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Electrochemical investigation of electrodeposited Fe-Pd alloy thin films

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ABSTRACT

In the present study, the electrodeposition of Fe, Pd and Fe–Pd alloys, in alkaline solutions, has been investigated. Using ammonium hydroxide and trisodium citrate as the complexing agents, it has been shown that the co-deposition of Fe and Pd is achieved due to diminishing the difference between the reduction potentials of these two metals. Cyclic voltammetry results clearly show that the electrodeposition processes are diffusion-controlled and the diffusion coefficients of Fe^{2+} and Pd^{2+} are 1.11×10^{-6} and 2.19×10^{-5} cm² s⁻¹, respectively. The step potential experiments reveal that nucleation mechanism is instantaneous with a typical three-dimensional (3D) growth. At low overpotentials, addition of Pd^{2+} to Fe^{2+} solution leads to a dramatic reduction in the number of nucleation sites, due to this fact that at such overpotentials, the electrodeposited films and the number of nucleation sites indicate that at higher overpotential, Fe^{2+} is deposited preferentially, thus the electrodeposition of iron–palladium alloys was classified as an anomalous co-deposition.

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1. Introduction

Fe–Pd thin films have many potential applications due to their specific chemical composition. Shape memory properties at alloys including 28–31 at.% Pd [1–6] and high magnetic anisotropy at about 50 at.% Pd [7–13] make them as promising materials for microelectromechanical systems (MEMS). Moreover, invar anomalies (30–35 at.% Pd) [14,15] and catalytic properties of palladium-rich thin films (including high hydrogen absorption capacity [16–18] and dechlorination of organic compounds [19,20]) can be considered as reasons of increased attention to the Fe–Pd thin films.

Different methods have been proposed to synthesize Fe–Pd thin films; including electron-beam evaporation and sputtering [15,21,22], melt spinning [5,23], arc melting [3–5,12] and electrodeposition [6–9,24]. Among these techniques the electrodeposition is more desirable both economically and practically [8,9].

There are some reports on the electrodeposition of Fe–Pd alloys in ammonium citrate [8,24], ammonium tartrate [6,9] and sulfosalicylic acid solutions [7,16]. Although all of the electrolytes are effective to co-deposition of Fe–Pd alloys, it is difficult to achieve a wide range of chemical composition of the thin layers without varying the electrolyte composition [8,16]. In addition, most studies on electrodeposition of Fe–Pd alloys have been dedicated to investigation of their physical properties whereas their deposition process from electrochemical point of view has been less attended.

Characterization of alloy electrodeposition is useful to recognize the relation between thin films properties and the mechanism of electrodeposition [25,26]. Therefore, the need of a comprehensive study with a focus on the mechanism of Fe–Pd alloy electrodeposition seems to be essential.

The aim of present study is to develop a stable electrolyte to achieve a wide range of Fe–Pd alloy thin films. Moreover, cyclic voltammetry and chronoamperometry techniques were applied to study the mechanism of the electrodeposition process. The effect of cathodic potential on overpotential deposition (OPD) and also on the number of nucleation sites has been investigated.

2. Experimental

2.1. Materials

Electrolytes were prepared using analytical grade of $FeSO_4 \cdot 7H_2O$ and $PdCl_2$ as the parent metal ions with the different concentrations ratio. NH_4OH and $Na_3C_6H_5O_7 \cdot 2H_2O$ were used as the complexing agents for palladium and iron ions, respectively. H_3BO_3 and $(NH_4)_2SO_4$ were utilized as additive and supporting electrolyte. The chemical compositions of the solutions are listed in Table 1. The pH of the electrolytes was adjusted to 8 using ammonia solution. At such levels of pH, hydrogen evolution on the cathode surface is not an issue of concern. The working electrode was a copper wire with surface area about 1 cm^2 and roughness less than 20 nm. The counter electrode was a 316L

