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# Electrodeposition of Cu–Li alloy from room temperature ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate

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ABSTRACT

Electrodeposition of Cu–Li alloy from 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][$BF_4$]) ionic liquid was investigated. The cyclic voltammetry behaviors of [BMIm][$BF_4$] containing Cu(II), Li(I), and mixtures of Cu(II) and Li(I) were studied at a copper working electrode, separately. The Cu–Li alloy produced by direct current electrodeposition was characterized by inductively coupled plasma atomic emission spectrometry (ICP), X-ray photoelectron spectroscopy (XPS), and scanning electron microscope (SEM). The function of 2-butyne-1,4-diol was studied by linear sweep voltammetry. The result shows that the 2-butyne-1,4-diol could improve Li content in deposit, and make the Cu–Li alloy deposits denser and finer.

## 1. Introduction

Room temperature ionic liquids (RTILs) are typically a large organic cation with an inorganic or organic anion with melt points at or below room temperature. From the 1950s to about 1995, most research focused on RTILs with aluminate anions. These RTILs are moisture sensitive [1], leading to the development of water stable RTILs in 1992 with $BF_4^-$ anions [2]. RTIL's possess a number of attractive characteristics, including a wide electrochemical window, undetectable vapor pressure, high thermal stability, good conductivity, and no hydrogen evolution [3–5]. These characteristics make RTIL's strong candidate as replacements for classical solvents in electrochemical deposition [6], Li-ion battery [7], organic synthesis [8], liquid–liquid extraction [9], nanomaterial syntheses [10], and absorption of harmful gas [11].

RTILs have proven to be particularly good non-aqueous solvents for electrodeposition of various metals and alloys. For example, Sun et al. [12] obtained hexagonal hollow copper–tin tube arrays by direct cathodic electrolysis in the [EMIm][DCA] containing Cu(I) and Sn(II) without using a template at 313 K. Kondo et al. [13] investigated the electrodeposition of neodymium in a triethyl-pentyl-phosphonium bis(trifluoromethyl-sulfonyl)amide ([P2225][TFSA]) room temperature ionic liquid. RTILs are especially useful for the deposition of reactive metals and semiconductors that cannot be deposited from aqueous solutions due to hydrogen evolution interference, such as Se, Al, Mg, Si, Ge and their alloys. Endres et al. [14] investigated the electrodeposition of Se, In and Cu from [BMP][$Tf_2N$]. Endres et al. [15] found that nanocrystalline aluminium can be electrodeposited without any additives in the ionic liquid 1-butyl-1-methyl pyrrolidinium bis(trifluoromethylsulfonyl)imide saturated with $AlCl_3$ for the first time. Cheek et al. [16] carried out deposition of magnesium in pyrrolidinium systems. In comparison, deposition of magnesium from propylene carbonate tetraethylammonium tetrafluoroborate was studied. Endres et al. [17] obtained $Si_xGe_{1-x}$ nanowires by a simple electrochemical template synthesis from the air- and water-stable ionic liquids [$Py_{1,4}$][$Tf_2N$] and [EMIm][$Tf_2N$] containing $GeCl_4$ and $SiCl_4$ as precursors.

Reduction potential of Li is the lowest of all metals, so it cannot be obtained in aqueous solution through electrodeposition. It has been reported that lithium layer was obtained using electrodepositing in RTILs. Endres et al. [18] demonstrated deposition of the macroporous aluminium electrodes by template assisted electrodeposition from ionic liquids [EMIm]Cl/$AlCl_3$ (40/60 mol%). Sano et al. [19] investigated the behavior of Li electrodeposition on nickel electrodes in RTILs using in situ optical microscopy with/without an organic additive, vinylene carbonate (VC), in the RTILs. These studies proved that electrodeposition of lithium in ionic liquid was feasible. It is hard to codeposition two metals that have a large separation of the reduction potentials, however the codeposition may

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be realized from RTILs. Chen et al. [20] studied electrodeposition of Cu–Mn alloy from air and water stable RTILs.

