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The Electroreduction of Carbon Dioxide on Porous Copper Nanoparticles

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THE ELECTROCHEMICAL REDUCTION OF

CARBON DIOXIDE ON POROUS

COPPER NANOPARTICLES

by

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Dedication

This work is dedicated to my dad- you finally got your engineer.

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The Electroreduction of Carbon Dioxide on Porous Copper Nanoparticles

by

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ABSTRACT

Copper nanoparticles of porous, controlled structure were synthesized using the sacrificial support method (SSM). The precursor weight percent (wt%) of copper (Cu) and fumed silica (EH-5) was varied to determine the optimum ratio for this material. The precursors were reduced at i) 350°C in a 7% H_2 atmosphere and ii) at 250°C in a 100% H_2 atmosphere. The specific surface areas of the nanoparticles was measured by Brunauer-Emmett-Teller N_2 absorption. The morphologies and widths of the nanoparticles were confirmed by imaging the nanoparticles by scanning electron microscopy (SEM). The bulk composition of the nanoparticles was determined by X-ray diffraction (XRD). Results of these characterizations are discussed in detail. The nanoparticles with a precursor Cu content of 5 and 10wt% exhibited the most controlled morphology with smallest particle widths when reduced at 250°C in 100% H_2 (21.5 ± 6.7 nm and 29.3 ±

11.3 nm, respectively) and at 350°C in 7% H_2 (29.8 ± 9.4 nm and 60.5 ± 21.5 nm, respectively).

Carbon dioxide (CO_2) electroreduction (CER) on the Cu nanoparticles synthesized by SSM was confirmed with rotating disk electrode experiments (RDE) using cyclic voltammetry at 25°C in CO_2 saturated 0.1M potassium bicarbonate solution ($KHCO_3$) at atmospheric pressure. The electrochemical stability of these nanoparticles was tested via bulk electrolysis for one hour at -1.2, -1.6, and -2.2 V *vs.* Ag/AgCl in kinetic and diffusion limited regimes. All nanoparticles exhibited activity towards CER and displayed excellent stability for at the potentials tested. The current densities observed during bulk electrolysis at -2.2 V *vs.* Ag/AgCl were between ca. -23 and -40 mA cm^{-2} for the nanoparticles reduced at 350 °C in 7% H_2 atmosphere and ca. -12 and -20 mA cm^{-2} for the nanoparticles reduced at 250°C in 100% H_2 atmosphere. The magnitude and stability of these particles makes them ideal candidates for further studies that will determine their relative efficiencies towards specific CER products by liquid and gas quantification.

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1. Introduction

Carbon dioxide (CO_2), a greenhouse gas, is generated by the complete oxidation of carbon containing fuels in processes such as the burning of methane or coal that accounted for approximately 82% of the worldwide energy supply in 2014 [1]. The unregulated, continuous release of CO_2 by industrial scale processes since the 1850s has increased atmospheric concentrations from 278 ppm to 400 ppm [2] – quantities that strain the balance of the earth's natural carbon cycle, leading to acidified oceans and irregular weather patterns [1,3-5]. The accumulation of CO_2 has been identified by climate scientists as a major contributing factor in rising global temperatures. Climate models predict drastic changes in precipitation and temperature which will impact regional and global economies, as shown in a model exploring the likelihood of a semi-permanent drought in North America (see Fig. 1) [5]. Recent discussions no longer focus
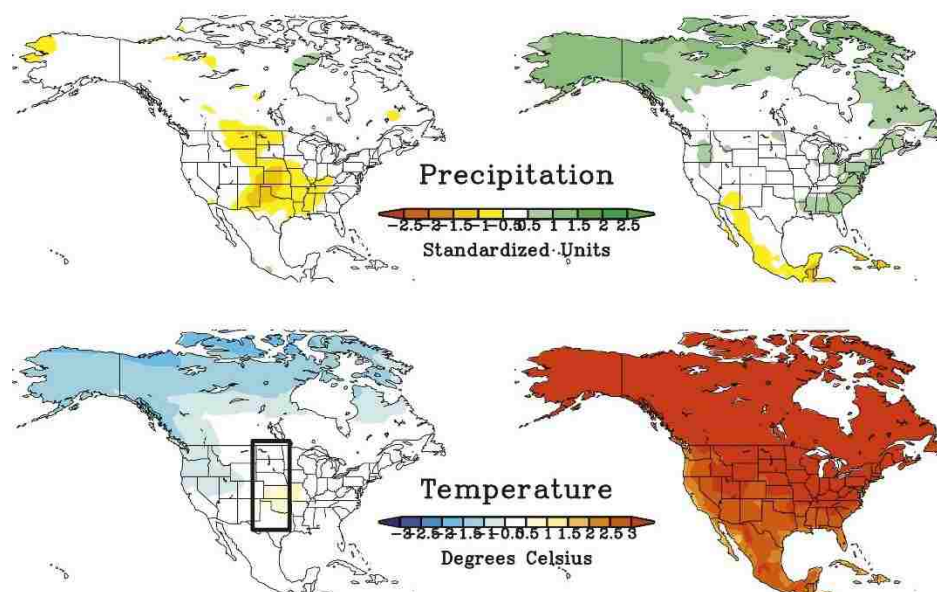
Figure 1. Projected changes in precipitation and temperature modeled from current atmospheric conditions without greenhouse gas reduction. On the left are trends observed from 1865-1875, on the right are predictions for 2045-2055 [5].

on *if* CO_2 emission rates should be decreased, but by how much and how soon they should be mitigated to avoid exceeding a global mean temperature rise of 1.5-2.0°C by 2100 [6]. The rate of CO_2 emission that is predicted to correspond with this limit is 44 gigatons of CO_2 per year ($GtCO_2$) by 2020, which is approximately 55% of the 1991 emission rates and will require a 12 $GtCO_2$ decrease from the projected 2020 rate of 59 $GtCO_2$ (for the "no action" case) [6-7]. Consensus that CO_2 emissions will continue to increase necessitates that the massive scale of these ambitious emission reductions will be mitigated by the development and improvement of technological discoveries in the next few decades.

Currently, there are many possible solutions for decreasing CO_2 emissions; among them are increasing the percentage of energy generated from renewable or nuclear sources and utilizing CO_2 capture and storage (CCS) at point sources (e.g. power plants) [6, 8-9]. While CCS fundamentally prevents CO_2 release, it can be improved by CO_2 capture and conversion (CCC) into fuels or value added products (defined as chemical products or precursors that have an increased monetary value). This would simultaneously decrease the rate of emissions and possibly reintroduce CO_2 into the energy cycle – essentially converting carbon emitting energy sources into carbon neutral sources. This process can be implemented in batch or flow reactors, typically with low fluid quantities, and has been shown to selectively reduce CO_2 to specific products. One example of this is the CO_2 reduction to formic acid, which in optimized systems has been reported at conversion rates as high as 94.1% on lead (Pb) and between 70-80% on tin (Sn) [10]. Formic acid is used extensively in agricultural applications: as a pesticide, as an

anti-bacterial preservative, and as a food additive for feed stocks. Another example is the accomplishment of "one-pot" synthesis of syn-gas (carbon monoxide and hydrogen gas) on Ag, which requires producing the gases at a controlled molar conversion ratio of 1:2 [11-13]. Syn-gas is used in gasoline synthesis, thus having a simple method of producing this mixture is extremely desirable. A final example is the synthesis of precursors for non-steroidal anti-inflammatory drugs (NSAIDS), such as ibuprofen or naproxen, which has been reported with conversions as high as 75-80% for the electrochemical carboxylation of organic intermediates to produce acids [8]. Further, CCC could facilitate the integration of intermittent renewable energy sources (e.g., solar or wind) by storing energy for later use as reduced CO_2 in liquid or gas products.

In general, CO_2 conversion can be achieved by reduction in solid state fuel cells, on metal electrodes in aqueous solutions, or by metal complexes [9, 11]. Possible reduction products of CO_2 include, but are not limited to, C_1-C_3 chained molecules such as carbon monoxide (CO), formic acid (HCOOH), methane (CH_4), ethylene (C_2H_4), and alcohols ($C_xH_{2x+1}OH$) [14-28]. Solid state fuel cells are currently limited to producing CO, which is attributed to their high operating temperatures [9, 21, 29-30]. Most metal complexes that have been studied contain either platinum or palladium catalytic sites, and thus are not economically viable at their current efficiencies on the industrial scale [9]. Metal electrodes in aqueous media can be incorporated into established technologies, such as proton exchange membrane fuel cells (PEMFCs) and gas diffusion electrodes (GDEs), replacing catalysts typically employed for the hydrogen evolution reaction (HER) with catalysts designed for CO_2 electroreduction (CER) at the cathode

while maintaining the oxygen evolution

reaction (OER), from H_2O, at the anode

[9,11-12, 31-32]. However, very few

catalysts exhibit high current density and

low applied voltage, in addition to

selectivity towards a specific product and

durability, which are all criteria for viable

industrial application of CER on metals in

aqueous media as shown in a recent

survey by Jhong et al. (Fig. 2).

1.1 Statement of intent

Unique among metal catalysts,

copper (Cu) can reduce CO_2 to small

chained hydrocarbons and alcohols ($\geq C_1$)

at low temperatures and atmospheric

pressures with surprisingly high

conversion [24]. Since the 1980s much

Figure 2. *Survey of current densities (CD) of CO_2 reduction reported from 1985 to 2012 as compiled by Jhong et al. shows a) faradaic efficiencies (FE) towards three major products (CO, CH_4, HCOOH) and b) energy efficiencies (EE), exhibiting the lack of catalysts that exhibit both high CD and high FE or EE [33].*

effort has been made to elucidate the mechanism of CO_2 reduction on Cu with the

purpose of engineering a catalyst that will generate high hydrocarbon yields in fuel cells

[20-23, 34-40]. Based on these insights, this thesis will report the results of testing the

hypothesis that a porous, unsupported Cu catalyst, synthesized with the sacrificial

support method (SSM) can generate stable, large current densities previously only

observed for carbon supported Cu nanoparticles [41-42]. The effect of composition and morphology of the synthesized particles will be discussed in terms of electrochemical performance, with comparison to the published results of other Cu materials for CER. In probing this topic the main goals of this work are as follows: First, synthesize and characterize Cu with a porous and controllable morphology using the sacrificial support method. In doing so, determine an optimum ratio of Cu to silica in the precursor to produce a porous morphology. Second, determine if this Cu catalyst is stable when held at high potentials for periods of at least 1 hour – this criteria is essential to determine the selectivity of these materials towards a specific product in later product quantification tests. Third, determine if the SSM is a beneficial synthesis approach for CER on Cu; this will be determined on the basis of comparing current densities observed in previous studies with those of the synthesized particles.

2. Background

2.1 Carbon dioxide electroreduction on metals

CO_2 reduction is catalyzed on metals in aqueous solutions at 25°C, pH=6.8, V *vs.* the standard hydrogen electrode (SHE, Eq. 7) according to the following net reactions [10, 42]:

$$CO_2\ (g) + 2H^+\ (aq) + 2e^- \leftrightarrow CO\ (g) + H_2O\ (l),\ E^0 = -0.104\ V\ (1)$$

$$CO_2\ (g) + 2H^+\ (aq) + 2e^- \leftrightarrow HCOOH\ (l),\ E^0 = -0.225\ V\ (2)$$

$$CO_2\ (g) + 8H^+\ (aq) + 8e^- \leftrightarrow CH_4\ (g) + H_2O\ (l),\ E^0 = +0.169\ V\ (3)$$

$$CO_2\ (g) + 6H^+\ (aq) + 6e^- \leftrightarrow CH_3OH\ (l) + H_2O\ (l),\ E^0 = -0.020\ to\ -0.114\ V\ (4)$$

$$2CO_2\ (g) + 12H^+\ (aq) + 12\ e^- \leftrightarrow C_2H_4\ (g) + 4H_2O\ (l),\ E^0 = +0.079\ V\ (5)$$

$$2CO_2\ (g) + 12H^+\ (aq) + 12e^- \leftrightarrow C_2H_5OH\ (l) + H_2O\ (l),\ E^0 = +0.090\ V\ (6)$$

$$2H^+\ (aq) + 2e^- \leftrightarrow H_2\ (g),\ E^0 = 0\ V\ (7)$$
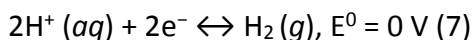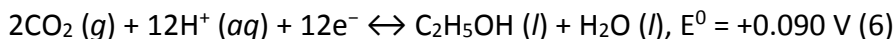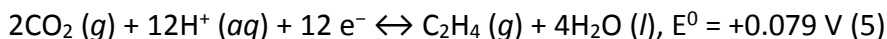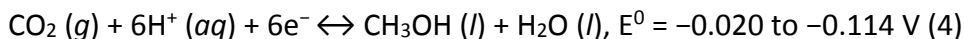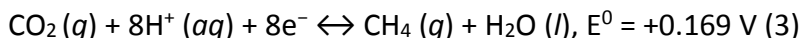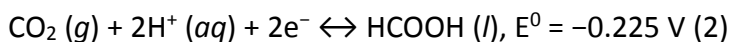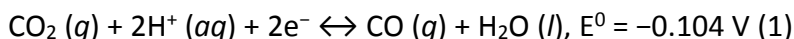
Where E^0 is the standard equilibrium potential, defined as $E^0 = E^0_{cathode} - E^0_{anode}$, *vs.* SHE.

Metal catalysts are categorized into four primary groups, based on their primary reduction products, as observed by Hori et al.: i) HCOOH (Pb, Tl, Hg, Sn, In, Cd), ii) CO (Au, Ag, Pd, Ga, Zn), iii) CH_4/C_2H_4 (Cu), and iv) H_2 (Pt, Ni, Fe, Ti) [25]. These product trends have been extensively confirmed by observation in many studies and suggest different surface affinities for CO_2 reduction intermediates and/or dissimilar reaction mechanisms for each class of materials [14-15, 18-19, 20-23, 25, 43-45]. The catalytic activity of all metals also depends on their surface characteristics such as roughness and

surface area to volume ratios, both which affect the plane edges exposed at the surface as is typical for a surface reaction [31, 34-35, 46]. Other parameters that influence product species and the distribution of yields include the reaction potential, the system pressure and temperature, and the solution concentration and type (e.g. aqueous versus non-aqueous, solution pH, specific cation and anion species, etc.). The remainder of this chapter will focus on the specific dependencies of Cu, although to some extent, these limitations and considerations apply to all metals.

