

## Supplementary Materials

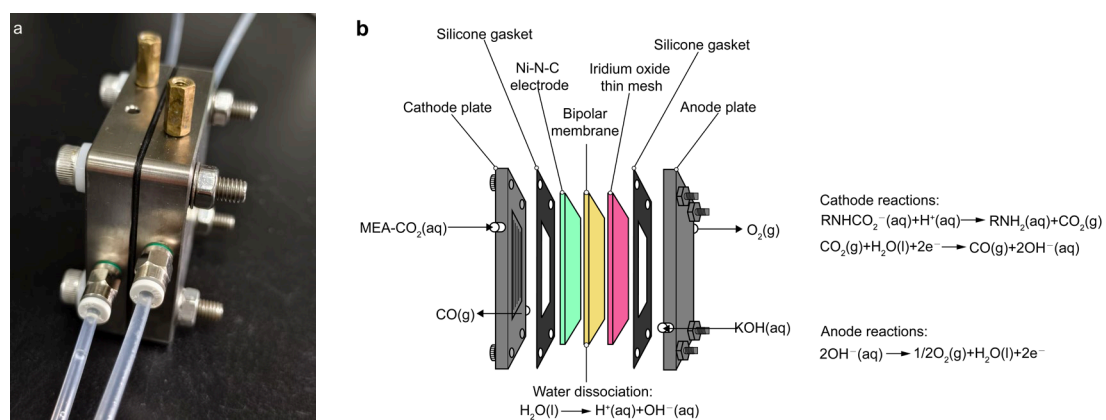
**Amine-mediated, oxygen-tolerant concerted capture and electrochemical conversion of CO<sub>2</sub> from flue gas**

**Manuscript Author:**

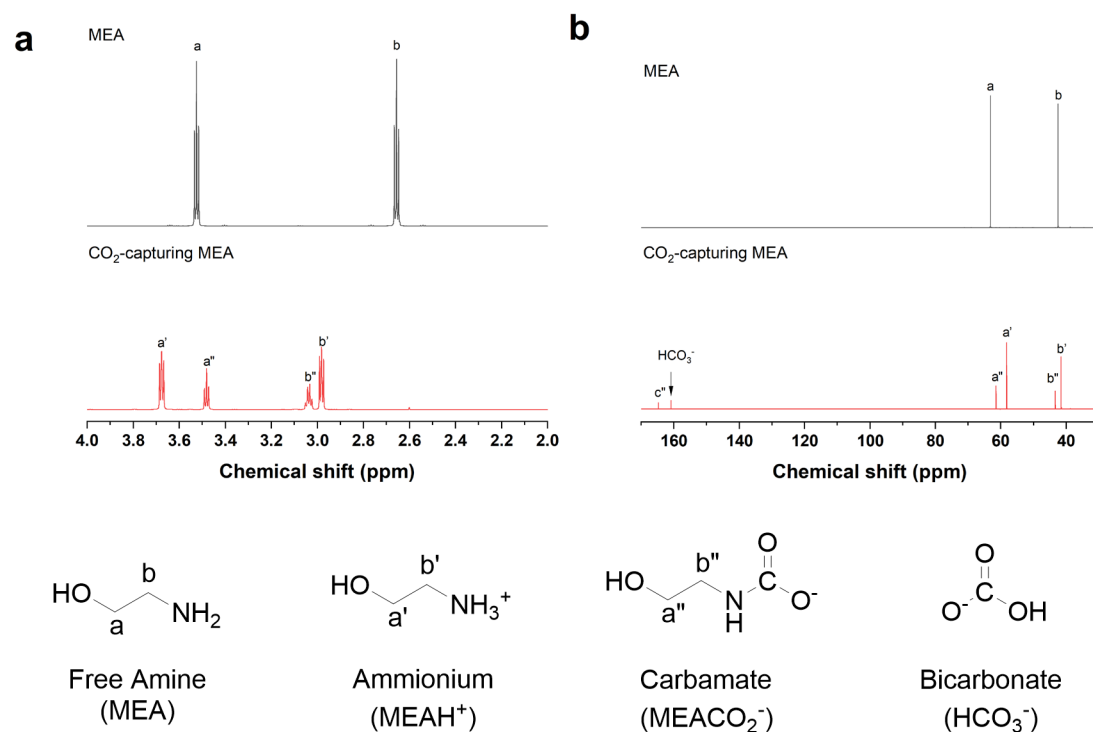
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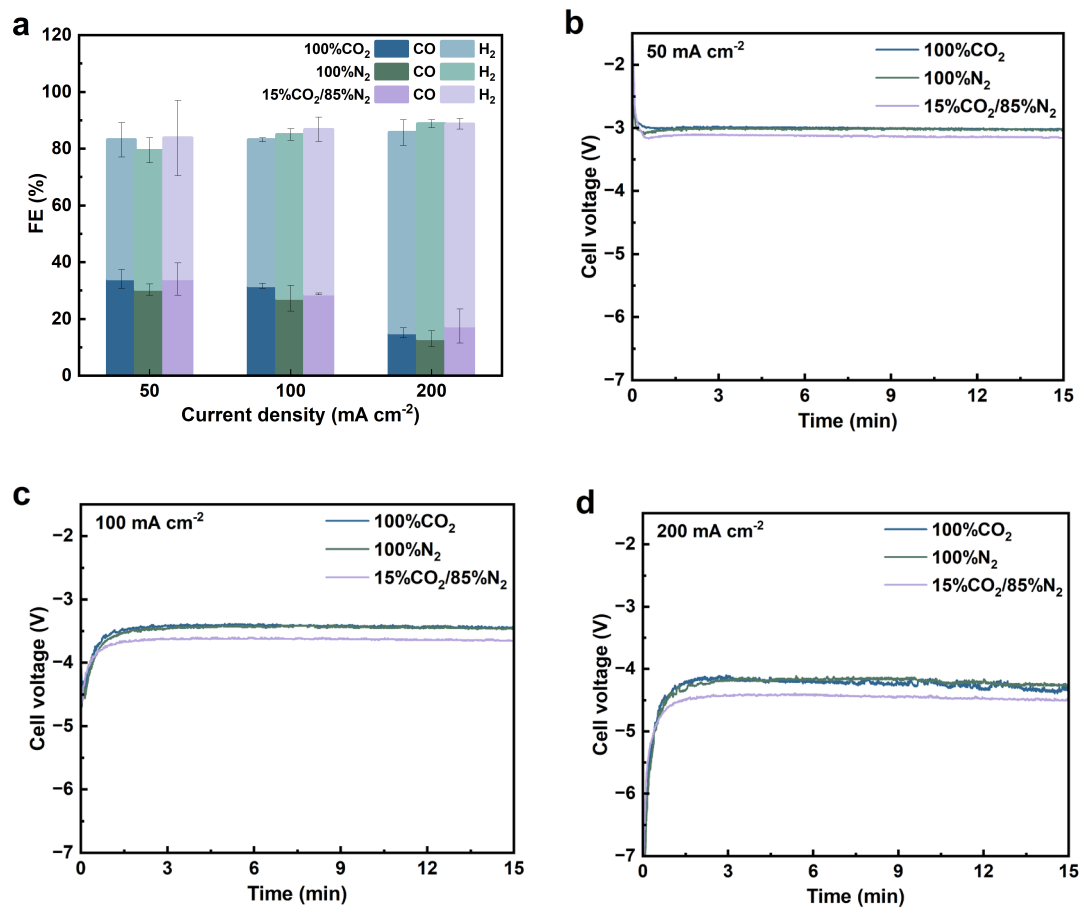
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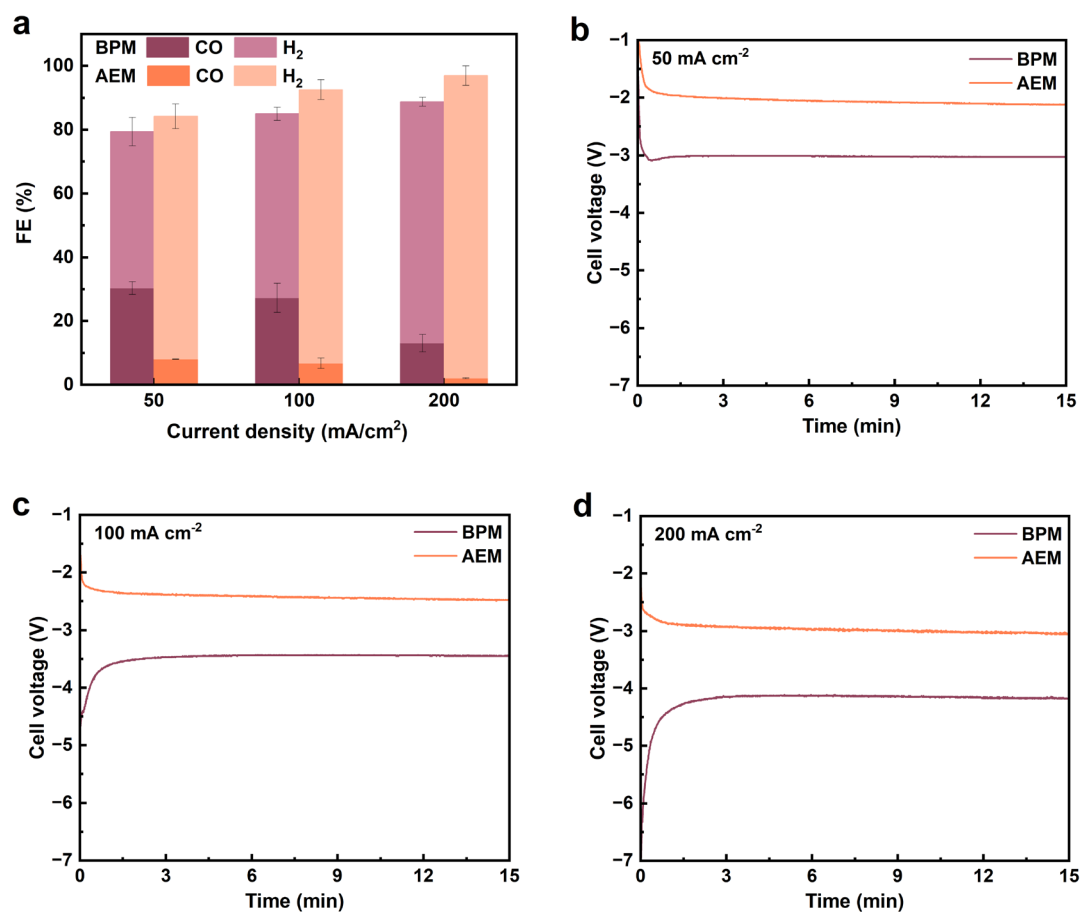
**Supplementary Figure 1.** (a) The photograph and (b) schematic diagram of the liquid-fed electrolyzer.



