

CO₂ Electrochemical Reduction to C1 Compounds

Deryn Chu⁽¹⁾, Jiangtian Li⁽¹⁾⁽²⁾, Terry DuBois⁽³⁾,
Annika Benson⁽⁴⁾, Tristan Weaver⁽⁴⁾, and Dr. Enoch Nagelli⁽⁴⁾

⁽¹⁾ U. S. Army Combat Capability Development Command
Army Research Laboratory, 2800 Powder Mill Rd., Adelphi, MD 20783

⁽²⁾ Oak Ridge Associated Universities (ORAU)

⁽³⁾ U. S. Army Combat Capability Development Command, C5ISR Center,
6631 Cyber Street, Aberdeen Proving Ground, MD 21005

⁽⁴⁾ Department of Chemistry & Life Science
United States Military Academy, West Point, NY

deryn.d.chu.civ@army.mil

Abstract

The development of renewable energy source is one of the most significant scientific challenges facing the world. In CO₂ reduction, its thermodynamic nature, coupled with the large activation energy associated with the multi-electron and multi-proton reduction, makes the conversion of CO₂ a grant challenge. The electrochemical reduction reaction pathway for CO₂ to C-1 chemical fuels is complicated. The electrochemical reactions for conversion of CO₂ on Cu and a fluorine-doped tin oxide (SnO₂:F, FTO) Sn electrodes surface to C1 chemical compounds are performed. This research proposes to characterize and understand electrochemical reduction of CO₂ and H₂O to C1 compounds on Cu and FTO electrode surfaces. The goal of this work is to study the feasibility of an electrochemical device to chemically synthesize fuels.

Key Words: Electrochemical Reduction, CO₂ Electrochemical Reduction, and Hydrogen Evolution.

Introduction

Sunlight is the most abundant renewable energy source and has intrinsic potential in meeting future global energy demand. Converting solar energy to chemical energy stored as chemical fuels has received enormous attention world-wide due to the renewable fuel generation and benefit to the environment. Solar fuels are the chemicals such as hydrogen and small organic hydrocarbon compounds that store the chemical energy converted from the solar energy. Since Fujishima and Honda reported water splitting with a titanium dioxide-based photo-electrochemical cell (PEC) in 1972 [1], photo-electrochemical water splitting with photoactive semiconductors has been extensively studied, especially under sponsorships from the U. S. Department of Energy Programs and the National Science Foundation Programs [2]. Hydrogen is an attractive clean fuel for general purpose. However,

hydrogen storage and transportation are challenging for practical applications. From a practical point view, high energy density liquid fuels are more favor due to their easy transportation and storage. Compared to hydrogen, carbon-based fuels have high volumetric energy density and easy integration into the present infrastructure. Figure 1 shows an ideal diagram for CO₂ reduction to high energy density liquid fuels.

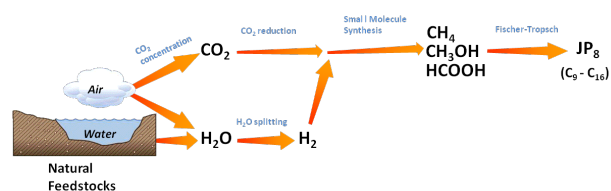


Figure 1: The schematic diagram is a renewable energy from CO₂ to liquid fuels.

Converting water and carbon dioxide into C1 hydrocarbon fuels is an important route for renewable energy development. Four different technical approaches have been reported in literature to synthesize C-1 hydrocarbon fuels from CO₂ with water: (1) conventional chemical catalytic technology, (2) biocatalysts enzyme technology [3], (3) photo-electrochemical technology [4-6], and (4) electrochemical technology [7-9].

