

Letter

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A Hybrid Catalyst-Bonded Membrane Device for Electrochemical Carbon Monoxide Reduction at Different Relative Humidities

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Keywords: Gas Diffusion Electrode, Carbon Monoxide Reduction, Relative Humidity,
Multiphysics modeling, Vapor-fed, *operando* X-ray Absorption Spectroscopy.

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3 **Abstract:** A hybrid catalyst-bonded membrane device using gaseous reactants for carbon
4 monoxide reduction (COR) reaction in the cathode chamber, an aqueous electrolyte for oxygen
5 evolution reaction (OER) in the anode chamber, and an anion exchange membrane (AEM) for
6 product separation was modeled, constructed and tested. The Cu electrocatalyst was
7 electrodeposited onto gas diffusion layers (GDLs) and was directly bonded to AEM by
8 mechanical pressing in the hybrid device. The impacts of relative humidity at the cathode inlet
9 on the selectivity and activity of COR were investigated by computational modeling and
10 experimental methods. At a relative humidity of 30%, the Cu-based catalyst in the hybrid device
11 exhibited a total operating current density of 87 mA cm⁻² at -2.0 V vs. Ag/AgCl reference
12 electrode, a Faradaic Efficiency (FE) for C₂H₄ generation of 32.6%, and an FE for liquid-based
13 carbon product of 42.6%. Significant improvements in the partial current densities for COR were
14 observed in relative to planar electrodes or flooded gas diffusion electrodes (GDEs). In addition,
15 a custom test-bed was constructed to characterize the oxidation states of the Cu catalysts in real
16 time along with product analysis through the backside of the GDLs via *operando* X-ray
17 absorption (XAS) measurements.
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Introduction

Gas diffusion electrodes (GDEs) have been recently used for the selective reduction of CO₂ and CO to ethylene, ethanol, and other carbon products at high current densities and Faradaic efficiencies.^{1–8} GDE configurations, consisting of a three phase interface of reactant gas (CO or CO₂), liquid or polymer electrolyte, and solid electrocatalyst have contributed to the improved performances due to increased concentration of reactant gas at the electrocatalyst surface compared to the limited solubility in liquid electrolytes.⁹ Vapor-fed GDEs also provide opportunities for the catalyst materials to operate under a wide range of pH conditions, and favorably steer selectivity through suppression of hydrogen evolution reaction (HER) by controlling the concentration of CO₂ and water vapor.⁹ In comparison, while often operated at much lower current densities, traditional cells with bulk aqueous electrolytes are typically used to gain fundamental insights for reaction mechanisms under well-controlled conditions.^{10–16}

CO is an important intermediate in CO₂R and is widely accepted as the first intermediate to multi-carbon products.^{1,11,17,18} COR not only has shed light on mechanistic pathways of CO₂R, but also has the advantage of producing an overall more efficient CO₂R system in a two-step, cascade CO₂ reactor, in which CO₂ is first electrochemically reduced to CO, followed by a second catalytic reactor in which CO is reduced to C₂₊ products such as ethanol, ethylene, or propanol.¹⁹ Using this approach could lead to a relative improvement in solar-to-fuel (STF) conversion efficiency as high as 54% in certain operating regions for the electrocatalysts.^{19,20}

Herein, a hybrid catalyst-bonded membrane device that contains gas only reactants in the cathode chamber and a liquid electrolyte in the anode chamber, separated by an anion exchange membrane (AEM) was constructed, and the impacts of the applied potential and the relative humidity in this hybrid device configuration were studied. As most GDE configurations

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3 contained aqueous catholyte, we aim to investigate the impacts of water content in the GDE
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5 through controlling the relative humidity of vapor streams. Our goal was to optimize the water
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7 content to suppress HER while maintaining facile ionic conduction to the anode chamber.
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9 Unlike many previously reported flow cells,^{3,5,6,21,22} the electrodeposited Cu catalyst in the
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11 vapor-fed device was in direct physical contact with the AEM via mechanical pressing. In the
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13 hybrid device configuration, the AEM not only directly facilitates the ionic transport between the
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15 cathode and anode chamber, but also controls and dictates the local reaction environments at the
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17 reaction sites of the Cu-catalyst for COR. In a slightly modified cell configuration (See
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19 Supporting Information Figure S1), *operando* X-ray absorption spectroscopy (XAS)
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21 measurements were carried out at device relevant operating current densities to understand the
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23 impact of Cu oxidation state on the selectivity of reduced CO products.
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Results and Discussion

