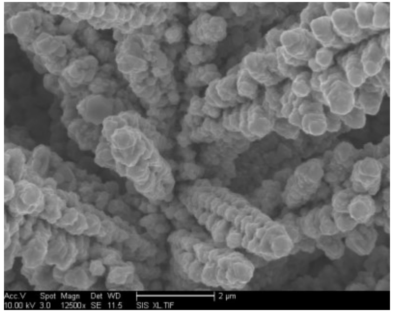
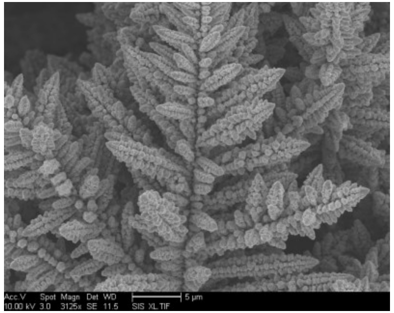
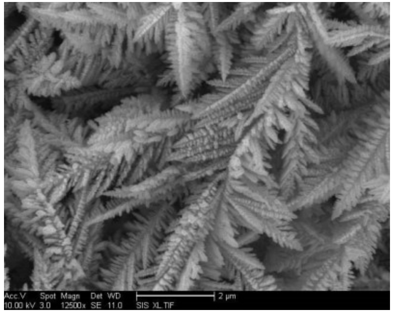
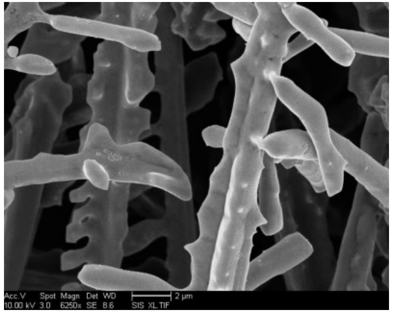


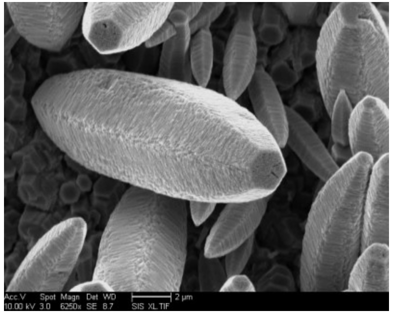


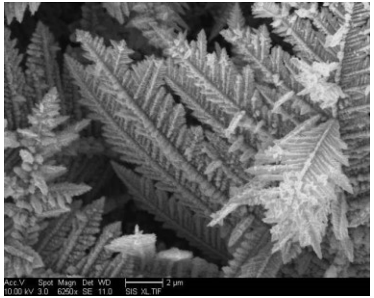


CO_2 Reduction on Nanoporous Copper Alloys

Jeffrey Whitridge, Mitchell Leers, Tyler Lindow



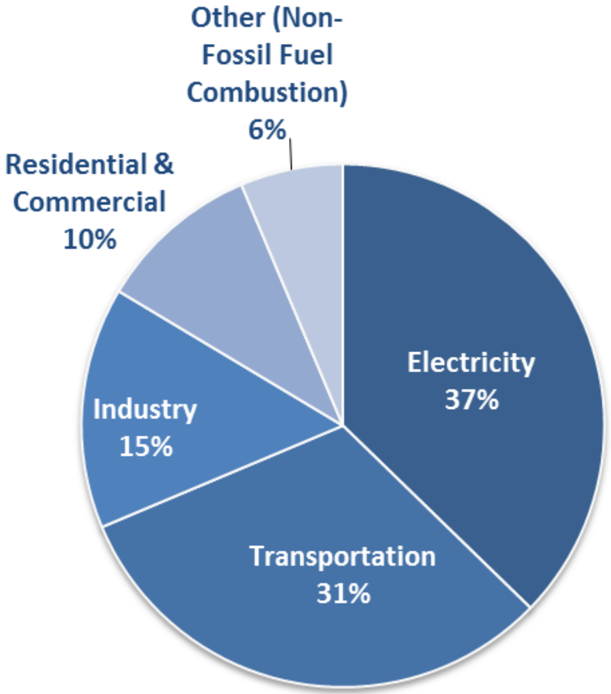




Motivation

1. CO_2 is a major greenhouse gas.

2. CO_2 can be recycled via reduction with copper by converting CO_2 to a variety of useful hydrocarbons fuels.



Overview of Geenhouse Gases: Carbon Dioxide, www.epa.gov/climatechange/ghgemissions/gases/co2.html

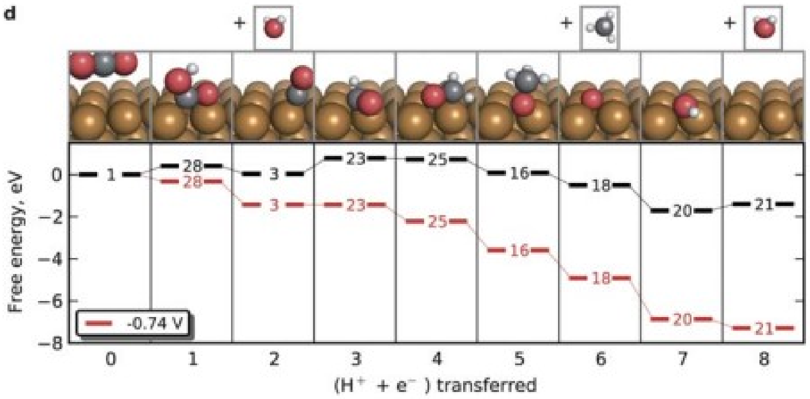
Note: All emission estimates from the *[Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2014]*.

Jeff

Background

Copper is the best known reduction agent for CO_2 because it is the most thermodynamically favorable at transferring protons from solution to substrate

Copper orients CO_2 in order to reduce it more readily.



“How copper catalyzes the electroreduction of copper dioxide into hydrocarbon fuels” Peterson et. al.

Jeff

Background cont.

Copper orients CO_2 in order to reduce it into different forms

- Multiple pathways allow for the conversion into several hydrocarbon products:

$$2H^+ + 2e^- \rightleftarrows H_2 \quad E_0 = 0.0\ \text{V vs. SHE} \tag{1}$$

$$2CO_2 + 12H^+ + 12e^- \rightleftarrows C_2H_4 + 4H_2O \quad E_0 = 0.079\ \text{V vs. SHE} \tag{2}$$

$$CO_2 + 8H^+ + 8e^- \rightleftarrows CH_4 + 2H_2O \quad E_0 = 0.169\ \text{V vs. SHE} \tag{3}$$

$$CO_2 + 2H^+ + 2e^- \rightleftarrows CO + H_2O \quad E_0 = -0.103\ \text{V vs. SHE} \tag{4}$$

$$CO_2 + H^+ + 2e^- \rightleftarrows HCOO^- \quad E_0 = -0.225\ \text{V vs. SHE} \tag{5}$$

Product	# e⁻	E	Product	# e⁻	E
Formate	2	−0.02	Acetaldehyde	10	0.05
Carbon monoxide	2	−0.10	Ethanol	12	0.09
Methanol (CH_3OH)	6	0.03	Ethylene	12	0.08
Glyoxal	6	−0.16	Hydroxyacetone	14	0.46
Methane (CH_4)	8	0.17	Acetone	16	−0.14
Acetate	8	−0.26	Allyl alcohol	16	0.11
Glycolaldehyde	8	−0.03	Propionaldehyde	16	0.14
Ethylene glycol	10	0.20	1-Propanol	18	0.21

Kuhl et. al, 2012

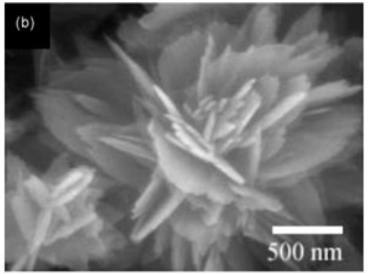
Jeff

Background cont.

