



Makale / Research Paper

Electrochemical Behavior of Tin Based Film Cathodically Deposited from Non-Aqueous Media

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Abstract: A platinum electrode was coated with Sn in order to study the electrochemical behavior of the Sn-based modified electrode in an acidic electrolyte. A deep eutectic solvent consisting of ethylene glycol and choline chloride (called Ethaline) was used as a deposition electrolyte by applying different voltage and time at two different temperatures (room temperature and 55 °C). The tin-coated platinum electrode was immersed in Na₂SO₄ and KOH solutions for the formation of tin oxide and tin hydroxide, respectively. Tin hydroxide and tin oxide films cycled in H₂SO₄ were not electroactive and these films cannot be used in acidic media for electrochemical devices. Sn electrode electrodeposited at high temperature was more than 500 times thicker than that at room temperature (20±2 °C). Thick SnO and Sn(OH)₂ films were not electroactive in acidic media the same as thin ones. Sn electrode electrodeposited from deep eutectic solvent at 55 °C and treated with an acidic solution was cycled in alkaline electrolyte. The reduction of the resulted film in KOH appeared at higher potential. This electrode could be used for the hydrogen evolution reaction in alkaline media.

Keywords: Electrodeposition, Ionic liquid, Tin, Tin oxide, Tin hydroxide

Sulu Olmayan Ortamlarda Katodik olarak elde edilen Kalay Esaslı Filmin Elektrokimyasal Davranışı

Öz: Platinum elektrot, Sn bazlı modifiye edilmiş elektrodun asidik elektrolit içindeki elektrokimyasal davranışını incelemek için Sn ile kaplandı. İki farklı sıcaklıkta (oda sıcaklığı ve 55 °C) farklı voltaj ve zaman uygulanarak kaplama elektroliti olarak etilen glikol ve kolin klorür (Ethaline olarak adlandırılan) içeren derin bir ötektik çözücü kullanıldı. Kalay kaplı platin elektrot, sırasıyla kalay oksit ve kalay hidroksit oluşumu için Na₂SO₄ ve KOH çözeltilerine daldırıldı. H₂SO₄ içinde taranan kalay hidroksit ve kalay oksit filmler elektroaktif değildi ve bu filmler asidik ortamda elektrokimyasal cihazlar için kullanılamaz. Yüksek sıcaklıkta elektrokaplanmış Sn elektrodu, oda sıcaklığındakinden (20±2 °C) 500 kat daha kalındı. Kalın SnO ve Sn(OH)₂ filmleri, asidik ortamda ince filmler gibi elektroaktif değildi. 55 °C'de derin ötektik çözücünden elektrokaplanmış ve asidik çözelti ile muameleye maruz bırakılmış Sn elektrodu bazik elektrolit içinde tarandı. Nihai filmin KOH içerisinde yüksek voltajda indirgenmesi ortaya çıktı. Bu elektrot, bazik ortamdaki hidrojen ortaya çıkma reaksiyonu için kullanılabilir.

Anahtar kelimeler: Elektrodepolama, İyonik sıvı, Kalay, Kalay oksit, Kalay hidroksit

Bu makaleye atıf yapmak için

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1. Introduction

Electrolytes (changing additives) and deposition conditions (applied potential, time, and temperature) are critical for electrodeposition [1-2]. Different electrolyte and deposition conditions have been researched for the electrodeposition of tin and tin alloys [3]. Electrodeposition could be applied either constant potential (potentiostat) or constant current (galvanostat). Pulsed electrodeposition could also be used to obtain metals and alloys. As electrodeposition is a simple and inexpensive method, it is widely used in industry for metal plating. The thickness and surface morphology of coating could be tailored by changing deposition parameters [4-5]. It is well known that the mass of metals/alloys (reduction of materials in electronics) is directly proportional to charge passed through electrode (Faraday's Law) [6]. Nucleation and growth of tin have been studied in detail depending on additives and deposition methods [7].

Sn and its alloys have been studied in the electronic industry instead of Pb which is highly toxic. Sn has been used as an alternative solder [8]. Tin coatings can protect the surface of bulk material from corrosion [9]. Tin and tin alloys have can be used as anode materials in lithium-ion batteries instead of graphite [10]. Metals including steel, copper have been coated by tin and tin alloys in order to improve not only corrosion resistivity but also to the appearance of bulk materials.

Electrolytes used to electrodeposit tin and its alloys could be the aqueous and non-aqueous solution. Aqueous electrolytes commonly used for tin growth are acidic or alkaline. Non-aqueous electrolytes can be ionic liquids that have studied commonly last decade [11]. Tin is electrodeposited from Sn^{2+} electrolyte by applying direct current. It is known that alkaline baths having hydroxide ions could be used without adding ligands. However, complexing agents are necessary to add acidic bath used for Sn deposition [12]. In this study, an ionic liquid that has only ions have been used to obtain Sn. Generally, current efficiency is low when an aqueous bath is used. However, the current efficiency for metal/alloy deposition in the ionic liquid is high [13]. A deep eutectic solvent has been used as an ionic liquid electrolyte for Sn electrodeposition in this work.

Deep eutectic solvent consists of a quaternary ammonium salts and hydrogen bond donor. Physical properties of ionic liquids and deep eutectic solvents are similar [14]. Tin and tin alloy (with zinc) were electrodeposited from choline chloride-based deep eutectic solvent (with ethylene glycerol and urea) containing Sn salt [15]. Structure, morphology and deposition kinetic of tin obtained from ionic liquid were different than these of tin electrodeposited from aqueous solution [16]. However, the electrochemical behavior of resulting films was not studied in different media.