Figure 1a shows a schematic illustration of the hybrid catalyst-bonded membrane device. The hybrid catalyst-bonded membrane device consists of a cathode chamber and an anode chamber separated by an anion exchange membrane (AEM). In the anode chamber a flowing 1.0 M KOH aqueous electrolyte was used for oxygen evolution reaction (OER), while in the cathode chamber CO gas at a controlled relative humidity (RH) was introduced at a flow rate of 10.0 sccm. The relative humidity of CO was controlled using two mass flow controllers, which controlled one dry stream, and one stream flowing through a bubbler filled with deionized water, as shown in the Supporting Information (Figure S2). Relative humidity, the ratio of the partial pressure of water to the equilibrium partial pressure of water, is given by Equation (1):

$$RH = \frac{P_{H_2O}}{P^*_{H_2O}} \quad (1)$$

Where P_{H_2O} is the controlled partial pressure of water vapor, and $P^*_{H_2O}$ is the equilibrium partial pressure of water vapor at a given temperature. By controlling the individual flow rates of a fully humidified stream (100% RH) and a dry stream (0% RH) a range of RH can be achieved.

A traditional three-electrode configuration was used in the hybrid device with the Cu-GDE as the working electrode, Pt mesh as the counter electrode, and Ag/AgCl as the reference electrode. The Pt mesh was mechanically pressed against the AEM, and Cu/AEM/Pt formed the membrane-electrode-assembly (MEA) for COR in the hybrid device. As the cathode chamber does not contain any liquid electrolyte, the Ag/AgCl reference electrode was placed in the anolyte reservoir (Fig. 1a). The non-traditional three-electrode configuration, in which the reference electrode was placed at the opposite of the counter electrode, was validated experimentally to provide accurate potential points for the working electrode (Figure S3). Total