2.2 Carbon dioxide electroreduction on copper

2.2.1 Measures of merit: efficiency and selectivity

Before introducing the limiting parameters of CER in aqueous media, it is sensible to discuss the challenges of characterizing this system in which the concurrent generation of numerous, multi-phase (liquid and gas), small-chained carbon molecules requires simultaneous measurement of electrochemical performance and either/both liquid and gas phase product quantification. Electrochemical performance is measured in half-cell or fuel cell apparatuses, under potentiostatic or galvanostatic conditions, as appropriate. Liquid and gas phase products are quantified by techniques such as gas chromatography (GC), nuclear magnetic resonance analysis (NMR), or mass spectroscopy (MS) to assess the selectivity of the reaction towards a specific product. This is necessary for assignation of the fractional charge distributions of current densities generated in saturated CO_2 solutions, which concomitantly generates H_2 from aqueous solutions. Accepted measures of product selectivity and efficiency are typically expressed as energetic and faradaic efficiency, defined in Eq. 8 and Eq. 9 [34]:

$$\varepsilon_{energetic} = \sum_k \frac{E_k^0 \varepsilon_{k,Faradaic}}{E_k^0 + \eta} \quad (8)$$

where E_k^0 is the standard potential of product k, $\varepsilon_{k,Faradic}$ is the Faradaic efficiency (FE) of

product k, and η is the cell overpotential (Eq. 10, below).

$$\varepsilon_{Faradic} = \frac{z \cdot n \cdot F}{Q} \quad (9)$$

where z is the number of electrons exchanged (e.g. $z = 2$ for reduction of CO_2 to CO), n is

the stoichiometric number of moles for a given product, F is Faraday's constant (96,485

C mol^{-1}), and Q (C) is the charge passed. Faradaic efficiencies of CER towards

hydrocarbons on Cu range from < 3-79% (see Table 1). In many of the discussions that

follow, only partial quantification of products (one phase is quantified) are reported in

published literature. However, in most cases the materials exhibit high total faradaic

efficiency (nearing 100%), indicating that the quantity of products in the excluded phase

Table 1 Examples of faradaic efficiencies (FE) for gaseous products methane (CH_4), ethylene (C_2H_4), and hydrogen (H_2) for CO_2 or CO electroreduction, as reported for Cu of different morphologies (foils, nanofoams, reduced Cu-oxides) and supported nanoparticles, with their corresponding current densities and potentials. Values not given are listed as not reported (NR). All products were generated in 0.1M KHCO$_3$.

Material (Catalyst/ Reactant)	Potential (vs. SHE)	Current Density (mA cm^{-2})	Total Hydro-carbon FE	CH$_4$ FE	C$_2$H$_4$ FE	H$_2$ FE
Cu / CO$_2$ [25]	-1.44 V	5	78.8	33.3	25.5	20.5
Cu / CO [25]	-1.40 V	2.5	37.5	16.3	21.2	45.5
Cu / CO$_2$ [25]	-1.41 V	5	59.1	29.4	30.1	10.9
Cu / CO$_2$ [25]	-1.39 V	5	62.3	32	30.3	14.5
Cu from Cu$_2$O / CO$_2$ [47]	-1.50 V	NR	35-40	NR	NR	NR
Cu nanofoams / CO$_2$ [48]	-1.50 V	8	< 3.0	1.3	1.4	60.0
20 wt% Cu nanoparticles on C / CO$_2$ [42]	-1.60 V	3	ca. 50	ca. 25	ca. 25	ca. 25

is a very small amount and does not diminish the value of these analyses.

2.2.2 Overpotential and the mechanism of carbon dioxide electroreduction

A significant challenge to the application of CO_2 electroreduction in a PEM-type cell is the large overpotential exhibited by the reaction (η, defined by Eq. 10), which is typically in the range of approximately 1.0 Volt [49, 25]:

$$\eta = E_{theoritical} - E_{observed} \quad (10)$$

where $E_{theoritical}$ is the thermodynamically predicted reaction potential and $E_{observed}$ is the experimentally measured reaction potential. While it is generally accepted that the large overpotential of CER is due to a slow and inefficient kinetics, determining which intermediate step in the reaction mechanism is rate limiting for such a complex system is extremely difficult [22, 38-39, 50-51]. Beyond signifying a much higher energy cost than is thermo-dynamically predicted, this η shifts the reaction potential of CO_2 reduction into the region where H_2 evolution is theoretically possible, at -0.03 V *vs.* the reference hydrogen electrode (RHE) [10], defined by Eq. 11:

$$E_{RHE} = E^0 - 0.059 \times pH \quad (11)$$

where E^0 is the standard hydrogen potential (Eq. 7), and *pH* is measured from the bulk electrolyte [49]. The dependence of product efficiencies on applied potential was observed by Hori et al., with less negative potentials predominantly generating H_2 and more negative potentials generating a range of products (Fig. 3) [22]. The source of this change in product distribution was illuminated by Peterson et al. who calculated that H_2 formation is likely the first open reaction pathway on Cu, but is limited by the formation

of surface oxides on Cu in aqueous solutions and at potentials more positive than -0.40 V *vs.* RHE [39]. Although adsorbed atomic hydrogen (H_{ad}) is a surface species that participates in CO_2 reduction, it is hypothesized that HER occurs at a faster rate, and at less negative potentials, so the competitive occupation of active sites by adsorbed CO_2 is slow and limits the availability of adsorbed CO intermediates (CO_{ad}) at these potentials [22, 38-39]. Beyond potentials of ca. -1.2 V *vs.* SHE there are several different reaction pathways that are energetically possible, as evident by

Figure 3. *A graph depicting the range of products and their faradaic efficiencies for CO_2 reduction on Cu as a function of potential, generated and reported by Hori et al. Total faradaic efficiency is depicted in the top segment [22].*

the simultaneous appearance of CO, CH_4, C_2H_4, and HCOOH – all seemingly sharing a rate limiting step that Jordan and Smith proposed is the ionization of CO_2 to its anion radical ($CO_2^{\cdot-}$) which could either be in solution or weakly adsorbed to Cu [52]. Hori et al. elaborated on this hypothesis, proposing that $CO_2^{\cdot-}$ was reduced and adsorbed as CO (Eq. 12), and subsequently further reduced and hydrogenated to form one of two carbonyl forms: either adsorbed COH (COH_{ad}) or CHO (CHO_{ad}).

$$CO_{2ad}^- + H_2O~(l) \rightarrow HCOOH_{ad} + e^- \rightarrow CO_{ad} \quad (12)$$

The adsorption, reduction, and subsequent hydrogenation of CO_2^-, observed via *in-situ* Fourier transfer spectroscopy (FTIR) on other metal electrodes, was thought to be stabilized by the d-orbitals of transition metals in a side-on or C-on orientation with the active site, similar to the electronic configuration of adsorbed CO_2, although this is not a universally accepted step in the reaction pathway [22]. Additional studies experimentally demonstrated that $HCOO^-$ is not further reduced on Cu while CO is, confirming that CO_{ad} is the intermediate in the CO_2 reduction mechanism [22]. Peterson et al. calculated the free energies for possible reaction intermediates using a computational hydrogen electrode (CHE) model coupled with density functional theory (DFT) adsorption energies to confirm that an adsorbed CHO intermediate is likely in the intermediate species in the pathway to both CH_4 and C_2H_4, shown in Eq. 13-14 [38]:

$$CO_{ad} + H^+ (aq) + e^- \rightarrow CHO_{ad} + H^+ (aq) + e^- \rightarrow CH_2O_{ad} + H^+ (aq) + e^- \rightarrow$$

$$CH_3O_{ad} + H^+ (aq) + e^- \rightarrow O_{ad} + CH_4 (g) \quad (13)$$

$$CO_{ad} + H^+ (aq) + e^- \rightarrow CHO_{ad} + H^+ (aq) + e^- \rightarrow 2CH_2O_{ad} \rightarrow O_{ad} + C_2H_4 (g) \quad (14)$$
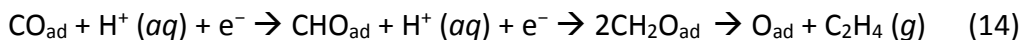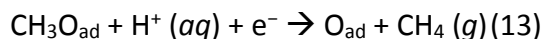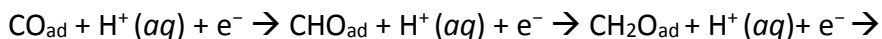
After the formation of adsorbed CO (CO_{ad}) at potentials less than -0.41 V *vs*. RHE, the additional reduction to CHO_{ad} was calculated as energetically favorable at potentials greater than -0.74 V *vs*. RHE. The potentials at which H_2 and CO_{ad} are possible energetic pathways for CER are nearly identical (-0.40 and -0.41 V vs. RHE, respectively), but clearly the further reduction of CO_{ad} has a larger energy barrier and thus explains the preferential formation of H_2 at less negative potentials. Although these studies are useful as a basis for understanding a possible mechanism of CER on Cu, they are less

predictive for Cu alloys or for Cu particles distributed on carbon supports because the electronic and surface properties of active sites are altered enough to change adsorption energies of intermediate species [39].

2.2.3 Influence of copper surface structure on selectivity

Studies on the effect of single and poly-crystalline Cu have revealed that CER faradaic yields are very sensitive to surface structure. Hori et al. show that C_2H_4 is produced in larger quantities on Cu (110), while CH_4 is the favored product on Cu (111), when compared with the products generated at the same potentials on Cu foil [34-35]. Higher index facets, such as Cu (311), Cu (511), and Cu (711) were shown to produce higher quantities of C_2H_4, in addition to a mixture of longer chained aldehydes, ketones, acids, and alcohols ($\geq C_2$). As discussed by Baturina et al., these differences predict the change in product distributions due to morphology as seen in several studies on Cu surfaces developed with different techniques [42]. Electrodeposited 3-dimensional foams of varying thickness produced C_2H_4 at a faradaic efficiency of 13%, while Cu mesh produced more CH_4 than C_2H_4 (ca. 12% and 8%, respectively) [53]. Further, Baturina et al. suggest that because nanoparticles of Cu are comprised of low-coordination sites and low-index facets (edges, defects, and corners), and would be expected to generate mostly C_2 products in CER because of the similarity of these sites to Cu (311), Cu (511), and Cu (711). This is supported by the observations of Tang et al. that Cu particles of 50-100 nm produced primarily C_2H_4 and little CH_4 (faradaic efficiencies of ca. 37% and 1%, respectively) [54]. Sen et al. studied hierarchal structured Cu nano-foams and observed a +200 mV improvement for the onset of CER (detection of products), and an increase in

faradaic efficiency towards HCOOH, which they attribute to an increased ratio of Cu

(111) : Cu (200) in the material [48]. These examples suggest that product distributions

of hydrocarbons can be controlled by developing Cu morphologies with specific product

affinities.

2.2.4 Modifications to copper: influence of alloying and conductive supports

As previously stated, predicting the performance and selectivity of alloys or

carbon supported Cu materials is difficult from a theoretical vantage. Peterson and

Norskov conclude their discussion of possible CER mechanisms with recommendations

for improvements of CER, such as alloying Cu with an element having a higher oxygen

affinity to increase the stability of CER CO intermediates [39]. In an early study,

Wanatabe et al. observed differences in CER onset and product distribution (CO,

HCOOH, and CH_3OH) of CER when alloying Cu with Ni, Sn, Zn, Pb, Cd and Ag [55]. They

observed that the η was decreased in all cases; CO production increased for Cu alloyed

with Zn, Cd, or Ag, while HCOOH production was increased for Cu alloyed with Sn or Pb,

and CH_3OH (rarely produced in measurable quantities) was generated on Cu alloyed

with Cd or Ni. In a recent study, Kim et al. synthesized bimetallic gold and copper (Au-

Cu) nanoparticles, observing that increasing the atomic ratios of Au : Cu increases CO

faradaic yields, decreases hydrocarbon production while simultaneously suppressing H_2

generation, and conclude that tuning the electronic affinities of intermediate CER

surface species is possible and also dependent on the relative geometric positioning of

elements [56]. Baturina et al. observed the effects of Cu nanoparticles (10-30 nm) on

the selectivity of CER towards hydrocarbons on various carbon supports. Increased

selectivity towards CH_4 at -1.4 V *vs.* SHE is attributed to carbon induced HER spillover at potentials greater than -1.0 V *vs.* SHE. Well dispersed nanoparticles (12-19 nm diameter) displayed a lower η (+200 mV) for C_2H_4 production, suggesting increased activity towards this species that may be resultant from the increased low-coordination sites of these particles [42]. Hossain et al. varied the weight percent of Cu nanoparticles loaded on carbon nanotubes (CNTs), reporting an optimum value of 20wt% with a CH_3OH faradaic efficiency of ca. 35%, but it is impossible to determine the effect on relative efficiencies of H_2 and hydrocarbons because they failed to report gas phase quantification and the total faradaic efficiency [57]. With the above examples of possible Cu surface variations, it can be understood that the surface sensitivity of CER, extends to alloys and carbon supports, and requires the development of well-controlled synthesis methods to produce surfaces of specific geometric and compositional parameters.

2.3 Copper nanoparticles: challenges in material synthesis

The synthesis of Cu nanoparticles is challenging because of the tendency of Cu to oxidize to cupric oxide (CuO, Cu^{2+}) and cuprous oxide (Cu_2O, Cu^+), both which spontaneously form at room temperatures in the presence of air and minimal moisture [58]. Methods for successful synthesis of Cu nanoparticles ranging in size from 15 to 100 nm implement thermal reduction and chemical reduction with many different types of solvents [42, 59-60]. It is difficult to make these sized particles without oxidation, further it is difficult to control the degree and type of oxidation that occurs, which explains the distinct lack of Cu nanoparticles of varied morphologies in nanoparticles. As

a result, most patterned structures are typically grown electrochemically on flat surfaces, as in the case of honey-comb and 3-D structures, just discussed [48, 53]. The thermal decomposition of a common precursor, Cupric nitratetrihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), has been extensively studied and shown to generate multiple nitrogen and oxygen containing gas phase products upon decomposition (between 150°C and 225°C) [61]. L'vov et al. propose that decomposition of $Cu(NO_3)_2 \cdot 3H_2O$ occurs in three stages: i) "deaquanation" up to 127°C ii) incomplete thermal decomposition by gasification mechanism at 187°C with the formation of $Cu_2(OH)_3NO_3$ iii) further decomposition to CuO at 257°C (Eq. 15) [62-63]:

$$Cu(NO_3)_2 \cdot 3H_2O \rightarrow CuO + 2NO_2 + 3H_2O + 0.5O_2 \quad (15)$$
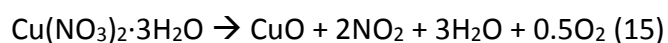
Additionally, L'vov et al. postulated that the reduction of nitrogen dioxide (NO_2) is catalyzed on CuO, resulting in the formation of nitric oxide (NO) according to the following reaction (Eq. 16) [62]:

$$2NO_2 \rightarrow 2NO + O_2 \quad (16)$$

Ryu et al. observed a similar intermediate ($Cu_2(OH)_3NO_3$) in their study of the thermal decomposition of $Cu(NO_3)_2 \cdot 3H_2O$ on activated carbon fibers, where they observed the formation of CuO at 200°C, CuO/Cu_2O between 230°C and 255°C, and Cu_2O/Cu between 300°C and 350°C [64]. Both Ryu et al. and L'vov et al. note that the thermal decomposition $Cu(NO_3)_2$ begins within the temperature range where dehydration may be incomplete, thus water is present in small amounts in the reactive phase of this decomposition and makes it difficult to control the amount, extent and type of oxide

formation, even in a reductive environment [62, 64]. Further, at temperatures greater than 350°C, Cu readily sinters and nanoparticles formed begin to aggregate into larger particles.

2.4 Electrolyte

2.4.1 The limited solubility of carbon dioxide in solution and the effect of pressure

Beyond catalyst considerations, CER is limited by the low solubility of CO_2 in both aqueous and non-aqueous solutions, which restricts the reactant concentration at atmospheric pressure (see Table 2) [22, 43, 53]. While increasing CO_2 pressure to increase its solubility may seem a straight-forward response to this limitation, it has been shown that Cu selectivity shifts towards CO and HCOOH and away from hydrocarbons with changes in pressure. Hara et al. demonstrated that hydrocarbon selectivity decreases from 60% to 15% with an increase in pressure from 1 atm to 30 atm. They posit that pressure controls CO_2 flux at the electrode surface; shifts in product distribution occurs when the current applied during galvanostatic experiments exceeds an optimum CO_2 flux, resulting in a shift in adsorbed species and altering the reaction pathway [45].

