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## The Electrochemical Deposition of Zn-Mn Coating from Choline Chloride-urea Deep Eutectic Solvent

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# **The electrochemical deposition of Zn-Mn coating from choline chloride-urea deep eutectic solvent**

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# **The electrochemical deposition of Zn-Mn coating from choline chloride-urea deep eutectic solvent**

Electrochemical and microscopic techniques were used for characterization of Zn-Mn coatings electrodeposited from choline chloride-urea deep eutectic solvent. Cyclic voltammograms show that there was no discernible Mn reduction peak when only  $\text{Mn}^{2+}$  was present in DES solution. The distinct Mn peak developed only upon addition of  $\text{Zn}^{2+}$  to the solution, probably due to previous Zn nucleation on the steel substrate. It was found that 22-27 wt.% Mn, was deposited at current densities of  $3\text{-}8\text{ mA cm}^{-2}$ , amounts significantly higher than in aqueous electrolytes. Since higher deposition current densities resulted in the formation of a porous surface consisting of clusters of nodular crystallites, the optimal deposition c.d was determined to be  $3\text{ mA cm}^{-2}$ .

Keywords: Zn-Mn coating; electrodeposition; deep eutectic solvent; choline chloride; urea; ionic liquid; cyclic voltammetry; alloy

## **1. Introduction**

There is a growing interest in electroplated Zn-Mn coatings for sacrificial corrosion protection of steel substrates, owing to the fact that Zn-Mn alloys of a certain chemical and phase composition, exhibit the highest corrosion resistance in an aggressive media, among all Zn alloy coatings.<sup>1</sup> Electrodeposition of Zn-Mn coating has mainly been performed in aqueous electrolytes, containing metal chlorides or sulphates, which may be acidic (boric acid)<sup>2</sup> or alkaline (potassium pyrophosphate).<sup>3</sup> In addition, in order to bring reduction potentials of  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$  closer, various complexing agents have been utilized in water electrolytes, eg. EDTA,<sup>4</sup> sodium citrate,<sup>5</sup> or pyrophosphate ion.<sup>3</sup> Unfortunately, aqueous electrolytes can suffer from bath instability, low current

efficiency or poor deposit morphology due to the intensive water reduction at high plating current densities.<sup>6</sup>

The avoidance of such disadvantages and attainment of higher electrodeposition current efficiency may be achieved by utilising aprotic ionic liquids as electroplating solutions. However this type of electrolyte has usually involved high production costs.<sup>7</sup> Since 2002, affordable, simple and stable ionic liquids, based on choline chloride (ChCl) type deep eutectic solvents (DES), have been developed for industrial application. Some important benefits of these ionic liquids include good solvation of many metal salts, low vapour pressure, good ionic conductivity, environmental friendliness (green solvents) and good thermal stability.<sup>8</sup> The electroplating of pure Zn<sup>9</sup> and its various alloys, for instance Zn-Ni,<sup>10</sup> Zn-Co<sup>11</sup> or Zn-Sn<sup>12</sup> in DES has been extensively investigated. Similarly, the electrodeposition of pure Mn<sup>13</sup> and Ni-Mn alloy<sup>14</sup> in DES has been achieved.

As regards the Zn-Mn coating, there are only few reports on its electrodeposition in DES, and the reported processes were performed on Cu and Pt substrates.<sup>15,16</sup> We are not aware of any reports of Zn-Mn electrodeposition on steel electrodes. Furthermore it is known that in ChCl based DES, the substrate significantly influences the overpotential for metal ions reduction, as well as the electrochemical degradation of supporting electrolyte.<sup>17</sup> Therefore, this work presents the electroplating of Zn-Mn coating on steel electrodes from DES, since Zn alloy coatings are widely used for corrosion protection of steel.<sup>1</sup>

## **2. Experimental methods**

### ***Electrolyte preparation***

Deep eutectic solvents were obtained by combining urea with ChCl in a 2:1 molar ratio and heating to a temperature of 70 °C, with continuous magnetic stirring, until a colourless liquid was formed.<sup>18</sup> Both ZnCl<sub>2</sub> and MnCl<sub>2</sub>·H<sub>2</sub>O, at concentrations of 0.1 mol dm<sup>-3</sup>, were then added to the mixture. The transformation of hydrated MnCl<sub>2</sub>·4H<sub>2</sub>O into its mono hydrated state MnCl<sub>2</sub>·H<sub>2</sub>O was achieved by heating at 200 °C under vacuum for 2 hours in a vacuum furnace, i.e. by using a method described in literature.<sup>15</sup> The prepared DES solutions were dried in vacuum chamber at 80 °C for 3 h, at  $p < 10$  mbar, and then stored in a dessicator. All electrochemical experiments were performed in open atmosphere.

