Electrolytic CO₂ Reduction in Tandem with Oxidative Organic Chemistry

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ABSTRACT: Electrochemical reduction of CO₂ into carbon-based products using excess clean electricity is a compelling method for producing sustainable fuels while lowering CO₂ emissions. Previous electrolytic CO₂ reduction studies all involve dioxygen production at the anode, yet this anodic reaction requires a large overpotential and yields a product bearing no economic value. We report here that the cathodic reduction of CO₂ to CO can occur in tandem with the anodic oxidation of organic substrates that bear higher economic value than dioxygen. This claim is demonstrated by 3 h of sustained electrolytic conversion of CO₂ into CO at a copper–indium cathode with a current density of 3.7 mA cm⁻² and Faradaic efficiency of >70%, and the concomitant oxidation of an alcohol at a platinum anode with >75% yield. These results were tested for four alcohols representing different classes of alcohols and demonstrate electrolytic reduction and oxidative chemistry that form higher-valued carbon-based products at both electrodes.

INTRODUCTION

Significant resources have been committed to realizing scalable and cost-effective electrolytic hydrogen production as a means of storing electrical energy, but there remain economic challenges in using electrolyzer technologies to store renewable energy. Even at the strikingly cheap clean electricity prices that are known today, hydrogen still costs approximately twice as much to produce through the electrolysis of water as it does when extracted from fossil fuels. This scenario has constrained electrolytically produced hydrogen to merely ~5% of total global hydrogen production. CO₂ electrolysis is therefore an appealing alternative to water electrolysis for long-term energy storage because the carbon-containing products can penetrate a wider range of global fuels and chemicals markets that have the requisite infrastructure in place. Electrolyzer technologies for CO₂ conversion are, however, at an early stage of development, and innovative technology solutions are needed.

In a conventional water electrolyzer where the hydrogen evolution reaction (HER) takes place at the cathode, it is still the oxygen evolution reaction (OER) at the anode that requires the larger overpotential due to the kinetic and thermodynamic barriers associated with dioxygen formation. The negligible economic value of dioxygen has prompted several groups to consider whether alternative reactions can be driven at the anode to lower the operating voltage while generating a higher-value product. Choi and Sun have independently demonstrated a successful embodiment of this concept by driving alcohol oxidation at the anode in tandem with HER at the cathode to produce carbonyl compounds and hydrogen fuels (Figure 1). Baran recently reported the more synthetically challenging allylic oxidation at the anode while performing HER at the cathode. Choi and our group have also independently demonstrated the photoelectrochemical oxidation of organic compounds coupled with HER.

Given that each of the preceding oxidative studies relies on the HER at the cathode, we set out to explore the possibility of instead driving the electrochemical reduction of CO₂. This notion was inspired by the significant recent advances in converting CO₂ to CO at a metal (alloy) electrode at moderate temperatures and pressure conditions. For example, Kanan and co-workers have shown that CO₂ can be electrochemically reduced into various types of chemical fuels (e.g., formic acid, CO, methane, etc.) with high current densities and selectivities in different nanoparticle/nanowire systems for the (photo)-electrochemical reduction of CO₂ while Sargent and co-workers demonstrated an enhanced electrocatalytic CO₂ reduction via a high local CO₂ concentration created by nanostructured electrodes. Of relevance to this study are recent reports that efficient electrochemical reduction of CO₂ into CO can take place at certain copper–indium alloy

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compositions. While each of these heterogeneous electrochemical CO2 reduction studies relied on OER at the counter electrode, studies of molecular CO2 reduction catalysts have utilized sacrificial oxidizing reagents such as ferrocene to bypass the use of OER as the oxidative half-reaction.