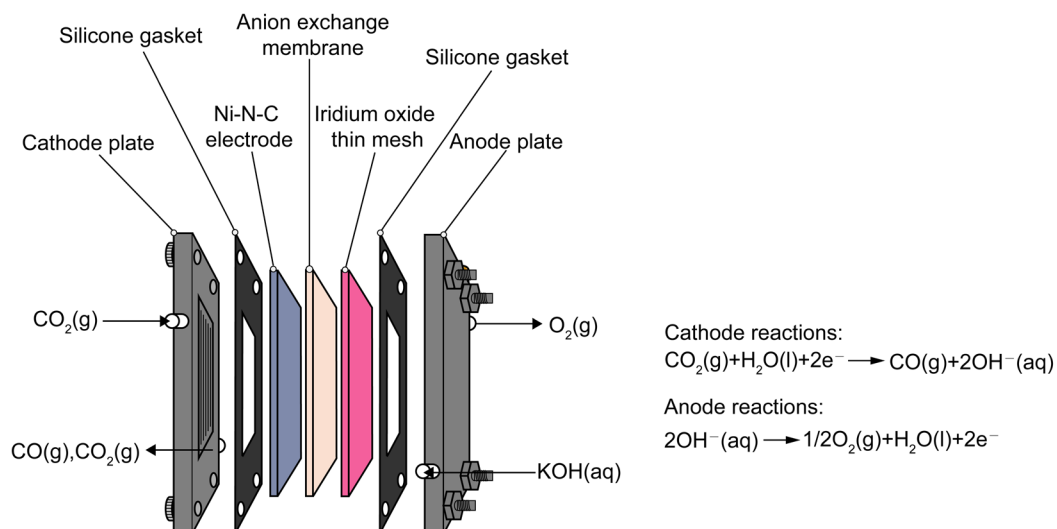
**Supplementary Figure 2.** (a) <sup>1</sup>H and (b) <sup>13</sup>C NMR spectra of 5 M MEA solution and CO<sub>2</sub>-capturing MEA solution.



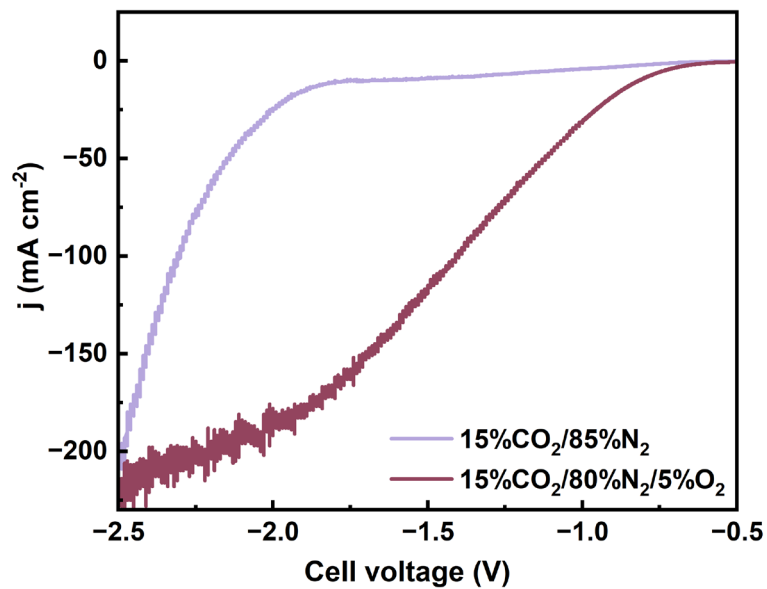
**Supplementary Figure 3.** FE and cell voltage recorded for electrolysis of CO<sub>2</sub>-capturing 5 M MEA solution at current densities of 50, 100, and 200 mA cm<sup>-2</sup> under 100%CO<sub>2</sub>, 100%N<sub>2</sub>, and 15%CO<sub>2</sub>/85%N<sub>2</sub> conditions.