### ***Electrochemical analysis and coating characterization***

Electrochemical measurements (cyclic voltammetry, CV, and galvanostatic deposition) were carried out using a ZRA Reference 600 Potentiostat/Galvanostat, from Gamry Instruments. A laboratory sand bath was used to maintain the temperature of the bulk electrolyte at 70 °C for all electrochemical measurements in the DES.

A three-electrode electrochemical cell was employed with a working electrode of steel plate, with a surface area of 0.25 cm<sup>2</sup>. The electrode was mechanically prepared using abrasive emery papers down to 2000 grit, degreased in a saturated solution of NaOH in ethanol, pickled with 2 mol dm<sup>-3</sup> HCl for 30 s, and finally rinsed with distilled water, acetone and dried in air by a fan. The counter electrode was a high purity Zn panel. In the experiments where Zn<sup>2+</sup> was not present in the solution (CV of metal-free DES and of DES with only Mn<sup>2+</sup> ions), the counter electrode was Pt wire placed in a separate compartment, in order to reduce the likelihood of working electrolyte contamination with the oxidation products. The reference electrode was a saturated calomel electrode (SCE), connected to the cell through a Luggin capillary tip. Although conventionally used in aqueous electrolytes, this reference electrode has also been

successfully used in deep eutectic solvent, without any special treatment.<sup>19</sup> After deposition at 70 °C the electrodeposited coatings on steel were thoroughly cleaned with acetone.

The surface morphology and composition of the samples were analyzed by a JEOL JSM 5800 scanning electron microscope (SEM), operated at 20 keV, equipped with an Oxford Instruments energy dispersive X-ray spectrometer (EDS). For SEM/EDS measurements, each Zn-Mn sample was deposited by the same charge density of 20 C cm<sup>-2</sup>, at 70 °C.

### 3. Results and Discussion

#### *Voltammetric measurements*

The reduction of Zn<sup>2+</sup> and Mn<sup>2+</sup> ions on a steel cathode, when either one or both species were present in DES, was studied by cyclic voltammetry in the potential range between -1900 and -600 mV (vs SCE), at a scan rate of 100 mV s<sup>-1</sup>.

#### *Voltammetry of DES with Mn<sup>2+</sup>*

The voltammetric responses of a pure DES and a DES with 0.1 mol dm<sup>-3</sup> MnCl<sub>2</sub> are shown in Fig. 1. Upon scanning from the open circuit potential of the steel electrode to negative potential in the blank DES, it can be noted that, prior to the sharp current increase related to the bulk electrolyte decomposition at around -1450 mV, there are two reduction peaks. The first cathodic current increase commenced at about -660 mV, giving the peak C<sub>1</sub> at -880 mV and the second wave begins at about -990 mV, with the peak C<sub>2</sub> at -1170 mV. The processes responsible for these waves were described in detail in,<sup>17</sup> where it was concluded that the peak C<sub>1</sub> was related to the Cl<sup>-</sup> ion reductive desorption. The intensity of the peak C<sub>2</sub> was enhanced upon water addition in ChCl–

urea DES, thus proving that C<sub>2</sub> probably represents the hydrogen evolution process from water impurity or other hydrogen bond donors, i.e. urea.<sup>17</sup> Although the prepared DES solutions were dried and stored in a desiccator before use, it is well known that some moisture may be easily absorbed into the deep eutectic solvent electrolyte during manipulation and experiments, or incorporated via hydrated salts,<sup>20,21</sup> so the peak C<sub>2</sub> response is accounted for in this work.

