Int. J. Electrochem. Sci., 7 **(2012)** 8436 - 8443

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Raman Study of Benzylideneacetone on Silver

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Received: 22 February 2012 / *Accepted:* 13 April 2012 / *Published:* 1 September 2012

Raman spectroscopy complemented by cyclic voltammetry was used to provide some insight towards understanding the interaction between Benzylideneacetone (BDA) and the substrate electrode. It was verified that the adsorption of BDA on the surface of an Ag electrode moderately inhibits the Zn underpotential deposition (UPD). It was observed that BDA did not form complexes with Zn (II). Certainly, the reduction mechanics associated with Zn (II) electrodeposition involve the species $ZnCl_4^{2-}$ and undoubtedly, the additive BDA blocks active sites and impedes the transport of ions to the surface. It is postulated that C-C=C-C=O bond is located close to the silver electrode and the phenyl group is positioned far from surface.

Keywords: electrodeposition, benzylideneacetone, zinc electroplating bath, Raman, Zn UPD.

1. INTRODUCTION

Coatings of zinc and its alloys are of great practical importance due to their capacity to protect ferrous substrates against corrosion [1-4]. Various factors affect the mechanism of zinc electrodeposition, and thus influence the composition and morphology of the coatings obtained. These factors include the concentration of zinc ions [5], complexing agents [6], anions [7-8] and additives [9-26], all of which play fundamental roles in zinc electrodeposition. The use of additives in electrolytic baths is very important due to their influence on the growth and structure of the deposits obtained. Typically, additives are added to the electrolytic bath at concentrations on the order of parts per million and their presence promotes the formation of soft and shiny coatings. In recent years, mixtures of benzylideneacetone (BDA) and alcohols have increasingly been used as additives in the electrodeposition of zinc [9-26]. The superior quality of the coatings obtained in the presence of BDA has generated an growing interest in the mechanism by which this additive affects zinc electrodeposition. Danciu [13] suggested that the adsorption of BDA onto active sites on the substrate BDA controls the roughness of Zn coatings. On the other hand, the underpotential deposition (UPD) of Zinc (II) has significant influence on the growth of bulk thin films[5,15]. In this regard, Trejo et al. [15], from the EQCM study, in the UPD region of the voltammograms, showed that the presence of BDA reduces the quantity of Zn deposited by UPD by up to 44%.

The inhibition of the UPD of Zn (II) ions by BDA may have important technological implications due to the important role played by the UPD of metal, in the anomalous codeposition of alloys. Thus, the addition of BDA to inhibit the UPD of Zn (II) ions could partially inhibit the anomalous codeposition of Zn alloys (e.g., Zn-Fe, Zn-Ni and Zn-Co), making it possible to obtain a more homogeneous composition of Zn alloy coatings.

Despite the work carried out in this area[9-26], the adsorption characteristics of BDA/alcohol and its mechanism of action during electrodeposition remain largely unknown. All studies made the assumption that the additives do not modify the chemical solution of electrodeposition baths (do not form complexes with zinc ions). Moreover, the influence of additives on the UPD of Zn has been studied on the assumption that the principal Zn (II) species present is $ZnCl_4^{2-}$. Therefore, the main argument of this work was based on the following postulates: 1) BDA did not form complexes with Zn (II), and 2) $ZnCl_4^{2-}$ was the principal Zn (II) species present in surface; therefore, this study was made in order to obtain corroborating evidence for these premises. Furthermore, this study focused on the potentials that correspond to Zn (II) UPD region.

It is also worth mentioning that BDA adsorption has not yet been studied systematically by in situ Raman spectroscopy. This method for the understanding of the BDA effect is original and provided reliable evidence for our premises.

2. EXPERIMENTAL

All solutions were prepared using analytical grade reagents and Millipore Milli-Q water. It is noteworthy that BDA (Benzylideneacetone or 4-Phenyl-3-buten-2-one) was an additive used in aqueous media, although it is insoluble in water. Therefore, it was dissolved in methanol before being added to solutions. The solution was prepared by adding the substances in the following order: 2.8M KCl, 0.32M H_3BO_3, 0.6M $ZnCl_2$ and 4mM BDA (previously dissolved in 3ml methanol). Afterwards, the pH of the solution was adjusted to 5 by the addition of 1 M HCl.

The Raman spectra were recorded on the lab-built spectrometer, which was extensively detailed in our previous work [27]. The 514.5 nm line of an Argon ion laser was used as the excitation source and the laser was focused by using a 20× microscope objective (1.5 µm spot and 20 mW power on sample). Three fresh solutions were prepared and the spectra of each one were obtained immediately.

