Electrodeposition of Bismuth in a Choline Chloride/Ethylene Glycol Deep Eutectic Solvent under Ambient Atmosphere

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The electrochemical behavior of bismuth(III) is investigated under ambient atmosphere in the ethaline deep eutectic solvent (DES) that is obtained by mixing 1 mol eq. of choline chloride and 2 mol eq. of ethylene glycol using Bi(NO₃)₃ as the Bi(III) source. Cyclic voltammetry indicates that the presence of water adsorbed from the atmosphere reduces the viscosity of the DES, and hence facilitates the reduction of Bi(III) to Bi. The presence of high water contents, however, suppresses the solubility of Bi(NO₃)₃ in the DES. Chronoamperometry experiments indicate that while the deposition of bismuth at a glassy carbon electrode involves with an overpotential-driven three dimensional instantaneous nucleation/growth process, the deposition of bismuth at the platinum, and nickel electrode involves with a progressive nucleation/growth. Crystalline bismuth films are deposited on Ni electrode by constant potential electrolysis. Scanning electron microscope images reveal that making the deposition potential more negative and/or increasing the temperature will reduce the deposited particle size. X-ray powder diffraction patterns suggest preferred orientation of the crystal growth. Bismuth coating can also be formed on copper substrate by galvanic displacement reaction between Bi(III) and Cu.

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Bismuth and its alloys are interesting chemicals largely used in various applications. For example, due to its unusual physical properties including electronic, thermostoelaic, and magnetoelectricity, Bi is used for electrochromic and piezoelectric devices. Moreover, due to their catalytic properties and mechanical stability, bismuth-modified electrodes have been employed for electrochemical sensors in place of mercury electrodes. Electrodeposition of Bi and its alloys has therefore attracted much attentions. Electrodeposition of Bi films with various morphologies and particles from micrometer to nanometer has been intensively studied in acid containing aqueous electrolytes without and with additives. Electrodeposition of Bi has also been studied in organic and molten salts.

Recently, ionic liquids (ILs) that are liquid at temperature below 100 °C have been considered more advantageous than organic electrolytes and high temperature molten salts because ILs are non-flammable, non-volatile, high thermal stability, and have a relatively good conductivity, as well as wide electrochemical window. Consequently, ILs have been considered as electrolytes for electrochemical applications including electrodeposition. Different types of ILs have been developed including hydrophobic and hydrophilic, and many of the traditional ILs are either moisture sensitive or expensive. More recently, Abbott and coworkers have reported a new class of ILs known as deep eutectic solvents (DESs) which are mixtures of hydrogen bond donor such as quaternary ammonium salt like choline chloride and hydrogen bond acceptor such as urea or ethylene glycol. The DESs are non-toxic, low cost and stable against moisture compared to many known ILs. One more advantage of DES is their capability of dissolving various metal compounds including oxides, chlorides, and others, enabling the preparation of solutions for electrodeposition. To date, several different DESs including choline chloride/malic acid, choline chloride/oxalic acid, and choline chloride/ethylene glycol have been studied for the electrodeposition of Bi and Bi-containing alloys. While Bi(NO₃)₃ is usually used as the Bi(III) source for electrodeposition of Bi from aqueous baths, bismuth(III) chloride (BiCl₃ or BiCl₄) is used as the Bi(III) source in the DESs. Because the solubility of BiCl₃ in these DESs is low at room temperature, a temperature of 60 °C is generally employed in these studies. In all of these studies, the electrodeposition is carried out under an inert atmosphere. Considering that the large scale electrodeposition in industrial applications cannot be conducted under inert atmosphere without significant increase in costs. Here, we evaluate the electrodeposition of Bi in the ethaline DES under ambient atmosphere using Bi(NO₃)₃ as the Bi(III) source. The influence of water present in the DES is studied. Cyclic voltammetry, chronoamperometry are employed to evaluate the redox behavior of Bi(III) and the Bi deposition nucleation/growth process. Bismuth deposits are prepared on nickel foils and characterized by SEM and XRD techniques.

