Int. J. Electrochem. Sci., 8 **(2013)** 1443 - 1458

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Platinum Electrodeposition in an Ionic Liquid Analogue. Solvent Stability Monitoring

E. Gómez[*], *E. Vallés*

Electrodep, Departament de Química Física and Institut de Nanociència i Nanotecnologia (IN^{2}UB),
Universitat de Barcelona, Martí i Franquès 1, E-08028 Barcelona, Spain.
[*]E-mail: e.gomez@ub.edu

Received: 16 November 2012 / *Accepted:* 11 December 2012 / *Published:* 1 January 2013

The use of ionic liquid analogues as solvents has increased in order to substitute the aqueous solvents in some applications in which the side reactions are undesirable. However these solvents prepared from the mixture in the eutectic proportion of species establishing hydrogen bonds are susceptible of electrochemical reactions. The study of platinum deposition on vitreous carbon in an ionic liquid analogue (2 urea: choline chloride) is presented; the electrochemical study has permitted to interpret the sequence of the metal deposition process and simultaneously to analyze the behavior of the ionic liquid analogue along the process. Reduction reactions of the solvent related both to the electronation of choline and hydrogen formation have been detected. Different substrata have been used in order to test the possibility and the extent of these reactions depending on the nature of material. The results indicate that the feasible electrochemical window of the substrate/solvent is highly dependent of the kind of substrate; the negative limit is tied by the massive hydrogen reaction, reaction enhanced by the electrocatalytic character of the substrate.

Keywords: platinum electrodeposition, ionic liquid analogue, electrochemical window, voltammetric characterization.

1. INTRODUCTION

Electrolytes for application in electrodeposition should have a high resistance against electrochemical reduction and oxidation, especially against the reduction process when the goal is to obtain metallic deposits. For this reason, it is well known that an important aspect to consider during the design of an electrochemical process is the stability of the solvent. But, it is also necessary to take into account the changes occurring in the substrate when the new phase is formed. The knowledge of the reactions that could occur over the freshly deposited material will allow avoiding or minimizing the effect of side-reactions that could damage the deposit properties or control the energy cost or both.

The electrodeposition of metals in aqueous solutions often is accompanied by the known side-reaction at the cathode of water to hydrogen gas:

$$2H_2O+2e^- = 2OH^- + H_2$$

Although water is the preferred solvent because of its versatility and cost, depending on the species to be deposited, the above reaction may be undesirable, either because the basic local environment generated or by the production of hydrogen. As more important is the above reaction, further away of 100% the current efficiency. But not only these factors could discourage the use of aqueous medium in the electrodeposits preparation, this medium is useless when its electrochemical window is not sufficient wide to achieve metallic deposits, this occurs for species which the deposition potential is more negative than that of the water reaction over the selected substrate.

As possible alternative, the use of ionic liquids as electrolytes for electrochemical purposes has gone gaining interest in the last years. Especially at present, with the use of air and water stable and relatively inexpensive ionic liquid analogues [1], named as deep eutectic solvents (DES). For these solvents an electrochemical window wide enough to deposit some species [2-6], impossible in water, is observed in some electrodes [7, 8]. But, also an important goal is that the electrochemical window maintains along the complete deposition process.

Only a few studies have been carried out on the possible reactions of ionic liquids [9, 10] and less during metal deposition when them are used as solvents. The same is true for investigations on how affects to the overall electrochemical process the possible ionic liquid reaction. The ionic liquid analogue used in this work is based on 2 urea: 1 choline chloride, for which previous FTIR studies [9] demonstrates the existence after liquid preparation of more hydrogen bonds than those in urea.

This work seeks to present the substrata influence over possible DES reactions, especially during electrodeposition processes. We reported that, when DES solvents are used, it is not only necessary to consider the behavior of the solvent against the substrate, but also against the formed deposit. Related with this, the effect of the substrate over the solvent response was analyzed. Taking advantage of the different electrocatalytic character of substrate and deposit, the electrodeposition of platinum on vitreous carbon in the DES solvent is shown as a tool to describe the effect of the appearance of the first deposited nuclei over the stability of the solvent.

Cyclic voltammetry has been the main tool used to establish the general trends of the electrochemical behaviour, to display the corresponding electrochemical window and provide information about the processes involved at different potential during the scan on the different substrata and experimental conditions. Substrata as vitreous carbon, copper, cobalt, nickel and platinum were considered.

This paper evidences that with these liquids is not always possible to minimize the hydrogen reaction, increasing efficiency significantly compared to that in the aqueous medium, because upon depending of the substrata, parallel reactions can be done that involve consume. The information derived from this work will be a tool or a criterion to select the potential ranges in which no side reactions occur and if this is not possible, consider if any.

2. EXPERIMENTAL PART

Solvent was prepared using choline chloride (from Across Organics) and urea (from Merck) of analytical grade. Choline chloride was dried in an oven at 70ºC during 48 h and subsequently placed in a dessicator. The solids, in the molar proportion 1 choline chloride: 2 urea, were warmed and removed constantly to achieve the liquid state, solutions were prepared using this DES solvent. Sodium hexachloroplatinate (IV) from Alfa Aesar of analytical grade was used. In all experiments the [Pt(IV)] was maintained at 2.10 10^{-2} M , this concentration is near the highest that allows the solubility of the platinum salt used in the DES at room temperature. After preparation, the solution was placed in a dessicator in order to avoid uptake of water by higroscopicity. No support electrolyte was added taking advantage that DES acts both as solvent and as electrolyte.

A cylindrical three electrode cell of one single compartment was used. Electrochemical experiments were carried out using an Autolab with PGSTAT30 equipment and GPES software. Basic electrochemical study was made using as working electrodes vitreous carbon (from Metrohm), platinum, cobalt, nickel and cooper rods and glass/indium tin oxide (ITO). Vitreous carbon electrode was polished to a mirror finish using alumina of different grades (3.75 and 1.87 μm), cleaned ultrasonically for 2 min in water and dried with air prior to be immersed in the solution. Prior electrochemical experiment platinum was immersed in a solution of nitric acid and subsequently submitted to the flame. Cobalt, nickel and cooper were polished using diamond (6 and 1 μm) and alumina (0.3 μm) suspended in distilled water and cleaned ultrasonically for 2 min in water.ITO was rinsed successively in acetone, ethanol and pure water and conveniently dried in nitrogen stream. The counter electrode was a spiral of platinum. The reference electrode was an Ag|AgCl/NaCl 3M mounted in a Luggin capillary containing the DES solvent [8]. Stable and reproducible values of the potential were obtained with this reference electrode. Before measurements, solutions were deaerated by bubbling argon and maintained under argon atmosphere during the experiments.