Table 2. *Solubility of CO_2 in various solvents at 1 atm and 25°C [25].*

Solvent	Concentration (M)
Aqueous media	0.033
Tetrahydrofuran (THF)	0.205 ± 0.008
Acetonitrile (AN)	0.279 ± 0.008
Dimethylformamide (DMF)	0.199 ± 0.006
Dimethylsulphoxide (DMSO)	0.138 ± 0.003

This hypothesis is supported by other studies which demonstrate a shift in selectivity away from hydrocarbons at atmospheric pressures beyond some limiting current density [44, 67-70]. Clearly, CO_2 pressure influences CER products, but it would best be optimized at some later stage, after a catalyst has been shown to perform at atmospheric pressure and there is a general understanding of the reaction mechanism. Other alternatives to solubility limitations include using aprotic solutions, but this restricts possible products to CO due to the absence of protons, and are not useful in discussion of CER to hydrocarbons [25]. As a final comment on pressure, the decrease of solubility at very low or high temperatures should be considered, where the concentration dependence of a gas dissolved in solution can be approximated by Eq. 17:

$$p = k_H(T) \times c \quad (17)$$

where p (atm) is the partial pressure of the gas above the solution, c (mol L^{-1}) is the concentration of the gas in solution, and k_H (mol-atm L^{-1}) is Henry's constant, which is not truly a constant because of its functional dependence on temperature [71]. There are very few studies that maintain constant pressure for temperature changes.

2.4.2 The effect of solution pH

In addition to solution type sensitivity, the product distribution of CER is influenced by the pH of aqueous solutions and can vary widely depending on the bulk pH of the solution [22]. Potassium bicarbonate ($KHCO_3$) is frequently used as the solution in CER because the potassium cation (K^+) has the highest faradaic selectivity towards C_2H_4 (14%) and CH_4 (16%), with the lowest selectivity towards H_2 [47]. Hori et

al. probed the effect of varying $KHCO_3$ from 0.03 to 1.5 M (Fig. 4), observing that faradaic yields of hydrocarbons drop off after 0.5 M, with the highest yield of C_2H_4 at low $KHCO_3$ concentrations, suggesting that selectivity is shifted because of changes in local pH [22]. Gupta et al. confirmed this suggestion with their mathematical model of the surface pH as a function of bulk pH concentration for $KHCO_3$ solutions. Calculations predicted that the pH near the boundary layer more closely resembled the bulk pH for higher

Figure 4. The effect of pH on product distribution for $KHCO_3$ solutions varied from 0.03 to 1.5M where: □ -H_2, Δ -C_2H_4, ◊ -C_2H_5OH, ○ -CH_4, $Δ^{-1}$ - C_3H_7OH [22].

$KHCO_3$ concentrations, with large pH differences for lower concentrations (e.g. bulk pH = 6.8, local pH = 9.8 for 0.1 M $KHCO_3$ with a boundary layer thickness of 0.01 cm) [43]. Until now, these pH data have been used to explore possible mechanistic pathways, but they will be important considerations for later applications in fuel cells.

Another possible effect of high pH solutions is the destabilization of metallic Cu, which can decrease activity by reducing Cu cat alytic sites. Metallic Cu can traverse regions of instability, as shown in the Pourbaix diagram for Cu (Fig. 5) [72], in the range of potentials and in low solution concentrations (<0.1 M), where pH gradients near the surface can vary substantially (as in 0.1 M $KHCO_3$ which is modeled as having a surface

pH of 9.8 and a bulk concentration of 6.8 under saturated CO_2 conditions for highly active surfaces) [10-11, 42]. However, this effect can also be exploited: Kas et al. electrochemical reduced thin films of Cu_2O to Cu at neutral pH at potentials greater than -0.3 V *vs.* RHE, essentially exposing plane-indices and edges associated with reduced C_2O, and increasing selectivity towards CH_3OH [47].
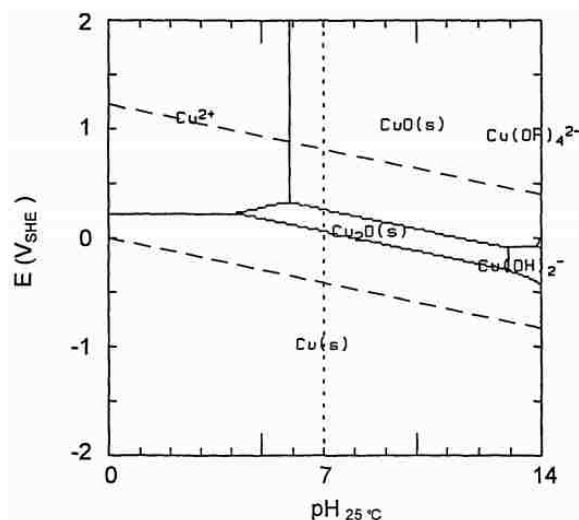
Figure 5. *The Pourbaix diagram for Cu in aqueous solutions; note the phase boundary between Cu and Cu_2O exists near 0 V vs. SHE at pHs 9-10 [72].*

2.4.3 Deactivation of copper by trace metals

A final consideration of Cu in aqueous solutions is its observed sensitivity to the poisoning of its active catalytic surface sites by very low quantities of Fe and Zn over time. These trace elements are present in even very high purity salts used for solutions, ≤ 5 ppm in materials ≥ 99.95% purity [66]. Pre-electrolysis of solutions used as an electrolyte is one method developed to remove these trace amounts of metals, but it would be more convenient for large scale applications to either develop a more robust catalyst or to incorporate another material that would filter out these trace amounts from solutions used in electrolysis [24].

2.5 Temperature

Increasing the temperature of electrolysis for CER has been shown to increase overall efficiency (i.e., higher current density), while decreasing selectivity towards

hydrocarbons. Hori et al. showed that increasing the temperature of reaction from 0°C to 40°C decreases the hydrocarbon selectivity from ca. 62% to 5%, respectively [20]. These conditions also resulted an increase in the faradaic efficiency of C_2H_4 from ca. 0% to 20%. Wanatabe et al. describe an optimum reaction condition for CER at a temperature of 0°C [73]. As briefly mentioned earlier, either extremely high or low temperatures can decrease the concentration of CO_2 in solution by altering its solubility – an effect that convolutes extracting kinetic parameters for CO_2 conversion towards any of its possible products. It is worth noting that most studies of high temperature CER (albeit on other metals) have shown high faradaic yields for CO and H_2, even when combined with high pressures [9, 21, 73]. Until the mechanism of multi-product reduction at room temperature and atmospheric pressure is well understood, it is unlikely that temperature dependent kinetic parameters will be forthcoming.

2.6 Further considerations for integration into application

Discussion thus far has focused on distinguishing important variables of CER on Cu to contextualize the complexity of this system. Despite all these challenges, Cu is still an attractive catalyst because it generates hydrocarbons with high faradaic yields at mild conditions, at atmospheric pressure and temperatures between 18.5°C and 25.0°C [20-23, 34]. If Cu is to be employed in PEM-type fuel cells as an approach to decrease CO_2 emissions, as suggested earlier, it will need to be optimized for high conductivity, low mass transport limitations, low η, fast kinetics, with long-term stability, preferably using low cost materials and synthesis methods. Material synthesis techniques that have typically been used to improve these characteristics for PEMFC catalysts include

dispersion of nanoparticles on carbon supports (increased activity, conductivity, and

mass transport) and alloying elements as nanoparticles (decreased cost, increased

activity and conductivity). As outlined above, many of these methods have been

employed to develop Cu as a CER catalyst, with some varied results. This distinguishes a

major setback to understanding the feasibility of Cu for fuel cells applications: there are

no comprehensive studies into the statistical significance of variables known to

influence CER total and product faradaic efficiencies. Current methodology separates

catalyst characterization into two primary approaches: 1) electrochemical

characterization of catalysts as thin films in a kinetically limited regime under

potentiostatic or galvanostatic conditions, as in rotating disk electrodes and 2)

electrochemical characterization of membrane electrode assembly cells (MEA), where

more realistic diffusion limitations can be resolved under galvanostatic conditions.

Major failings of each include: 1) studies cannot model and predict possible changes in

mechanism in the expansion of thin film to 3-dimensional structure 2) studies rarely

include deconvolution of $E_{cathode}$ from the total cell potential and do not deviate from

standard procedures to determine the effect of supports and ionomers on the cell.

Although both characterization approaches provide valuable insight into catalyst

performance, at present there is no way to reconcile the two into a unified body of data

about the general system, essentially these failings make it impossible to compare the

results of MEA and half-cell studies, which will be especially important for a system as

sensitive as Cu for CER [33]. With this in mind, the purpose of this thesis is to probe the

effect of morphology on CER product distribution, in other words it is an exploration

into the kinetics of this system, with the understanding that this is a partial qualification

of its suitability for application.

3. Experimental Methods

3.2 Synthesis of Cu nanoparticles

Cu nanoparticles were synthesized using the sacrificial support method, a method developed by UNM [74-83]. The weight percent (wt%) of Cu to fumed silica was varied from 5-40wt% and calculated for 500 mg batches. For each ratio the calculated amount of Cupric nitratetrihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, 98.0-103%, Sigma-Aldrich) was dissolved in 10 mL ultrapure deionized water (DI H_2O, Millipore, 18.2 MΩ cm). The corresponding amount of fumed silica (Carb-O-Sil ©, EH-5, 380 m^2 g^{-1}) was whetted with DI H_2O and dispersed by ultrasonic force (Tekmar Sonic Disruptor). The $Cu(NO_3)_2 \cdot 3H_2O$ solution was combined and dispersed in the colloidal silica suspension by ultrasonic force. The resultant solution was stored at 85°C until completely dry (12-24 hours) and ground into a fine powder with an agate mortar and pestle. The final weight of the powder was recorded and divided into two parts for thermal reduction. Each half was reduced for 2 hours at the following conditions: i) at 350°C in a 7% H_2 (7% H_2, 93% N_2, Argyle) atmosphere ii) at 250°C in a 100% H_2 (Matheson Tri-gas) atmosphere. Table 3 summarizes the Cu to silica ratios, reduction environments, and reduction temperatures used.

Table 3. *Precursor materials and environmental conditions used for synthesis of Cu nanoparticles using the sacrificial support method.*

Precursor weight percent ratios of Cu : EH-5					Atmosphere	Temperature (°C)
5 : 95	10 : 90	20 : 80	30 : 70	40 : 60	7% H_2, 93% N_2	350
5 : 95	10 : 90	20 : 80	30 : 70	40 : 60	100% H_2	250

Once cooled, the powders were sealed by Parafilm© in their respective environments and allowed to equilibrate with an oxygen containing environment (air) for one week. The reduced powders were combined and etched for 12 hours with 25 mL 7M potassium hydroxide (KOH) prepared from DI H_2O and KOH pellets (≥85%, EMD).The nanoparticles were separated from solution using centrifugal force (Labnet Hermle Z400) and rinsed with DI H_2O until pH= 7.

3.3 Characterization

3.3.1 Material characterization

The specific surface area of the catalysts was measured using Brunauer-Emmett-Teller measurements (BET, Micrometrics Gemini BET Analyzer). The physical morphology of the catalysts was observed by imaging using scanning electron microscopy (SEM, Hitachi S-5200). The bulk composition of the catalysts was determined using X-ray diffraction (XRD, Scintag Pad V, Cu anode).

3.3.2 Electrochemical characterization

The electrochemical activities of the catalysts were characterized by rotating disk electrode method (RDE, Pine Wavedriver and Pine Biopotentiostat AFCBP1) in a 0.1M $KHCO_3$ solution (pH=6.8) prepared from deionized water and granular $KHCO_3$ (99.7-100.5%, Macron Chemicals). Inks were prepared from 2.0 mg of catalyst dispersed in a solution of 0.30 mL 0.5wt% ionomer (5wt%, Nafion™), 0.74 mL isopropyl alcohol (≥99.7%, Sigma Aldrich), and 2.96 mL DI H_2O (final concentration: 0.5 mg mL^{-1}). Inks were deposited at a loading of 20 µg cm^{-2} on a glass carbon electrode (surface areas: 0.196 cm^2 and 0.2475 cm^2, Pine Instruments) and dried in air at room temperature. All

electrochemical experiments were performed with 100 mL CO_2 (99.5%, Argyle) or N_2 (Argyle) saturated solution in a standard five neck electrochemical cell (200 mL, Pine Instruments) at 25°C using a Pt wire counter-electrode and a Ag/AgCl reference electrode (saturated KCl solution, +0.197 V *vs.* SHE, Radiometer Analytics). Prior to all experiments the working electrode was stabilized by cyclic voltammetry at 100 mV s^{-1}. Cyclic voltammetry was performed at a scan rate of 20 mV s^{-1} at 1600 rotations per minute (RPM) between 0.6 and -2.0 V *vs.* Ag/AgCl. Cyclic voltammetry was also performed at scan rate of 1 mV s^{-1} without rotation between 0.6 and -2.0 V *vs.* Ag/AgCl. Bulk electrolysis was performed at -1.2, -1.6 and -2.2 V *vs.* Ag/AgCl for 1 hour with and without rotation (1600 RPM, 0 RPM respectively).

4. Results and Discussion

A series of catalysts were prepared using the sacrificial support method (SSM) by varying the precursor wt% of Cu to silica and the reduction environment with the intent of producing porous Cu nanoparticles. The designations to identify these Cu nanoparticles according to their synthesis conditions are listed in Table 4. The criteria for successful implementation of this synthesis method for producing Cu nanoparticles includes an open, sponge-like morphology, a relatively high BET surface area, high Cu^0 content/low oxide content, and exhibited stable electrochemical activity with current densities between or greater than 0.5 to 20 mA cm^{-2} within the potential range of CER (-1.0 to -2.2 V *vs.* Ag/AgCl) [10, 33].

