



High carbon efficiency in CO-to-alcohol electroreduction using a CO reservoir

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SUMMARY

The electrochemical CO₂ reduction reaction (CO₂RR) has progressed but suffers an energy penalty from CO₂ loss due to carbonate and bicarbonate formation and crossover. Cascade CO₂ to CO conversion followed by CO reduction (CORR) addresses this issue, but the combined figures of carbon efficiency (CE), energy efficiency (EE), selectivity (Faradaic Efficiency, FE), and stability require improvement. We posited that increased CO availability near active catalytic sites could maintain selectivity for CORR even under CO-depleted conditions – a requirement for achieving high carbon efficiency, since CO is sparse near the outlet of a high-CE reactor. Here we present a heterojunction carbon reservoir catalyst (CRC) architecture that combines catalytic copper nanoparticles with porous carbon nanoparticles. The latter possesses pyridinic and pyrrolic functionalities that absorb CO: operando Raman spectroscopy reveals the coordination of adsorbed CO with N-groups and the presence of binding sites that promote alcohol selectivity. By implementing and optimizing this design strategy, we achieve ethanol FE and carbon efficiency of 50% and 93% (CE*FE = 47%) in a flow cell at 200 mA cm⁻², fully doubling the best prior CE*FE to ethanol. In an MEA system, we show sustained efficiency over 85 hours at 100 mA cm⁻².

Keywords - CO₂ reduction; CO electroreduction; carbon monoxide; catalyst design; nitrogen-doped carbon; carbon utilization; electrocatalysis; ethanol; renewable fuels; CO₂ valorization

INTRODUCTION

The electroproduction of alcohols such as ethanol and propanol from CO₂ can potentially provide low-carbon-intensity fuels and platform chemicals. Toward this goal, it will be important to continue to improve carbon efficiency (CE, the fraction of CO₂ and CO converted into desired products in a single pass), Faradaic efficiency (FE, the selectivity to specific products), and energy efficiency (EE). System design and selective carbon-efficient catalysts are required to address these challenges.²

In gas-phase electrolyzers, the catalyst layer (CL) is adjacent to the catholyte and gas flow channel, forming a three-phase boundary (**Figure 1A-B**). The reactant gas diffuses into the porous gas diffusion layer (GDL) and reaches the electrocatalytic active sites in the catalyst layer. The water-based electrolyte acts as the proton source, which can react with electrons and lead to C-products. These systems can realize CO₂RR and CORR at high reaction rates (above 100 mA cm⁻²) and compelling energy efficiency (EE) thanks to the large availability of the reactants at the active sites. However, this approach comes with the disadvantage of significant carbon losses.

It is challenging to achieve, simultaneously, high CE and FE to C-products (CE*FE). One cause of low CE is carbonate formation in the electrolyte and crossover through the membrane; another is the competing hydrogen evolution reaction (HER). It is challenging to achieve, simultaneously, high CE and FE to C-products (CE*FE), because the CO concentration near the outlet of such systems is low, leading to the competing hydrogen evolution reaction (HER).³⁻⁹

Cascade electroreduction of CO₂ to CO followed by CO reduction reaction (CORR) offers a route to high CE by addressing carbon losses from carbonate formation.^{9,10} Commercial solid oxide electrolyzer cells (SOEC) provide a convenient source of CO.¹¹ However, previous electrochemical CORR systems suffered low carbon efficiency and product selectivity leading to CE*FE_{alcohols} < 25%^{9,10,11} reducing the net energetic benefit.^{4, 8-10}

We posited that increasing the CO concentration, through local/nanoscale effects, near the catalytic active sites, could preserve FE to C-products. Experimentally, we found that – in reference, catalysts based on Cu alone (**Figure 1C**) – when we tune operating conditions to

Context & Scale

Electrochemical reduction of CO₂ and CO provides ways to produce added-value chemicals, and the potential to achieve carbon neutrality when powered with renewable electricity. Efficient conversion of CO₂ and CO is paramount to making these approaches sustainable and cost-competitive compared to traditional fossil-energy-based ones. We report a catalyst design strategy where a CO-capturing component provides catalytic copper with high local concentration of CO even at a conversion rate close to unity (above 90%), preventing other parasitic reactions and providing control over the product selectivity.



achieve CE above 30%, the selectivity to C-products drops, resulting in limited adsorbed CO adjacent to metallic copper active sites.

We sought, therefore, to incorporate Cu-NPs into a microporous CO-capturing matrix to ensure CO availability at the catalytic sites (**Figure 1D**). We implemented this strategy using porous carbon nanoparticles (C-NPs) having functionalized nitrogen groups, which we call carbon reservoir catalyst (CRC) active layers.¹²⁻¹⁵ The C-NPs with pyridinic- and pyrrolic-nitrogen groups promote CO adsorption while favoring high CORR selectivity to C₂₊ alcohols at high CE. By controlling the reactant diffusion into the porous C-NPs and varying the ratio of pyridinic and pyrrolic nitrogen atoms, we achieved CE*FE_{ethanol} >47%, and EE_{C2+} = 40% sustained for 85 hours of continuous operation.

RESULTS AND DISCUSSION

Electrochemical finite-element studies

Since CO solubility in KOH is much lower than that of CO₂,¹² the availability of CO as a reactant will be limited, especially when higher electrolyte concentrations are used and when high current densities are applied. Such a low reactant concentration is expected to result in increased H₂ evolution, limiting the energy and carbon efficiencies of the electrolyzer. Previous investigations have used finite element modeling (FEM) to study how electrolyzer properties affect performance.¹⁶⁻²³ FEM enables the estimation of local species concentrations.

We explored the distribution of CO in different gas diffusion electrode architectures (**Figure 1E-G and Supplementary Note 4**). We studied how the catalyst performance changes as the reactant distribution varies inside the catalyst layer under high CE regimes (high reaction rate, 200 mA cm⁻², and low CO flow rate, *ca.* 1.1 sccm). To do this, we modulated the CO adsorption (S_{CO}) in the CL, investigating two scenarios. In the first, the CL contains only catalytic Cu-NPs (without appreciable CO adsorption ability, $S_{CO}^* = 0$, **Figure 1F**). In the second, we introduced nanoparticles inside the CL with a markedly different CO adsorption value (S_{CO}^* , **Figure 1G**). As S_{CO} increases, the CO concentration in the gas and in the liquid phase, which wets the catalyst, also increases (**Figure 1F-G and Figure S1**), potentially enabling higher reactant availability at high CE regimes. A higher S_{CO} is expected to sustain large CO conversion at high CE without an appreciable increase in the HER (**Figure S2-3**). Conversely, without the carbon reservoir catalyst strategy, regions of the CL with limited CO availability result in pronounced HER at high CE conditions (**Figure S4-5**).



