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Electrodeposition of aluminium from 1-butyl-1-methylpyrrolidinium chloride/AlCl₃ and mixtures with 1-ethyl-3-methylimidazolium chloride/AlCl₃

P. Giridhar^a, S. Zein El Abedin^{a,b}, F. Endres^{a,*}

^a Institute of Particle Technology, Clausthal University of Technology, Arnold-Sommerfeld-Strasse 6, 38678 Clausthal-Zellerfeld, Germany ^b Electrochemistry and Corrosion Laboratory, National Research Centre, Dokki, Cairo, Egypt

ARTICLE INFO

Article history: Received 4 February 2012 Received in revised form 1 March 2012 Accepted 13 March 2012 Available online 23 March 2012

Keywords: Electrodeposition Aluminium Ionic liquids Ionic liquid mixtures XRD SEM

ABSTRACT

In this paper we show that nanocrystalline aluminium can be electrodeposited from the ionic liquid 1-butyl-1-methylpyrrolidinium chloride ($[Py_{1,4}]Cl/AlCl_3$) (40/60 mol%). The study comprises electrochemical experiments such as cyclic voltammetry, constant potential electrolysis, SEM and XRD measurements. Thick and uniform layers of aluminium are obtained from $[Py_{1,4}]Cl/AlCl_3$ with an average crystal size of 20 nm at 100 °C. Aluminium deposits obtained from 90:10 vol% and 80:20 vol% of $[Py_{1,4}]Cl/AlCl_3$ and $[EMIm]Cl/AlCl_3$ are nanocrystalline at 100 °C. The presence of imidazolium cations seems to alter the electrode/electrolyte interface to some extent as nanocrystalline and microcrystalline aluminium deposits are obtained from the ionic liquid mixtures at compositions of 70:30 vol% of $[Py_{1,4}]Cl/AlCl_3$ and $[EMIm]Cl/AlCl_3$ and below.

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1. Introduction

The Electrodeposition of aluminium and its alloys from ionic liquids has been extensively studied in ionic liquids composed of organic halides and aluminium halides. Already in 1928, an attempt to electrodeposit aluminium from a mixture of tetraethyl ammonium bromide and aluminium bromide (as a source of aluminium) at 100 °C was reported [1]. Later, Hurley and Wier electrodeposited aluminium and some metals such as Cu, Zn and others from solutions composed of ethylpyridinium bromide and the respective metal chlorides [2,3]. These ionic liquids (sometimes called first generation ionic liquids) are hygroscopic in nature, which might limit their applications. Nevertheless, a lot of work was done on the electrodeposition of aluminium from chloroaluminate ionic liquids with imidazolium halides and in most of the cases a microcrystalline aluminium deposit was obtained [4-19]. In [20] we showed that nano- and microcrystalline aluminium can be electrodeposited from the ionic liquids [Py14]TFSA and [EMIm]TFSA, respectively. At the first glance it was suggested that the speciation and/or the cation of the ILs might be the reason of such effect. Therefore, we systematically investigated the biphasic mixtures by means of RAMAN/IR and ²⁷Al- as well as ¹⁹F-NMR together with DFT (density functional theory) calculations [21]. Interestingly, we found that [Py1,4]TFSA/AlCl3 and [EMIm]TFSA/AlCl3 mixtures show the same behaviour and the electrochemically active Al-species in both mixtures was found to be [AlCl₂(TFSA)₂]⁻. Therefore we supposed that the $[Py_{1,4}]^+$ cation acts as a grain refiner and it might play its role by adsorption on the substrates and on growing nuclei, thus hindering the further growth of crystallites. Together with Atkin we further confirmed this interpretation by probing the interfacial structure at the electrode/ionic liquids interface using atomic force microscopy (AFM) and scanning tunneling microscopy measurements (STM) [22]. The AFM results showed that several solvation layers form at the electrode/ionic liquids interface, and that the strength of the interaction between the innermost layer and the substrate is dependent on the cation type. The force required to rupture the solvation layers is greater for $[Py_{14}]TFSA$ than for [EMIm] TFSA, signifying the increased strength of interaction for the [Py_{1.4}] cation compared to [EMIm] cation. Furthermore, the STM results revealed that the interaction of [Py_{1,4}]TFSA with Au(111) leads to strongly structured surface and on the contrary [EMIm]TFSA/Au(111) does not show surface restructuring [22]. Thus, it can be stated without doubt that the difference in surface interactions of the ionic liquid species can totally influence the electrochemical behaviour of ionic liquids leading to interesting effects. Even a slight change in the substitution of an imidazolium cation, such as incorporation of a methoxy group into the side chain, significantly influences the electrochemical behaviour as nanocrystalline, shiny aluminium deposits can be obtained from 1-(2-methoxyethyl)-3-methylimidazolium chloride/AlCl₃ [23].