4.1 Characterization

4.1.1 Scanning electron microscopy

The morphology of the catalysts was confirmed by SEM (Fig. 6-7). The mean and standard deviation of these particle widths are reported in Table 5 (for details refer to Appendix 1). Widths measured are the chords of non-spherical and the diameters of

Table 4. *The designations for Cu nanoparticles synthesized by SSM, as distinguished by their precursor Cu content and reduction environment.*

Weight % Cu : EH-5 in precursor	7% H$_2$ atmosphere 350 °C	100% H$_2$ atmosphere 250 °C
5 : 95	Cu$_{A1}$	Cu$_{B1}$
10 : 90	Cu$_{A2}$	Cu$_{B2}$
20 : 80	Cu$_{A3}$	Cu$_{B3}$
30 : 70	Cu$_{A4}$	Cu$_{B4}$
40 : 60	Cu$_{A5}$	Cu$_{B5}$

spherical particles. The Cu_{A1} and Cu_{A2} particles (Fig. 6a-6b) exhibit morphology typical of

the SSM, with voids from the etched silica clearly visible. The size of these voids

correspond to the particle radius range reported for EH-5 [82]. The particles made from

Cu_{A3}, Cu_{A4}, and Cu_{A5} fail to exhibit this morphology (Fig. 6c-6e); additionally, these

particles are larger and exhibit more varied particle shapes, such as hexagonal (Fig. 6d)

and rectangular shapes (Fig. 6c), and shard-like structures (Fig. 6e). The Cu_{B1}, Cu_{B2}, and

Cu_{B3} particles exhibit morphology typical of SSM (Figs. 7a-7c). The Cu_{B4} particles exhibit

some variance of shape (Fig. 7d), and maintain some of the connective, void shaped

morphology. The Cu_{B5} particles do not exhibit the sponge-like, void shaped morphology

(Fig. 7e), and similar to the Cu_{B4} and Cu_{B5} particles (Fig. 6d-6e) are quite varied in shape

and size. The consistency of morphology and shape visible for most of the Cu_{BX} (X=1-5)

particles can be attributed to temperature effects – the Cu_{AX} (X=1-5) particles are

produced at temperatures where sintering may begin to occur (350 °C) and the surface

energy of small particles are thermodynamically unfavorable, thus the SSM morphology

may be destroyed by larger particles forming from small near neighbors [61]. In both the

Table 5. *BET surface areas measured for all particles with their means and standard deviations in nanometers, as calculated from SEM images of each particle. Nearly all display an approximately normal distribution, with the exception of Cu_{A5} and Cu_{B5}, which display multiple populations of distinct sizes (see Appendix 1).*

Sample (x)	Cu_{AX}			Cu_{BX}		
	Width (nm)	σ (nm)	BET Surface Area (m^2 g^{-1})	Width (nm)	σ (nm)	BET Surface Area (m^2 g^{-1})
1	29.8	9.4	20.0	21.5	6.7	25.1
2	60.5	21.5	10.4	29.3	11.3	20.8
3	82.7	34.4	6.0	48.1	20.9	11.1
4	78.3	35.0	3.8	48.6	19.9	11.8
5	60.0	30.2	3.4	78.8	33.6	7.0
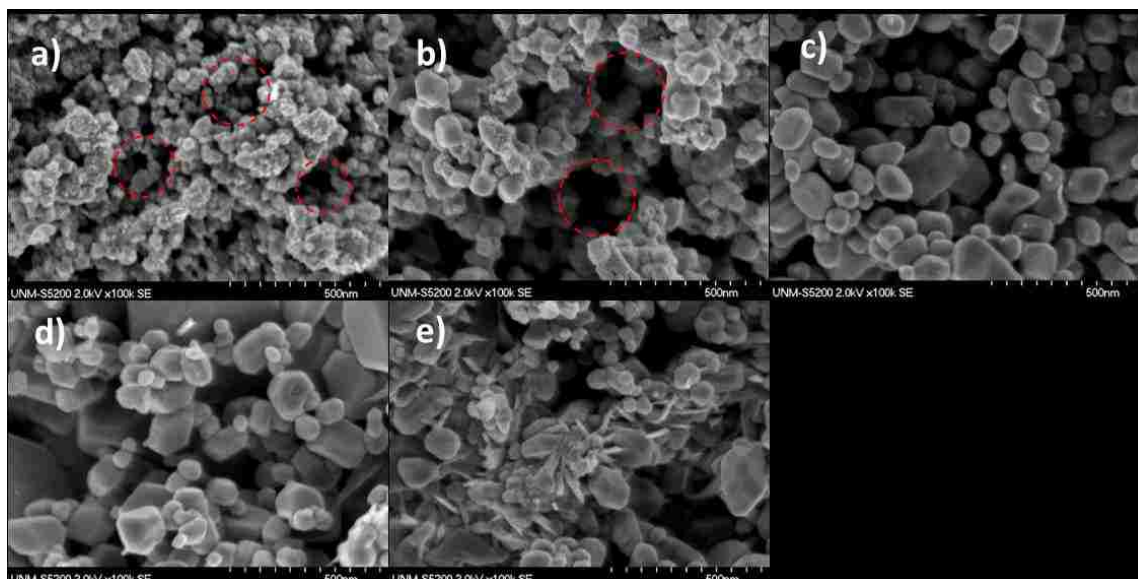
Figure 6. *SEM images of Cu nanoparticles synthesized at 350 °C in a 7% H_2 reduction atmosphere: a) Cu_{A1}, b) Cu_{A2}, c) Cu_{A3}, d) Cu_{A4}, and e) Cu_{A5}. The Cu_{A1} & Cu_{A2} particles (a-b) exhibit sponge-like morphology consistent with the sacrificial support method (voids from EH-5 indicated in red).*
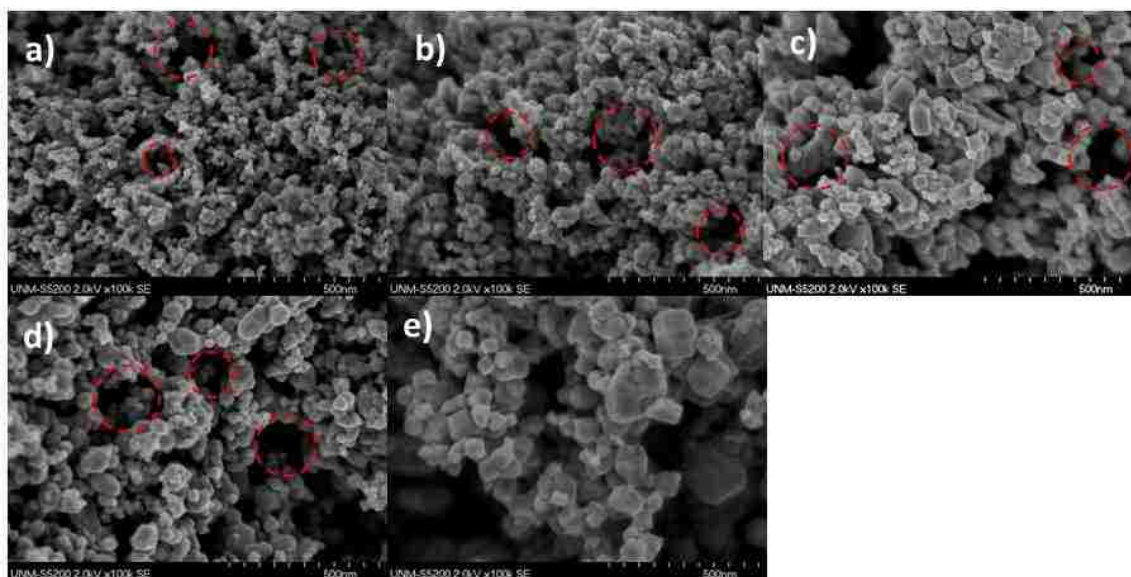
Figure 7. *SEM images of the Cu nanoparticles synthesized at 250 °C in a 100% H_2 reduction: a) Cu_{B1}, b) Cu_{B2}, c) Cu_{B3}, d) Cu_{B4}, and e) Cu_{B5}. The Cu_{B1}, Cu_{B2}, Cu_{B3}, and Cu_{B4} particles (a-d) exhibit sponge-like morphology consistent with the sacrificial support method (voids from EH-5 indicated in red).*

7% and 100% H_2 reduction atmospheres smaller particles were synthesized for lower wt% of Cu in the precursor (Fig. 8). This may be due to dispersion of the $Cu(NO_3)_2$ in a silica matrix, which deters the formation of larger particles with aggregation of smaller particles during the reduction step.

4.1.2 Brunauer-Emmett-Teller surface area

The specific surface area for all catalysts, as measured by BET, are listed in Table 5. In general, the BET surface area decreases with increasing particle

Figure 8. *The effect of precursor Cu weight percent (wt%) on the average particle width during synthesis using the sacrificial support method.*

size; this trend is particularly supported by the nearly identical surface areas of the Cu_{B3} and Cu_{B4} particles (11.4 vs. 11.8 $m^2\,g^{-1}$, respectively) and their similar average particle widths and distributions (48.6 ± 19.9 nm vs. 48.1 ± 20.9 nm, respectively).

Table 6. *The mole percent (mol%) of Cu, CuO, and Cu_2O, as determined from phase fitted XRD data for all particles synthesized using the sacrificial support method.*

Sample (x)	Cu_{AX}			Cu_{BX}		
	Cu (mol %)	CuO (mol %)	Cu_2O (mol %)	Cu (mol %)	CuO (mol %)	Cu_2O (mol %)
1	25.2	12.7	62.2	32.5	0	67.5
2	47.0	1.58	51.4	51.9	8.47	39.7
3	15.7	-	84.3	46.4	12.1	41.5
4	67.6	-	32.4	20.8	-	79.2
5	76.2	4.61	19.2	52.9	-	47.1

Figure 9. *The effect of the precursor Cu weight percent and the reduction environment on the final Cu^0 content in the particles prepared using the sacrificial support method where a) 100% H_2 (250°C) and b) 7% H_2 (350°C).*

4.1.3 X-ray diffraction

XRD patterns from all particles were fitted using Jade 2010 (MDI) to determine

the mole percent (mol%) of Cu (Cu^0), Cu_2O (Cu^+), and CuO (Cu^{2+}) in the materials (for

XRD patterns see Appendix 2) and are listed in Table 6. From this point forward, Cu will

be designated as Cu^0 to distinguish it is not the same type of Cu as is present in the

mono- or divalent Cu-oxides. No more than 13 mol% CuO was calculated for any

particle, with the major phases Cu_2O and Cu^0 exhibited in varied ratios. As previously

discussed, the oxidation of Cu^0 to CuO and Cu_2O is thermodynamically favorable in

oxygen containing atmospheres at low temperatures and atmospheric pressure [59-62].

Additionally, although Cu^0 forms from $Cu(NO_3)_2$ after its decomposition there is a

simultaneous formation of CuO and Cu_2O beginning at 200°C. Subsequent reduction of

CuO to Cu_2O, and a final reduction of Cu_2O to Cu^0 occurs between 200°C and 300°C [62].

Determining which of these two oxide formation sources accounts for the degree of

oxidation in these particles is difficult, but it is important to distinguish that a thin oxide layer formed in air and a particle consisting of significant quantities of oxides in its bulk will display different catalytic surfaces during electrochemical reduction. There appears to be no correlation between the wt% Cu in the precursor and the final mol% Cu^0 in the particles reduced in 100% H_2 (Fig. 9b). This suggests that the rate of oxide reduction is similar for all particles, at this temperature. The final mol% of Cu^0 for the particles reduced in 7% H_2 shows a positive correlation (Fig. 9a), with the highest Cu^0 content exhibited in the highest precursor wt% Cu (Cu_{A5}, 76.2 mol% Cu^0). The difference in trends can be attributed to the temperature of the reducing atmosphere. Until 250°C the effect of temperature would be identical for both atmospheres, because the temperature ramp rate for both reactions was the same (5°C min^{-1}) – however, these particles were formed at different temperatures. While held at 250°C, the continued decomposition of gaseous intermediates would be accompanied by the slow reduction of oxides to Cu for the particles reduced in 100% H_2. The eventual formation of Cu from its oxide forms does occur at this temperature, but may require a longer reduction period, even at such a high concentration of H_2. The particles reduced in 7% H_2 were further heated to 350°C, undergoing the same reactions just discussed, but at a faster rate. The increase of final mol% Cu^0 for higher precursor Cu may be caused by rapid reduction of oxides (primarily Cu_2O at this temperature) to Cu as the particle forms, because of the high temperature. So while more Cu^0 is formed at a higher temperature, during the same reduction time, the rate is accelerated to the point the particles begin to aggregate and overpower the template of silica, forming irregular sizes and shapes.

The particles with the highest Cu^0 mol% were formed at 350°C in low concentrations of H_2, thus displaying the greatest extent of this precursor reduction, but they also are the largest and have the lowest BET surface area. The particles reduced in 100% H_2 at 250°C show a maximum Cu^0 content of c.a. 50 mol%, but in general less CuO. This suggests that a longer reduction time at the lower temperature and high H_2 concentration may increase the reduction of Cu_2O to Cu^0 while maintaining the desired morphology.

4.2 Electrochemical characterization

4.2.1 Cyclic voltammetry

The electrochemical performance of the catalysts was tested in both diffusion and kinetically limited thin film regimes. Catalysts were initially screened by comparison of the cathodic sweep of cyclic voltammograms (CVs) captured at a scan rate of 20 mV s^{-1} in N_2 and CO_2 saturated solutions (Appendix 3). For all catalysts the current density produced in a CO_2 saturated solution was less than in a N_2 saturated solution, an observation that confirms CER; a net decrease in current in the presence of CO_2 indicates competitive occupation of active sites of HER and CER.

Next, pseudo-steady state, diffusion limited performances were measured by cyclic voltammetry without rotation at a scan rate of 1 mV s^{-1} (see Fig. 10-11). The maximum current densities of the Cu_{AX} (X=1-5) particles range from -3.0 to -8.0 mA cm^{-2} at -2.2 V *vs*. Ag/AgCl. The Cu_{A1}, Cu_{A2}, Cu_{A3}, and Cu_{A5} particles exhibit a characteristic limiting current at ca. -1.45 V *vs.* Ag/AgCl which has been previously identified as saturation of active sites by reduction of both H_2O and CO_2 on Cu^0 surfaces (Fig. 10, inset) and can also be attributed to diffusion limitations of species to and from the
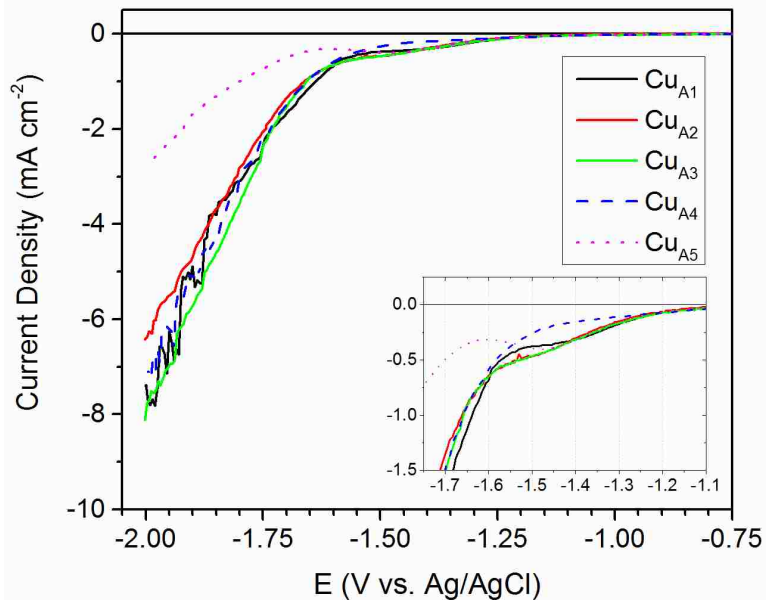
Figure 10. *The cathodic sweep of voltammograms performed at 1 mV s⁻¹ of Cu particles synthesized using SSM in 7% H₂ at 350°C (CuₐX, where X=1-5). Conditions: 0.1M KHCO₃, 25°C, no rotation.*
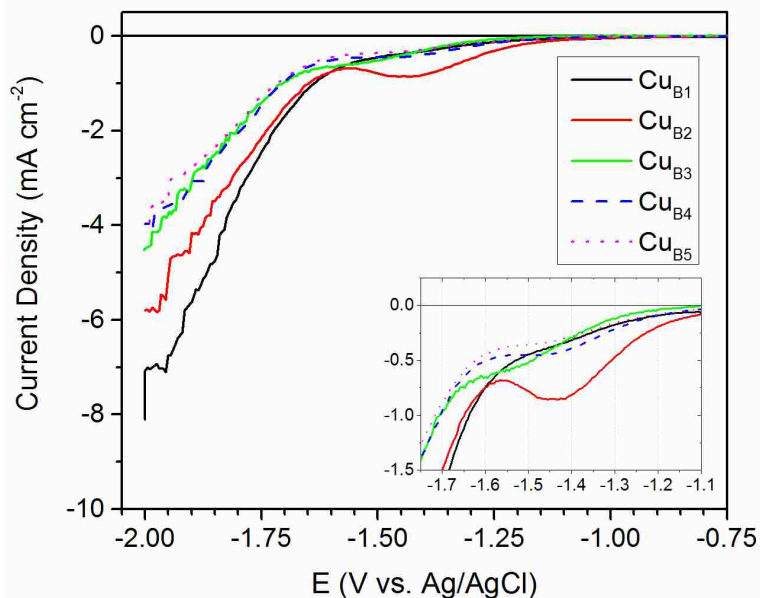
Figure 11. *The cathodic sweep of voltammograms performed at 1 mV s⁻¹ of Cu particles synthesized using SSM in 100% H₂ at 250°C. (CuₐX, where X=1-5). Conditions: 0.1M KHCO₃, 25°C, no rotation.*

catalytic sites [41]. The Cu_{A5} particles exhibit the highest inhibition of activity (a decrease

of ca. 0.20 mA cm^{-2}) from -1.45 to -1.65 V vs. Ag/AgCl (Fig. 10, inset), and have the

lowest total current density (-2.5 mA cm^{-2}). The high activity towards CER can be

attributed to thehigh Cu^0 content in these particles (76.2 mol%), with the low

performance due to the large particles size (60.0 ± 30.2), corresponding to a lower

surface area and fewer catalytic sites. The current densities of Cu_{A1}, Cu_{A2}, Cu_{A3}, and Cu_{A4}

particles are nearly identical from -1.75 to -2.00 V *vs.* Ag/AgCl. Differences are visible in

the slope of their limiting currents (Fig. 10, inset). The Cu_{A1} particles exhibit a constant

limiting current density for ca. 35 mV until it begins to increase at -1.55 V *vs.* Ag/AgCl.