Experimental

Chemicals.—Choline chloride (ChCl, 98+%, Alpha Aesar), ethylene glycol (EG, 99.3+%, J.T. Baker), Bi(NO₃)₃ · 5H₂O (98%, Alfa Aesar), and Cu(NO₃)₂ · 3H₂O (98.0-103%, Sigma Aldrich) were used as received without further purification. Copper foils (99.9%, 0.127 mm thick) and Nickel foils (99+%, 0.127 mm thick) were cleaned by ultra sonication in acetone, 2 M nitric acid, and deionized water in sequence. Afterwards, the metal foils were dried and transferred to a glove box before being used as the substrate for deposition. Pt spiral wire was used as the counter electrode. The ethaline (ChCl/EG) deep eutectic solvent was prepared by mixing ChCl and EG with a 1:2 molar ratio in a beaker, and continuously stirred at 50 °C for 30 minutes until a transparent liquid was obtained. The water content of the freshly obtained ethaline DES was determined to be 18669 ppm (1.87 wt%) using Karl Fischer’s titration. The humidity of our laboratory is typically around 50%, and the water content of the DES increased to 7.2 wt% after exposed to the ambient atmosphere for 20 days.

Instruments.—Electrochemical experiments were conducted under ambient atmosphere. The electrochemical experiments were performed using an Autolab model PGSTAT 30 potentiostat/galvanostat controlled by the Nova 1.10 electrochemical software. A conventional three-electrode electrochemical cell was used for all electrochemical experiments. For voltammetric and amperometric experiments, the working electrode was a glassy carbon (GC), geometric area (A) = 0.071 cm², platinum (A = 0.031 cm²), gold (A = 0.024 cm²) or nickel (A = 0.071 cm²) disk electrode. The counter electrode was a piece of Pt spiral, and the reference electrode was a piece of Ag wire respectively immersed in neat ethaline DES contained in a glass tube with a fine-porosity tip. For the electrodeposition of Bi, a piece of Ni foil (A = 0.25 cm²) and a piece of Pt spiral wire were respectively used as the working and the counter electrodes. Electrodeposition was conducted via potentiostatic electrolysis in the baths steadily stirred using a magnetic stirrer. The surface morphology of the bismuth electrodeposits was characterized with a high-resolution scanning electron microscopy (HITACHI, SU8000). The crystalline nature of the bismuth electrodeposits was determined with a powder X-ray diffractionmeter (XRD, Shimadzu XRD-7000) using Cu Kα radiation. The
Cyclic voltammetry of bismuth(III).—The voltammetric behavior of Bi(III) in the freshly prepared ethaline DES (water content = 1.87 wt%) is illustrated by the voltammograms shown in Fig. 1 recorded on polycrystalline GC, Pt, Au, and Ni disk electrodes in the DES containing 10 mM Bi(NO$_3$)$_3$ at 30 $\degree$C under ambient atmosphere. As shown in Fig. 1A, the CV recorded at the GC electrode with a potential sweep rate of 50 mV s$^{-1}$ shows that the negative potential scan from the open circuit potential (OCP) gives a single reduction peak commences at about $-0.25$ V and reaches its peak at about $-0.40$ V, after which the current decreases as the diffusion layer gets thicker. On the reverse potential scan a current crossover is observed at $-0.10$ V after which an oxidative stripping peak is observed at about 0.20 V. This current crossover indicates that the cathodic deposition of Bi on the GC requires an overpotential to initiate the nucleation