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1. REPORT DATE (DD-MM-YYYY) 02/23/2011		2. REPORT TYPE Final		3. DATES COVERED (From - To) 1/30/2009-1/30/2011	
4. TITLE AND SUBTITLE Surface Chemistry and Tribology of Copper Surfaces in Carbon Dioxide and Water Vapor Environments				5a. CONTRACT NUMBER N00014-09-1-0595	
				5b. GRANT NUMBER CFDA 12.300	
				5c. PROGRAM ELEMENT NUMBER Modification A00001	
6. AUTHOR(S) Miquel Salmeron				5d. PROJECT NUMBER 10PR05200-00	
				5e. TASK NUMBER CAGE 50853	
				5f. WORK UNIT NUMBER EDI/EFT 6164AH	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of California, Berkeley Engineering Research Support Organization 558 Cory Hall Berkeley, CA 94704-5940				8. PERFORMING ORGANIZATION REPORT NUMBER 24884-23845-44-EJMBS	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) University of California, Berkeley Sponsored Projects Office 2150 Shattuck Ave, Room 313 Berkeley, CA 94704				10. SPONSOR/MONITOR'S ACRONYM(S) SPO	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) 026977-003	
12. DISTRIBUTION/AVAILABILITY STATEMENT					
<h1>20110316015</h1>					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT By combining several in situ techniques, the surface chemistry of Cu and its related oxide surfaces have been systematically investigated under ambient and aqueous conditions. Using the state-of-the-art ambient pressure X-ray spectroscopy (AP-XPS), we have revealed that metallic copper, cuprous oxide (Cu ₂ O) and cupric oxide (CuO) exhibit strikingly different behaviors with regard to water (H ₂ O) and carbon dioxide (CO ₂) adsorption in the presence of 0.5 Torr of gases. A novel in situ liquid X-ray absorption spectroscopic technique (XAS) has been developed to real time monitor the corrosion processes of Cu films in bicarbonate solution.					
15. SUBJECT TERMS In situ techniques, Cu corrosion, Cu oxide, tribology, electrochemistry, XPS, XAS, QCM, AFM, STM					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Theresa Short
U	U	U	UU	1	19b. TELEPHONE NUMBER (Include area code) 510-486-4886



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Contract Information

Contract Number	N00014-09-1-0595
Title of Research	Surface Chemistry and Tribology of Copper Surfaces in Carbon Dioxide and Water Vapor environments
Principal Investigator	Miquel Salmeron
Organization	University of California, Berkeley

Technical Section

Technical Objectives

Engineering reports state that the copper brushes in the superconducting homopolar motor experience wear at rates greater than 3×10^{-11} wear /distance traveled when biased positively. It has been found the motor operates best in an atmosphere of carbon dioxide and water vapor. The objective of our research therefore is provide the basic science to understand the phenomena involved in the detrimental wear of the electrodes so that engineering solutions can be found for improved designs. To that effect we investigate the chemical nature of Cu surfaces in the presence of water and CO₂ during the passage of electrical current with the goal to correlate it with the friction and wear properties.

Specific objectives for this year include:

- 1) Determination of the structure and thickness of water layers on several of the Cu oxides that were identified in the past cycle using our unique ambient pressure x-ray photoelectron spectroscopy apparatus (APPES). In the past year we studied the adsorption of water on Cu₂O. This year we extend this study to the adsorption on other Cu substrates that were found to be present under different electrochemical potentials:
 - a. Cu metal with one chemisorbed O layer (present at negative bias)
 - b. Cu₂O (present near zero and slightly positive bias). While this was studied last year, additional experiments will be carried out for comparison with the other Cu substrates under identical conditions.
 - c. CuO (present at positive bias)
- 2) Continue our investigation of the electrochemical modifications of Cu under potentiostat control and solution pH
- 3) Determine the loss of mass of Cu when in carbonate containing solutions under different bias potentials
- 4) Use Scanning Tunneling Microscopy to obtain a detailed molecular level understanding of the water structure in thin films and its dissociation to OH, H and O that result in oxidation of the Cu.

