOR at various current densities at 50 °C. GOR products were also quantified using HPLC, see Fig. S13. f The CO$_2$ and O$_2$ flow rates (normalized by electrode geometric area) in the anodic gas streams at 50 °C. The simulated CO$_2$ is assessed by the stoichiometry of generated OH$^-$ and transferred electrons, assuming CO$_2$ is converted to CO$_3^{2-}$.
The theoretical CO2 crossover (mol s\(^{-1}\)) = \frac{I(A)}{F(C_{\text{mol}}^{-1})} \times \frac{1}{2} \quad (3)

where \(I\) refers to the current and \(F\) the Faraday constant. Here, the CO2 crossing over to the anode is in the form of carbonate\(^{17}\). The experiment suggested that the amount of CO2 collected at the anode is in good agreement with the stoichiometry of OH\(^-\) generated and electrons transferred\(^{17}\) (Fig. 3f), indicating a CO2 recovery efficiency approaching 100% (Fig. 3g). In addition, the anodic CO2 flow rate is three orders of magnitude larger than that of O\(_2\) (Fig. 3f), indicating a purity of CO2 recovered from the anodic gas stream exceeding 99% (Fig. 3g). This low level of O\(_2\) enables direct recycling of this anode gas stream in the cathode without the need for separation and associated energy costs. Notably, an oxygen fraction of over 1.8% deteriorates the CO2RR selectivity, as seen in control studies in Fig. S3. Specifically, the cathodic gas product FE distribution (Fig. 3d) of the CO2-RR-ORR, with the anodic CO2 stream directly fed into the cathode, approaches to within 5% absolute the CO2-RR-ORR electrolyser (Fig. S3). The control experiments (Figs. S13, S14) and 13C mass balance analysis (Table S4) show that >99.8% of the anodic CO2 is not from the overoxidation of glucose. These experimental observations are in good agreement with the mass balance analysis provided in Fig. 1c.

Avoiding the cathode-side CO2RR liquid products crossover. Ethylene production via CO2RR is accompanied by liquid-phase products such as ethanol, acetate, and propane, much of which crosses the membrane to the anode stream\(^4\). Cathode-to-anode crossover of liquid products is a challenge in CO2RR as these products risk oxidation and dilution in the anolyte. With ORR on the anode side, there is the additional risk that cathode-produced liquids will contaminate the liquid anode product stream and the gaseous CO2 stream\(^{2,27}\). When we increased the temperature from 20 to 50 °C, we found that the FE of the major gas products of CO2RR (C\(_2\)H\(_4\) and CO) increased from 48 to 56% at a constant current density of 100 mA cm\(^{-2}\) (Figs. S4, 3d and h). This observation agrees with previous studies, attributable to the positive entropy change of the CO2RR\(^{45,46}\). The FE toward the liquid products of CO2RR decreased from 24 to 9%—a trend consistent with a previous report\(^4\). The higher temperature significantly reduced the crossover of ethanol and n-propanol (Fig. S8) to the anode side, a finding we assign to the increased rate of evaporation into the cathode gas stream. As a result, the weight ratio of the liquid CO2RR products to the GOR target products in the anolyte stream was <1% at 50 °C (Fig. S9), in contrast to 1.4% at 35 °C (Fig. S9). In light of the evidence that: (i) the total CO2RR FF is close to 100% (Fig. 3d, negligible loss due to anode oxidation) and (ii) the ethanol oxidation signal is absent in the CV profiles of the anolyte (Fig. S14), we conclude the oxidation of the CO2RR liquid products at the anode is insignificant. Thus, operating at modestly elevated temperatures benefits the CO2RR-GOR system by reducing full-cell voltage and suppressing the formation and crossover of liquid CO2RR products.

