Investigation of Current on Dendritic Copper Growth and the Morphologies of Dendritic Copper Alloys

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A11620225

6/7/16

Summary

This project will look into modifying copper to be able to turn carbon dioxide, a greenhouse gas which contributes to global warming, into useful fuels such as methane. This copper metal will be made through electroplating, a process similar to the way in which chrome plating is made where a metal is submerged in a tub and an electrical current is run through the metal and the liquid to cause another metal to form on the surface of the submerged piece. When this is done to form copper plating, the result is nanoscopic sized pine tree-like structures built up on the surface of the original piece of metal.

The objectives of this project will include determining the shapes of copper which catalyze this process the best by using simulations to study the way carbon dioxide molecules interact with the surface of the copper. Then determining how to create these shapes by experimenting with adding other metals to the copper and by changing the electrical conditions that form the copper structures.

This project will advance knowledge in understanding how the carbon dioxide/copper catalytic interaction works and how to start making use of it. Society will benefit greatly from a new source of clean energy that is produced by capturing carbon dioxide where it is produced by industry, such as in electrical production facilities that burn fossil fuels, and instead recycle it into storable fuels such as methane. While the burning of this methane will convert it back to carbon dioxide and water, the carbon dioxide that will be trapped and converted into methane and kept in storage will no longer be kept as carbon dioxide floating free in the Earth's atmosphere, where it contributes to global warming. Additionally, this project will reduce the United States' dependence on foreign oil and create new jobs, helping the economy.

<u>Purpose</u>

To investigate effects of current on dendritic copper growth and the combination of copper with nickel, tin, and zinc to form new morphologies for use as a catalyst in the reduction of carbon dioxide into hydrocarbons that can be used as fuels.

<u>Background</u>

Copper metal serves as a catalyst for reducing carbon dioxide into useful hydrocarbons which can be used as fuels. The reason for this is not fully understood, however through density functional theory (DFT) simulations, approximations can be made for the electric potentials of the onset of product formation.[1] It is understood that this process is driven by the interaction of the CO_2 molecules with the copper metal surface at certain crystallographic planes which interact favorably with the atoms of molecules in the solution.

These hydrocarbon products are produced as a result of proton-electron pair exchanges which occur sequentially as a stepped process. One of the main products of interest is methane, which is formed in six steps of proton-electron pair exchanges, not considering the final two exchanges needed to remove the remaining hydroxide as water.

As a negative potential is applied to the system, the evolution of hydrogen gas is the first pathway to open at about -0.4V on the (211) copper surface stepped sites.[1,2] The pathway to methane formation instead does not open until around -1.0V.[2] The evolution of hydrogen gas impedes the the ability to synthesize hydrocarbons since it is the first formation pathway that becomes exergonic and requires the lowest amount of free energy it therefore is readily produced above the -0.4V threshold and occupies much of the proton-electron transfers that occur at the copper surface. The next most energetically favorable product is the evolution of carbon

monoxide gas. Carbon monoxide is not useful as a fuel, however, some studies have been looking into the use of copper to further reduce carbon monoxide into hydrocarbons.[3,4] Since the crystallographic planes of the copper surface are responsible for the formation of certain hydrocarbons, increasing the amount of certain planes is expected to increase the selectivity of certain products over others. One of the main goals in making the carbon dioxide reduction to hydrocarbon fuels process lucrative is to reduce the amount of hydrogen gas evolution as much as possible. This is important because hydrogen gas evolution detracts proton-electron pairs from participating in the formation of the other products of interest. By patterning a bare copper substrate surface with a number of particular crystal planes, a modified copper structure could be synthesized which would show a greater selectivity for certain hydrocarbons.

It is for this reason that the use of dendritic copper surfaces, formed through electrochemical deposition, or electroplating, was investigated for the purpose of increasing the amount of such higher order facets on the copper surface. Previous studies have investigated the use of copper dendrites for CO_2 reduction, however, in this study the effect of electric current on the dendritic structure formation as well as the resulting morphologies of the addition of nickel, tin and zinc to form alloys of copper via the same electrodeposition formation process was explored.

In the electrochemical deposition process, which is used to form the dendritic copper, H_2 gas is needed, unlike CO_2 reduction where H_2 gas is undesirable. The H_2 gas bubbles serve as a negative template in order to produce the pores, as can be seen in Figure 1.