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3 cell resistances measured before and after bulk electrolysis ranged from 2-5 Ω as measured by
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5 electrochemical impedance spectroscopy (EIS) (Figure S4).
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8 The Cu electrocatalyst layer was electrodeposited on graphite-based gas diffusion layers (GDL)
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10 with a microporous carbon layer in an aqueous solution containing 0.15 M CuCl_2 , 1.0 M HCl,
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12 and 20% ethanol. Electrodepositions were performed potentiostatically by applying -0.50 V vs.
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14 Ag/AgCl until 4.5 C cm^{-2} of total charge was passed. During the deposition, the GDL served as
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16 the working electrode, copper mesh served as the counter electrode, and Ag/AgCl (sat. KCl)
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18 served as the reference electrode. After electrodeposition, the Cu-GDE was dipped in deionized
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20 water several times to rinse off any residual deposition electrolyte, followed by drying in air.
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22 Figure 1b shows an optical image of the electrodeposited Cu catalyst on GDL. The morphology
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24 and chemical composition of the Cu catalyst was characterized by scanning electron microscopy
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26 (SEM), energy dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD) before and
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28 after deposition. Cross sectional SEM images (Figure 1c) of the Cu-GDE show a dendrite type
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30 morphology and the Cu catalyst mainly deposited on the surface of the GDL with no penetration
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32 into the microporous layer of the substrate as shown by SEM/EDX (Figure S5). High selectivity
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34 of C_2H_4 in GDEs has been largely attributed to Cu morphology, with nanoneedle and dendrite
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36 type morphologies resulting in high local pH environments amenable to C-C coupling.
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38 Polycrystalline Cu also results in the exposure of high index facets which also show increased
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40 selectivity for C_{2+} products.²³⁻²⁷ XRD patterns (Figure 1d) after deposition show peaks matching
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42 calculated polycrystalline Cu diffraction patterns, as well as a small amount of Cu_2O present in
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44 the bulk.
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51 Prior to bulk electrolysis experiments the Cu-GDE was allowed to equilibrate under a flow of
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53 CO (10 sccm) at room temperature and controlled RH for 1 hour at open circuit voltage (OCV)
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3 conditions. During this period of time EIS measurements were taken to determine the cell
4 resistance, and it was found over the course of an hour that the OCV typically changed from -0.2
5 V to -1.0 V, while the cell resistance reduced from $\sim 30 \Omega$ to $\sim 4 \Omega$ at equilibration due to wetting
6 of the anion exchange membrane (Figure S6). Bulk electrolysis experiments were performed
7 using a range of potentials from -1.6 V to -2.2 V vs. Ag/AgCl. Gas products from COR were
8 measured every 6 min during bulk electrolysis by gas chromatograph (GC) (see SI for more
9 details), while liquid products were collected after bulk electrolysis from the anode electrolyte
10 and measured by high performance liquid chromatograph (HPLC). We note that the liquid
11 products identified in the HPLC may not be the direct reduction products of the Cu catalyst in
12 the hybrid device, since the Pt anode could oxidize some liquid products that transported across
13 the AEM. Additional loss of liquid products may have resulted from escaping the cathode or
14 anode chamber in the vapor form or being absorbed within the AEM. Nevertheless, from almost
15 all measurements, $>85\%$ of electrons participating the reactions were accounted for COR
16 products using GC and HPLC. Figure 2a shows the total operating current densities as a function
17 of time at 100% RH. The total current densities increased for the first 5-10 minutes of operation
18 and reached a relatively steady value after ~ 20 minutes of operation. Figure 2b shows the
19 corresponding product distribution as a function of applied potentials for COR at 100% RH. At -
20 2.0 V vs. Ag/AgCl, a total carbon product selectivity of 51.1% (23.5% toward generation of
21 C_2H_4 , and 27.6% toward generation of liquid based carbon products) was observed. The
22 geometric partial current densities for C_2H_4 generation remained relatively stable between 30 mA cm^{-2}
23 to 35 mA cm^{-2} during the course of testing for COR (Fig. 2c). In comparison, aqueous-based
24 electrolytes exhibit geometric partial current densities $< 1 \text{ mA cm}^{-2}$ for COR due to the low
25 solubility and low diffusion coefficient of CO, even with a range of catalyst morphologies and
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3 nano-structures.^{13–16} The low partial current density in cells with bulk aqueous electrolytes can
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5 be simply explained by Fick's law of diffusion (Equation 2) in which j is the partial current
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7 density, n is the number of electrons involved in the electrochemical reduction step (4 for 2 CO
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9 to C₂H₄), D_0 is the diffusion coefficient (2×10^{-9} m² s⁻¹ at 20 °C) and C_0 is the solubility of CO in
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11 aqueous solution (1 mM at 20 °C), L is the hydrodynamic boundary layer thickness, and F is
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13 Faraday's constant (96485 C mol⁻¹). The mass transport limited current density for CO reduction
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15 to C₂H₄ was limited to ~0.81 mA cm⁻² at a boundary layer thickness of ~100 μm.
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$$j = nFD_0 \frac{c_0}{L} \quad (2)$$