Concerning the CV of DES with Mn<sup>2+</sup> ions, it is seen that apart from the broad peaks already identified in the blank DES, there is no other cathodic current peak which could be related to the Mn<sup>2+</sup>/Mn reduction, nor the corresponding anodic stripping peak. However, the current increase related to the Mn deposition was reported in literature concerning voltammetric analysis of Mn<sup>2+</sup> reduction in DES on Au<sup>13</sup> and Cu electrode.<sup>15</sup> This strongly suggests that Mn<sup>2+</sup> species are not reduced in ChCl-urea DES on steel substrate at potentials more positive to the potential of the electrochemical degradation of the bulk DES solution.

#### *Voltammetry of DES with Zn<sup>2+</sup> and Mn<sup>2+</sup>*

Cyclic voltammograms of 0.1 mol dm<sup>-3</sup> ZnCl<sub>2</sub> + 0.1 mol dm<sup>-3</sup> MnCl<sub>2</sub> in DES recorded on steel at different potential scan limits are presented in Fig. 2. Four current peaks are clearly evident, and may be ascribed, from positive towards negative potential to the processes in the blank electrolyte, Zn<sup>2+</sup> reduction and finally Mn<sup>2+</sup> reduction, respectively.

When the CVs of metal free DES (Fig. 1) are compared to the voltammograms of DES with metal ions (Figs. 1 and 2) it is clear that the bulk electrolyte decomposition, indicated by the sharp current increase, is shifted to more negative potentials when Zn<sup>2+</sup> and/or Mn<sup>2+</sup> ions are present in the solution. Similar behaviour was reported for example in sulphuric acid,<sup>22</sup> when it was shown that the addition of



$\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$  or  $\text{Cd}^{2+}$  to the sulphuric acid inhibited hydrogen evolution reaction on steel. This was used in order to inhibit iron corrosion in sulphuric acid, although the mechanism describing how the metal ions having more electronegative reversible potential than that of hydrogen evolution process, actually may influence this process, is still not completely understood.<sup>23</sup> Some of suggested mechanisms involve specific adsorption, underpotential deposition, or the effect on the potential at the outer Helmholtz plane of the double layer.<sup>22,23</sup>

Further analysis of the voltammograms reveals that, although the reduction of bulk Mn on the steel substrate was not observed in cyclic voltammogram of ChCl–urea DES containing  $\text{MnCl}_2$  (in Fig. 1), when  $\text{Zn}^{2+}$  ions are present in DES along with  $\text{Mn}^{2+}$ , a clear reduction peak appears at  $\sim -1770$  mV (in Fig. 2), which is due to the reduction of  $\text{Mn}^{2+}$  ions. Therefore the Mn co-deposition occurs at a more positive potential than that for bulk Mn deposition. Based on literature data on the electroreduction in ChCl–urea deep eutectic solvents,<sup>10,17</sup> it may be suggested that the peak at  $-1770$  mV, results from the reduction of Mn on the Zn nuclei that were freshly deposited at more positive potentials (the peak  $\text{C}_3\text{Zn}^{2+}/\text{Zn}$  in Fig. 2). Similarly to this suggestion, Birbilis et. al have shown that the peak related to  $\text{Zn}^{2+}$  reduction on Cu substrate was shifted to a more positive potential if  $\text{Ni}^{2+}$  ions were previously reduced on Cu,<sup>10</sup> while Gomez and Valles have shown that ChCl–urea DES decomposition occurred at a much more positive potential when fresh Pt nuclei were formed on vitreous carbon during the same voltammetric scan.<sup>17</sup>

### ***Chemical composition of Zn–Mn deposits***

In order to determine the influence of deposition current density on the chemical composition and the surface morphology of Zn–Mn deposits, the coatings were galvanostatically deposited at current densities (c.d.s) in the range from 2 to 8  $\text{mA cm}^{-2}$ .

