RESEARCH ARTICLE

Electrodeposition of nano tin film on different substrates in a choline chloride–ethylene glycol deep eutectic solvent containing boric acid

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ABSTRACT

In recent years, Tin has been used in coating of medical and orthopedic instruments, probes, alignment devices, implants and surgical cutting tools. This study examines the electrodeposition of nano tin film on several substrates, including brass, copper, and mild steel, while using a ChCl: EG-based liquid which also contained boric acid. It was found that adding larger amounts of boric acid improved the conductivities of Sn electrolytes; when boric acid was introduced to them, the redox current peaks of Sn decreased with increasing concentrations of boric acid and displayed negative shifts in the deposition peak when performing cyclic voltammetry. SEM was involved to examine the morphologies of Sn deposits. Boric acid was found to improve the homogeneity of the morphologies of the deposited Sn films, leading to the formation of smooth Sn coatings, the associated roughness of which was determined to be 7.642 nm. The Sn deposits’ crystal structure was investigated using X-ray diffraction spectroscopy.

How to cite this article


INTRODUCTION

Most surgical tools are often made from stainless steel, but these materials are suffering from corrosion so coat them with metal with high resistant to corrosion is necessary. Electroplating is used to deposit various kinds of metals and alloys because of its various advantages as a technique, the excellent purity of any resulting deposits, its reasonable handling pressures, and its low processing temperature [1].

Due to its nontoxic nature, ductility, and corrosion-resistant properties, tin and its alloy coatings are vital in various industrial fields [2]. Tin is used as an anodic material in lithium-ion rechargeable batteries, and as a coating to protect metals from corrosion. Tin is also used in foodstuff processes [3]. Previously, electrodeposition of tin was performed using acidic solutions (such as methane sulfonic acid, fluoborite, and phenol sulfonic acid), or from alkaline solutions. However, the primary disadvantage of alkaline solutions is that high temperatures are required for the deposition process; the main problem with acidic baths, by contrast, is the formation of precipitates of tin oxide, SnO₂ [4, 5].

Moreover, electrodeposition of metals from aqueous solutions have several further disadvantages: the current efficiency is low, hydrogen is evolved, the electroplating of certain elements requires toxic reagents such as cyanide, the process has a narrow potential window, the electrodeposition of water-sensitive elements such as W, Al, and Ti is difficult and, finally, some metals are poorly electrodeposited from aqueous electrolytes in general (such as Zn and Cr) [6].

Several ionic liquids have been utilized in the electrodeposition of tin, such as 1-n-methylpyrrolidinium bis-(trifluoromethyl sulfonil)imide (BMPTFSI) [7] and 1-ethyl-3-methylimidazolium dicyanamide (EMI-DCA) [8]. However, the major drawbacks of these liquids...
are their reactivity with water and their possible degradation in the presence of oxygen [9], as well as their high cost.

Recently, DESs, which are a sub-class of ILs, have begun to be used as alternative solvents in the electrodeposition process. DESs have some major advantages over conventional ionic liquids in the sense that they are easy to prepare, cheaper, biodegradable, and considerably less toxic [10]. Among the various applications of DESs, they are widely employed as electrolytes in metal electrodeposition and electropolimerization processes [11-23]. Porous Sn film electrodeposition from Ethaline and its lithium storage performance were investigated by Gu et al. [24].

The electrodeposition of tin from choline chloride in the presence of various hydrogen bond donors (HBD), was investigated by Sonia and coworkers, whose results demonstrated that choline chloride-based solvents can be successfully used to support such an electrodeposition [25].

The concentration of SnCl₂ can also affect the formation of complexes in ethylene, where Swatilekha et al. observed what appeared to be two stripping steps in polarization scans with increasing concentrations of tin salt (SnCl₂·2H₂O), which was due to the formation of complexes such as SnCl₃ and Sn₂Cl₅ [26].

In their investigation of the electrodeposition of tin from ChCl-urea-based DESs, Cao et al. looked on the influence of hotness and SnCl₂ concentration on the reduction behavior of the metal. [27].

Tin alloys were also studied by Vieira et al. [5], in particular tin-bismuth. Hasan et al. also looked into how additives affected the electrodeposition of such alloys [28].