Hydroxides and oxides form of manganese, cobalt, nickel are commonly studied for energy storage devices (supercapacitor and batteries) [17-18]. However, the study of energy storage devices regarding tin-based materials is limited. In this work, Sn was electrodeposited from a deep eutectic solvent and it was treated in an aqueous electrolyte to obtain SnO and $\text{Sn}(\text{OH})_2$. After hydroxide and oxide forms of Sn were obtained, they were transferred to acidic media in order to understand their electrochemical performances.

2. Materials and Methods

Na_2SO_4 (Sigma-Aldrich), KOH (Tekkim), H_2SO_4 (Merck), choline chloride (Merck), ethylene glycol (Merck), SnCl_2 (Sigma-Aldrich) were used directly. All experiments were carried out using Versastat 3 (AMATEK, Princeton Applied Research, USA). Pt flag (99.9% purity) and platinum-coated mesh were used as working and counter electrodes, respectively. The platinum working electrode was used because the potential window which is selected to study the electrochemical behavior of tin-based coating is not overlapped by the reaction of Pt. Silver wire and silver-silver chloride reference electrodes were used in non-aqueous ionic liquid and aqueous electrolyte. All

deposition potentials reported here are against the Ag wire reference electrode because the ionic liquid was used for electrodeposition. Sn coated Pt electrodes electrodeposited from ionic liquid were transferred to aqueous solutions (alkaline, acidic and neutral) for polarization treatment and cycling. Silver-silver chloride reference electrode having saturated potassium chloride was used in aqueous electrolytes. Before each electrodeposition of Sn, Pt electrodes were immersed in saturated HNO_3 in order to remove all coating from the surface. Then, the electrode was rinsed with deionized water and by ethanol. During the potentiostatic deposition, two constant potentials were applied at room temperature (20 ± 2 °C) for 300 sec and 55 °C for 500 sec in Ethaline. Ethaline was prepared by mixing one-part choline chloride with two-part ethylene glycol at 50 °C for 45 minutes. The Sn^{2+} solutions were prepared by dissolving tin chloride in Ethaline. Chronoamperometric and chronocoulometric data of Sn growth were obtained. The polarization of electrodes was performed operating at a scan sweep of 20 mV s^{-1} at 20 ± 2 °C.

3. Results and Discussion

Sn was electrodeposited from ethylene glycol and choline chloride mixture called Ethaline containing 0.1 M SnCl_2 . As the electrochemical behavior of tin coating was aimed to study, the substrate was platinum flag because platinum generally is electroinactive in the different electrolytes at a wide potential window [19]. It is known that deep eutectic solvent can be used for metal and alloy deposition generally at high temperatures [20]. However, Sn was deposited on a platinum working electrode at 20 ± 2 °C. The deposition potential of -0.9 V was applied to a platinum electrode immersed in Ethaline electrolyte containing 100 mM SnCl_2 for 300 seconds. The deposition potential was against the Ag wire reference electrode because the water in the Ag-AgCl reference electrode can contaminate the ionic liquid. Chronoamperometric and chronocoulometric responses of a platinum electrode in Ethaline ionic liquid are presented in Figure 1. The current density of the electrode was around $55 \mu\text{A cm}^{-2}$ as soon as -0.9 V was applied and the current density increased to $10 \mu\text{A cm}^{-2}$ after around 150 seconds. The response of the current density of the electrode became linear after that point. Negative current can occur when a reduction reaction occurs. The negative current shown in Figure 1 indicates that tin was electrodeposited on the substrate. Ethaline was used as a deposition electrolyte because hydrogen evolution does not occur when deposition potential around -1 V was applied. Hydrogen evolution reaction during electrodeposition can cause the growth of metal hydroxide especially in aqueous solutions and decrease current efficiency. The charge density of tin deposition (blue line of Figure 1) was approximately 3.2 mC cm^{-2} after 300 seconds. The charge was calculated from the integration of the current time graph. After Pt was polarized cathodically in Ethaline solution by application of -0.9 V, the surface became black and indicated that Sn coated Pt surface. A tin-coated platinum electrode was transferred to the different aqueous electrolytes for electrochemical characterization.

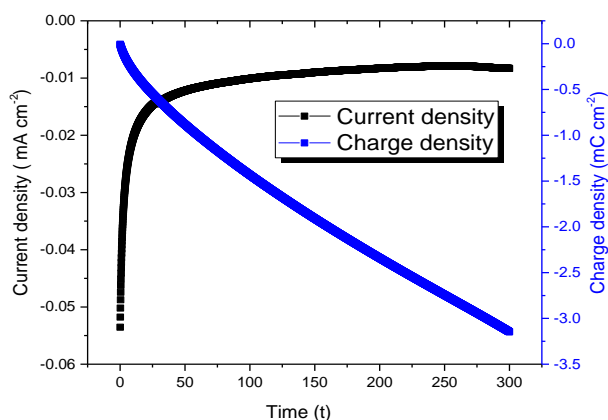


Figure 1. Chronoamperometry and chronocoulometry of Sn growth on Pt working electrode from Ethaline containing 0.1 M SnCl_2 by applying -0.9 V for 300 seconds at 20 ± 2 °C.