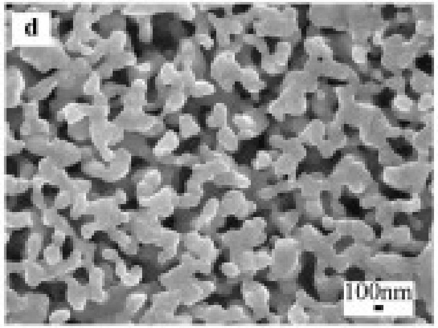
Fabrication nanostructures (various methods) can further increase efficiency and/or selectivity of conversion.

a. Increased surface area

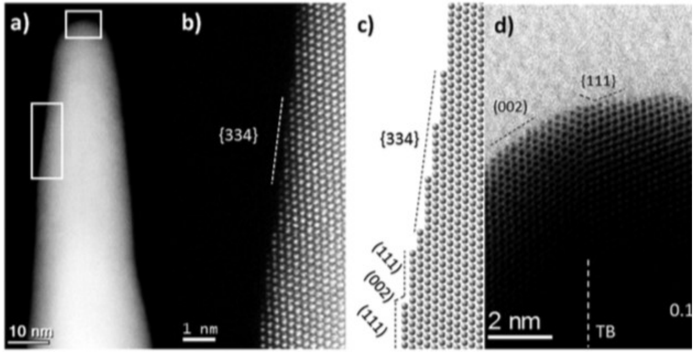
b. Exposed higher order/energy surface plar



Etched nano-flower
Xiang et. al, 2008



Dealloying of Al-Cu
Qi et. al, 2009



HAADF-STEM planes of gold copper nanostars
Bazan-Diaz et. al, 2015

Jeff

Project Design & Methodology

Project Design: Thought Process

Aimed to use **electrodeposition** to deposit several metals (Zn, Sn, Cu, Ni) to increase CO_2 reduction product formation selectivity.

CO_2 reduction involving never before used alloy for this purpose.

Created a design space to test variables for CO_2 reduction.

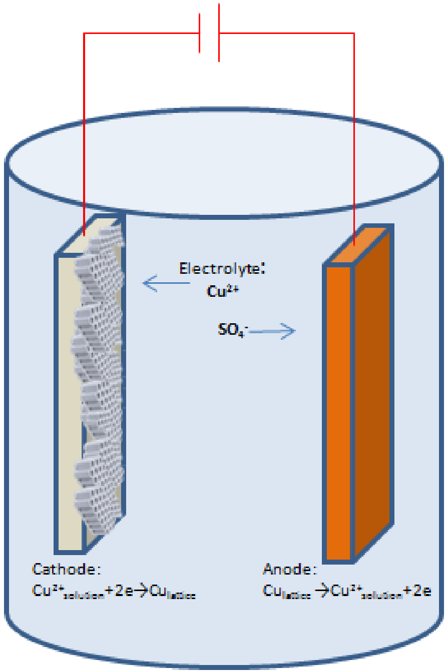
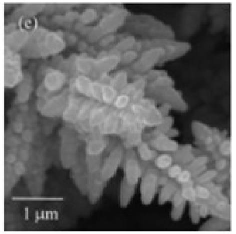


Image:http://ssp.physics.upatras.gr/Electrodeposition.html

Tyler

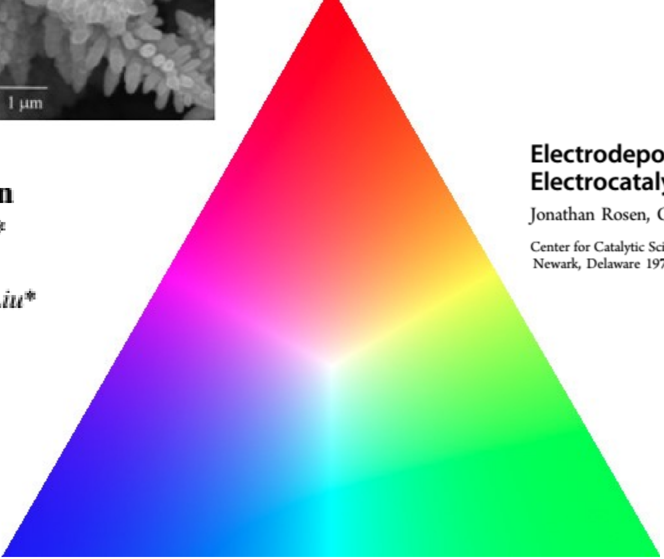
Our Design Space



% Copper

Nanoporous Structures Prepared by an Electrochemical Deposition Process**

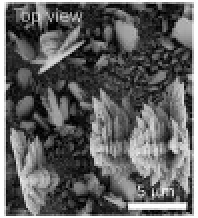
By *Heon-Cheol Shin*, *Jian Dong*, and *Meilin Liu**

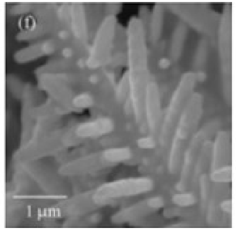


Electrodeposited Zn Dendrites with Enhanced CO Selectivity for Electrocatalytic CO_2 Reduction

Jonathan Rosen, Gregory S. Hutchings, Qi Lu, Robert V. Forest, Alex Moore, and Feng Jiao*

Center for Catalytic Science & Technology (CCST), Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware 19716, United States





% Tin

% Zinc

Tyler

Utilizing High Surface Area Structures: Hydrogen Evolution Negative Template

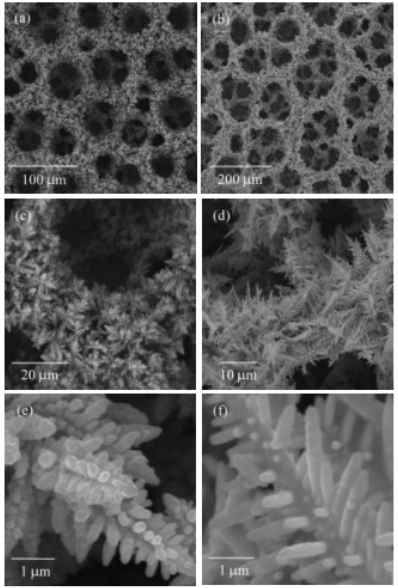
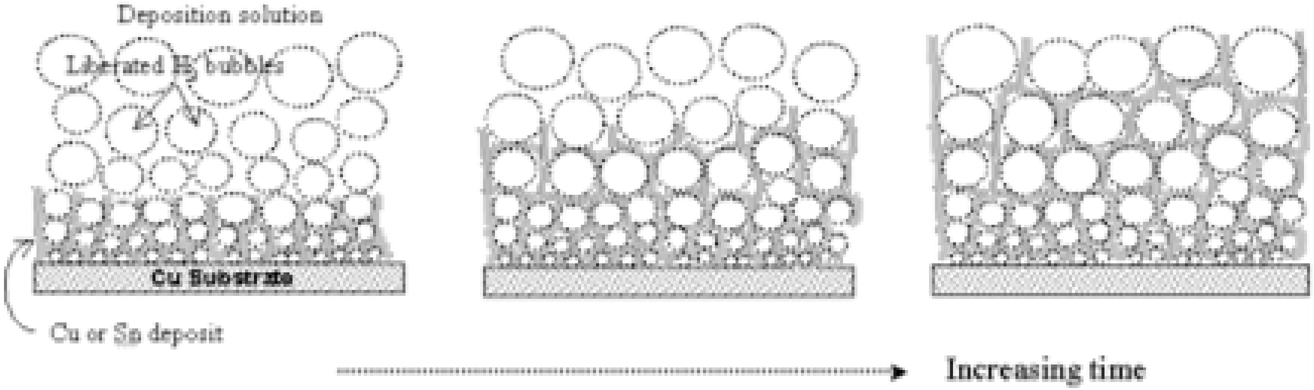


Fig. 3. 3D foam structures of copper (a,c,e), and tin (b,d,f) deposits at different magnifications. The copper and tin foam structures have been prepared by an electrodeposition for 20 s and 5 s, respectively.