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22 Figure 2c also shows the geometric partial current density for a flooded GDE, in which the Cu
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24 catalyst layer was intentionally flooded with KOH electrolyte ahead of the bulk electrolysis
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26 measurements. The partial current density for C₂H₄ generation reduced to ~1-2 mA cm⁻², which
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28 was comparable in value to many reported aqueous-based systems. In the flooded GDE, the
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30 catalyst layer was fully immersed in aqueous KOH electrolyte, which resulted in the disruption
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32 of three-phase interfaces that were responsible for the facile vapor CO transport to the catalytic
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34 sites. The flooded GDE, in which the reactant CO needed to transport through hundreds of
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36 micrometers of liquid layer, essentially reduced into a high surface area, nano-structured
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38 electrode that operated in a bulk aqueous electrolyte, resulting in significant decrease in partial
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40 current density for COR, as well as larger partial current densities and Faradaic efficiencies for
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42 HER (Figure S14).
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47 The impacts of relative humidity on the activity and selectivity of the Cu-GDE were carried out
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49 by experiment and by Multi-physics simulations. Figure 3a shows the linear sweep voltammetry
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51 (LSV) of Cu-GDEs at five different RHs from OCV to -2.2 V vs. Ag/AgCl reference electrode at
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53 a scan rate of 50 mV s⁻¹. The total operating current density exhibited an increasing trend as the
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3 RH increased from 5% to 100%. Current densities up to 350 mA cm⁻² were observed at -3.0 V
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5 vs. Ag/AgCl (Fig. S7), however at these high current density regions, the intense OER at the
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7 anode chamber, which was not optimized for this study, produced large amounts of O₂ bubbles
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9 and caused noisy electrochemical signals. Figure 3b, 3c and 3d show the product distributions of
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11 COR at various applied potentials for three different RH conditions. The applied potential had
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13 the largest impact on product distribution and in general, high selectivity for COR products were
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15 observed at more negative potentials, with the highest selectivity of total COR products of ~75%
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17 at -2.0 V and RH 30%. Product distributions were impacted in the RH range of 5% to 30%, with
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19 little change in the distribution at RH values >50% (Figure S8). Control experiments using a N₂
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21 stream resulted in >90% Faradaic efficiency for HER with no liquid products detected by HPLC
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23 (Figure S9). The major liquid product distribution consisted of acetate, ethanol, and propanol;
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25 with trace amounts of acetylaldehyde and ethylene glycol detected. As liquid products were
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27 formed and diffused across the AEM, they could be electrochemically oxidized to other
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29 products. Ethanol has been electrochemically oxidized in basic media to several products
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31 including acetate, acetylaldehyde, and CO₂.²⁸⁻³⁰ To determine the extent to which ethanol could
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33 be oxidized to any of these products, a control experiment was performed by spiking the anolyte
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35 with 1000 ppm ethanol with bulk electrolysis performed under N₂ flow. After 1 h of electrolysis
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37 at -2.2 V, the anolyte was analyzed by HPLC and it was found that the ethanol signal was
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39 significantly decreased, while the acetate signal increased significantly. Based on the
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41 stoichiometry, we calculated 22.8% of ethanol was oxidized to acetate, 35.3% to CO₂, while
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43 41.9% remained. Due to the complexity of the oxidation of COR products in the anode chamber,
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45 we cannot currently determine if the catalyst was directly responsible for the generation of
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47 acetate, or if the catalyst is selective for ethanol alone, which is then oxidized to acetate.
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3 The relatively small change in the activity and selectivity for COR at various RHs at the
4 cathode feed was investigated by a Multi-physics model that accounted for vapor and water
5 transport in the vapor-fed test-bed. Figure 4a shows a schematic illustration of the vapor-fed test-