Methods

The electrochemical deposition process was performed in a two electrode electrolytic cell, using a 30mL electrolytic solution. In following off the work of Shin et al.[5] for the preparation of
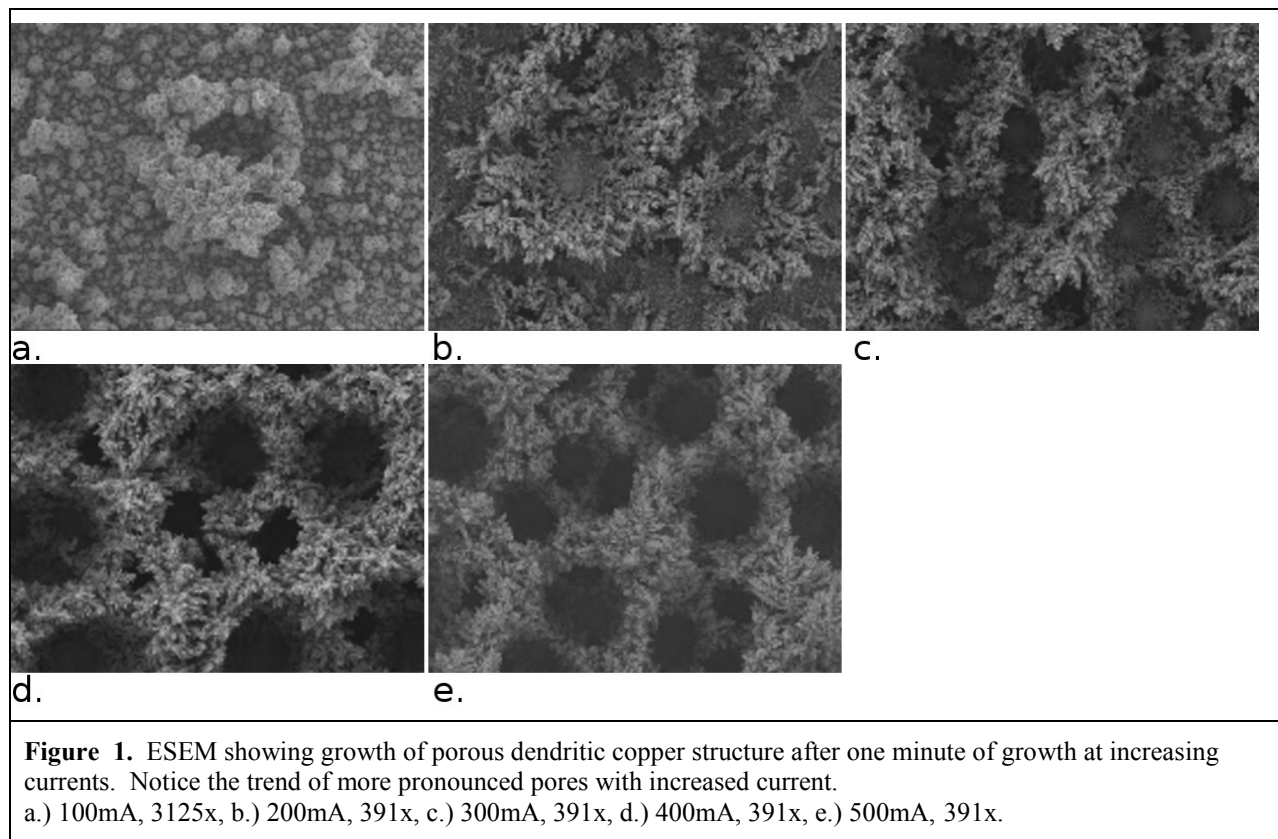
samples containing only copper, a solution of 1.5M sulfuric acid and 0.20M copper(II) sulfate pentahydrate in DI water was used. For the portions of the project where either copper and tin or copper and zinc bi-alloys were synthesized, in following off of Shin et al.[6], a 1.5M sulfuric acid, 0.24M copper(II) sulfate $\cdot 5H_2O$ and either 0.20M tin(II) sulfate $\cdot 7H_2O$ or 0.20M zinc sulfate $\cdot 7H_2O$ in DI water solution was used. For the portion involving copper and nickel, in following off of Jeong et al.[7], a 1.0M sulfuric acid, 0.01M copper(II) sulfate $\cdot 5H_2O$ and nickel(II) sulfate $\cdot 6H_2O$ in DI water solution was used.