The variation of Mn content in the coating as a function of deposition c.d., determined by EDS analysis, is shown in Fig. 3, as an average result of 3-5 measurements at three samples of each deposit. The sample deposited at  $2 \text{ mA cm}^{-2}$  was Mn free, denoting that the working potential of the electrode has not reached the value for  $\text{Mn}^{2+}$  reduction. By increasing c.d. to  $3 \text{ mA cm}^{-2}$ , the Mn content sharply increases to around 25 wt.%, and then, between 3 and  $8 \text{ mA cm}^{-2}$ , it reaches a plateau in the narrow range of 22 – 27 wt.%. Bearing in mind that the ratio of two metals in the alloy is proportional to their partial deposition current densities, i.e. to the rates of their reduction, the dependence shown in Fig. 3 is quite intriguing, in comparison to the studies of the chemical composition of Mn alloys deposited from aqueous solutions. Numerous literature reports suggest that the electrodeposition of Mn alloys with more noble metals (Zn, Sn, Ni) in aqueous electrolytes belongs to the regular codeposition type,<sup>2,4,6,24</sup> characterized by a steady increase in Mn percentage in the deposit, as the deposition c.d. increases or the deposition potential shifts to more negative values. This is due to the fact that in the regular codeposition the alloy is deposited under diffusion control conditions. A nobler metal, in this case Zn, is reduced preferentially, but at a certain deposition c.d. value, a diffusion limiting current density is exceeded for this metal, so only the content of the less noble metal (Mn) increases with further increase in current density.<sup>25</sup>

As regards the deposition of Zn-Mn coating from deep eutectic solvent in this work, this is also, undoubtedly, a regular codeposition, because Mn content increases with deposition c.d. and Mn reduction occurs at a more negative potential than Zn reduction. However, contrary to the continuous growth in Mn percent, typically seen in water solutions, in this case one may observe a sharp increase in Mn content at  $3 \text{ mA cm}^{-2}$  in DES, which is quite a low deposition c.d., and the further increase to  $8 \text{ mA cm}^{-2}$ , does not bring a significant change in Mn content, as Fig. 3 depicts. A similar

pattern was reported for potentiostatic electrodeposition of Zn-Mn in ChCl-urea DES in,<sup>15</sup> although the authors did not further discuss this issue.

The most reasonable explanation for such Zn-Mn ratio in the deposit obtained from DES, would be that, unlike in water-based electrolyte, where after reaching a certain cd., Zn deposition is under diffusion control, this is not the case in DES. In other words, in the range of c.d.s studied (3 - 8 mA cm<sup>-2</sup>), for both metal species, the rate of their reduction may be enhanced by shifting the deposition potential to more negative values, which would not be the case for a diffusion limiting step. To examine this suggestion, the cyclic voltammograms were recorded on a steel substrate from DES at different hydrodynamic conditions during deposition, provided by magnetic stirrer. They were compared with the one in stagnant electrolyte, as illustrated in Fig. 4. When the stirring rate is changed from 0 to 300 rpm, the intensity of all four cathodic peaks slightly increases. However, for several rates from 300 to 1500 rpm, all peaks for Zn<sup>2+</sup> reduction are of similar intensity, and the same stands for Mn. This suggests that, contrary to the results from water-based solution, the diffusion of Zn or Mn ions to the cathode is not the rate determining step in their electrodeposition. Such an assumption is consistent with the very recently proposed mechanism of Zn electrodeposition in DES.<sup>26,27</sup> Briefly, it is known that the main zinc species in choline chloride based eutectic solvents is tetrachlorozincate ion [ZnCl<sub>4</sub>]<sup>2-</sup>, having the rather negative reduction potential. So, it has been proposed<sup>26,27</sup> that instead of direct reduction of [ZnCl<sub>4</sub>]<sup>2-</sup> species, the Zn deposition occurs through the formation of an intermediate species [Zn(RO)<sub>x</sub>Cl<sub>4-x</sub>]<sup>2-</sup> and its subsequent reduction to Zn. The species [Zn(RO)<sub>x</sub>Cl<sub>4-x</sub>]<sup>2-</sup> is formed in the diffusion layer by replacement of one or more chloride ligands in the [ZnCl<sub>4</sub>]<sup>2-</sup> ion. Its formation has slow chemical kinetics and this may be a rate determining step for Zn deposition, instead of diffusion of Zn<sup>2+</sup> ions to the cathode.<sup>26,27</sup>

From the practical point of view, it appears that the change in deposition c.d. may not be a parameter which significantly alters the chemical composition of Zn-Mn electrodeposits from ChCl-urea DES, as is usually the case in water-based electrolytes.<sup>1,4,6</sup> However, the positive result is certainly the fact that in DES, as shown in Fig. 3, a quite high Mn content (22 - 27%) may be achieved at low deposition c.d., which is usually not feasible in water solutions.<sup>2,3,6</sup>