6 bed in Multi-physics modeling, with the calculation domain of the 2D model for water-vapor
7 transport available in the Supporting Information file. In the AEM domain, three mechanisms of
8 the water transport were considered in the model, including diffusion, water electro-osmotic
9 drag, and hydraulic permeation. The liquid-gas flow in GDL, MPL, and channel domains were
10 described by two separate Darcy's equations for liquid phase and gas phase, respectively. The
11 water saturation was predicted using Van Genuchten model which was expressed as capillary
12 pressure. The Hertz–Knudsen–Langmuir equation was used to predict the interfacial mass
13 transfer (evaporation and condensation) between liquid and gas phase.³¹ The 2D numerical
14 model was used to simulate local RH and water saturation in the catalyst layer as a function of
15 the relative humidity at the cathode inlet. Figure 4b shows the average RH inside the cathode
16 catalyst layer ranged from 88.5% to 99.3% while the external RH was controlled from 5% to
17 100%. The water saturation in the cathode catalyst layer was close to 0.52 regardless of
18 controlled inlet RH. This is mostly related to the domination of water transport through the AEM
19 by diffusion due to the aqueous-based electrolyte in the anode compartment. The relatively un-
20 changed local RH and water saturation in the catalyst layer resulted in limited impact to activity
21 and selectivity for COR by changing the inlet RH in the system. To further test this hypothesis,
22 an all vapor fed two-electrode configuration was employed by flowing 100% RH N₂ through the
23 anode at 10.0 sccm, and 5% RH CO in the cathode. The current density was set to 10 mA/cm²,
24 the average current density when applying -1.6 V in a three-electrode configuration. While the
25 Faradaic efficiency of HER was diminished to 7.5% in this all vapor configuration, the anion
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3 exchange membrane would dry out over a short period of time resulting in large cell resistances
4 and increased cell voltages (Figure S10). Further improvements to water transport and
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6 controlling RH at the anode could lead to decreased HER and better selectivity of COR products.
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10 A slightly modified GDE cell with an opening for incident X-rays was constructed to
11 accommodate *operando* XAS measurements. Figure 5a shows the experimental setup for
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13 *operando* XAS measurements at the Stanford Synchrotron Radiation Lightsource (SSRL).
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15 Multiple Cu oxidation states were observed by XANES measurements after deposition and
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17 during OCV conditions, and as the Cu-GDE was allowed to equilibrate an increase in the Cu₂O
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19 pre-edge was observed by XANES (Figure S11). There are several factors to consider during this
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21 equilibration period, including membrane wetting and oxidation state changes of the
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23 electrocatalyst which all play factors in the observed changes. The change in OCV correlates to
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25 the chemical oxidation state change of the Cu-GDE when exposed to a CO environment, while
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27 under N₂ flow, no significant change of OCV was observed (Figure S6). The decreased cell
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29 resistance is due to membrane wetting resulting in increased conductivity of the membrane.
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31 Figure 5b and 5c show the XANES measurements of the Cu-GDEs at OCV and under various
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33 applied potentials for COR. Under OCV conditions, a mixed oxidation state of Cu was observed
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35 (Figure 2b) with peaks matching both Cu and Cu₂O reference XANES spectra. However, during
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37 bulk electrolysis the Cu oxide was eventually reduced and peaks from the Cu-GDE matched the
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39 metallic Cu standard (Figure 5c). As Cu oxides are only observed at OCV conditions and
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41 metallic Cu is observed at every potential tested, we conclude that metallic Cu, instead of Cu
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43 oxides, was responsible for catalytic COR in the vapor-fed GDEs based on XANES
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45 measurements, in agreement with previous *operando* reports.³² The vapor-fed GDEs offered a
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47 unique platform, without the complications in the aqueous electrolyte, for investigating chemical
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3 and structural properties of the catalyst under device-relative operating conditions. In aqueous
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5 based cells, high current densities may result in bubble formation at the electrode surface
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7 blocking active sites and disrupting the *operando* measurements. However, in the vapor-fed
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9 configuration there is no liquid at the electrode surface and only water vapor is needed. This
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11 enables spectroscopic probing of the system at relatively high current density with little
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13 interference.
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Conclusion