Sn modified Pt electrode was immersed firstly in Na_2SO_4 solution in order to obtain a form of tin oxide. Cyclic voltammetry response of the Sn coated Pt electrode in Na_2SO_4 electrolyte is given in Figure 2a. In aqueous electrolyte, the reference electrode was Ag-AgCl having a saturated KCl solution as it is more stable than Ag wire which was used during electrodeposition of Sn in ionic liquid media. Oxidation of Sn started at around 0.25 V and reached to around $8 \mu\text{A cm}^{-2}$ at 0.7 V (see the first cycle of Figure 2a). Although obvious oxidation of Sn was observed, a reduction related to that oxidation was not seen because the tin film was oxidized but not reduced. The oxidized form of Sn was stable in Na_2SO_4 electrolyte. Sn was cycled again in the same electrolyte to elucidate its electrochemical response and that time oxidation was also not observed. The tin oxide coated platinum electrode was taken out and washed with deionized water and immersed in H_2SO_4 for cycling. The cyclic voltammogram of SnO coated Pt is shown in Figure 2b. Oxidation and reduction reaction of the modified electrode in H_2SO_4 was low (around $2 \mu\text{A cm}^{-2}$ at 0.7 V). It can be said that SnO modified electrode is not electroactive in acidic media. Tin was firstly electrodeposited on platinum and that electrode was treated in Na_2SO_4 electrolyte to obtain tin oxide. As tin oxide film cycled in H_2SO_4 was not electroactive, tin oxide films cannot be used in acidic media for electrochemical devices.

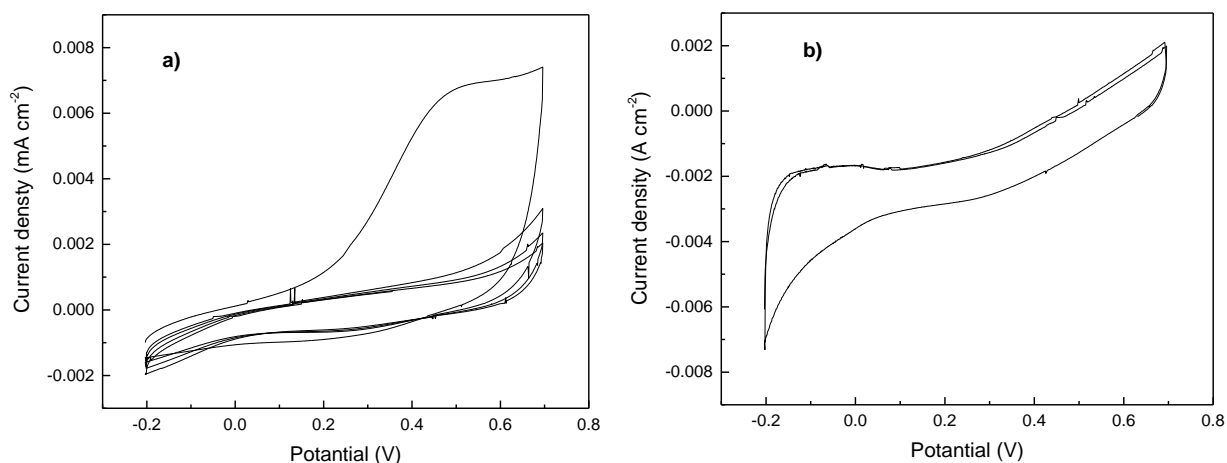


Figure 2. a) Cyclic voltammogram of Sn (electrodeposited on Pt from a deep eutectic solvent at $20 \pm 2 \text{ }^\circ\text{C}$) in 0.5 M Na_2SO_4 . b) Cyclic voltammogram of SnO (Sn treated in Na_2SO_4 given in panel a of this figure) was immersed in 0.1 M H_2SO_4 . The sweeping speed for both cyclic voltammetry is 20 mV s^{-1} .

A freshly prepared Sn modified Pt electrode (its typical growth response in Ethaline is presented in Figure 1) was transferred to a new aqueous KOH solution to oxidize tin to tin hydroxide by cathodic polarization before cycling in acidic medium. It was shown in Figure 2 that tin oxide was not electroactive in acidic media. In order to observe if $\text{Sn}(\text{OH})_2$ is electroactive or not in acidic media, Sn coated Pt electrode was firstly polarized in alkaline media to obtain a tin oxide-based electrode. Cyclic voltammetry response of the Sn modified electrode in KOH is presented in Figure 3a. As KOH was also an aqueous electrolyte, Ag-AgCl having saturated KCl was used as a reference electrode. Immediate application of 0 V to Sn electrode caused oxidation which could be the formation of tin hydroxide (around 0.03 mA cm^{-2}) and had a plateau-like current response from 0.1 V to 0.5 V (approximately 0.02 mA cm^{-2}) (shown in the first cycle of Figure 3a). Obvious oxidation of Sn was observed also here but a reduction peak was not seen as the tin film was oxidized and tin hydroxide film was formed. The hydroxide based tin film became stable in the KOH electrolyte. Sn coated Pt electrode was scanned again in an alkaline electrolyte to understand its electrochemical behavior. Oxidation of tin hydroxide film was again observed at around 0.45 V but this is not related to the transformation of tin to tin hydroxide. It is more related to the oxygen evolution reaction because bubbles were formed on Sn-based Pt electrode. Tin hydroxide based modified electrode was washed with deionized water after cycled in alkaline media and the treated

film was immersed in H_2SO_4 in order to understand its electrochemical properties in acidic media. Cyclic voltammogram data of $\text{Sn}(\text{OH})_2$ film is shown in Figure 3b. Oxidation and reduction peaks of tin hydroxide modified electrode in H_2SO_4 were also low (around $2 \mu\text{A cm}^{-2}$ at 0.7 V). Cyclic voltammogram of $\text{Sn}(\text{OH})_2$ in H_2SO_4 (Figure 3b) was the same as that of bare Pt in H_2SO_4 . Therefore, it can be said that $\text{Sn}(\text{OH})_2$ modified electrode was not electroactive in acidic media. Tin was firstly electrodeposited on platinum and that electrode was treated in KOH electrolyte to obtain tin hydroxide. As tin hydroxide film cycled in H_2SO_4 was not electroactive, tin hydroxide films cannot be used in acidic media for electrochemical devices.