These preceding observations prompted us to contemplate whether sacrificial oxidative chemistry could be bypassed during CO2 reduction for sustained electrolytic formation of usable products at both the anode and cathode. Following this line of inquiry, we report herein tandem CO2 reduction and organic oxidation in a single electrochemical cell using an NaHCO3 electrolyte where the anode and cathode are separated by a Nafion membrane. This proof-of-concept study focuses on the conversion of CO2 into CO at a copper−indium cathode, and oxidative chemistry at a platinum anode with the redox mediator 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) to mediate the oxidation of alcohols. Four different types of alcohols were investigated: namely, the primary and secondary benzylic and aliphatic alcohols listed in Figure 2. We were able to electrochemically convert each of these alcohols to their corresponding carbonyl compounds with >78% yield in less than 3 h while maintaining Faradaic efficiencies for both the cathode and anode at >70% prior to reagent depletion. These experiments represent the first demonstration of CO2 reduction in tandem with oxidation of organic compounds, and provide an alternative strategy for generating economically valuable products at both electrodes.

**RESULTS AND DISCUSSION**

A two-compartment electrochemical cell was used for all electrochemistry experiments where each compartment contains 25 mL of 0.5 M NaHCO3 in water and the compartments are separated by a Nafion proton exchange membrane (Figure S1). A platinum mesh served as the anode, and a copper−indium alloy film on titanium was used as the cathode for all experiments. The cathode catalyst layer was synthesized by irradiating copper(II) chloride dihydrate (0.075 mmol) and indium acetylacetone (0.025 mmol) dissolved in 6 mL of methanol that were spin-coated on planar titanium substrates with near-infrared light prior to electrochemical reduction. Powder X-ray diffractograms displayed dominant crystalline phases of Cu2In and Cu, confirming the composition and structure of the Cu−In films as previously reported (Figure S2). The solution in the cathodic compartment was purged with CO2 at a rate of 5.0 sccm for 30 min prior to and during electrochemical measurements. All potentials were measured against an Ag/AgCl reference electrode and reported versus reversible hydrogen electrode (RHE).

The cathode and anode reactions were each investigated independently by cyclic voltammetry. The cyclic voltammogram for CO2 reduction at a copper−indium cathode shows an onset potential at approximately −0.36 V and a current density of 3.7 mA cm−2 at −0.70 V (Figure 3a). The Faradaic efficiency at −0.70 V was confirmed to be 80% based on the relative amounts of CO and hydrogen detected by gas chromatography (GC). While superior CO2 reduction electrocatalyst activity
has been observed for complex nanostructures or with ionic liquids,\textsuperscript{35,40} the current density of 3.7 mA/cm\textsuperscript{2} for the copper–indium samples is among the highest activity reported to date for CO\textsubscript{2} reduction by a planar thin film, providing a reliable foundation for studying tandem CO\textsubscript{2} reduction and organic oxidation.

We then investigated the oxidative electrochemistry of each of the four alcohols indicated in Figure 2. The data for 1-phenylethanol (1-PEA) are provided in Figure 3; the other three alcohols exhibit similar behavior (the corresponding data are included in the Supporting Information). The oxidative scans of the alcohols in 0.5 M NaHCO\textsubscript{3} aqueous solutions (without TEMPO present) did not show any redox activity over the 0.7–2.1 V range using a platinum anode (Figure S3). Data recorded on 0.20 mmol of TEMPO in the same electrolyte (no alcohol present) produced a reversible redox couple at 1.3 V in accordance with literature values.\textsuperscript{21,25} Following these control experiments, 0.25 mmol of 1-phenylethanol was added to the electrolyte solution containing TEMPO, and a small increase in current was observed, suggestive of charge transfer between TEMPO and the alcohol (Figure 3). This response was observed for each of the acids. The much larger current response measured with TEMPO and the alcohol over that of the background indicates that TEMPO-mediated alcohol oxidation is more favorable than water oxidation over the 1.2–1.8 V potential window.\textsuperscript{21}