Technical Approach

To achieve our goals we will exploit the unique analytical capabilities developed in my laboratory. These include:

(a) *in situ* X-ray photoelectron spectroscopy (XPS) to provide chemical fingerprinting of the surface species and to measure the amount of liquid water condensed on the Cu contacts while in the presence of gases. There is no other electron spectroscopy that can do this currently.

(b) *in situ* X-ray absorption spectroscopy (XAS) of Cu in aqueous environments with bicarbonate ions that mimic the conditions of the wet brush-rotor contact. Electrochemical control of the surface by cyclic voltammetry makes it possible to prepare different chemical states of the Cu, as those produced in the motor electrodes under positive and negative bias. *In situ* XAS spectroscopy is a unique developed in my laboratory during the last year that allows us to unambiguously determine the chemical state of the Cu surface at each surface potential.

(c) tribological studies in wet CO₂ environments using atomic force microscopy (AFM). Our AFM apparatus permits measurement of friction in CO₂ and water vapor environments while passing current between the AFM tip and the Cu surface.

(d) Quartz crystal microbalance in an electrochemical cell for direct measurement of the loss or gain of mass of Cu as a function of bias and solution carbonate concentration.

(e) Scanning Tunneling Microscopy (STM) to obtain atomically resolved images of the surfaces: clean, with chemisorbed oxygen and CO₂, and oxidized.

Progress Statement Summary

- In 2010 we have studied the structures formed by water on surfaces of Cu metal (state of electrodes under negative bias, see below), cuprous oxide (Cu₂O, formed under zero or small positive voltages), and cupric oxide (CuO, at positive bias voltages of +100 mV and above). With XPS in our APPEs we have determined the hydroxilation state of the various surfaces in the presence of 0.5 Torr of water at room temperature (in progress).
- Simultaneous XAS and cyclic voltammetry of Cu in bicarbonate solutions under potentiostatic control at the Berkeley Synchrotron facility (Figure 1). Paper written and published in *Electrochemistry Communications* 12, 820 (2010) last April.
- We measured the changes of mass of Cu electrodes as a function of bias potential in bicarbonate solutions using a quartz crystal microbalance in an electrochemical cell. We found that while there is no measurable loss of mass at negative bias, from -100 mV to more positive voltages there is a rapid increase in mass loss due to dissolution of Cu⁺ ions. The rate saturates at approximately 1 mm/year at +100 mV. This result is highly significant due to its direct bearing on the observed wear of positive motor brushes.
- Using STM we have characterized the molecular structure of the first wetting layer on Cu metal. We are planning to continue using STM to characterize the structures on other Cu surfaces and oxidation states.

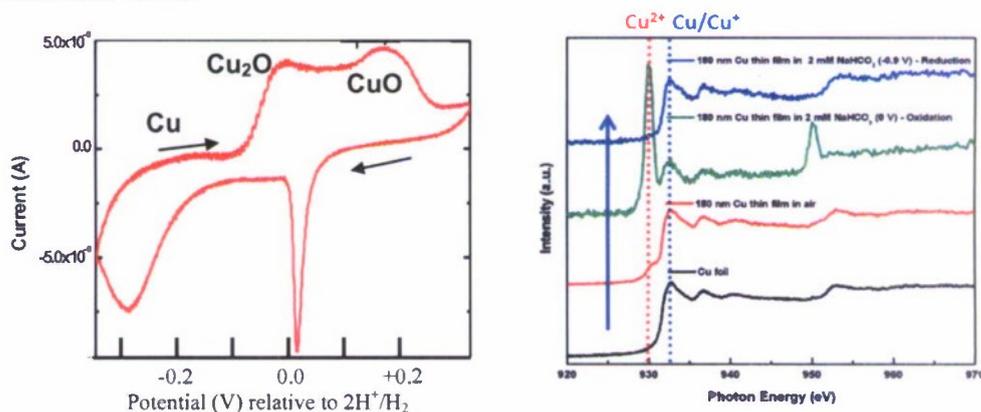


Figure 1. (Reported in Dec. 2009). Left: Cyclic voltammogram of a Cu film on the *in situ* electrochemical cell in 0.1 M solution of NaHCO₃. The voltage was measured with a Ag reference wire and then converted to the standard 2H⁺/H₂ reference electrode. Right: Simultaneously x-ray absorption spectra showing the oxidation state of Cu during the cycling