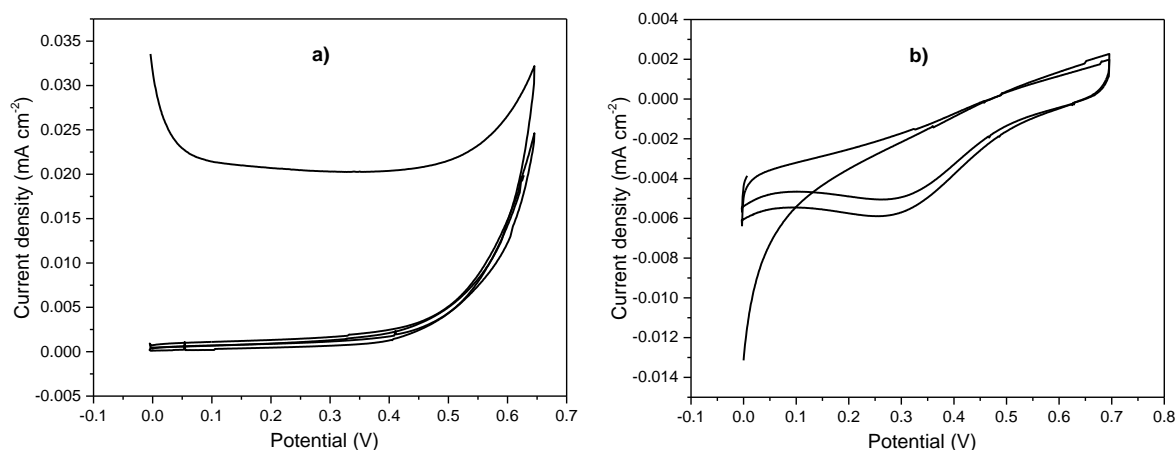


Figure 3. a) Cyclic voltammogram of Sn (electrodeposited on Pt from a deep eutectic solvent at $20 \pm 2 \text{ }^\circ\text{C}$) in 1 M KOH. b) Cyclic voltammogram of $\text{Sn}(\text{OH})_2$ (Sn treated in KOH given in panel a of this figure) was immersed in 0.1 M H_2SO_4 . The sweeping speed for both cyclic voltammetry is 20 mV s^{-1} .

Sn was electrodeposited from ethylene glycol and choline chloride mixture at $20 \pm 2 \text{ }^\circ\text{C}$ (Figure 1) and oxidized in Na_2SO_4 to form tin oxide (Figure 2a). The tin oxide was cycled in H_2SO_4 (Figure 2b) and it was not electroactive in acidic media. Tin deposited platinum electrode was also immersed in the KOH solution (Figure 3a) and tin hydroxide was formed and then tin hydroxide was cycled again in the acidic electrolyte (Figure 3b). All these coatings electrodeposited from choline chloride and ethylene glycol were thin. Sn was electrodeposited from Ethaline solution at high temperature in order to obtain electroactive tin-based film in acidic media. The substrate was again platinum the same as Figure 1. Deep eutectic solvents are usually used for metal and alloy deposition at high temperatures. The deposition potential of -0.6 V was again applied to a platinum electrode which was immersed in Ethaline media having 0.1 M SnCl_2 for 500 seconds. The time applied to electrodeposit Sn at high temperature was longer than that at $20 \pm 2 \text{ }^\circ\text{C}$ (Figure 1) because it was aimed to obtain a thicker film.

Chronoamperometric and chronocoulometric responses of a platinum electrode in choline chloride and ethylene glycol mixture (Ethaline) are shown in Figure 4. The current density of the electrode was 5 mA cm^{-2} immediately after the application of -0.6 V (see Figure 4) which was about 100 times greater than the current density of electrode obtained at $20 \pm 2 \text{ }^\circ\text{C}$. The current density reached around 2 mA cm^{-2} after approximately 50 seconds and cathodic current increased to about 10 mA cm^{-2} after 500 seconds. There was not hydrogen evolution and the current was directly related to the reduction of Sn^{2+} in Ethaline to tin metal. Cathodic current density (negative) shown in Figure 4 indicates that Sn was electrodeposited on the Pt working electrode at high temperature. The charge density of tin deposition at room temperature (blue line of Figure 1) was about 3.2 mC cm^{-2} . However, the charge density of tin deposition at high temperature (blue line of Figure 4) was 1750 mC cm^{-2} . It means that the Sn film electrodeposited in Ethaline at $55 \text{ }^\circ\text{C}$ was 500 times thicker than that at room temperature. After Pt was polarized cathodically in Ethaline solution by application of -

0.6 V at 55 °C, the modified electrode was transferred to the different aqueous electrolytes for electrochemical characterization.