and growth of the bulk Bi. In addition, it is observed that the cathodic peak potential, $E_{pc}$, shifts negatively with increasing potential scan rate. Such a shift also indicates that the cathodic deposition of Bi is an overpotential-driven nucleation/growth process; a slower potential scan rate gives more time for the nucleation process to complete and leads to the reduction current to occur at a more positive potential whereas a faster potential scan rate leaves less time for the nucleation process, and the current does not occur significantly until the potential is swept to more negative value. It is observed that the potential where the current crossovers from cathodic side to anodic side does not affect by the potential scan rates, indicating that the electro-dissolution of the Bi deposits is less dependent on the scan rate. The CV recorded for the same Bi(III) solution at Ni electrode is shown in Fig. 1B. Essentially, voltammetric behavior such as current crossover and $E_{pc}$ shifting similar to those observed on GC electrode is seen on the Ni electrode, indicating that the cathodic deposition of Bi on Ni is also involved with an overpotential-driven nucleation/growth mechanism. However, the deposition of Bi on Ni commences at potentials less negative than that at GC, indicating less overpotential is required for the Bi nuclei formation on Ni. Note that the anodic potential scan was limited at 0.05 V to avoid the anodic dissolution of the Ni substrate. As shown in Fig. 1C, more complicate behavior is observed when the CV is recorded on Pt electrode. More careful examination of this CV reveals that small cathodic current commences at about $+0.25$ V in addition to the main bulk cathodic deposition. This additional cathodic wave can be attributed to the underpotential deposition (UPD) of Bi on Pt. The UPD of Bi on Pt is not surprising since it is known that UPD of a metal often occurs on a substrate that has a larger work function value than the deposited metal.$^{25}$ The work function of Pt is larger than that of the Bi.$^{26}$ Due to the presence of the Bi UPD layer, the overpotential required for the nucleation/growth of the bulk Bi is reduced, and as a result, the commence of the bulk Bi deposition shifts to less negative potential (ca. $-0.15$ V) in comparison to that on the GC electrode. Meantime, two additional anodic stripping peaks appear at about 0.15 V and $+0.30$ V in addition to the main bulk Bi deposition.
stripping peak. The additional stripping peaks can be attributed to the stripping of the UPD Bi and the Pt-Bi surface alloy. As shown in Fig. 1D, when the CV is recorded on a Au electrode which also has a work function much larger than Bi,26 the UPD of Bi is even more clearly indicated by the reduction potential at about +0.05 V which is associated with the anodic stripping peak at +0.12 V. The UPD of Bi on Au electrode observed here is in agreement with the UPD of Bi on Au in a nitric solution that has been reported previously.25 Because of the presence of the Bi UPD layer on the Au, the overpotential required for the nucleation/growth of the bulk Bi is significantly reduced. Therefore, the onset of the cathodic bulk Bi deposition on the Au electrode shifts to much less negative potential (ca. −0.06 V) in comparison to that on the other electrodes, and current crossover is not apparent in this CV.