Progress

Water on Cu surfaces at different oxidation states

In previous cycles of this project we used *in situ* XPS to determine the nature of the surface species formed on Cu and Cu₂O exposed to water and CO₂. These species include hydroxyl (OH) groups, carbonate species (CO₃) and chemisorbed CO₂. Last year we have shown, using another *in situ* technique, XAS in an electrochemical cell that, in addition to Cu₂O, which is present at zero or small positive bias, at negative electrode bias Cu is in the metallic state and, at positive bias larger than 100 mV, in the form of cupric oxide (CuO). This is shown in figure 1.

Since January of 2010 we have extended our studies to include the structure of water in these other Cu surfaces with different oxidation states. First we determined the characteristic XPS spectrum of O as a function of its chemical surroundings. Our results at low humidity, presented in figure 2, show that water forms different amounts of OH on metallic Cu(110) with a chemisorbed oxygen layer, on Cu₂O and on CuO. These experiments, currently in progress, will shed more light into the chemistry of Cu and its oxides interacting with water *in ambient* conditions of humidity, from near zero to near 100% (in progress). They are particularly relevant in view of the recent results that show different oxidation states of Cu at various bias potentials (Fig. 1). Introduction of CO₂ in the gas environment will be done next.

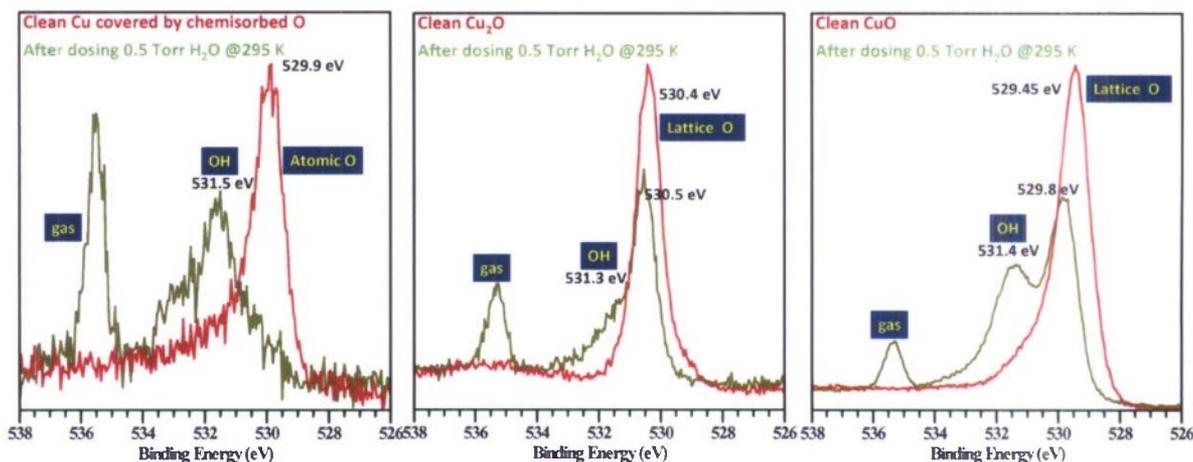


Figure 2. Oxygen 1s XPS spectra acquired in an ambient pressure of 0.5 Torr of water at room temperature before dosing water (red curves) and after dosing (green curves). Left: clean Cu(110) with one monolayer of chemisorbed oxygen. All O is converted to OH. Center: Cu₂O. Right CuO. Notice the much larger fraction of lattice O that is converted to OH in this case.

In situ study of mass loss of Cu as a function of bias in aqueous bicarbonate solutions

We have determined that the “wear” of the positive brush electrodes has several origins: chemical and mechanical. Mechanical wear was discussed in the previous year report (N000140810732), is most likely due to the increased friction of the more oxidized Cu, as revealed in AFM experiments where the tip was used to locally oxidize or reduce the Cu surface by application of + and – voltages. This is not

yet well understood and therefore we plan to continue investigating the correlation between oxidation state of Cu, friction and wear.