Nanoporous Structures Prepared by an Electrochemical Deposition Process**

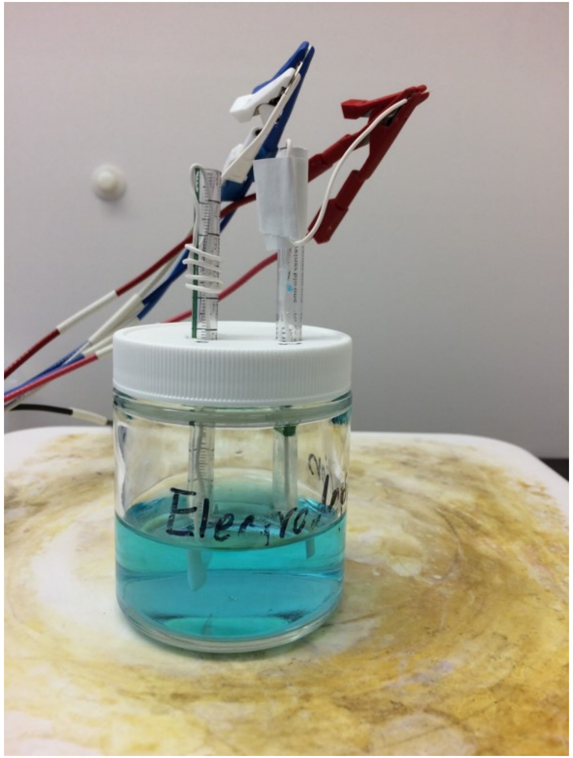
By *Heon-Cheol Shin*, *Jian Dong*, and *Meilin Liu**



Tyler

Methods Summary

1. Fabrication of a two electrode (Pt/Cu) cell
2. Preparation of pure copper sample and platinum electrode
3. Calculation/preparation of metal sulfates (Cu, Sn, or Zn) and sulfuric acid to create electrolyte
4. Calibration of power supply to desired current
5. Electrodeposition of Cu, Zn, and/or Sn for fixed amounts of time or fixed current
6. Wash, dry, store samples for preparation of

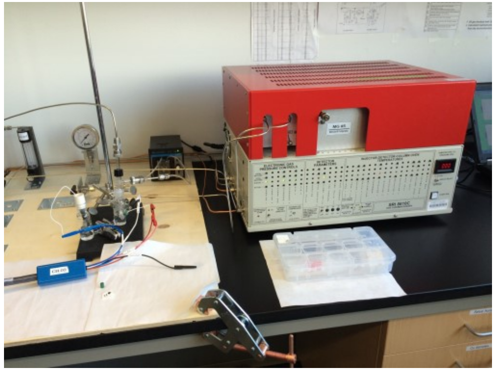


Two electrode (Pt/Cu) cell

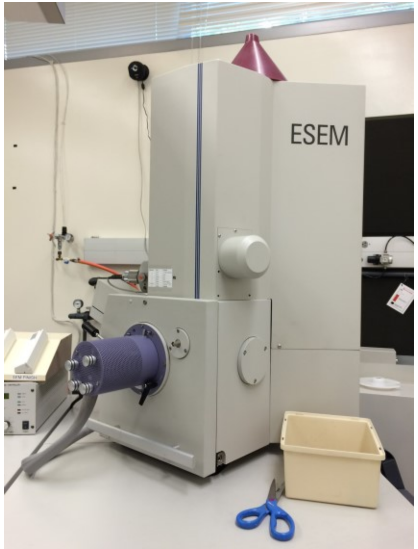
Mitch

Methods cont.

1. Characterization
    a. Qualitative Analysis
        i. SEM/EDX
        ii. Optical Microscope
    b. Quantitative Analysis
        i. UV-VIS Reflectance Spectroscopy
        ii. Optical Microscope
        iii. Faradaic Efficiency
        iv. Gas Chromatography



Gas Chromatograph



ESEM

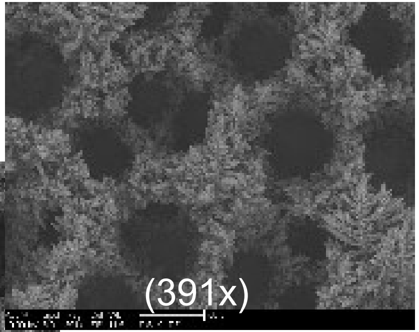
Mitch

Results & Analysis

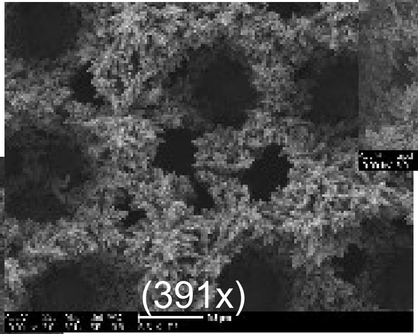
Initial Tests: Copper Deposition On Copper

