Int. J. Electrochem. Sci., 12 **(2017)** 8860 – 8867, doi: 10.20964/2017.10.01

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Electrochemical Behavior Zn(II) at Carbon Steel Electrode in Deep Eutectic Solvents Based on Choline Chloride

Evelin Gutiérrez[1], *José A. Rodriguez*[1,*], *Julián Cruz-Borbolla*[1], *Yolanda Castrillejo*[2], *Enrique Barrado*[2]

[1] Área Académica de Química, Universidad Autónoma del Estado de Hidalgo, Unidad Universitaria, km 4.5 Carretera Pachuca-Tulancingo, C.P. 42184 Pachuca-Hidalgo, Mexico.
[2] Dpto. de Química Analítica, Facultad de Ciencias, Universidad de Valladolid, Paseo de Belén 7, 47011, Valladolid, Spain.
[*]E-mail: josear@uaeh.edu.mx

Received: 26 May 2017 / *Accepted:* 19 July 2017 / *Published:* 12 September 2017

Deep eutectic solvents prepared by mixture of choline chloride with urea, thiourea and ethylene glycol (1:2 molar ratio) were used to study the electrochemical behavior Zn(II) at carbon steel 1018 electrode. Zn deposits were immersed in a corrosive media (NaCl 3%wt). Composition of the solvent employed causes a difference in electrodeposition and corrosion behaviors, being diffusion coefficient value a critical parameter associated to these processes.

Keywords: carbon steel; deep eutectic solvent; urea; thiourea; ethylene glycol.

1. INTRODUCTION

Electrochemical processing of metals is commonly realized in aqueous solutions that can be acidic or basic in presence of complexing agents [1]. Electrochemical processes require solvents with high conductivity capable to solubilize electrolytes and metal salts, aqueous systems is then employed for this purpose. On the other hand, some problems are associated such as hydrogen embrittlement of the substrate [2] and hydrogen evolution reaction during electrodeposition [3]. Electrodeposition of metallic films and alloys can improve the chemical and mechanical (hardness, ductility and wear resistance) properties of metals [4-6].

Recently, ionic liquids have been proposed as an alternative solvent to aqueous electrolytes in electrochemical processes such as: deposition of metals and alloys, generation of batteries, catalysis process and organic synthesis [7-10].

Deep eutectic solvents (DESs) belong to the family of ionic liquids; DESs are excellent electrolytes due to characteristics as melting points below 100 °C, low toxicity, easy preparation, low vapor pressure, non-flammability and low cost. Generally, DESs are a mixture composed of a quaternary ammonium salt and a hydrogen bond donor. The melting point of the DESs is lower than their individual components, this decrement is a consequence of the hydrogen bond between halide ion and hydrogen bond donor [2,11]. DESs are applied in many fields as organic synthesis, extraction process, material chemistry and electrodeposition of metals [12].

There are different DESs components, but the most popular is choline chloride (ChCl) which is considered an essential nutrient, biodegradable and non-toxic salt [13]. DES composed of choline chloride-urea (ChCl-U) has been used in electrodeposition of Ni coatings on magnesium for improve the corrosion resistance [14], Pb powder from PbO employing stainless steel [15]; Zn-Ni alloys onto platinum electrodes [6]; Zn, Cu-Zn alloys [16], Mg alloys [17], Zn-Co alloys on platinum [4]. In addition to choline chloride-urea, the DES based on choline chloride -ethylene glycol (ChCl-EG) has been applied to: formation of porous Pb [12] and electrodeposition of Zn [18].

There are different reports employing DESs as electrolytes in electrochemical processes employing inert working electrodes. Taking into account the advantages of non-aqueous solvents for the electrochemical applications, in this paper is performed an electrochemical characterization of $ZnCl_2$ in three DESs, ChCl-U, choline chloride-thiourea (ChCl-TU) and ChCl-EG, employing carbon steel as working electrode. Additionally, the effect of DESs composition on corrosion resistance is evaluated immersing the Zn electrodeposited surfaces in aqueous NaCl (3% wt).