Material preparation and characterization

To implement the CRC strategy, we sought catalyst layers having the CO reservoir property. We looked at gas-absorbing materials able to conduct the high current density required for reaction rates of industrial interest. Activated microporous carbon nanoparticles (C-NPs) are adsorbents for CO₂ capture and CO separation and have high structural stability, chemical resistance, and electrical conductivity.^{12–14} Nitrogen (N) functional groups in porous carbon structures tune surface molecular binding and selectivity in gas separation and electrocatalysis.^{15, 24–28} Pyridinic- and pyrrolic-N located at the edges of carbon structures (**Figure 2A**) create active sites interacting with reaction intermediates and driving selectivity in electrocatalytic processes.^{29, 30} We hypothesized that their assembly with Cu-NPs in a heterojunction CL would offer distinct domains whereby the C-NPs porous structure facilitates CO transport and distribution, and nitrogen groups promote selectivity and CO availability.

We used N-rich zeolitic-imidazolate framework (ZIF)-derived carbon as a material to prepare micro-, meso-, and macroporous carbon structures. As the heat-treatment temperature tunes physicochemical and structural properties, we prepared different types of C-NPs under different heat-treatment temperatures of 700, 800, 900, and 1000°C. Thermal treatment above 700°C removes most methyl groups of the organic framework. Higher temperature leads to the removal of carbon species and nitrogen, and the evaporation of the Zn metal species occurs above 900°C. The remaining Zn is removed by acid treatment with concentrated HCl (**Figure 2B**), resulting in Zn-free C-NPs. Additionally, we controlled the nanoparticle size by adjusting the synthesis temperature, obtaining ~ 25 nm and ~ 100 nm C-NPs at room temperature and 0°C, respectively.

The XPS spectra of the N 1s can be deconvoluted in four peaks: pyridinic-N (N_{pi} , at 398.0 eV), pyrrolic-N (N_{pr} , at 400 eV), graphitic-N (N_g , at 401 eV), and oxidized-N (N_o , at 403 eV) (**Figure 2A and 2C, Table S5**).^{23,24} Thermal treatment tuned the pyrrolic: pyridinic nitrogen atom ratio ($N_{pi}:N_{pr}$) from *ca.* 1.3 to 3.0 in the C-NPs treated at 700 and 1000°C (denoted as C-NPs - N1.3 and C-NPs - N3.0, respectively) without change in the morphology of the nanoparticles (**Figure 2E-G and Figure S13-16**). Cyclic CO adsorption and desorption experiments reveal that the C-NPs, regardless of the $N_{pi}:N_{pr}$ ratio, have a 6–9 cm³ g⁻¹ CO adsorption capacity (S_{CO}), which is reversible (**Figure 2D and Figure S9**).

The linear adsorption profile indicates relatively weak adsorbent-adsorbate interactions.⁴² At each relative pressure, CO molecules cluster around the most favorable sites in the C-NPs samples. The hysteresis in the complete loop confirms that the pores are partially filled with CO. These features in the adsorption-desorption cycle and the similar CO adsorption values at each nitrogen content and $N_{pi}:N_{pr}$ ratio are consistent with physisorption behavior.^{11,14}

Conversely, Cu-NPs have a low 1 cm³ g⁻¹ S_{CO} in the adsorption cycle linked to the presence of Cu²⁺ and Cu¹⁺ oxidized Cu sites (**Figure 2D**) at the surface due to the passivation of these commercial nanoparticles. The negligible CO desorption implies that Cu-NPs irreversibly chemisorb CO at room temperature.²⁵ These results suggest that C-NPs may capture and release CO under CORR conditions and increase the CO availability of nearby catalytic Cu-NPs. We assembled CRC gas diffusion electrodes with catalytic Cu NPs, C-NPs, and Nafion ionomer to extend ion and CO diffusivity. Scanning electron microscopy (SEM, **Figure 2E, Figure S11-16 and Figure S23** for the 100 nm C-NPs) shows that C-NPs and Cu-NPs aggregate in *ca.* 200 nm structures bound with Nafion. High-resolution transmission electron microscopy (**Figure 2F**) further indicates that C-NPs and Cu-NPs are homogeneously mixed in these structures. Elemental energy dispersive X-Ray spectroscopy of a CRC with C-NPs - N1.3 (CRC_N1.3, **Figure 2G and Figure S10-17** for CRC_N3.0) also confirms the presence of a continuous Cu and C-NPs network only with a few C-NPs agglomerates.



CO electroreduction performance in flow cells

Flow cells with a gas diffusion electrode (GDE) were used to study electrocatalytic performance at operating current densities $> 100 \text{ mA cm}^{-2}$ to explore ethanol FE and CE. The C-NPs with different sizes and $N_{\text{pi}}:N_{\text{pr}}$ were implemented into CRC active layers and tested at 100, 200, 300, and 400 mA cm^{-2} (**Figure S18**) using 4 M KOH and anion exchange membrane (AEM). At 200 mA cm^{-2} , CRC electrodes show enhanced selectivity to alcohols (ethanol and propanol) compared to pure Cu-NPs ($\text{FE}_{\text{C}_2+\text{alcohols}} \sim 48\%$ vs. 32% , respectively).