Another origin of “wear” is simply the loss of Cu due to dissolution of Cu^+ ions, which is enhanced at positive voltages. While this is not wear in the tribological sense, it has the same result of shortening the length (and thus the life) of the Cu brush electrodes. Dissolution of Cu (and other metals) is an old and well-known phenomenon that has practical applications in electroplating for example. Another manifestation of this phenomenon is the electropolishing process of Cu. Rough surfaces of Cu can be polished to a mirror like smooth appearance by the preferential dissolution of Cu at the surface asperities, where the electrical field is larger. With this in mind we designed an experiment using Cu films (~300 nm) evaporated on the electrode surface of a quartz crystal microbalance (QCM), shown in figure 3.

The QCM is an extremely sensity quartz crystal oscillator that is used to measure mass by the shift in its resonance frequency. It has a sensitivity of about 1/100 of a monolayer (ML) or better (0.01 ML of Cu is approx. 1 nanogram). We show in Figure 3 the set-up of the QCM used in our experiments. The sample was an evaporated film of Cu (~300 nm thick) on the Au electrode of the quartz resonator crystal. In the electrochemical cell, containing a 0.2 M NaHCO_3 solution, we measured the frequency shift of the resonator as a function of electrode bias. This shift was calibrated in terms of mass or equivalent thickness of Cu dissolved. As the graphs in Figure 4 demonstrate, there is a loss of Cu mass, above -0.1 V and increasing at more positive voltages. We know that the chemical state of Cu in this region is first

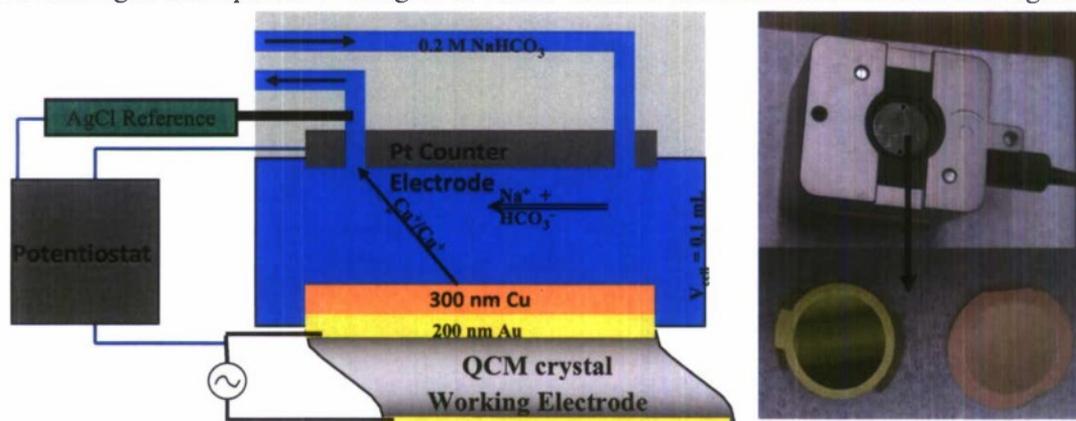


Figure 3. Left: Schematic of the electrochemical cell with quartz microbalance with an evaporated Cu film on top of the Au electrode. Right: Picture of the actual QCM with two quartz disc electrodes. The one on the left is before deposition of Cu and the right one after.