2. EXPERIMENTAL

2.1. Reagents

DESs were prepared by mixing ChCl with urea, thiourea or ethylene glycol (Sigma-Aldrich, St. Louis, Mo, USA) at 1:2 molar ratio (ChCl:hydrogen bond donor). The mixture was continuous stirring at 70 °C in case of ChCl-U and ChCl-EG, and 80 °C for ChCl-TU until a homogeneous colorless liquid was observed [13,15]. A concentration of 0.2 mol kg^{-1} was obtained by adding $ZnCl_2$ (Sigma-Aldrich) at the three DESs. The mixture was stirring until $ZnCl_2$ was completely dissolved; all the solvents prepared were stored at room temperature.

2.2. Electrodes and Instrumentation

Electrochemical studies were performed in an electrochemical system Autolab (Autolab PGSTAT 30, Eco Chemie B.V., Netherlands) controlled by GPES software version 4.5.

The electrochemical characterization was performed using a three electrode electrochemical cell. The working electrode consisted of a carbon steel surface AISI 1018 of 0.32 cm^2 (0.6-0.9% Mn, 0.15-0.2% C, 0.04% P, 0.05% S, balance% Fe), a platinum wire and Ag/AgCl (MW-2021 Basi, West Lafayette, IN, USA) were used as auxiliary and reference electrode, respectively. After finishing each experience, the working electrode was sequentially abraded using emery papers of 80, 600 and 1200 grid. Once renewed the surface, it was cleaned with acetone and finally washed by deionized water. The temperature of solvents was controlled using a recirculating system (Brinkmann Lauda Econoline RE106). Cyclic voltammetry was carried out starting from open circuit potential to cathodic potential, at a scan rate of 10 mV s^{-1}. The zinc signal was compared on the three DESs solvents employing a zinc foil (Meyer, Mexico) as working electrode

Potentiodynamic polarization of unmodified and Zn electrodeposited carbon steel surfaces was obtained in NaCl aqueous solution (3% wt). An anodic swept was applied in the potential interval of ±100 mV (scan rate of 1 mV s^{-1}) from open circuit potential.

3. RESULTS AND DISCUSSION

3.1 Electrochemical behavior of Zn(II) in DESs

The cathodic limit of is observed in discontinues black line on Figure 1 (a,b,c). The characteristic cathodic limit in the electrochemical window of DESs based on choline chloride employed is associated to the reduction of choline ions, formation of hydrogen gas associated to the presence of traces of water and reduction of hydroxyl group when ChCl-EG [18,19].

Figure 1 (a,b,c) presents in red line the cyclic voltammograms obtained at a carbon steel electrode at 10 mV s^{-1} employing ChCl-U, ChCl-TU and ChCl-EG respectively, with $ZnCl_2$ in concentration 0.2 mol kg^{-1}. The cathodic peak observed at -1.50 V in ChCl-U, -1.68 V in ChCl-TU and -1.44 V in ChCl-EG was attributed to the reduction of Zn(II) to Zn. The signal observed in the anodic scan at -0.95, -0.78 and -0.80 V (ChCl-U, ChCl-TU and ChCl-EG) is associated to oxidation of Zn deposit. In order to attribute the reduction signal observed by voltammetry to reduction of Zn(II) to metallic Zn was performed a voltammetry analysis at zinc electrode in the three DESs in absence of $ZnCl_2$. The results are observed in blue line on Figure 1 (a,b,c) in which is possible to observe that the maximum value of the reduction signal is in approximate potential value to observed in presence of $ZnCl_2$ using carbon steel as working electrode.

Differences observed on ChCl-U, ChCl-TU and ChCl-EG are congruent with results observed in electrodeposition using DESs. The nature of solvent plays an important role in electrochemical behavior of metallic ions and nucleation mechanism; differences in electrodeposition can be attributed to chloride activity in the solvent which modifies the concentration of metallic ion in the double layer [16]. The displacement observed cathodic potential is associated to solvent viscosity; an increment in this variable causes a decrement in convection, generating concentration gradients and in consequence an increase of electric resistance [1]. According to voltammograms (Fig. 1) the highest displacement is observed in ChCl-TU, this solvent has higher viscosity than ChCl-U and ChCl-EG.