Increasing Current

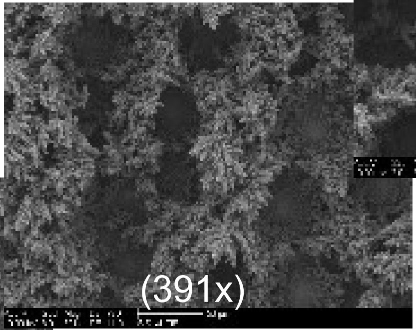
500mA



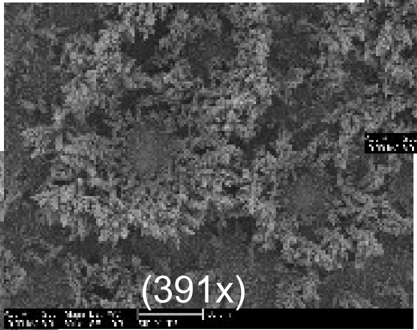
400mA



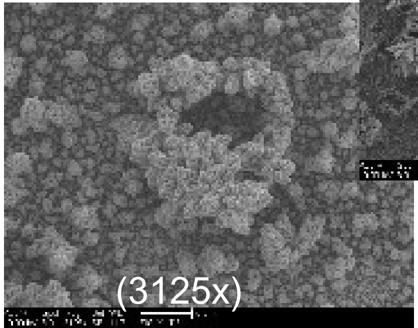
300mA



200mA



100mA

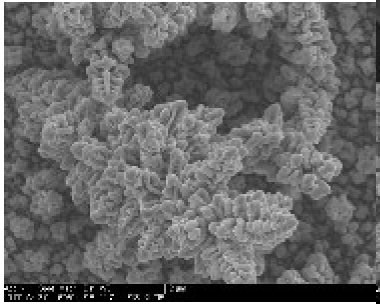


3-D structure dependent on current density

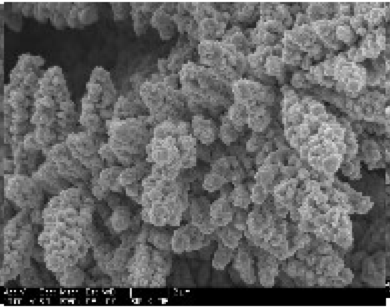
Tyler

Dendritic Copper NanoStructures

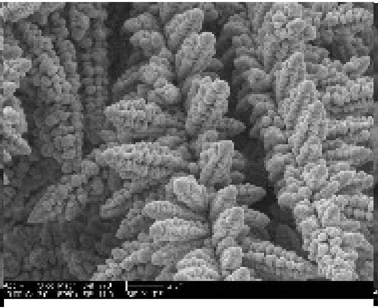
100mA



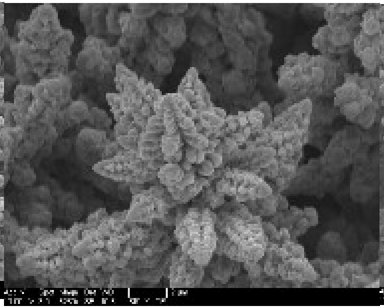
200mA



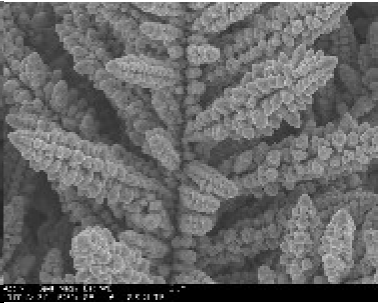
300mA



400mA



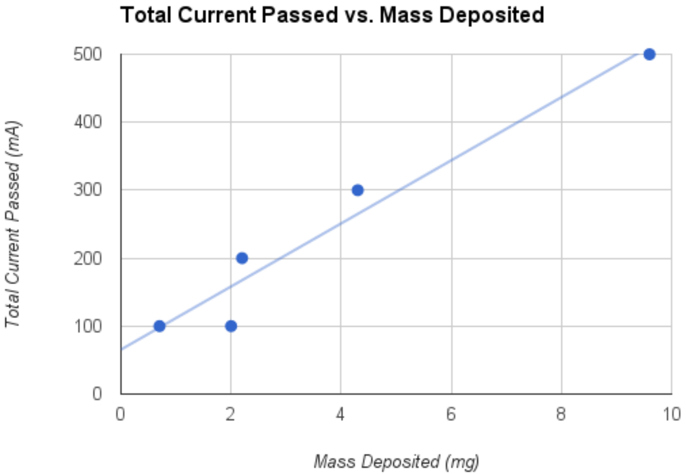
500mA



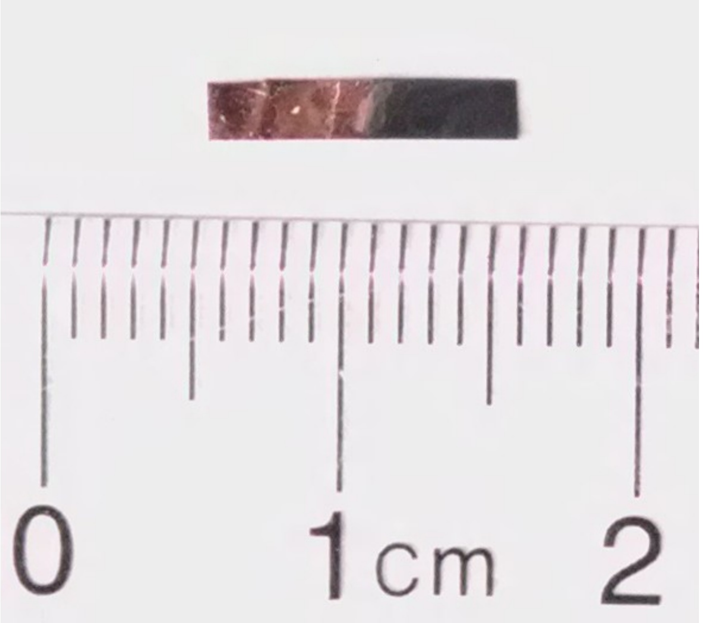
A qualitative look at the dendritic nanostructures across different currents shows little observable differences

Tyler

Mass of Deposition



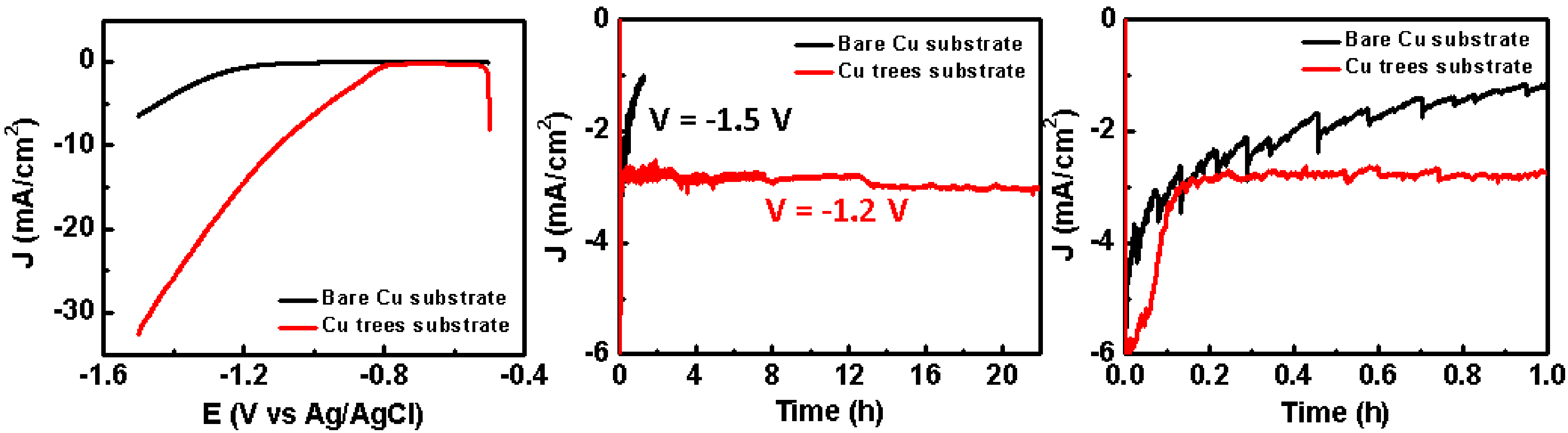
Mass of copper deposited from a copper (II) sulfate electrolytic solution on a copper substrate at different currents.