If the opposite is not said, voltammetric experiments were carried out scanning at first to negative potentials from 0.4 V at 50 mV s^{-1} and only one cycle was run in each voltammetric experiment. The temperature was selected at 70ºC to favour low viscosity and high conductivity of the solvent. Magnetic stirrer was used when the agitation effect was tested.

Deposits were prepared on ITO, the morphology was observed using a Field Emission scanning electron microscope Hitachi H-4100 FE.

3. RESULTS AND DISCUSSION

3.1. Solution containing Pt(IV)

3.1.1. Vitreous carbon substrate

On vitreous carbon electrode the first recorded voltammetric scan (Fig. 1 curve a) in the solution containing Pt(IV) shows during the negative scan a reduction peak (C_1) centered at around -0.12 V, which current decreases smoothly with the scan progress, following the scan a new current was detected from -1.05V. Reversing the scan at -1.5 V, a current loop was observed, however in any potential of C_1 peak it was possible to record a current loop after reversing the scan. Following the positive scan a small current band centered at -0.49 V was detected. Similar scan on vitreous carbon electrode using the Pt(IV)-free solution did not show faradaic current, and it is necessary to elongate the scan to -2 V to record the initio of significant current [8]. Stirring the solution during the scan, an evident current increase was observed as the scanning goes to the more negative potentials (Fig.1 curve b), confirming that the current related to C_1 peak corresponds to a process under mass control [3[. Reproducibility between independent experiments was very satisfactory.

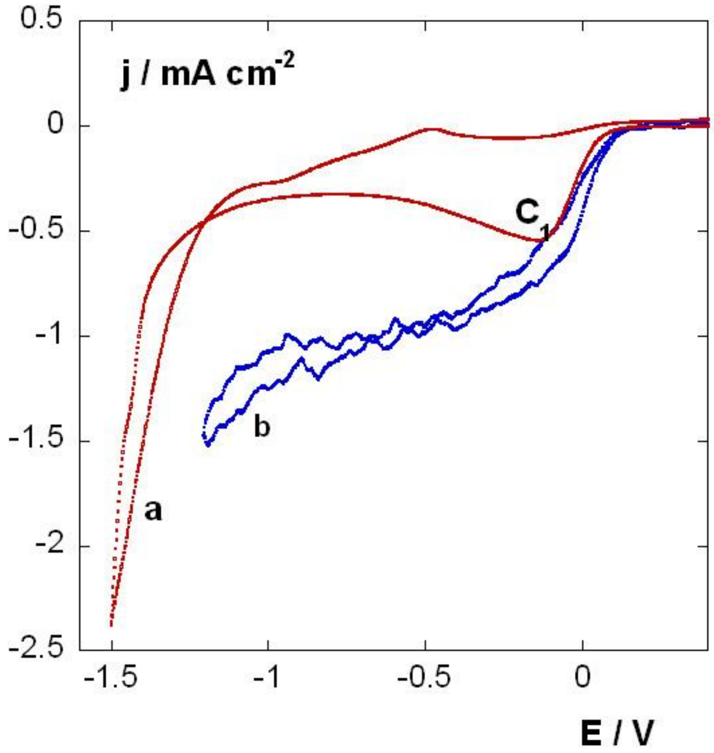


Figure 1. Cyclic voltammograms from 2.1 10^{-2} M Pt(IV) solution on vitreous carbon electrode, curves: a) stagnant conditions, b) stirred conditions. Scan rate 50 mV s^{-1}.

However the comparison between two consecutive scans showed some differences. Consecutive scans were recorded at stationary conditions maintaining the limits (Fig. 2), stirring the solution between the scans for a few seconds at +0.4 V, potential at which current was not detected. The second voltamètric profile (Fig.2 curve b) coincides with the first one to around -0.65V, but from this potential value a second peak (C_2) followed by the massive current was observed. In the positive scan, also, a clear oxidation peak (A_2) appears, joint to the little current band already observed. In consecutive scans the massive reduction current shifted towards more noble potentials [3]. Gas bubbling was observed on the working electrode during the massive reduction of the solvent.

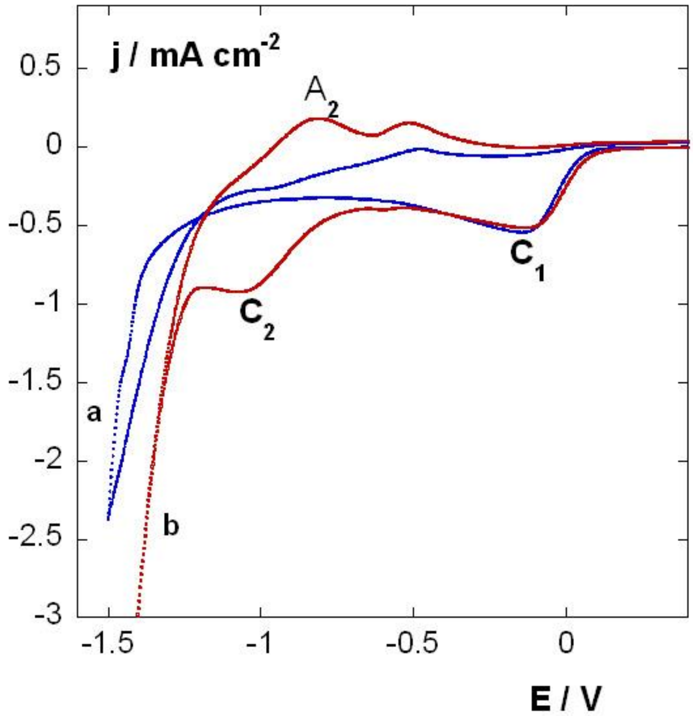


Figure 2. Cyclic voltammograms from 2.1 10^{-2} M Pt(IV) solution on vitreous carbon electrode, recorded at stagnant conditions, curves: a) first scan, b) consecutive second scan. Scan rate 50 mV s^{-1}.

These results indicate that the platinum deposition process on a foreign substrate as vitreous carbon causes changes in the overall electrochemical process. The presence of the first platinum nuclei seems able to modify the nature of the electrode, as the manner that reactions that occur at very negative potentials on vitreous carbon are significantly favored on the freshly deposited platinum. In order to confirm the effect of platinum presence it was analyzed the reduction process of Pt(IV) on platinum substrate.