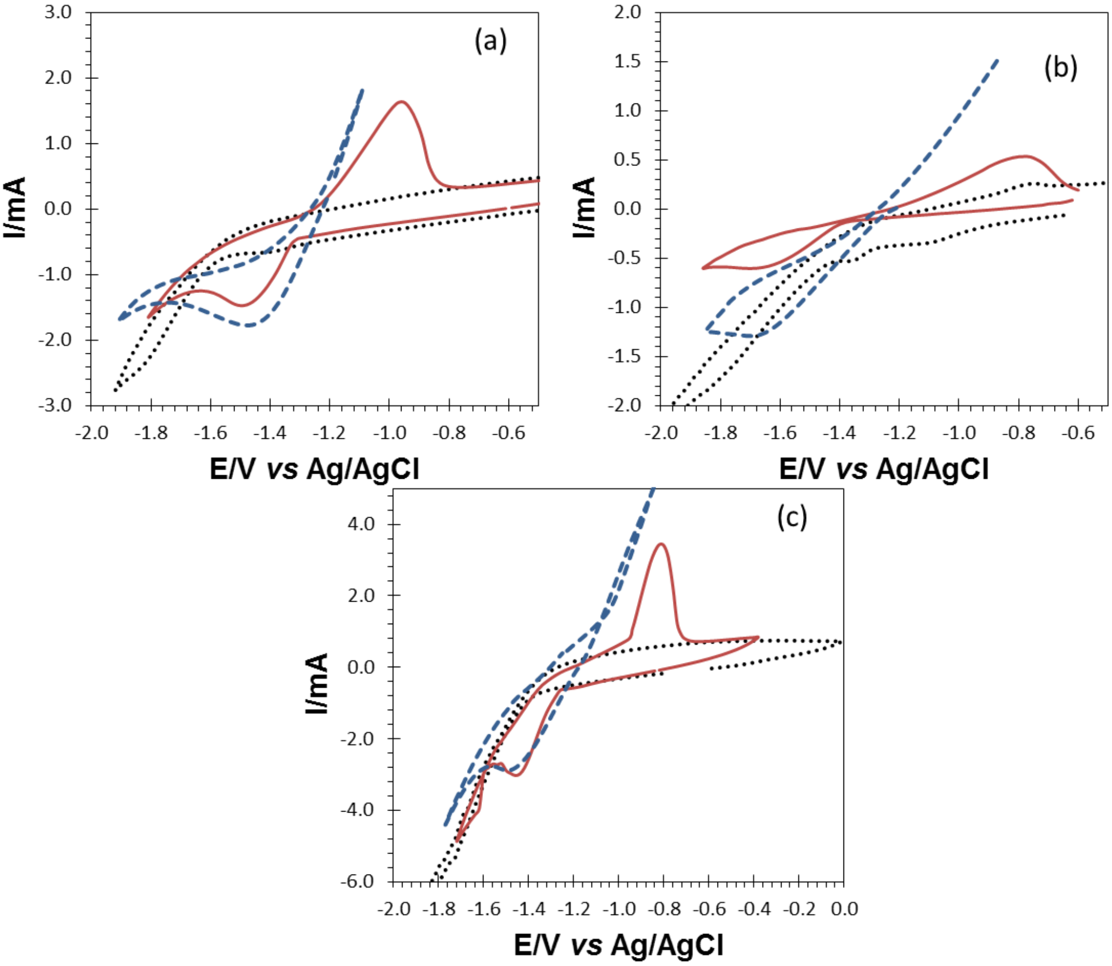

Figure 1. Cyclic voltammetry of Zn(II) at carbon steel 1018 in DESs (a) ChCl-U, (b) ChCl-TU and (c) ChCl-EG.