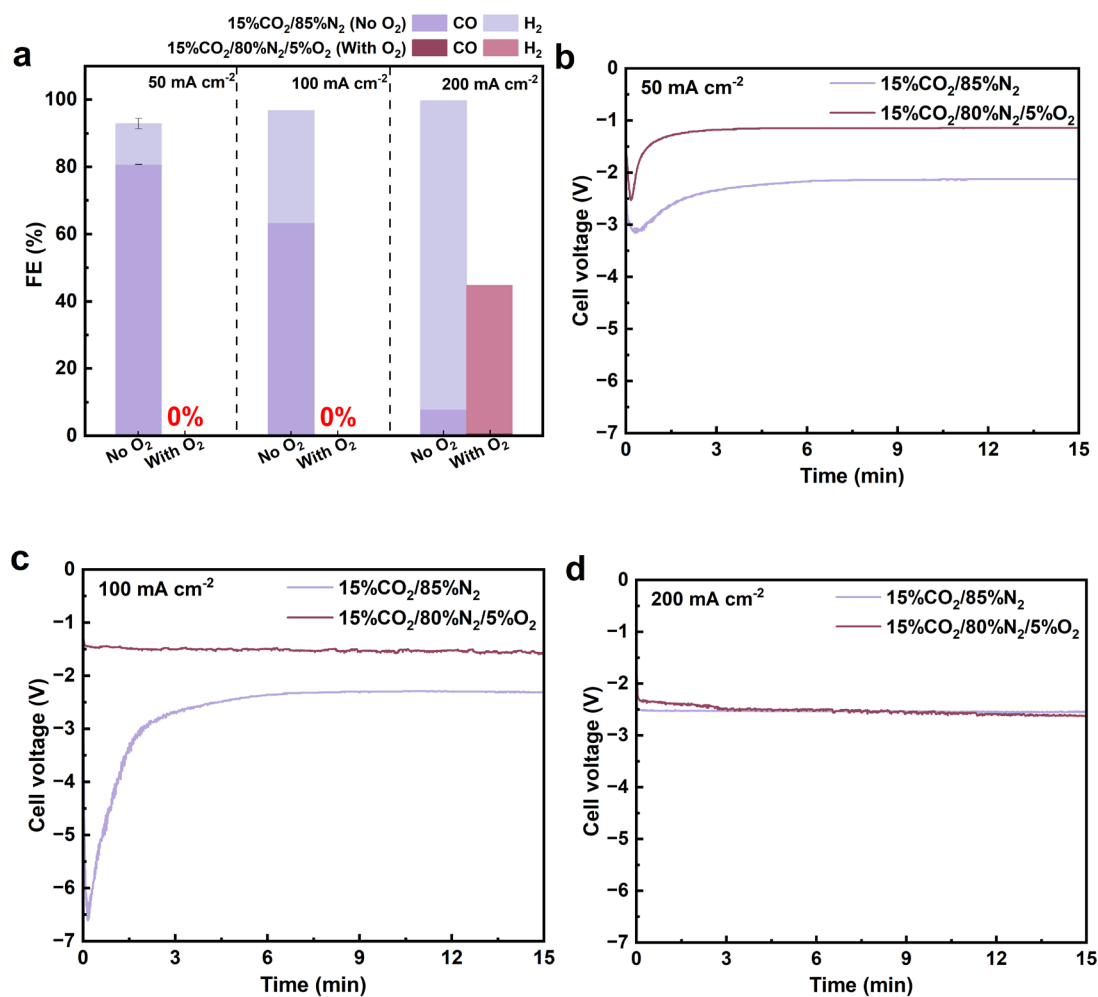
**Supplementary Figure 4.** FE and cell voltage recorded for electrolysis of CO<sub>2</sub>-capturing 5 M MEA at 50, 100, and 200 mA cm<sup>-2</sup> under N<sub>2</sub> atmosphere using a BPM and an AEM.



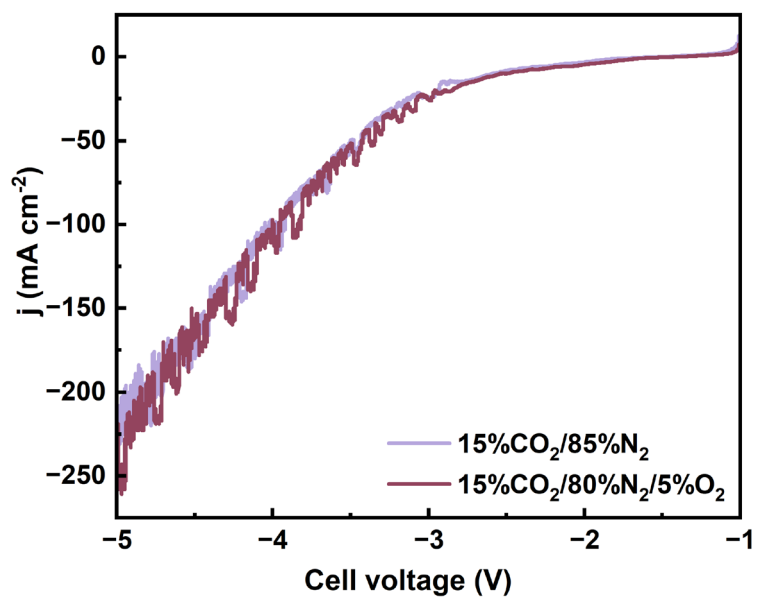
**Supplementary Figure 5.** Schematic diagram of the gas-fed electrolyzer.