^{*} Corresponding author. Tel.: +49 5323 722980; fax: +49 5323 722460. *E-mail address*: frank.endres@tu-clausthal.de (F. Endres).

^{0013-4686/\$ -} see front matter © 2012 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2012.03.056

Based on our earlier results described above we were interested to investigate, if and to which extent imidazolium cations added to $[Py_{1,4}]Cl/AlCl_3$ can alter the grain size of aluminium. For this purpose, various compositions of ionic liquid mixtures have been prepared. The ionic liquid mixtures were composed of 1-butyl-1-methylpyrrolidinium chloride, $[Py_{1,4}]Cl$ and $AlCl_3$ (40:60 mol%) and of 1-ethyl-3-methylimidazolium chloride [EMIm]Cl and $AlCl_3$ (40:60 mol%). Nanocrystalline aluminium deposits were obtained both from $[Py_{1,4}]Cl/AlCl_3$ ionic liquid and also from mixtures of ionic liquids up to a vol% of 80:20 of $[Py_{1,4}]Cl/AlCl_3$ vs. [EMIm]Cl/AlCl_3. In the case of [EMIm]Cl/AlCl_3, a microcrystalline aluminium deposit was obtained. These results indicate that the pyrrolidinium cation indeed seems to be responsible for the deposition of nanocrystalline Al.

2. Experimental

1-ethyl-3-methylimidazolium chloride, [EMIm]Cl and 1-butyl-1-methylpyrrolidinium chloride, [Py_{1,4}]Cl, were purchased from IOLITEC, Germany. The quality of the substances, [EMIm]Cl and [Py_{1,4}]Cl, given by the supplier are 99% and 99% respectively. The water contents of as received [EMIm]Cl and [Py_{1,4}]Cl, are 0.28% and 0.27% respectively (by Karl–Fischer Titration). Aluminium chloride grains (99.99%) were procured from FLUKA.

The organic halides were further dried for two days at 363 K and stored in closed bottles in an argon filled glove box. This procedure usually reduces the water content to values of about 20 ppm. The water and oxygen contents in the glove box are below 2 ppm (OMNI-LAB from vacuum atmospheres). Acidic chloroaluminate ionic liquids were prepared by careful mixing of 40 mol% of either [Py_{1,4}]Cl or [EMIm]Cl and 60 mol% of AlCl₃ in the glove box. A viscous and light yellow colour solution was obtained in the case of [Py1,4]Cl/AlCl3. The ionic liquids, i.e., pure [Py1,4]Cl/AlCl3 (40:60 mol%), pure [EMIm]Cl/AlCl₃ (40:60 mol%), and various compositions of ionic liquid mixtures (mixtures of [Py1,4]Cl/AlCl3 (40:60 mol%) and [EMIm]Cl/AlCl₃ (40:60 mol%) are clear at the studied temperature. A clear and light brown colour solution was obtained in the case of [EMIm]Cl/AlCl₃. According to results of Abbott's group the light brown colour of [BMIm]Cl/AlCl₃ has no considerable effect on the electrodeposition characteristics [24]. Since the viscosity of [Py_{1,4}]Cl/AlCl₃ is relatively high compared to [EMIm]Cl/AlCl₃, experiments were carried out at 100 °C in order to have comparable viscosities. Various compositions of ionic liquid mixtures, i.e., from 90 (vol%) of [Py_{1,4}]Cl/AlCl₃ and 10 (vol%) of [EMIm]Cl/AlCl₃ to 50/50 vol% of [Py_{1,4}]Cl/AlCl₃ and [EMIm]Cl/AlCl₃ mixtures were prepared. All the prepared acidic chloroaluminate ionic liquids and their mixtures were purified by electrolysis between an Al anode and a stainless steel cathode for up to 2 days at 100 °C and used for the reported studies. The electrochemical measurements were carried out using a PARSTAT 2263 potentiostat/galvanostat controlled by PowerCV and PowerStep software. A 25 mL glass beaker was used as an electrochemical cell. Gold substrates (gold on glass) from Arrandee Inc. and mild steel sheets were used as working electrodes, Al sheets and Al wires were used as counter and reference electrodes respectively. Prior to use the working electrodes were annealed in a hydrogen flame to red glow for a few minutes. High resolution SEM (Carl Zeiss DSM 982 Gemini) was employed to investigate the surface morphology of the deposited films. X-ray diffraction patterns were recorded using a Siemens D-5000 diffractometer with Co K α radiation.