The aim of this work was to improve a deeper understanding of how tin electrodeposits on various substrates (brass, copper, and mild steel) when a 1:2 mixture of 1:2 ChCl:EG is used as the deposition medium, both with and without the addition of boric acid. We studied electrodeposition of nano tin film on different substrates in a 1:2 ChCl:EG deep eutectic solvent containing boric acid which can be used in coating of medical and orthopedic instruments, probes, alignment devices, implants and surgical cutting tools to increase resistance of these tools to the corrosion. Such tin films’ surface morphologies, roughnesses, and crystallities were examined using SEM, AFM, and XRD, respectively.

**EXPERIMENTAL**

Choline chloride (Biochem Chemopharma, 98%) and ethylene glycol (Thomas Baker, 99%) were combined in 0.1 M SnCl₂·2H₂O was added to the Ethaline 200 and mixed at 80°C until the associated Sn solution had been prepared with and without BA.

A Pt disc served as the working electrode, a Pt flag served as the counter electrode, and Ag served as the reference electrode in a three-electrode cyclic voltammetry system with a PGSTAT20 potentiometric. The cyclic voltammetry was carried out within a potential range of 0.2 V to -1.0 V.

The electrical conductivities of Sn solutions were measured at various temperatures in the range 25-90°C. The surface morphologies of Sn films were characterized using a TESCAN Mira3 instrument with an accelerator voltage of 25 keV.

SEM was used to study morphologies of Sn deposition, An NT-MDT Netgra AFM device was used to conduct atomic force microscopy in order to analyze the 3D surface morphologies of the Sn deposits and assess the roughnesses of the films.

A PHILIPS PW1730 was used to conduct the associated powder X-ray diffraction experiments. A Cu anode with 1-deg, 1-deg, and 0.2 mm slit monochromatic-filtered radiation made up the X-ray tube, which was operated at 30 mA and 40 kV.

**RESULTS**

**Physical Properties**

Most ionic liquid electrodeposition investigations to date have paid little attention to how the addition of boric acid actually affects the physical characteristics of Ethaline 200. Viscosity has a direct impact on the rate of transport of the reactive material to the electrode surface for deposition, which in turn affects coating rate. In this paper, we demonstrate that boric acid has an obvious effect on the viscosity and conductivity of Ethaline 200. Moreover, viscosity is one of the more significant properties of ionic liquids which are
used as solvents and electrolyte solutions. This physical property of ionic liquids is acquired via van der Waals and hydrogen bonding interactions [29]. The viscosity of SnCl$_2$H$_2$O in 1ChCl:2EG is described in Fig. 2 (a) as a function of temperature and concentration of boric acid. As can be observed, boric acid has no appreciable impact on a substance's capacity to flow and only very slightly increases the viscosity of the SnCl$_2$H$_2$O in a 1:2 ChCl:EG solution. The establishment of large numbers of hydrogen bonds typically results in an increase in the viscosity of the associated ionic liquid. This might be caused by the liquid disrupting the lattice and changing the coordination of the Cl$^-$ dialogue.

The corresponding change in conductivity with respect to the concentration of boric acid in 1:2 ChCl: EG is shown Fig. 2(b). Here, the conductivity is presented in an analogous manner to the viscosity and decreases as a function of the concentration of boric acid. Fig. 2(b) depicts the conductivity of SnCl$_2$H$_2$O in 1:2 ChCl:EG as a function of temperature and different amounts of boric acid. As a result, the conductivity with different concentrations of boric acid shows a differing pattern to that of the viscosity, as the conductivity of the metal salt solution decreases significantly with increasing concentration of boric acid. As a result, these species more probably exhibit inhibition conductivity of SnCl$_2$H$_2$O in Ethaline 200. It is also shown in Fig. 2(b) that

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**Fig. 1.** Image of the Sn electrodeposition apparatus, as run at 80°C for 30 min.