Diffusion coefficient (*D*) is a critical factor in electrochemistry processes; this value involves the movement of Zn(II) from DESs to the electrode surface. There are different methodologies for determining the diffusion coefficient from cyclic voltammetry data; however most of these only consider the peak current and potential values which cause not to take into account all possible information. Convolution principle transforms voltammogram data into a curve intensity-potential, the accuracy for determination of *D* value is better since it is used all the information contained in the signal [20,21].

A robust estimation of *D* values was obtained from convolution of a series of voltammograms realized in ChCl-U, ChCl-TU and ChCl-EG at scan rates of 2 to 10 mV s^{-1}. Values of $2.4(\pm 0.5)\times 10^{-7}$ cm^2 s^{-1}, $1.1(\pm 0.2)\times 10^{-7}$ cm^2 s^{-1} and $11.3(\pm 1.1)\times 10^{-7}$ cm^2 s^{-1} were obtained, respectively. *D* values in DESs have the following tendency $D_{Zn(II),ChCl-EG} > D_{Zn(II),ChCl-U} > D_{Zn(II),ChCl-TU}$, this trend is in agreement with the viscosity of DESs. Higher *D* values are obtained in lower viscosity electrolyte solutions. *D* values of Zn(II) in DESs are smaller than those obtained in aqueous media, where the corresponding values are in the interval of 0.52-0.74 $\times 10^{-5}$ cm^2 s^{-1} [22,23]. *D* value is inversely proportional to the viscosity [24] experimental results have shown that the rate of mass transport can be accelerated by increasing temperature [25].

3.2 Electrochemical nucleation of Zn(II) at carbon steel electrode

Nucleation process of Zn was evaluated by chronoamperometry. Electrodeposition potential was set from a value in which Zn(II) reduction was not observed to cathodic values until nucleation and growth processes were observed. After each experience, Zn electrodeposit was removed by polarizing the working electrode anodically. Current-time transients obtained in ChCl-U, ChCl-TU and ChCl-EG are shown in Figure 2. The sharp of current-time transients involves: charging of the double layer, formation and growing of Zn nuclei achieving i_{max} and t_{max} and a decrease of the current. The i_{max} increases while the t_{max} shortens when higher cathodic potentials were applied [3].

