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# Electrolysis of solid copper oxide to copper in Choline chloride-EG eutectic melt

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ABSTRACT

Electrochemical deoxygenation of porous CuO pellet to prepare copper was investigated in the 33.3-66.7 mol% Choline chloride (ChCl)-EG eutectic melt at 353 K. Cyclic voltammetry of the Pt-powder cavity microelectrode loaded with CuO powder exhibited that the solid CuO can be electrochemically reduced in solid state in the eutectic melt. Constant-voltage (2.0 to 2.4 V) electrolysis, with an assembled cathode of a sintered porous CuO pellet and a graphite anode, that performed in the eutectic melt demonstrated the conversion process of oxide-to metal as confirmed by scanning electron microscopy, energy-dispersive X-ray, and X-ray diffraction spectra. A mechanism for this reduction process has been proposed on the basis of the in situ formation of numerous gas at the cathode, emphasizing that the oxidation of cathodically generated $O^{2-}$ ions occurred nearby along with the copper electroreduction, in which the new formed metal was served as a temporary anode, oxygen was generated at the interface of the reduced copper and electrolyte inside the cathode.

## 1. Introduction

Metal oxides are important raw materials for metal electrodeposition/winning [1]. For this purpose, aqueous acids or alkalis are predominantly used to dissolve these metal oxides as they are insoluble in most molecular solvents [2]. However, these acids or alkalis aqueous solutions are highly corrosive and generally fail as solvents because hydrogen evolution is inevitable during the metal electrodeposition process, which lowers the cathodic current efficiency [3]. In this context, room temperature ionic liquids (RTILs) have been developed as promising electrolytes for electrodeposition application due to their wide electrochemical windows and good conductivity [4]. In this field, haloaluminate based ILs with metal chlorides as metal sources have been widely investigated for metals electrodeposition [5]. However, the cost and hygroscopic nature of haloaluminate based ILs has delayed progress in their use [6]. Alternative, primarily ionic systems called deep eutectic solvents (DESs), which are made from quaternary ammonium salts mixed with simple hydrogen bond donors [7,8], are found to have considerable preparation advantages such as cheap, convenience, and electrochemical stability and make them more attractive solvents for large-scale technological applications. Additionally, these DESs show high selective dissolubility of metal oxides, which are found to be insoluble in common RTILs [9,10]. This unanticipated solvating power attracts metal oxides processing and opens a new route for preparation of metals in the DESs media from metal oxides precursors. Hussey et al. [11] studied the electrochemistry of copper (I) oxide in the ChCl-urea based DES on account of its relatively high solubility in the DES of more than 8ppt and found that high quality Cu films could be electrodeposited on nickel substrate through control potential electrolysis. Also, these DESs may prove to be a kind of important solvents for direct electroreduction of certain poorly soluble metal oxides to prepare metals without the necessity for dissolving operation based on their air-and water insensitive, relatively wide electrochemical windows, and acceptable conductivity [12,13].

In the present work, we have investigated the direct electrolysis process of bulk solid copper oxide to solid copper metal in the ChCl-EG eutectic melt by means of cyclic voltammetry and constant voltage electrolysis. Based on experimental evidence, a new elucidated mechanism is proposed to account for the reduction process. Our work demonstrates not only copper oxide thin film [14] but also its bulk pellet can be direct electrochemically reduced in the DES media at room temperature. These findings promise a novel and simple route for preparation of metals in the DESs from their metal oxides precursors at room temperature.

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## 2. Experimental

Choline chloride (ChCl; Aladdin, 99%) and ethylene glycol (EG) (Aladdin, >99%) were dried under vacuum at 373 K prior to use. The eutectic mixture (the molar ratio was 1:2 for ChCl with EG) was formed by mixing together the appropriate amount of each component in a capped glass bottle under an argon-gas atmosphere at 333 K until a homogeneous, colorless liquid formed. The eutectic melt was dried under vacuum for 12 h at a temperature of 323 K and stored in an argon filled glove box. The water content of the melt was determined by using a Metrohm Karl Fischer model 870 coulometric titration apparatus and was typically less than 200 ppm. CuO powder (>99.9%, Aladdin) were used as purchased.

All electrochemical measurements in the eutectic melt were performed under a purified argon atmosphere using a CHI 760D Electrochemical System (Shanghai Chenhua, China). Electrochemical experiments were performed in a three-electrode cell. The powder cavity microelectrode [15] was used as a working electrode to record cyclic voltammograms (CVs) curves of the oxide powder in the eutectic melt and prepared as follows. A platinum (99.995% Pt) wire was fabricated by sealing a 100 μm dia in a glass tube and grinded its end to form a plane perpendicular to the axis of the tube. Then, the disk microelectrode was etched with aqua regia to create a cavity at its tip. The cavity electrode was ground on a glass plate with the powder of sample to obtain the powder microelectrode. The reference electrode was an Ag wire placed in a fritted glass tube containing the eutectic melt and a platinum bar (Ø 1 mm, 10 mm) directly immersed in the bulk eutectic melt was used as the counter electrode.