In summary, we report a hybrid catalyst-bonded membrane device using only gas reactants for the electrochemical reduction of CO to ethylene, and various liquid products with a selectivity of up to 75% for C₂₊ products. The identified liquid products included acetate, ethanol, and propanol. At a relative humidity of 30%, the Cu-based catalyst in the hybrid device configuration exhibited a total operating current density of 87 mA cm⁻² at -2.0 V vs. Ag/AgCl reference electrode, a Faradaic Efficiency (FE) for C₂H₄ generation of 32.6%, and a FE for liquid based carbon product of 42.6% for CO reduction. Significant improvements in the partial current densities for COR were observed relative to planar electrodes or flooded gas diffusion electrodes (GDEs). The local RH and water saturation at the catalyst layer were dictated by the diffusional water transport through the AEM and exhibited little change over a wide range of the cathode vapor feed from 5% to 100%. As a result, relative humidity at the cathode had little impact on the product selectivity and activity in the hybrid catalyst-bonded membrane device. In addition, while different oxidation states of Cu were observed by *operando* XAS measurements in a custom test-bed, these were quickly reduced to metallic Cu and had no direct correlation on the selectivity of ethylene or H₂.

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3 **Supporting Information:** Detailed descriptions of the Cu electrodeposition, cell design, cross
4 sectional SEM/EDX data, relative humidity control schematic, details for numerical modelling
5 for water-vapor transport, cell resistance before and after bulk electrolysis, CV scans of
6 ferrocyanide in a GDE configuration, OCV and EIS data during equilibration, XANES data at
7 equilibration, and SEM images before and after bulk electrolysis, can be found in the Supporting
8 Information file.
9

10
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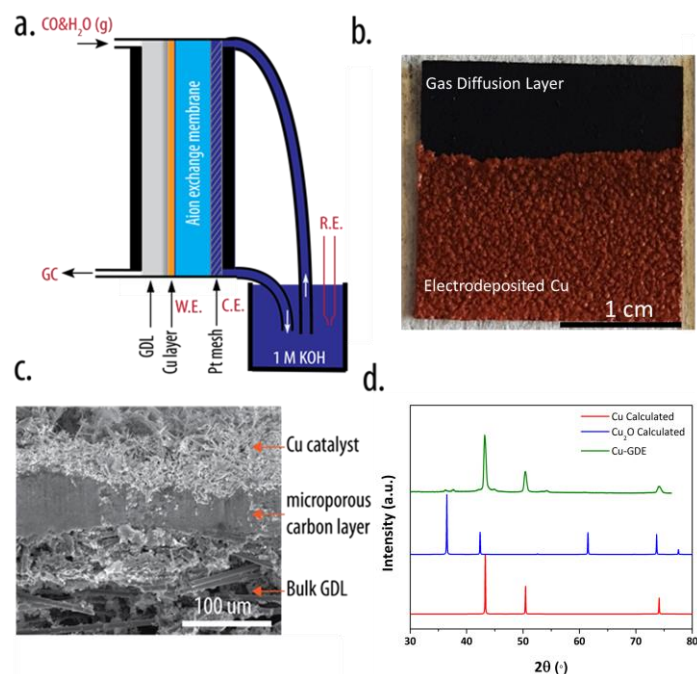


Figure 1. (a) A schematic illustration of the hybrid catalyst-bonded membrane device. (b) Optical image of the electrodeposited Cu catalysts on GDL. (c) Cross sectional SEM images of the Cu catalysts on GDL. (d) XRD pattern of the electrodeposited Cu catalyst on GDL.

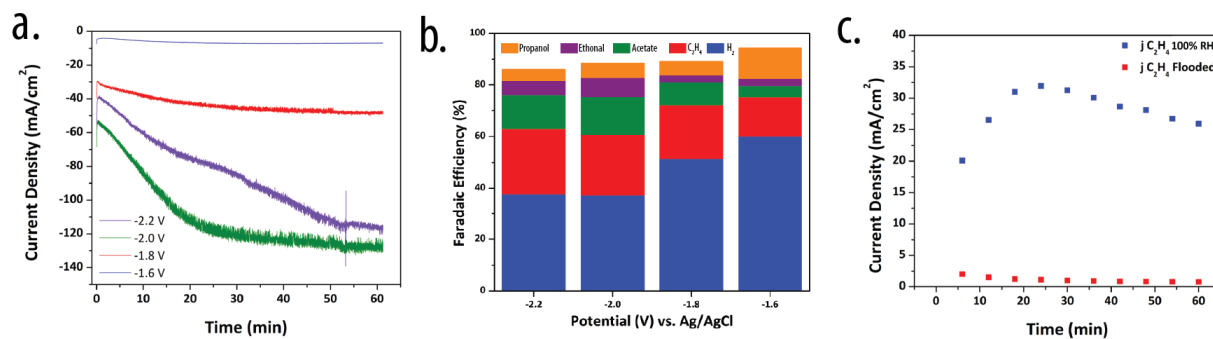


Figure 2. (a) Total operating current densities as a function of time at different applied potentials for COR at 100% RH. (b) Product distribution as a function of applied potentials for COR at 100% RH. (c) Partial current densities for C₂H₄ generation at -2.0 V as a function of time for the flooded cell and the vapor cell at 100% RH.