### ***Deposit's surface morphology***

Figure 5 shows the morphological characteristics of several samples obtained from SEM investigation. These SEM micrographs indicate that the coatings deposited at 2, 3 and 4 mA cm<sup>-2</sup> consist of closely packed and randomly oriented platelets, producing at low magnifications visibly smooth and light surfaces, which is typical for Zn coatings deposited at low overpotentials.<sup>28</sup> However, it can be seen that an increase in c.d. to 5 mA cm<sup>-2</sup> resulted in the formation of a porous surface consisting of clusters of nodular crystallites. Furthermore, the deposition at 8 mA cm<sup>-2</sup> led to a surface with pyramidal shaped dendrites and with evidence of gas evolution. Gaseous products formed as a result of ChCl-urea DES electrochemical decomposition, have been proven to be hydrogen and triethylamine.<sup>17,26,29</sup> Therefore, it may be inferred that the optimal deposition c.d would be 3 mA cm<sup>-2</sup>, since at a higher c.d. there is a negligible increase in Mn content. However the surface morphology and appearance become less acceptable for protective coating applications.

## **4. Conclusions**

Cyclic voltammograms recorded in choline chloride-urea deep eutectic solvent, show that there was no observable Mn reduction peak when only Mn<sup>2+</sup> was present in DES solution. The distinct Mn peak developed only upon addition of Zn<sup>2+</sup> to the solution,

probably due to previous Zn nucleation on the steel substrate. The EDS analysis of the Zn–Mn deposits obtained with current densities of  $3 - 8 \text{ mA cm}^{-2}$ , reveals that Mn content is in the range of  $22 - 27 \text{ wt.}\%$ , and it does not increase significantly with increased deposition current density. The possible explanation for such an interesting observation could be the slow formation of  $[\text{Zn(RO)}_x\text{Cl}_{4-x}]^{2-}$ , as an intermediate species in Zn reduction. At  $3 \text{ mA cm}^{-2}$ , a Zn–Mn coating of dense and homogeneous appearance may be formed, having around  $25 \text{ wt.}\%$  Mn, which is considerably higher than typical Mn content in Zn–Mn coatings deposited from aqueous electrolytes.

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### Figure Captions:

Figure 1. Cyclic voltammograms of blank 2:1 urea -  $\text{ChCl}$  electrolyte and 2:1 urea -  $\text{ChCl}$  electrolyte +  $0.1 \text{ mol dm}^{-3} \text{ MnCl}_2$ , on steel substrate, at  $70^\circ\text{C}$ . Scan rate  $100 \text{ mV s}^{-1}$ .

Figure 2. Cyclic voltammograms of 2:1 urea -  $\text{ChCl}$  +  $0.1 \text{ mol dm}^{-3} \text{ MnCl}_2$  +  $0.1 \text{ mol dm}^{-3} \text{ ZnCl}_2$  electrolyte on steel substrate, at  $70^\circ\text{C}$ , for three potential scan limits. Scan rate  $100 \text{ mV s}^{-1}$ .

Figure 3. Variation of Mn content, determined by EDS, in Zn-Mn coatings deposited at  $70^\circ\text{C}$ , with electrodeposition current density.

Figure 4. Cyclic voltammograms of 2:1 urea -  $\text{ChCl}$  +  $0.1 \text{ mol dm}^{-3} \text{ MnCl}_2$  +  $0.1 \text{ mol dm}^{-3} \text{ ZnCl}_2$  electrolyte on steel substrate, at  $70^\circ\text{C}$ , at different stirring rates. Scan rate  $100 \text{ mV s}^{-1}$ .

Figure 5. SEM micrographs of Zn-Mn coatings deposited on steel substrate, at  $70^\circ\text{C}$ , from 2:1 urea -  $\text{ChCl}$  +  $0.1 \text{ mol dm}^{-3} \text{ MnCl}_2$  +  $0.1 \text{ mol dm}^{-3} \text{ ZnCl}_2$  electrolyte at (a)  $2 \text{ mA cm}^{-2}$ , (b)  $3 \text{ mA cm}^{-2}$ , (c)  $4 \text{ mA cm}^{-2}$ , (d)  $5 \text{ mA cm}^{-2}$  and (e)  $8 \text{ mA cm}^{-2}$ . All deposits were obtained with the same charge density of  $20 \text{ C cm}^{-2}$ .