Scale of samples

Jeff

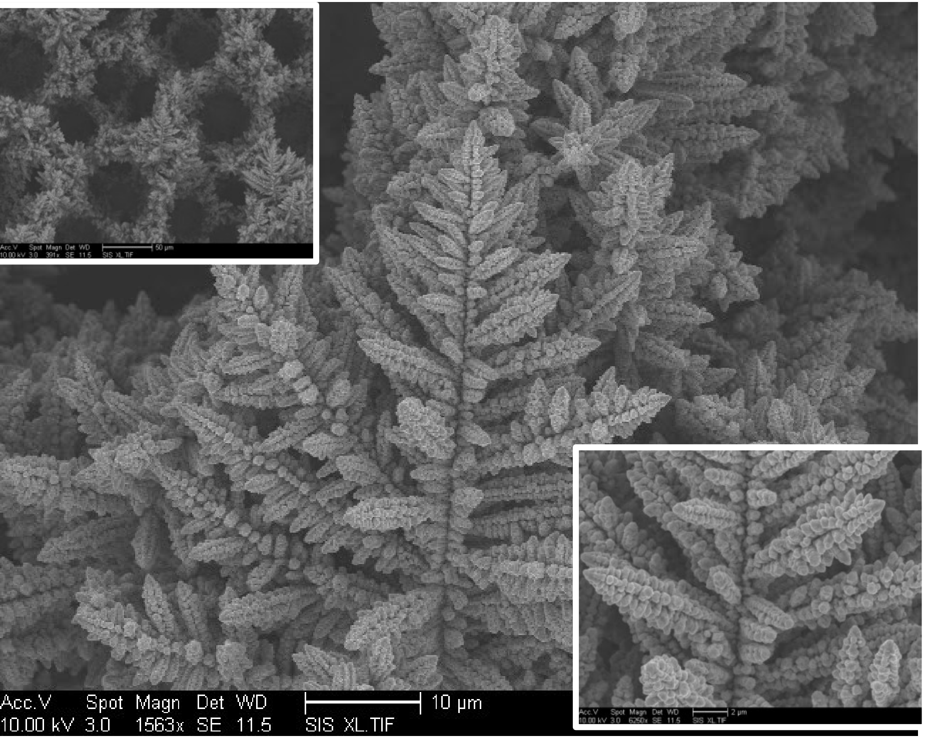
CO_2 Reduction NanoPorous Copper Sample



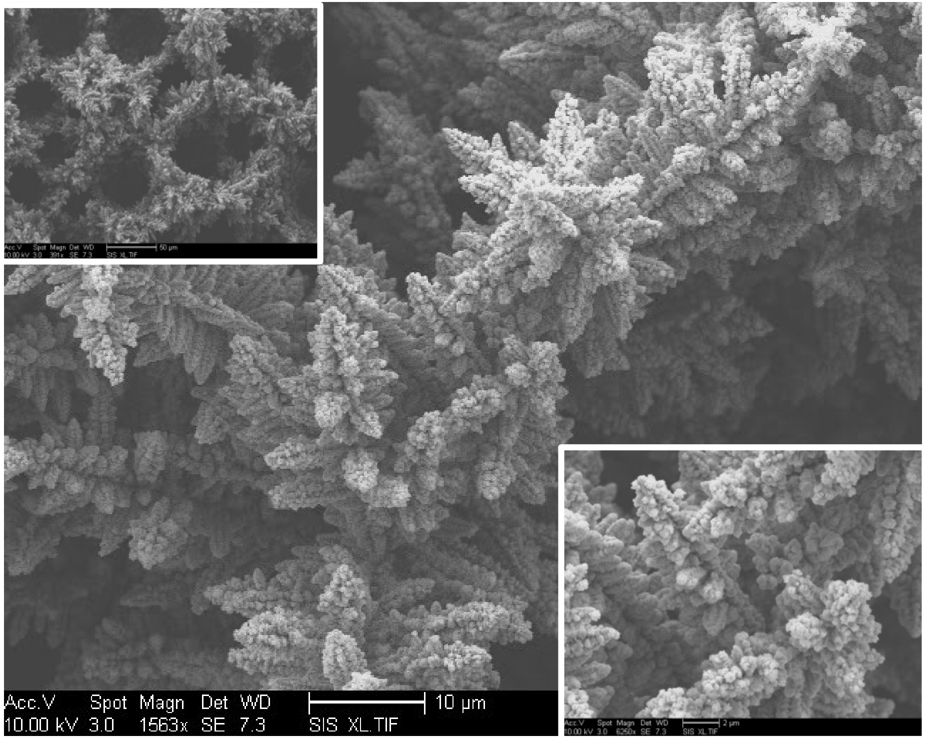
Jeff

Cu #11 - Before and after CO2 Test (6250x zoom)

Before

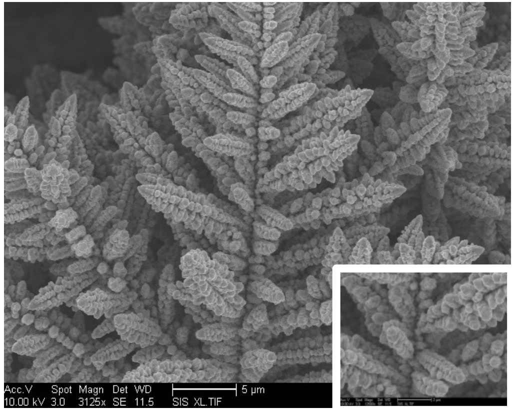


After 4hrs (Degradation/erosion of trees)

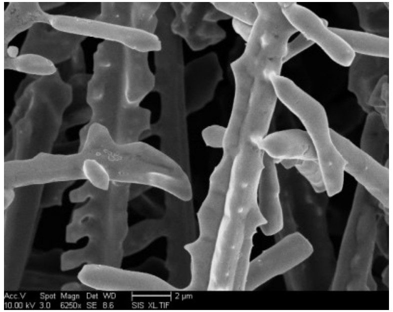


Jeff

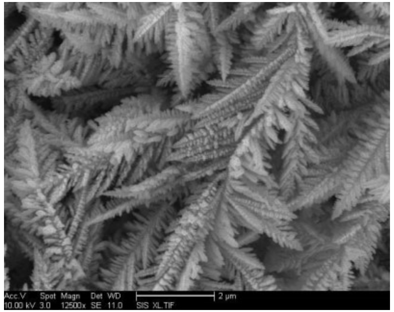
Next Tests: Morphologies of various copper alloys



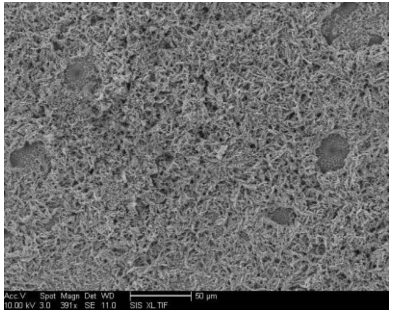
Pure Copper (12,500x)



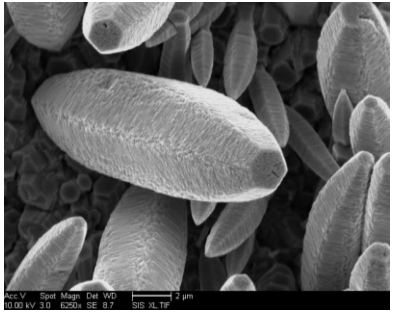
Pure Tin (6250x)



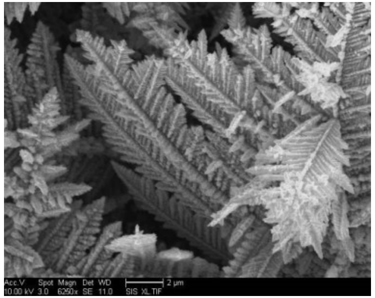
Copper-Tin (12,500x)