3.1.2. Platinum substrate

On platinum electrode, the voltammograms recorded of Pt deposition process show a profile very similar to that obtained during the second scan on vitreous carbon (Fig.3 curve a). In the negative scan similar C_1 and C_2 peaks appeared followed by massive current. Moreover, a new small peak (C_{21}), previous to the C_2 appeared. Reversing the scan at limits exceeding the onset of the massive current, in the positive-going sweep an albeit broader, oxidation peak A_3, centered around -1 V, was observed. Recording the voltammograms under stirring, the reduction current increased, the peak C_{21} also appeared and negative current was detected in the positive scan (Fig. 3 curve b). The presence of the C_2 voltammetric peak from the first scanning when platinum was used as substrate confirms that C_2 peak and the massive current advancement observed from the second scan on vitreous carbon are related to some reaction that takes place on the freshly platinum deposited, reaction that on vitreous carbon is not feasible at this potential range.

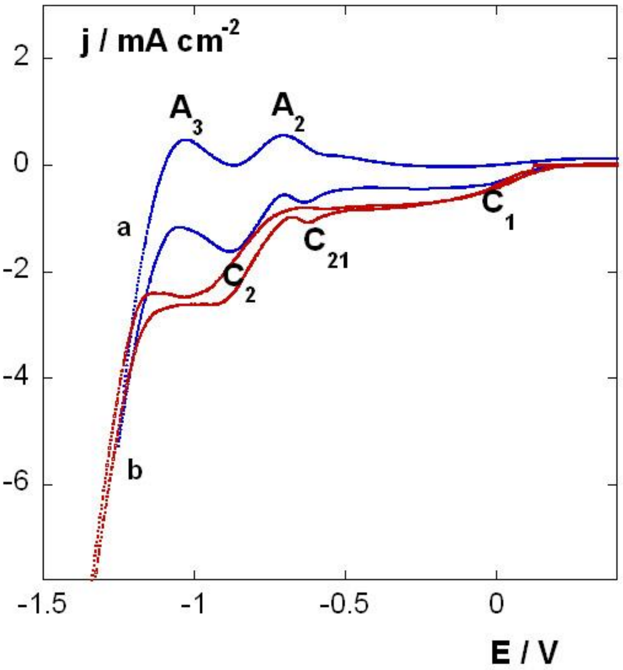


Figure 3. Cyclic voltammograms from 2.1 10^{-2} M Pt(IV) solution on platinum electrode, curves: a) stagnant conditions, b) stirred conditions. Scan rate 50 mV s^{-1}.

3.1.3 Preparation of deposits and identification of C_1 peak

As nucleation loop was not observed after reversing the scan along the onset of the C_1 peak, the potential range at which platinum deposition occurs was investigated.

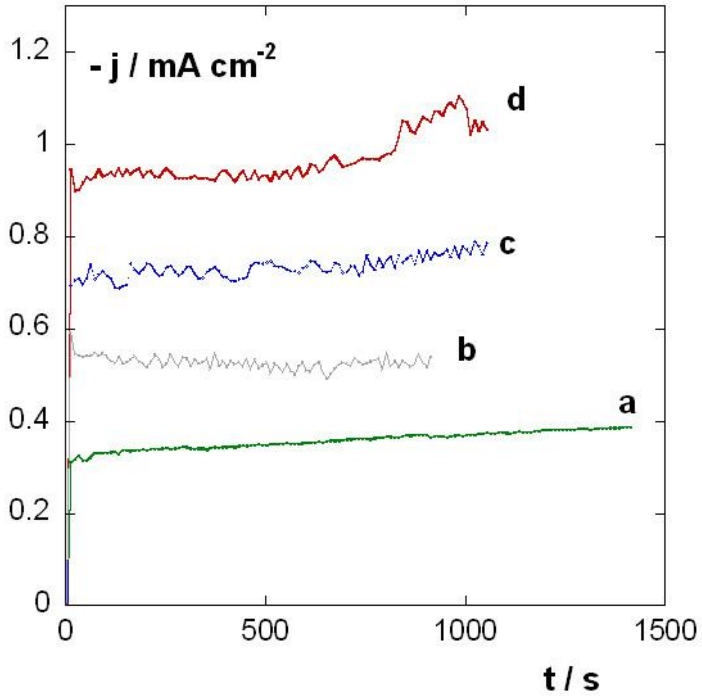


Figure 4. j-t transients from 2.1 10^{-2} M Pt(IV) solution on glass / ITO electrode under stirred conditions at different potentials: a) -730 mV, b) -760 mV, c) -790 mV and d) -840 mV.

Glass/ITO electrode was selected to prepare platinum deposits due to its transparent character and good adherence between conductive layer and the substrate. Over this substrate, the voltammetric response of the platinum deposition process was similar than that over vitreous carbon although the reduction processes shifted slightly to negative values due to the lower conductivity of the substrate. Platinum deposits were prepared potentiostatically under agitation.

The j-t transients show the current of the charge of double layer followed by a quasi-stationary current, that remains stable during the deposition process at moderate potentials and increases with deposition time at the most negative (Fig. 4). Although on glass/ITO electrode, reduction current was observed in the voltammetric curves from around 0 V, in no case, applying potentials more positive than -0.65 V deposit was obtained.

