

Electrochemical study of the activating solution for electroless plating of polymers

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Abstract This paper presents an electrochemical study about the activating solutions of the electroless plating of polymers, containing Pd(II), Sn(II) and Sn(IV) mixtures in HCl as main components. The objective of the study is the voltammetric characterization of these solutions by cyclic and linear voltammetry in order to study the recovery of tin and palladium from these solutions. The effect of concentration and rotation rate on the current–potential curves was studied using the RDE technique. The electrochemical behaviour of solutions prepared in the laboratory was performed as a prior step to the further study of real activating rinsing solutions. The electrochemical reduction of Pd(II) takes place in two one-electron transfer steps which are mass transport controlled. The electrochemical reduction of Sn(II) and Sn(IV) is also mass transport controlled and takes place with direct formation of metallic tin, although the electrochemical reduction of Sn(IV) only takes place in solutions with HCl concentrations higher than 1 M. The presence of additives in the real solutions prevent the chemical reduction of Pd(II) and the formation of Sn(IV) hydroxylated complexes. This causes the appearance of well defined diffusion waves attributable to the electrochemical reduction of Pd(II) and Sn(IV). Hence, the recovery of both species simultaneously as well as separately could be carried out, if appropriate conditions are selected.

Keywords Activating solution · Palladium · Tin · Electrochemical deposition · Cyclic voltammetry · Electroless plating

1 Introduction

Electroless plating is widely applied because it may be used to obtain metal deposits on non-conducting materials [1]. Initially, articles plated were mainly decorative, but due to technological advances in chemical processing techniques, plating on plastics began on a commercial level. Industries that use plated plastics include the automotive, microelectronics, electrotechnics, instrument-making electronics, etc. [2, 3].

Electroless deposition is an autocatalytic process that must be preceded by an activation pretreatment consisting of the formation of catalytic sites on the dielectric surface [1]. For this purpose, solutions of SnCl₂ and PdCl₂ in HCl as diluting agent are used. This is a solution of complex ions and colloidal particles which form a palladium–tin hydrosol, whose activity and stability depend on the chloride and stannous ion concentrations. The optimal composition of this solution should contain a mixture of SnCl₂ and SnCl₄ [4–7]. Palladium ions are reduced on the polymer surface by stannous ions to a palladium layer that serves as a catalyst for the subsequent electroless deposition of copper or nickel [8–10].

However, the activating solutions are not stable because of various chemical reactions which may occur, such as hydrolysis and Sn(II) and Sn(IV) complex formation [1, 11]. On the other hand, as a consequence of the activation process and because of direct oxidation by air, Sn(II) ions are continuously oxidized to Sn(IV), increasing the concentration of Sn(IV) ions in the solution and making the

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solution unusable [4]. Therefore, Sn(IV), Sn(II) and Pd(II) ions in HCl are the main components of the generated activating-wasted solution, where palladium is the minor specie. Since tin and palladium are two valuable metals, it is interesting to develop new techniques that allow their recovery from waste activating baths and from rinsing baths.

Thus, the selective electrochemical separation of the metals depends on their relative deposition potentials, so that if the deposition potentials are significantly different then it is possible to separate the metals. However, a previous study of the chemical and electrochemical behaviour of the metal ions must be done in order to examine the kinetic characteristics for the desired reactions and to take into account complexation of the cations as well as the irreversible nature of the electrodeposition processes.

In spite of the wide commercial applications of plated plastics, very little work has been reported regarding the electrochemistry of the activating solutions. The present work deals with the investigation of the electrochemical behaviour of the activating rinsing solutions of the electrodeless plating of polymers. Cyclic and linear voltammetry using a rotating disc electrode were used to characterize the kinetics of the electrodeposition of tin and palladium, and to find the optimum conditions for the electrochemical deposition of both metals. This information is relevant to the feasibility of the electrochemical recovery of tin and palladium from waste activating solutions or from rinsing baths. Due to the complexity of the activating solutions and to the presence of different additives such as hydrolysis retardants and colloid stabilizers that may affect the electrochemistry of tin and palladium [6], solutions of the two metals simulating the composition of the activating rinsing baths were firstly prepared and studied as a previous step to the further investigation of the real rinsing baths.