**CO2RR-GOR system performance.** Encouraged by these findings, we explored the carbon efficiency upper limits in the CO2RR-GOR system. A widely employed approach\(^{14,21}\) to determine carbon efficiency upper limits is restricting the CO2 availability at the cathodic stream and measuring the ratio between F3 (CO2 converted to products) and F1 (CO2 feeding). The current and FE distributions determine F2 and F3. F1 is regulated to tune the CO2 availability. In the CO2RR-GOR system, F1 = F3 + F4, meaning that F4 needs to be suppressed by lowering F1 to achieve high carbon efficiency. In principle, in a given electrolysis system, the relative values of F1, F2, F3, and F4 are proportional to the electrolyser area. We thus normalize all the flow rates by the electrolyser area in this study to focus in on the intrinsic properties of this system.

Decreasing the input CO2 flow rate increases the carbon efficiency, as is typical in these systems (Table S10 and Fig. 4b). At an inlet CO2 flow rate of 0.18 sccm cm\(^{-2}\) (flow rates are normalized by electrode area), the system delivered a total C\(_2\)+ FE of ~34% at a constant current density of 100 mA cm\(^{-2}\) and a full-cell voltage of 1.90 ± 0.1 V, corresponding to a carbon efficiency of 75% toward all CO2RR products (total carbon efficiency, Fig. 4a and b), exceeding the upper limit of carbon efficiency in neutral media CO2RR electrolyses\(^{46,14}\). At these conditions the ethylene FE stabilizes at ~26%, corresponding to a CO2-to-ethylene carbon efficiency of ~36% (Fig. 4b). This carbon efficiency is 1.4-fold greater than the theoretical upper limit of 25% in CO2-to-ethylene conversion in conventional, neutral-media, AEM-based electrolyses\(^{14}\). Restricting the flow rate results in a significant increase in the hydrogen FE (Fig. 4a), which we and others\(^{46,14}\) attribute to the mass transfer limitation of CO2. GOR maintains consistent selectivity and productivity at the anode, independent from CO2 availability in the cathodic gas stream (Fig. 4a and Table S11).

A trade-off between carbon efficiency and ethylene FE is typical of CO2-to-ethylene electrolyses\(^{4,6,14}\) (Fig. 4a and b). A higher carbon efficiency reduces the energy demand for cathode separation, but the accompanying decrease in ethylene FE increases the specific electrolyser energy demand. To reconcile these metrics, we assess the total input energy (electricity, cathode separation, and anode separation per ton of ethylene produced) of various CO2RR approaches (see “Methods”\(^6\)). We find that the CO2RR-GOR system achieves the lowest energy consumption of 262 GJ per ton ethylene, and achieves this with the input CO2 flow rate of 0.36 sccm cm\(^{-2}\), a total carbon efficiency of 48% toward all CO2RR products. Under this condition, the FE toward C\(_2\)+ and ethylene are 45% and 32%, respectively (Table 1).

Compared to state-of-art conventional CO2-to-ethylene systems (i.e., MEAs based on AEM and neutral electrolyte), the CO2RR-GOR system eliminates the anodic separation energy (>53 GJ per ton ethylene, Supplementary note 1). The overall energy intensity of ethylene production is ~46% less than the most energy-efficient prior CO2RR systems among neutral and acidic CO2-to-ethylene electrolyses (Table 1).

**Stability with high carbon efficiency.** Stability is a prerequisite for the industrial application of CO2RR. However, long-term operation of CO2RR with a high carbon efficiency (e.g., CO2 carbon efficiency >40%) has not been achieved to date. The best CO2 carbon efficiency achieved for a run duration of 100 h was <4%\(^6\).