For electrolysis experiments in this work, $NH_4HCO_3$ as a pore-forming agent was used for the preparation of high-porosity CuO precursors (pellets) [16]. About 0.6 g of the mixture powders ($CuO:NH_4HCO_3 = 5:1$) was moisturized with a few organic binder (5wt% PVA solution) and pressed into cylindrical pellets (13 mm diameter and 1.0-1.2 mm thickness) under 10 MPa. The pellets were then sintered in air at 1073 K for 3 h, which were found to be about 50% in porosity. The sintered oxide pellets were wrapped with the stainless steel (SS) wire mesh, and then attached to a Ti current collector. This oxide cathode was then inserted into the ChCl-EG eutectic melt and electrolyzed for a prescribed time (20 h) under constant voltages (2.0-2.4 V) with a graphite rod anode. During electrolysis process, the reactor was continuously flushed with argon. The temperature was increased to and kept at 353 K with continuously stirring by a magnetic paddle (500 rpm). The electrolysis was controlled by an adjustable DC power supply (Zhejiang Yueqing Yizhan Electronics Co. Ltd., China). For gas determination, the effluent gas from the reactor was monitored by a FULI-9790 gas chromatography (GC) equipped with an ECD system (Fuli Anal. Instrument Ltd., Wenling, China) and a GDX-104 column. Air was chosen as the reference system. Before measurements, the headspace of the reactor was degassed with ultrapure nitrogen (99.999%) for 5 min to avoid any air residue. The ultrapure nitrogen was also used as the carrier gas of GC at a flow rate of 1.5 mL/min. The injector and detector temperatures were 373 K. The column temperature was kept at 303 K, and sample running time was 20 min/sample.

After electrolysis, the cathode products were cooled in argon, removed from the melt, and then washed with water in air to dissolve the liquid salt on the cathode, and dried at 323 K for 6 h in vacuum before further analysis. The electrolyzed pellets were then broken into two halves whose cross-sections were examined under optical microscope. The surface morphology and elemental compositions of the electrolytic products were examined with scanning electron microscope (SEM, FEI-quanta-200F Field Emission Gun SEM system) together with energy dispersive X-ray (EDX) analysis. For X-ray diffraction analysis (XRD, Rigaku D/max 2200 X-ray diffractometer by using Cu Kα radiation), the electrolyzed pellets were manually ground into powders with a mortar and pestle.

## 3. Results and discussion

### 3.1. Cyclic voltametric studies

The cyclic voltammograms (CVs) that were recorded on a Pt-powder cavity microelectrode filled with and without CuO powder in the ChCl-EG eutectic melt at 353 K are shown in Fig. 1. For the sample filled case, the CVs exhibit two cathodic peaks labeled c1 and c2, which should be attributed to the reduction of $Cu^{2+}$ to $Cu^{+}$ and subsequent reduction, producing metallic copper. This is accompanied by two anodic waves labeled a2 and a1 during scan reversal. Increasing the scan rate from 20 to 50 mV $s^{-1}$, the cathodic peak potentials are observed to shift to a negative direction with anodic peaks positively shifting. Interestingly, slight fluctuations appear at the high potential portion as compared with the background voltammetry. This phenomenon may be indicative of a follow-on reaction that the oxidation of oxygen ions take place in situ along with copper electroreduction, in which copper is served as a temporary anode, oxygen is generated at the interface of reduced copper and the melt [17]. Obviously, the CV observation confirms that solid CuO can be electrochemically reduced in the eutectic melt.

### 3.2. Constant voltage electrolysis

To confirm the electroreduction process, different cell voltages (2.0-2.4 V), that were below the decomposition voltage of eutectic melt ($\sim$ 2.45 V at 353 K), were performed in the experiments. The sintered copper oxide pellets were electrolyzed for 20 h with different voltages in a 50 mL electrolysis bath at 353 K, respectively. The current value is found to sharply increase with increasing the applied voltage from 2.0 to 2.4 V, which is generally attributed to the enhancement of driving force for the electrode reaction. Upon electrolysis, the CuO pellet quickly turns metallic like on the surface (Fig. 2a), and the interior changes from dark to purple red (Fig. 2b). This metallized proceeding from the superficial to the profound is consistent with the electroreduction process taking place at the metal |oxide| electrolyte three phase interline (3PIs) [18–20].

Fig. 3 compares the SEM images of the sintered CuO pellets before (Fig. 3a) and after (Fig. 3b) electrolysis at 2.4 V for 20 h. The high porosity of the presented oxide pellet, which was sintered

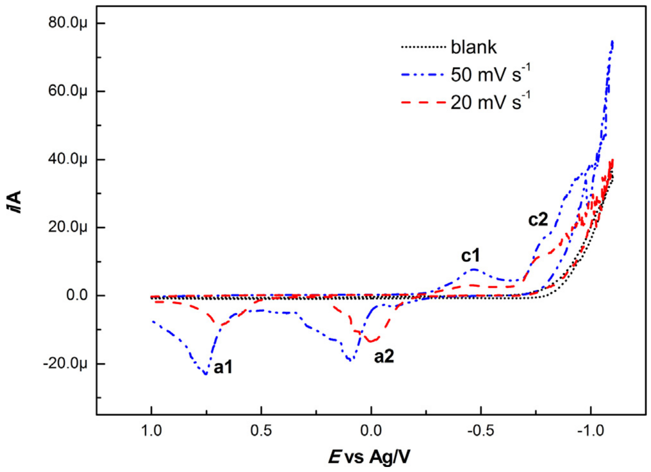

**Fig. 1.** CVs of a Pt-powder cavity microelectrode (diameter: 100 μm) filled with and without CuO powder at different scan rates, as indicated, in the ChCl-EG eutectic melt at 353 K.