Alcohol FE increases at the expense of ethylene and hydrogen in the CRC system compared to relevant Cu-NP controls (**Figure 3A**). Tuning the ratio of pyridinic:pyrrolic nitrogen atoms shifts the alcohol selectivity. The CRC with $N_{\text{pi}}:N_{\text{pr}}$ 1.3 synthesized at 700°C , provides the highest propanol productivity, 32% FE, at 200 mA cm^{-2} . The nucleophilicity of pyridinic-N may facilitate $^*\text{OCCO}$ and $^*\text{CO}$ bonding, a route to increase propanol at the expense of ethanol.²⁶⁻²⁸ A larger ratio of pyrrolic vs pyridinic nitrogen within CRC-N3.0 inhibits C_{3+} alcohol formation, leading to the highest ethanol FE, 30% FE, at 200 mA cm^{-2} while maintaining total alcohol FE (ethanol selectivity over total alcohol increases from 38% to 63% as the amount of pyrrolic nitrogen increases).²⁶

We then further explored the ratio of Cu-NPs and C-NPs – N3.0 (CRC-N3.0) to maximize CE by acting on the CO flow rate (from 0.5 to 10 sccm , **Figure 3B-C**). Detailed experimental data on gas flow rate, CE, and FE are described in the Supporting Information (**Table S7**). Different catalyst loading, C-NPs: Cu-NPs ratios, and ionomer loading ratios were also performed to optimize FE and CE (**Figure S20-21**).

A GDE containing only Cu-NPs achieved 32% CE and 20% FE of EtOH ($\text{CE}^*\text{FE}_{\text{ethanol}} = 6\%$) and overall, 84% FE to C_{2+} (**Figure 3B**). In this case ethylene was the dominant product, and HER steeply increased at CE above 30% , suggesting that the local concentration of CO decreased, disfavoring CO-CO coupling to C_{2+} products and limiting CE.

CRC electrodes extend C_{2+} production above 30% CE. We tested the two C-NPs sizes (25 nm and 100 nm) and found that, with 100 nm C-NPs, HER takes over even in CO rich environment (**Figure S23**). We then characterized in detail the pore size distribution and structure of the C-NPs using N_2 adsorption-desorption isotherms and pore size distribution analysis. All the C-NPs samples have a high specific surface area (from Brunauer-Emmett-Teller, BET, **Figure S7**). Both C-NPs show similar micropores and mesopores (below 1 nm and *ca.* $2\text{-}3 \text{ nm}$ diameter, respectively) distributions. However, the 100 nm C-NPs present larger macropores (with a diameter of $70\text{-}90 \text{ nm}$ compared to $20\text{-}30 \text{ nm}$ for the smaller C-NPs). Macroporous structures are due to the interparticle voids and promote kinetic accessibility to the available active sites favoring mass- and ionic transport.^{29,30,34} In 100 nm C-NPs heterojunction CRC electrodes, Cu-NPs could segregate in the large macropores with limited CO distribution, causing HER (**Figure S23**).

CRC electrodes assembled with 25 nm C-NPs achieve CE and C_{2+} production above 90% (**Table S6**). We optimized the CRC-N3.0 electrode and achieved 50% FE to EtOH and CE 90% ($\text{CE}^*\text{FE}_{\text{ethanol}} = 47\%$) with, overall, 93% FE to C_{2+} (**Figure 3C**), outperforming previous reports, especially in terms of simultaneous achievement of CE and ethanol FE (**Figure 3D and Table S8**). Moreover, ethanol selectivity over total alcohol increases from 63% to 90% at a low CE of 12% CE to 90% CE, respectively. The CRC catalyst functions as a CO reservoir which can modulate the local concentration of CO even in a low CO supply. The modulation of CO local concentration would suppress deoxygenation of HOCC^* which favors the formation of alcohol and maintains high C_{2+} FE at low CO supply.^{26,41,45}

In situ characterization

To analyze the oxidation state of the catalyst under CORR conditions, we performed X-ray absorption spectroscopy (XAS) at the Cu K-edge of control samples (Cu_2O , CuO , and Cu metal), of the Cu-NPs and the CRC-N3.0 electrodes as prepared, and during CORR (EXAFS in **Figure 4A**). Before the reaction, the Cu nanoparticles are partially oxidized at the surface with



oxidation number +1. In operando conditions, the EXAFS spectrum of CRC shows that the copper oxide shell becomes fully reduced, suggesting an active catalyst composed of Cu metal.

We used in situ and operando Raman spectroscopy to query the reaction in different catalyst architectures - Cu-NPs, CRC-N1.3, and CRC-N3.0) during CORR (**Figure 4B**). The signal intensity under $-0.25 V_{RHE}$ (which corresponds to a low current density, *ca.* 5 mA cm^{-2}) we took to be a qualitative indicator of the CO^* saturation coverage.³⁵ Under this potential, the bands at 280 cm^{-1} and 360 cm^{-1} associated with a frustrated rotation and stretching of CO^* on the Cu, respectively, show a shift to lower frequencies in the CRC catalysts. This shift implies a weaker Cu-CO bond which suggests partial coordination of the adsorbed CO with the N-functional groups of the carbon nanoparticles.³⁶⁻³⁷ As the applied potential stepped to more negative values, the peaks shifted to higher frequencies indicating the prevalence of the stronger Cu-CO bond at high reaction rates.

The band in the range of $1,900 - 2,100 \text{ cm}^{-1}$ arises from the $\text{C}\equiv\text{O}$ stretching atop-bound, which is an on-pathway intermediate to C_{2+} .³⁸ The peak is present at the surface of CRC electrodes at more negative voltages than Cu-NPs. These voltages correspond to reaction rates at which CO is depleted in the reactant gas and are compatible with CO-diluted conditions occurring at high $\text{CE}^*\text{FE}_{\text{C}_{2+}}$. Additionally, the broad peak on CRC electrodes indicates that the presence of the many different nitrogen groups of NDC nanoparticles modulates the CO binding sites, and leads to high alcohol selectivity.³⁹ In CRC electrodes, the catalytic sites are present only at the surface of Cu-NPs which are surrounded by C-NPs (**Figure 2E-G** and **Figure S17**). Prior studies showed that surface Cu^{2+} binds pyridinic and pyrrolic nitrogen,^{43,44} in catalytic materials and suggests that, in the CRC electrode, C-NPs can coordinate with the partially oxidized Cu-NPs (**Figure S8**). Operando, the heterojunction structure can provide confined spaces where catalytic Cu surface sites and nitrogen groups are within distances to bind reaction intermediates and affect the selectivity.

Taken together, operando XAS and Raman show that C-NPs influence the CO adsorption on the active catalytic sites of metallic copper and correlate the enhanced CE and FE to C_{2+} alcohols to the extended availability of CO and the multitude of binding sites in the CRC catalysts.