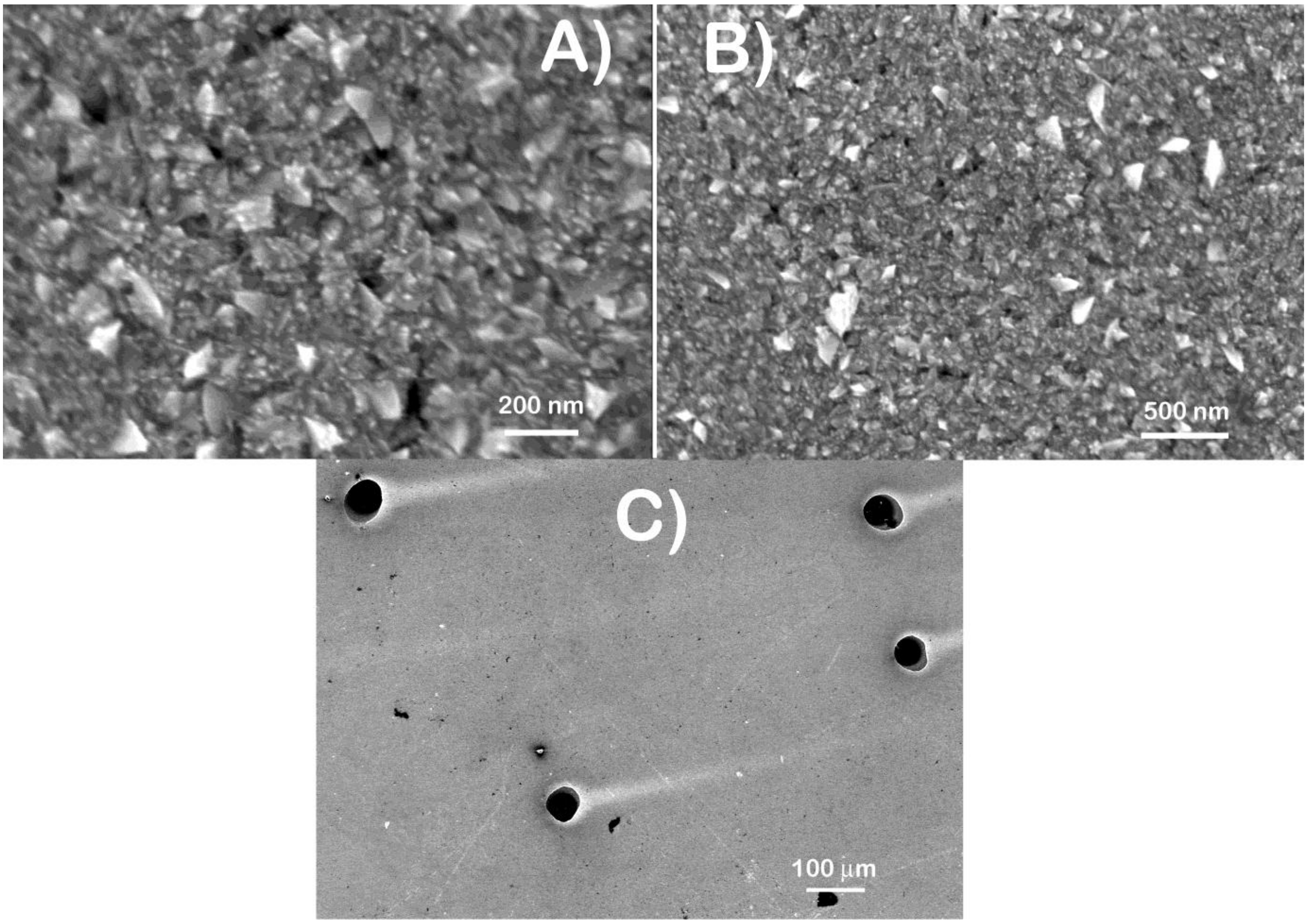


Figure 5. SEM images of platinum deposits obtained at: A) and B) -760 mV and C) -910 mV

The glass/ITO substrate, just removed from the solution continues as transparent as when it was immersed in the solution. It was necessary to apply potentials more negative than -0.7 V, to observe, after a few minutes, a light gray color on the transparent substrate. Decreasing the applied potential, continuous layers were obtained at long deposition times. The layers prepared at moderate potentials were fine-grained (grain size about 50 nm), show a needled morphology (Fig. 5A) and compact coverage after apply the potential during a few hundred of minutes (Fig. 5B).

Decreasing the applied potential to values more negative than -0.90 V, less adherent continuous deposits were obtained, deposits that show distributed empty circles of tens of microns in which the deposit has not grown (Fig. 5C). These circles are a consequence of the gas formation observed during the deposition process; bubbles attached to the deposit inhibit locally the growth.From these results (deposit was not obtained in the C_1 potential range and absence of voltammetric nucleation loop when the potential was reversed on the onset of the C_1 peak), it's possible to conclude that the C_1 reduction peak does not correspond to a nucleation and growth process. C_1 peak is associated to the partial reduction of Pt(IV), probably to Pt(II) species. The true Pt nucleation – growth process occurs at more negative potentials, as it has been demonstrated by means deposits preparation.

3.2. DES solvent. Blank solution

3.2.1. Behavior of Pt in DES solvent

In order to analyze the electrochemical behavior of the solvent and to identify the processes associated to it on platinum substrate, the voltammetric study was made in a blank solution. Different negative limits were tested (Fig. 6).

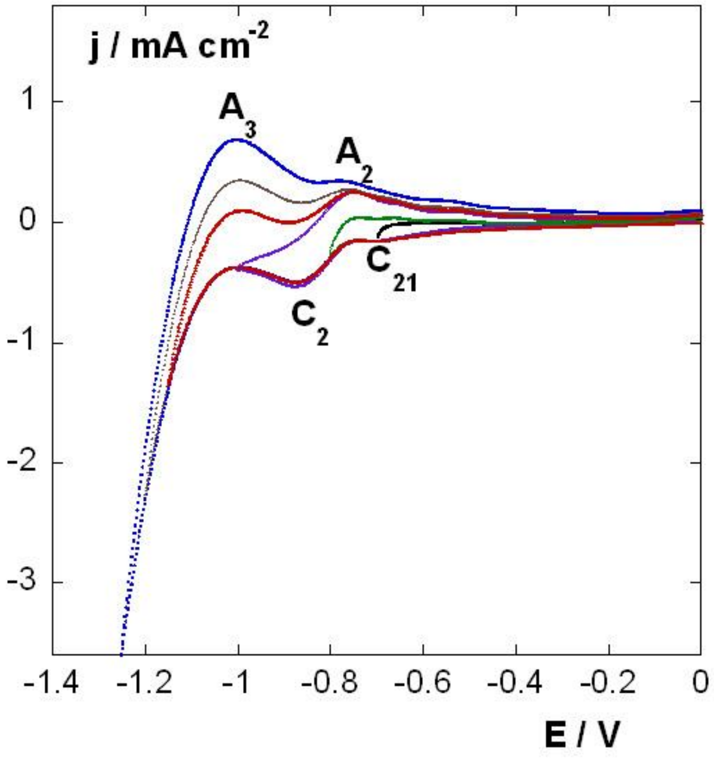


Figure 6. Cyclic voltammograms in the DES solvent on platinum electrode at different negative limits at stagnant conditions. Scan rate 50 mV s^{-1}.

Scanning to negative potentials, the C_{21} peak, followed by C_2 one and the massive solvent reduction were recorded. Reversing the scan from -0.9 V, potential that exceeds the C_2 peak, the corresponding A_2 peak in the positive scan was detected. By reversing the scan in the massive reduction zone (when gas bubbling was detected, as in the Pt(IV) solution), the A_3 oxidation peak appeared in the positive scan, being the involved charge increased as the limit was made more negative.

However, lowering the scan rate, the A_3 peak quasi-disappears (Fig.7 curve a) because the gas bubbles can be detached from the electrode and their oxidation is nor possible. The voltammograms recorded under stirring evidence that the C_2 peak corresponds to a mass-controlled process (Fig. 7 curve b). In all conditions, the cyclic voltammograms obtained after successive cycles do not show differences.