Electrochemical measurements were performed in situ, in a Teflon cell with a flat optical glass window. A polycrystalline silver disk of 1.1 cm^2 area, and Pt wire were used as the working electrode and the counter electrode respectively. The reference electrode was Ag/AgCl and all electrode potentials refer to this electrode. A Bas/Epsilon potentiostat was employed to control the electric potential.

The silver surface was polished and washed with copious amounts of distilled water. Immediately after, the surface roughening for Ag electrodes was performed in 0.1M KCl, using electrochemical oxidation-reduction cycles. These cycles began at -0.25V for 15s, switched to 0.25V for 8s, and returned back to -0.25V for another 30s. At the end of the cyclic process, the surface appeared brownish-yellow [28].

Raman spectra recordings were taken for 120 seconds while the potential was held at constant value. A scan rate of 10 mV/s was applied between test potentials.

3. RESULTS

A cyclic voltammogram of silver electrode in the base solution containing 0.6 M $ZnCl_2$ (Fig. 1) presents a cathodic peak at -0.89 V associated with the underpotential deposition (UPD) of zinc. Also the voltammogram shows an anodic peak at -0.84 V upon reversing the direction of the sweep, which is associated to the dissolution of zinc UPD. Mendez [15] observed that the presence of Cl^{-} ions in high concentration does not interfere with the UPD of Zn (II). In addition, this author [6] also observed that the process of zinc UPD on Pt occurs simultaneously with hydrogen adsorption, thus the integration of the charge for the zinc UPD layer is difficult and it is not clear to what extent zinc UPD forms preferentially with respect to hydrogen adsorption. However, it is well established that Ag presents a poor electrochemical catalytic activity for hydrogen adsorption and reduction [29,30], therefore the charges of the peaks were only associated to the Zn UPD process.

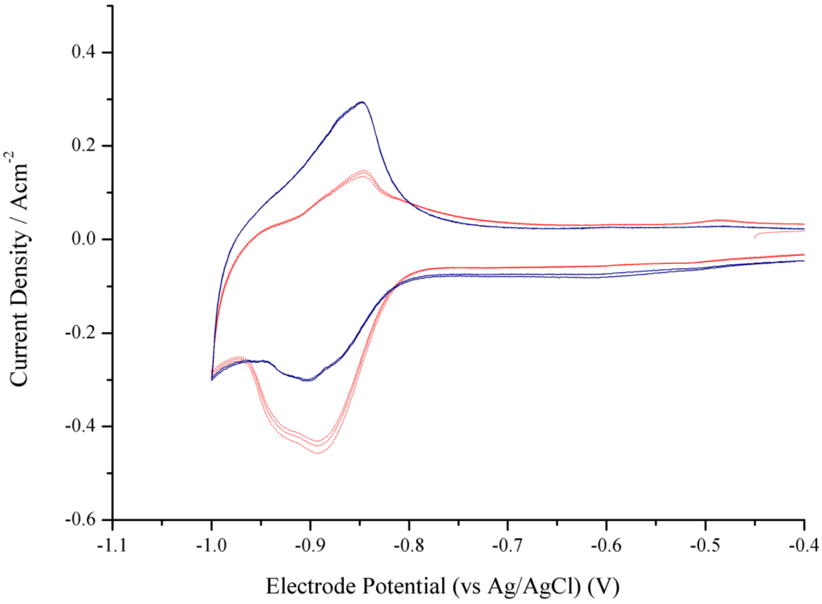

Figure 1. Cyclic Voltammetry of silver electrode in a) 8M KCl, 0.32M H_3BO_3, 0.6M $ZnCl_2$ pH 5 (—) and b) 2.8M KCl, 0.32M H_3BO_3, 0.6M $ZnCl_2$, 0.342 M BDA/MeOH pH 5 (—). Scan rate at 25 mV/s.

The addition of BDA resulted in an increase of the cathodic peak, which indicates that the adsorption of additive and UPD occurs simultaneously. Moreover, the decrease of the anodic peak was produced by the adsorption BDA; thus the additive reduced the quantity of Zn deposited by around 43%.

The Raman spectrum of silver electrode obtained at open circuit potentials in the presence of Zn(II) (Fig. 2) shows the largest band at 279 cm^{-1}, which is attributable to the Zn-Cl vibration in $ZnCl_4^{2-}$ in aqueous solution [31-32]. Particularly, Quicksall [31] assigned this vibration to the A1 Zn–Cl stretching mode. The wavenumber of the Raman active symmetric stretching vibration was determined theoretically by Tossel [32] who concluded that the vibration of $ZnC1_4^{2-}$ was observed in the range of 272-288 cm^{-1}.