2 Experimental

The measurements were performed in a three-electrode electrochemical cell with a 3 mm in diameter glassy carbon rotating disk electrode as working electrode, a platinum electrode as auxiliary electrode and a Ag/AgCl saturated KCl as reference electrode. All potentials were referred to this electrode. The system was kept at open circuit potential for 2 min. Then, cyclic and linear voltammetric experiments were carried out at a scan rate of 10 mV s^{-1} using a Solartron SI 1287 potentiostat/galvanostat interfaced with a computer. Prior to each experiment the working electrode surface was mechanically polished using $0.05 \text{ }\mu\text{m}$ alumina powder and rinsed with distilled water. Dissolved oxygen was removed from the test solution by bubbling nitrogen for 10 min. This inert atmosphere was

maintained during the whole measurement. The experiments were carried out at different rotation rates within a range 500–3,000 rpm. All experiments were carried out at room temperature.

Solutions of tin and palladium were prepared in a concentration range similar to that present in the real activating rinsing baths. Palladium concentration was varied from 1×10^{-4} to 4×10^{-4} M, while tin concentration ranged from 1×10^{-3} to 4×10^{-3} M. The supporting electrolyte was 0.1 M HCl. Analytical grade chemicals used were $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, PdCl_2 and hydrochloric acid. All solutions were prepared with distilled water. Sn(II) solutions were prepared daily immediately before the experiments in nitrogen deaerated HCl and kept in dark to prevent oxidation by air.

For the study of the real activating baths, the determination of tin was performed by polarography [12], while the determination of palladium was performed by atomic absorption spectrometry on a Perkin-Elmer model AAnalyst 100 atomic absorption spectrometer using a Pd hollow cathode lamp at 247.6 nm wavelength, 0.2 nm spectral bandwidth and an operating current of 15 mA.

3 Results

3.1 Electrochemical behaviour of palladium in aqueous HCl

A typical voltammogram of 4×10^{-4} M PdCl_2 in 0.1 M HCl at a rotation rate of 2,000 rpm is shown in Fig. 1. The potential range was between 1.3 and -0.3 V. Two reduction waves, C_I and C_{II} , with similar magnitude and shape, at 0 and -0.1 V, respectively, can be observed in the negative scan shown in the inset of Fig. 1. These reduction waves correspond to diffusion controlled limiting current

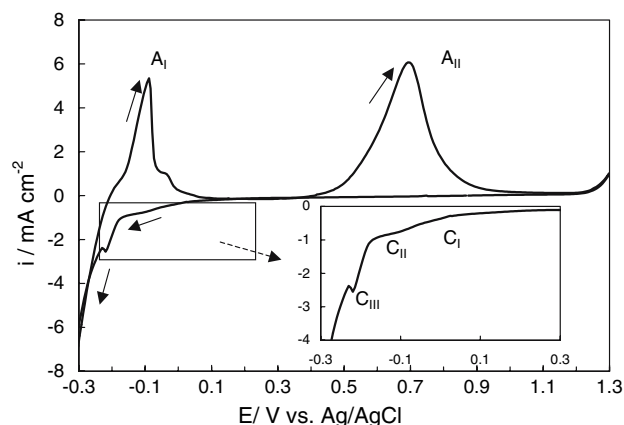
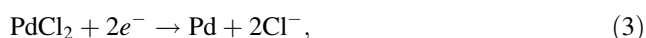


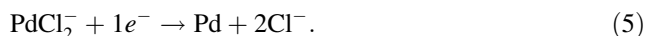
Fig. 1 Cyclic voltammogram of 4×10^{-4} M Pd(II) in 0.1 M HCl at a RDE rotation rate of 2,000 rpm

densities and can be attributed to palladium electrodeposition. A reduction peak, C_{III} , at approximately -0.2 V is also observed, which can be attributed to the formation of palladium hydrides ($\text{Pd} + x\text{H}^+ \rightarrow \text{PdH}_x$). These hydrides are formed when the deposition of palladium is carried out with the codeposition of hydrogen [13–16]. At more cathodic potentials, the current density increases rapidly and hydrogen evolution becomes significant. In the positive scan, two oxidation peaks are observed. The first peak, A_I , at -0.1 V corresponds to the oxidation of hydrogen from the palladium hydride, while the second anodic peak, A_{II} , at 0.7 V represents dissolution of the deposited palladium [14, 16–18].