The two half-reactions were then tested in tandem by performing chronoamperometry of a two-electrode cell where CO\textsubscript{2} was bubbled into the catholyte, and 0.20 mmol of TEMPO and 0.25 mmol of an alcohol were added to the anolyte. Electrolysis carried out at a constant potential of ∼0.70 V maintained a stable current density of ∼3.7 mA cm\textsuperscript{-2} for 3 h (Figure 3a). During electrolysis, gases in the cathodic compartment were automatically vented into the gas-sampling loop of a gas chromatograph (GC) and analyzed every 30 min. Aliquots of the liquid in the anodic compartment were manually collected by syringe and analyzed by proton nuclear magnetic resonance (\textsuperscript{1}H NMR) every 30 min (Figures S5, S7, S8, and S10). The competing HER and OER reactions at the cathode and anode, respectively, were accounted for by measuring the relative amounts of hydrogen and oxygen formation by GC. The Faradaic efficiencies for CO\textsubscript{2} to CO conversion were maintained at >70% over the course of the 3 h experiment (Figure 4a). The Faradaic efficiency of the anodic oxidation of 1-phenylethanol (1-PEA) to acetoephone (ACP) was ∼95% for the first 30 min of the reaction, but then started to diminish toward ∼70% at 1.5 h into the experiment (Figure 4b). The OER was dominant for the last half of the 3 h experiment, and thus the Faradaic efficiency for ACP formation was merely ∼36% over the course of the entire experiment. However, this rapid drop in Faradaic efficiency at the anode is merely because 95% of 1-PEA is consumed in the first 1.5 h of the reaction (Figure 4b) and can be increased by adding more alcohol or starting with higher concentrations. These collective data indicate that the formation of CO and ACP is favored over hydrogen formation by GC. The Faradaic conversion were maintained at >70% over the course of the 3 h experiment (Figure 4b). The Faradaic conversion were maintained at >70% over the course of the 3 h experiment (Figure 4b).

The four alcohols chosen to demonstrate the viability of oxidizing different classes of alcohols were all oxidized with meaningful yields (78%–93%) after 3 h reaction (Table 1). Product selectivity is one of the key figures of merit for alcohol oxidation, particularly for primary alcohols that can be oxidized to aldehydes or oxidized further to carboxylic acids (aldehydes can be hydrated to geminal diols in aqueous solution and subsequently oxidized to carboxylic acids).\textsuperscript{41} The oxidation of secondary alcohols (1-phenylethanol and isopropanol) in our study yielded the respective ketones in exclusivity, whereas the oxidation of primary alcohols (4-methoxybenzyl alcohol and ethanol) produced mixtures of the aldehydes and carboxylic acids during the initial stages of the reaction but yielded higher product selectivity over 3 h of electrolysis. For the ethanol oxidation reaction, acetaldehyde was accumulated over the first 1 h of reaction (yield ∼16%, Figure S9) prior to further oxidation to acetic acid. Acetic acid was the dominant product after 3 h of electrolysis (Table 1), suggesting a relatively fast oxidation of acetaldehyde into acetic acid.\textsuperscript{41} The oxidation of 4-methoxybenzyl alcohol, however, terminated at the corresponding aldehyde to yield 4-methoxybenzaldehyde as the major product (Table 1 and Figure S6). This observation indicates that the oxidation rate of 4-methoxybenzaldehyde is much slower than that of 4-methoxybenzyl alcohol. The divergent oxidation product selectivity of ethanol and 4-methoxybenzyl alcohol is consistent with previous studies on TEMPO-mediated oxidation of primary alcohols.\textsuperscript{25,42} The differences were attributed to the strongly electron-donating effect and steric encumbrance of the methoxyphenyl group that render hydration of 4-methoxybenzaldehyde much more unfavorable than that of acetaldehyde (hydration constant of acetaldehyde ∼10\textsuperscript{8}, whereas the hydration constant of 4-methoxybenzaldehyde is <10\textsuperscript{−2}, Figure S12).\textsuperscript{41}