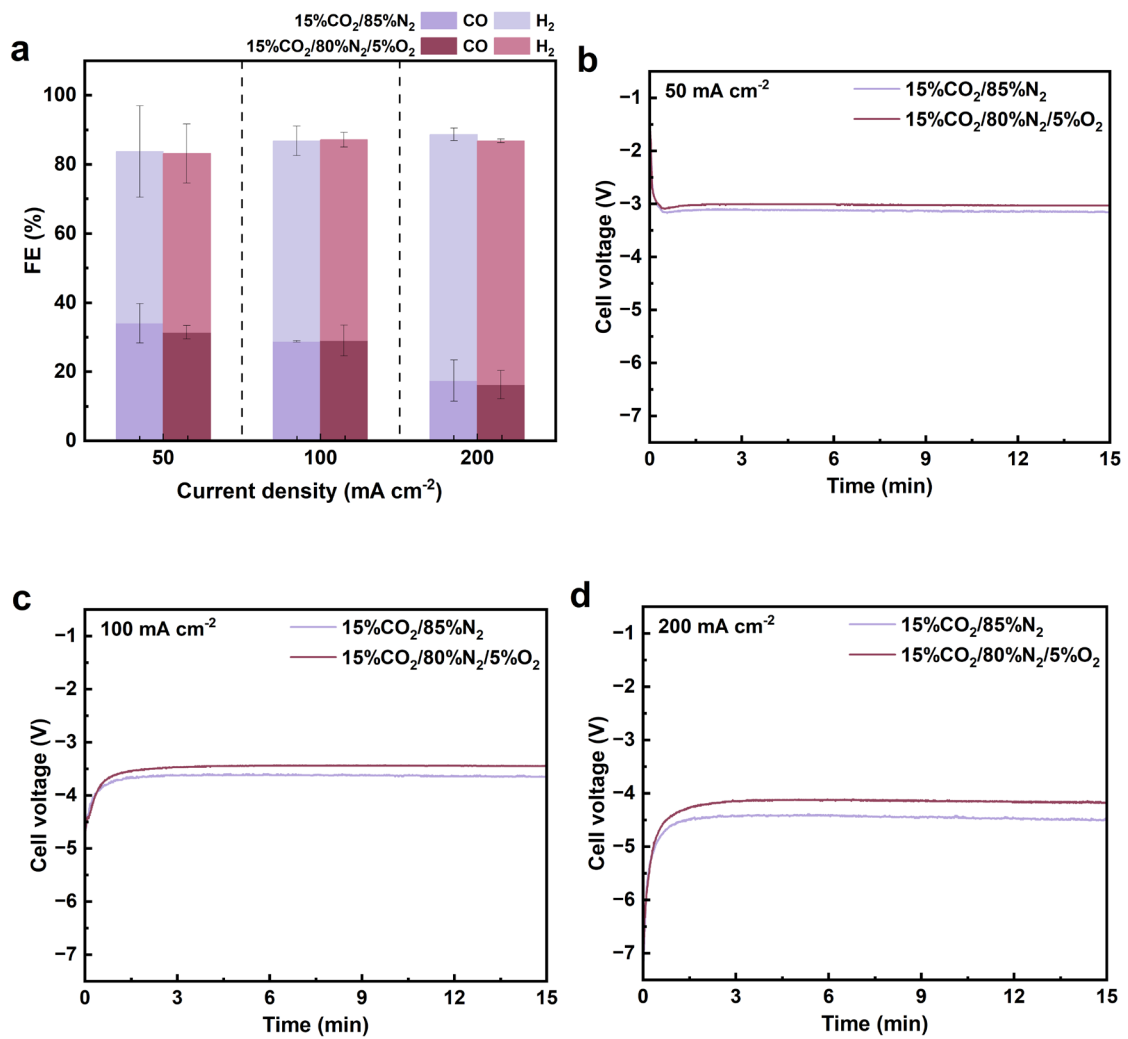
**Supplementary Figure 6.** LSV curves obtained in the gas-fed electrolyzer under 15%CO<sub>2</sub>/85%N<sub>2</sub> and 15%CO<sub>2</sub>/5%O<sub>2</sub>/80% N<sub>2</sub> conditions. Scan rate: 10 mV/s.



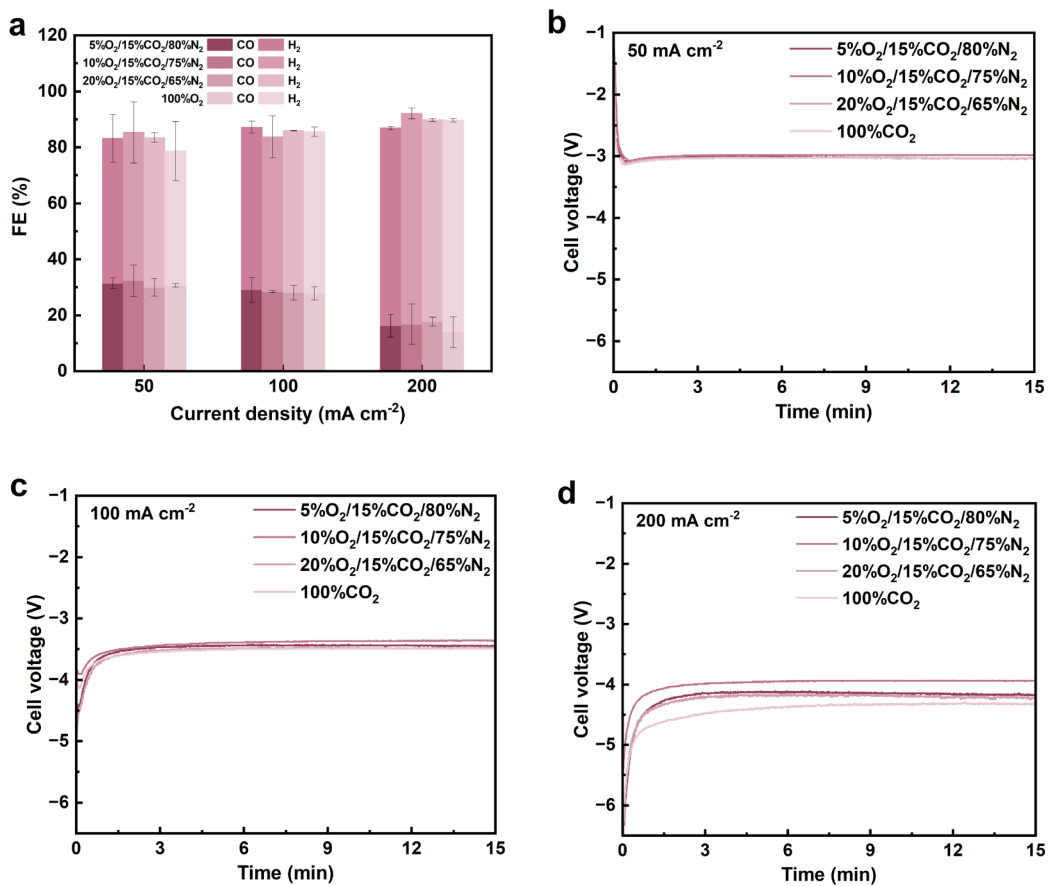
**Supplementary Figure 7.** FE and cell voltage recorded for electrolysis of 15%CO<sub>2</sub>/85%N<sub>2</sub> and 15%CO<sub>2</sub>/5%O<sub>2</sub>/80%N<sub>2</sub> at 50, 100, and 200 mA cm<sup>-2</sup> in the gas-fed electrolyzer.



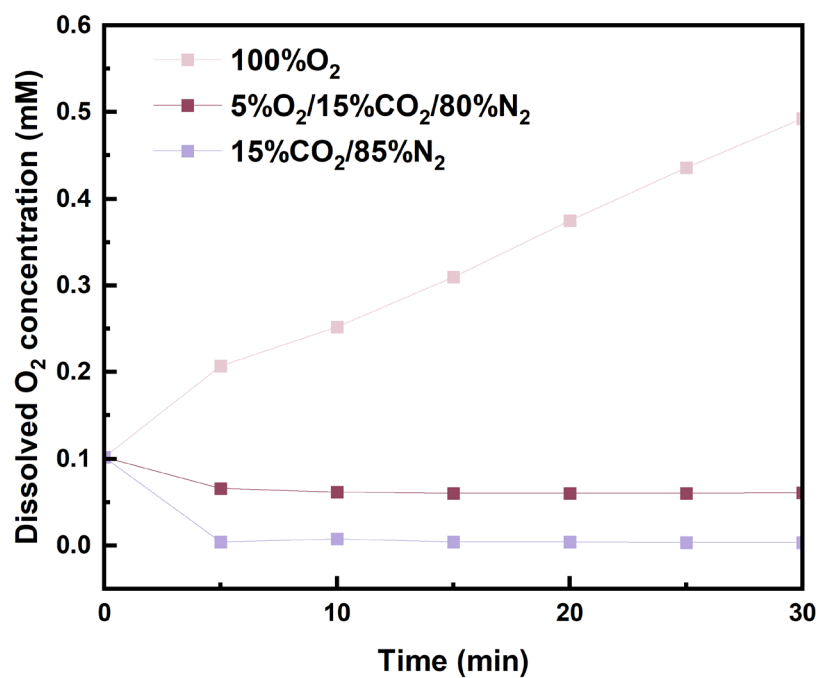
**Supplementary Figure 8.** LSV curves of CO<sub>2</sub>-capturing 5 M MEA liquid-fed electrolyzers under 15%CO<sub>2</sub>/85%N<sub>2</sub> and 15%CO<sub>2</sub>/5%O<sub>2</sub>/80%N<sub>2</sub> conditions. Scan rate: 10 mV/s.