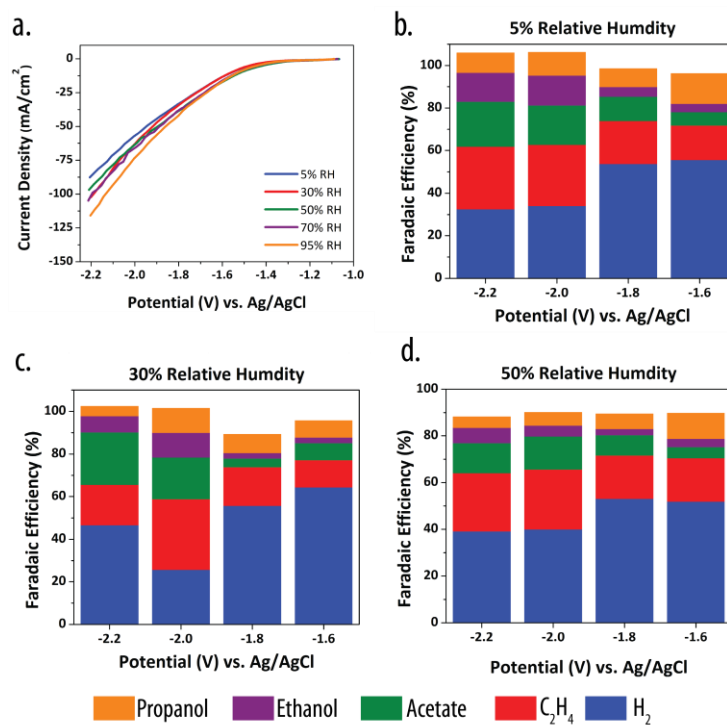


Figure 3. (a) LSV scans of Cu-GDE at various relative humidities. (b)-(d) Product distribution after 1 h bulk electrolysis as a function of applied potential and controlled relative humidity for COR.

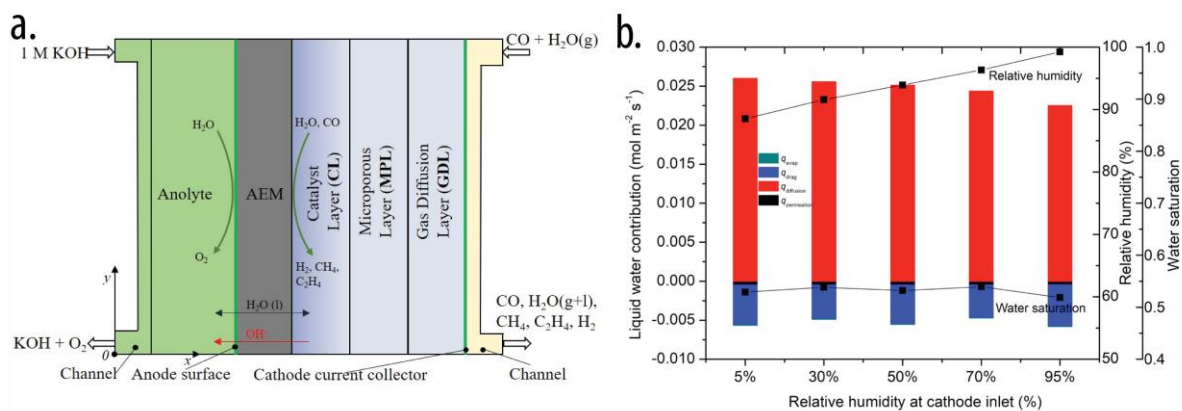
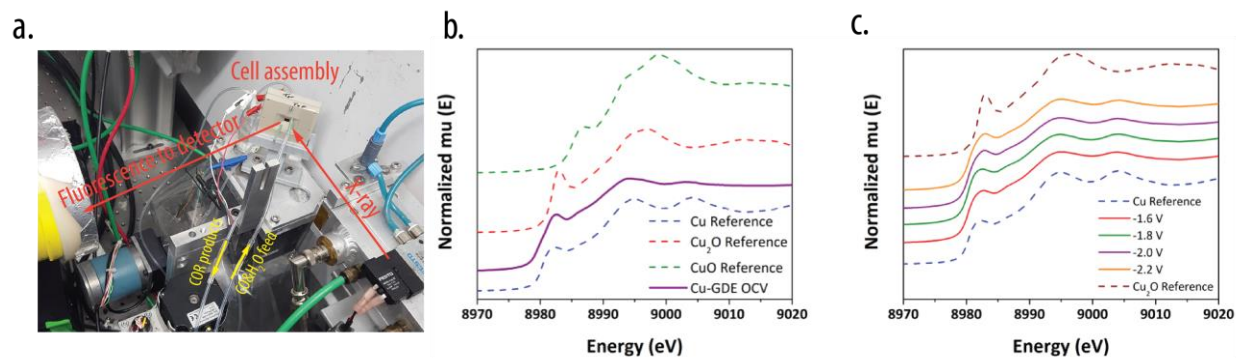