The Cu_{A2} and Cu_{A3} particles exhibit a constant slope in current densities from -1.30 to -

1.60 V *vs*. Ag/AgCl before it beings to increase, with a slight inflection at -1.45 V *vs.*

Ag/AgCl indicating a limiting current density. The Cu_{A4} particles do not show any

inflection to indicate the competitive activity of CER, instead slowly increasing in current

density until -1.55 V *vs.* Ag/AgCl. These particles are dissimilar in size, composition and

morphology, so it is likely the similarity in current is due to diffusion limitations – which

is more visible for the smaller particles (Fig. 6a) than for larger particles with a more

open framework (Fig. 6b-6d). This diffusion limitation depends on the activity of the

catalyst, as is evident from differences observed near the onset of CER (ca. -1.20 *V vs.*

Ag/AgCl), but to what extent the activity of these particles varies is unclear from this

data.

The maximum current densities of the Cu_{BX} (X=1-5) particles range from -4 to

-8.0 mA cm^{-2} at -2.0 *vs.* Ag/AgCl (Fig. 11). The Cu_{B2}, Cu_{B4}, and Cu_{B5} particles exhibit the

characteristic limiting current near -1.45 V *vs.* Ag/AgCl, while the Cu_{B3} particles exhibit a limiting current at ca. -1.55 V *vs.* Ag/AgCl (Fig. 11, inset). The Cu_{B1} particles exhibit the highest current density (-8.0 mA cm^{-2}) with a downward inflection between -1.30 and -1.55 V *vs.* Ag/AgCl, before exhibiting a sharp increase in current density. This inflection could correspond to a low amount of CER activity, but is not conclusive. The Cu_{B2} particles exhibit the second highest current density, with a distinct limiting current at -1.45 V *vs.* Ag/AgCl, previously attributed to high Cu^0 content (in the Cu_{A5} particles, Fig. 10 inset), which agrees well with the relatively high Cu^0 content in these particles (51.9 mol%). The current densities of the Cu_{B3}, Cu_{B4}, and Cu_{B5} particles are nearly identical after -1.75 V *vs.* Ag/AgCl, with a maximum of ca. -4.0 mA cm^{-2}; prior to this potential, differences in activity are visible starting at -1.20 V *vs.* Ag/AgCl (Fig. 11, inset). The Cu_{B3} particles exhibit the lowest current until -1.40 V *vs.* Ag/AgCl after which its current density is higher than both Cu_{B4} and Cu_{B5} (0.25 mA cm^{-2}), reaching an inflection point and a slowing rate of increasing current density at ca. -1.55 V *vs.* Ag/AgCl. The Cu_{B4} and Cu_{B5} particles exhibit similar behavior between -1.30 and -1.60 V *vs.* Ag/AgCl. However, the limiting current density of the Cu_{B4} particles is more pronounced (ca. -0.5 mA cm^{-2}) than that of the Cu_{B5} particles – this behavior is unexpected considering their relative Cu^0 content (20.8 mol%, 52.9 mol% respectively) which would suggest a reverse relationship. This reveals a significant shortcoming when relying on XRD compositional analysis of these particles – its bulk analysis does little to describe the surface species and suggests further surface sensitive analysis would be beneficial to understanding the surface concentrations of Cu^0, Cu^+, and Cu^{2+}, especially in cases where the previously

observed behavior of the electrochemical performance of Cu^0 is contradicted. The consistent morphology of the particles reduced in 100% H_2 illuminates some effect due to particle size, with a clear increase in current densities for smaller particles, but the degree to which this is influenced by concurrent restrictions to catalytic sites developed under diffusion limitations is unclear from this data.

4.2.2 Bulk electrolysis

The electrochemical stability of the catalysts was tested by bulk electrolysis at three potentials of interest: -1.2, -1.6 and -2.2 V *vs*. Ag/AgCl. At -1.2 V *vs*. Ag/AgCl, the relative onset of CER can be determined; this is very near the theoretically calculated rate limiting potential of 0.74 V *vs.* SHE, associated with the reduction of a CO_{ad} to a carbonyl proposed by Peterson and Norskov [39]. It is expected that the major product at this potential will be H_2. Many fundamental studies report CER at -1.6 V *vs*. Ag/AgCl, with current densities of 3-5 mA cm^{-2} on polycrystalline Cu and can thus serve as a benchmark for comparison (Table 1) [25, 42, 47-48]. Substantial quantities of CER gas phase products have been reported in studies at -2.2 V *vs*. Ag/AgCl, and thus can illuminate more realistic limits of conversion for appreciable quantities of CER and the energetic cost of associated current densities. Stability at all potentials is important, as it indicates the surface is chemically stable in the entire CER potential range, but is especially important at -1.6 and -2.2 V *vs*. Ag/AgCl because these are the potentials which are associated with measurable quantities of CER products that are essential to determine selectivity towards observed products by quantification of gas, liquid, or both gas and liquid phases as previously discussed. To this end, bulk electrolysis was

performed for 1 hour with and without rotation. The experiments without rotation were performed to determine if diffusion limited pseudo-steady state CVs are predictive of actual steady state performance. Experiments with rotation were performed to determine the kinetically limited steady state current, and to confirm stability to allow for quantification of gas products.

The current densities of all particles reached and maintained a steady current density for the duration of the diffusion limited experiments (Appendix 4). Comparison of the steady state and pseudo-steady state performance of the particles for both 7% and 100% H_2 reduction atmospheres indicates that the steady state current densities predicted at -1.2 and -1.6 V vs. Ag/AgCl by slow scan voltammetry at 1 mV s^{-1} are not indicative of either rank of performance or actual current densities under potentiostatic conditions (Fig. 12). Bulk electrolysis current densities are reported as 30 minute averages, while voltammogram current densities are reported as averages of ± 20 mV of the potential state.
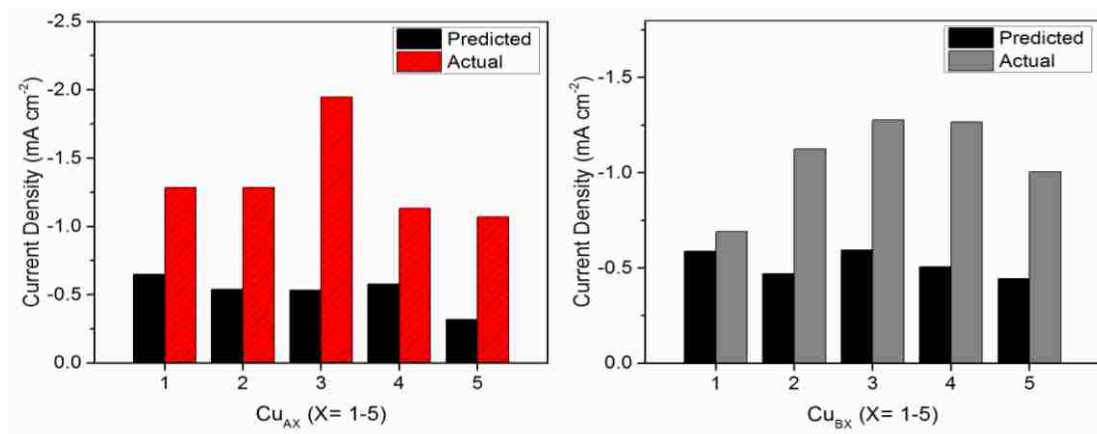
Figure 12. Comparison of average current densities from particles reduced in a) Cu_{AX} and b) Cu_{BX} (X=1-5) for bulk electrolysis and slow scan voltammetry at -1.6 V vs. Ag/AgCl illustrating the discrepancies between expected and observed steady state values.

The steady state performance of the Cu_{AX} and Cu_{BX} (X=1-5) particles were tested to observe their kinetically limited current densities at -1.6 and -2.2 V *vs*. Ag/AgCl (Fig. 13-14) while held for 1 hour. Current densities under rotation were greater than those without, as is expected for a system with diffusion limitations. The magnitude of the current densities (10s of mA cm^{-2}) produced are comparable to those reported by Baturina et al. for similar catalyst loadings (20 μg cm^{-2}) [42].

Figure 13. *Bulk electrolysis of Cu particles reduced at 350°C in a 7% H$_2$ atmosphere at a) -1.6 and at b) -2.2 V vs. Ag/AgCl. Conditions: 0.1M KHCO$_3$, 1600 RPM, 25 °C.*

The Cu_{AX} (X=1-5) particles were relatively stable when held for one hour at -1.6 V vs. Ag/AgCl (Fig. 13a) and very stable when held for one hour at -2.2 V *vs.* Ag/AgCl (Fig. 13b). While held at -1.6 V *vs.* Ag/AgCl the Cu_{A1} and Cu_{A2} particles exhibited a stable current density after 20 minutes, the Cu_{A4} particles exhibited a continuously increasing current density (although the rate of increase slowed after 30 minutes), and the Cu_{A3} and Cu_{A5} particles exhibit a very stable current density after several minutes. The improvement of current in the Cu_{A1}, Cu_{A2}, and Cu_{A4} particles is

likely due to reduction of reordering of the catalyst surface at this negative potential.

Recall that surface oxides begin to be electrochemically reduced after -0.60 V *vs.*

Ag/AgCl, as discussed by Peterson [38], thus all surface oxides should be completely

reduced to Cu^0, but the facets exposed may be unstable since they are essentially

patterned from oxygen vacancies [46-47]. This process increases the current densities of

the Cu_{A1} and Cu_{A2} particles less (an increase of ca. 0.50 mA cm^{-2}) than for the Cu_{A4}

particles (an increase of ca. 2.0 mA cm^{-2}). It unclear why the Cu_{A4} particles experience

such a dramatic improvement in current density, since they possess a high Cu^0 content

(67.2 mol%), and would thus be expected to have a more stable surface (as in the Cu_{A5}

particles, which are 76.2 mol% Cu^0). The stability of the Cu_{A3} and Cu_{A5} particles may be

due to both possessing ca. 80 mol% of a single phase (Cu_2O and Cu, respectively), which

may lend increased resistance of these particles against substantial surface reordering

after a brief reduction of a thin oxide layer. While held at -2.2 V *vs.* Ag/AgCl, the Cu_{A1}

and Cu_{A2} particles achieve stable current densities after 20 minutes, exhibiting similar

behavior as observed at -1.6 V *vs.* Ag/AgCl. The Cu_{A3}, Cu_{A4}, and Cu_{A5} particles are

immediately stable, remaining at near constant current densities for the duration of the

experiment. The rapidity of this stabilization can be attributed to the very high potential

of this electrolysis, any surface changes occurring would be expected to occur more

quickly at lower potentials. The changes in current density performance ranks at -1.6

and -2.2 V *vs.* Ag/AgCl are noticeably different, and allude to differences in reduction

mechanism, but further deductions from this observation are not possible with this

data.

The Cu_{BX} (X=1-5) particles were relatively stable when held for one hour at -1.6 V *vs.* Ag/AgCl (Fig. 14a) and very stable when held at -2.2 V *vs*. Ag/AgCl (Fig. 14b). The Cu_{B1}, Cu_{B2}, and Cu_{B3} particles exhibit increasing current densities; the Cu_{B1} particles stabilize at 15 minutes, while the Cu_{B2} and Cu_{B3} particles both asymptotically approach a maximum value by the lapse of an hour. For these particles, the final current density is more than doubled the initial current density. As discussed previously (for the Cu_{A1} and Cu_{A2} particles, Fig. 12a)
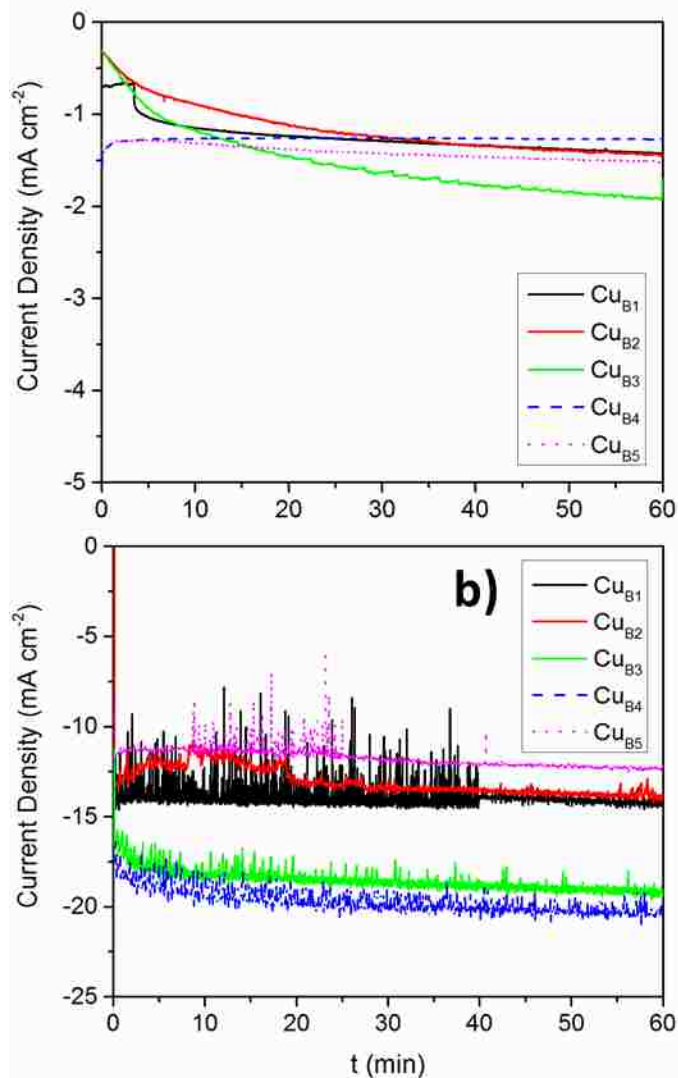

Figure 14. *Bulk electrolysis of Cu particles reduced at 250°C in a 100% H_2 atmosphere at a) -1.6 and at b) -2.2 V vs. Ag/AgCl. Conditions: 0.1M $KHCO_3$, 1600 RPM, 25°C.*

this is likely due to electrochemical reordering of the catalyst surface. The Cu_{B4} and Cu_{B5} particles stabilize in minutes and remain so for the duration of the experiment. Again, there is no apparent correlation between the Cu^0 and Cu_2O content and the relative stability of these particles. When held at -2.2 V *vs*. Ag/AgCl for 1 hour, all particles were stable after 20 minutes. As observed for the Cu_{AX} (X=1-5) particles, performance ranks of

these particles are inconsistent between -1.6 and -2.2 V *vs.* Ag/AgCl, consistent with different CER reduction pathways at different potentials.