Membrane electrode assembly for stability testing

We implemented the CRC in a membrane electrode assembly (MEA) system, allowing longer operating times and low resistive losses.⁸ We achieved a full cell voltage of -2.35 V at a current density of 100 mA cm^{-1} using 2 M KOH as anolyte and observed stable operation for over 85 h (**Figure 5A**). This corresponds to a full cell C_{2+} energy efficiency of 39% and alcohol EE of 24% . We carried out techno-economic (**Supplementary Note 1**) and carbon footprint analyses using experimental data from the CORR MEA system (**Supplementary Note 2**).^{38,40}

We estimated the plant-gate levelized cost per ton of ethanol assuming CO_2RR to CO via SOEC and CORR as studied herein (details in **Supplementary Note 1**). In the MEA configuration, the total plant-gate levelized cost (including estimated separation costs) per ton of ethanol is less than the sum of hydrogen, ethylene, propanol, and ethanol product values (**Figure 5B**). The energy cost of CO_2RR and CORR is $\sim 200 \text{ GJ tonne}^{-1}_{\text{EtOH}}$ (**Figure 5B** and **Supplementary table 2**). With 83% carbon efficiency, the CORR system based on the optimized catalyst has (cradle-to-gate) projected at $-1.1 \text{ tonne}_{\text{CO}_2}/\text{tonne}_{\text{EtOH}}$ (**Supplementary Note 1**).

Conclusion

The carbon reservoir catalyst provides catalysts that are not limited by CO depletion near the outlet of an electrolysis system, enabling alcohol selectivity to be maintained at high carbon



efficiency. The choice of nitrogen in the CRC increases the selectivity toward ethanol ($50 \pm 3\%$) against propanol in flow cell system, driven by pyridinic vs. pyrrolic nitrogen. In an MEA, the catalyst performed > 85 h of electrosynthesis at 100 mA cm^{-2} , with a carbon efficiency of 83%, 40% ethanol FE, and 40% EE_{C_2+} . With energy analysis over the cascade system, the performance of the CRC catalyst suggests the CORR-to-ethanol has a path to carbon-negative ethanol electrosynthesis, paving the way to the decarbonization of the chemical industry.



EXPERIMENTAL PROCEDURES

Resource Availability

Lead Contact

Further information and requests for resources and materials should be directed to and will be fulfilled by the Lead Contact, Edward H. Sargent (ted.sargent@utoronto.ca)

Data and Code Availability

The original data supporting the current study are available from the Lead Contact on request.

Preparation of catalyst and gas diffusion electrode

Materials

2-Methylimidazole 99%, Zn (NO₃)₂ ethanol, HCl (37 wt.%), KOH, dimethyl sulfoxide, deuterated water (D₂O), and methanol were used as purchased from Aldrich. Carbon monoxide (grade 4) was purchased from Praxair, and Ar (grade 5) was purchased from Messer. Nickel foam was purchased from MTI Corporation. Carbon-based gas diffusion electrode (Freudenberg H23C9), anion exchange membrane (Fumasep FAA-PK-130), Nafion 212, 5% Nafion perfluorinated resin solution 5 wt. % (D520 EW=1000) were purchased from the Fuel Cell Store. Deionized water (18.2 MΩ) was used in all experiments.

Synthesis of electrocatalysts

Synthesis of the 25 nm zeolitic-imidazolate framework (25-ZIF): At room temperature, add a solution of 500 mL of methanol containing 2-methylimidazole (13.57 g) to a solution of 500 mL of methanol containing Zn(NO₃)₂ (12.29 g) under stirring. After a few minutes, the solution turns white, and after 20 minutes, stop the stirring and leave the solution settling for 24 hours at room temperature. Then, decant the supernatant clear solution, separate the white precipitate by centrifugation, wash it with methanol three times, and finally dry it overnight under a vacuum.

Synthesis of the 200 nm zeolitic-imidazolate framework (200-ZIF): Dissolve 2-methylimidazole (3.24 g) in 175 mL of methanol and dissolve Zn(NO₃)₂ (2.94 g) in 175 mL of methanol. After cooling the two solutions in an ice bath, add the methylimidazole solution to the Zn solution under stirring at 300 rpm. Stir for 2 minutes, remove from the stirrer, and leave settling undisturbed for 24 hours at room temperature. Then, decant the supernatant clear solution, separate the white precipitate by centrifugation, wash with methanol three times, and finally dry it overnight under vacuum.

Thermal treatment: We used a thermal treatment to remove the Zn from the organic structure and obtain the carbon particles (C-NPs) powder. White ZIF powder (500 mg) was placed in a quartz boat and annealed in a tube furnace under an inert atmosphere by flowing Ar at 100 cm³ min⁻¹. The final temperature was reached with a two-ramp process. Initially, the powder was heated at a rate of 5°C min⁻¹ up to 650°C and left at this temperature for 1 h. Then the temperature was increased at a rate of 5°C min⁻¹ to the final annealing temperature (700, 800, 900, and 1000°C), which was maintained for 2 h. During the annealing process, the weight loss was ca. 50, 40, 35, and 30% for the samples treated at 700, 800, 900, and 1000°C, respectively.

Acid treatment: We treated the obtained C-NPs powder with concentrated HCl to remove the residual Zn. C-NPs (100 mg) were stirred with 10 mL of concentrated HCl for 24-72 h. Then, the powder was separated by centrifugation, washed with deionized water four times, and finally with ethanol.

Preparation of gas-diffusion electrode

The catalyst was airbrushed on a Freudenberg H23C9 (Fuel Cell Store) gas diffusion electrode (GDE) with dimensions of 3 x 3 cm² or 2 x 2 cm². The ink was prepared by adding Cu NPs and the NDC to 2 mL of propanol. After a few seconds of sonication, a 5% Nafion solution (Fuel Cell Store D520, EW=1000) was added. A typical ink contained 80 μL of Nafion, 20 mg Cu-NPs, and 2 mg of NDC. The ink was sonicated for more than 1 h before being deposited on the GDE.



Adsorption Measurements

Gas sorption measures were performed with a Micromeritics 3Flex instrument. The specific surface areas were determined from the N₂ desorption isotherm at 77 K in the pressure range between 0.05 and 0.3 (relative pressure, p/p°), according to the Brunauer-Emmett-Teller (BET) method. CO sorption studies were carried out at room temperature and up to 1 bar. Before N₂ and CO adsorption analyses, the samples were thermally treated at 393 K for 12 h under high vacuum (10^{-6} Torr).