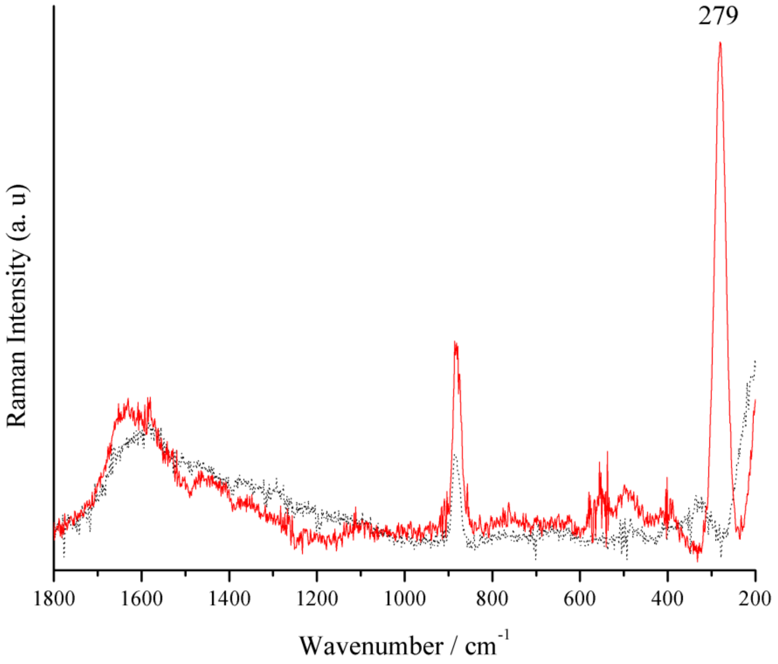

Figure 2. Raman spectra of silver electrode obtained at open circuit potential (OCP) of a) – 0.15 mV in 2.8M KCl, 0.32M H_3BO_3, 0.5 M $ZnCl_2$ pH 5 (—), and b) – 0.72 mV in 2.8M KCl, 0.32M H_3BO_3, 0.5 M pH 5 (·····).

El-Shafei [33] suggested that various surface borate structures are produced at a relatively slow reaction rate under deposition condition of the electroplating, however these structures were not identified. The concentration distribution diagram of borate [34] contains ten equilibrium reactions in the aqueous system and it shows that the concentration of HB_4O^{7-} increases significantly at pH 5. In this work, the broad bands at 1109 cm^{-1} and 494 cm^{-1} were certainly assigned to the tetraborate anion $HB_4O_7^{-}$ [35]. In addition, boric acid was also detected in the dissolution because, in the Raman spectrum, the symmetrical BO_3 stretching vibration [35] appears at 882 cm^{-1}.

The potential dependent survey spectra of the silver electrode in presence of Zn (II) are reported in Fig. 3. The position and intensity of the band associated with the zinc complex were unchanged from the initial potential to -0.9 V, with intensity changes at cathodic potentials higher than

-0.9 V due to the UPD of zinc. The Raman spectra assert that the mechanics of Zn (II) UPD in solutions without additives involves the species $ZnCl_4^{2-}$.