### Biographical notes:

Mihael Bučko is an Associate Professor in the Department of Military Chemical Engineering, at Military Academy, University of Defence in Serbia, where he teaches metal corrosion and protection. His research interests focus on the electrochemical deposition of alloys on steel substrate, from aqueous and non-aqueous electrolytes. He has published 11 scientific articles and attended 23 scientific conferences until now.

Dr. David Cullion is an Early Stage Researcher (having completed his Ph.D. in 2011) and Project Manager in Mechanical Engineering. His main areas of research include surface degradation phenomena and treatments, adapted electrochemical technologies, light metal alloys, renewable energies and mechanistic water-transfer systems. In his



Ph.D he developed a novel conformal anti-tribocorrosion surface technology. The technology is the subject of a number of on-going industrial projects in the wastewater and electronics industries and a patent has been filed. Dr. Culliton combines this with extensive experience in Project Management covering the IT, Construction and Research environs. He is currently involved in the development of pan-European and Global research projects.

Dr Tony Betts is the Head of Research in the College of Sciences and Health in the Dublin Institute of Technology (DIT), Ireland. He cofounded the Institute's Applied Electrochemistry Group with Professor John Cassidy. Especially interested in materials-oriented electrochemistry, he was previously a corrosion scientist performing research and consultancy work in Forbairt (now Enterprise Ireland). Dr Betts obtained his PhD degree in electrochemistry from the University of Auckland, New Zealand. Before moving to Ireland in 1998 he undertook a similar role in the Materials Performance Technologies Group of Industrial Research Ltd (formerly the DSIR) in Auckland.

Dr Jelena Bajat is Professor at the Department of Physical Chemistry and Electrochemistry at the Faculty of Technology and Metallurgy, University of Belgrade, Serbia. She teaches several courses: Physical Chemistry, Surface Engineering, Metallic and Non-metallic coatings at graduate studies and Galvanic technique at postgraduate studies. Her main research fields are surface treatments, electrodeposition of alloys and composites, corrosion protection by metallic and non-metallic coatings, sol-gel coatings, oxide based plasma electrolytic oxidation layers, adhesion, light metal alloys for biomedical applications, inhibitors.

Figure 1.

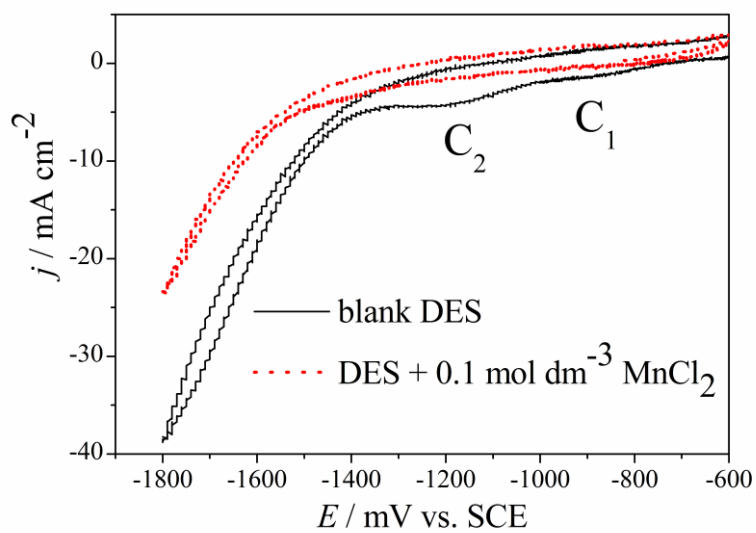


Figure 2.