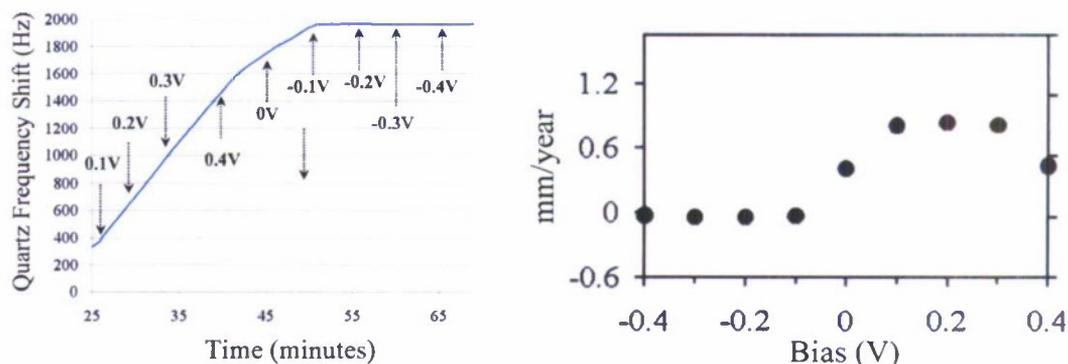


Figure 4. Left: Frequency shift of the quartz crystal resonator due to Cu dissolution as a function of applied bias in a 0.2 M solution of NaHCO_3 . The rate of dissolution and the resulting mass loss becomes important above -0.1 V towards more positive bias. Right: Mass loss from the calibrated frequency shift converted to mm of material lost per year.

Cu₂O and then CuO. At negative voltages, when the stable form of Cu is metallic, there is no loss of mass. The measured rate is about 1 mm/year. While we cannot yet compare this rate with the quoted figure of 3×10^{-11} wear/distance traveled (there is not travel in our dissolution experiments !), it is very clear that dissolution is greatly enhanced at positive bias and therefore it is a very important contributor to “wear”. When combined with the APPES results, a picture immerges of this being a potential mechanism contributing to “wear” since the interface is essentially “solution like” with a thin film of water under ambient relative humidity conditions, thereby allowing for the dissolution of Cu⁺ under positive bias.

If funding becomes available we would like to continue this work and to establish more quantitative relations, in particular the effect of pH in the solution, temperature, etc. We would like also to determine which of the two mechanisms, dissolution and mechanical wear, is more important. Interestingly at positive bias the friction is higher leading to an increase in wear.

Scanning Tunneling Microscopy (STM)

We have initiated studies of the structure of water on Cu(110), when clean, when covered with chemisorbed oxygen and when oxidized. Our first results obtained on clean and O-covered Cu show that on the clean surface at temperatures below 130K water forms a honeycomb layer of molecular water as shown in Figure 5. Above 140 K water dissociates and forms OH group and above 230 K a chemisorbed oxygen layer from the dissociated water. These studies, still in progress, will be expanded if funding is available, to include ambient temperature, and oxide films, both with Cu₂O and CuO structure. We will also study the effects of coadsorbed CO₂.

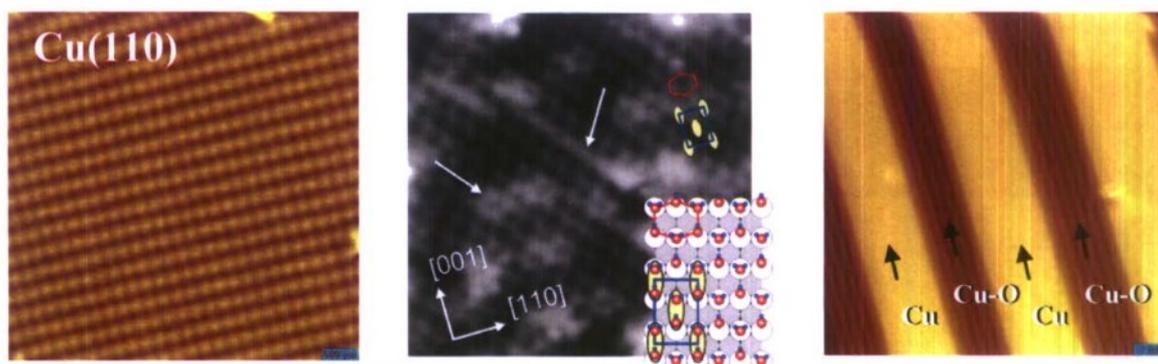


Figure 5. STM images of Cu(110). Left: clean surface with the Cu atoms atomically resolved. Center: monolayer of water forming a honeycomb structure (as shown in the schematic). Right: Partially O-covered surface after heating in oxygen gas.