



# Electrochemical Kinetics of Reduction of Zinc Oxide to Zinc Using 2:1 Urea/ChCl Ionic Liquid



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## ABSTRACT

Electrochemical reduction of zinc oxide to zinc was investigated in 2:1 urea/choline chloride electrolyte at applied cell potentials of 3.2 - 3.5 V. Concentration polarization was observed at the beginning of electrochemical reduction process. The diffusion coefficient of zinc species in the electrolyte was calculated to be  $7.85 \times 10^{-13} \text{ m}^2/\text{s}$  at 363 K. An increase in the current density was observed after a sharp initial decrease due to activation polarization, in which case, a linear relationship was established between  $\log$  (current density) and over-potential. The electrochemical kinetic parameters was investigated in the steady-state current region. The transfer coefficient was calculated to be 0.2 indicating an irreversible charge transfer process. The XRD analysis confirmed that the electrodeposits consists of high purity zinc. The SEM analysis showed the formation of dendrites at higher over-potential ( $\geq 0.65 \text{ V}$ ), which is comparable to the calculated critical over-potential for Zn dendrite formation. The estimated energy consumption varied from 3.04 to 3.66 kWh/kg and current efficiency from 78.5 to 88.9%.

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## 1. Introduction

Zinc is commonly recognized as an effective coating material for reactive metal surfaces due to its anti-corrosive property [1]. The long-established method for deposition of zinc from sulfuric acid electrolyte baths involve complicated processes that poses various problems and therefore, require further improvements. Hydrogen evolution is inevitable and it results in low current efficiency and embrittlement of the products. In addition, difficult secondary purification processes are required due to high sensitivity of Zn deposition to the electrolyte impurities that occur as byproducts of electrowinning in sulfuric acid [2].

To overcome the major difficulties involved in the zinc sulfate electrolytic process, it is important to find an alternative electrolyte that is eco-friendly and highly efficient. Recently, ionic liquids (ILs) have been widely investigated as novel green solvents for metal extraction and deposition. Ionic liquids have many attractive properties such as: (1) non-corrosive, (2) non-flammable, (3) low vapor pressure, (4) wide electrochemical window, (5) good thermal stability, (6) high electrical conductivity, etc. [3,4]. However, large-scale industrial application of ionic liquids are limited mainly due to handling issues and relatively high costs.

More recently, deep eutectic solvents (DES) have attracted many scientists due to their low price, non-toxicity, and high stability in air and moisture. The most commonly used component of DES is choline chloride (ChCl), a biodegradable quaternary ammonium salt. ChCl can easily form DES at very low temperatures through its hydrogen bond donor functional groups [5]. The eutectic mixture of urea and choline chloride (2:1 molar ratio) is considered for the current study because of its stability in ambient environment, affordability, and availability [6]. Also, the low melting point (285 K) of urea/ChCl mixture indicates a potential for energy savings [7]. Reddy et al. have reported a relatively large electrochemical window (2.5 V) for Urea/ChCl mixture [8]. Moreover, the capability of eutectic urea/ChCl mixture to selectively dissolve metal oxides greatly simplifies the purification procedure. It is reported that only  $\text{PbO}_2$ ,  $\text{Cu}_2\text{O}$ , and  $\text{ZnO}$  show appreciable solubility, whereas other metal oxides, such as  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$ , have negligible solubility in the studied eutectic solvents [7]. In our previous studies, successful deposition of Zn and Pb from corresponding metal oxides was carried out in urea/ChCl, and in particular, ZnO showed great solubility ( $\sim 1.23 \text{ mol/L}$ ) at 373 K. Electrochemical measurements, using cyclic voltammetry (CV), confirmed that the onset reduction potential for  $\text{Zn}^{2+}$  to Zn occurs at  $\sim -1.05 \text{ V}$  via a one step, two electron transfer process. In addition, from CVs with different scan rates, the charge transfer process is characterized as an irreversible, diffusion-controlled, over-potential driven, and nucleation mediated process [9]. The

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earlier studies on ZnO solubility in urea/ChCl and electrochemical measurements of Zn deposition provides the preliminary data for further studies on electrowinning of zinc. In the current study, a thorough investigation was carried out on electrowinning process of zinc in eutectic mixture of urea/ChCl. Specific objectives of the research are: (i) to study the kinetic parameters of zinc electrowinning process, (ii) to examine the effect of over-potential on the surface morphology of zinc deposits, (iii) to calculate and compare the current efficiency and energy consumption during the zinc electrochemical reduction process.

## 2. Experimental procedure

### 2.1. Preparation of ionic liquid and materials

Urea ( $\text{CO}(\text{NH}_2)_2$ ) (Alfa Aesar, 99.3%) and ChCl ( $\text{C}_5\text{H}_{14}\text{ClNO}$ ) (Alfa Aesar, 98%) were dried under vacuum at 373 K for 2 hours before electrolyte preparation. The eutectic mixture was prepared by combining urea and ChCl (2:1 in molar ratio) at a temperature of 363 K for 12 hours until a homogeneous colorless solution was obtained. One gram of Zinc oxide (Fisher Scientific, certified ACS,  $\geq 99.0\%$ ) was dissolved in 30 mL of 2:1 urea/choline chloride mixture with constant stirring for 12 hours at a temperature of 363 K. Concentration of ZnO additions was fixed throughout the experiment.