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Solution	$FeSO_4 \cdot 7H_2O$	PdCl ₂	H_3BO_3	$(NH_4)_2SO_4$	$Na_3C_6H_5O_7{\cdot}2H_2O$	NH ₄ OH
1	200	-	-	-	-	-
2	200	-	250	600	300	900
3	_	20	-	_	_	-
4	_	20	250	600	300	300
5	-	20	250	600	300	450
6	-	20	250	600	300	750
7	-	20	250	600	300	900
8	200	10	250	600	300	900
9	200	20	250	600	300	900
10	200	40	250	600	300	900

 Table 1

 Chemical composition of the solutions (mmol/dm³).

stainless steel plate with surface area about 8 times larger. A saturated calomel electrode (SCE, +0.241 V vs. SHE) was used as reference electrode.

2.2. Methods and analysis

All experiments were performed in a deaerated threeelectrode electrochemical cell without agitation using a potentiostat/galvanostat Autolab[®] model PGSTAT302N equipped by Nova 1.5 software. The reduction regions of Fe²⁺ and Pd²⁺ ions at the different concentrations of the complexing agents were determined applying linear sweep voltammetry (LSV). In addition, cyclic voltammetry was employed to identify the type of reduction process. The scan rate variety was in the range of 20–150 mV s⁻¹. The potentiostatic *j*-*t* transients were recorded every 100 mV in the range of -800 to -1100 mV for a pulse time of 10 s. The films were deposited for 10 min and then removed from the substrate by a 2:1 mixture of HCl and HNO₃ solutions as the acidic solvent. The concentrations of Fe and Pd in the obtained solutions were performed using atomic absorption spectroscopy (AAS) (model Perkin Elmer Instruments, Analyst 800).

3. Results and discussion

3.1. Thermodynamics of Fe and Pd co-deposition

As iron is more active than palladium, for co-deposition of Fe^{2+} and Pd^{2+} , it is thermodynamically essential to make near the reduction potential of these two ions. In order to achieve such these conditions, addition of the given complexing agents and/or changing of Fe^{2+} and Pd^{2+} ions concentrations seems to be effective methods [8].

It has been shown that the difference between the standard reduction potential of Pd^{2+}/Pd (+0.95 V vs. SHE) and Fe^{2+}/Fe (-0.44 V vs. SHE) can be reduced, if $[Pd(NH_3)_4]^{2+}$ complex form of Pd is present in the medium [27]. It is due to the lower standard reduction potential of $[Pd(NH_3)_4]^{2+}$ according to:

$$Pd^{2+}(aq) + 4NH_3 \Rightarrow [Pd(NH_3)_4]^{2+}(aq) \quad \Delta G_1^0 = -RT \ln \beta_4$$
 (1)

$$[Pd(NH_3)_4]^{2+}(aq) + 2e^- \Rightarrow Pd(s) + 4NH_3 \quad \Delta G_2^0 = -nFE_2^0$$
(2)

$$Pd^{2+}(aq) + 2e^{-} \Rightarrow Pd(s) \quad \Delta G_3^0 = -nFE_3^0$$
 (3)

where β_4 is the constant stability of $[Pd(NH_3)_4]^{2+}$ complex, *F* is the Faraday's constant and Eq. (3) is the sum of Eqs. (1) and (2). Using Nernst equation for 20 mM concentration of Pd²⁺, the value of E_3^0 is calculated +0.66 V vs. SCE. Accordingly, the value of E_2^0 can be determined using following equations:

$$\Delta G_1^0 + \Delta G_2^0 = \Delta G_3^0 \tag{4}$$

$$E_2^0 = E_3^0 - \frac{RT}{nF} \ln \beta_4$$
 (5)

Regarding the value of $\beta_4 = 10^{30.5}$ [28], if whole Pd²⁺ ions are present in the form of [Pd(NH₃)₄]²⁺ complexes, the value of E_2^0 will be -0.24 V vs. SCE.

Addition of NH_4OH into the solution leads to an increase in pH. Under this condition, the possibility of Fe precipitation and/or the formation of Fe(OH)⁺ enhances significantly. Such these reactions can be hindered using citrate ions to form iron citrate complex [8] and boric acid to reduce the (OH)⁻ concentration near the surface [29], resulting in stability of Fe²⁺ ions.