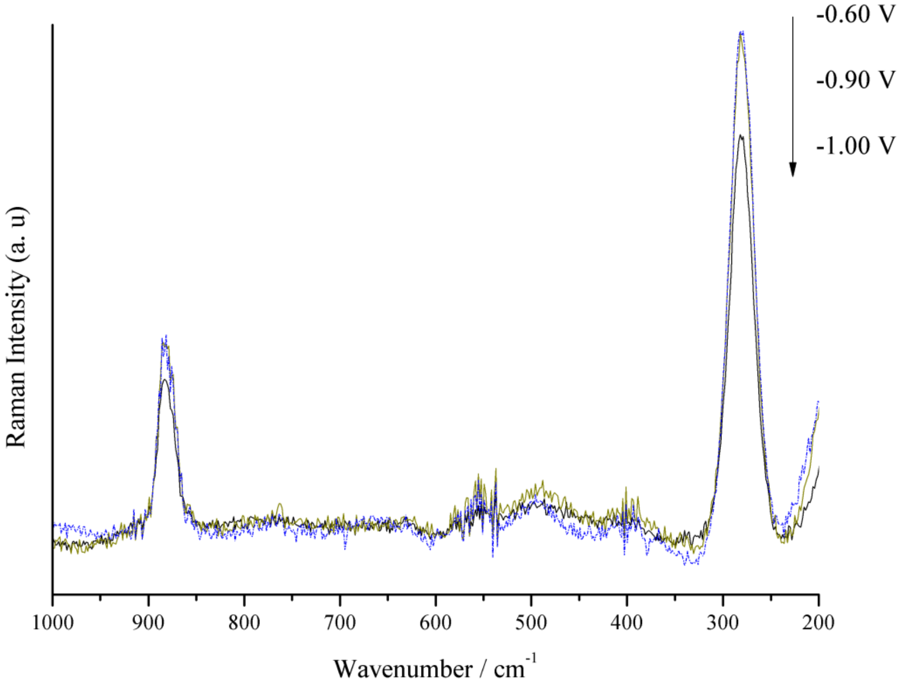

Figure 3. Raman spectra of silver electrode obtained at different potentials in a solution of 22.8 M KCl, 0.32M H_3BO_3, 0.6 M $ZnCl_2$, pH 5. The scan rate was at 1 mV/s and potential test was -0.6 (---), -0.9 (—) and -1.0 V (—) in which the Raman spectra were recorded during 120 sec.

In order to discern between adsorption and reaction of BDA, potential-dependent Raman spectra of the silver electrode immersed in zinc plating bath were obtained (Fig. 4). The band at 279 cm^{-1} is not showed in order to maintain clarity; to be more precise, Fig. 4 was adjusted to show only areas that correspond to bands of BDA. The Zn(II) band behaves identically in Fig. 3, indicating that the UPD of metal ions in presence of additives involves the species $ZnCl_4^{2-}$. A strong band observed at 1609 cm^{-1} was assigned to ν_s (C–C=C–C) based in our previous Raman and DFT studies [36]. In addition, bands in the region between 1200-1600 cm^{-1} were primary associated with ν(C-C) ring stretching modes. The intensity of the bands between 1600 cm^{-1} and 1700 cm^{-1} was increased as the potential decreased after -0.37 V, with the most significant increase observed in the band at 1609 cm^{-1}, the stretching vibrations of exocyclic –C=C–C. Consequently, it can be assumed that the bonds of –C–C=C–C=O were located sufficiently close to the surface as to be affected by the electrical potential. Bands observed at 1192 cm^{-1} and 1205 cm^{-1} were associated with the stretching vibrations ring of the phenyl group. The insignificant change observed in the intensity of the 1192 cm^{-1} band at increasing negative potential, establishes that the phenyl group was distant from surface as it was not affected by the electrical potential at the electrode.

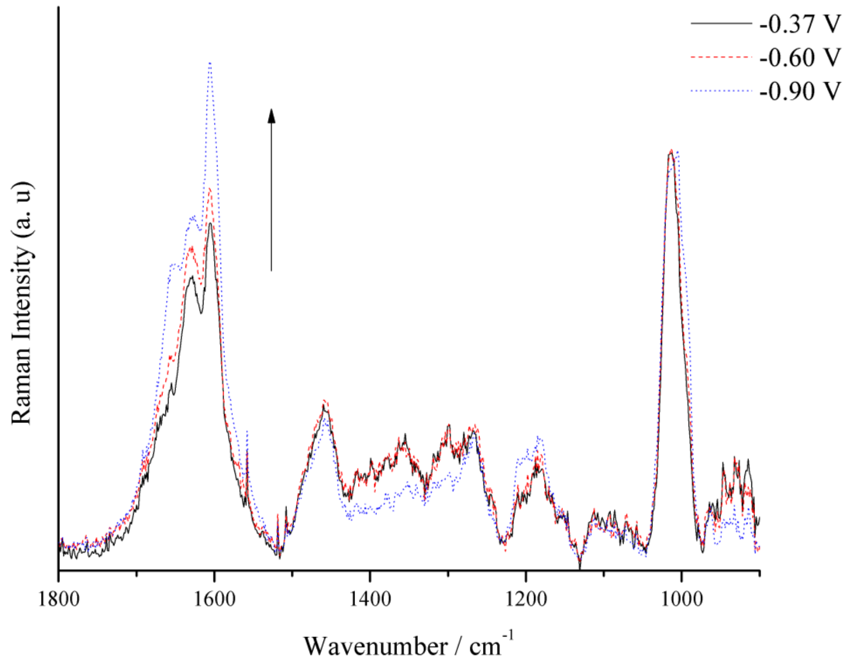

Figure 4. Raman spectra of silver electrode obtained at different potentials in a solution of 22.8 M KCl, 0.32M H_3BO_3, 0.6 M $ZnCl_2$, 4mM BDA/3ml MeOH, pH 5. The scan rate was at 1 mV/s. The potential test was -0.37 (—), -0.6 (---) and -0.9 V(⋯).