The electrochemical reduction of palladium in acidic chloride media, takes place through the dissociation of the PdCl_4^{2-} complex followed by the reduction of PdCl_2 according to the following reactions [19–21]:



where at high- Cl^- concentrations, reaction (3) takes place through two one-electron transfer steps [22]:



Whether a reaction should be regarded as a simple reaction or two or more simple reactions depends on how unstable the active intermediate is. In the case of palladium, although the complexes of Pd(I) are rare, there are many complexes that can be formally regarded as Pd(I) species [23, 24], and the implication of Pd(I) species has been suggested for several red-ox processes [25]. Then, if the intermediate Pd(I) ions are not completely unstable and if reaction (4) is faster than reaction (5), the Pd(I) ions produced in reaction (4) can diffuse away from the electrode surface instead of reacting immediately through reaction (5). This reduction mechanism would justify the presence of the two diffusion waves, C_I and C_{II} , in the voltammogram of Fig. 1, where C_I can be attributed to the reduction of Pd(II) according to reaction (4) and C_{II} corresponds to the reduction of Pd(I) according to reaction (5).

The cathodic reduction of palladium at the RDE was studied at different rotation rates (Fig. 2) and palladium concentrations (Fig. 3) by linear voltammetry. Potential scans in the negative direction were applied from the open circuit potential to -0.3 V. The limiting current densities corresponding to C_I and C_{II} diffusion waves increase with

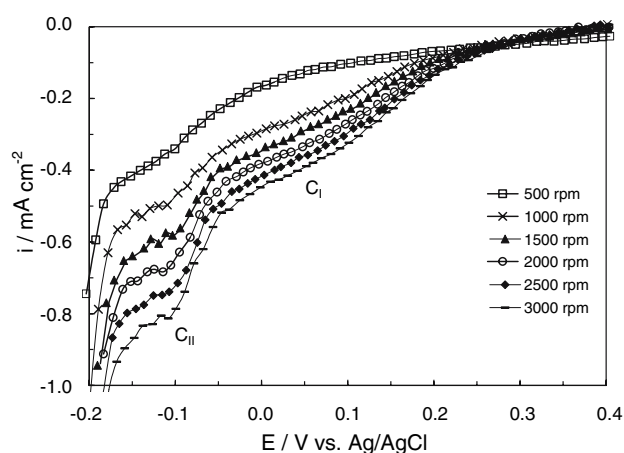


Fig. 2 Effect of the RDE rotation rate on the cathodic polarization curves of 3×10^{-4} M Pd(II) in 0.1 M HCl

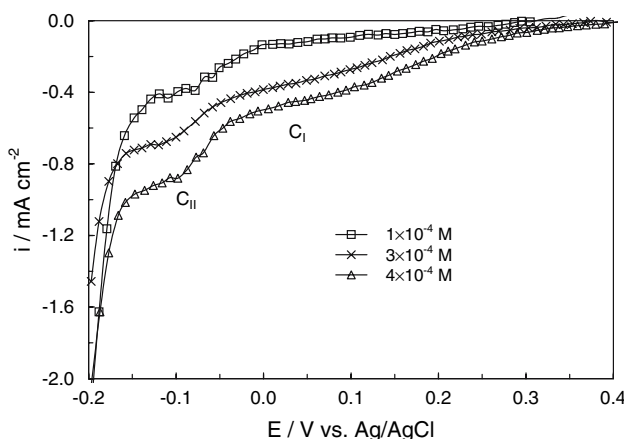


Fig. 3 Effect of Pd(II) concentration on the cathodic polarization curves at a RDE rotation rate of 2,000 rpm

both rotation rate and palladium concentration. Then, since the palladium concentration in the activating solution is much lower than that of Cl^- , and since an increase in Pd(II) concentration produces a proportional increase in the two diffusion waves, C_I and C_{II} , it can be concluded that the electrochemical reduction of Pd(II) proceeds according to the model proposed by Astakhova and Krasikov [22] following reactions (4) and (5).

The nature of the limiting current densities was verified using the Levich equation [26]. The plots for the disk electrode at 0 and -0.12 V can be seen in Fig. 4. The limiting current density corresponding to the second wave, C_{II} , is twice that of C_I . The variation of limiting current density with $\omega^{1/2}$ is linear and the plots pass through the origin, which suggests convective diffusion control. Under these conditions the Levich equation is satisfied:

$$i_L = 0.62nFD^{2/3}v^{-1/6}\omega^{1/2}C_b, \quad (6)$$

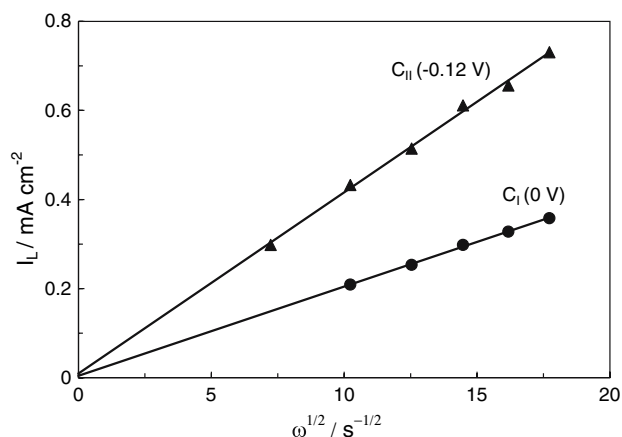


Fig. 4 Effect of the RDE rotation rate on the limiting current densities for the electrochemical reduction of 3×10^{-4} M Pd(II) in 0.1 M HCl

where i_L is the limiting current density, n the number of electrons transferred, F the Faraday constant, D the diffusion coefficient, ν the kinematic viscosity, ω the electrode rotation rate and C_b is the bulk concentration of palladium. The diffusion coefficient of palladium calculated from the slope of the line corresponding to the limiting current density of wave C_{II} , assuming a two electron transfer for the global reaction, has a value of 1.17×10^{-9} m² s⁻¹, which is similar to other reported values [15, 27].

3.2 Electrochemical behaviour of tin in aqueous HCl

Since tin may be present as Sn(II) and as Sn(IV) in the activating solutions, it is interesting to study the electrochemical behaviour of both oxidation states. Figure 5 shows a typical voltammogram of 10^{-3} M Sn(II) in 0.1 M

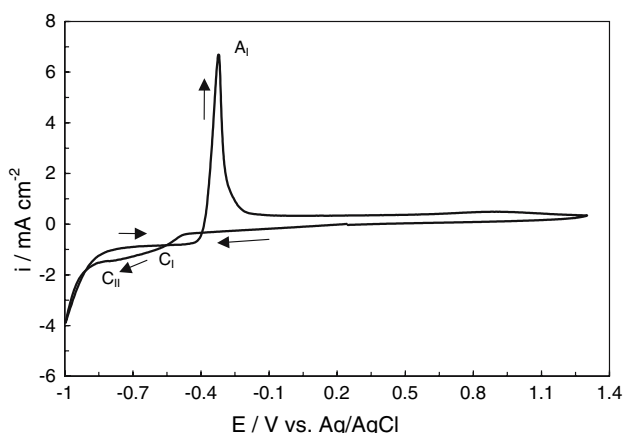
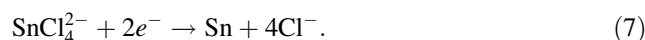


Fig. 5 Cyclic voltammogram of 1×10^{-3} M Sn(II) in 0.1 M HCl at a RDE rotation rate of 2,000 rpm

HCl at a rotation rate of 2,000 rpm, where the potential range was varied between 1.3 and -1 V. Two reduction waves, C_I and C_{II} , at approximately -0.6 and -0.8 V, respectively, can be seen, and a limiting current density is reached. At more cathodic potentials hydrogen evolution takes place. In the positive scan a pronounced oxidation peak, A_I , at about -0.3 V, is observed. This peak corresponds to the dissolution of the tin electrodeposited during the negative scan [28, 29].

The existence of the two reduction waves, C_I and C_{II} , may be a consequence of complexing equilibria in solution between the metal and chloride ions and indicates the existence of at least two complexes in equilibrium with each other. The reduction of Sn(II) ions proceed following the reaction [30]:



In acidic solutions Sn(II) compounds probably exist in the form of Sn^{2+} aquoion [31]. The stannous ion may react with the Cl^- present in the activating solution giving rise to the SnCl_4^{2-} complex, which is reduced following reaction (7).

The effect of the rotation rate on the current–potential reduction curves is depicted in Fig. 6. At low overpotentials the curves show a slight dependence on electrode rotation rate, but this dependence is more evident at high overpotentials and different plateaus can be observed corresponding to the limiting current densities. The limiting current density increases with rotation rate but the plateau width diminishes because the hydrogen evolution reaction is favoured.