**Fig. 2:**

(a) The viscosity of 0.1 M SnCl$_2$H$_2$O in Ethaline 200 as a function of temperature and various concentrations of BA, and (b) the conductivity of 0.1 M SnCl$_2$H$_2$O in Ethaline 200 as a function of temperature and various concentrations of BA.
the conductivity of SnCl$_2$.2H$_2$O, with different concentrations of boric acid, increases significantly with increasing temperature.

Cyclic voltammetry
Voltammograms were produced using a Pt disc, a Pt flag, and Ag wire as the working, counter, and reference electrodes, respectively. Fig. 3 displays the cyclic voltammograms of 0.1 M SnCl$_2$.2H$_2$O in Ethaline 200. The cyclic voltammetry was performed starting at 0.2 V and moving in a negative direction until reaching -1 V before being reversed back to 0.2 V. The cyclic voltammetry of 0.1 M SnCl$_2$.2H$_2$O at different temperatures was investigated, as shown in Fig. 3(a), where increasing cathodic and anodic peak intensities were observed with increasing temperature. Elevated temperature increases the free volumes in the IL, increasing the mass transport towards the electrode surface as a result of the decrease in viscosity and increase in the movement of ions, which then accelerates the oxidation-reduction processes. Fig. 3(b) shows the cyclic voltammograms performed at different scan rates at 80°C, which indicate that there are two different reduction processes responsible for the reversible Sn$^{2+}$ to Sn$^0$ couple at -0.4 V, whereas Sn dissolution (from Sn$^0$ to Sn$^{2+}$) is responsible for the stripping peak at -0.3 V. The cathodic and anodic peaks in this case are unaffected by scan rate. The cyclic voltammetry response of a 0.1 M SnCl$_2$.2H$_2$O in Ethaline 200 solution at 80°C in both the absence and presence of various boric acid concentrations is shown in Fig. 3(c). When BA is present, the Sn deposition peak at negative potential somewhat decreases; this is because BA adheres to the electrode surface and prevents Sn deposition. As BA was added to the Sn electrolyte, the Sn reduction potential also shifted negatively by around 30 mV. The adsorption of BA on the electrode surface, which necessitates more energy to discharge the Sn ions, is responsible for the negative shift in the overpotential for the reduction of Sn.

![Cyclic voltammetry graphs](image)
Deposit properties

Effect of temperature on the electrodeposition of Sn

In this work, to study influence of temperature on the morphology of the Sn deposit, the electrodeposition process was achieved at low (room) and high (80°C) temperatures, as shown in Fig. 4, where each of these films was deposited on a copper substrate at 30 mA cm\(^{-2}\) for 30 min.

Dark-colored and heterogeneous film was observed when electrodeposition was performed at room temperature, as illustrated in Fig. 4(a), in comparison to that performed at 80°C, where a bright, uniform Sn coating was formed when the deposition was achieved at the higher temperature. As shown above, temperature has a significant impact on conductivity, as per Fig. 2(b), and on the cyclic voltammetry of the electrolyte during Sn deposition, as per Fig. 3(a), and thus has an effect on the morphology of the Sn film so deposited. At high temperature, the Cl\(^-\) anion concentration decreases, which allows Sn deposition to proceed at a high rate and thus with high current efficiency [30]. Additionally, the reduced viscosity of the Sn electrolyte brought on by the higher temperatures can exacerbate the effects of mass movement. The electrodeposition of Sn from Ethaline 200 at high temperature is thus advised for the production of a bright, uniform Sn coating, as based on cyclic voltammetry and morphological data. Consequently, in this work, the electrodeposition of Sn from Ethaline 200 has been carried out at 80°C in both the absence and presence of boric acid.

Effects of boric acid on the electrodeposition of Sn

Fig. 5 demonstrates the pictures, SEM image and AFM images (right) for Sn electrodeposition in a 0.1 M SnCl\(_2\)·2H\(_2\)O electrolyte at a constant bath temperature of 80°C without/with varying concentrations of BA. In each experiment, the Cu substrates were electroplated for 30 minutes at a CD of 30 mA cm\(^{-2}\). In fact, in employing boric acid, excellent adhesion was attained for all Sn coatings. As can be seen in the inset of Fig. 5, the morphology of the electrodeposited additive-free Sn film was discovered to be a rough layer with bigger grains (a). However, as demonstrated in Figs. 5(b), (c), and (d), we observe that the surface morphologies of the Sn deposits are changed when the BA additive is added to the Sn plating bath. An enhancing concentrations of BA in the plating bath, the particle sizes were obviously noticeably reduced, and the grain sizes of the particles steadily shrank. In comparison to Sn deposition without BA, the surface morphology also improved with concentration. This is a consequence of the smaller crystal size brought on by the addition of different BA additive concentrations. This suggests that BA may be effective because film deposition requires