4.3 Correlations between electrochemical performance material properties

To understand how performances relate to material properties, possible correlations between Cu^0 content and BET surface area were explored (Fig. 15-18). (Note: BET surface areas were previously correlated with particle size, where higher surface areas are associated with smaller particle size listed on Table 5, and as such particle size will not be explicitly compared because it is redundant.) The Cu_{AX} (X=1-5) particles exhibit decreasing current density at both -1.2 (Fig. 15, top) and -2.2 V *vs.* Ag/AgCl (Fig. 15, bottom) as Cu^0 content increases, with no clear effect for -1.6 V *vs.* Ag/AgCl (Fig. 15, middle). Recall that -1.2 V *vs.* Ag/AgCl is the potential at which CER begins, but H_2 production dominates because of energy barriers to reduction of adsorbed CER intermediates [38-39]. A decrease in current can correspond to reduction of HER by this mechanism. At decrease in current at -2.2 V *vs.* Ag/AgCl can be attributed to competitive reduction by CER and HER, hence a decrease in the slope of this correlation. The magnitude of the current densities generated by all particles at -1.6 V *vs*. Ag/AgCl are comparable to those reported for polycrystalline Cu (-2.0 to -4.0 mA cm^{-2}, Table 1). At this potential the energy barrier to reduction of CO_{ad} is overcome, and multiple pathways open – this may account for the inconclusive current densities observed; while CER is likely occurring at a more rapid rate, the adsorption affinities of intermediates and products may obscure this effect. A reverse trend is observed for BET surface area, with increasing current density corresponding to higher surface area for
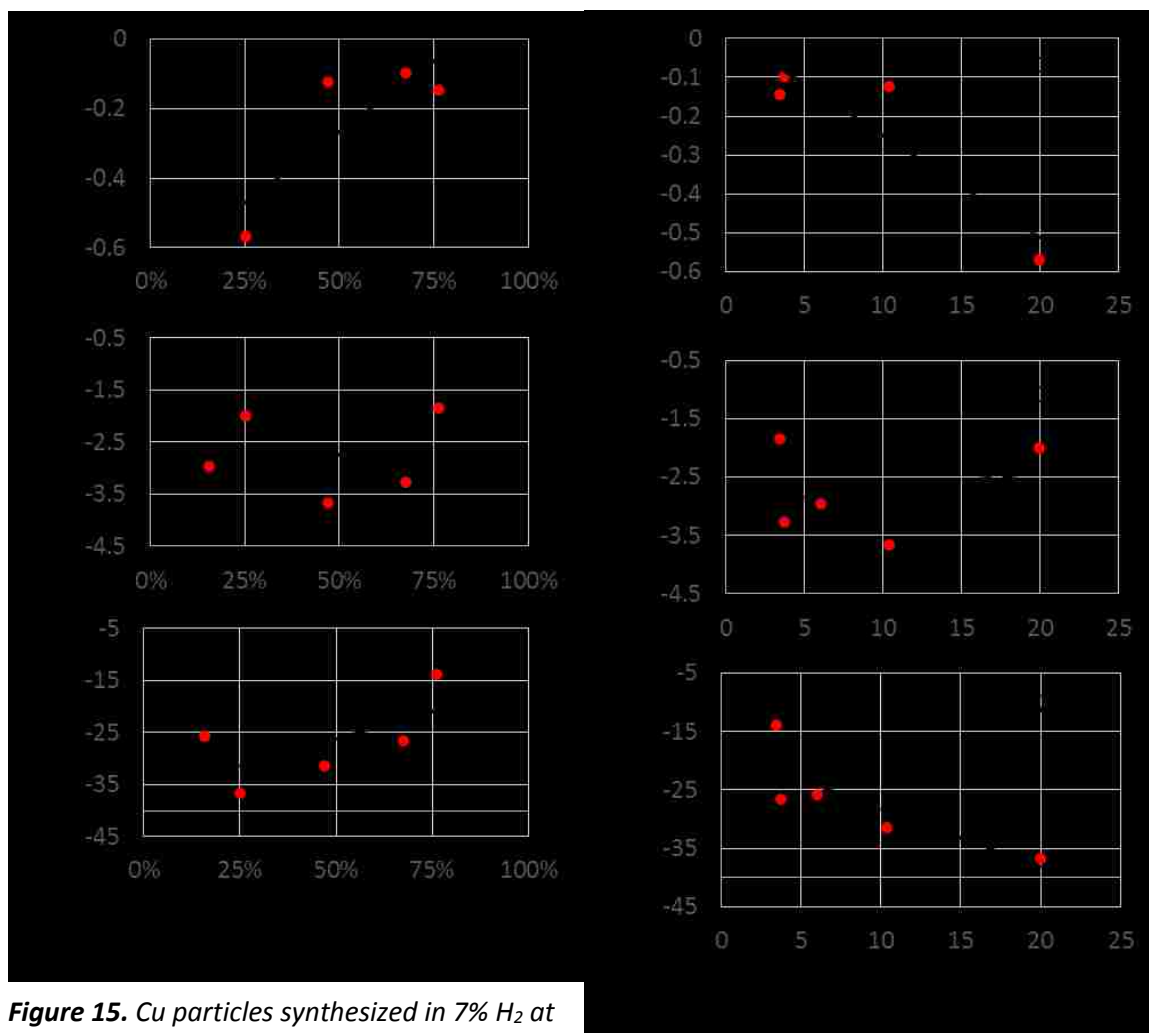
Figure 15. *Cu particles synthesized in 7% H_2 at 350°C exhibit decreasing current density as Cu^0 content increases at -1.2 (top) and -2.2 (bottom), with no apparent correlation at -1.6 (middle) V vs. Ag/AgCl. Conditions: 0.1M $KHCO_3$, 1600 RPM, 25°C.*

Figure 16. *Cu particles synthesized in 7% H_2 at 350°C exhibit increasing current density for increasing BET surface area at -1.2 (top) and -2.2 V vs. Ag/AgCl (bottom), with no clear effect at -1.6 (middle) V vs. Ag/AgCl. Conditions: 0.1M $KHCO_3$, 1600 RPM, 25°C.*
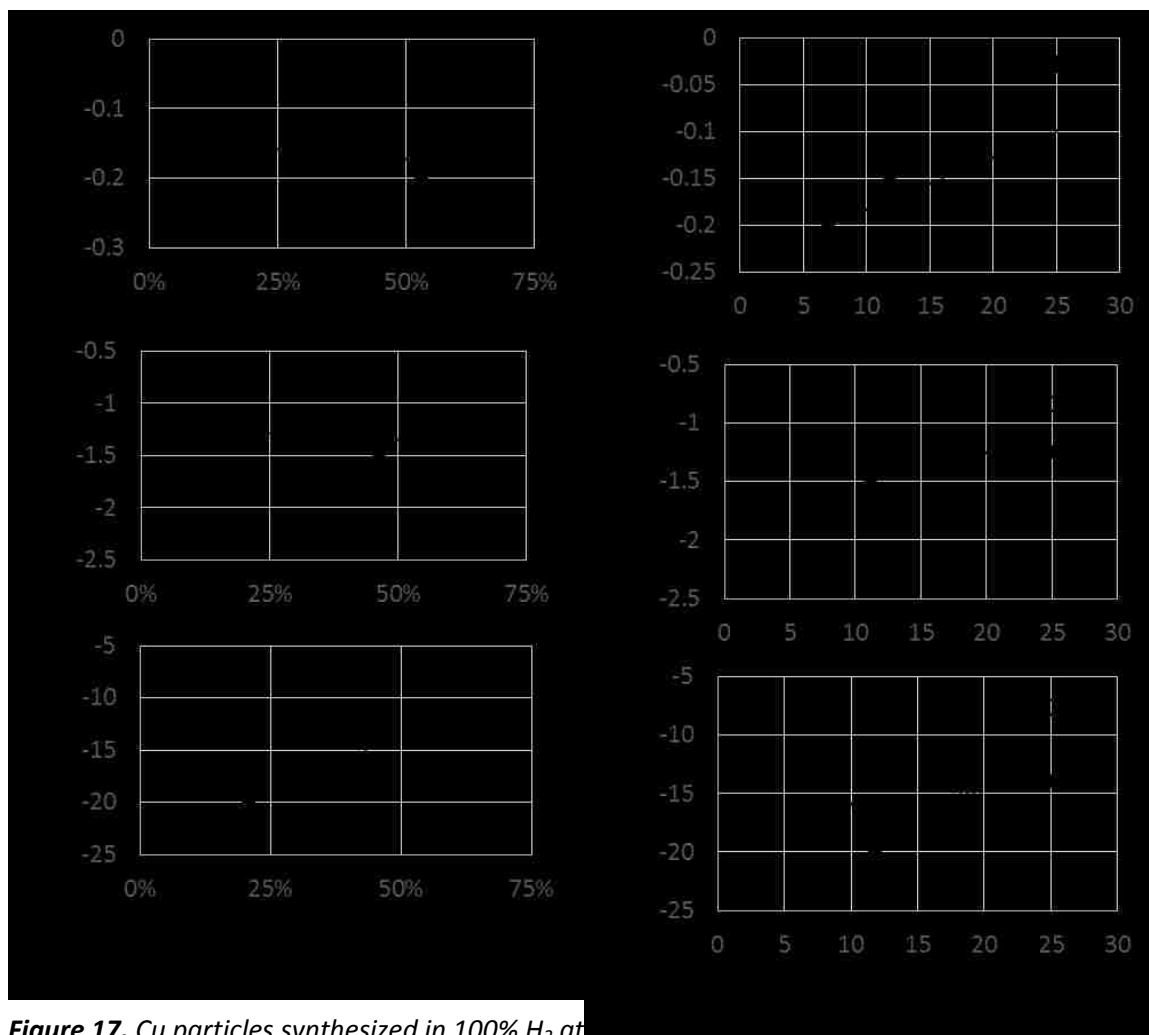
Figure 17. Cu particles synthesized in 100% H_2 at 250°C exhibit decreasing current for increasing Cu^0 content at -2.2 (bottom), with no apparent correlation at -1.2 (top) and -1.6 (middle) V vs. Ag/AgCl. Conditions: 0.1M $KHCO_3$, 1600 RPM, 25°C.

Figure 18. Cu particles synthesized in 100% H_2 at 250°C exhibit decreasing current density for increasing BET surface area at -1.2 (top) and -1.6 (middle), with near clear effect at -2.2 (bottom) V vs. Ag/AgCl. Conditions: 0.1M $KHCO_3$, 1600 RPM, 25 °C.

-1.2 and -2.2 V *vs.* Ag/AgCl (Fig. 16, top and bottom); these observations are consistent

with behaviors observed in CVs – higher Cu^0 results in competitive CER/HER, thus

reducing net current but also corresponds to larger particles (and correspondingly lower

surface areas), while smaller particles increase surface area and access to catalytic sites

resulting in increased total current. From these observations, the highest performing

catalyst should have both high Cu^0 content and high surface area to maximize CER,

which corresponds to the Cu_{A2} particles, which were thus selected for further testing by

gas chromatography.

The Cu_{BX} (X=1-5) particles exhibit increasing current for increasing Cu^0 content at

-2.2 V *vs.* Ag/AgCl, with no clear trend for -1.2 and -1.6 V *vs.* Ag/AgCl (Fig. 17). At -1.2 V

vs. Ag/AgCl there is no obvious suppression of HER as in the previous case (Fig. 15),

which may be attributed to the similar surface chemistries of these particles near the

onset of CER (i.e., they are producing H_2 at similar rates, and may be inhibited at similar

rates as well) but this cannot be conclusively asserted. The magnitude of the current

densities generated by all particles at -1.6 V *vs*. Ag/AgCl is between -1.0 and -1.5 mA

cm^{-2}, slightly lower than those typically reported for polycrystalline Cu (lowest: 2.5 mA

cm^{-2}, Table 1). As with the Cu_{AX} (X=1-5) particles, this can signify a complex interplay

between adsorbed intermediates, products, and HER, but cannot signify any one specific

cause. Although less persuasive than the previous case, this could suggest CER

suppression of HER, as previously discussed, at -2.2 V *vs*. Ag/AgCl. Current densities

decrease slightly for higher BET surface areas at -1.2 V *vs*. Ag/AgCl, with no clear trend

observed at -1.6 and -2.2 V *vs*. Ag/AgCl (Fig. 18). This could indicate competitive

CER/HER rates on higher surface areas, but is not conclusive. A lack of clear trends in

this material set necessitates implementing the same criteria applied to the previous

particles: the particles with the highest Cu^0 content and the highest surface area were

Cu_{B2}, and thus were selected for further testing of gas phase products.

5. Conclusions

The synthesis of Cu nanoparticles using the SSM method is promising. Implementation of this synthesis method to develop particles with a controlled and specifically structured morphology was successfully achieved for lower precursor Cu contents (5wt% and 10wt%) in both reduction environments. The Cu_{A1} and Cu_{A2} were within the typical Cu nanoparticle range (15-100 nm) with widths of 29.8 ± 9.4 and 69.5 ± 21.5 nm, respectively, although their Cu^0 content was correspondingly low – 25.2 and 47.0 mol%, respectively. Comparatively, the Cu_{B1} and Cu_{B2} particles exhibited an even higher degree of control over morphology with smaller particle widths, 21.5 ± 9.4 nm and 29.3 ± 21.5 nm, respectively. However, these particles were similarly low in final molar Cu^0 content, with 32.5 and 51.9 mol%, respectively. The consistently high amount of oxidation for these particles may be mediated by modifications to the synthesis approach such as completely evaporating water vapor from precursors prior to synthesis at low temperatures, exploring more complex temperature treatments (involving multiple temperature and time intervals), and developing a more controlled method of passivation after reduction, which may all optimize the final Cu^0 content while maintaining the desired morphology. Further, studies into the surface content of these particles may reveal if such concerns are even necessary, since Cu_2O has been shown to be catalytically active towards CER [42,46-47]. When tested for electrochemical stability, the Cu_{A1}, Cu_{A2}, Cu_{B1}, and Cu_{B2} particles were adequately stable when bulk electrolysis was performed for 1 hour at -1.6 and -2.2 V *vs.* Ag/AgCl (Fig. 13-14). This confirms they are suitable for further analysis of gas and liquid phase products

to determine their selectivity towards specific CER products. These particles exhibit higher current densities when a kinetically limited regime, as is typical of a system with diffusion limitations, although this is not necessarily a negative attribute since it may increase the residence time of intermediates and increase product selectivity towards a single product. This can be determined by further studies that quantify liquid and gas phase products of the Cu_{A2} and Cu_{B2} nanoparticles. The highest current densities at -2.2 V $vs.$ Ag/AgCl were ca. -40 mA cm^{-2} for Cu_{A2} and ca. -35 mA cm^{-2} for Cu_{A1}. The Cu_{B1} and Cu_{B1} particles exhibited lower current densities of ca. -15 mA cm^{-2}. These are all of the same magnitude of current densities reported for similar catalyst loadings and in similar conditions for carbon supported Cu [42] but are significantly more stable, suggesting this synthesis method may achieve even higher current densities once optimized for higher Cu^0 content and can be deployed in an bench-scale fuel cell apparatus.