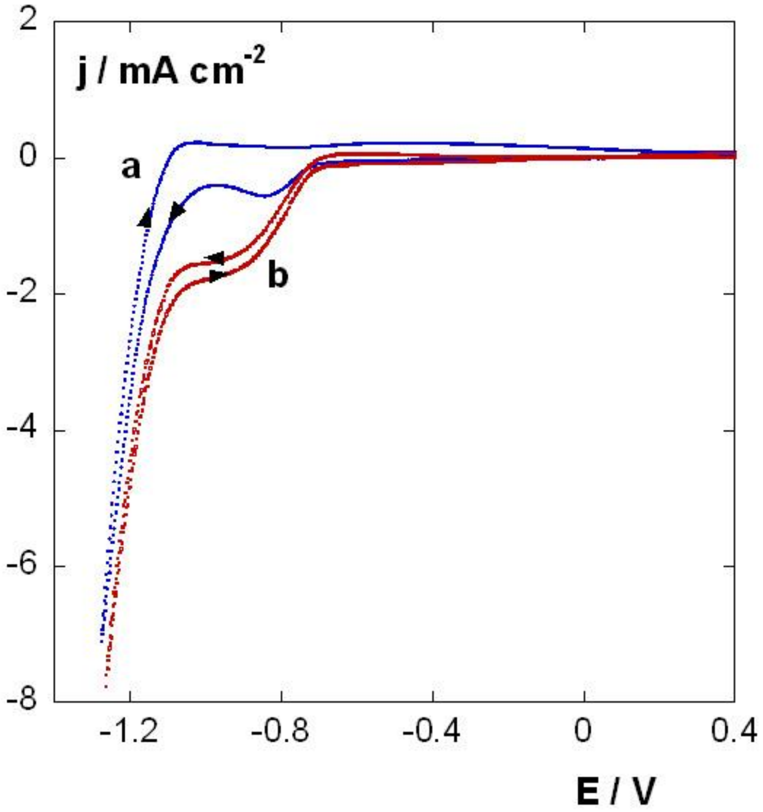


Figure 7. Cyclic voltammograms in the DES solvent on platinum electrode curves: a) stagnant conditions, b) stirred conditions. Scan rate 20 mV s^{-1}.

In order to analyze the solvent reduction upon depending on the substrate nature, potentiostatic and galvanostatic experiments were performed at similar conditions on both vitreous carbon and platinum electrodes. Potentiostatic experiments, were made at fixed sufficient negative potential (-1500 mV) to test the solvent reduction. Negligible current was recorded on vitreous carbon, even under stirring conditions, whereas on platinum, significant current was recorded, greater when the solution was stirred (Fig 8A), highlighting that the solvent reduction process is affected by the contribution of solvent to the electrode. The chronopotentiometric experiments were developed at low current densities, -50 and -100 μA cm^{-2}. A potential decay just stabilization was recorded in all experiments. On platinum, applying these low currents, the attained potential values corresponded to those of the first currents in the voltammetric experiments, whereas when vitreous carbon was used as working electrode, the attained potential was more negative than those recorded on platinum (Fig. 8B). Then, for maintain a small current of solvent reduction on vitreous carbon; the system must reach potential values much more negative than on platinum. Chronopotentiometric and chronoamperometric experiments were in agreement, and were indicative that the solvent reduces and this reduction is clearly favoured on platinum, as can be also seen from the voltammetric experiments. The platinum presence catalyses the reduction reaction of the solvent.

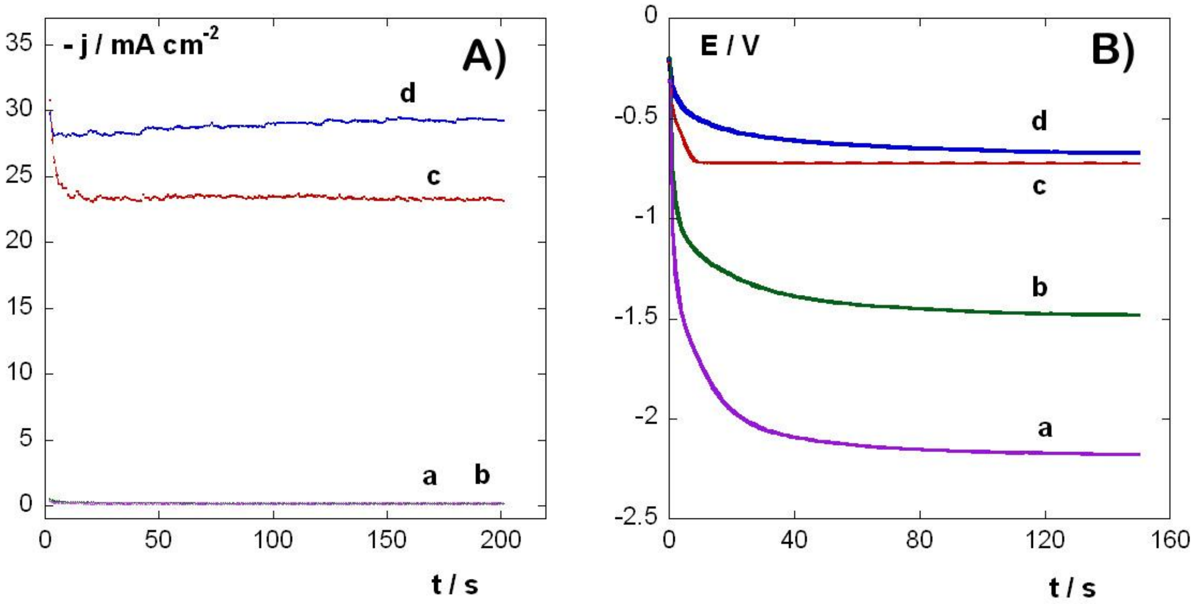


Figure 8. From DES solvent. A) j-t transients at -1500 mV on: a) vitreous carbon, quiescent conditions, b) vitreous carbon, stirred conditions, c) platinum, quiescent conditions, d) platinum, stirred conditions. B) E-t transients under stirred conditions on: a) vitreous carbon at -0.1 mA cm^{-2}, b) vitreous carbon at -0.05 mA cm^{-2}, c) platinum at -0.1 mA cm^{-2}, and d) platinum at -0.05 mA cm^{-2}.

An analysis of the voltammetric potential range at which both C_2 and C_{21} peaks appeared was performed. Cyclic voltametries were recorded at different scan rates, reversing the scan just past the potential range of the pair C_2/A_2 (Fig. 9).