![Fig. 4. SEM images of 0.1 M SnCl\(_2\)·2H\(_2\)O electrodeposited on Sn in Ethaline 200. Both films were formed using a copper electrode with a CD of 30 mA cm\(^{-2}\) at two different temperatures: (a) room temperature, and (b) 80°C.](image-url)
a finer grain, which would slow the growth rate of the Sn deposit. Roughness of the tin deposits achieved from 1:2 ChCl :Cl on the copper were studied via AFM in both the absence and presence of BA. A 20 x 20 mm area was the subject of AFM scans. Average surface roughnesses of Sn films are shown in Table 1, where it is evident that the roughness of the Sn film decreased as BA concentration in the plating liquid increased.

The morphologies of Sn deposits on the copper, mild steel, and brass substrates were characterized via SEM, as shown in Fig. 6. The depositions were accomplished using Ethaline 200 that contained 0.05 M BA and at a CD of 30 mA cm² for 30 minutes at 80°C. As shown in Fig. 6, Sn deposits on the brass substrate were not uniform and showed different particle sizes. This deposit is more uniform than that obtained on the copper electrode. Small particles were found to be distributed along the surface on the mild steel

![AFM images of Sn deposits](image-url)
substrate, as shown in Fig. 6(c). The EDX spectra in Fig. 6 confirm that the films are formed from Sn.

In this study, XRD was used to examine the crystal structures of the Sn deposits generated from the electrolyte on copper, brass, and mild steel surfaces. The XRD patterns for Sn deposits are displayed in Fig. 7. Sn deposits at 2θ values of 30.5°, 32°, 44.2°, 44.9°, 55.3°, 62.5°, 64.6°, 73.8°, and 79.5° were associated with the (200), (101), (220), (211), (301), (112), (321), (420), and (312) planes, respectively.

<table>
<thead>
<tr>
<th>Metal salt</th>
<th>Conc. BA / M</th>
<th>Average roughness / nm</th>
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<tr>
<td>SnCl₂.2H₂O</td>
<td>0.00</td>
<td>32.08</td>
</tr>
<tr>
<td>SnCl₂.2H₂O</td>
<td>0.01</td>
<td>20.9</td>
</tr>
<tr>
<td>SnCl₂.2H₂O</td>
<td>0.03</td>
<td>12.5</td>
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<tr>
<td>SnCl₂.2H₂O</td>
<td>0.05</td>
<td>7.9</td>
</tr>
</tbody>
</table>

Table 1. Average surface roughnesses of Sn films

Fig. 6. SEM images and EDAX spectra for the electrodeposition of SnCl₂.2H₂O on copper, brass, and mild steel substrates, respectively. Each experiment was run for 30 minutes at 80°C.
CONCLUSION
This study examines the Sn deposits produced by Ethaline 200 on copper, brass, and mild steel substrates when boric acid is used as an additive. It was discovered that when the process was carried out using electrolytes containing BA, a bright, uniform Sn deposit was generated. When boric acid’s effects on the Sn electrolyte’s electrochemical behavior were investigated, it was found that BA could be deposited onto the surface of electrode and thereby prevent Sn deposition. Additionally, performing the electrodeposition in electrolytes containing BA had a significant impact on the morphology, composition, nucleation, and roughness of the resultant Sn deposits. Utilizing XRD, the crystal structures of the resulting Sn deposits were analyzed.

ACKNOWLEDGEMENTS
The MHERS of Iraq provided financial assistance for this project, and the authors would also like to thank the University of Kerbala for supplying the supplies and equipment needed.

CONFLICT OF INTEREST STATEMENT
On behalf of all authors, the corresponding author states that there is no conflict of interest.

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