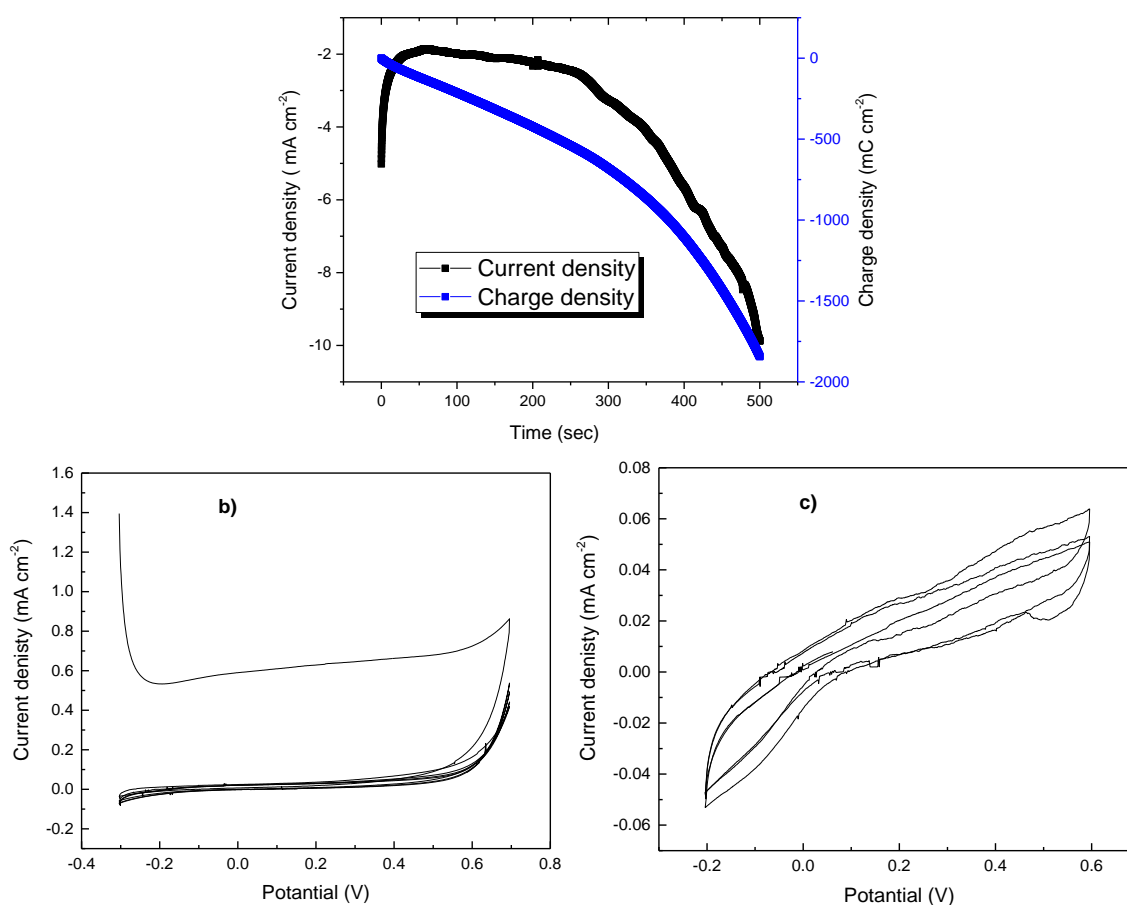


Figure 4. Chronoamperometry and chronocoulometry of Sn growth on Pt working electrode from Ethaline containing 0.1 M SnCl₂ by applying -0.6 V for 500 seconds at 55 °C. b) Cyclic voltammogram of Sn (electrodeposited on Pt from a deep eutectic solvent at 20±2 °C) in 1 M KOH. c) Cyclic voltammogram of Sn(OH)₂ (Sn treated in KOH given in panel b of this figure) was immersed in 0.1 M H₂SO₄. Sweeping speed for panel b and panel c of this figure is 20 mV s⁻¹.

Sn electrodeposited from Ethaline at high temperature (shown in Figure 4a) was cycled firstly in alkaline solution (1 M KOH) to transform thick Sn to Sn(OH)₂. It was shown in Figure 3b that thin tin hydroxide was not electroactive in acidic media. In order to observe if thick Sn(OH)₂ could be electroactive or not in acidic media, thick Sn coated Pt electrode was firstly oxidized in alkaline media to obtain tin hydroxide. Cyclic voltammetry data of Sn modified electrode electrodeposited from hot (55 °C) Ethaline in KOH is given in Figure 4. Immediate application of -0.3 V to Sn electrode caused oxidation which could be the formation of tin hydroxide (around 1.4 mA cm⁻²) and had a plateau-like current response from -0.2 V to 0.5 V (approximately 6 mA cm⁻²) (shown in the first cycle of Figure 4b). The behavior of thick Sn coating in KOH (Figure 4) was the same as that of thin Sn in KOH presented in Figure 3a but the only difference is the high current density value of thick Sn. Oxidation of Sn with the absence of reduction was again seen (Figure 4) similar to the thin Sn film shown in Figure 3a. The hydroxide based thick tin film was stable in KOH electrolyte as repetitive cycles follow the same i-E route. Sn(OH)_x coated Pt electrode was cycled in H₂SO₄ electrolyte to compare its electrochemical behavior with thin Sn(OH)₂ in H₂SO₄. Before immersing the electrode in acidic media, it was washed with deionized water. Cyclic voltammogram data of Sn(OH)₂ film in the acidic electrolyte is shown in Figure 4. Oxidation response of thick tin hydroxide film in H₂SO₄ (around 6 μA cm⁻² at 0.7 V) was greater than that of thin Sn(OH)₂ film in acidic media (around 2 μA cm⁻² at 0.7 V) which could be related to oxygen evolution reaction

(compare Figure 4c and Figure 3) because the reduction of both Sn(OH)₂ electrode was similar. Sn(OH)₂ modified electrode was not electroactive in acidic media. Tin was electrodeposited on platinum at room temperature and 55 °C. These electrodes were treated in the KOH electrolyte to obtain tin hydroxide. As tin hydroxide film cycled in H₂SO₄ was not electroactive, thick and thin tin hydroxide films cannot be used in acidic media for electrochemical devices.