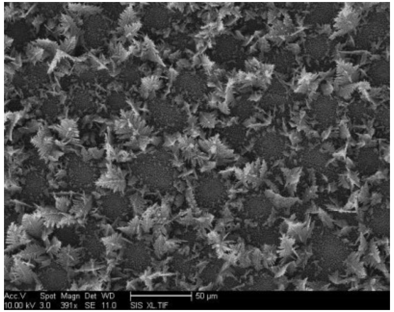
Copper-Tin (391x)



Pure Zinc (6250x)



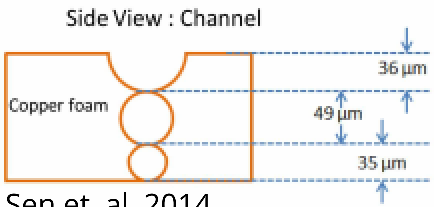
Copper-Zinc (6250x)



Copper-Zinc (391x)

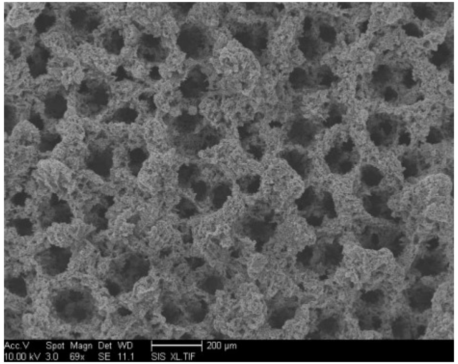
Mitch

Alloy composition vs. pore size



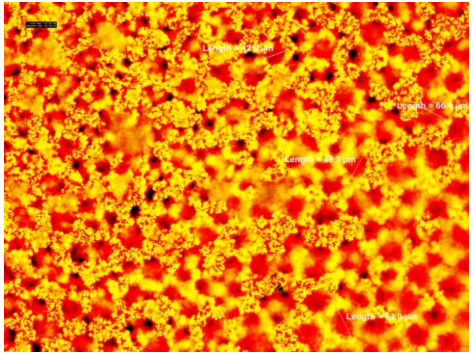
Sen et. al, 2014

391x SEM



Cu-Zn, smaller pores (~.025 - .13 mm)

20x Optical (colorized)



Cu-only, larger pores (~.05-.15mm)

TABLE 17.1 Standard Reduction Potentials at 25 °C

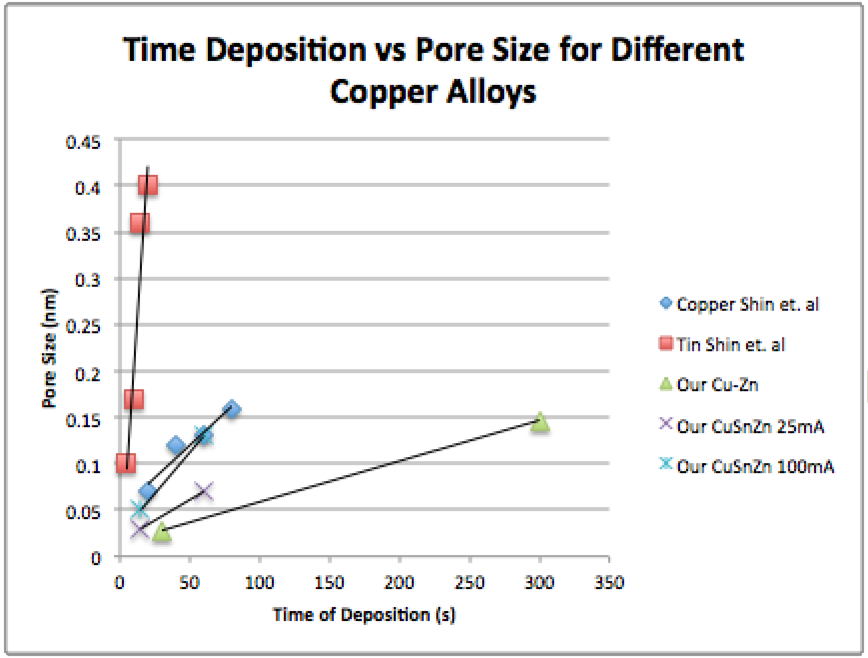
	Reduction Half-Reaction		$E°$ (V)	
Stronger oxidizing agent	$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51	
	$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33	
	$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23	
	$Br_2(aq) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54	
	$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	-0.13	
	$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	-0.26	
	$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	-0.40	
	$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	-0.45	
	$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	-0.76	
	$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	-0.83	
	$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	-1.66	
Weaker oxidizing agent	$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	-2.37	Stronger reducing agent
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	-2.71	
	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	-3.04	

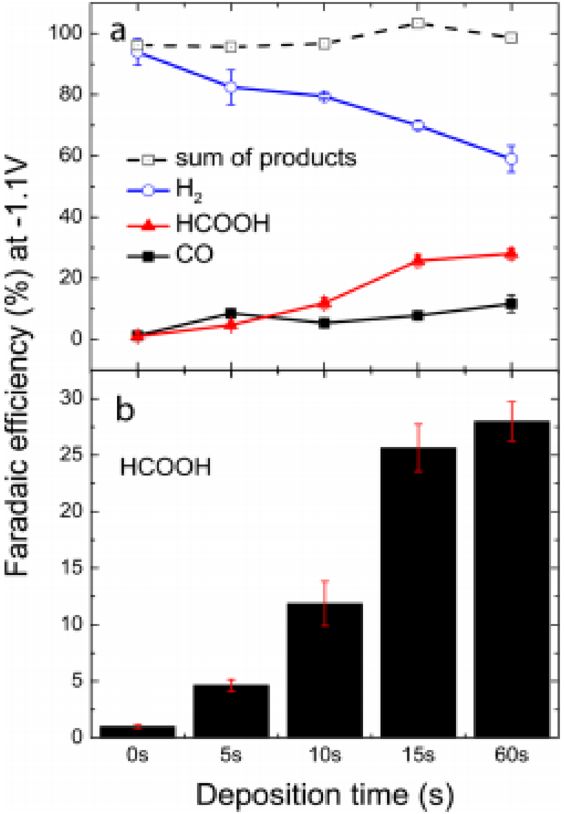
Table 17-1 Chemistry, 5/e

Image:https://www.premedhq.com/reduction-potential-and-cell-potential

Tyler

Tuning Pore Size with Alloy Composition

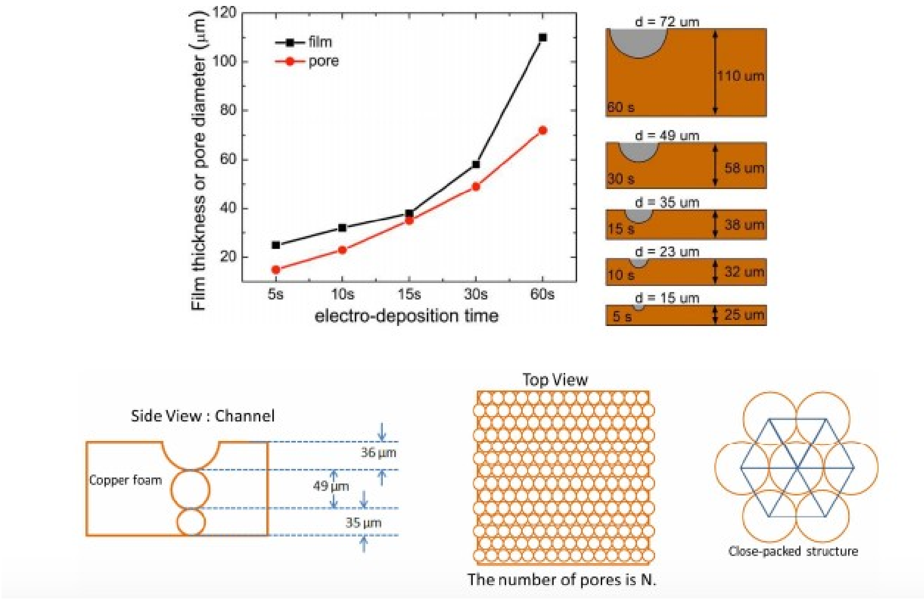




Sen et. al, 2014

Tyler

Using Pore Size to Approximate Surface Area



Geometrical surface area approximation using assumption of close packed structure and 3 layer hydrogen bubble template (Sen et. al, 2014)