We performed extended CO2RR under the operating conditions that enable the lowest energy intensity of ethylene production. The CO2RR-GOR system achieves stable electro-synthesis of cathodic C\(_2\)+ and anodic products for over 80 h at a constant current density of 100 mA cm\(^{-2}\), comparable to the stability of conventional MEAs\(^4\). The system maintains an average full-cell voltage of 1.90 ± 0.1 V, an average total C\(_2\)+ FE of 42%, and an average carbon efficiency of ~45% toward all CO2RR products (Fig. 4c, Table S12). Similarly, we detected stable GOR productivity throughout (Fig. 4c, Table S13). Notably, this CO2- to-C\(_2\)+ electrolyser demonstrates high stability while maintaining high carbon efficiency.
and CO2-to-C2H4 (mole ratio of the input CO2 converted to C2H4) at various CO2 input geometric area of the electrodes.

100 mA cm−2 achieves a low full-cell potential of 1.90 V at a current density of high CO2 conversion of up to 75%. The combined system simultaneously. The CO2 that crosses to the anode was recovered returning CO2 to the cathodic upstream, this strategy achieves a from the anodic downstream with a high purity of >99%. By accounting for the total electricity and downstream separation energy costs, this method achieves a total energy intensity of 262 GJ per ton of ethylene produced, ~46% lower than that of previous CO2RR electrolyses. This work contributes a route to high carbon efficiency in CO2RR electrolysis.

Discussion

We demonstrate that pairing CO2RR with an all-liquid anodic reaction in neutral media combines high carbon efficiency and low energy input in the electrosynthesis of renewable chemicals and fuels. One key to implementing this strategy is pairing the catalyst mass loadings on the cathode and anode to maximize CO2RR product selectivity and minimize anodic OER selectivity simultaneously. The CO2 that crosses to the anode was recovered from the anodic downstream with a high purity of >99%. By returning CO2 to the cathodic upstream, this strategy achieves a high CO2 conversion of up to 75%. The combined system achieves a low full-cell potential of 1.90 V at a current density of 100 mA cm−2 and stable electroysis of C2H4 products for over 80 h while maintaining a high CO2 conversion of 45%. Accounting for the total electricity and downstream separation energy costs, this method achieves a total energy intensity of 262 GJ per ton of ethylene produced, ~46% lower than that of previous CO2RR electrolyses. This work contributes a route to high carbon efficiency in CO2RR electrolysis.

Methods

Materials. Potassium bicarbonate (KHCO3, 99.7%), D-glucose (99.5%), copper nanoparticles (25 nm), Nafion™ 1100 W (5 wt.% in a mixture of lower aliphatic alcohols and water) and Pt/C (40 wt.% Pt on Vulcan XC72) were purchased from Sigma Aldrich and used as received. Aquивion D79-25BS ionomer was purchased from Fuel Cell Store. Piperion (40 μm) was used as the anion-exchange membrane, purchased from W7Energy and stored in 0.5 M KOH. The water used in this study was 18 MΩ Milli-Q deionized (DI-) water.

Electrodes. For the CO2RR, we prepared the gas diffusion electrodes (GDEs) by spray-depositing a catalyst ink dispersing 1 mg mL−1 of Cu nanoparticles and 0.25 mg mL−1 of Nafion™ 1100 W in methanol onto a PTFE substrate that pre-sputtered with a 200 nm thick polycrystalline Cu layer. The substrate was prepared by sputtering Cu target, at a rate of 1 Å s−1 onto a piece of PTFE membrane in a Magnetron sputtering system3. The mass loading of Cu nanoparticles on the GDE was tuned between 0.5 and 1.0 mg/cm2. The GDEs were dried in the air overnight prior to experiments.

For the GOR anode electrodes, a commercially available Pt/C was first physically mixed with ionomer (Aquивion D79-25BS) in a glass beaker and then sonicated for 1 h. The resulting catalyst ink was then spray coated on both sides of the hydrophilic carbon cloth until the Pt loading of 0.5−3.2 mg cm−2 was achieved.

Characterizations. Scanning electron microscopy (SEM) images of cathode and anode were captured by an FEI Quanta FEG 250 environmental SEM. X-ray photoelectron spectra (XPS) of the electrodes were determined by a model 5600, PerkinElmer using a monochromatic aluminum X-ray source.