This study focuses on converting water and CO₂ to C1 chemical fuels through an electrochemical reaction pathway. The thermodynamic nature of the CO₂ reduction reaction, coupled with the large activation energy associated with the multi-electron and multi-proton reduction, makes it a great challenge. Dr. Thomas Jaramillo at Stanford University has observed a total of 16 different CO₂ reduction products (C₁-C₃) from a polycrystalline copper electrode [7-9]. This research is to evaluate catalysts (such as Cu and Sn) for the electrochemical reduction of CO₂ and H₂O to C1 hydrocarbon fuels,

aiming to study feasibility for an electrochemical device for chemically synthesize fuels.

Experimental:

The experiments were carried out with a Cu electrode or FTO/Sn glass electrode in a conventional electrochemical glass cell with three separate compartments for the working, counter, and reference electrodes. A platinized platinum gauze was used as the counter electrode. A saturated calomel electrode (SCE) saturated with KCl was used as the reference electrode. The reference electrode was connected to the main compartment (working electrode) via a luggin capillary that acts to minimize the IR drop and to prevent Cl⁻ ion reacting with working electrode. The counter electrode was connected to main compartment (working electrode) via a fine glass filter to separate reaction products generation from counter electrode to working electrode compartment. A Pine instrument potentiostat was employed for all electrochemical experiments. All potentials reported here are referred to SCE.

High purity potassium bicarbonate (KHCO₃) was procured from Sigma Chemical Company. 0.5 M KHCO₃ solution was prepared by solving KHCO₃ in distilled water. The 0.5 M KHCO₃ electrolyte was saturated with ultrapure CO₂ (99.99%, Airgas, USA) by bubbling for at least 30 minutes before performing CO₂ electrochemical reduction. Continuous CO₂ flow was maintained over the tested electrolyte during the experiment. Chronoamperometry and Cyclic voltammetry techniques were used for experiments. Cyclic voltammetry technique was performed to obtain the electrochemical potentials vs. electrochemical current response for CO₂ electrochemical reaction (reactant adsorption/reduction and products desorption) at the Cu and FTO/Sn (Fluorene Doped Tin Oxide) electrodes. Chronoamperometry is the current-time transient following a potential step and used to study the CO₂ electrochemical reaction at the Cu and FTO electrodes. In this study, the potential was set up to step from -0.2V (vs. SCE) to a potential at which the CO₂ electrochemical reduction occurs potentials.

Products Analysis:

The analysis of gas products from the electrochemical reduction of CO₂ was analyzed on an SRI Gas Chromatography (GC) -Flame Ionization and Thermal Conductivity Detectors (GC-FID&TCD) (SRI, GC 8610). Liquid phase products were analyzed by nuclear magnetic resonance (NMR).

Results and Discussion:

There have two electrochemical reduction reactions at cathodic sweep direction for CO₂ saturated 0.5M

KHCO₃ electrolyte: CO₂ reduction reaction (CO₂ + m (H⁺ + e⁻) → C_xH_yO_z + nH₂O) and H₂ evolution reaction (2H⁺ + 2e⁻ → H₂). Two reactions compete dependent on applied potentials. Table I shows theoretical thermodynamic electrochemical reduction potentials (E⁰) for CO₂ to various products through two or multi-electron and multi-proton reduction reactions. The CO₂ potentials are calculated for aqueous solutions at pH=7.

Table I. Theoretical thermodynamic electrochemical reduction potentials (E⁰) for CO₂ to various products through two or multielectron reduction reactions. n represents the involved electron numbers for the corresponding reactions.

Water Splitting:	n	E ⁰
2H ⁺ + 2e ⁻ → H ₂	2	E ⁰ = 0.00V
H ₂ O → ½ O ₂ + H ₂	2	E ⁰ = 1.23V
CO ₂ Electrochemical Reaction		
CO ₂ + 2H ⁺ + 2e ⁻ → CO + H ₂ O	2	E ⁰ = -0.53V
CO ₂ + 2H ⁺ + 2e ⁻ → HCOOH	2	E ⁰ = -0.61V
CO ₂ + 4H ⁺ + 4e ⁻ → HCHO + H ₂ O	4	E ⁰ = -0.48V
CO ₂ + 6H ⁺ + 6e ⁻ → CH ₃ OH + H ₂ O	6	E ⁰ = -0.38V
CO ₂ + 8H ⁺ + 8e ⁻ → CH ₄ + 2H ₂ O	8	E ⁰ = -0.24V
CO ₂ + 12H ⁺ + 12e ⁻ → C ₂ H ₄ + H ₂ O	12	E ⁰ = 0.079V