Structural characterization

The TEM imaging was conducted on a JEOL EM-2010 microscope operated at 200 kV. STEM imaging and EDS measurements were performed in STEM mode equipped with a single drift detector (X-MAX^N Oxford Instruments). SEM imaging was conducted on a Hitachi FE-SEM SU5000 microscope operated at 30 kV. The powder samples were deposited on a carbon tape before SEM imaging. XRD analysis was performed on a MiniFlex600 system employing Cu K α radiation. XPS measurements were conducted using the PerkinElmer model 5600, equipped with 1,486.6 eV monochromated Al K α X-ray source. The samples were prepared on conductive glass substrates by drop-casting a few droplets of ink solution.

Electrochemical CO reduction measurements

Electrochemical rate measurements were performed in both a flow cell and a membrane electrode assembly configuration. For the flow cell setup, the catalyst-deposited GDE was used as the working electrode (cathode) and nickel foam (MTI Corporation) as the counter electrode (anode). An anion exchange membrane (Fumasep FAA-PK-130) was used to separate the anodic and cathodic compartments. The flow cell assembly constituted of the GDE, anion exchange membrane, and nickel anode, while liquid electrolyte (1 M KOH, Sigma Aldrich) was circulated in both anodic and cathodic compartments using a peristaltic pump (McMaster-Carr). Carbon monoxide (Praxair, Grade 4.0) was passed behind the GDE using a mass flow controller (Sierra SmartTrack 100), while an Ag/AgCl reference electrode was inserted inside the cathodic compartment for half-cell potential measurement. For the MEA setup, the catalyst-deposited GDE was used as the working electrode (cathode), and an IrO₂-Ti felt (Sigma Aldrich) as the anode. A Nafion 212 (Fuel Cell Store) cation-exchange membrane was used to keep separation between the anolyte and the cathodic liquid products. The MEA was assembled by layering the GDE, Nafion, and IrO₂-Ti felt and pressing them between the cathode plate (1 cm² flow field, stainless steel) and the anode plate (5 cm² titanium, flow field). A 1 M NaOH solution was circulated through the anodic flow field using a peristaltic pump, while carbon monoxide was flown into the cathodic flow field using a mass flow controller. The liquid products were collected inside a cooled container (2–6°C) from the outlet of the cathode plate. For both configurations, the carbon monoxide flowrate was 25–40 standard cubic centimeters (SCCM), and the electrolyte flow was 10–15 mL min⁻¹. Electrochemical reactions were performed using an electrochemical workstation (Autolab PGSTAT302N) connected to a current booster (Metrohm Autolab, 10 A). Electrode potentials were rescaled to the RHE reference by:

$$E_{Vs\ RHE} = E_{Vs\ Ag/AgCl} + 0.235V + 0.059 \times pH$$

An electrochemical impedance spectroscopy (EIS) measurement using an Autolab PGSTAT302N electrochemical workstation was performed to obtain a cell resistance of 3.51 Ω . iR corrections to the potential were then performed using the following equation:

$$E_{iR-free} = E_{Vs\ Ag/AgCl} - 0.85R_{cell}i_{cell}$$

where $E_{iR-free}$ is the corrected potential at the cathode, $E_{Vs\ Ag/AgCl}$ is the applied potential, and i_{cell} is the total current (a negative value at the cathode). A correction factor of 0.85 is used due to the 1 M KOH electrolyte's high conductance and low voltage drop across the electrolyte.

The full-cell energy efficiency of the MEA system is obtained from the following equation:

$$EE_{Full-cell} = FE_{Product} * \frac{E_{cell}^0}{V_{Full-cell}}$$



where $EE_{Full-cell}$ is the full-cell energy efficiency of the system, $FE_{Product}$ is the system's faradaic efficiency towards specific product, and $V_{Full-cell}$ is the average full cell voltage over the length of the stability experiment. The standard reduction potential of the cell is obtained from the standard Gibbs free energy of the reaction $2CO + 2H_2O \rightarrow CH_3COOH + 2O_2$:

$$E_{cell}^0 = \frac{-\Delta G_{2CO+2H_2O \rightarrow Acetate+2O_2}^0}{zF}$$

where z is equal to 4 and F is the faraday constant (96485 C mol^{-1}).

Product analysis

The gas products from CORR were analyzed by sampling 1 mL of the electrolyzer outlet gas with an air-tight syringe (Hamilton, 5 mL). The gas sample was injected into a gas chromatograph (Shimadzu GC-2014) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). A Molecular Sieve 5A and Carboxen-1000 column were installed upstream from the TCD and FID respectively to separate the H_2 , CO and gaseous hydrocarbons. The liquid products were quantified using nuclear magnetic resonance spectroscopy (NMR, **Figure S14** shows two representative analyses of the liquid products). A 1 mL sample of the electrolyte was taken at various times during the reaction. 1H NMR spectra of the analyte samples were taken using an Agilent DD2 600 spectrometer with dimethyl sulfoxide (DMSO) as an internal standard. Faradaic efficiency (FE) of CORR gas product was calculated by the following equation:

$$FE_{i,gas} = y_{i,g} \dot{V} z_i F \frac{P_0}{RT} j_{total}$$

where y_i is the volume fraction of gas product i , $\dot{V}$ is the outlet gas flow rate in sccm, z_i is the number of electrons associated with producing one molecule of i , F is the Faraday constant, P_0 is atmospheric pressure, R is the ideal gas constant, T is the temperature and j_{total} is the total current density. The FE of liquid product was calculated using the following equation:

$$FE_{i,liquid} = n_{i,liquid} z_i F \frac{1}{Q_{total}}$$

where n_i is the number of moles of liquid product i , and Q is the total charge passed prior to the liquid sample being taken.

Electrochemical characterization

Cyclic voltammetry characterization with electrodes assembled in a flow cell was performed with the same equipment used for CORR experiments. iR correction of the applied potential was not performed.

Operando and ex situ spectroscopic analysis

We carried out operando and ex situ XAS Cu K-edge measurements at the European Synchrotron Radiation Facility (ESRF) at beamline ID26 which is equipped with high energy resolution fluorescence detectors (HERFD). We employed a flow cell electrolyzer modified to host a X-ray transparent window facing the cathode backside.