These results collectively demonstrate that our integration of CO\textsubscript{2} reduction and oxidative electrochemistry can be used to form CO and convert alcohols with high product selectivity and high Faradaic efficiencies. This cell architecture successfully converted four primary and secondary aliphatic and benzylic alcohols into their corresponding carboxyl compounds with yields >70% within the first hour of the experiment. At the current densities investigated here, the losses in cell efficiency are due to the depletion of the organic reagents. Future studies will test the efficacy of these reactions in a flow cell configuration that enables constant delivery of the substrate to the cathode. This electrochemical study showcases the opportunity to create an electrolyzer that generates products at both electrodes that are of higher commercial value than the hydrogen and oxygen fuels produced in a conventional electrolyzer.

\section*{METHODS}

\textbf{Materials.} Indium acetylacetone (98%), copper(II) chloride dihydrate (98%), methanol (98%), NaHCO\textsubscript{3} (99%), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 98%), 4-methoxybenzyl alcohol (98%), 4-methoxybenzaldehyde (98%), 4-methoxybenzoic acid (98%), 1-phenylethanol (racemic, 98%), acetoephone (99%), ethanol (dried, 99%), acetaldehyde (99%), acetic acid (99%), isopropanol (99%), acetone (99%), benzene-1,3,5-tricarboxylic acid (98%), and deuterium oxide (D\textsubscript{2}O, 99.9 atom % D) were purchased from commercial vendors (Alfa Aesar, Fisher Scientific, or Sigma-Aldrich). No unexpected or unusually high safety hazards were encountered.

\textbf{Electrode Preparation.} Copper–indium cathodes were prepared in accordance with our previously reported procedures.\textsuperscript{36} Solutions of metal precursor complexes were prepared by dissolving 0.075 mmol of copper(II) chloride dihydrate and 0.025 mmol of indium acetylacetone in 6 mL of methanol, and 0.75 mL of precursor solution was dropped onto
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0.04 piece of Na and a gas-tight two-compartment electrochemical cell with collected between 2 contained 25 mL of 0.5 M NaHCO3 aqueous solution. The used for all electrochemistry experiments. Each compartment were measured against an Ag/AgCl reference electrode (3.0 M 30 min prior to electrochemical measurements. All potentials under an IR lamp overnight. The resulting metal oxide solution in the cathodic compartment was purged with CO2 for 6. Cyclic voltammetry of alcohol oxidation, platinum working electrode and copper-indium counter electrode were used, and 0.20 mmol of TEMPO and 0.25 mmol of alcohol were added successively into anolyte; a constant bias of −0.7 V vs RHE was applied over 3 h. During electrolysis, CO2 gas was delivered into the cathodic compartment at a rate of 5.0 sccm and gas sample in the cathodic compartment was taken into analysis by gas chromatography (GC) every 30 min; whereas liquid sample in the anodic compartment was taken into analysis by proton nuclear magnetic resonance (1H NMR) every 30 min.

Product Quantification. The GC (SRI Instruments) was equipped with a packed MolSieve 5A column with an interior diameter of 2 mm and a length of 0.274 mm. Argon (Praxair, 99.999%) was used as the carrier gas and set at a flow rate of 20 sccm. A flame ionization detector (FID) with methanizer was used to quantify CO, and a thermal conductivity detector (TCD) was used to quantify H2. Calibration curves for CO and H2 were created by plotting peak area versus concentration in standard calibration gas purchased from Norlab. 1H NMR spectroscopic data were collected on a Bruker AV III HD 400 MHz spectrometer equipped with Bruker BBFO smart probe with ATMA at 25 °C. Benzene-1,3,5-tricarboxylic acid was added to reaction sample taken from anolyte as internal standard, and deuterium oxide (D2O) was added to make a H2O:D2O (1:9 v/v) solution for 1H NMR measurements. Water signal was suppressed by using watergate W5 pulse sequence with double gradient echo.43 A series of standard solutions with known concentrations of pure reactants and products were prepared and analyzed by 1H NMR, and the relative peak areas of reactants and products were normalized to the peak of benzene-1,3,5-tricarboxylic acid (singlet, δ = 8.29 ppm). Calibration curves were created by plotting relative peak areas versus concentration of standard solutions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.7b00207.