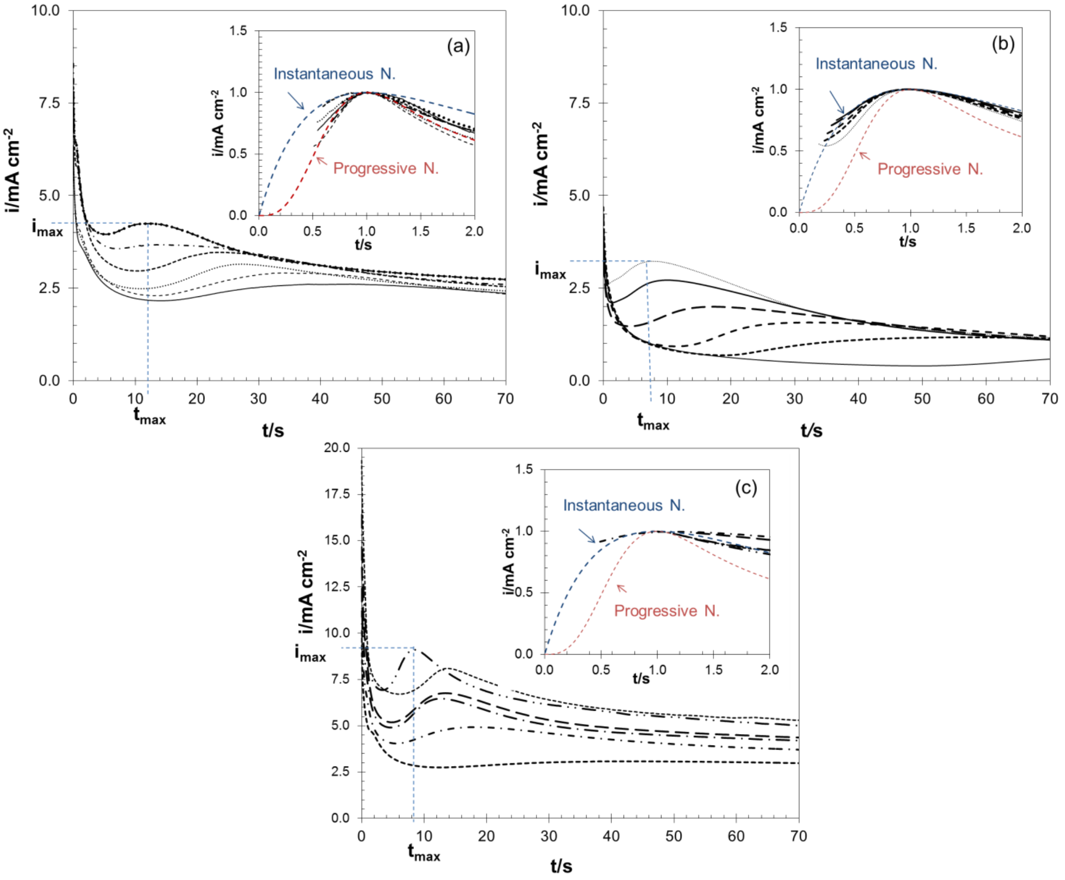

Figure 2. Experimental and dimensionless curves for instantaneous and progressive nucleation. (a) ChCl-U (b) ChCl-TU and (c) ChCl-EG

Nucleation mechanism was analyzed by employing dimensionless models. Instantaneous nucleation mechanism implies an immediate activation of all nuclei sites and the rate of formation of additional nuclei is negligible during the experiment. On the other hand, during progressive nucleation mechanism the nuclei formation is time dependent, involving an increment of the number of nuclei during electrodeposition experiment [26].

Dimensionless curves obtained from chronoamperometric data in ChCl-U, ChCl-TU and ChCl-EG is shown in Figure. According to Figure 2 there is an adjustment to progressive model in ChCl-U and instantaneous model in ChCl-TU and ChCl-EG.

3.3 Polarization analysis

In order to compare the effect of a DES composition on the formation of zinc metallic deposits and the resistance to an aggressive media, electrodeposition at 10 minutes was realized onto a carbon steel surface by chronoamperometry. The potentials employed for Zn electrodeposition on three different DESs were established according to the observed reduction potential values from cyclic voltammetry: -1.50 V (ChCl-U), -1.68 V (ChCl-TU) and -1.44 V (ChCl-EG) *vs* Ag/AgCl.

Modified surfaces were immersed in a corrosive media (NaCl, 3% wt) and analyzed employing potentiodynamic polarization each hour during 6 hours. The electrodeposition time selected allows study the deposit behavior against corrosion at short periods of time. Figure 3(a) shows Tafel curves of modified and unmodified surfaces with Zn in three HBDs, (a) ChCl-U, (b) ChCl-TU and (c) ChCl-EG obtained initially.