The limiting current densities of Sn(II) ions are plotted against the square root of the rotation rate in the inset of Fig. 6. The straight line obtained obeys the Levich equation. The diffusion coefficient of tin calculated from the

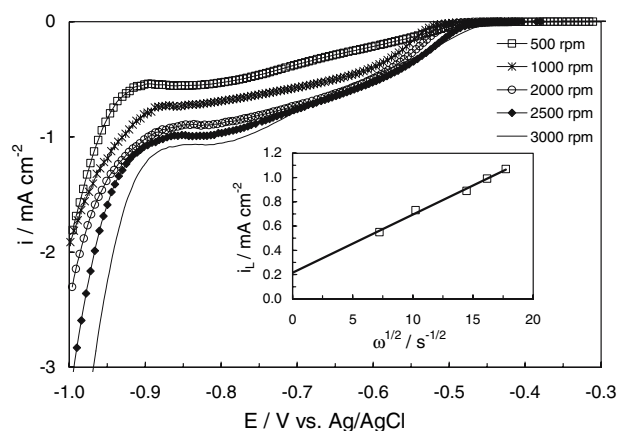


Fig. 6 Effect of the RDE rotation rate on the cathodic polarization curves of 3×10^{-3} M Sn(II) in 0.1 M HCl. Inset: effect of the RDE rotation rate on the limiting current density

slope of the latter straight line using Eq. 6 is $2.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. This value is similar to those obtained by Kiekens et al. ($1.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) [32] and by Broggi et al. ($1.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) [33], but higher than the values calculated by Bazan and Bisang ($1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) [34]. The extrapolation of the i_L versus $\omega^{1/2}$ curve to the origin leads to a non-zero current density, suggesting the existence of other phenomena coupled to the charge transfer process. These increase the current density.

Since pH has a significant influence on the electrochemical reduction of Sn(IV) the electrodeposition of this species has been studied for different hydrochloric acid concentrations. Figure 7 shows the cyclic voltammograms of 10^{-3} M Sn(IV) at a rotation rate of 2,000 rpm, for two different HCl concentrations of 0.1 M, curve (a) and 1 M, curve (b).

The current density measured in 0.1 M HCl (Fig. 7 curve (a)) is very low, and the voltammogram does not present reduction or oxidation waves, probably because of the formation of hydroxylated complexes, such as $\text{Sn}(\text{OH})_6^{2-}$ which is difficult to reduce [35–37]. For the highest HCl concentration (Fig. 7 curve (b)), the current density increases exponentially when the applied potential is more cathodic than -0.7 V , approximately, due to hydrogen evolution. By reversing the negative scan a hysteresis loop was obtained, involving a cathodic current density greater than that recorded in the preceding negative scan. In the negative scan the reduction of tin takes place on the glassy carbon electrode at more negative potentials than that of the hydrogen reaction, whereas in the negative part of the positive scan, the reduction of Sn(IV) ions takes place on the previously deposited tin, causing the observed hysteresis loop. In the positive scan a steep anodic peak, around -0.3 V , can be observed. This peak, similar to that obtained in the electrochemical study of Sn(II) (Fig. 5), can

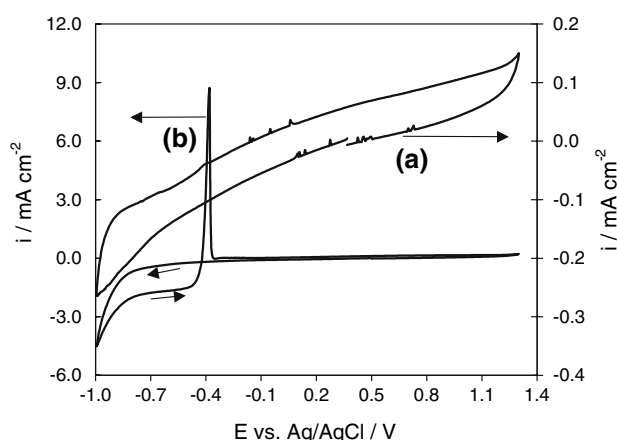
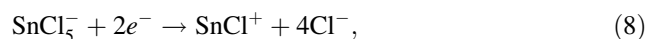


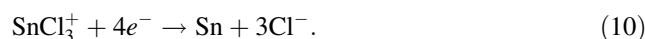
Fig. 7 Cyclic voltammogram of $1 \times 10^{-3} \text{ M}$ Sn(IV) at a RDE rotation rate of 2,000 rpm. Curve (a) 0.1 M HCl, curve (b) 1 M HCl

be attributed to the dissolution of the previously deposited tin.

In strongly concentrated chloride solutions the reduction of Sn(IV) takes place in two steps. The species responsible for this mechanism could be the SnCl_5^- complex and the reaction mechanism occurs as follows [32, 36–38]:



whereas in the presence of lower chloride concentrations the reduction of Sn(IV) proceeds with direct formation of metallic tin. The species responsible for this mechanism is probably the SnCl_3^+ complex:



Under the present experimental conditions, the electrochemical reduction of Sn(IV) takes place in one single step, as proposed in Eq. 10.