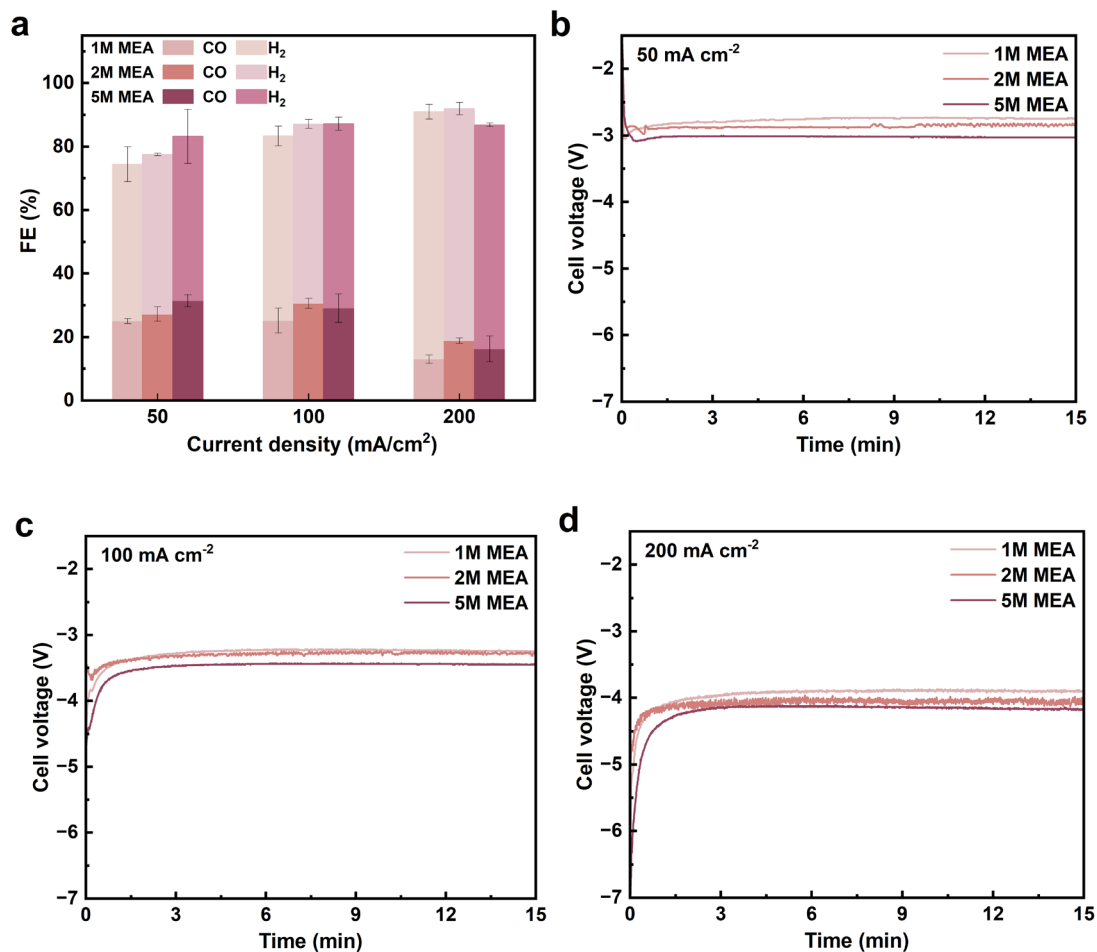
**Supplementary Figure 9.** FE and cell voltage recorded for electrolysis of CO<sub>2</sub>-capturing 5 M MEA in the liquid-fed electrolyzer at 50, 100, and 200 mA cm<sup>-2</sup> under 15%CO<sub>2</sub>/85%N<sub>2</sub> and 15%CO<sub>2</sub>/5%O<sub>2</sub>/80%N<sub>2</sub>.



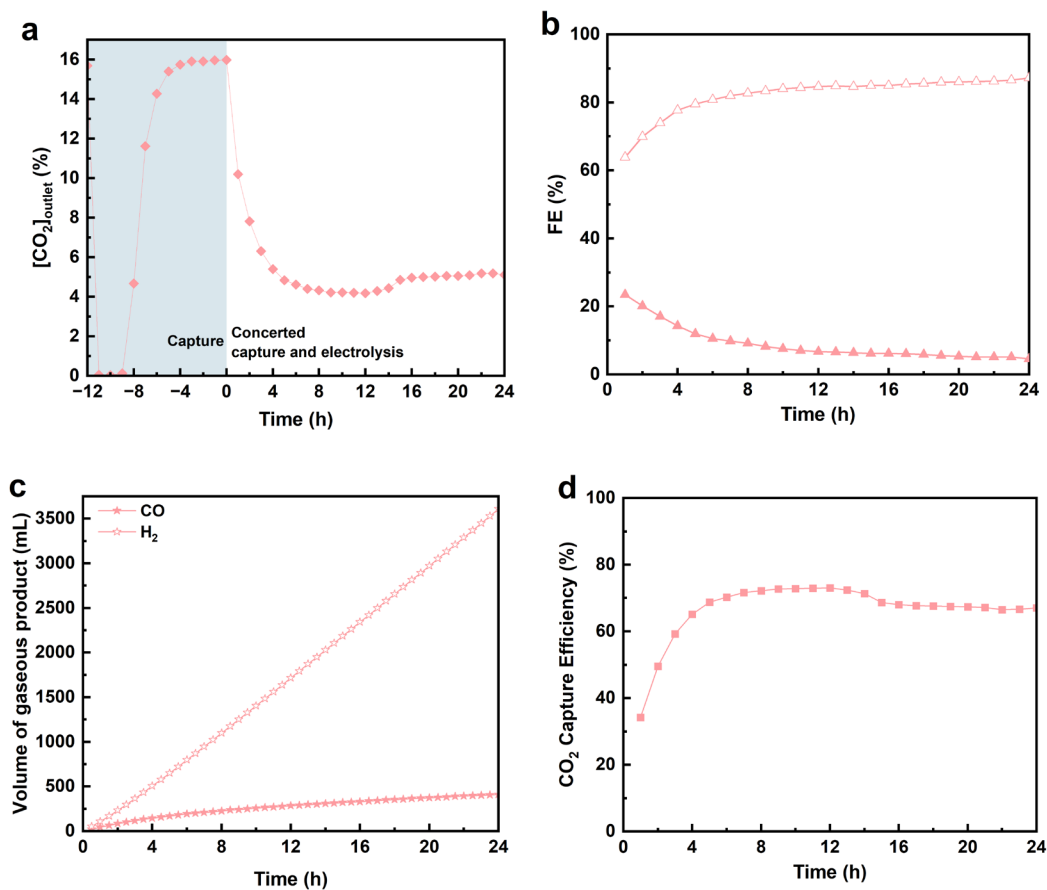
**Supplementary Figure 10.** FE and cell voltage recorded for electrolysis of CO<sub>2</sub>-capturing 5 M MEA in the liquid-fed electrolyzer at 50, 100, and 200  $\text{mA cm}^{-2}$  under atmospheres with varying O<sub>2</sub> content: 5%O<sub>2</sub>/15%CO<sub>2</sub>/80%N<sub>2</sub>, 10%O<sub>2</sub>/15%CO<sub>2</sub>/75%N<sub>2</sub>, 20%O<sub>2</sub>/15%CO<sub>2</sub>/65%N<sub>2</sub>, and 100%O<sub>2</sub>.