3. Results and discussion

The cyclic voltammogram of $[Py_{1,4}]Cl/AlCl_3$ (40/60 mol%) on gold at 100 °C is shown in Fig. 1. The electrode potential was

Fig. 1. Cyclic voltammogram of $[Py_{1,4}]Cl/AlCl_3~(40/60\,mol\%)$ at a scan rate of $10\,mV\,s^{-1}$ on gold at $100\,^\circ C.$

scanned initially from the open circuit potential (OCP) to the negative direction at a sweep rate of 10 mV s⁻¹. The cyclic voltammogram exhibits a sharp rise in reduction current below -50 mV (c₄) followed by a stripping peak (a₄) upon scan reversal. The observed crossing of forward and backward scan close to 0V can be attributed to nucleation and growth of aluminium on the working electrode. Fig. 1 reveals that the aluminium bulk deposition is reversible. In addition, three cathodic processes have been observed $(c_1, c_2, and c_3)$ prior to the bulk deposition of aluminium. The processes at c₁ and c₂ might be attributed to the under potential deposition of Al and the corresponding counter parts are observed at a_1 and a_2 . The cathodic wave at c_3 might be attributed the alloying of Al with gold before the onset of the nucleation and growth process of three dimensional particles [25-27]. The anodic wave at a_3 is associated with the cathodic process at c_3 , which is attributed to the dissolution of this aluminium-gold alloy. It is worth mentioning that in the case of the aluminium deposition from [Py1,4]TFSA/AlCl₃, where TFSA is bis(trifluoromethylsulfonyl)amide, no underpotential processes were observed [25]. Furthermore, the deposition was not reversible.

In order to get information on the deposit, a constant potential electrolysis was carried out at -0.3 V for 1 h. The obtained deposit was washed and then analyzed by high resolution scanning electron microscopy and X-ray diffraction. A bright and uniform deposit was obtained and the high resolution SEM image shown in Fig. 2a reveals fine crystallites with some aggregations.

For XRD analysis, Al was deposited on mild steel under the same conditions reported for gold. The XRD patterns of Al made at -0.3 V and -0.5 V on mild steel for 1 h are shown in Fig. 2b. As seen, the deposited Al is crystalline and a strong diffraction peak (200) is obtained along with other characteristic diffraction peaks (111), (220), (311), and (222). At a more negative potential (-0.5 V), the (111) peak vanishes, indicating a preferential orientation of the deposit. Furthermore, the diffraction peaks are quite broad, and the average crystallite size could be determined by the Scherrer equation [28]. The average size was found to be about 55 nm. Fig. 2a shows smallest grain size of about 20 nm, which is more or less in agreement with the XRD result.

Fig. 3 shows how the cyclic voltammogram is altered if both ionic liquids are mixed. All cyclic voltammograms exhibit a similar electrochemical behaviour, i.e., a nucleation loop is observed when the scan is reversed and a corresponding anodic peak associated with the complete stripping of deposited aluminium is observed





Fig. 2. (a) SEM image of electrodeposited Al obtained on gold in $[Py_{1,4}]Cl/AlCl_3$ (40/60 mol%) at -0.3 V for 1 h at 100 °C. (b)XRD patterns of electrodeposited Al layer on mild steel from $[Py_{1,4}]Cl/AlCl_3$ (40/60 mol%) at two different potentials -0.3 and -0.5 V for 1 h at 100 °C.

in all cases. In the case of [EMIm]Cl/AlCl₃, the oxidation waves slightly differ from those ones obtained in ionic liquid mixtures. Furthermore, an increase in the current is observed from pure [Py_{1,4}]Cl/AlCl₃ to pure [EMIm]Cl/AlCl₃, which is mainly attributed to the decrease of viscosity. Constant potential electrolysis was



Fig. 3. Cyclic voltammograms recorded on gold at various compositions of ionic liquid mixtures at 100 $^\circ\text{C}.$



Fig. 4. XRD patterns of electrodeposited aluminium layers on mild steel from various compositions of ionic liquid mixtures at 100 °C.

carried out to deposit Al from the ionic liquid mixtures at -0.3 V for one hour at 100 °C either on gold or on mild steel.

The obtained deposits were washed in a stream of isopropanol and water. The washed samples are analyzed by high resolution scanning electron microscopy and X-ray diffraction. The XRD patterns of the electrodeposited aluminium at an applied potential of -0.3 V on mild steel for 1 h are shown in Fig. 4. As shown, the diffraction peaks of the deposits obtained in the ionic liquid mixtures are broad indicating the small particle size of the deposit. However, the diffraction peaks for the deposit obtained from [EMIm]Cl/AlCl₃ (40/60 mol%) are comparably narrow. SEM images of the deposits obtained from various compositions and from [EMIm]Cl/AlCl₃ are shown in Fig. 5a-f. The deposits are uniform with very fine crystals (~25 nm) obtained from 90:10 vol% and 80:20 vol% mixtures (Fig. 5a and b). In the case of Al deposits obtained from 70:30, 60:40, and 50:50 vol% mixtures and from pure [EMIm]Cl/AlCl₃ (40/60 mol%), coarse and cubic particles are seen in the SEM images (see Fig. 5c, d and f). However, with a higher magnification nanostructures are seen on the microcrystals at compositions below 80:20 vol%.