3.3 Electrochemical behaviour of mixtures of tin and palladium

The voltammograms obtained for laboratory mixtures containing both Sn(IV) and Pd(II) in 0.1 M HCl (not shown) is very similar to that obtained for palladium (Fig. 1). In the negative scan two diffusion waves and one peak are observed, which correspond to the two-step electrochemical reduction of palladium and to the formation of palladium hydrides, respectively. In the positive scan two anodic peaks are obtained, which are related to the oxidation of palladium hydrides and the oxidation of metallic palladium, respectively. Hence, under these conditions the electrochemical reduction of Sn(IV) does not take place, probably due to the formation of hydroxylated complexes, which are very difficult to reduce.

On the other hand, the electrochemical behaviour of laboratory mixtures containing Sn(II) and Pd(II) in 0.1 M HCl (not shown) differs from that reported previously. In this case, only one clear oxidation peak is observed at around -0.4 V which can be assigned to the oxidation of the tin deposited during the negative scan. In the interval between -0.1 and 0.5 V , an oxidation background is present, which could be related with palladium oxidation as it is probable that some Pd(II) is reduced on the electrode surface forming unstable or metastable species. However, the reduction and oxidation peaks corresponding to the electrochemical reactions of palladium cannot be clearly observed since most of Pd(II) ions are chemically reduced in bulk solution due to the presence of Sn(II), which acts as a reducing agent.

The real activating solutions may contain additives, such as hydrolysis retardant agents and colloid stabilizers [6] which affect the electrochemical behaviour. These additives cause stabilization of Pd(II) ions that are not reduced by Sn(II), unlike the solutions prepared in the laboratory. Moreover, the presence of Pd(II) ions in the real activating bath was confirmed by atomic absorption spectrophotometry. On the other hand, it was confirmed by polarography [12] that in the real rinsing baths Sn(II) is completely oxidized to Sn(IV).

Figure 8 shows a typical voltammogram obtained for an activating rinsing bath in the range 1.3 to -1 V. In the positive scan a steep anodic peak, A_I , at a potential of -0.3 V can be observed and in the inset figures two peaks of lower current densities, A_{II} and A_{III} , are placed at potentials of -0.1 and 0.4 V, respectively. On the other hand, in the negative scan a well defined diffusion wave, C_{III} , is observed which corresponds to a diffusion limiting current density whose plateau extends from -0.6 to -0.8 V, approximately. Hydrogen evolution occurs at about -0.9 V. Two reduction waves, C_I and C_{II} , are also obtained at potentials of -0.3 and -0.4 V, respectively, whose current densities are lower than that of wave C_{III} . These two diffusion waves are better observed in Fig. 9, where the effect of rotation rate on the current–potential curves is evaluated. An increase in rotation speed produces an increase in the three reduction waves, as expected for mass transport controlled processes.

Comparing this behaviour with that of the individual ions (Figs. 1, 7b) a first wave or peak assignment can be suggested. The cathodic diffusion waves C_I and C_{II} obtained at -0.3 and -0.4 V can be attributed to two-step Pd(II) electrochemical reduction via Pd(II)-chloride complexes, while the wave C_{III} corresponds to the electrochemical reduction of Sn(IV). In the real solutions, the reduction waves of Pd(II) move negatively in comparison