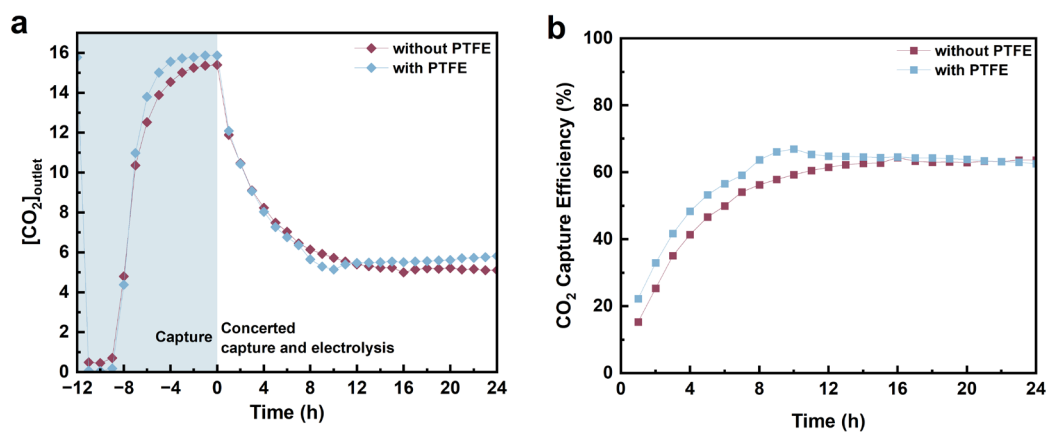
**Supplementary Figure 11.** Concentrations of dissolved O<sub>2</sub> in a CO<sub>2</sub>-capturing 5 M MEA electrolyte under non-electrolytic conditions. The electrolyte was bubbled for 30 min with different gas: 15% CO<sub>2</sub>/85% N<sub>2</sub>, 15%CO<sub>2</sub>/80%N<sub>2</sub>/5%O<sub>2</sub> and 100% O<sub>2</sub>.



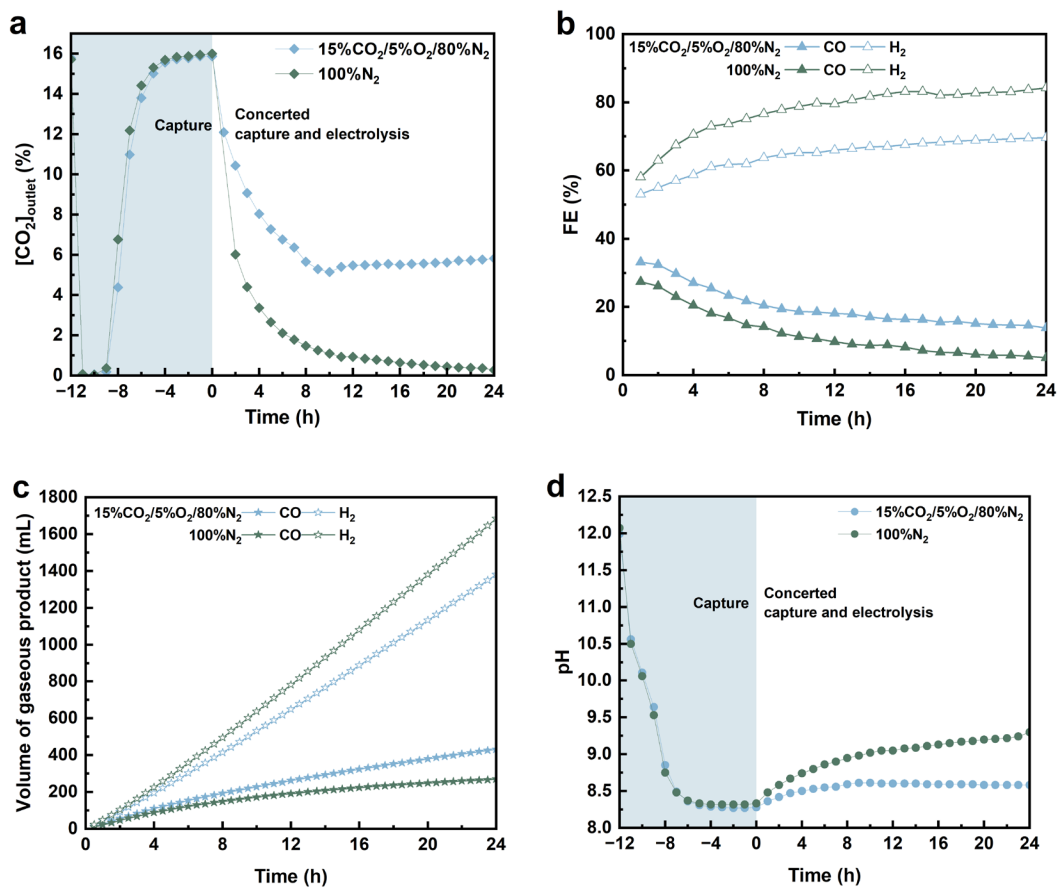
**Supplementary Figure 12.** FE and cell voltage recorded for electrolysis of CO<sub>2</sub>-capturing MEA solutions prepared using different MEA concentrations (1, 2, and 5 M) under 15%CO<sub>2</sub>/5%O<sub>2</sub>/80%N<sub>2</sub> at 50, 100, and 200 mA cm<sup>-2</sup>.



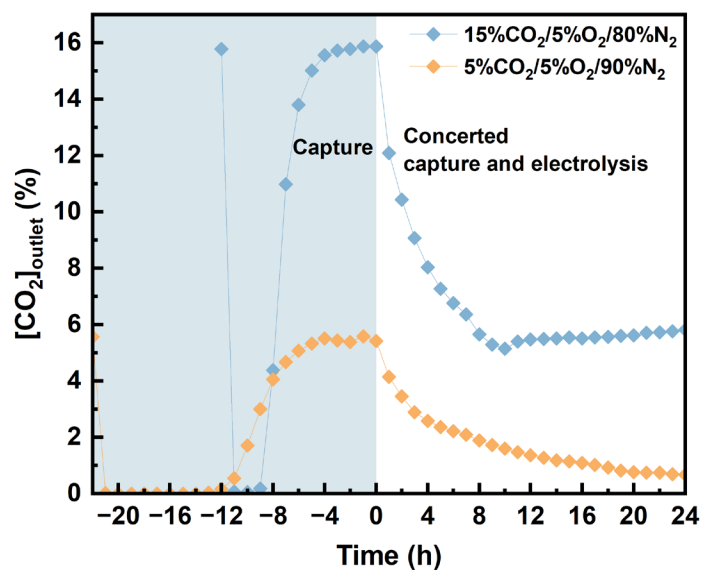
**Supplementary Figure 13.** Efficiency of the concerted CO<sub>2</sub> capture and conversion system using 2 M MEA to capture CO<sub>2</sub> from a flus gas containing 15%CO<sub>2</sub>/5%O<sub>2</sub>/80%N<sub>2</sub> and performing electrolysis of the CO<sub>2</sub>-capturing MEA at 100 mA cm<sup>-2</sup> for 24 h: (a) concentration of CO<sub>2</sub> leaving the concerted system ([CO<sub>2</sub>]<sub>outlet</sub>); (b) FE for CO and H<sub>2</sub>; (c) cumulative volume of gaseous products; (d) CO<sub>2</sub> capture efficiency.