2-Butyne-1,4-diol is a common additive for deposition of metal in aqueous solution. It is thought that 2-butyne-1,4-diol adsorbs on the electrode to make deposition potential of metal shifted to more negative potential, increasing cathodic polarization. As a result, the rate of nucleation increases and grain becomes smaller [21–23]. In this study, referring to electrodeposition theory in aqueous solution, we added 2-butyne-1,4-diol into ionic liquid to improve the appearance of CuLi. Unexpectedly, we found 2-butyne-1,4-diol not only improve the appearance but also increase the content of lithium in deposit.

Cu–Li alloys are of strong interest as a Li-ion battery anode material to improve cycling. The copper in the alloy is thought to prevent formation of lithium dendrite. In the present study, Cu–Li alloy coatings were electrodeposited on copper substrates in [BMIm][$BF_4$] ionic liquid to demonstrate the feasibility. The voltammetric behaviors of Li(I), Cu(II), and mixtures of Li(I) and Cu(II) in RTILs were also studied. Alloy deposits were characterized with a scanning electron microscope (SEM), inductively coupled plasma atomic emission spectrometry (ICP), and X-ray photoelectron spectroscopy (XPS).

## 2. Experimental

### 2.1. Chemical and reagents

1-Buthyl-3-methylimidazolium tetrafluoroborate ([BMIm][$BF_4$]) was purchased from Shanghai Chengjie Chemical Co., Ltd., China. Ionic liquids were dried under vacuum for 24 h at 120 °C and stored in an argon-filled glove box. The water content in the ionic liquid was measured with a coulometric Karl Fischer titrator (SFY-3000, Haifen Instment Ltd. Co., China) at 20 ppm. Anhydrous $Cu(BF_4)_2$ was prepared by direct reaction of $Cu_2(OH)_2CO_3$ and $HBF_4$, and $LiBF_4$ was prepared by direct reaction of $Li_2CO_3$ and $HBF_4$, then stored under argon atmosphere. 2-Butyne-1,4-diol was purchased from Shenyang Xinxi Regent Factory, China.

A solution of $Cu(BF_4)_2$ in [BMIm][$BF_4$] ionic liquid was prepared by adding $Cu(BF_4)_2$ to [BMIm][$BF_4$] under dry argon and stirring with a magnetic stirrer for several minutes until dissolution of $Cu(BF_4)_2$ was complete. Solutions of $LiBF_4$ and mixture of $Cu(BF_4)_2$ and $LiBF_4$ in [BMIm][$BF_4$] ionic liquid were prepared in the same manner. Electrodepositions were carried out on Cu foil. The deposits were washed in acetone to remove the ionic liquid residue.

### 2.2. Measurement procedures and apparatus

Electrochemical experiments were carried out under dry argon. [BMIm][$BF_4$] ionic liquid was poured into a homebuilt glass electrolytic cell in the glove box. The electrochemical measurements were performed in a conventional three-electrode cell using CHI630B. A copper wire (0.38 mm diameter) was used as the working electrode (WE). The counter electrode (CE) was a platinum plate and the quasireference electrode was a platinum wire. For the electrochemical experiments, the electrolyte temperature was kept constant at 25 °C. The surface morphologies of deposits were characterized by field-emission scanning electron microscope (FE-SEM, Hitachi S4700). The copper foil was weighed before electrodeposition, $m_1$. After the electrodeposition, the Cu–Li coated foil was weighed, $m_2$, and then dissolved into aqueous nitric acid solution. The difference between $m_1 - m_2$ gives the mass of the deposits. Inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin Elmer, 300DV) was used to determine the amounts of Li and Cu. The weight of Li, $m_{\mathrm{Li}}$, and the weight of Cu, $m_{\mathrm{Cu}} = m_2 - m_1 - m_{\mathrm{Li}}$, were converted to their atomic ratio. Electrochemical impedance spectra was measured by Potentio-Galvanostat (EG&G Princeton Applied Research, M273). The frequency range is from 100 kHz to 100 mHz and an AC signal of 5 mV in amplitude as the perturbation. X-ray photoelectron spectroscopy (XPS) analysis was taken by PHI 5700 ESCA System with monochromatic Al Kα radiation (1486.6 eV). All spectra were calibrated to the binding energy of the C 1s peaks at 284.6 eV.