Assembling of the CO2RR-GOR system. The MEA set (5 cm2) was purchased from Dioxide Materials. A cathode was cut into a 2.5 cm × 2.5 cm piece and placed onto the MEA cathode plate with a flow window with a dimension of 2.23 cm × 2.23 cm. The four edges of the cathode were sealed by copper tapes and then Kapton tapes, and make sure the tapes did not cover the flow window. A Piperion AEM (40 μm, 3 cm × 3 cm) was carefully placed onto the cathode. A gasket with a 2.23 cm × 2.23 cm window was placed on the cathode. The Pt/C loaded carbon cloth anode (2 cm × 2 cm) was placed onto the AEM.

Electrochemical measurements. All the data in this work were collected with 0.5 mg/cm2 Cu (cathode) and 2 mg/cm2 Pt (anode) unless otherwise specified. All the performance metrics were recorded after at least 1000 s of stabilization at a specific condition. The full-cell voltages reported in this work are not iR corrected. All the error bars are presented as standard deviation based on three measurements. The potential cut-off was set to 10 V, and the current applied on the cell was in the range of 0.2–1.0 A.
To evaluate the performance of the CO₂RR-GOR system under different conditions, the cathode side of the MEA was fed with CO₂ flow (0.18–10 scm cm⁻² of electrode area, 10 sccm cm⁻² if not specified) that comes from both CO₂ feedstock and anodic gas stream unless specified. The anode side was circulated with a solution containing 1 M KHCO₃ and glucose with various concentrations (0.1–2 M) at 10 mL/min by a peristaltic pump. A gas-tight glass bottle with four in/out channels (gas inlet, gas outlet, liquid inlet and liquid outlet) was used as the anolyte reservoir and gas-liquid separator. In typical CO₂RR-GOR performance evaluations, the gas inlet channel was sealed, and the gas outlet channel is connected to a ‘Y’ shape tubing connector. Since the anolyte reservoir/gas-liquid separator is gas-tight, the CO₂ pressure between the feedstock stream and anodic stream will eventually be balanced and promote a steady flow rate from both sides. The electrochemical measurements were performed with a potentiostat (Autolab PGSTAT204 with 10 A booster).

The auxiliary system for heating the CO₂RR-GOR electrolyser is shown schematically in Fig. S15. To evaluate the performance of the CO₂RR-GOR system, the cathode was replaced by a Pt/C catalyst spray-coated onto a hydrophobic carbon paper with a loading of 0.7 mg cm⁻². The anolyte and the GOR liquid products in a certain period were deduced from the collected liquid from the cathode side and the anode gas. The FE of a gas product is calculated as follows:

\[
FE = \frac{n_F}{n_i} \times \frac{V_P}{RT}
\]

Where \(x_i\) is the volume fraction of the gas product, \(i\) is the MEA cathode outlet gas flow rate in L s⁻¹ (measured by a bubble flow meter), \(P\) is atmosphere pressure 101.325 kPa, \(R\) is the ideal gas constant 8.314 J mol⁻¹ K⁻¹, \(T\) is the room temperature in K, \(n_i\) is the number of electrons required to produce one molecule of product \(F\) is the Faraday Constant 96485 C mol⁻¹, and \(J\) is the total current in A. To analyse the anodic gas stream component, the gas outlet channel of the anolyte reservoir was disconnected from the tubing for circulating to the cathode. A 20 sccm argon flow was input from the ‘gas inlet’ channel of the anolyte reservoir as the carrier gas to promote the accurate analysis of CO₂ and O₂ components in the anode gas.