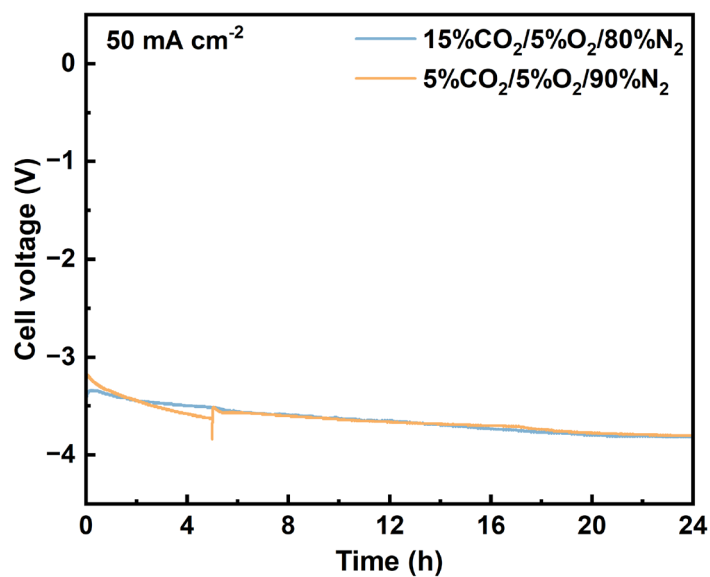
**Supplementary Figure 14.** (a) [CO<sub>2</sub>]<sub>outlet</sub> and (b) CO<sub>2</sub> capture efficiency of CO<sub>2</sub>-capturing 2 M MEA in the concerted CO<sub>2</sub> capture and conversion system using Ni-N-C and Ni-N-C-PTFE electrode at 50 mA cm<sup>-2</sup> under 15%CO<sub>2</sub>/5%O<sub>2</sub>/80%N<sub>2</sub>.



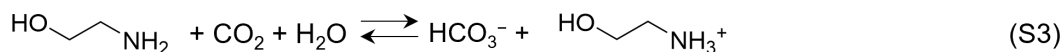
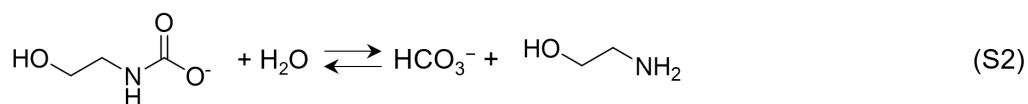
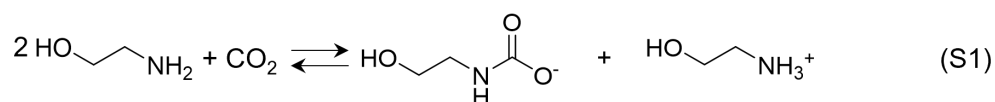
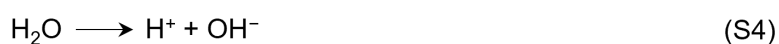
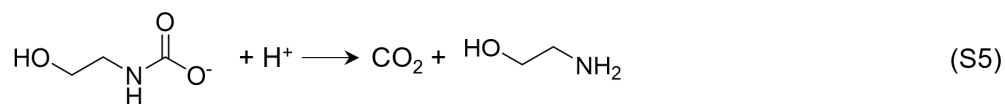
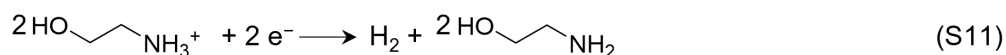
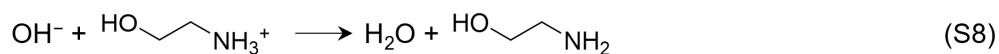
**Supplementary Figure 15.** Efficiency of electrolysis of 15%CO<sub>2</sub>-capturing 2 M MEA at 50 mA cm<sup>-2</sup> with the flow of 15%CO<sub>2</sub>/5%O<sub>2</sub>/80%N<sub>2</sub> and 100%N<sub>2</sub>: (a) [CO<sub>2</sub>]<sub>outlet</sub>; (b) FEs for CO and H<sub>2</sub>; (c) cumulative volume of products; (d) pH evolution during CO<sub>2</sub> capture and follow-up conversion.



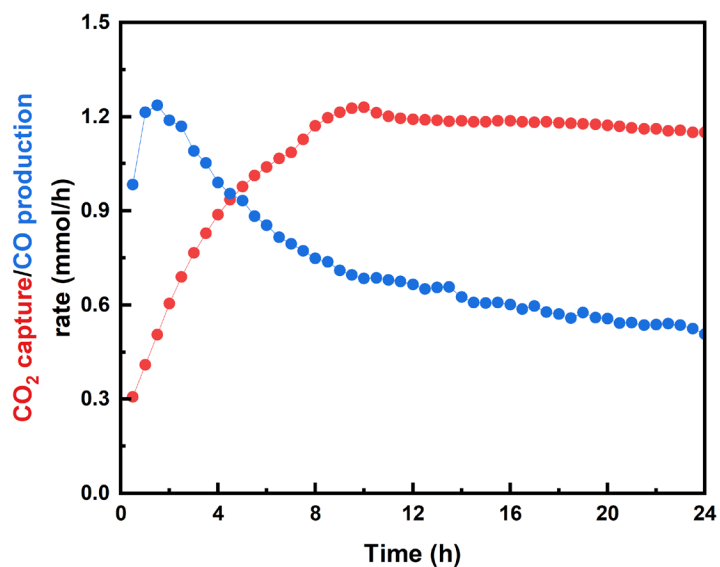
**Supplementary Figure 16.**  $[\text{CO}_2]_{\text{outlet}}$  in the concerted CO<sub>2</sub> capture and conversion system using 2 M MEA as the capture medium and performing electrolysis at 50 mA cm<sup>-2</sup> under 15%CO<sub>2</sub>/5%O<sub>2</sub>/80%N<sub>2</sub> and 5%CO<sub>2</sub>/5%O<sub>2</sub>/90%N<sub>2</sub> supply.



**Supplementary Figure 17.** Cell voltages recorded in the concerted CO<sub>2</sub> capture and conversion system using 2 M MEA as the capture medium and performing electrolysis at 50 mA cm<sup>-2</sup> under 15%CO<sub>2</sub>/5%O<sub>2</sub>/80%N<sub>2</sub> and 5%CO<sub>2</sub>/5%O<sub>2</sub>/90%N<sub>2</sub> supply.