For the evaluation of Fe²⁺ and Pd²⁺ reduction process, the linear sweep voltammetry curves of the electrolytes number 1 and 3 (without any complexing agents) and the electrolytes 2, 4-7 (with additives and different concentrations of ammonium hydroxide) are depicted in Fig. 1(a) and (b), respectively. Based on the obtained results, complexing agents decrease the reduction potential of both Fe (from -0.11 to -0.27 V vs. SCE) and Pd (from +0.64 to -0.25 V vs. SCE); and at the same time, the difference between reduction potential of these two metals shifts to a lower value. The thermodynamically determined values of reduction start potential for Pd²⁺ and [Pd(NH₃)₄]²⁺ show acceptable agreements with the empirical results (Table 2). According to Nernst equation, it is expected that the reduction of Fe²⁺ in solution (1) (200 mM Fe²⁺) start at -0.70 V vs. SCE, while based on the results of Fig. 1(a), the start point occurs at about -0.11 V vs. SCE. This difference can be related to the underpotential deposition (UPD) of Fe which is a common phenomenon in the deposition process of iron group metals on a noble substrate [30,31]. For instance, Mallett et al. [32] have observed the UPD process of Fe²⁺ on platinum substrate. In addition, Leistner et al. [33] have shown that the underpotential deposition of a 100 mM Fe²⁺ solution on copper substrate starts at about E = -0.1 V vs. SCE.

The same calculation procedure can be employed in the case of reduction start potential of iron citrate complex using Eqs. (6)-(9):

 $\operatorname{Fe}^{2+}(\operatorname{aq}) + \operatorname{Cit}(\operatorname{aq}) \Rightarrow \left[\operatorname{Fe-Cit}\right]^{2+}(\operatorname{aq}) \quad \Delta G_1^0 = -RT \ln K \tag{6}$

$$[Fe-Cit]^{2+}(aq) + 2e^{-} \Rightarrow Fe(s) + Cit(aq) \quad \Delta G_2^0 = -nFE_2^0$$
(7)

$$Fe^{2+}(aq) + 2e^{-} \Rightarrow Fe(s) \quad \Delta G_3^0 = -nFE_3^0$$
(8)

$$E_2^0 = E_3^0 - \frac{KT}{nE} \ln K$$
 (9)

Assuming that $E_3^0 = -0.11$ V vs. SCE (according to Fig. 1(a)) and $K = 10^{4.4}$ [34], the value of E_2^0 is estimated as -0.24 V vs. SCE. This value is close to that of presented in Table 2.

Fig. 1(b) indicates that electrodeposition of Fe^{2+} from solution (2) and Pd^{2+} from solution (7) initiates from nearly close potential. As it was mentioned before, addition of ammonium hydroxides leads to an increase in $[Pd(NH_3)_4]^{2+}$ concentration and consequently, this event resulted in a decrease in the both palladium reduction potential and deposition rate (Fig. 1(b), curves 1–4). As a consequence, an overlapping in the reduction regions of Fe (curve 4) and Pd (curve 5) is occurred. Such a solution can be potentially introduced as an effective electrolyte solution for Fe–Pd alloy electrodeposition.

Table 2	
The value of reduction start potential vs. SCE	/V.

Electroactive species	Fe ²⁺ (sol. 1)	Pd ²⁺ (sol. 3)	[Fe-Cit] ²⁺ (sol. 2)	$[Pd(NH_3)_4]^{2+}$ (sol. 7)
<i>E</i> ⁰ (calculated value)	-0.70	+0.66	-0.24	-0.24
<i>E</i> ⁰ (empirical value)	-0.11	+0.64	-0.27	-0.25