Figure 2 compares cyclic voltammetry (CV) for Cu electrode in 0.5M KHCO₃ electrolyte saturated with Argon (Ar) (curve A) and CO₂ (curve B), respectively. To get a real transient CV curve for a Cu electrode by suppressing H₂ reduction reaction, the sweep potential range was limited between -0.2V to -0.8V vs. SCE. Curve A shows a well-defined CV for a bare Cu electrode. Three small reduction peaks (~-0.25V, ~-0.375 and ~-0.65V) at the cathodic scan direction have been attributed to CuO, Cu₂O or Cu₄O₃ reduction reactions. To the best of our knowledge, this is the first time to have a CV curve for a Cu electrode in this potential range since Cu surface is too unstable and easily being oxidized to get a well-define Cu CV curve. Curve B shows the CO₂ electrochemical reduction reaction on Cu electrode in CO₂ saturated 0.5M KHCO₃. The cathodic peak at ~-0.6V obviously indicates the CO₂ electrochemical reduction. A close comparison for curves A and B current scale, CO₂ reduction current is almost 5 time less than that of Ar saturated electrolyte. This is probably attributed to the strong adsorption of CO₂ reduction product (such as CO) on Cu surface, poisoning Cu electrode and therefore blocking the Cu activity available surface.

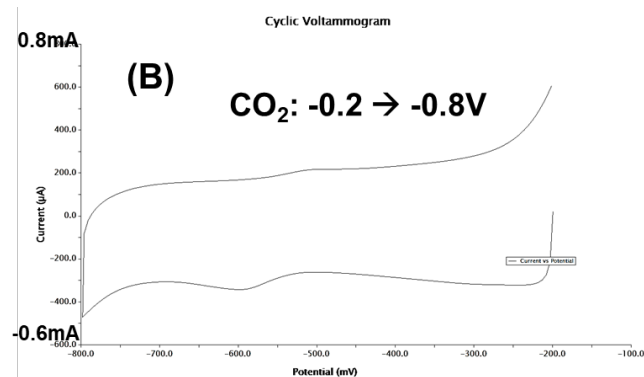
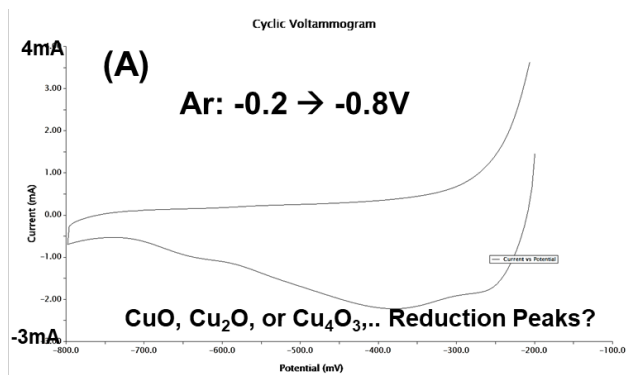


Fig. 2 Cyclic voltammetry for a Cu electrode in 0.5M KHCO₃ saturated with Ar (A) and CO₂ (B), Scan rate: 50mv/s, Potential from -0.2 V to -0.8V.

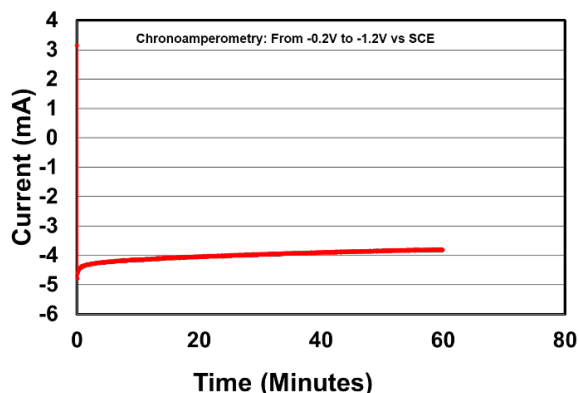


Fig. 3 Chronoamperometry experiment for a Cu electrode in 0.5M KHCO₃ saturated with CO₂, Potential Step from -0.2 V to -1.2V vs SCE.