Operando Raman was operated with a water immersion objective with a Renishaw inVia Raman microscope using a 785 nm laser. To avoid damaging the samples, we collected full spectrum in two ranges (centered at 700 and 1700 cm^{-1}) using 0.05% full laser intensity, 0.1s integration time, and 200 repetitions. The raw data were base corrected by using Origin 2019 software. An open-structured flow cell was utilized for the measurements. An Ag/AgCl electrode (with saturated aqueous KCl solution) and a platinum wire were the reference and counter electrode, respectively. We collected the spectra at different current densities per each catalyst layer.



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SUPPLEMENTAL INFORMATION

AUTHOR CONTRIBUTIONS

E.H.S. supervised the project. S.P., I.G. and E.H.S. conceived the idea. S.P. and I.G. synthesized catalyst, carried out the experiments and performed characterization. F.B. and J.K. performed N₂ and CO adsorption and desorption experiment. I.G. T.A. performed theoretical calculations. B.H.L., E.S., R.D., G.L., Y.L., A.S., D.S. and D.K. contributed to the manuscript editing. S.P., I.G., T.A. and E.H.S. co-wrote the manuscript. J.A. performed in-situ XAS measurement. B.H.L., J.K., E.D.J., and D.K. assisted with the discussions.

DECLARATION OF INTERESTS

The authors declare no competing interests.

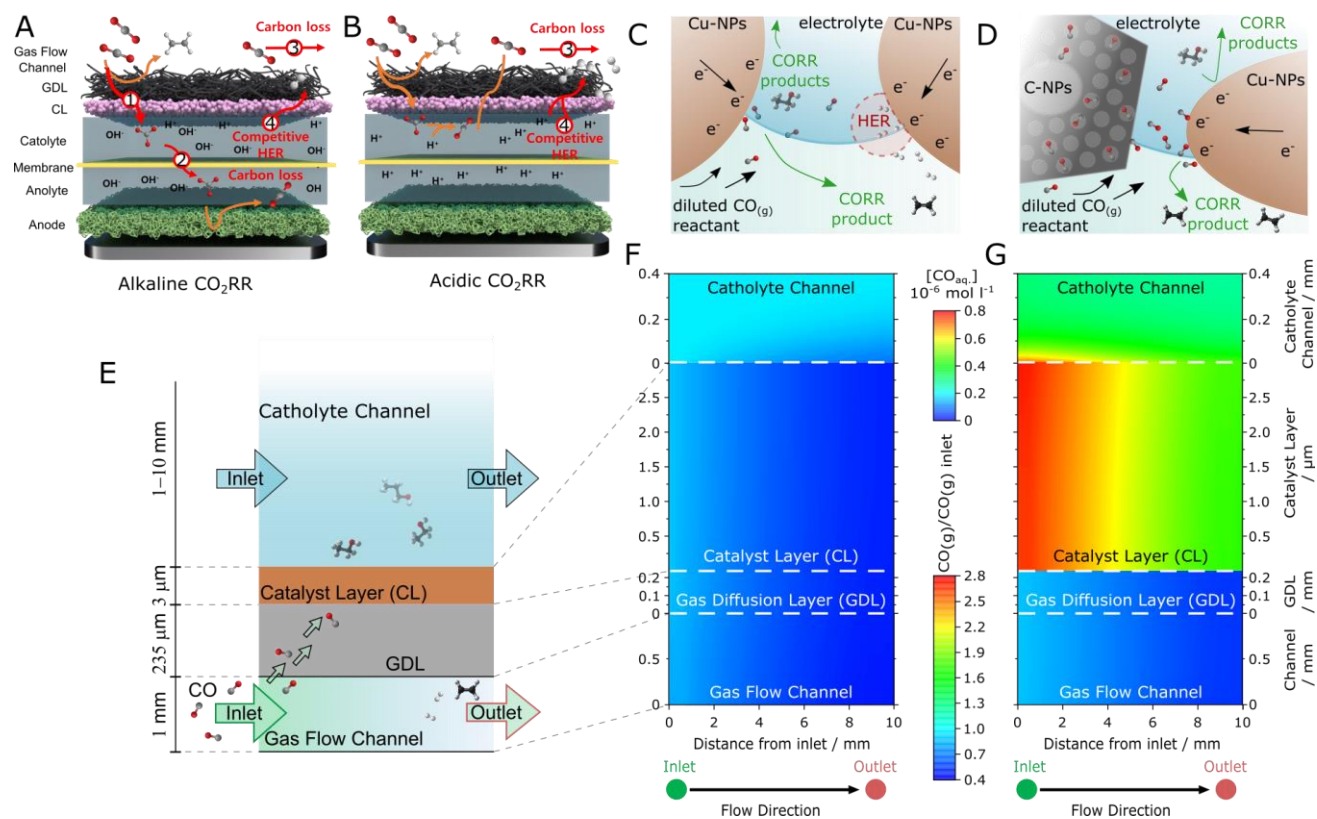


Figure 1. CO availability in the gas phase electrolyzer.

CO₂RR in (A) basic and neutral media using anion exchange membrane, (B) acidic media using cation exchange membrane. CE losses arise from carbonate formation (1), crossover to the anode side (2) unreacted CO (3). Competition with the hydrogen evolution reaction (4) leads to FE losses. (C) Catalyst regions where the reactant gas is sparse promote by-product reactions such as HER. (D) When CO distribution is promoted at the catalytic active sites, CORR to desired C-products can occur at diluted CO conditions. (E) Schematic of the electrolyzer gas cell: the electrolyzer is fed with CO from the gas flow channel inlet. The CO passes through the 10 mm long channel (thickness = 1 mm) and moves into the gas diffusion layer (GDL, thickness = 235 μm) and the catalyst layer (CL, thickness = 3 μm) through convection and diffusion. In the CL, a triple-phase boundary region exists between gaseous CO, solid electrode, and liquid electrolyte (from the catholyte channel, thickness >1 mm). The gas stream at the gas flow channel outlet is depleted in CO and enriched in C-products and H₂. The CO profile is modeled at 200 mA cm⁻² and an inlet CO flow rate of ca. 1.1 sccm in the catholyte layer, electrolyzer gas flow channel, inside the unreactive GDL, through a standard CL (F) and a CL with increased carbon monoxide adsorption (S_{CO}) ability (G) and in the catholyte channel. The top scale bar is for the CO dissolved in the electrolyte of the catholyte channel and the bottom scale bar is for the gaseous CO in the CL, GDL, and gas flow channel. Regions of the CL where CO concentration is low favor undesired reactions such as HER (Figure S4). The increased S_{CO} in the carbon reservoir catalyst (CRC) layer extends the dissolved CO availability along the electrode length (in the CL and in the catholyte layer), resulting in favored CORR over HER.