Figure 4. (a) A schematic illustration of the vapor-fed device in Multi-physics modeling (b) Simulated average relative humidity and water saturation in the cathode catalyst layer.



16 **Figure 5.** (a) Experimental setup for *Operando* XAS at SSRL (b) *Operando* XANES
17 measurements at OCV and (c) under various applied potentials.
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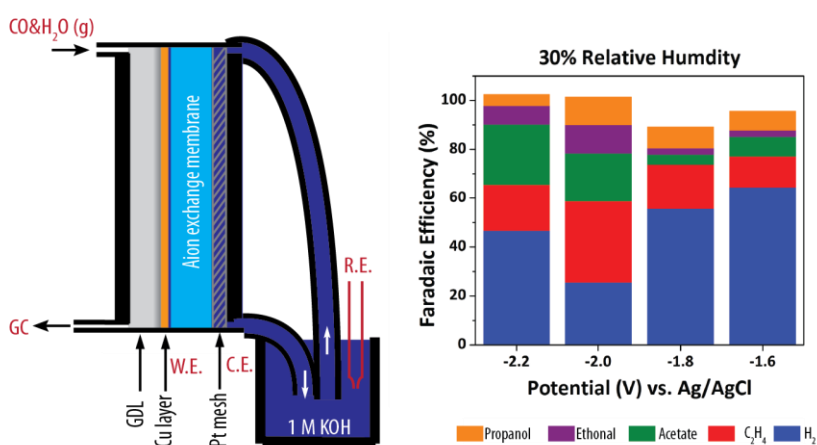
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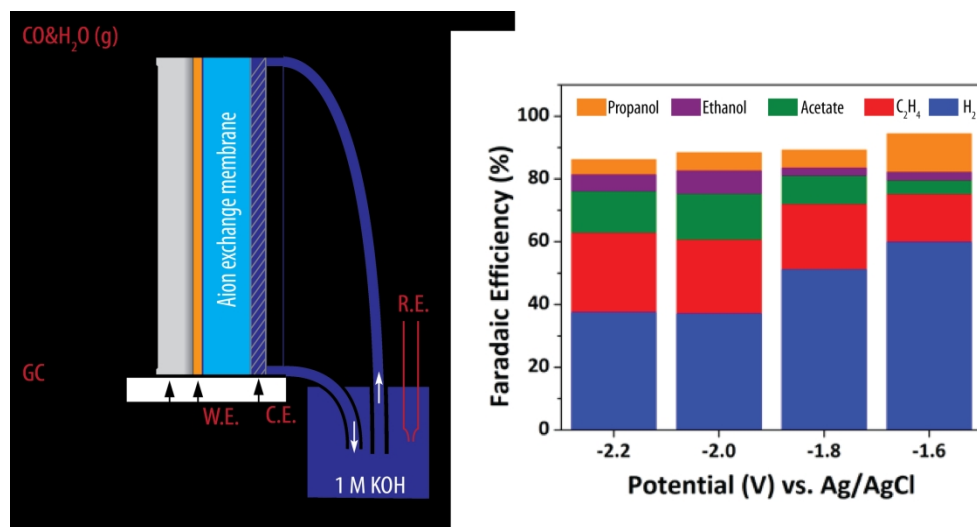
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Synopsis: Modeling and experimental study of a hybrid catalyst-bonded membrane device for electrochemical carbon monoxide reduction at different relative humidities.



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