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In situ soft X-ray absorption spectroscopy investigation of electrochemical corrosion of copper in aqueous NaHCO₃ solution

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Abstract: A novel electrochemical setup has been developed for soft x-ray absorption studies of the electronic structure of electrode materials during electrochemical cycling. In this communication we illustrate the operation of the cell with a study of the corrosion behavior of copper in aqueous NaHCO₃ solution via the electrochemically induced changes of its electronic structure. This development opens the

way for in situ investigations of electrochemical processes, photovoltaics, batteries, fuel cells, water splitting, corrosion, electrodeposition, and a variety of important biological processes.

1. Introduction

Understanding the mechanism of electrochemical reactions is important from the basic science point of view, as well as for the development of electrochemical applications, such as batteries, solar and fuel cells, etc [1-6]. It is also important in studies of the corrosion and wear of copper brushes in electrical motors [7]. This is best accomplished by the combination of electrochemical measurements with spectroscopic techniques. However, ex situ characterization methods suffer from a number of experimental limitations. For instance, transferring samples from one instrument to another can easily result in chemical changes in the state of the sample and introduce artifacts. In order to avoid the unwanted change of composition and electronic structure, in situ techniques are required. Several in situ techniques have been used to investigate electrochemical processes, including scanning probe microscopy, x-ray diffraction, infrared reflection absorption spectroscopy, surface-enhanced Raman spectroscopy, sum frequency generation, etc [8,9]. However, these techniques have limited capabilities in providing direct electronic structure information, which is the key for monitoring changes in the oxidation state.

In this communication we demonstrate a novel liquid flow cell for in situ soft x-ray absorption studies under controlled electrochemical conditions. This setup allow the real time monitoring of the element specific electronic structure changes of a system at all stages of the electrochemical cycle. Using this technique we have investigated the oxidation of Cu in NaHCO_3 solution under controlled electrochemical conditions.

2. Experimental

X-ray absorption spectroscopy (XAS) is an element specific technique with the capability to determine the unoccupied density of states, and thus to provide the oxidation state of the material [10]. In the last decades, due to the relatively simple instrumentation, XAS using hard x-rays has been widely utilized to carry out in situ investigation of important electrochemical processes [11-13]. Nevertheless, the electronic information about the 3d electrons in transition metals and their compounds is inaccessible from K-edge spectra due to dipole selection rule. The sharp L-edge in the soft x-ray range on the other hand, can provide more valuable chemical information in this aspect. Moreover the K-edge of light elements is also accessible with soft x-rays. The large absorption cross-section of most gases and liquids in this energy range requires the use of UHV instrumentation. However by using ultrathin membranes to separate the

samples from the UHV environment, soft x-rays can be used for studies under real conditions, such as high-pressure gas and liquid environments [14-21].

Several groups have investigated the electronic structure of liquid water by using such in situ XAS techniques [16-18]. Recently, the changes of electronic structure of Cu thin films in various aqueous solutions have also been studied in situ. However, due to the lack of potential control, these studies were limited to “static” electrochemical conditions [19]. In situ electrochemical reactions have also been studied by scanning transmission x-ray microscopy, where liquid cells without the capability of flowing the electrolyte solution were used [20,21]. These setups suffered from the formation of gas bubbles during electrochemical reactions and the difficult exchange of electrolytes [17,20].

Our experiments were performed at beamline 7.0.1 of the Advanced Light Source in Berkeley, California, USA. The schematic design of the cell is shown in Figure 1. The body (Fig 1c) of the cell was made of a UHV compatible and chemically inert polymer (polyether ether ketone, PEEK). A thin (~100 nm) silicon nitride (Si_3N_4) membrane, held by a Si frame (a, in Fig 1), separated the cell chamber from the UHV environment, with base pressure of 5×10^{-9} Torr during measurements. A thin Cu film (~300 nm) with 5 nm adhesive Cr layer was thermally deposited on the cell side of the membrane and used as working electrode (b^1 , Fig 1) in a three-electrode setup. The thickness of the Cu film was selected to allow the penetration of the incident x-rays and the escape of the fluorescence photons. A Pt wire as the counter electrode (b^3 , Fig 1) and a Ag wire as pseudo-reference electrode (b^2 , Fig 1) were inserted in the cell body through small holes on the sides. The electrolyte was flowing through two holes located at the backside of the body. The body was attached to a support tube, which was fixed on an XYZ adjustable manipulator. The potential was controlled by a VersaSTAT4 (Princeton Applied Research) potentiostat. XAS spectra were recorded in the total fluorescence yield mode using a channeltron detector and the intensities were normalized to a reference signal recorded simultaneously on a gold mesh. The energy scale was calibrated by using metallic Cu foil as reference.

3. Results and Discussion

Figure 2a) shows the cyclic voltammetric curve of the Cu thin film at a scan rate of 0.02 V/s in 0.1 M NaHCO_3 solution in this cell setup. The characteristic oxidation and reduction peaks of copper are clearly observable. Anodic peaks I and II correspond to the formation of Cu^+ and Cu^{2+} , respectively. Cathodic peaks II and I are related to the reduction of Cu^{2+} to Cu^+ and Cu^+ to Cu^0 , respectively. These observations and assignments are consistent with previous reports [22,23].