APPENDICES

Appendix 1. Particle size, defined as the length of the chord for non-spherical particles and diameter for spherical particles, distributions of Cu nanoparticles synthesized using the SSM, as determined by SEM.
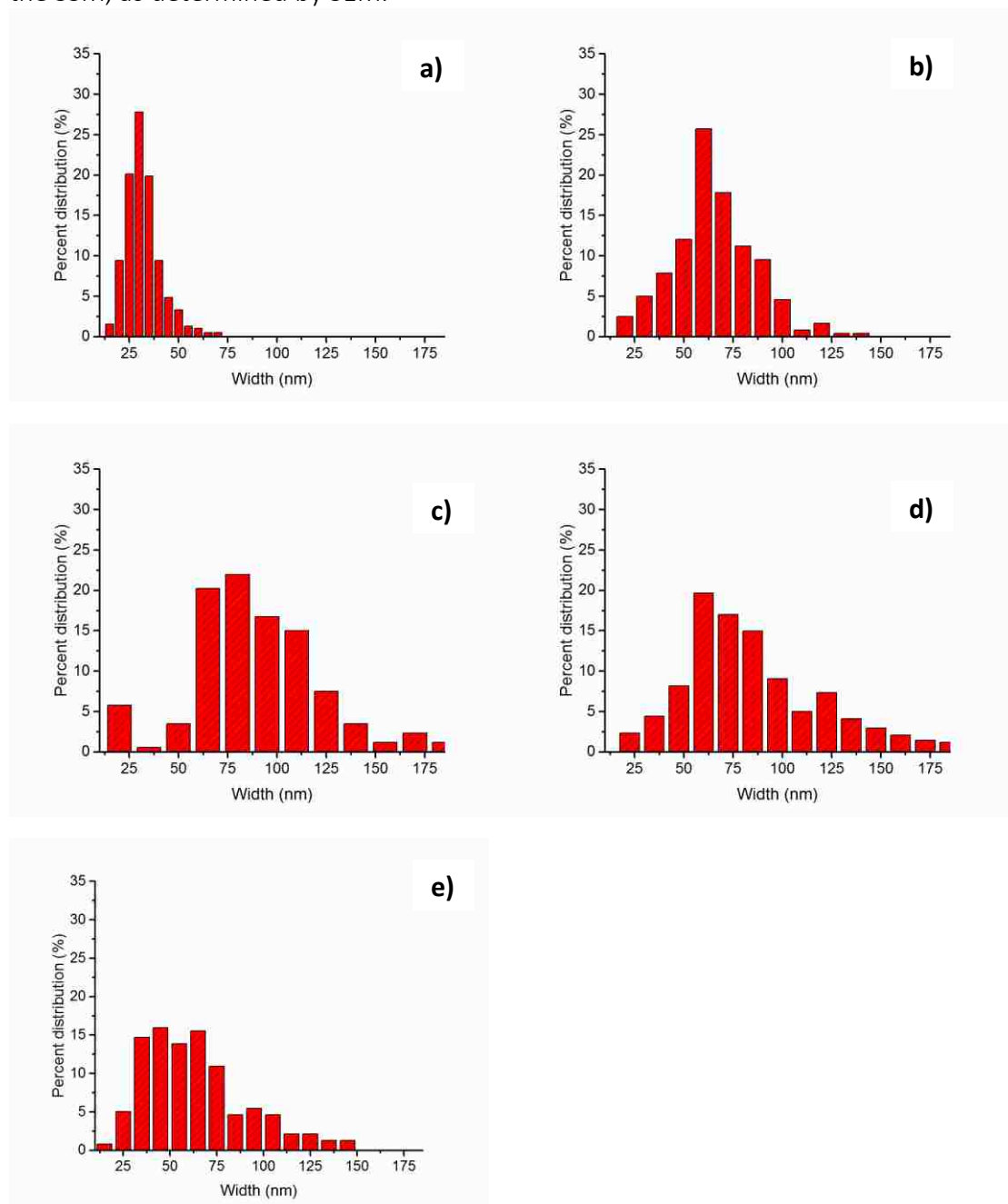
Figure 19. *Particle width distributions of Cu synthesized in 7% H_2 at 250°C: a) Cu_{A1}, b) Cu_{A2}, c) Cu_{A3}, d) Cu_{A4}, e) Cu_{A5}. The Cu_{A1}, Cu_{A2}, and Cu_{A3} particles appear to have a normal distribution (a-c); Cu_{A4} (d) is skewed left and exhibits two populations at ca. 60 and 118, while Cu_{A5} (e) similarly exhibits a skewed left distribution with two populations at ca. 55 nm and 95 nm.*
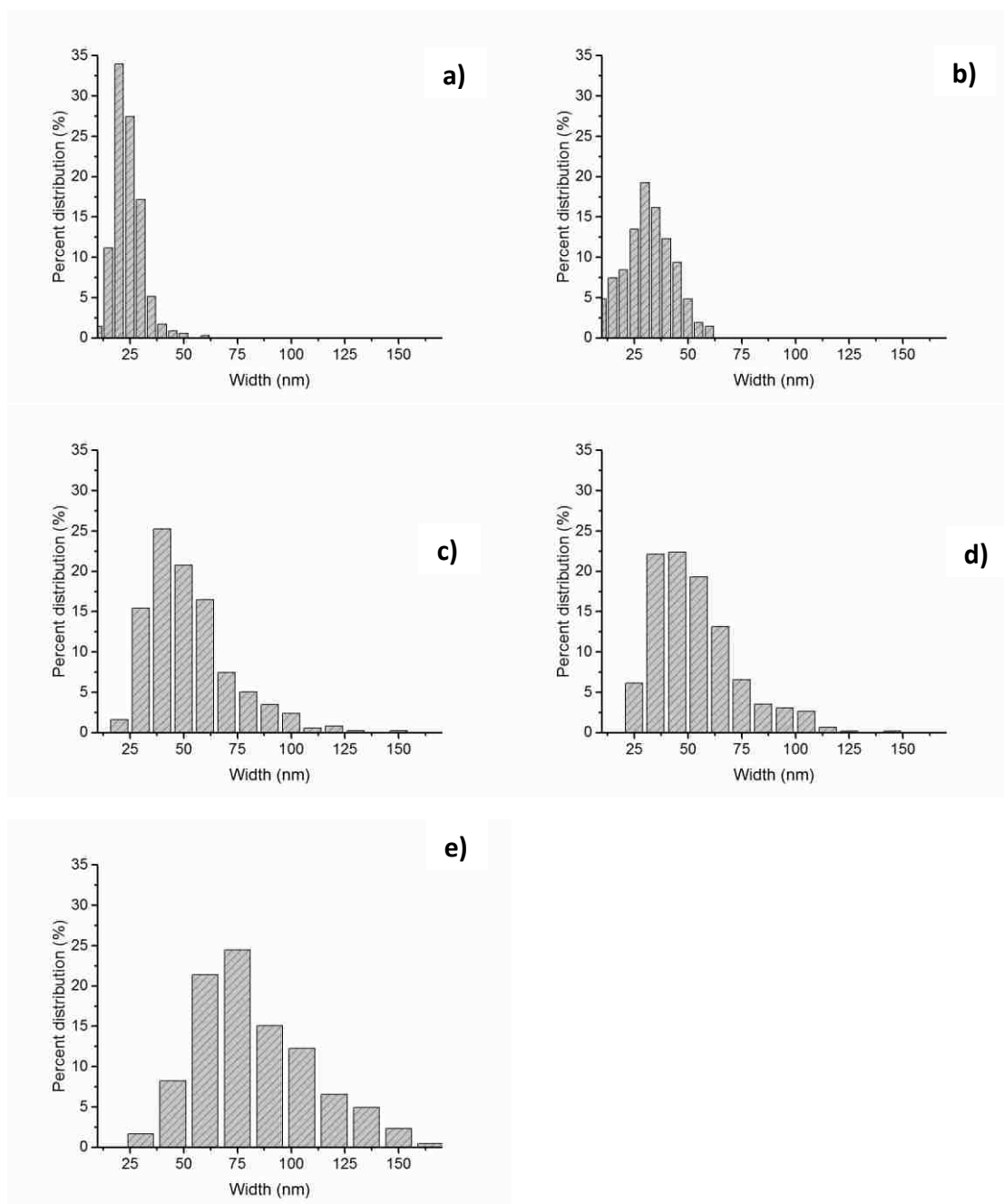
Figure 20. *Particle width distributions of Cu synthesized in 100% H₂ at 350 °C: a) Cu_{B1}, b) Cu_{B2}, c) Cu_{B3}, d) Cu_{B4}, e) Cu_{B5}. The Cu_{B1} and Cu_{B2} (a-b) particles appear to have a normal distribution. The Cu_{B3}, Cu_{B4}, and Cu_{B5} (c-e) distributions are skewed left, but exhibit singular population means (ca. 40, 45, and 75 nm respectively).*

Appendix 2. XRD patterns taken of Cu nanoparticles synthesized using the SSM.
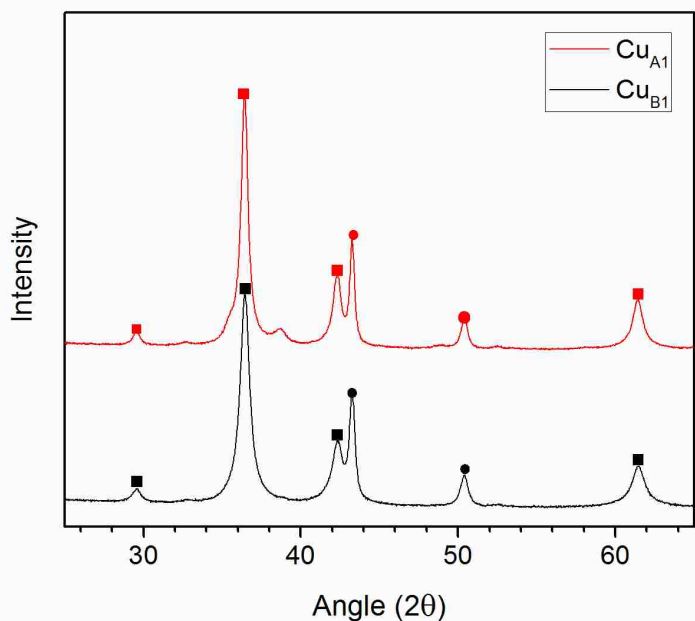
Figure 21. *XRD patterns of catalysts prepared from 5wt% Cu precursors in 7% (Cu_{A1}, red) and 100% H_2 (Cu_{B1}, black) atmospheres. Cu_2O (squares): 29.6° - (110), 36.4° – (111), 42.3° – (200), 61.4° - (220). Cu (circles): 43.2° – (111), 50.4° – (200). CuO is a minor phase included in refinements for the particles reduced in 7% H_2, at 12.7mol%.*
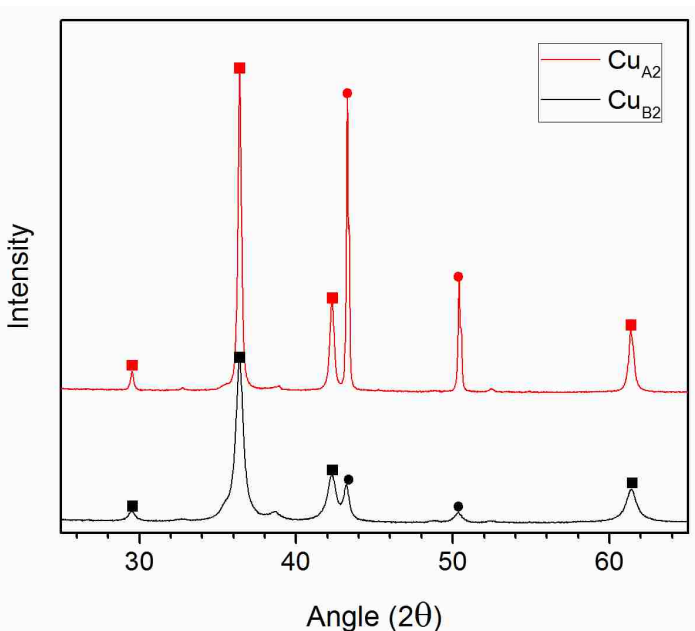
Figure 22. *XRD patterns of catalysts prepared from 10wt% Cu precursors in 7% (Cu_{A2}, red) and 100% H_2 (Cu_{B2}, black) atmospheres. Cu_2O (squares): 29.6° - (110), 36.4° – (111), 42.3° – (200), 61.4° - (220). Cu (circles): 43.2° – (111), 50.4° – (200). CuO is a minor phase included in refinements for the particles reduced in 7% H_2 and 100% H_2, at 1.58 at 8.47 mol%, respectively.*
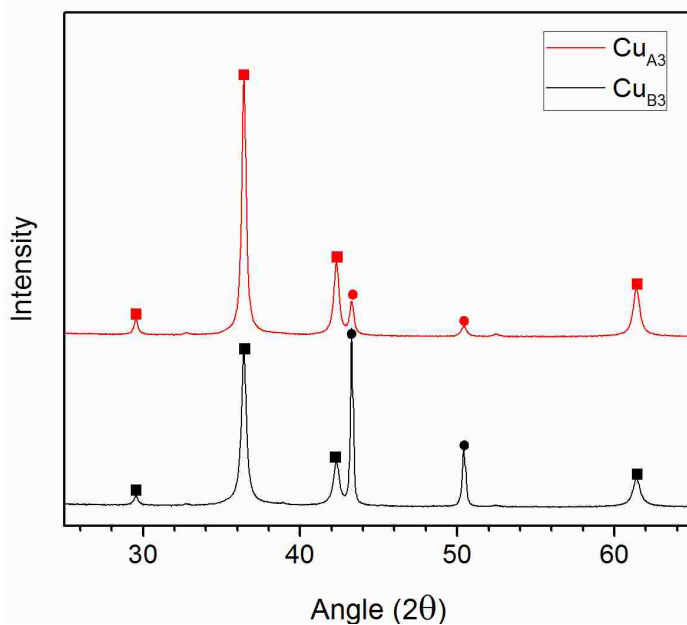
Figure 23. XRD patterns of catalysts prepared from 20wt% Cu precursors in 7% (Cu$_{A3}$, red) and 100% H$_2$ (Cu$_{B3}$, black) atmospheres. Cu$_2$O (squares): 29.6° - (110), 36.4° – (111), 42.3° – (200), 61.4° - (220). Cu (circles): 43.2° – (111), 50.4° – (200). CuO is a minor phase included in refinements for the particles reduced in 100% H$_2$, at 12.1 mol%.
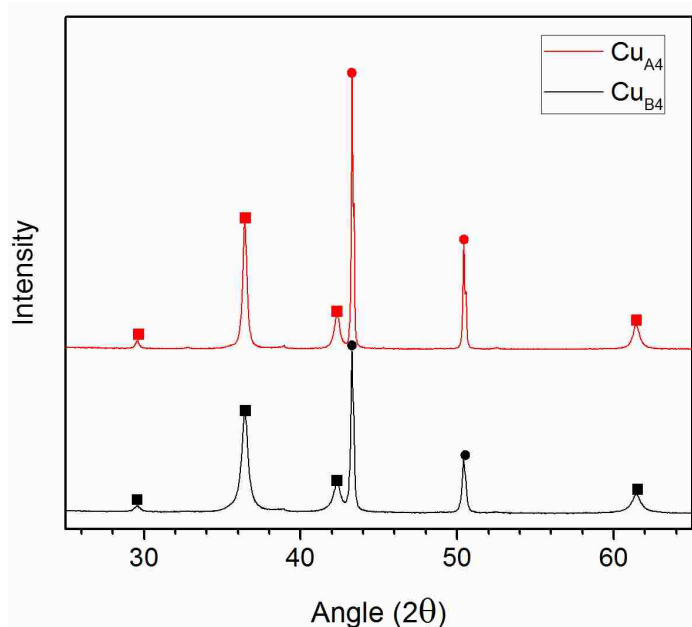
Figure 24. XRD patterns of catalysts prepared from 30wt% Cu precursors in 7% (Cu$_{A4}$, red) and 100% H$_2$ (Cu$_{B4}$, black) atmospheres. Cu$_2$O (squares): 29.6° - (110), 36.4° – (111), 42.3° – (200), 61.4° - (220). Cu (circles): 43.2° – (111), 50.4° – (200). CuO was not detected as a minor phase.
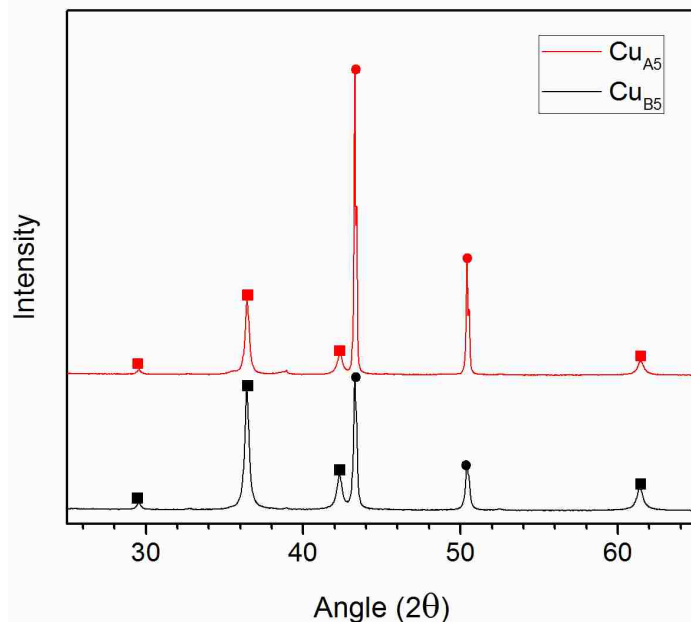
Figure 25. *. XRD patterns of catalysts prepared from 40wt% Cu precursors in 7% (Cu$_{A5}$, red) and 100% H$_2$ (Cu$_{B5}$, black) atmospheres. Cu$_2$O (squares): 29.6° - (110), 36.4° – (111), 42.3° – (200), 61.4° - (220). Cu (circles): 43.2° – (111), 50.4° – (200). CuO is a minor phase included in refinements for the particles reduced in 7% H$_2$, at 4.61 mol%.*