At the lower scan rate tested (20 mV s-^{1}) no well defined current was observed in the potential range of C_{21} peak, but as the scan rate was increased, a more clear splitting of the recorded peaks was observed and the C_{21} peak presence evidences. Reversing the scan a not so clear counterpart A_{21} manifests at potentials more positive than A_2 peak. The relative contribution of both C_{21} and A_{21} peaks to the overall current in this potential range increases as the scan rate increases, being at the highest scan rates tested majoritary respect to C_2 and A_2 peaks respectively. A rough estimation of the charges involved in the C_{21} peak shows that this charge is, regardless the scan rate, similar (Table 1), whereas the involved under the C_2 peak decreases progressively as the scan rate increases. As the manner that, the overall current recorded in this potential range decreases upon increasing the scan rate.

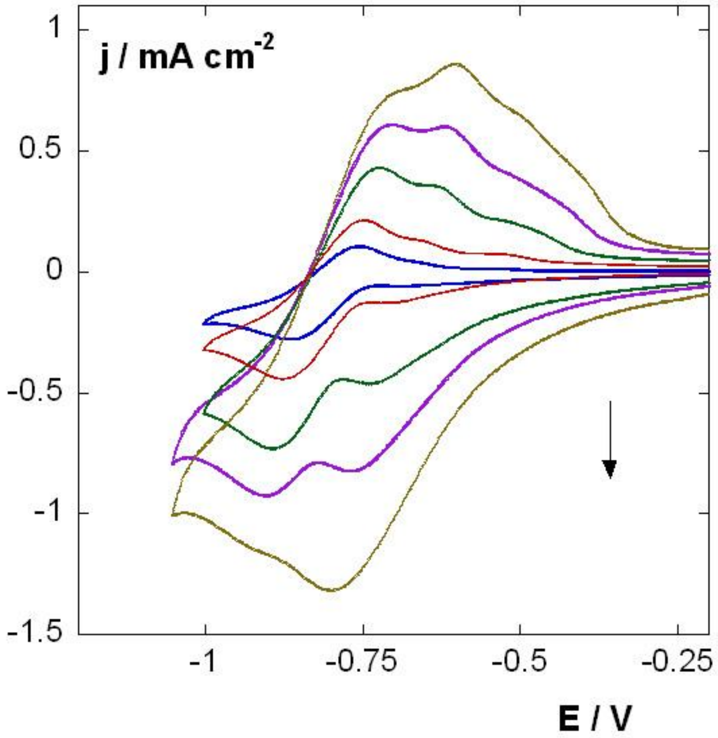


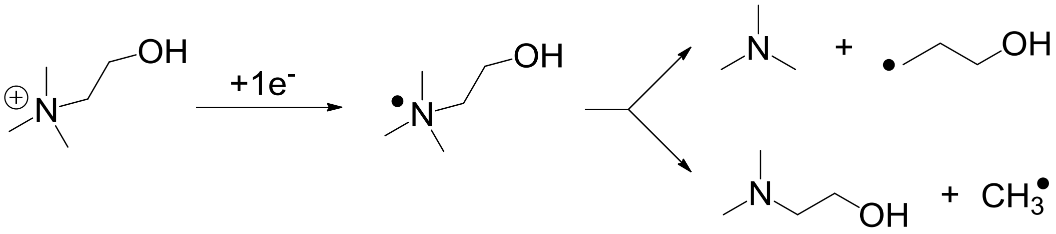
Figure 9. Cyclic voltammograms in the DES solvent on platinum electrode at different scan rates under quiescent conditions, curves in increasing sequence: 20 mV s^{-1}, 50 mV s^{-1}, 200 mV s^{-1}, 400 mV s^{-1}and 750 mV s^{-1}.

The fact that the involved charge under the C_{21} peak was similar regardless of the scan rate, leads to raise that it corresponds to an reductive adsorption process being the process fast enough, whereas that related to the processes associated to C_2 peak seems slow, due to their involved charge decreases at the scan rate increases. Hold experiments in both C_{21} and C_2 peaks in stationary conditions, make in evidence that a hold in the C_{21} peak leads to a sudden current decrease to zero current, whereas if the hold is made in the C_2 peak the process continues, as the manner that when the scan follows, some reduction current was recorded previous to the massive reduction current. On the other hand, when the solution was stirred, no evident modification was observed in the C_{21} peak morphology, whereas an important increase of current in C_2 peak was observed under agitation as already was stated (Fig 3).

Table 1. Charge under voltammetric peaks C_{21} and C_2 and C_{21} measured at different scan rates

Scan rate /mV s^{-1}	10^4* $Q_{(C21 + C2)}$ / C	10^5* $Q_{(C21)}$ / C
20	5.41	-
50	3.56	8.8
75	2.97	10.
100	2.64	10
200	1.94	9.1
400	1.52	8.4
500	1.36	8.6
750	1.16	8.9
1000	0.999	9.4

The interpretation of the solvent reduction processes assigned to C_{21}, C_2 and massive reduction features is analyzed. According to the literature [9, 10], the C_2 peak could be associated to the reduction of the choline. Yue and al. proposed that the choline decomposition occurs by electronation of the quaternary ammonium, that after the addition of one electron forms a radical that could decompose to different subproducts as trimethylamine or dimethylaminoethanol, according to the scheme:



Scheme 1. Electronation of choline ion at the cathode

On the other hand, the urea- choline chloride ionic liquid analogue presents different possible hydrogen bonds between associations of urea and choline [9]. Any of the possible associations that can be established may be involved in the reduction process and could be the responsible of the appearance of the massive reduction current, facilitated by the reduction of hydrogen donor species present in the solvent. This reaction, that it becomes only evident at high potentials on vitreous carbon, is favored on platinum probably due by the known electrocatalytic character of the platinum substrate versus hydrogen reduction [11, 12]. The formation of H_2, agrees with the gas bubbling observed over the working electrode, more important as the potential was made more negative.

In order to confirm the hypothesis that hydrogen donor species could induce the massive current appearance, experiments in which controlled volumes of water (0.5-5 ml) were added to 50 ml of DES solution, were performed. The voltammograms over platinum substrate were recorded from 0.4 V, potential value at which current was not detected, and scanned to negative values (Fig. 10).

From the first addition (0.5 ml), the C_2 peak enhanced and the massive reduction slightly advanced. Simultaneously, the A_2 peak increased.