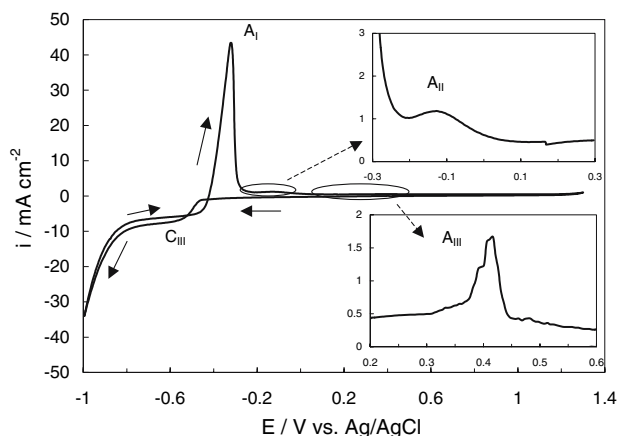


Fig. 8 Cyclic voltammogram for the real rinsing activating solutions

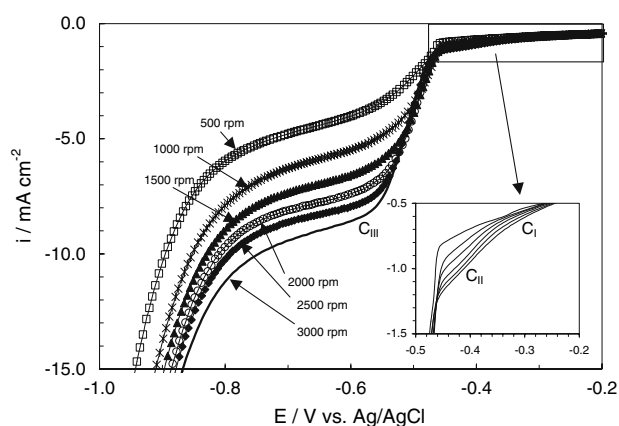


Fig. 9 Effect of the RDE rotation rate on the cathodic polarization curves of the real rinsing activating solutions

with the Pd(II) solutions previously studied, while the reduction wave of Sn(IV) appears in the same potential range. The peak corresponding to the palladium hydride formation is not observed because it is masked by the large diffusion wave of Sn(IV) located within the potential range -0.6 to -0.8 V. On the other hand, hydrogen evolution takes place at the same potential values as those occurring in the solutions containing Sn(II) or Sn(IV) previously studied.

In the positive scan of Fig. 8, the oxidation peak A_I at -0.3 V is due to the oxidation of tin deposited during the negative scan. This peak appears around the same potential as that for the individual Sn(II) and Sn(IV) solutions (Figs. 5, 7b, respectively). The oxidation peaks A_{II} and A_{III} observed in the insets of Fig. 8 are attributable to the oxidation of hydrogen from the palladium hydrides and to the oxidation of palladium, respectively. These potentials are similar to those obtained for the individual Pd(II) solutions shown in Fig. 1. The current density corresponding to the peak assigned to tin is greater than those assigned to palladium, due to the difference in concentrations between these two ions. In the real rinsing activating baths the concentration of Sn(IV) is more than ten times greater than that of Pd(II).

In order to corroborate that the diffusion waves observed in Fig. 9 are effectively due to the electrochemical reduction of Sn(IV) and Pd(II), the effect of the addition of Sn(IV) and Pd(II) on the cathodic current–potential curves of Fig. 9 is presented in Figs. 10 and 11, respectively. An increase in Sn(IV) concentration produces a proportional increase in current density corresponding to the diffusion wave between -0.6 and -0.8 V (Fig. 10). Thus, the latter wave is related to the electrochemical reduction of Sn(IV). On the other hand, an increase in Pd(II) concentration results in an increased current density for the potential range between -0.2 and -0.45 V (Fig. 11). Hence, these diffusion waves correspond to the reduction of Pd(II).

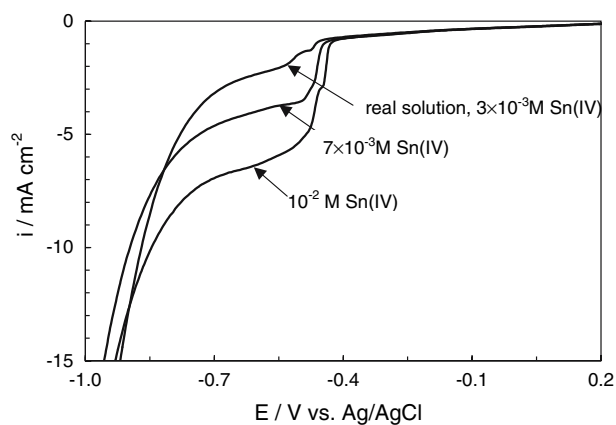


Fig. 10 Effect of the addition of Sn(IV) on the electrochemical behaviour of the real rinsing activating solutions

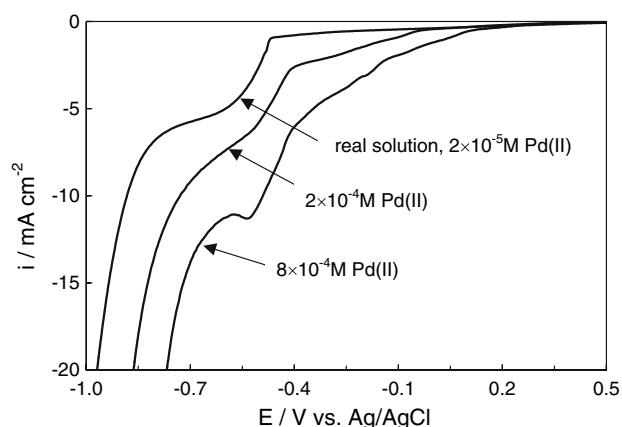


Fig. 11 Effect of the addition of Pd(II) on the electrochemical behaviour of the real rinsing activating solutions