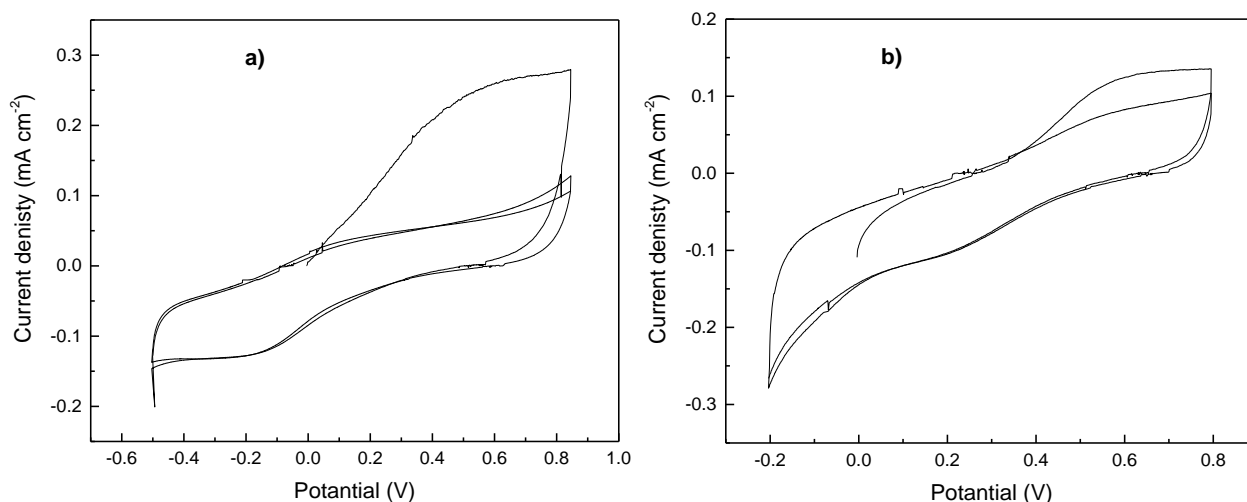


Figure 5. a) Cyclic voltammogram of Sn (electrodeposited on Pt from a deep eutectic solvent at 55 °C) in 0.5 M Na₂SO₄. b) Cyclic voltammogram of SnO (Sn treated in Na₂SO₄ given in panel a of this figure) was immersed in 0.1 M H₂SO₄. The sweeping speed for both cyclic voltammetry is 20 mV s⁻¹.

Thick tin modified Pt electrode was immersed again in Na₂SO₄ solution for the formation of SnO. Cyclic voltammetry data of the Sn coated Pt electrode in Na₂SO₄ electrolyte is presented in Figure 5a. Oxidation current of thick Sn electrodeposited from hot Ethaline was around 300 μA cm⁻² at 0.7 V in Na₂SO₄ (see the first cycle of Figure 5a). This current density was more than 35 times greater than the current density of thin Sn in Na₂SO₄ (8 μA cm⁻² at 0.7 V shown in Figure 2a). Although obvious oxidation of Sn was observed, a reduction related to that oxidation was not that high. The oxidized form of Sn was stable in Na₂SO₄ electrolyte. Sn was cycled in acidic electrolyte to elucidate its electrochemical response. Before cycling in H₂SO₄, thick tin oxide coating was washed with deionized water. The cyclic voltammogram of thick SnO coated Pt is shown in Figure 5b. Oxidation and reduction reaction of the modified electrode in H₂SO₄ was low (around 0.1 mA cm⁻² at 0.8 V). The cyclic voltammogram of SnO in H₂SO₄ (Figure 5b) was similar to the 2nd and 3rd cycles of Sn in Na₂SO₄ (Figure 5a). Thick or thin SnO modified electrode is not electroactive in acidic media. Thick and thin Sn electrodeposited on platinum from deep eutectic solvent at high (55 °C) and room temperature (20±2 °C) was treated in Na₂SO₄ electrolyte to obtain tin oxide. As tin oxide film cycled in H₂SO₄ was not electroactive, tin oxide films cannot be used in acidic media for electrochemical devices.

Sn modified electrode was also treated with H₂SO₄ and then cycled in KOH. Thick Sn film electrodeposited from a deep eutectic solvent at 55 °C (similar to the film shown in Figure 4) was cycled in acidic media (see Figure 6a). Cycling started at -0.2 V and quick oxidation was observed at around 80 mA cm⁻². This could be the dissolution of Sn as tin could be dissolved in acidic media. As the main aim of this work is to characterize the electrochemical behavior of Sn-based film in different electrolytes, the mechanism of Sn coated Pt in acidic media was not studied in detail. Instead, Sn film which was treated in acidic media (Figure 6a) was transferred to 1 M KOH to understand its cycling behavior in alkaline media. Cyclic voltammetric response of Sn-based film (after polarized in acidic media) in KOH electrolyte is shown in Figure 6b. Oxidation peak of Sn-

based film in KOH was not observed but a strong reduction of the film in KOH appeared due to probably of hydrogen evolution.