Figure 3 shows a chronoamperometry experiment for for a Cu electrode in 0.5M KHCO₃ saturated with CO₂, Potential Step from -0.2 V to -1.2V vs SCE.

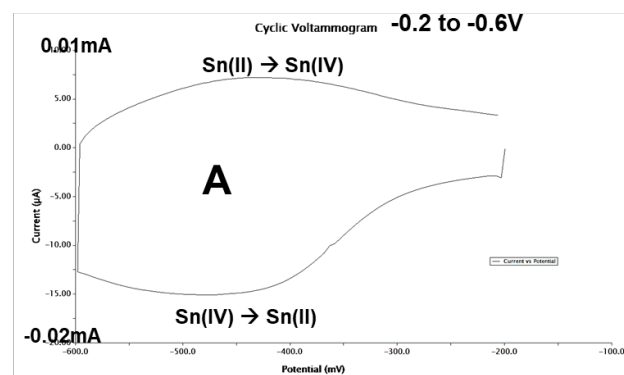
Table 2 tabulates the products of CO₂ reduction on a Cu electrode at different potentials. The results are based on GC analysis of gas products and NMR analysis of liquid phase product (HCOOH). The Chronoamperometry experiment results for CO₂

reduction to CO agreed well with the cyclic voltammetry experiment results.

Table II. CO₂ reduction reaction on Cu electrode generates various products at different potentials vs SCE.

Cu	H ₂	CO	CH ₄	C ₂ H ₄	C ₂ H ₂	HCOO ⁻	CH ₃ OH
-0.65V		V					
-0.8V		V					
-1.0V	V	V					
-1.2V	V	V					
-1.4V	V	V	V	V	V		
-1.6V	V	V	V	V	V	V (trace)	
-1.8V	V	V	V	V	V	V (trace)	

Figure 4 compares cyclic voltammetry curves for a FTO electrode in 0.5M KHCO₃ electrolyte saturated with Argon (Ar) (curve A) and CO₂ (curve B), respectively. The potential was scanned between -0.2V to -0.6V vs. SCE. The cathodic/anodic peak couple in curve (A) is related to Sn (II) and Sn (IV) redox reaction. The reaction is reversible. Curve (B) shows the CO₂ electrochemical reduction on FTO electrode. The CO₂ reduction starts at -0.3V and reaches a plateau at -0.5V vs SCE, respectively. A comparison of current scale for curves A and B, CO₂ reduction current is almost 10 time larger than that of Ar saturated electrolyte. As shown in Table 3, only H₂ and CO reaction products have been detected for the FTO/Sn electrode, even the electrode potential reaching -2.0V vs SCE, indicative of high CO₂ reduction selectivity on FTO electrode.



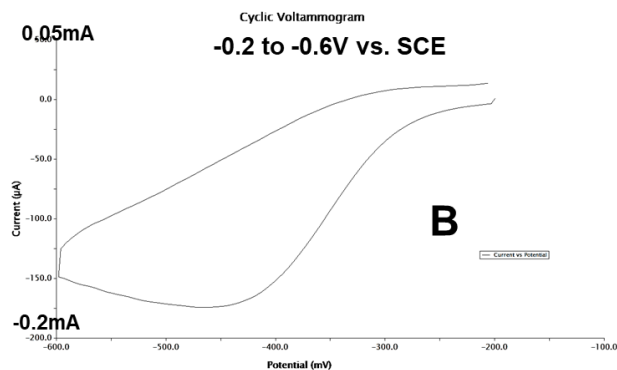


Fig. 4 Cyclic voltammetry for a FTO electrode in 0.5M KHCO_3 saturated with Ar (A) and CO_2 (B), scan rate: 50mv/s, potential from -0.2 V to -0.6V.