There are some significant differences between the electrochemical behaviour of the real rinsing activating solutions and that for solutions prepared in the laboratory containing mixtures of palladium and tin. In the laboratory solutions hydrogen evolution takes place at less negative potentials, therefore, the diffusion wave of tin cannot be observed during the negative scan for laboratory solutions. The presence of different additives in the activating solution increases the hydrogen overpotential and the diffusion wave of tin can be observed in Fig. 8. On the other hand, the presence of hydrolysis retardants in the real solution prevent the formation of Sn(IV) hydroxylated complexes and, consequently, Sn(IV) reduction may take place. Finally, in real solutions the stabilizing agents avoid the chemical reduction of Pd(II) in bulk solution.

From the results obtained about the electrochemical reduction of the activating solution, it is inferred that the reduction of Pd(II) to its metallic state takes place within a potential range -0.3 to -0.4 V and this reduction is mass transport controlled. If the potential is swept to more

negative values, the reduction of Sn(IV) to its metallic form occurs between -0.6 and -0.8 V. This reaction is also mass transport controlled and a limiting current density is reached. Hence, two well defined and separated zones for palladium and tin electrodeposition are obtained and, as a consequence of this, the recovery of these species, simultaneously as well as separately, could be carried out. The selective recovery of palladium would be possible in potentiostatic operation selecting a potential close to -0.4 V, or in galvanostatic operation at a sub-limiting current density. Then, tin could be recovered in potentiostatic operation at a potential of -0.6 V or in galvanostatic operation at a sub-limiting current density. On the other hand, the simultaneous recovery of tin and palladium could be carried out at a potential close to -0.6 V in potentiostatic operation or at a current density lower than the limiting current density of tin in galvanostatic operation.

4 Conclusions

The electrochemical study of solutions of tin and palladium prepared in the laboratory, with concentration values similar to those present in the activating rinsing baths of the electroless plating of polymers, was carried out as a prior step to the study of the real solutions. In the case of the solutions prepared in the laboratory, the electrochemical reduction of Pd(II) takes place in two one-electron transfer steps and two limiting current densities are obtained. From the variation of the limiting current densities with the rotation rate a diffusion coefficient of $1.17 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ is obtained. The electrochemical reduction of Sn(II) and Sn(IV) takes place with direct formation of metallic tin, although the electrochemical reduction of Sn(IV) only takes place in solutions of high-HCl concentration, which prevent the formation of hydroxylated complexes. The electrochemical reduction of Sn(II) in 0.1 M HCl shows a diffusion limiting current density. From the variation of this limiting current density with the RDE rotation rate a diffusion coefficient value of $2.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ is obtained for Sn(II). The electrochemical behaviour of the laboratory solutions containing mixtures of Pd(II), Sn(II) and Sn(IV) is similar to that observed for Sn(II) solutions, as Pd(II) ions are almost reduced in bulk solution by Sn(II).

The electrochemical behaviour of the activating rinsing solutions is different from that of the laboratory solutions due to the presence of additives. In the real solutions, Pd(II) ions are stabilized, and the electrochemical reduction of Pd(II) to metallic palladium takes place within a potential range -0.3 to -0.4 V, and is mass transport controlled. On the other hand, the presence of hydrolysis retardants makes possible the electrochemical reduction of Sn(IV) to its

metallic form in a potential range between -0.6 and -0.8 V, this process being mass transport controlled.

The study of the real solutions revealed that it is possible to electrochemically recover both tin and palladium. The selective recovery of palladium would be possible in potentiostatic operation at a potential close to -0.4 V, or in galvanostatic operation at a sub-limiting current density. Once the palladium has been recovered, it would be possible to recover tin by operating at a potential of -0.6 V in potentiostatic operation or in galvanostatic operation at a sub-limiting current density. Alternatively, the simultaneous recovery of tin and palladium would be possible at an electrode potential close to -0.6 V in potentiostatic operation or at a current density lower than the limiting current density of Sn(IV).

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