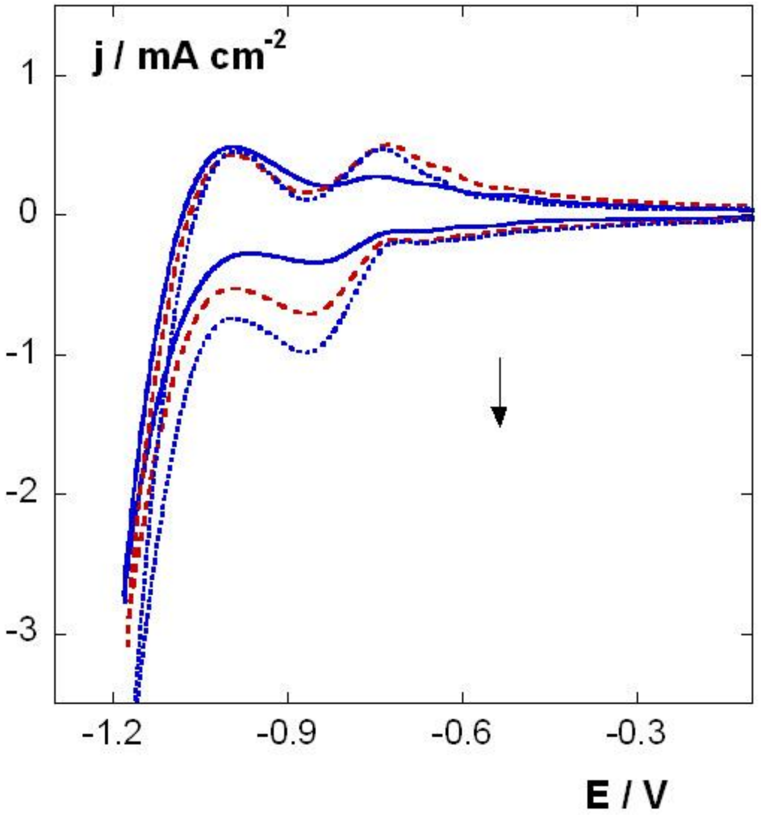


Figure 10. Cyclic voltammograms recorded after addition of different water volumes (x) in 50 ml of DES solvent on platinum electrode at quiescent conditions, curves: a) x = 0 ml continuous line, b) x = 0.5 ml dashed line and c) x= 1.5 ml dotted line. San rate 50 mV s^{-1}.

When similar experiments were made over vitreous carbon, the only remarkable effect observed after adding a few milliliters of water was the advancement of the onset of massive reaction as expected. Only for experiments where the water volume added was around 10 ml, a reduction band previous to the massive reaction began to be observed.

Hydrogen evolution takes place in the massive reduction current, but it is also evident that in the C_2 peak, an important contribution of hydrogen formation exists. In the C_2 peak potential range the reduction of tetrametyalmoniun cation occurs [9], but also takes place the hydrogen formation, as the manner that when the surface is saturated, hydrogen recombination occurs.

The broad oxidation peak A_3 corresponds to the oxidation of some H_2 that has not yet diffused away from the Pt electrode after being formed. When the scan rate was reduced, the time available to spread the gas is increased, and thus the A_3 peak is not as evident in the positive scan.

More difficult at these conditions it is to assign the process associated to the couple C_{21}/ A_{21}, some FTIR studies have been made but the results are inconclusive. As a possibility, it could be proposed that the C_{21} peak is due to chloride reductive desorption, chloride is an abundant species in this solvent and it is well known that chloride adsorbs strongly on the platinum [13]. Once the platinum has reached very negative potentials, the chloride, that remains adsorbed on platinum, desorbs and C_{21} peak appear, being the A_{21} peak, recorded during the positive going sweep the corresponding adsorption peak associated to the oxidative adsorption. The possibility of urea adsorption also has been considered, urea adsorption has been extensively studied on platinum [14,15], but the potential range of the couple C_{21} / A_{21} seems excessively negative to formulate the proposal of its desorption/adsorption process even in this medium and maybe could be related to oxidative processes.

3.2.2. Behavior of DES solvent on Ni, Co and Cu electrodes.

From the results it is confirmed that the nature of the substrata exerts an important effect over the observed DES reduction process. Other metals (Co, Ni, Cu) were tested to analyze the behavior of the ionic liquid analogue on them. It is well known that in aqueous solutions cobalt and nickel show electrocatalytic character to hydrogen formation [16-18] whereas for copper it is low [19]. These metals were selected to test their behaviour over the solvent that shows important number of hydrogen bonds.

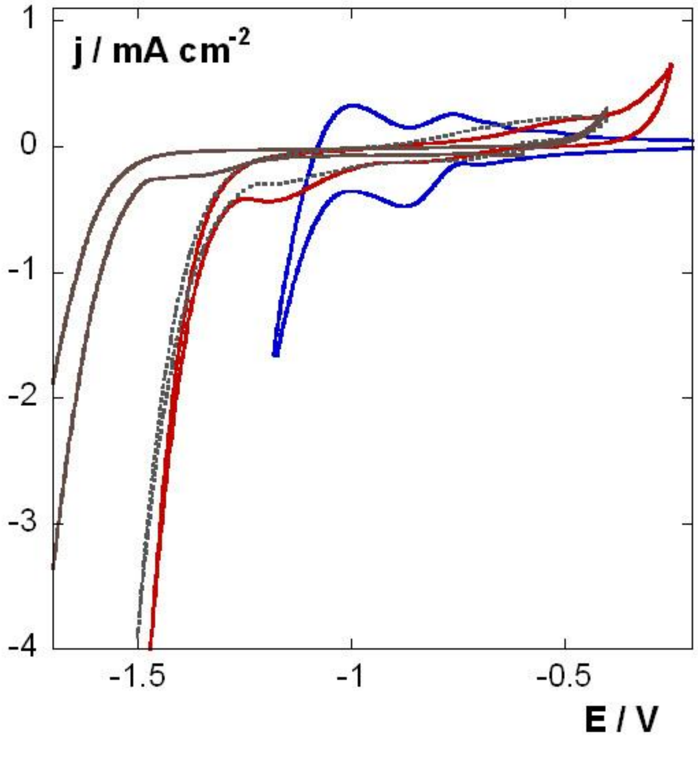


Figure 11. Cyclic voltammograms in the DES solvent at quiescent conditions on: a) platinum, b) cobalt, c) nickel and d) copper electrodes. Scan rate 50 mV s^{-1}.