Table III. CO_2 reduction reaction at FTO/Sn electrode only generates H_2 and CO products at different potentials vs SCE. The Gas phase products from GC analysis.

FTO	H_2	CO	CH_4	C_2H_4	C_2H_6	CH_3OH
-0.65V		✓				
-0.8V		✓				
-1.0V	✓	✓				
-1.2V	✓	✓				
-1.4V	✓	✓				
-1.6V	✓	✓				
-2.0V	✓	✓				

Summary

We performed the electrochemical CO_2 reductions on Cu and FTO/Sn electrodes and compared the products by varying the applied potentials. Based on the electrochemical experimental results from this study, we have a couple of preliminary conclusions. Cu electrode is unstable and easily oxidized to Cu oxides in the electrolyte, whereas Sn surface is very stable under CO_2 electrochemical reduction conditions. CO is the only gas product at -0.65 & -0.8V vs SCE, for CO_2 electrochemical reduction on both Cu and Sn electrodes. The CO adsorption on Cu surface is strong, while weak on Sn surface. Observed CO product concentration is high at the initial electrochemical reaction and then decreases with increasing time for experiment on Cu. CO generation rate is constant at the Sn surface. H_2 generation reaction starts from potential $\sim -1.0\text{V}$ vs SCE. At higher potentials $> -1.4\text{V}$ vs SCE, H_2 , CO, CH_4 and C_2H_4 are products for CO_2 electrochemical reduction reaction on Cu.

Electrochemical reaction can convert CO_2 with water to C1 hydrocarbon compounds. However, the

thermodynamic potential for hydrogen generation reaction is more favorable than that of CO_2 electrochemical reduction. The electrochemical device for CO_2 reduction suffers from low stability and efficiency, preventing them to become a practical application. There are also grand challenges with the separation and collection of liquid hydrocarbon products. Developing multi-functional catalysts or selective surface catalysts for the simultaneous carbon dioxide and water chemical conversion to syngas is pivotal for further research and development efforts. Continued improvements in efficiency, durability, and cost are still needed for practical applications.

References:

1. A. Fujishima and K. Honda, *Nature*, 238 (1972), 37-38.
2. Oscar Khaselev and John A. Turner, *Science*, 280 (1998), 425-427
3. Stefanie Schlager and Niyazi S. Sariciftci, *Energy Technology*, 5 (2017), 812-821.
4. Bocarsly, A. B.; Gibson, Q. D.; Morris, A. J.; L'Esperance, R. P.; Detweiler, Z. M.; Lakkaraju, P. S.; Zeitler, E. L.; Shaw, T. W., *ACS Catalysis* 2012, 2 (8), 1684-1692.
5. Morris, A. J.; McGibbon, R. T.; Bocarsly, A. B., *Chemsuschem* 2011, 4 (2), 191-196.
6. Cole, E. B.; Lakkaraju, P. S.; Rampulla, D. M.; Morris, A. J.; Abelev, E.; Bocarsly, A. B., *Journal of the American Chemical Society* 2010, 132 (33), 11539-11551.
7. K. Kuhl, E.R. Cave, D.N. Abram, T.F. Jaramillo, *Energy & Environmental Science*, 5 (2012), 7050-7059.
8. D. Koshy, S. Chen, D. Un Lee, M.B. Stevens, A. Abdallah, S. Dull, G. Chen, D. Nordlund, A. Gallo, C. Hahn, D.C. Higgins, Z. Bao, T.F. Jaramillo, *Angewandte*, (2020). DOI: 10.1002/ange.201912857
9. L.Wang, D.C. Higgins, Y. Ji, C.G. Morales-Guio, K. Chan, C. Hahn, T.F. Jaramillo, *Proceedings of the National Academy of Sciences*, (2020).