The electrolytic cell was made from a small glass jar with a plastic lid. The lid had 2 holes drilled in it, into which two sawed-off plastic pipettes were inserted and held in place by friction alone. These served to insert and fix in place two wires; one into each tube. From one of these wires a 1mm x 5mm x 7.5mm piece of platinum, which would serve as the counter electrode, was soldered onto the end with the solder covered with Loctite® 1C™ Hysol® Epoxi Patch® Adhesive Resin and Hardener. The other wire was connected to an alligator clip used to hold the bare copper sample substrates. These two wires suspended the substrate of the sample and the platinum in the solution a distance of 2cm apart. It was ensured before each run that the copper alligator clip was above the surface of the electrolytic solution and not wetted.
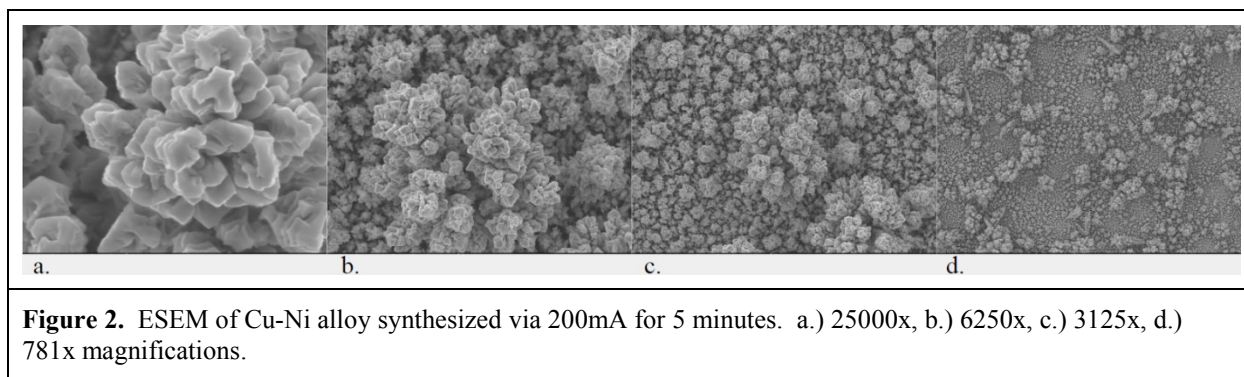
In following Shin et al.[6], electrodeposition was done using constant current, rather than constant voltage. A power supply was preset to the desired current connected to the electrolytic cell setup and a timer was used to know when to shut off the power supply to stop the process.
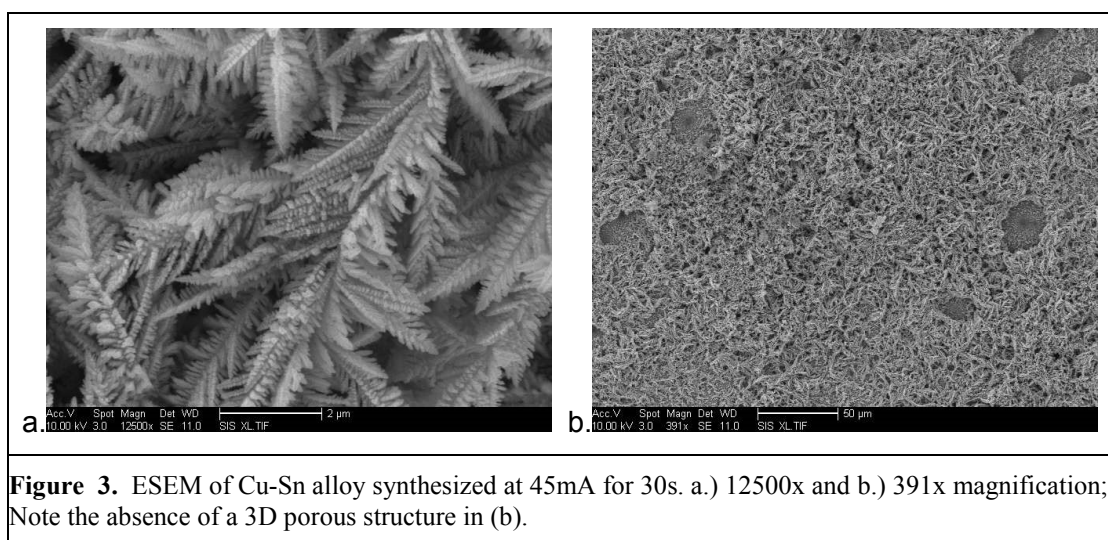
Results

A qualitative analysis via environmental scanning electron microscopy (ESEM) was performed

on select samples to verify dendritic growth.

Figure 1. ESEM showing growth of porous dendritic copper structure after one minute of growth at increasing currents. Notice the trend of more pronounced pores with increased current.
a.) 100mA, 3125x, b.) 200mA, 391x, c.) 300mA, 391x, d.) 400mA, 391x, e.) 500mA, 391x.