As mentioned earlier that the cathodic peak potential, \( E_{pc} \), shifts negatively with increasing potential scan rate because the cathodic peak deposition of bulk Bi is involved with an overpotential-driven nucleation/growth potential process. When the values of the \( E_{pc} \) extracted from Fig. 1 at the various electrodes and scan rates are plotted in Fig. 2, it becomes clear that the \( E_{pc} \) is dependent on the nature of the electrode material, and varies from negative value toward positive value following the order: GC < Pt < Ni < Au, indicating that the deposition of Bi on GC requires the largest overpotential to initiate the nucleation/growth, whereas it requires the least overpotential on Au. This order agrees with the order of the formation of a UPD Bi layer. Furthermore, this figure shows that the slope of the \( E_{pc} \) shifting versus increasing potential scan rate on these electrodes follows the trend: GC > Ni > Pt > Au. This fact suggests that the nucleation rate of Bi is slowest on GC and fastest on Au.

The temperature effect on the electrochemical behavior of Bi(III) is illustrated by the CVs shown in Fig. 3 recorded on a Ni electrode in the DES containing 10 mM Bi(NO₃)₃ at 30°C and 60°C, respectively. Both CVs exhibit similar deposition and stripping peaks, but the peak currents obtained at 60°C are much higher than that obtained at 30°C, indicating the electrochemical reaction rate increases with increasing temperature due to the more efficient mass transfer rate resulting from lower viscosity at higher temperature. Furthermore, the onset potential of cathodic deposition of bulk Bi shifts to more positive value, and the current crossover disappears at 60°C in comparison with that observed at 30°C, indicating that the overpotential required for initiating the nucleation/growth of the bulk Bi deposition is greatly reduced by raising the temperature. The current efficiency was estimated by the ratio of the anodic charge to the cathodic charge (Qa/Qc). These charges were obtained by integrating the current under the anodic and cathodic transients resulting from such experiments conducted to further study the nucleation/growth process. In each of the experiments, the electrode potential is stepped from an initial value where no reduction would occur to a potential negative enough to initiate the nucleation/growth process, and the current resulting from the process is recorded as a function of time. Examples of a series of current-time transients resulting from such experiments carried on GC, Pt, and Ni, respectively, in a DES containing 10 mM Bi(III) are shown in the insets of Fig. 4. All of these current-transients show the typical behavior of a diffusion-limited reaction for a nucleation/growth process. Specifically, after the decay of double-layer charging, the current increases rapidly due to an increase in the electroactive area resulting from the formation and growth of bismuth nuclei on the electrode. The current transients increase to a current maximum, \( i_{max} \), at a time, \( t_{max} \). After \( t_{max} \), the current decreases as the diffusion zones around the nuclei begin to overlap. Finally, all the current transients converge and approach to the characteristic response for linear diffusion to a planar electrode surface that obeys the Cottrell condition (linear \( i \) vs. \( t^{-1/2} \) relationship).27 It can be seen from Fig. 4 that \( i_{max} \) increases whereas \( t_{max} \) shortens as the applied potentials is more negative (increased overpotential), indicating that both the nucleation/growth rate and the number of nuclei increase with increasing applied overpotential. Cottrell plots constructed from the current during the final seconds of the current-time transients recorded on GC electrode at 30°C is used to calculated the diffusion coefficient, \( D \), of the Bi(III) species in this solution at this temperature. The calculated \( D \) is \( 3.04 \times 10^{-7} \text{ cm}^2\text{s}^{-1} \), which is larger than that obtained for the Bi(III) species in a water-free DES at 60°C.23 Apparently, the absorption of water in the DES reduces the viscosity of the solution, and results in the larger \( D \). Nevertheless, the \( D \) value obtained here is smaller than that obtained for Bi(III) in a nitric solution because the water-containing DES is still more viscous than the aqueous nitric solution.

According to the Scharifker-Hills model of nucleation,28 the nucleation/growth mechanism is generally classified between two limiting cases; progressive and instantaneous. The nucleation sites are gradually activated with time after applying the potential step for the progressive nucleation/growth process. On the other hand, all the nucleation sites are activated at the same time upon applying the

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**Figure 2.** Plots of the cathodic peak potential, \( E_{pc} \), vs. scan rate of the cyclic voltammograms shown in Fig. 1.

**Figure 3.** Cyclic voltammograms of 10 mM Bi(III) introduced as Bi(NO₃)₃ in ethaline DES recorded on a Ni electrode at 30°C and 60°C, respectively. The scan rate was 50 mV s⁻¹.
Figure 4. Comparison between theoretical and experimental \((i/i_m)^2\) vs. \((t/t_m)^2\) plot for Bi deposition at 30 °C on (A) GC, (B) Pt, (C) Ni, and at 60 °C on (D) Ni electrodes in ethaline DES containing 10 mM Bi(III). Inset shows chronoamperometric current-time transients obtained at indicated potentials.

Potential step for the instantaneous nucleation/growth process. The two nucleation mechanisms can be distinguished by comparing the experimental current-time transient to the dimensionless theoretical \((i/i_m)^2\) vs. \((t/t_m)^2\) curves derived by Scharifker-Hills for three-dimensional (3D) instantaneous and progressive, respectively, nucleation/growth processes. \(^{26}\) Plots of \((i/i_m)^2\) vs. \((t/t_m)^2\) curves that were generated from the experimental data along with the theoretical curves are shown in Fig. 4. This figure clearly suggests that the nucleation/growth process of Bi deposition is dependent on the electrode material. At 30 °C, Bi deposition onto GC favors the instantaneous nucleation more than the progressive nucleation (Fig. 4A), while Bi deposition onto Pt and Ni electrodes proceeds by progressive nucleation (Figs. 4B, and 4C, respectively). Due to the UPD of Bi on Pt, the progressive nucleation mechanism observed on the Pt electrode may not precisely reflect the real mechanism, and should be considered with caution. Fig. 4D shows that raising the temperature to 60 °C does not significantly change the nucleation model for Bi deposition on Ni electrode.