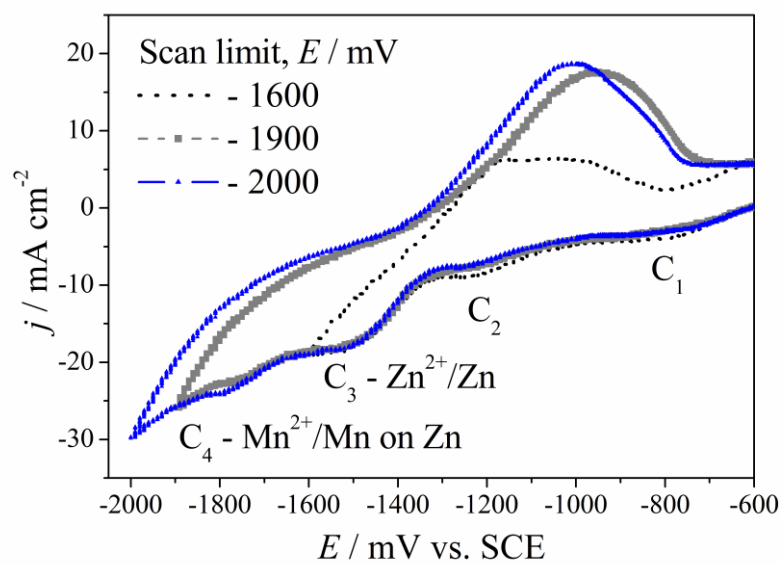


Figure 3.

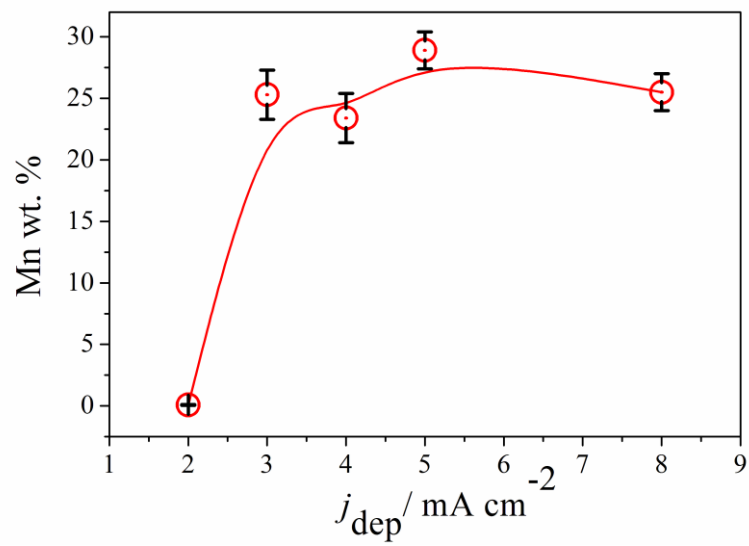


Figure 4.

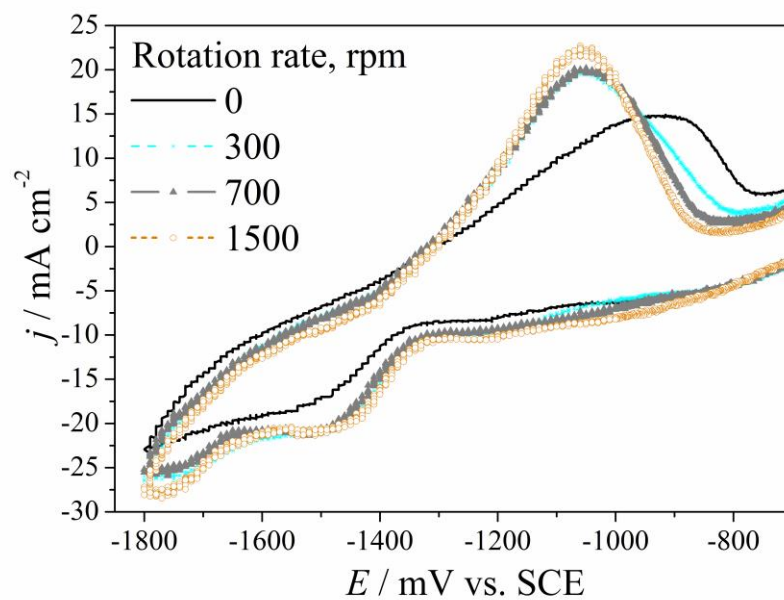


Figure 5.