In investigation of the effects of current on the resulting dendritic structure, it was found that

when holding growth time constant, at higher currents such as 400 and 500mA, the deposition

was visibly observation to be much thicker and encrusted over substrate, as well as being

mechanically more brittle. Upon ESEM imaging (Figure 1) of the samples it can be seen that the

3D porous structure of the dendrites increases with increased current and that the pores become

more pronounced as more layers of them are formed as the thickness increases. Further study

could be done into examining thickness of growth as a function of growth time and current.

Figure 2. ESEM of Cu-Ni alloy synthesized via 200mA for 5 minutes. a.) 25000x, b.) 6250x, c.) 3125x, d.) 781x magnifications.

The copper-nickel alloys resulted in morphologies resembling succulent plants (Figure 2) rather than the pine tree-like structures formed by copper. None of the copper-nickel alloys tested with energy dispersive x-ray spectroscopy (EDX) results showed the presence of nickel. It was later found that this was due to the fact that we had deviated from Jeong et al.[7] by using nickel(II) sulfate hexahydrate, rather than nickel(II) chloride hexahydrate, as the chloride ion plays a significant role in facilitating the deposition of nickel onto copper.

Figure 3. ESEM of Cu-Sn alloy synthesized at 45mA for 30s. a.) 12500x and b.) 391x magnification; Note the absence of a 3D porous structure in (b).

The copper-tin alloys (Figure 3) showed dendritic structures similar to copper, however, the presence of tin was found to cause the structure to have a more drooping morphology than the pure copper, resembling fern leaves. It was noted however that the copper-tin alloys required lower currents and time for synthesis, however failed to produce a 3D structure. When run at 200mA for 40s it produced a visibly black and thickly caked sample which was very brittle.
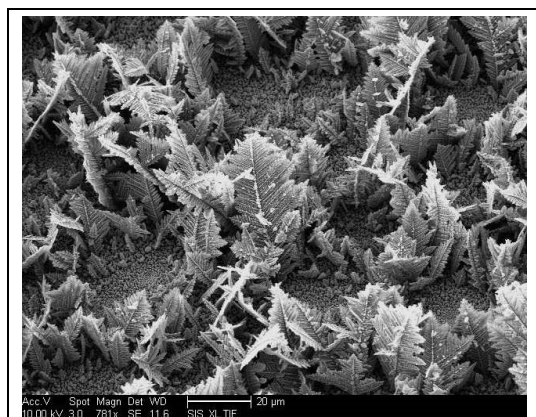
Figure 4. ESEM of Cu-Zn alloy synthesized at 200mA for 30s, 781x magnification.

Less brittle but much thinner samples were produced by using substantially lower currents such as the sample shown in Figure 3 synthesized at 45mA for only 30s.
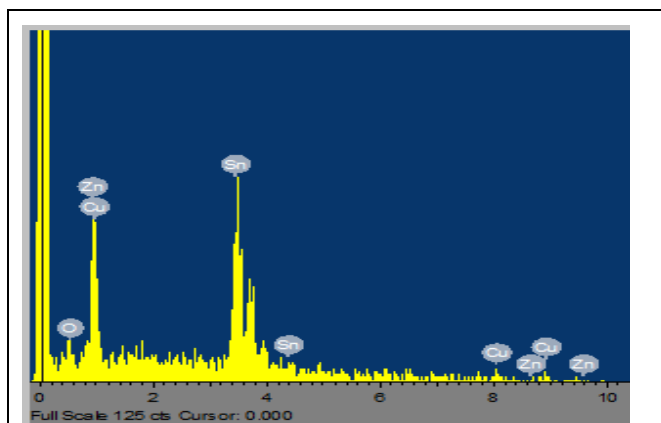
In contrast to the copper-tin alloys, the copper-zinc alloys instead had the opposite effect, creating a more erect and sharp morphology (Figure 4).
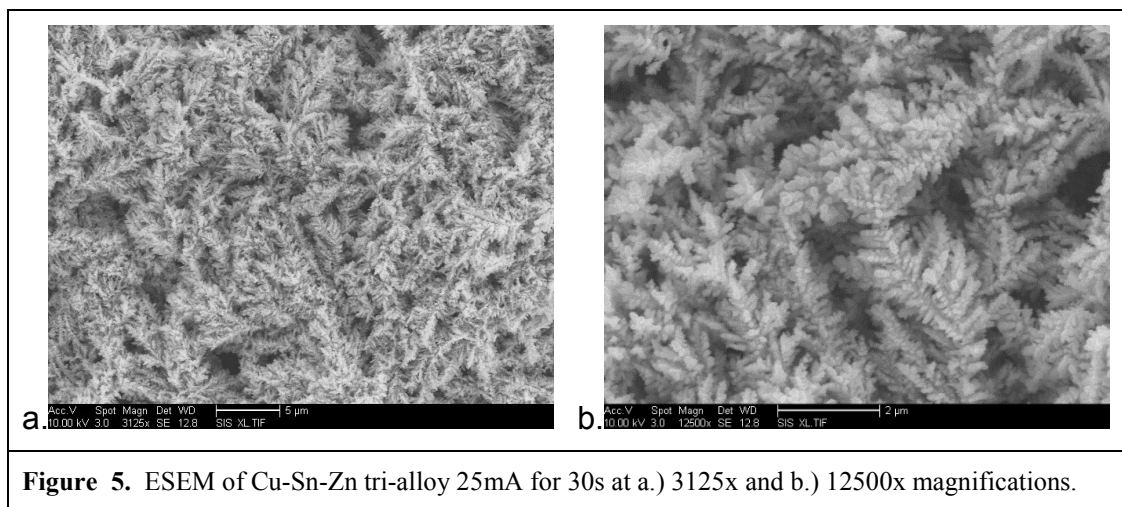
Figure 5. ESEM of Cu-Sn-Zn tri-alloy 25mA for 30s at a.) 3125x and b.) 12500x magnifications.