The films were potentiostatically electrodeposited in a solution (9) which contains both species of solutions (2) and (7). The effect of applied cathodic potential on Fe and Pd contents of the films is shown in Fig. 2. The Fe content of the deposits increases from 12.1 to 93.2 at.% when the potential changes from -650 to -1200 mV. It can be related to underpotential co-deposition of Fe–Pd same as what occurs in Fe–Pt co-deposition [33]. Also, the other reason can be the drop in concentration of Pd²⁺ near the electrode surface due to long time of 10 min or anomalous co-deposition of Fe–Pd



Fig. 1. Linear sweep voltammetry curves for electrodeposition of Fe and Pd: (a) without complexing agents and (b) with complexing agents, scan rate = 2 mV s^{-1} .

same as Fe–Ni co-deposition [25]. It should be mentioned that the underpotential co-deposition only in low overpotentials (less than –700 mV vs. SCE) can occur. Since in whole range of applied potentials, the Fe content of the films (as less noble metal) increases by an increase in overpotential and, also, the analysis of the number of nucleation sites shows anomalous nucleation (Section 3.3), this phenomenon cannot be only due to diffusion of Pd²⁺. Because the nucleation process occurs only in the initial times when there is no diffusion process. Therefore, it is more probable and rational that the coupling of anomalous co-deposition together with diffusion process is responsible for the increasing of Fe content due to an increasing in overpotential.

3.2. Kinetics of electrodeposition

Fig. 3(a) and (b) illustrates the reduction behavior of Fe and Pd at various scan rates from electrolytes 2 and 7. In Fig. 3(a), there is a single wide peak in Fe voltammograms. It is specific property of the Fe voltammetric curves when the deposition is diffusion-controlled [25]. In Fig. 3(b), two peaks (a and b) for Pd electrodeposition is observed. Peak (b) completely disappears when the scan rate increases from 20 to 150 mV s^{-1} . This behavior shows that two serial reactions may have occurred [35]. Since the electrodeposition of some metals such as Ni and Pt (platinum group metals), which shows similar behaviors like Pd, obeys two-step reduction mechanism [29,36,37], it may be related to the two-step reduction of Pd²⁺ as follows:

$$Pd^{2+} + e^{-} \Rightarrow Pd^{+}(slow) \tag{10}$$

$$Pd^+ + e^- \Rightarrow Pd(fast)$$
 (11)

This two-step reaction during the palladium electrodeposition has been already suggested by Kravtsov [38]; the first reaction is considered as the rate determining step, while the second reaction is a fast reaction [37].



Fig. 2. Influence of cathodic potential on the Fe and Pd contents of Fe–Pd alloy; deposition times 10 min.



Fig. 3. Cyclic voltammograms for deposition of Fe, Pd and Fe–Pd alloys: (a) Fe in solution (2), (b) Pd in solution (7), (c) Fe and Pd at more positive potentials range and (d) Fe–Pd in solutions (8–10).

At reverse path, for both Fe and Pd voltammograms (Fig. 3(c)), there are long distances between the reduction peaks (C_{Fe} and C_{2Pd}) and oxidation peaks (A_{Fe} and A_{2Pd}), so that the electrodeposition of Fe and Pd can be considered as the irreversible reactions [35].

In the case of Fe–Pd voltammograms (Fig. 3(d)), two distinct diffusion regions are observed. By an increase in Pd^{2+} concentration in solution (from 10 to 40 mM) the reduction current increases at first zone and the increase in current at second zone is related to the current increase in first zone. As a consequence, the first peak in Fig. 3(d) can be related to Pd^{2+} reduction and the second one corresponded to Fe^{2+} . Moreover, the voltammograms of Fe–Pd alloys show that in the presence of Fe^{2+} ions, the reduction peak of Pd^{2+} shifts to less cathodic potentials.