Using geometrical calculation we find that on a ~0.1cm^2 copper substrate:

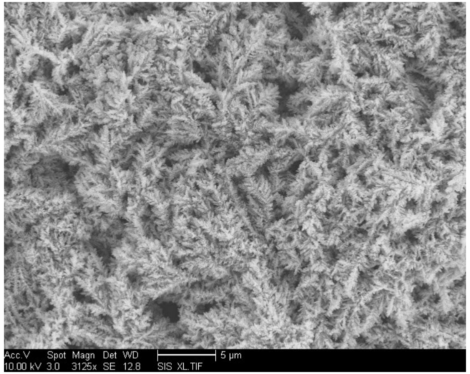
Nanoporous Cu 0.9cm^2 surface area

9x!

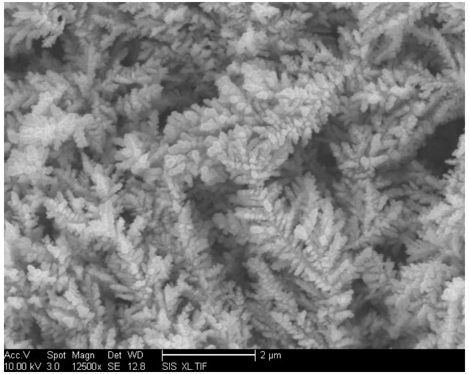
Measurement closely approximate double layer capacitance surface areas (Sen et. al, 2014)

Mitch & Tyler

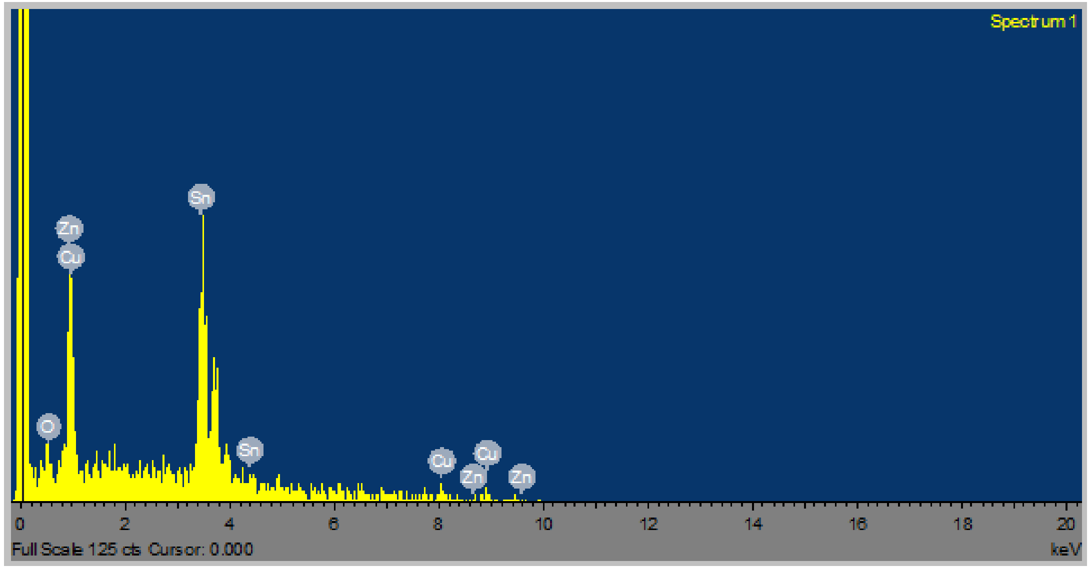
Final Tests: Developing a dendritic Zn-Sn-Cu Alloy