## 3. Results and discussion

### 3.1. Voltammetric study of [BMIm][$BF_4$] containing Li(I), Cu(II), and mixtures of Cu(II) and Li(I)

Fig. 1a shows the cyclic voltammogram of [BMIm][$BF_4$] containing 1.7 mol/L Li(I) recorded at the Cu electrode. The potential was initially scanned from −0.5 V toward −4.1 V and then back to −0.5 V. The reduction peak $c_1$ (about −2.0 V) in Fig. 1a represents the underpotential deposition (UPD) of lithium. It is known that when the electronic work function of the deposited metal is smaller than the work function of the electrode substrate, underpotential deposition (UPD) of the metal may occur at the electrode substrate. In view of the fact that the work function of Li (2.39 eV) is smaller than that of Ni (4.84 eV), Pt (5.29 eV), Au (4.58 eV) and Cu (4.47 eV) [24]. According to the researches that the UPD of lithium happened at the Ni, Pt and Au electrodes [3,25–27], the UPD of Li at Cu electrodes is reasonable. The peak $c_2$ (−4.0 V) that is much more negative is assigned to bulk deposition of lithium. It is known that the addition of lithium salt to RTILs causes significant enlargement of the cathodic branch of the electrochemical window [18,28]. It is believed that a solid electrolyte interphase (SEI) forms on the cathodic electrode surface that is $Li^+$-conductive and prevents the electrolyte reduction [27,29].

The pair of redox peak shown in Fig. 1b at −0.6 V ($c_1'$) and at 0.2 V ($a_1'$) represent the deposition of Cu and the stripping of deposited Cu, respectively. According the theory of metal electrodeposition, redox of copper is 2-steps one electron process. However, there is just set of redox peaks for copper rather than the two couples in Fig. 1b. Because the concentration of cupric ion is very high (0.8 mol/L), the concentration polarization of the Cu(II) → Cu(I) reaction is shifted to where it is hard to distinguished from the Cu(I) → Cu(0) peak. However, there is one anodic peak at about 0.2 V in Fig 1b. The stripping peak that appeared at 0.2 V may be

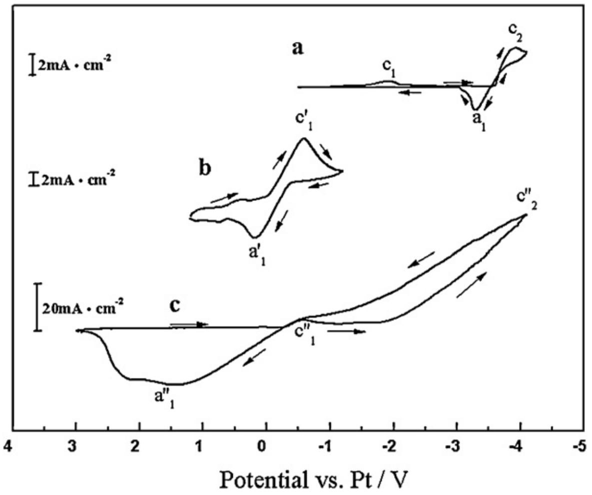

**Fig. 1.** Cyclic voltammograms recorded at the Cu electrode in [BMIm][$BF_4$] containing 1.7 mol/L Li(I) (a), 0.8 mol/L Cu(II) (b) and a mixture of 0.8 mol/L Cu(II) and 1.7 mol/L Li(I) (c), respectively. Scan rate: 10 mV/s. Temperature: 298 K.