The Cu-Sn-Zn tri-alloy (Figure 5) showed a combination of the Cu-Sn and Cu-Zn alloys to a varying degree, resembling the Cu-Sn more than the Cu-Zn. Further time is required to investigate, using EDX or XRD, to determine the composition of the three metals in the alloy as a function of the concentration of the sulfates in the electrolytic solution used, the growth time allowed, and the current used. Figure 6 shows the EDX of the sample shown in Figure 5, where it can be seen that the presence of all three metals was successfully detected in the sample.

Figure 6. EDX of Cu-Sn-Zn tri-alloy shown in Figure 5 above. Note the presence of all three metals detected.
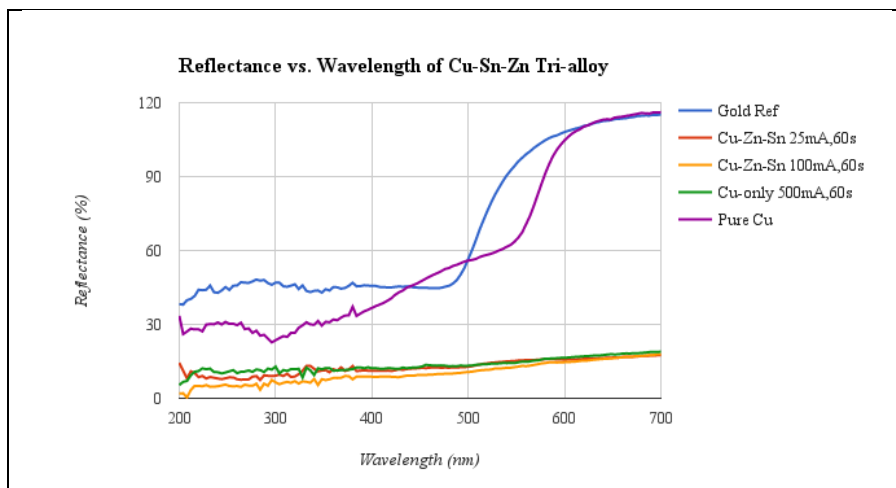
Figure 7. Graph of Reflectance vs. wavelength for the Cu-Sn-Zn tri-alloy when synthesized at 25, 100, and 500 mA, as well as the results of a gold reference used for initial calibration and a pure bare copper sample.

The reflectance measurements shown in Figure 7 show that the samples indeed have altered surface morphology which absorbs a great amount of the light incident upon it as compared with an unmodified sample.

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Conclusions

The ESEM assisted in confirming a positive correlation between electric current and growth of the 3D dendritic porous structure. The addition of other metals to form alloys of copper to enhance CO_2 reduction requires further investigation which was not possible due to unforeseen technical problems with getting the gas chromatograph to work properly.

Based on the range of these morphologies produced in this study, it is evident that there is great room for further investigation into the chemistry which governs their formation. Because of SEM becoming more commonly available at universities and in industry in recent years, it can be expected that research in this field of study will continue to grow.

References

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