From the above results and discussion the following features can be summarized. The electrochemical behaviour of Al species in all ionic liquids or mixtures seems to be quite similar and in all cases the deposition is reversible at 100 $^\circ\text{C}$. Nanocrystalline deposits were obtained from [Py1,4]Cl/AlCl3 (40/60 mol%) and from the ionic liquid mixtures with a vol% of \geq 80:20. Below this composition rather nanocrystalline and microcrystalline Al deposits were obtained together. The electrode/electrolyte interface does not seem to be significantly affected upon the addition of [EMIm]Cl/AlCl₃ to the [Py14]Cl/AlCl3 till 80:20 vol%. This result supports an earlier interpretation that the pyrrolidinium ion interacts with the substrate in a different manner than the imidazolium ion does. As the deposition experiments were performed at 100 °C it is unlikely that the viscosity contributes to the obtained effect. At such temperature the viscosity of both [EMIm]Cl/AlCl₃ and [Py₁₄]Cl/AlCl₃ are almost comparable. Furthermore, it was shown that the pyrrolidinium based ILs are about 4 times more strongly adsorbed on the electrode surface than imidazolium based ILs [22]. Therefore, the increased strength of adsorption of [Py1,4]⁺ compared to [EMIm]⁺ can lead to the difference in the microstructure of the obtained deposits. The strong adsorption of $[Py_{1,4}]^+$ to the surface of the growing nuclei hinders their further growth, leading to very fine particles with sizes in the nanometer regime. However, the exact nature of the



Fig. 5. (a and b) SEM micrographs of Al deposits obtained from electrolysis of 90:10 vol% and 80:20 vol% of (40/60 mol%) [Py_{1,4}]Cl/AlCl₃: [EMIm]Cl/AlCl₃ on gold at -0.3 V for 1 h at 100 °C. (c and d) SEM images of Al deposits (and their magnified images) obtained from 70:30 vol% and 60:40 vol% of (40/60 mol%) [Py_{1,4}]Cl/AlCl₃: [EMIm]Cl/AlCl₃ on gold at -0.3 V for 1 h at 100 °C. (e and f) SEM images of electrodeposited aluminium on gold after constant potential electrolysis of 50:50 vol% of (40/60 mol%) [Py_{1,4}]Cl/AlCl₃: [EMIm]Cl/AlCl₃ : [EMIm]Cl/AlCl₃ : [EMIm]Cl/AlCl₃ (its magnified image) and pure [EMIm]Cl/AlCl₃ (40/60 mol%) at an applied potential of -0.30 V for 1 h at 100 °C.

electrode/electrolyte interface cannot be commented based on the present results alone. Quite recently, we showed that interfacial structures of electrode/ultrapure ionic liquids are strongly influenced by addition of a simple salt like LiCl even with very low concentrations [29]. Therefore, we cannot account for the nature of the electrode/employed electrolytes interface without in situ STM and AFM experiments. However, such experiments with these liquids at 100 °C are extremely difficult at the moment. In the near future we will be able to perform in situ AFM experiments in the employed electrolytes. One can also think in nucleation studies which can give useful information on the nucleation and growth at the early stages; however it is not straightforward to get reproducible results in such systems. Au-Al alloying and underpotential processes can influence the results leading to a lack of reproducibility. Therefore, substrates such as graphene or even glassy carbon should be employed to avoid the problems associated with alloying or underpotential deposition. But also this would not assure reproducibility of nucleation results as formation of IL interfacial layers and their interactions with the substrate can also influence the nucleation processes.

4. Conclusions

In this paper we have shown that nanocrystalline aluminium can be electrodeposited from a 40/60 mol% mixture of $[Py_{1,4}]Cl/AlCl_3$ at 100 °C. Nanocrystalline aluminium is also obtained from various ionic liquid mixtures comprising both pyrrolidinium and imidazolium cations. This study supports earlier results that pyrrolidinium cations interfere differently with the substrate than imidazolium cations do. At mixtures of 70:30 vol% of both ionic liquids and below ([Py_{1,4}] vs [EMIm]) microcrystalline deposits are obtained. However, even in these mixtures the pyrrolidinium ion plays a role in the grain size of the Al deposit as nano on microcrystalline deposits were obtained from these mixtures.

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