Appendix 3. Confirmation of CO_2 electroreduction on Cu nanoparticles with cyclic voltammetry at 20 mV s^{-1} in N_2 and CO_2 saturated 0.1M $KHCO_3$ solutions.
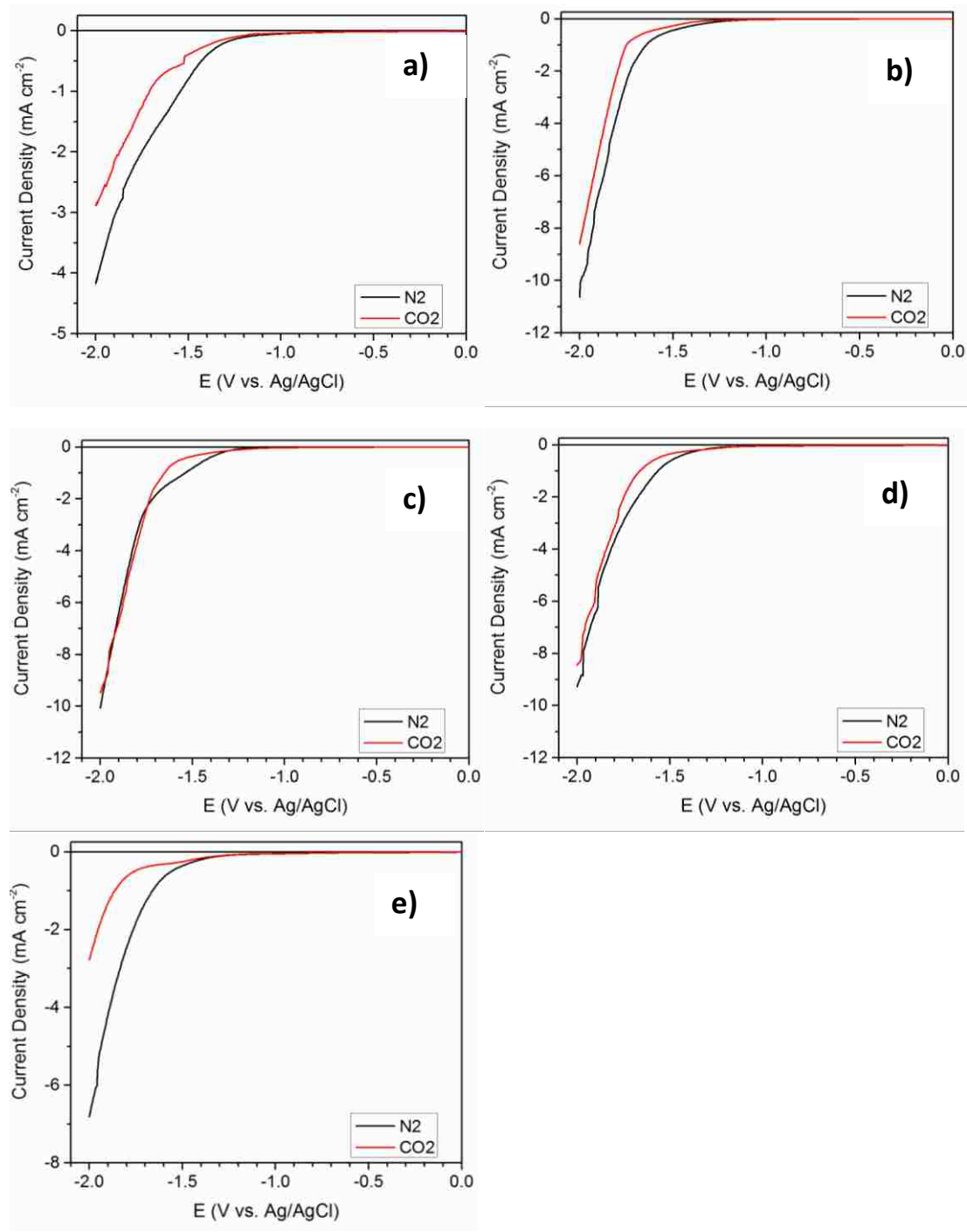
Figure 26. *Confirmation of CER activity by comparison of cathodic voltammograms of Cu nanoparticles reduced at 350 °C in 7% H$_2$. Conditions: N$_2$ or CO$_2$ saturated 0.1M KHCO$_3$, 1600 RPM, 25°C. Particles are as follows: a) Cu$_{A1}$, b) Cu$_{A2}$, c) Cu$_{A3}$, d) 3 Cu$_{A4}$, and e) Cu$_{A5}$.*
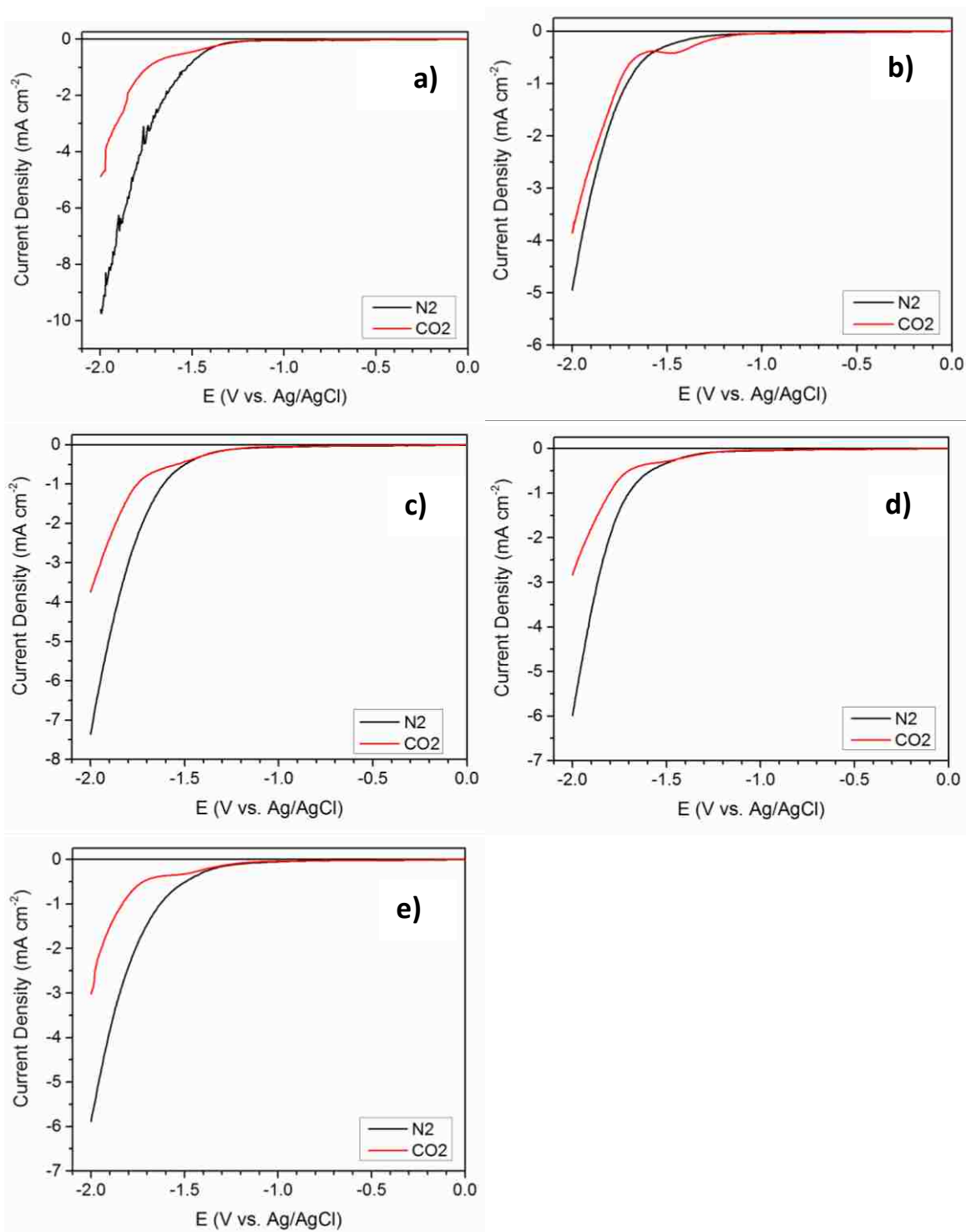
Figure 27. *Confirmation of CER activity by comparison of cathodic voltammograms of Cu nanoparticles reduced at 250°C in 100% H_2. Conditions: N_2 or CO_2 saturated 0.1M KHCO3, 1600 RPM, 25°C. Particles are as follows: a) Cu_{B1}, b) Cu_{B2}, c) Cu_{B3}, d) 3 Cu_{B4}, and e) Cu_{B5}.*

Appendix 4. Bulk electrolysis for carbon dioxide electroreduction of Cu nanoparticles held for one hour at -1.6 and -2.2 V *vs.* Ag/AgCl in 0.1M KHCO₃, without rotation.
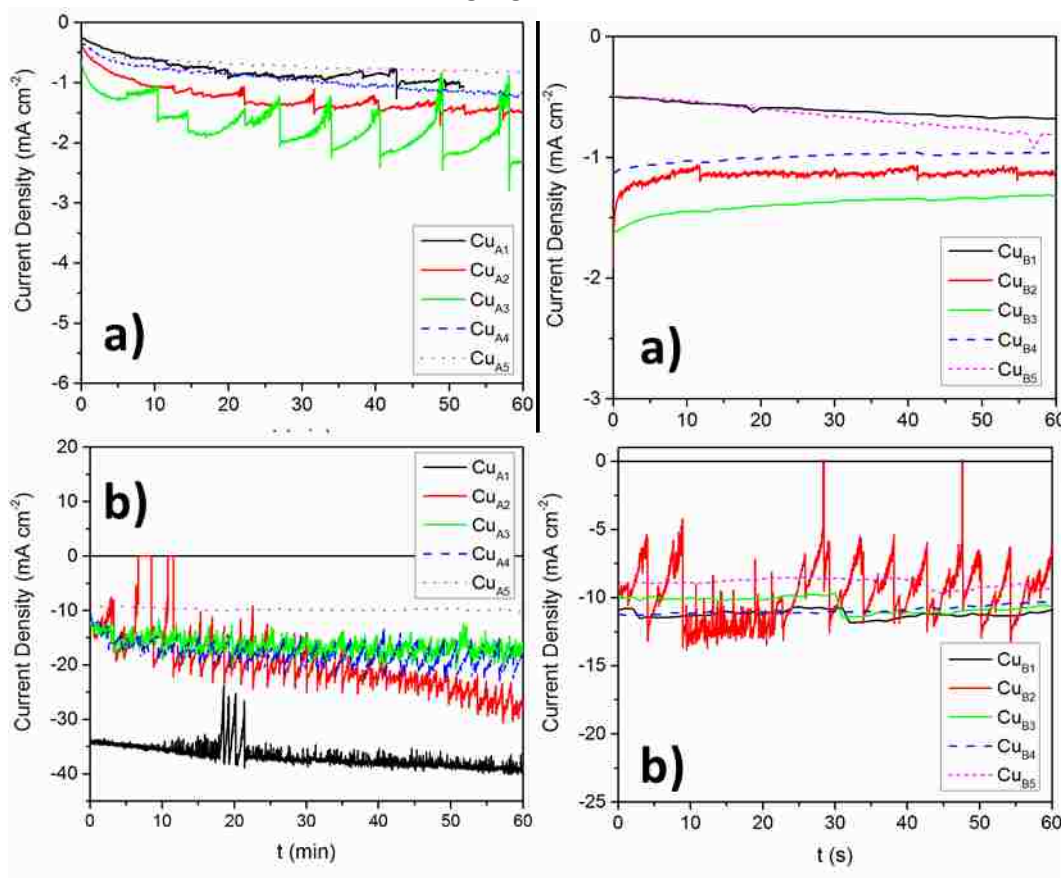
Figure 28. *Bulk electrolysis of Cu_{AX} (X=1-5) particles reduced at 350°C in a 7% H_2 atmosphere at a) -1.6 and at b) -2.2 V vs. Ag/AgCl. Conditions: 0.1 M KHCO₃, 1600 RPM, 25°C. Large spikes in current densities are caused by coverage of the working electrode surface by gas.*

Figure 29. *Bulk electrolysis of Cu_{BX} (X=1-5) particles reduced at 250°C in a 100% H_2 atmosphere at a) -1.6 and at b) -2.2 V vs. Ag/AgCl. Conditions: 0.1 M KHCO₃, 1600 RPM, 25°C. Large spikes in current densities are caused by coverage of the working electrode surface by gas.*

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