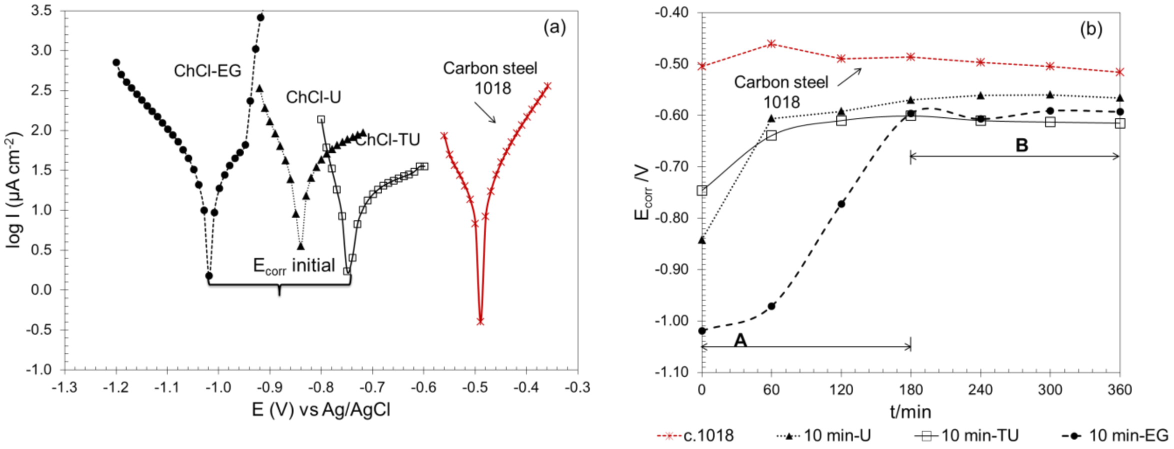

Figure 3. (a) Potentiodynamic polarization of electrodeposits formed in ChCl-U, ChCl-TU and ChCl-EG, immersed in NaCl (3.0% wt). (b) Variation of corrosion potential *vs* exposition time of zinc electrodeposits obtained in different DESs.

A tendency is observed in corrosion potential, Zn film electrodeposited in three DESs initially exhibits poor corrosion resistance respect to unmodified carbon steel. Taking into account that Fe is a more noble metal than Zn, dissolution of Zn deposit occurs firstly, a displacement of corrosion potential was then observed to achieve the potential of unmodified surface. This behavior is similar to the observed in the electrodeposition of Zn on a Cu substrate, which is a more noble metal respect to Zn. The presence of electrodeposited Zn causes a displacement at lower corrosion potentials respect to unmodified copper substrate [6, 16]. A higher value of corrosion potential respect to electrodeposited metallic film implies that corrosive medium reacts with electrodeposited film firstly, acting as a sacrificial anode [14].

Figure 3(b) shows the behavior of corrosion potential *vs* time of zinc electrodeposits immersed in corrosive media for six hours. Different zones are indicated, the first one (A) can be associated to dissolution of electrodeposited Zn while (B) can be related to formation of compounds with passivating characteristics in corrosive media (oxide). In consequence, corrosion potential does not achieve the value obtained for unmodified electrode. Similar behavior is observed on Fe-Zn alloys, where is it possible to identify the dissolution of Zn and Fe [27]. The time required for Zn dissolution is highest when Zn is electrodeposited ChCl-EG, according to diffusion coefficient value a thicker film is obtained in this DES, a longer time is required then to dissolve the deposit from the metal surface.

The observed behavior of the Zn electrodeposits obtained in the DESs studied in the corrosive medium has the same tendency than Zn-Fe electrodeposits onto carbon steel prepared in aqueous medium. In aqueous medium it is not possible to observe a clear reduction signal of Zn(II), however a nucleation phenomenon is verified by the formation of loops in the cathodic zone in cyclic voltammetry [28, 29].

The electrodeposition of Zn-Mn on 35NCD16 steel has been performed in aqueous KCl 2.31 M+ H_3BO_3 0.4M, at potential intervals between -1.5 and -1.75 V (*vs* saturated calomel electrode). In these conditions reduction of Zn-Mn and hydrogen evolution occurs at the same time. The substrate selected has an apparent influence in the limit of cathodic window [30]. The formation of Zn electrodeposits on carbon steel in DESs showed that the reduction of Zn(II) occurred in a potential close to the cathodic limit, showing a similar behavior than aqueous media.

4. CONCLUSIONS

In three DESs, (ChCl-U, ChCl-TU and ChCl-EG) it is possible to identify the reduction signal of Zn(II). Nucleation mechanism is dependent on the employed DESs. Corrosion behavior of electrodeposited Zn is similar in the three DESs employed, but time require for dissolution of Zn deposited in ChCl-EG is higher than the require using ChCl-U and ChCl-TU. A thicker Zn film was obtained in ChCl-EG, as a result of higher diffusion coefficient value. Diffusion coefficient value is a critical parameter associated to electrodeposition and corrosion processes. The corrosion resistance is similar than the obtained for Zn electrodeposits in aqueous media.

ACKNOWLEDGEMENTS

This work was supported by CONACYT (grant number 266926); UAEH-PAI; Junta de Castilla y Leon (Project VA171U14)

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