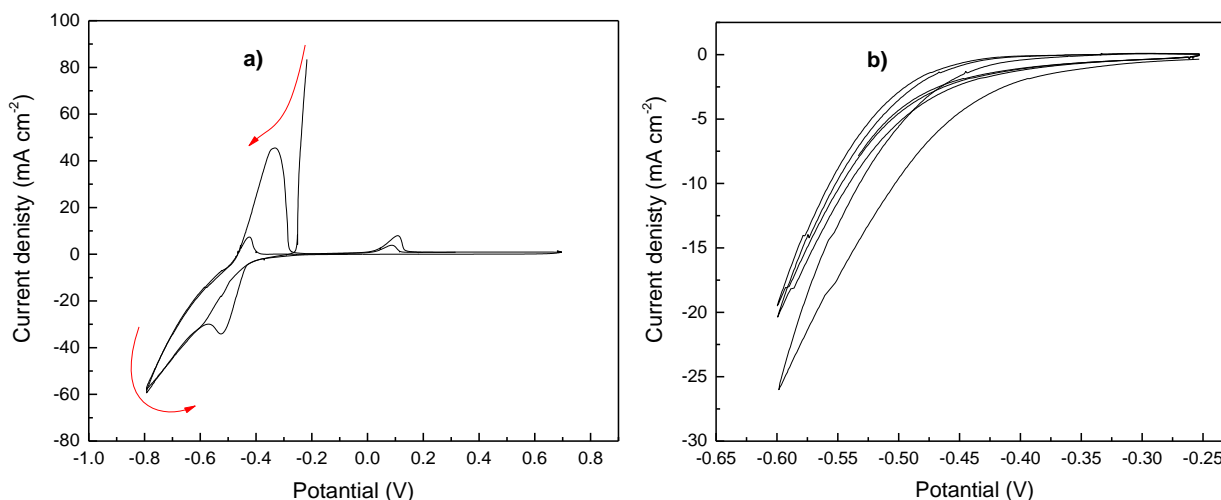


Figure 6: a) Cyclic voltammogram of Sn (electrodeposited on Pt from a deep eutectic solvent at 55 °C) in 0.5 M H₂SO₄. b) Cyclic voltammogram of tin-based electrode (Sn treated in H₂SO₄ given in panel a of this figure) was immersed in 1 M KOH. The sweeping speed for both cyclic voltammetry is 20 mV s⁻¹.

This kind of electrode could be used for hydrogen evolution reaction in alkaline media which is an important issue for fuel cell applications. However, Sn electrodeposited on Pt from deep eutectic solvent at high temperature (55 °C) and treated in H₂SO₄ electrolyte was not electroactive in KOH electrolyte.

4. Conclusions

Sn was electrodeposited on a platinum substrate from Ethaline ionic liquid (ethylene glycol and choline chloride mixture) containing 100 mM SnCl₂ by applying -0.9 V for 300 seconds. A tin-coated platinum electrode was immersed in a different aqueous electrolyte to understand its electrochemical behavior. As it is known that Sn can be dissolved in acidic media, Sn was firstly electrodeposited from a deep eutectic solvent and then treated with Na₂SO₄ (neutral) and alkaline solution. Sn coating was immersed firstly in Na₂SO₄ solution to form tin oxide. Oxidation of Sn was observed but a reduction was not appeared as Sn was oxidized but not reduced and Sn was stable in Na₂SO₄ electrolyte. SnO coated modified electrode was immersed in H₂SO₄. As oxidation and reduction reaction of the modified electrode in H₂SO₄ was low, SnO modified electrode is not electroactive in acidic media.

Sn was electrodeposited on platinum and was treated in the KOH electrolyte to obtain tin hydroxide. Sn(OH)₂ coating became stable in the KOH electrolyte. As oxidation and reduction peaks of tin hydroxide modified electrode in H₂SO₄ was low Sn(OH)₂ modified electrode was not electroactive in acidic media. As tin hydroxide and tin oxide film cycled in H₂SO₄ were not electroactive, tin oxide and hydroxide films cannot be used in acidic media for electrochemical devices.

Thick Sn was electrodeposited from Ethaline at 55 °C and hydrogen evolution did not occur. Mass of Sn film electrodeposited at high temperature was more than 500 times greater than that at room temperature (20±2 °C). Sn coated Pt was oxidized in Na₂SO₄ and tin oxide was formed. This thick tin oxide was cycled in H₂SO₄ and it was not electroactive in acidic media. Thick tin modified Pt electrode was immersed in Na₂SO₄ solution to form SnO. Sn film electrodeposited from hot

Ethaline in Na₂SO₄ electrolyte had higher oxidation current than Sn film electrodeposited from Ethaline at room temperature. Thick and thin SnO modified electrodes are not electroactive in acidic media.

Sn modified electrode electrodeposited from deep eutectic solvent at 55 °C was treated with an acidic solution and then cycled in alkaline electrolyte. The oxidation peak of Sn-based film in KOH was not observed but a strong reduction of the film in KOH appeared due to hydrogen evolution. This electrode can be used for hydrogen evolution reaction in alkaline media which is critical for fuel cell applications.