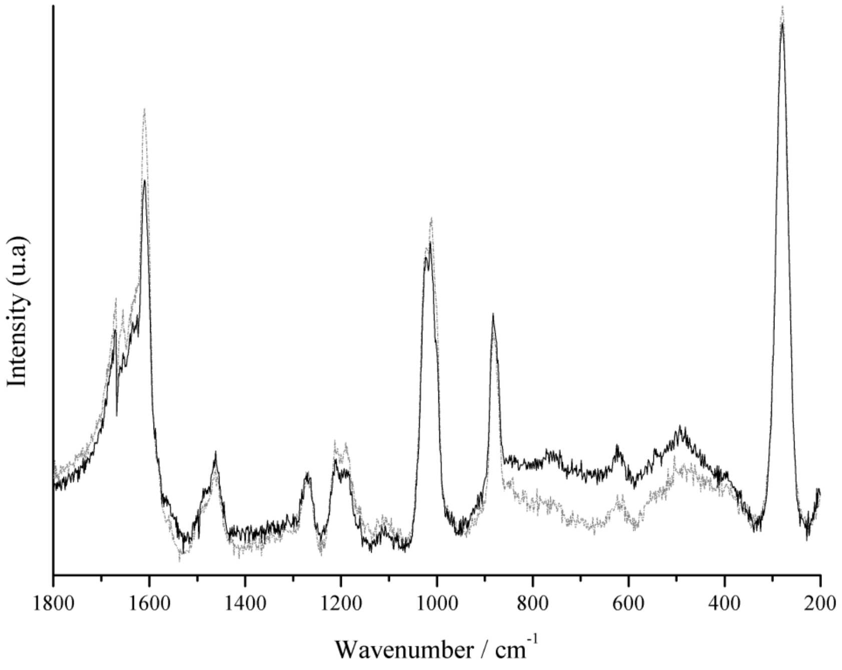

Figure 5. Raman spectrum obtained after 12 (—) and 20 (⋯) min polarization at -0.9 V. The solution was 2.8 M KCl, 0.32M H_3BO_3, 0.6 M $ZnCl_2$, 4m M BDA/3 mL MeOH, pH 5.

Fig. 5 shows a Raman spectrum obtained after a lengthy polarization at -0.9 V. The band positions were constant during the electrolysis test, which indicates a high chemical stability of $ZnC1_4^{2-}$ and BDA in the electroplating bath. This spectrum verified that under the standard electrodeposition conditions of Zn, the predominant species in the solution is the $ZnC1_4^{2-}$ complex. No evidence was found of the formation of covalent bonds between Zn (II) ions and oxygen or carbon atoms. Thus, on the basis of the above results, we have confirmed that at the concentrations used in this work, Zn(II) ions do not form complexes with the additive $ZnC1_4^{2}$ on surface. Thus, the additive acts principally at the electrode surface, blocking active sites and impeding the transport of ions to the surface.

Barriola [20,37] and Mockute [12] suggested that the BDA decomposes into diverse compounds during the cathodic polarization. Barriola [20] proposed that the hydrogenation of C=C occurred through the hydrogen adsorbed on substrates at high cathodic potentials used for the bulk deposition of zinc. Conversely, this study indicates that the organic molecules remain unreactive on the silver polycrystalline if Zn (II) is electrodeposited at potentials in the underpotential deposition potential (UPD) range. Undoubtedly, the primary effect of the additive BDA is to block active sites, with the additive adsorption causing a decrease in the nucleation rate observed in our previous studies [15-17].

3. CONCLUSION

The results corroborate our premise that Benzylideneacetone (BDA) did not form complexes with Zn (II) in the surface of electrode. Besides, it was observed that the presence of BDA partially inhibits the Zn UPD, in other words, the additive molecule adsorbed on the surface of Ag electrode reduces the number of active sites for the formation of nuclei and causes a decrease in the nucleation rate.

The second postulate of this study and our previous studies [15-17] proposes that $ZnCl_4^{2-}$ was the principal Zn (II) species present in surface and also this premise was verified. Therefore, the reduction mechanics associated with the Zn (II) electrodeposition involves the species $ZnCl_4^{2-}$, which is reduced to Zn (0) metal via the following reaction:

$$ZnCl_4^{2-} + 2e^- \rightarrow Zn^{(0)} + 4Cl^-$$

Finally, it is postulated that C–C=C–C=O bond is found close to the silver electrode (probably perpendicularly oriented to surface) and the phenyl group is positioned far from surface. This reorientation of the BDA molecule was proposed because the spectral wavenumbers of each band were unchanged during periods of polarization.

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