Deposition and characterization of Bi film.—To accelerate the deposition rate, bulk electrodeposition of Bi was conducted by potentiostatic electrolysis of a ethaline DES containing 1.87 wt% of water and a higher concentration of 50 mM Bi(NO₃)₃ at 30 °C with stirring. The presence of water adsorbed from the ambient atmosphere, reduces the viscosity of the solution, and enhance the Bi(III) diffusion rate. The same accumulated charge density of 2 C cm⁻² was used for each of the electrolysis experiments. A CV of this solution was recorded at the Ni electrode before the constant potential electrolysis experiments in order to decide the applied potential for the electrolysis. As shown by the CV shown in the inset of Fig. 5A that due to the presence of water the reduction potential of Bi(III) under this condition onsets at about +0.0 V which is more positive than that is observed for the 10 mM Bi(III) solution shown in Fig. 1B. Moreover, the reduction current is much higher than that is observed in Fig. 1B. From this CV, three potentials, −0.04 V, −0.07 V, and −0.10 V are chosen for the bulk Bi electrodeposition experiments. The reduction current during each of the electrolysis experiments is recorded as a function of time, and the resulted current-time curves are shown in Fig. 5A. The deposition time period for complete the electrolysis gets shorter with increasing current density as the potential is made more negative. At a lower electrodeposition potential (−0.04 V), the current initiates and stays at a low value, suggesting the formation of a low nuclei number density, and the formation of a relatively compact layer of electrodeposits is expected. As the electrodeposition potential is shifted negatively to −0.07 V, the deposition initiates at a higher current which increased gradually with time. When the deposition is conducted even more negatively at −0.1 V, the deposition current increased rapidly with deposition time, suggesting a fast increase of the deposited Bi surface, and the formation of a coarse coating. The surface morphologies of the Bi-deposited samples are
shown by the SEM images in Figs. 5B–5D. In all cases, well defined microcrystallites were produced. The production of particles in these samples with different sizes agrees with the progressive nucleation process concluded from Fig. 4B. The average particle size of the crystallites decreases as the deposition gets more negative because the number of nuclei produced during the deposition increases at more negative potential. Therefore, the deposits obtained at −0.04 V and −0.07 V (Figs. 5B, 5C) are compact and dense, whereas the Bi-deposited sample obtained at −0.10 V is coarse. More close examine of Fig. 5D, reveals that the growth of the deposits seems to favor the direction vertical to the substrate more than the lateral direction. This kind of growth leads to the increase in the deposit surface area, and agrees with the increasing deposition current shown in the inset of Fig. 5A. Moreover, similar to that was observed for the electrodeposition of Bi in a nitric acid bath,6 step faceting is seen in some of the particles shown in the SEM images, suggesting that although the macrodeposit grows by three-dimensional nucleation and growth, each particle grows primarily by two-dimensional, layered growth which has also been observed in a nitric acid aqueous bath.8 Potentiostatic electrolysis of a ethaline DES containing 50 mM Bi(NO3)3 were also conducted at 60 °C with stirring. Shown in Fig. 6A are the current-time curves recorded for the electrolysis conducted at −0.04 V and −0.07 V, respectively. The currents seen in this figure are higher than that shown in Fig. 5A in accordance with the decreased viscosity. The surface morphologies of the Bi-deposited samples from these experiments are shown in Figs. 6B, 6C. Crystallographic features similar to Fig. 5 are observed in this figure. However, the average particle size of the crystallites in Fig. 6 is smaller than in Fig. 5, implying that the deposition current-time curves recorded during the constant potential deposition of Bi on Ni foils from an ethaline DES containing 50 mM Bi(III) at the indicated potential at 30 °C. Inset in (A) is the CV recorded for this solution. The SEM images of the deposits obtained at (B) −0.04 V, (C) −0.07 V, and (D) −0.10 V.