The kinetic parameters of Fe²⁺ and Pd²⁺ reduction can be determined using Nicholson and Shain analysis [39]. Fig. 4(a) shows the variation of $E_p - E_{p/2}$ vs. the *S.R.*^{1/2}. For an irreversible reaction, charge transfer coefficient can be calculated using Delahay equation as following [39]:

$$E_p - E_{p/2} = \frac{-1.857RT}{\alpha n_{\alpha} F} \tag{12}$$

where E_p , $E_{p/2}$, n_{α} and α are the peak potential, the potential where $j = j_p/2$, the number of electrons in the rate determining step and the charge transfer coefficient, respectively. Charge transfer coefficient is independent of the concentration of the solution but a function of potential [39], therefore using the intercept of Fig. 4(a) curves, these values for iron and palladium can be obtained [40].

Fig. 4(b) shows the linear dependence of peak current against the square root of scan rate. Thus, it can be confirmed that the reduction of Fe²⁺ and Pd²⁺ on copper electrode are irreversible and diffusion-controlled processes. The diffusion coefficient can be, therefore, calculated from Randles–Sevick equation as following [39]:

$$j_p = -0.496 n F^{3/2} C^{\infty} D^{1/2} \upsilon^{1/2} \left(\frac{\alpha n_{\alpha}}{RT}\right)^{1/2}$$
(13)

where *n*, C^{∞} , *D* and υ are the number of exchanged electron involved in the electrode process, the solution bulk concentration, the diffusion coefficient and the potential scan rate, respectively. Also, the kinetic constant of the reduction reactions can be determined using Gokhshtein equation from intercept of curves in Fig. 4(c) as following [39]:

$$j_p = -0.227 n F C^{\infty} K^0 \exp\left(\frac{-\alpha n_{\alpha} F}{RT} (E_p - E^{0'})\right)$$
(14)



Fig. 4. Analyzed curves extracted from cyclic voltammograms for deposition of Fe and Pd: (a) $E_p - E_{p/2}$ vs. $S.R.^{1/2}$, (b) $-j_p$ vs. $S.R.^{1/2}$ and (c) $\ln(-j_p)$ vs. $E_p - E^{0'}$ solutions (2) and (7).

The kinetic parameters of Fe²⁺ and Pd²⁺ electrodeposition obtained by voltammetric analysis are listed in Table 3. It should be pointed out that, based on Eq. (10), as the rate determining step, the stoichiometric coefficient of electron (e^-) is 1. Assuming this value, $D_{pd^{2+}}$ can be calculated and compared with the value obtained from chronoamperometry analysis (Section 3.3). Additionally, the result of Table 3 reveals that the Fe²⁺ charge transfer coefficient (as coefficient of the activation energy) is lower than that of Pd²⁺ and the kinetic constant of Fe²⁺ electrodeposition is higher than that of

Pd²⁺. These explanations can shown that at higher overpotentials, iron is deposited with higher rate than palladium.

3.3. Nucleation and growth mechanism

Chronoamperometric analysis was applied, in order to study the mechanism of Fe, Pd and their binary alloy electrodeposition. Fig. 5 shows a series of potentiostatic current transient obtained from OCP (-0.25 V vs. SCE) to potential of -0.8, -0.9, -1.0 and -1.1 V

Table 3The kinetic parameters of the Fe and Pd electrodeposition.

Ion	α	D/cm ² s ⁻¹			$K^0/\mathrm{cm}\mathrm{s}^{-1}$
		Voltammetric analysis	Chronoamperometric analysis (Cottrel equation)	$j_{ m max}$, $t_{ m max}$ analysis	
Fe ²⁺ (sol. 2) Pd ²⁺ (sol. 7)	0.1460 0.8057	$\begin{array}{c} 1.11 \times 10^{-6} \\ 2.19 \times 10^{-5} \end{array}$	$\begin{array}{c} 1.11 \times 10^{-6} \\ 2.27 \times 10^{-5} \end{array}$	$\begin{array}{c} 1.07\times 10^{-6} \\ 2.20\times 10^{-5} \end{array}$	$\begin{array}{c} 6.7 \times 10^{-4} \\ 6.4 \times 10^{-5} \end{array}$



Fig. 5. Potentiostatic j-t transients and linear dependence of $j-t^{-1/2}$ accordance to Cottrell relation for deposition of: (a) 200 mM Fe (sol. 2), (b) 20 mM Pd (sol. 7) and (c) 200 mM Fe + 20 mM Pd (sol. 9) at the different cathodic potentials: (1) E = -800, (2) E = -900, (3) E = -1000 and (4) E = -1100 mV vs. SCE. The inset figure corresponds to E = -1100 mV vs. SCE.