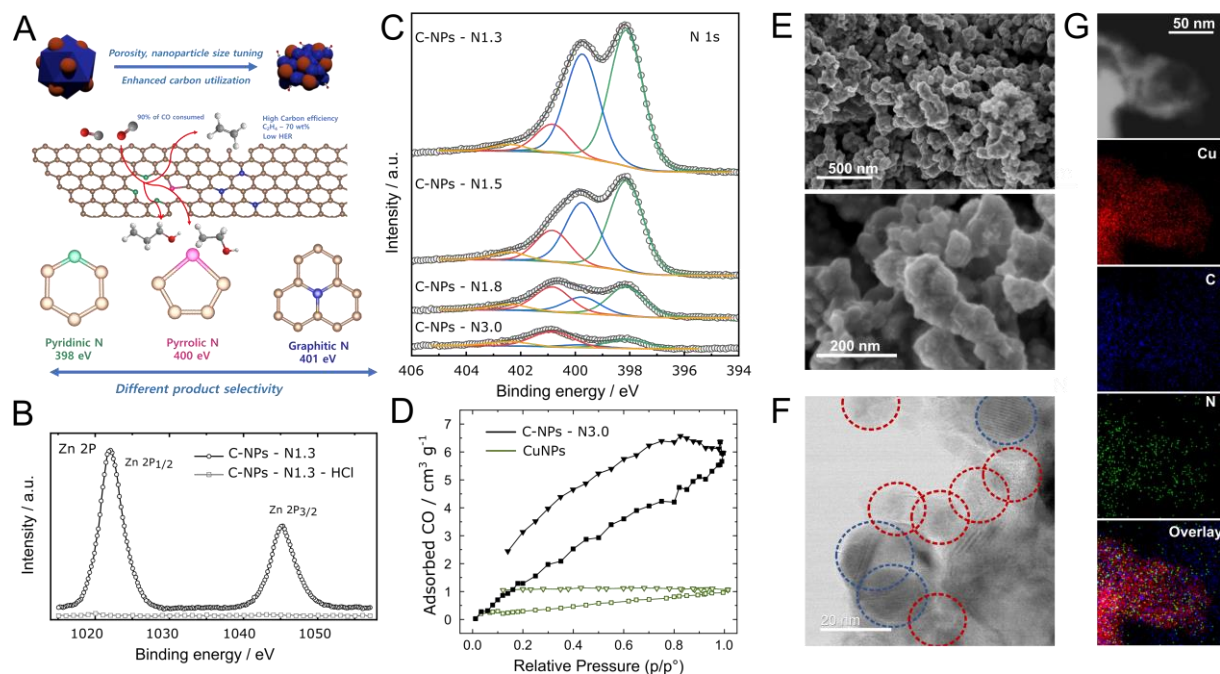


Figure 2. The C-NPs and Cu-NPs CRC heterojunction active layers

(A) Scheme of the different nitrogen groups in N-doped carbon nanoparticles. (B) Zn 2p in the C-NPs with a N_{pi}:N_{pr} ratio of 1:3 before and after acid treatment. (C) N 1s XPS spectra of C-NPs samples with different pyridinic:pyrrolic nitrogen ratios (N_{pi}:N_{pr}) of 1.3, 1.5, 1.8 and 3.0 (in the samples treated at 700, 800, 900, and 1000°C, respectively) (D) CO adsorption (squares) and desorption (triangles) isotherms for C-NPs with 3.0 N_{pi}:N_{pr} ratio and Cu-NPs (black and green symbols and traces, respectively) (E) SEM, (F) HR-TEM and (G) HR-TEM with elemental mapping of the 3D carbon reservoir catalyst (CRC) electrode.