**Deposition of Bi on Cu via galvanic displacement reaction.—**Fig. 8A compares the cyclic voltammograms recorded at a GC electrode in the ethaline DES containing Bi(NO3)3 and Cu(NO3)2, respectively, at 30 °C. As can be seen, the Cu(NO3)2 solution exhibits two redox couples attributed to the Cu(I)/Cu(II) and Cu(I)/Cu reactions. It is clear that the redox potential of the Cu(I)/Cu couple overlaps with the redox potential of the Bi(III)/Bi couple. This fact suggests that Cu can be galvanic oxidized by Bi(III) species, and Bi can be deposited on the Cu substrate via this galvanic displacement reaction in this DES. To prove this, a Cu foil is immersed in a ethaline DES containing 50 mM Bi(NO3)3 at 30 °C. During the immersion, the color of the Cu foil changes from brown into gray, indicating that the displacement deposition of Bi is taking place. Fig. 8B shows the SEM micrograph of the Cu foil after being immersed in the Bi(III) solution for 15 min. This figure shows that the surface of the Cu is covered by a layer of particles. An enlarged SEM of this sample shown in Fig. 8C further reveals the presence of aggregates formed with crystals having sizes less than 2 µm. Fig. 8D shows the XRD patterns of this sample. This figure clearly shows that in addition to the reflections due to the Cu substrate (designated by •), all the diffraction patterns can be assigned to Bi.6,8,23 It is noted from this figure that the texture of the Bi deposits varies with deposition potential. For example, at 30 °C, the intensity of the 012 and 024 reflections increases while the intensity of several other reflections, such as 003, 022, 107, decreases as the potential is made more negative, suggesting preferred orientation of the growth. This phenomenon is similar to that was reported in the electrodeposition of Bi in a nitric solution.6 However, the preferred orientation of growth is less evident at 60 °C because the intensity of all the reflections decreases relatively equally when the deposition potential was made more negative. On the other hand, the half-peak width of the reflections increases when the potential is made more negative. This may reflect that the grain size of the deposits decreases with increasing applied overpotential.

![Figure 5](image-url)

**Figure 5.** (A) The i-t curves recorded during the constant potential deposition of Bi on Ni foils from an ethaline DES containing 50 mM Bi(III) at the indicated potential at 30 °C. Inset in (A) is the CV recorded for this solution. The SEM images of the deposits obtained at (B) −0.04 V, (C) −0.07 V, and (D) −0.10 V.
Figure 6. (A) The $i$-$t$ curves recorded during the constant potential deposition of Bi on Ni foils from an ethaline DES containing 50 mM Bi(III) at the indicated potential at 60°C. The SEM images of the deposits obtained at (B) $-0.04$ V, and (C) $-0.07$ V.

**Influence of water content on the voltammetry of Bi(NO$_3$)$_3$ in the DES.—**This study focuses on the electrochemistry of the Bi(III) in the ethaline DES under ambient atmosphere. Because the ambient atmosphere contains certain amounts of water that will be taken up by the DES, it is necessary to study the influence of the water contents on the voltammetry of the Bi(III). For this purpose, portions of water were added to a 6.0 mL DES containing 8.6 mM Bi(NO$_3$)$_3$ at 30°C, and cyclic voltammograms were recorded on a GC electrode after each addition. Typical voltammograms are shown in Fig. 9. Similar to what has been observed for the electrodeposition of zinc from ionic liquid/water mixture. This figure shows that both cathodic peak current and anodic peak current increase with increasing water content. Meanwhile, the peak potential of the Bi(III)/Bi redox couple shifts positively upon the addition of water. This phenomenon may be partly attributed to the reduced viscosity and increased conductivity of the DES solution upon the addition of water. The potential shifting upon addition of water may be the results of several phenomena. Firstly, the improved conductivity of the solution upon introducing water may reduce the overpotential caused by the solution resistance for the reduction of Bi(III), leading to positive potential shift. Secondary, the positive potential shift may also be related to the change in the electrified electrode/solution interface (ESI) structure. It has been reported that in ionic liquids, ILs (or DES), the ESI consists of a multilayer structure which may hinder the approaching of the solute ions from contacting the electrode surface to exchange electrons, and adds an overpotential required for reduction. The multilayer structure is reduced toward a double layer structure when water is mixed with the ILs (or DES), and as a result, reduces the overpotential for reduction to take place. Thirdly, in the absence of water the ethylene glycol in the DES (in addition to chloride ions) may act as a ligand coordinating to the Bi(III). When water is present, hydrogen bonding interaction may occur between the hydrogen atom of water and the hydroxyl-oxygen atoms of ethylene glycol, weakens the interaction between ethylene glycol and Bi(III), contributing to the