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References

- [1]. Sano, H.; Sakaebe, H.; Matsumoto, H. Observation of Electrodeposited Lithium by Optical Microscope in Room Temperature Ionic Liquid-Based Electrolyte. *J. Power Sources* 2011, 196 (16), 6663–6669.
- [2]. A. Gürten, K. Tehçi, İzoniazid Çözeltisinde Üç Değerlikli Kromun İndirgemesinin Elektrokimyasal Mekanizması, *El-Cezeri J. Sci. Eng.* 4 (n.d.) 156–164.
- [3]. Low, C. T. J.; Walsh, F. C. Electrodeposition of Tin, Copper and Tin–copper Alloys from a Methanesulfonic Acid Electrolyte Containing a Perfluorinated Cationic Surfactant. *Surf. Coatings Technol.* 2008, 202 (8), 1339–1349.
- [4]. Bicelli, L. P.; Bozzini, B.; Mele, C.; D’Urzo, L. A Review of Nanostructural Aspects of Metal Electrodeposition. *Int. J. Electrochem. Sci.* 2008, 3 (4), 356–408.
- [5]. S. Bahçeci, F. Daldaban, Dağıtım Şebekelerinde Güneş Panelleri ve Enerji Depolama Sistemi Uygulaması, *El-Cezeri J. Sci. Eng.* 4 (n.d.) 308–313.
- [6]. Tang, A.; Li, Z.; Wang, F.; Dou, M.; Liu, J.; Ji, J.; Song, Y. Electrodeposition Mechanism of Quaternary Compounds Cu₂ZnSnS₄: Effect of the Additives. *Appl. Surf. Sci.* 2018, 427, 267–275.
- [7]. Arafat, Y.; Sultana, S. T.; Dutta, I.; Panat, R. Effect of Additives on the Microstructure of Electroplated Tin Films. *J. Electrochem. Soc.* 2018, 165 (16), D816–D824.
- [8]. Neveu, B.; Lallemand, F.; Poupon, G.; Mekhalif, Z. Electrodeposition of Pb-Free Sn Alloys in Pulsed Current. *Appl. Surf. Sci.* 2006, 252 (10), 3561–3573.
- [9]. Collazo, A.; Figueroa, R.; Nóvoa, X. R.; Pérez, C. Corrosion of Electrodeposited Sn in 0.01 M NaCl Solution. A EQCM and EIS Study. *Electrochim. Acta* 2016, 202, 288–298.
- [10]. Wurm, C.; Oettinger, O.; Wittkaemper, S.; Zauter, R.; Vuorilehto, K. Anode Materials for Lithium-Ion Batteries. In *Lithium-Ion Batteries: Basics and Applications*; Springer, 2018; pp 43–58.
- [11]. Soulimi, N.; Porrás-Gutiérrez, A.-G.; Mordvinova, N. E.; Lebedev, O. I.; Rizzi, C.; Sirieix-Plénet, J.; Groult, H.; Dambournet, D.; Gaillon, L. Sn (TFSI) 2 as a Suitable Salt for the Electrodeposition of Nanostructured Cu₆Sn₅–Sn Composites Obtained on a Cu Electrode in an Ionic Liquid. *Inorg. Chem. Front.* 2019, 6 (1), 248–256.
- [12]. Mahapatra, S. Das; Dutta, I. Co-Electrodeposition of Tin with 0.2–20% Indium: Implications on Tin Whisker Growth. *Surf. Coatings Technol.* 2018, 337, 478–483.
- [13]. Abbott, A. P.; Frisch, G.; Ryder, K. S. Electroplating Using Ionic Liquids. *Annu. Rev. Mater. Res.* 2013, 43, 335–358.

- [14]. Smith, E. L.; Abbott, A. P.; Ryder, K. S. Deep Eutectic Solvents (DESs) and Their Applications. *Chem. Rev.* 2014, 114 (21), 11060–11082.
- [15]. Abbott, A. P.; Capper, G.; McKenzie, K. J.; Ryder, K. S. Electrodeposition of Zinc–tin Alloys from Deep Eutectic Solvents Based on Choline Chloride. *J. Electroanal. Chem.* 2007, 599 (2), 288–294.
- [16]. Srivastava, M.; Yoganandan, G.; William Grips, V. K. Electrodeposition of Ni and Co Coatings from Ionic Liquid. *Surf. Eng.* 2012, 28 (6), 424–429.
- [17]. Cao, F.; Zhao, M.; Yu, Y.; Chen, B.; Huang, Y.; Yang, J.; Cao, X.; Lu, Q.; Zhang, X.; Zhang, Z.; et al. Synthesis of Two-Dimensional CoS_{1.097}/Nitrogen-Doped Carbon Nanocomposites Using Metal-Organic Framework Nanosheets as Precursors for Supercapacitor Application. *J. Am. Chem. Soc.* 2016, 138 (22), 6924–6927.
- [18]. S. Bahçeci, F. Daldaban, Economic Analysis of Demand Side Management with Residential PV System and Energy Storage System, *El-Cezeri J. Sci. Eng.* 7 (2020) 67–78.
- [19]. Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G. An Electrochemical Study of the Oxidation of Hydrogen at Platinum Electrodes in Several Room Temperature Ionic Liquids. *J. Phys. Chem. B* 2007, 111 (18), 5000–5007.
- [20]. Abbott, A.P.; Ballantyne, A.; Harris, R.C.; Juma, J.A.; Ryder, K.S.; Forrest, G.A., Comparative Study of Nickel Electrodeposition Using Deep Eutectic Solvents and Aqueous Solutions. *Electrochim. Acta* 2015, 176, 718–726.