### 2.2. Electrodeposition set-up

All experiments were conducted in a 100 mL glass beaker. Cu plate (0.02" thickness) was used as the cathode and a controlled area (1.92  $\text{cm}^2$ ) was immersed in the ionic liquid. Platinum wire (0.004" in diameter) and silver wire (0.004" in diameter) were used as the anode and quasi-reference electrode respectively. The purpose of reference electrode was to measure the cathodic and anodic potentials using a multimeter (Keithley 2000 Multimeter). The constant cell potential difference was applied between cathode and anode using EG&G PARC model 273A potentiostat/galvanostat. The instrument was controlled from a desktop computer using Power Suite (Princeton Applied Research) software to conduct the polarization studies. A thermometer was inserted in the solution to monitor the temperature [10–13].

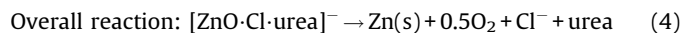
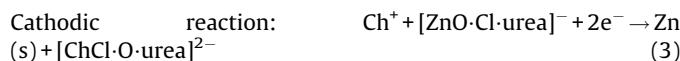
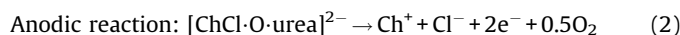
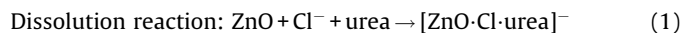
### 2.3. Characterization of the deposits on the substrate

The characterization of zinc deposits on the cathode were analyzed using the X-ray diffraction pattern, obtained from a Phillips MPD XRD that utilizes a monochromatic  $\text{Cu } \alpha$  radiation. The resulting pattern was compared with the standard ICDD card. The morphology and elemental analysis of the deposits were carried out using Scanning Electron Microscope (SEM), model JEOL 7000, equipped with an Energy Dispersive Spectrometer (EDS). The SEM images were obtained by setting the accelerating voltage at 20 kV, and a working distance of 10.0 mm.

## 3. Results and discussions

### 3.1. Electrochemical reduction of Zn in Urea/ChCl eutectic mixture

The potentiostatic electrochemical reduction of Zn was conducted at 363 K for one hour from 3.2 to 3.5 V. ZnO was dissolved in the electrolyte to form predominant  $[\text{ZnO}\cdot\text{Cl}\cdot\text{urea}]^-$  species, which was also confirmed from the previous literature [9,14,15]. The isolated  $\text{Ch}^+$  ions reacts with  $[\text{ZnO}\cdot\text{Cl}\cdot\text{urea}]^-$  species and the anode supplies two electrons needed for the reduction of  $\text{Zn}^{2+}$  to Zn on the cathode. Therefore, the possible electrode reactions are shown as follows:



A typical XRD pattern of the electrodeposits is shown in Fig. 1. The XRD peaks of electrodeposits matches with the standard ICDD diffraction peaks of Zn, except for a peak at  $\sim 50.4^\circ$ , which is due to Cu substrate (ICDD 00-004-0836), and thus, verifying that the zinc deposits obtained are of high purity.

Current output was recorded at regular time intervals and the current density was calculated by dividing the current with the surface area of zinc deposited on the cathode. Fig. 2 shows the current density ( $\text{A}/\text{m}^2$ ) as a function of time (s) at applied cell potential differences from 3.2 to 3.5 V and at a temperature of 363 K. A typical current density against time curve is obtained for all applied cell potentials and the plot is divided into three sections. A steep decrease marked as section A is observed during the first 50 seconds. To further analyze the sharp decrease of the curve, a chronoamperometry study was conducted using a three electrode system, which consisted of Cu as the cathode, Ag as a quasi-reference, and Pt as the anode. Cathodic potential has been delicately set from  $-1.09$  to  $-1.37$  V and the conversion to cell potentials (3.2 to 3.5 V) can be realized from the measurements between the cathode and anode using a multimeter. Fig. 3 is plotted for the first six seconds of the electrochemical reduction process. A short rising trend of the curve, which occurred in the first 0.1 s, can be attributed to the nucleation process: the number of nuclei increases with the increase in electroactive area of the electrode [16]. More clearly, it is then followed by a decreasing portion from 0.5 to 6 s. The decaying current density is plotted as a linear function of  $t^{-1/2}$  (Fig. 4), which is in agreement with the Cottrell equation given below [17]:

$$j = nFC(D/\pi)^{1/2}t^{-1/2} \quad (5)$$

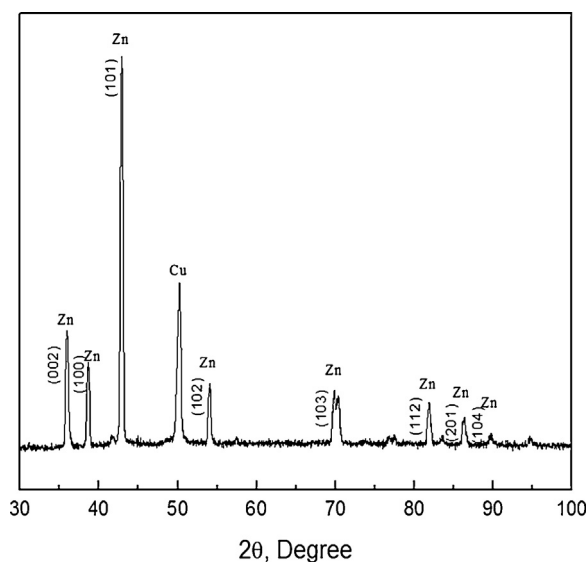


Fig. 1. X-ray diffraction pattern of deposited Zn on copper electrode.

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