Figure 7. XRD patterns of Bi electrodeposited on Ni foil from ethaline DES containing 50 mM of Bi(NO$_3$)$_3$ at (A) 30°C, and (B) 60°C. The applied electrodeposition potentials are indicated in the figures. The reflection patterns of the Ni substrate are indicated with (●).
Figure 8. (A) Cyclic voltammograms recorded at a GC electrode for the solutions of ethaline DES containing Bi(NO$_3$)$_3$, and Cu(NO$_3$)$_2$, respectively, at 30°C. The scan rate was 50 mV s$^{-1}$. (B) and (C) are the SEM micrographs of the Bi-deposited Cu foil by galvanic displacement of Bi on Cu in an ethaline DES containing 50 mM Bi(NO$_3$)$_3$ at 30°C. (D) XRD patterns of the Bi-deposited Cu foil sample shown in (C).

Potential shift. However, the use of a quasi-reference electrode in this study somewhat reduces the reliability of the observed potential shift, and therefore, the water content effect on the potential shift needs be further checked more quantitatively using other metal redox systems in the future. White precipitates drop out when the water contents exceed 3.11 mL, which corresponds to an water to DES volume ratio of 0.5, indicating that the solubility of the Bi(NO$_3$)$_3$ is limited by the water contents. The above results show that the addition of water to the DES has both positive and negative effects on the use of DES for electrochemical studies.

Conclusions

This work investigates the voltammetry and electrodeposition of bismuth in the ethaline DES under ambient atmosphere using Bi(NO$_3$)$_3$ as the Bi(III) source. Water taken up from the ambient atmosphere reduces the viscosity of the DES, and hence, facilitates the reduction reaction. However, the solubility of Bi(NO$_3$)$_3$ is suppressed by the presence of high water content. Cyclic voltammetry shows that the reduction of Bi(III) to Bi on the GC requires a higher overpotential than on the Pt, Au, and Ni electrodes. UPD of Bi on Au and Pt electrode is observed in accordance with the work function of the materials. Increasing the temperature decreases the viscosity of the solution and the required deposition overpotential, and therefore facilitates the reduction. Chronoamperometry experiments indicate that while the deposition of bismuth at a glassy carbon electrode involves with an overpotential-driven three dimensional instantaneous nucleation/growth process, the deposition of bismuth at the platinum, and nickel electrode involves with a progressive nucleation/growth process. Bismuth deposits were prepared by constant potential electrolysis on Ni foils. SEM images show that the particles size of the deposits decreases with more negative potential and/or higher temperature. SEM images also reveal that although the macrodeposit grows by three-dimensional nucleation and growth, each particle grows...
primarily by two-dimensional, layered growth. The intensity of reflections observed in the XRD patterns of the Bi deposits varied with potential, suggesting preferred orientation of the growth. Because the redox potential of Bi(III)/Bi couple overlaps with that of the Cu(I)/Cu couple in the DES, crystalline Bi can be deposited on Cu by the galvanic displacement reaction. The ability of operating the deposition under ambient atmosphere suggests the possibility for using the DES in practical electrochemical applications. More detailed quantitative studies on the effects of solution water content on the nucleation process and the morphology of the deposits shall be conducted further.

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