Table 4	
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The effect of overpotential on the number of nucleation sites.

Cathodic potential vs.	The number of nucleation sites, $(N_0/10^{+6})/cm^{+2}$			
SCE/mV	Fe (sol. 2)	Pd (sol. 7)	Fe-Pd (sol. 9)	
-800	19.1	1.99	2.21	
-900	26.8	3.81	5.06	
-1000	32.2	8.72	10.0	
-1100	38.3	11.5	23.5	

vs. SCE. The *j*-*t* transients have a normal dependence to overpotential, whereas the current density increases with an increase in overpotential. Based on the characteristic shape of the chronoamperometry curves, it seems that a nucleation and growth process can describe the electrodeposition process; and the rate of growth is limited by electroactive species diffusion toward the surface [25,26,40,41]. Fig. 5 shows that for all step potentials at initial times, the current increases due to the nucleation and growth process [25,41]. Afterwards, the current drops by increasing the concentration gradient of electroactive species on the surface [42], according to Cottrel equation:

$$i = -0.564nFC^{\infty}D^{1/2}t^{-1/2} \tag{15}$$

The encountering of the nucleation and growth with the diffusion phenomenon has resulted in the creation of a maximum current at all overpotentials [41]. The critical time (t_{max}) for the transient of Fe decreases from 113 to 62 ms, for Pd from 113 to 22 ms and for Fe–Pd from 319 to 65 ms as the potential is made more cathodic (dash lines).

According to the linear plots of Fig. 5 (*j* vs. $t^{-1/2}$) at the high overpotentials, the diffusion coefficients can be calculated from the sum of least square method using Levenberg–Marquardt algorithm (LMA). The values of *D* were 1.11×10^{-6} and 2.27×10^{-5} cm² s⁻¹ for Fe and Pd, respectively. As seen in Table 3, there is a good agreement between the calculated values from chronoamperometry and those obtained form voltammetry analysis. On the other hand, to determine diffusion coefficient by voltammetry analysis, it was assumed that the controlling step in palladium reduction is Eq. (10) (n = 1). Since the obtained values of *D* from chronoamperometry and voltammetry analysis are close together, this assumption is now reasonable.

The partial differences between the values of *D* obtained in this work and those reported in the literature may be related to different concentration of the applied electrolytes [25,43].

In order to investigate the nucleation type of the deposition, *j* vs. $t^{1/2}$ curves were plotted for Fe, Pd and Fe–Pd alloys at initial times (Fig. 6). The linear relationship in this region approves the applicability of the proposed model for instantaneous nucleation and diffusion-controlled growth [44]:

$$j = -5.012nFD^{3/2}C^{\infty 3/2}V_m^{1/2}N_0(t-t_0)^{1/2}$$
(16)

where t_0 is the representative of the induction period; V_m and N_0 are the molar volume and the number of nucleation sites, respectively. The values of N_0 , obtained from slope of $j-t^{1/2}$, are listed in Table 4. The number of nucleation sites for Fe is higher than Pd which could be related to the lower concentration of Pd²⁺ in the electrolyte. By an increase in the applied electrode potential from -800 to -1100 mV, the Pd nucleation sites rises to 6 times higher than initial value, while in the case of Fe this value is 2. Therefore, N_0 for Pd electrodeposition is more affected by an increase in overpotential compared with Fe. According to the results presented in Table 4, addition of the Pd²⁺ to Fe²⁺ electrolyte leads to a dramatic reduction in the number of nucleation sites, especially at low overpotentials. A comparison between the values of N₀ for solutions (2), (7) and (9) reveals that the value of N_0 for solution 9 (deposition of Fe–Pd alloy) is between N_0 of solution (2) (deposition of pure Fe)