Cu $L_{2,3}$ -edge XAS of Cu thin film on Si_3N_4 membrane before contacting any solution is shown in Fig. 2b) (2). The main component can be assigned to the L_3 edge (932.7 eV) of metallic Cu, consistent with the metallic Cu reference sample (Fig. 2b, curve (1)) [19,24,25]. Except the main peak, there is one

additional peak at the lower photon energy side (930 eV), which can be ascribed to Cu^{2+} species. These features indicate that a thin oxidized layer is formed on the surface of the evaporated Cu film due to oxidation in air during transfer. These observations indicate the importance of in situ measurements for investigations of electrochemical reactions in order to avoid introducing artifacts and misinterpreting experimental data.

The in situ XAS spectra acquired during electrochemical reactions are presented in Fig. 2b) (3) and (4). The intensity of the Cu^{2+} peak (930 eV) increased significantly when the potential was set to a nominal value of 0.2 V. In contrast, the Cu^{2+} oxidation peak disappears when reduction occurs at nominally -0.9 V. By keeping the potential constant, we could follow the oxidation and reduction kinetics of the Cu thin film. In Fig. 3 (a), the XAS intensity of Cu^{2+} peak increases gradually during oxidation process, while the intensity of Cu^{2+} peak decreases during reduction, as shown in Fig. 3 (b). The oxidation and reduction processes could be repeated several times, until the thin Cu film was completely dissolved [22,23].

4. Conclusions

In summary, we have shown how in situ soft x-ray absorption spectroscopy can be performed under electrochemical control. We have used the technique to successfully study the corrosion behavior of Cu in aqueous NaHCO_3 solution. Our novel technique combines the capabilities of element specific soft x-ray absorption spectroscopy and electrochemistry, thus opening the way for in situ investigations of electrochemical applications in photovoltaics, batteries, fuel cells, water splitting, corrosion, electrodeposition, and a variety of important biological processes.

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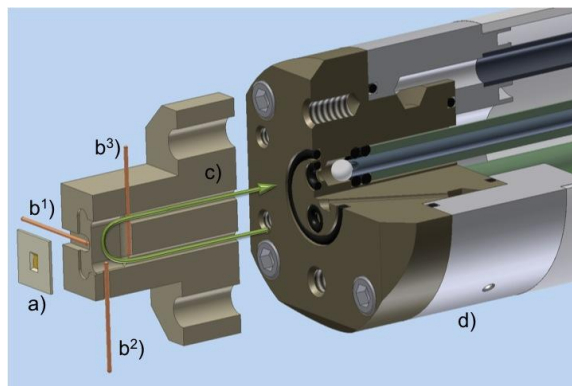


Figure 1. Schematic drawing of the electrochemical cell assembly for in situ x-ray absorption spectroscopy studies. a) Si_3N_4 window, b^1) electrical connection to Si_3N_4 window (working electrode), b^2) reference electrode, b^3) counter electrode, c) PEEK body, d) support tube assembly. The green arrow indicates the liquid flow.

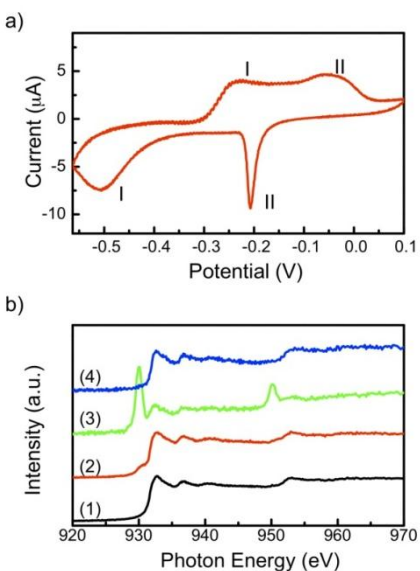


Figure 2. a) Cyclic voltammogram of a Cu thin film working electrode in 0.1 M NaHCO_3 solution at a scan rate of 0.02 Vs^{-1} . Pt and Ag wires were used as counter and pseudo-reference electrodes, respectively. b) Total fluorescence yield XAS of Cu $L_{2,3}$ -edge. (1) Reference metallic Cu foil. (2) Cu thin film (~ 300 nm) evaporated on the Si_3N_4 membrane (oxidized during transfer in air). Spectra (3) and (4) were recorded after in situ oxidation at nominally 0.2 V and after reduction at nominally -0.9 V in 2 mM NaHCO_3 solution, respectively.

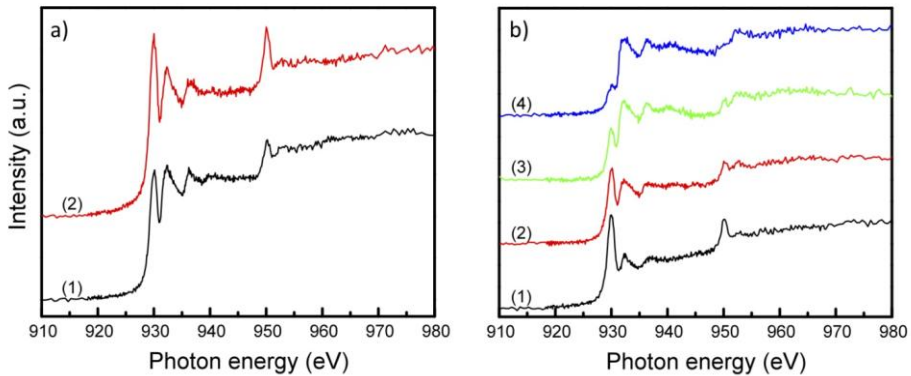


Figure 3. Time evolution of the Cu L_{2,3}-edge XAS spectra showing the a) oxidation and b) reduction kinetics in 2 mM NaHCO₃ solution at nominal potential of -0.1 V and -1.0 V, respectively. The spectra were collected sequentially with a time difference of approximately 15 minutes.