The liquid products from the cathode side of the SC-MEA were collected using a cold trap containing 5 mL 0°C water. The collected liquid from the cathode side and the anolyte were quantified separately by the proton nuclear magnetic resonance spectroscopy (¹H NMR) on an Agilent DD2 500 spectrometer in D₂O using water suppression mode and dimethyl sulfoxide (DMSO) as the internal standard. Typical ¹H NMR spectra of GOR can be found in Fig. S11. Fresh anolyte was used for each liquid product quantification plot, and the collection duration was 30–60 minutes. The FE of a liquid product is calculated as follows:

\[
FE = m_l \times \frac{n_F}{n_i} \frac{V_P}{RT}
\]

Where \(m_l\) is the quantity of the liquid product in mole, \(t\) is the duration of product collection (1800–3600 seconds).

To evaluate the stability of the CO₂RR-GOR system, the CO₂RR gas and cathodic product were evaluated using the above-mentioned methods. 50 μL of anolyte (the total volume is 10 litres) was periodically (every 15–20 h) sampled for ¹H NMR analysis. The quantity of the CO₂RR liquid products that cross over to anolyte and the GOR liquid products in a certain period were deduced from the concentration increment from the beginning to the end of this period.

The by-products of the GOR were also measured by high-performance liquid chromatography (UltiMate 3000 HPLC) equipped with an Aminex HPX-87H column (Bio-Rad) and a reflective index detector. The eluent is 0.05 M H₂SO₄ and the column was kept at 60 °C.

The anodic CO₂, CO, and H₂O were analyzed for gLIC at the Geobiology Isotope Laboratory at the University of Toronto using a Finnigan Gas Bench coupled with a Thermo-Finnigan MAT 253 gas source isotope ratio monitoring mass spectrometer. The Finnigan Gas Bench sample tray was heated to 72 °C and loaded with vials of CO₂ gas samples. Sample vials were first flushed with helium gas. CO₂ samples from the anodic gas stream and cylinder were directly injected into the vials. The CO₂ samples reacted with phosphoric acid to release CO₂. The glucose sample (60–300 μg) reacted with 1 μL oxidant solution (100 mM H₂O₂ + 4.0 g K₂S₂O₈ + 200 mL of 85% H₃PO₄) to release CO₂. Measured carbon isotopes were compared to the reference materials, CaCO₃, MERCK (in-house standard), IAEA-CO-8, NBS-19 and IAEA-CO-1 (International Atomic Energy Agency Reference Products for Environment and Trade). Carbon isotope data are reported in the standard delta (δ) notation relative to Vienna Pee Dee Belemnite (VPDB).

Energy assessment. We evaluated the energy consumptions for electrolyser electricity, cathodic separation, and anodic separation in the context of ethylene—<sub>1</sub>CO₂—feeding to the processes. We consider the state-of-the-art CO₂RR systems from the literature, including neutral MEA electrolyzers, acidic flow-cell, and MEA. This consideration is based on the performance metrics, including selectivity, productivity, and full-cell voltage—a combination of them reflects as energy intensity of producing multi-carbon products (i.e., ethylene). The proximity of these performance metrics will help refine the effect of anodic and cathodic separation on the energy requirement for producing ethylene. We summarize the input parameters to the model for all the systems. The majority of these input parameters listed in Table 1 are from literature and this work. Cathodic gas separation was modeled into two steps: (i) pressure swing adsorption to remove CO₂; (ii) cryogenic distillation to separate ethylene from hydrogen and CO. We employed one of the most widely used models (i.e., biogas upgrading) for evaluating the energy cost associated with cathode gas separation. The energy assessment on anodic CO₂/O₂ separation is evaluated in Supplementary note 1 of SI.

For acidic flow-cell and MEA electrolyzers, we assume no energy cost associated with the anodic separation considering no CO₂ availability at the anodic gas stream. The separation energy of the anodic GOR products is not included in this assessment. A previous techno-economic assessment on the electrochemical GOR suggested that the overall process of the electrochemical GOR is economically feasible. We, therefore, assume that the energy consumed for anodic GOR product purification can be fully covered by selling the value-add GOR products and does not include it in the comparison between different CO₂RR devices.

Data availability

The data generated in this study are provided in Supplementary Information and Source Data file. Source data are provided with this paper.

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