**CO<sub>2</sub> absorption:****Water splitting happens at the BPM:****CO<sub>2</sub> release:****Cathodic reaction:****Anode reaction:****Overall reaction:**

**Supplementary Figure 18.** The reactions involved in CO<sub>2</sub> capture and electrolysis processes.



**Supplementary Figure 19.** CO<sub>2</sub> capture and CO production rates during the concerted CO<sub>2</sub> capture and electrochemical conversion in 2 M MEA using Ni-N-C-PTFE electrode and 15%CO<sub>2</sub>/80%N<sub>2</sub>/5%O<sub>2</sub> gas at 50 mA cm<sup>-2</sup>.

## Supplementary note 1

### Energy consumption analysis for syngas production.

The energy consumption of the concerted route for capturing and electrochemically converting CO<sub>2</sub> from flue gas was calculated. For comparison, the energy consumption of the conventional sequential capture-conversion systems and recently reported concerted capture-conversion system based on carbonate absorbent were also calculated.<sup>[S1-S3]</sup> Based on the data we obtained and reported in the literature, we calculated the overall energy consumption for CO<sub>2</sub> capture and utilization, focusing on four main stages that contribute to the total energy costs: CO<sub>2</sub> release, electrolysis, product separation, and water electrolysis.

**Energy consumption for CO<sub>2</sub> release.** We calculated the energy required to release sufficient CO<sub>2</sub> for the production of 1 mol of CO by considering the energy needed to liberate 1 mol of CO<sub>2</sub> from the CO<sub>2</sub>-capturing solution and the CO<sub>2</sub> utilization efficiency during electrolysis. This calculation assumes CO<sub>2</sub> capture from flue gas using an industrial amine scrubbing method, in which releasing CO<sub>2</sub> from the CO<sub>2</sub>-amine adduct consumes 179 kJ mol-CO<sub>2</sub><sup>-1</sup>.<sup>[S4]</sup> Thus, the sequential system relying on a pure CO<sub>2</sub> feed for electrolysis incur this additional energy cost. In contrast, the concerted capture and electrochemical conversion approach avoids this extra energy expenditure. Furthermore, because CO<sub>2</sub> electrolysis typically suffers from CO<sub>2</sub> loss due to crossover and low single-pass efficiency, an additional amount of CO<sub>2</sub> must be supplied to generate 1 mol of CO. By analyzing the experimental or reported data from each example, the percentage of each loss can be quantified, with the remaining percentage representing the CO<sub>2</sub> utilization. To produce 1 mole of syngas with a H<sub>2</sub>/CO ratio of 3, 0.25 mol of CO is generated. Therefore, the energy associated with CO<sub>2</sub> release for syngas production was calculated according to Eq. S15.

$$\text{Energy required for CO}_2 \text{ release} = \frac{179 \text{ kJ mol-CO}_2^{-1}}{\text{CO}_2 \text{ utilization efficiency}} \quad (\text{S15})$$

**Energy consumption for electrolysis.** The energy required for the CO<sub>2</sub> electrolysis in the gas-fed or the concerted CO<sub>2</sub> capture and conversion systems was calculated

according to Eq. S16.

$$\text{Energy required for CO}_2 \text{ electrolysis} = I \times U \times t \quad (\text{S16})$$

where  $I$  is the current for the electrolysis,  $U$  is the operating cell voltage of the electrolyzer, and  $t$  is the electrolysis time required to produce 1 mole of product.

**Product separation.** As CO<sub>2</sub> removal is generally the most energy-intensive step in downstream step,<sup>[S5]</sup> only the energy required for separating CO<sub>2</sub> from the product stream was considered in our calculations. The reported energy cost varies widely, ranging from 100 to 900 kJ mol-CO<sub>2</sub><sup>-1</sup> depending on the separation method used. In this work, amine scrubbing was adopted for CO<sub>2</sub> removal, consistent with the capture process described above, resulting in an energy consumption of 179 kJ mol-CO<sub>2</sub><sup>-1</sup> for removing unreacted CO<sub>2</sub> from the gaseous products. Additionally, in the CO<sub>2</sub>-fed electrolyzer, bicarbonate is formed during electrolysis and subsequently transported across the membrane.<sup>[S6]</sup> Based on the previous reported simulation model, the CO<sub>2</sub> loss associated this crossover was estimated to be 5%.<sup>[S7]</sup> Taking these factors into account, the energy consumption for production separation was calculated according to Eqs. S17-S20.

$$\text{Separation energy} = 179 \text{ kJ mol-CO}_2^{-1} \times n_{\text{CO}_2 \text{ outlet}} \quad (\text{S17})$$

$$n_{\text{CO}_2 \text{ outlet}} = n_{\text{CO}_2 \text{ inlet}} - n_{\text{CO}_2 \text{ loss}} - n_{\text{CO}_2 \text{ utilization}} \quad (\text{S18})$$

$$n_{\text{CO}_2 \text{ inlet}} = \frac{n_{\text{CO}_2 \text{ utilization}}}{\text{CO}_2 \text{ utilization efficiency (\%)}} \quad (\text{S19})$$

$$n_{\text{CO}_2 \text{ loss}} = n_{\text{CO}_2 \text{ inlet}} \times 5\% \quad (\text{S20})$$

where  $n_{\text{CO}_2 \text{ utilization}}$  is 1 mol when considering 1 mol of CO is produced for electrolysis.

A syngas with a H<sub>2</sub>/CO ratio of 3 was assumed in the analysis. Accordingly, the production of 1 mol of syngas requires 3/4 mole of H<sub>2</sub> and 1/4 mole of CO. The energy required to produce 1 mol of CO was calculated using the above Eqs. S1-S6. The energy required for H<sub>2</sub> via water electrolysis was taken as 365 kJ-mol<sub>H<sub>2</sub></sub><sup>-1</sup>.<sup>[S8]</sup> Based on these values, the total energy consumption for syngas production was determined and summarized in Supplementary Table 1.

**Supplementary Table 1.** CO<sub>2</sub> capture-conversion Performance in different systems.

System	Sequential 1 (Ref. S1)	Sequential 2 (Ref. S2)	Carbonate- based concerted (Ref. S3)	MEA-mediated concerted ( <b>this work</b> )
Feedstock	High-purity CO <sub>2</sub> gas	High-purity CO <sub>2</sub> gas	K <sub>2</sub> CO <sub>3</sub> solution (20%CO <sub>2</sub> /80% N <sub>2</sub> )	MEA-CO <sub>2</sub> solution (15%CO <sub>2</sub> /80%N <sub>2</sub> /5%O <sub>2</sub> )
Catalyst	Ni single atoms on carbon black	Nanoporous Au	Ag nanoparticles	Ni-N-C
FE <sub>CO</sub>	90%	88%	30%	32%
$j_{\text{total}}$	80 mA cm <sup>-2</sup>	100 mA cm <sup>-2</sup>	100 mA cm <sup>-2</sup>	50 mA cm <sup>-2</sup>
$j_{\text{CO}}$	72 mA cm <sup>-2</sup>	88 mA cm <sup>-2</sup>	30 mA cm <sup>-2</sup>	16 mA cm <sup>-2</sup>
Stability	6 h	0.25 h	46 h	24 h
CO <sub>2</sub> capture efficiency	N/A	N/A	30%	63%
Energy consumption	1160 kJ mol- syngas <sup>-1</sup>	1110 kJ mol- syngas <sup>-1</sup>	761 kJ mol- syngas <sup>-1</sup>	922 kJ mol- syngas <sup>-1</sup>

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