A very careful treatment of the substrata has been necessary to attain reproducibility because the reactions were very sensitive to the state of the metal surface. Voltammograms in the ionic liquid analogue were recorded at fixed both temperature and scan rate (Fig. 11). Similar voltammetric profiles were observed over the different substrates, although the potential range at which current appeared was different. The initio of the reduction process was in the sense Pt>Co>Ni>Cu>vitreous carbon. The reduction process amended C_2 was always detected previous to the massive reduction current, but its charge was lower than the observed on platinum, especially for copper substrate. The C_{21} peak was not detected in any condition. The massive reduction current on nickel and cobalt appears at similar potential, a few hundred millivolts more negative than on platinum, whereas the appearance of massive current on copper electrode occurs even at more negative potentials, but more positive than on vitreous carbon. In the positive scan, the oxidation current gradually increased from Cu to Pt electrodes, previous to their oxidation. The A_3 peak, recorded on platinum, did not appear over the other substrates.

The reactions of solvent reduction also occur on these metallic substrata, being the facility of the reduction dependent on the nature of substrate. The electrocatalytic character for hydrogen reaction of both cobalt and nickel seems continuing effective in this medium, as occurs on platinum, because an advancement of the massive current respect to copper was observed. The catalytic behaviour of the metals on the DES solvent maintains respect to the behaviour observed on aqueous solutions.

According to the stated in previous sections the charge recorded under the C_2 peak in the blank solution corresponds to both the choline electronation [9, 10] and the hydrogen formation. As the peak C_2 recorded on copper was lower than those recorded on nickel or cobalt and especially on platinum, this confirm the stated above, because the contribution of the hydrogen reaction on copper substrate decreases due to its lower electrocatalytic character versus this kind of reaction.

The lower adsorption of chloride species on the selected metals than platinum is consistent with the no appearance of C_{21} peak, that tentatively was assigned to chloride reductive desorption.

4. CONCLUSIONS

During the platinum deposition on vitreous carbon in the ionic liquid analogue (2 urea: choline chloride) important changes occur that modifies superficial properties as the manner that the electrochemical window is substantially narrowed due to the reactions associated to solvent reduction. Voltammetric technique has been used as the main tool to detect these changes. Different peaks were detected, that have been assigned to two steps in the platinum deposition and to solvent reduction reactions. Deposits preparation has helped to define the potential range at which the true platinum deposition occurs.

The use of this deep eutectic solvent as electrolytic solvent in any electrodeposition process implies the need of a qualitative analysis of the possible DES reactions both on the substrate and over the freshly deposited material in order to establish the effective electrochemical window in a feasible manner. Simultaneously, it is necessary to take into account the possible interferences caused by processes associated to the solvent reduction and its effect on current efficiency.

For the solvent analyzed, choline reduction and hydrogen formation occurred, being the second reaction more important as the electrocatalytic character of the material versus the hydrogen reaction is. Higher electrocatalytic effect leads to a narrowing of the electrochemical window. The presence of platinum, as well as substrate as a coating leads to greater narrowing of the electrochemical window. Also, the presence of electrocatalytic metals versus hydrogen reaction, as nickel or cobalt and predictably their alloys will exert also sufficient influence as the manner that could be responsible of modifications in the experimental conditions along the electrodeposition process.

The use of this kind of solvents is not indifferent to the coating to be prepared, however its use, even in the least favorable conditions widen the electrochemical window compared to that of aqueous solvent and obtain coatings that in aqueous conditions are impossible.

The study confirm that on these metal substrata, reduction of the solvent needs to be considered, and depending of either substrate nature or the nature of the deposited species, electrochemical window will have more or less wideness, factor that should be always taken into account when an electrochemical process is designed using ionic liquid analogues in order to improve the current efficiency and minimize the damage of the coating.

ACKNOWLEDGEMENTS

This paper was supported by contract CTQ2010-20726 (subprogram BQU) from the *MINECO*. The authors wish to thank the *Centres Científics i Tecnològics de la Universitat de Barcelona (CCiTUB)* for the use of their equipment.

References

1. K. Haerens; E. Matthijs; A. Chinuelarz; B. van der Bruggen; *J. Environmental Management* 90(11) (2009) 3245-3252
2. N.M. Pereira, P.M.V.Fernandes, C.M. Pereira, A.F. Silva, *J. Electrochem. Soc* 159(9)(2012)D501-D506
3. P. Guillamat, M. Cortés, E. Vallés, E. Gómez, *Surf. Coating Technol*. 206(21) (2012) 4439-4448
4. P. Martis, V. Dilmon, J. Delhalle, Z. Mekhalif, *Electrochim. Acta* 55(19)(2010)5407-5410
5. B. Pollet, J-Y Hihn, T. Mason, *Electrochim. Acta* 53(12)(2008) 4248-4256
6. L. Wei, Y-J Fan, H_H Wang,N. Tian, Z-Y Zhou, S-G Sun, *Electrochim. Acta* 57 (2012) 468-474
7. X. Lu, G. Burrell, F. Separonc, C. Zhoo, *J. Phys. Chem*. B 116(30) (2012) 9160-9170
8. E. Gomez, P. Cojocaru, L. Magagnin, E. Valles, *J. Electroanal. Chem*. 658 (1-2) (2011) 18-24
9. D. Yue, Y. Jing, Y. Yao, J. Sun, Y. Jia, *Electrochim. Acta* 65(2012)30-36
10. Haerens K.; Matthijs E.; Chinuelarz A.; van der Bruggen B., *Green Chem*. 11 (2009) 1357-1365
11. R. Gomez, A. FernandezVega, J.M Feliu, A. Aldaz, *J. Phys. Chem*. 97 (19) (1993) 4769-4776
12. T.N. Andersen, B.S. Dandapani, J.M. Berry, *J. Electroanal. Chem*. 357 (1993) 77-89
13. N. Li, J. Lipkowski, *J. Electroanal. Chem* 491 (1-2) (2000) 95-102
14. V. Climent, A. Rodes, J.M. Orts, A. Aldaz, J.M. Feliu, *J. Electroanal. Chem*. 46 (1999) 65-75
15. V. Climent, A. Rodes, J.M. Orts, J.M. Feliu, J.M. Pérez, A. Aldaz, *Langmuir* 13 (1997) 2380-2389
16. K. Lian, D. Kirk, S.J. Thorpe, *Electrochim. Acta* 36 (3-4) (1991) 537-545
17. R. Solmaz, A. Gundojdu, G. Kardas, *Intern. J. Hydrogen Energy* 37 (11) (2012) 8917-8922
18. P. Vermeiren, R. Leysen, H. van den Borre, *Electrochim. Acta* 30 (3-4) (1985) 1253-1255
19. M. Cortes, E. Gomez, A. Perez-Rodriguez, C. Serre, E. Valles, *J. Electroanal. Chem*. 619-620 (2008) 176-182