3125x



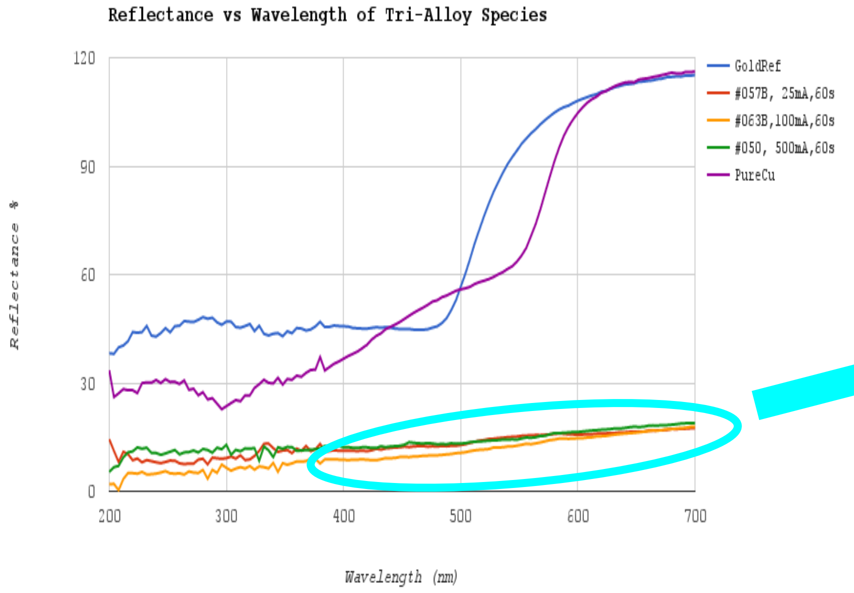
12500x

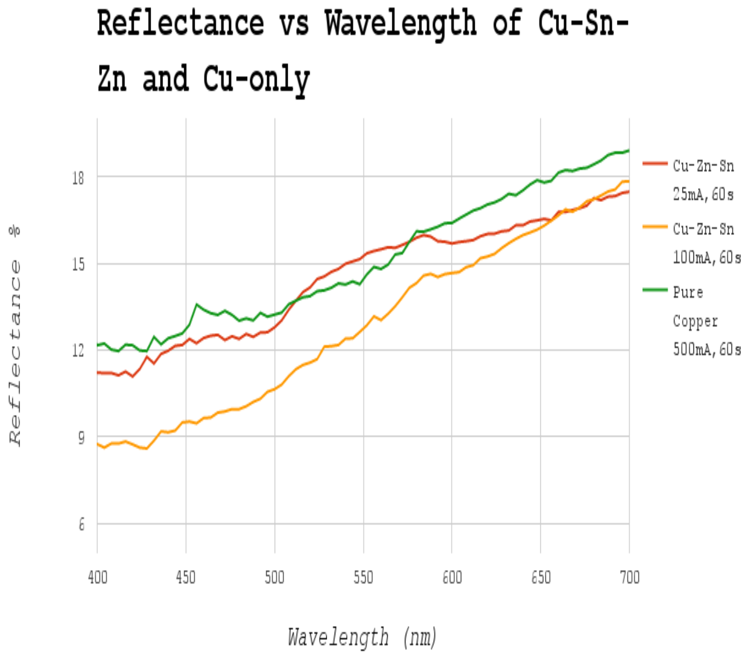


Energy Dispersive X-ray Spectrograph of Cu-Zn-Sn alloy

Mitch

Preliminary Cu-Zn-Sn Tests: UV-VIS Reflectance





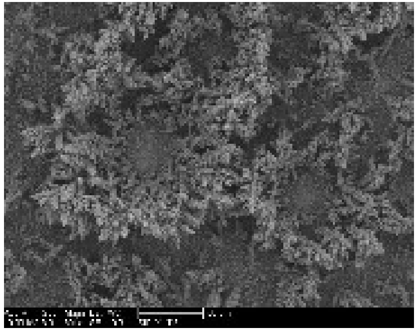
Mitch

Conclusions

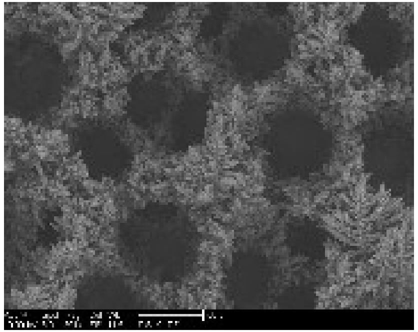
Which samples would we want to run for future CO_2 reduction tests?

Multi-layer hydrogen evolution/3-D porous template

Current density



Cu 100mA 1min

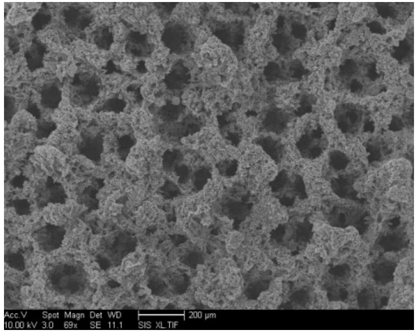


Cu 500mA 1min

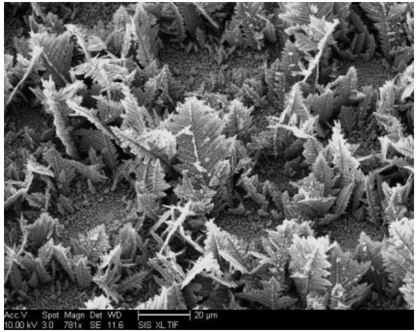
Pore Size/Nanostructure Planes

Time of deposition

Alloy composition



Cu-Zn 200mA 5 min



Cu-Zn 200mA 30s

Tyler

Implications/Future Work

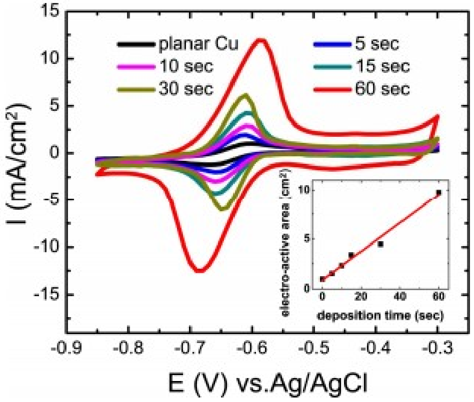
Further testing is necessary for standardization of sample preparation

Account for sources of error in order to gain better measurements of quantitative data

Additional quantitative measurements such as UV - VIS reflectivity, GC, pore size, faradaic efficiency, and DLC to continue defining “best” conditions.

Further controlling nanostructures

Application in a useful CO_2 reduction device



Cyclic Voltammetry - Double Layer Capacitance

- Sen et. al, 2014

Jeff

What were some of our takeaways in doing this project?

Tyler, Mitch, & Jeff

Acknowledgements

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Mentor: Professor, Dr. David Fenning

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- All faculty and TAs involved in NANO 120B

Mitch

Additional References

Hirunsit, Pussana, Wiwaporn Soodsawang, and Jumras Limtrakul. "CO2 Electrochemical Reduction to Methane and Methanol on Copper-Based Alloys: Theoretical Insight." *The Journal of Physical Chemistry C* 119.15 (2015): 8238-8249.

Hori, Yoshio, et al. "Electrocatalytic process of CO selectivity in electrochemical reduction of CO 2 at metal electrodes in aqueous media."*Electrochimica Acta* 39.11 (1994): 1833-1839.

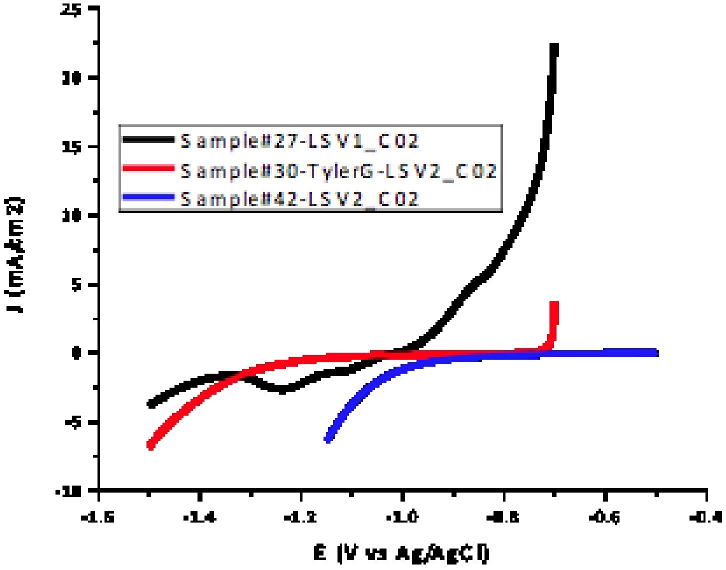
Shin, H-C., and Meilin Liu. "Three-Dimensional Porous Copper–Tin Alloy Electrodes for Rechargeable Lithium Batteries." *Advanced Functional Materials* 15.4 (2005): 582-586.

Thank You!
Questions?

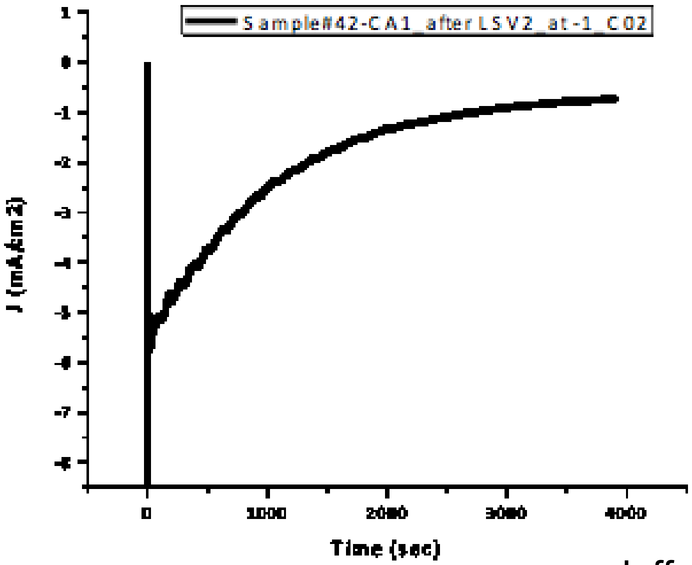
Additional Slides

CO_2 Reduction of Dendritic/Porous Copper Alloys

CO_2 Reduction Efficiency



Stability Test over 1 hour



Jeff