Electrochemistry Experiments. A CHI 660D potentiostat and a gas-tight two-compartment electrochemical cell with a piece of Nafion proton exchange membrane as a separator were used for all electrochemistry experiments. Each compartment contained 25 mL of 0.5 M NaHCO3 aqueous solution. The solution in the cathodic compartment was purged with CO2 for 30 min prior to electrochemical measurements. All potentials were measured against an Ag/AgCl reference electrode (3.0 M KCl) and converted to the RHE reference scale using E (vs RHE) = E (vs Ag/AgCl) + 0.22 V + 0.059 V*pH. For cyclic voltammetry of CO2 reduction, copper-indium working electrode and platinum counter electrode were used. For cyclic voltammetry of alcohol oxidation, platinum working electrode and copper-indium counter electrode were used, and 0.20 mmol of TEMPO and 0.25 mmol of alcohol were added successively into anolyte. For overall electrolysis, copper-indium working electrode (immersed surface area of 2.7 cm2) and platinum counter electrode were used, and 0.20 mmol of TEMPO and 0.25 mmol of alcohol were added into anolyte; a constant bias of −0.7 V vs RHE was applied over 3 h. During electrolysis, CO2 gas was delivered into the cathodic compartment at a rate of 5.0 sccm and gas sample in the cathodic compartment was taken into analysis by gas chromatography (GC) every 30 min; whereas liquid sample in the anodic compartment was taken into analysis by proton nuclear magnetic resonance (1H NMR) every 30 min.

Figure 3. (a) Reductive scan of a copper-indium cathode immersed in 25 mL of H2O containing 0.50 M NaHCO3 where CO2 is bubbled through at a rate of 5.0 sccm. (b) Cyclic voltammetry profiles of a blank 0.50 M NaHCO3 aqueous solution (black) prior to the successive addition of 0.20 mmol of TEMPO (orange) and 0.25 mmol of 1-phenylethanol (1-PEA, blue). All data recorded at a scan rate of 10 mV/s in 25 mL of aqueous solution.

Figure 4. (a) Rate of product formation (blue trace) and Faradaic efficiencies (columns) over 3 h of tandem electrolysis at an external bias of −0.70 V that converts CO2 into CO and 1-phenylethanol (1-PEA) into acetophenone (ACP). The Faradaic efficiencies for the cathodic products CO (green) and H2 (black) and anodic products acetophenone (orange) and O2 (gray) are indicated. (b) Relative concentrations of 1-phenylethanol (blue) and acetophenone (orange) over the course of the 3 h experiment that were quantified by 1H NMR spectroscopy.

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Table 1. Yields of Alcohol Oxidation Following 3 h of Sustained Electrolysis

| Class of Alcohol | Reactant | Product A | Product B |
|------------------|----------|-----------|-----------|
| Primary benzyl alcohol | ![Chemical Structure](image1) | 84% | < 1% |
| Secondary benzyl alcohol | ![Chemical Structure](image2) | 93% | — |
| Primary aliphatic alcohol | ![Chemical Structure](image3) | < 1% | 91% |
| Secondary aliphatic alcohol | ![Chemical Structure](image4) | 78% | — |

Electrolysis scheme, XRD diffractogram, CV profiles, $^1$H NMR spectra, relative concentrations of electrolysis reactants and products over time, and mechanism of oxidations of 4-methoxybenzyl alcohol and ethanol in water (PDF)

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### Author Contributions

C.P.B. supervised this project; T.L. and C.P.B. designed the experiments; T.L. performed the electrolysis; Y.C. helped with characterization; J.H. prepared the cathodes; T.L. and C.P.B. wrote the manuscript.

### Notes

The authors declare no competing financial interest.

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