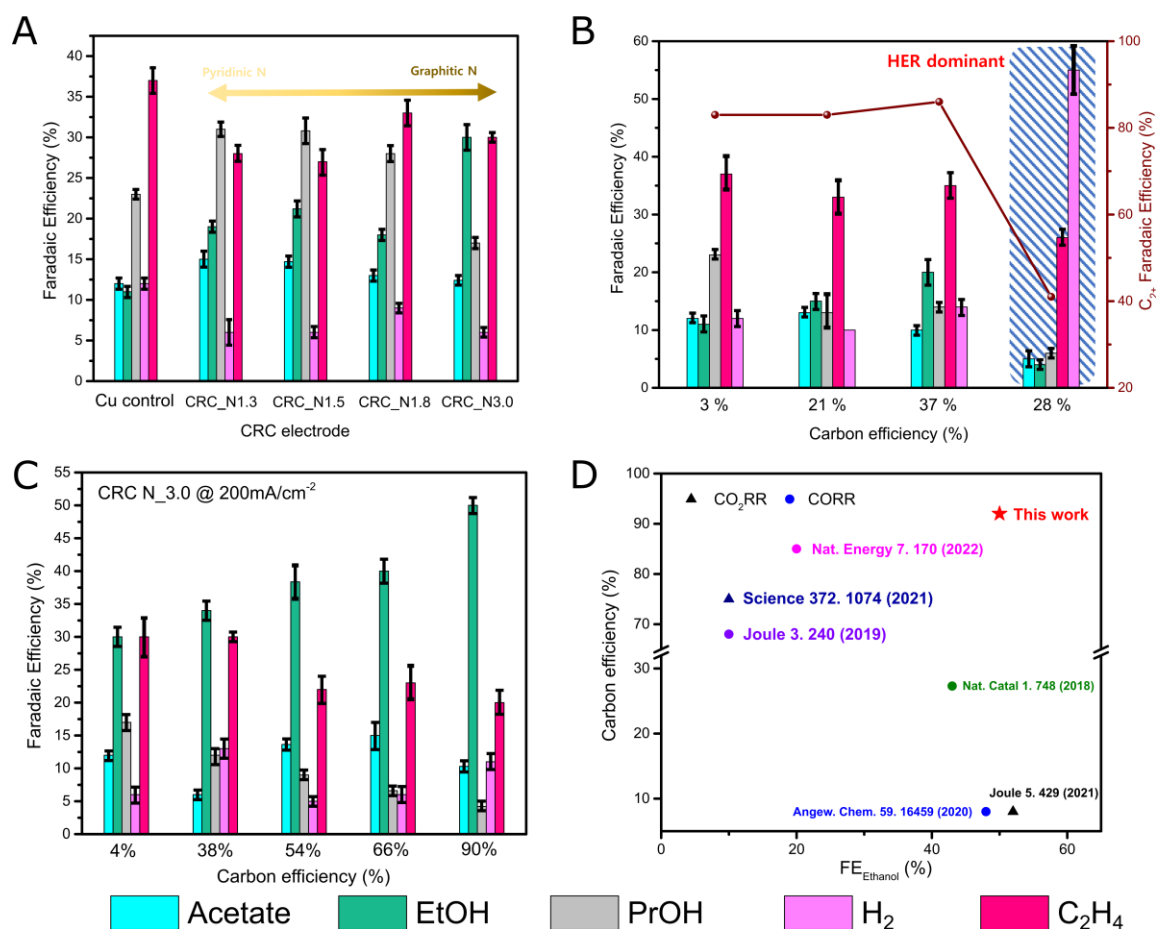


Figure 3. Heterojunction carbon reservoir catalysts for carbon-efficient CO electroreduction to alcohols.

(A) Comparison of product distribution at 200 mA cm⁻² and 20 sccm of CO on different CRC GDEs comprising C-NPs with different N_{pi}:N_{pr} ratios and catalytic Cu-NPs catalysts. FE distribution of CORR products at 200 mA cm⁻² for (B) control Cu-NPs and (C) CRC_N3.0 tested at different CE and CO flow (detailed information in the **Table S6** and **Table S7**) (D) Plot of FE ethanol versus external carbon efficiency for various catalysts in CO₂RR / CORR (detailed information in the **Table S8**).

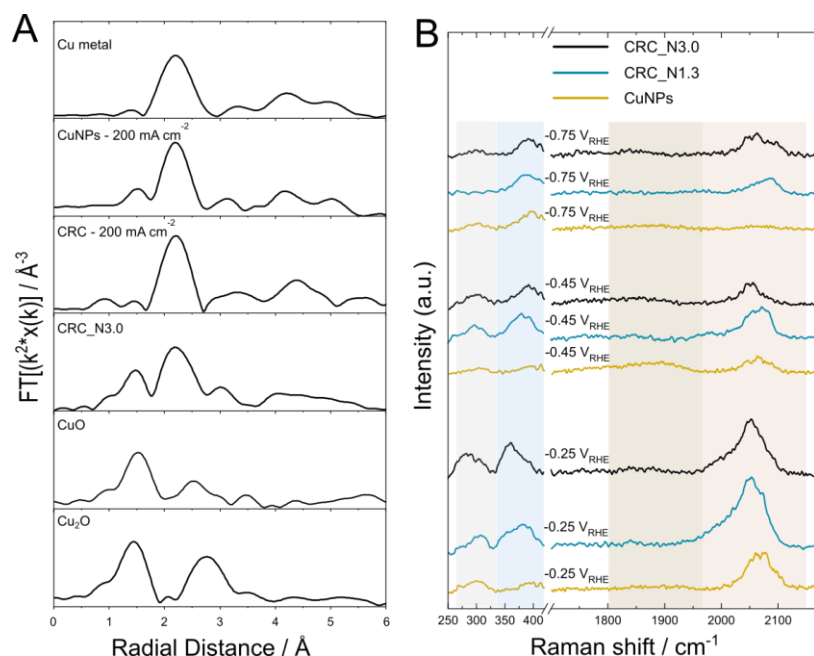


Figure 4. Operando characterization of carbon reservoir catalyst electrodes.

(A) Cu K-edge EXAFS spectra of Cu_2O , CuO , and Cu metal reference materials, a C-NPs/Cu-NPs electrode (CRC_N3.0) ex-situ and CRC_N3.0 & Cu-NPs electrode under CORR operando condition at 200 mA cm^{-2} .

(B) Operando Raman spectra of Cu-NPs, CRC_N1.3 and CRC_N3.0 (yellow, blue, and black traces, respectively) electrodes under CORR at different applied potentials. The region of $250\text{--}325 \text{ cm}^{-1}$ (*CO frustrated rotation), $325\text{--}425 \text{ cm}^{-1}$ (*CO stretching), $1850\text{--}2000 \text{ cm}^{-1}$ (stretching of bridge bound *CO) and $2000\text{--}2150 \text{ cm}^{-1}$ (stretching of atop bound *CO) are marked by gray, blue, brown, and orange, respectively. The Raman shift between 425 and 1700 cm^{-1} is marked by the break in the x axis.

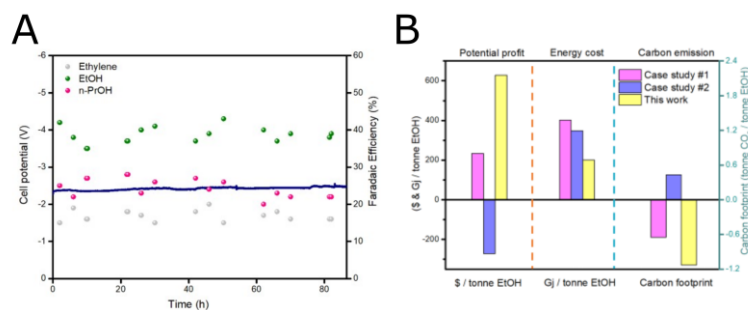


Figure 5. Techno-economic & carbon footprint analysis comparison for different case studies and stability test.

(A) Chronopotentiometry stability test of CRC_N3.0 at 100 mA cm⁻² in MEA cell configuration.

(B) TEA and carbon footprint analysis and comparison with different case studies (detailed information in the **Supplementary Note 1,2 and 3**)^{3,41}



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