Fig. 6. Potentiostatic $j-t^{1/2}$ curves for deposition of: (a) Fe (sol. 2), (b) Pd (sol. 7) and (c) Fe–Pd (sol. 9) at the different cathodic potentials.

and N_0 of solution (7) (deposition of pure Pd). It should be noted that, at the lower cathodic potentials, N_0 for the alloy is close to that of pure Pd (N_0 of solution (7)), while at the higher cathodic potentials this value approaches to that of pure Fe (N_0 of solution (2)). This phenomenon can confirm that at the lower cathodic potentials the



Fig. 7. Non-dimensional $(j|j_{max})^2 \text{ vs. } t|t_m \text{ curves for deposition of: Fe (sol. 2), Pd (sol. 7) and Fe–Pd (sol. 9) at <math>E = -1100 \text{ mV vs. SCE.}$

nucleation pattern of alloy is very similar to that of Pd whereas to that of Fe at the higher cathodic potentials. This behavior confirms the anomalous co-deposition of Fe–Pd alloys.

According to the model of diffusion-controlled growth of 3D hemispherical particles presented by Scharifker and Hills [44], the deposition transients for progressive and instantaneous nucleation can be expressed by the non-dimensional equations (17) and (18):

$$\left(\frac{j}{j_{\text{max}}}\right)_{\text{prog}}^{2} = \frac{1.2254}{t/t_{m}} \left\{ 1 - \exp\left[-2.3367 \left(\frac{t}{t_{m}}\right)^{2}\right] \right\}^{2}$$
(17)

$$\left(\frac{j}{j_{\text{max}}}\right)_{\text{inst}}^2 = \frac{1.9542}{t/t_m} \left\{ 1 - \exp\left[-1.2564\left(\frac{t}{t_m}\right)\right] \right\}^2 \tag{18}$$

Fig. 7 shows the dimensionless theoretical plots of $(j/j_{max})^2$ vs. t/t_m in both form of instantaneous and progressive nucleation. It can be seen that the nucleation process of Fe, Pd and Fe–Pd at E = -1100 mV, obeys an instantaneous nucleation with diffusion controlled growth. This behavior can be confirmation of the results obtained through analysis of $j-t^{1/2}$ in Fig. 6.

Verification of the mechanism of nucleation and growth can be performed through determination of the diffusion coefficient, and comparison with previously calculated values. For instantaneous nucleation, these values calculated by following equation [44]:

$$D = \frac{j_{\text{max}}^2 t_{\text{max}}}{0.1629 (nfC)^2}$$
(19)

From Eq. (19), the diffusion coefficients at potential -1100 mV are calculated 1.07×10^{-6} and $2.20 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for Fe and Pd, respectively. A comparison between these diffusion coefficients and values obtained from the slope of $j-t^{-1/2}$ can be further evidence for the proposed mechanism (Table 3).

4. Conclusions

In the presence of complexing agents, the reduction potential of Fe^{2+} and Pd^{2+} shift to more negative potentials which is more severe for Pd^{2+} ; therefore Pd^{2+} was electrodeposited in the range of Fe^{2+} reduction region. The Fe content of the deposits increased from 12.1 to 93.2 at.% with an increase in potential from -650 to -1200 mV vs. SCE. The mechanistic analysis of the cyclic voltammetry clearly showed that the electrodeposition of the Fe, Pd and Fe–Pd alloys on copper substrates are diffusion-controlled processes and the reduction of palladium is a two-step reaction. Regarding to *j*-*t* tran-

sient analysis, the nucleation mechanism is instantaneous with a 3D hemispherical growth. The number of nucleation sites increased with an increase in overpotential. By analyzing the number of nucleation sites, it was found that at low overpotentials, the N_0 for the alloy is close to that of Pd and at high overpotentials as a consequence of the anomalous co-deposition of iron-palladium, the N_0 becomes larger and closer to its values for single Fe deposition.

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