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STUDIES ON THE POSSIBILITY OF USING CAFFEINE AS ADDITIVE IN A WATTS NICKEL ELECTROPLATING BATH

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Abstract

The possibility of using caffeine as additive in a Watts-type bath has been investigated in this paper. Caffeine was chosen because it is a non-toxic and environmental-friendly compound and highly accessible, being found in many plant materials as major constituent. It is one of the many organic molecules having required properties of an inhibitor for cathodic processes, acting by adsorption onto the electrode surface.

Electrochemical studies were carried to evaluate the behavior of caffeine and its influence on cathodic processes. Voltammetric studies showed that caffeine used as additive in a Watts electroplating bath influence the kinetics of the deposition process by adsorption onto the electrode, which increases along with caffeine concentration.

Keywords: expired drug, caffeine, additive, nickel electrodeposition, Watts electroplating bath

INTRODUCTION

The electrodeposition of nickel and nickel alloys processes are highly investigated by electrochemists (Kruglikov S.S. et al, 1965, Oriňáková R. et. al, 2006, Rudnik E. et. al. 2012) due to the possibility to obtain nanostructures and materials with special properties (Rudnik E. et. al. 2012, Oliveira E.M. et. al, 2006). Nickel coatings are very often used for the ornamental effect and anticorrosive efficiency (Oriňáková R. et. al, 2006, Rudnik E. et. al. 2012, Oliveira E.M. et. al, 2006, Hassani S. et. al, 2009). Presently, the most widely used nickel electroplating bath at industrial level is the Watts bath, providing high quality cathodic deposits (Tudela I, et. al, 2015).

Nickel coatings quality can be improved by adding various agents, such as leveling, brighteners, wetting or buffering agents (Kruglikov S.S. et al, 1965, Rudnik E. et. al. 2012, Oliveira E.M. et. al, 2006, Tudela I, et. al, 2015, Spanou S. et. al, 2009). Many organic molecules are recognized as additives for the electroplating process. It is known that they act by preferential adsorption onto the surface of metal, blocking the electrode area (Kruglikov S.S. et al, 1965, Sílvio de Souza F. et. al, 2012). As a result, the properties of metal/electrolyte interface are significantly modified, along with double layer capacitance and kinetics parameters (Sílvio de Souza F. et. al, 2012).

The aim of present study is to use caffeine, an environmental-friendly compound (Sílvio de Souza F. et. al, 2012, Fallavena T. et. al, 2006), as additive in the nickel electrodeposition process from Watts bath. Caffeine (IUPAC name: 3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6-dione) is a natural alkaloid from N-methyl derivatives of xanthine (Švorc L., 2013, Alizadeh T. et. al, 2010). Thanks to its stimulant properties, caffeine is the most commonly used legal drug worldwide (Rosal R. et. al, 2009). It is found in soft drinks, coffee, chocolates and tea (Rosal R. et. al, 2009, Trovó A.G. et. al, 2013, Goyal R.N. et. al, 2011, Jeevagan A.J. et. al, 2012) and acts by stimulating central nervous and cardiovascular systems of human body (Goyal R.N. et. al, 2011, Jeevagan A.J. et. al, 2012).

MATERIALS AND METHODS

Platinum electrode was used to characterize caffeine behavior in 0.5 mol L^{-1} Na_2SO_4 + 30 g L^{-1} H_3BO_3 (named SB) solution. Copper and nickel disks with active surface of 1 cm^2 were used as substrate for nickel deposition in SB + 5 g L^{-1} Ni^{2+}. To determine the effect of caffeine as additive in nickel deposition process, different concentrations, between 10^{-6} and 10^{-2} mol L^{-1}, have been used.

Studies on the electrodeposition of nickel were done in SB + 5 g L^{-1} Ni^{2+} solution, prepared using $NiSO_4 \cdot 6H_2O$ (Sigma Aldrich p.a.≥99 %), $NiCl_2 \cdot 6H_2O$ (Sigma Aldrich p.a.≥98 %), H_3BO_3 (Merk p.a. ≥ 99 %) in the same mass ratio as in Watts-type bath. Kinetics studies of the deposition process were done in this solution to provide wider range of potential to characterize the influence of caffeine on the electrode process. Caffeine used in experiments was purchased from Sigma–Aldrich.

To study the caffeine voltammetric behavior, cyclic voltammetry was performed. In order to determine the influence of caffeine adsorption onto the electrode surface on hydrogen evolution reaction and nickel deposition process, linear voltammograms were drawn. Kinetic parameters were determined from Tafel polarization plots. All measurements were performed at room temperature.

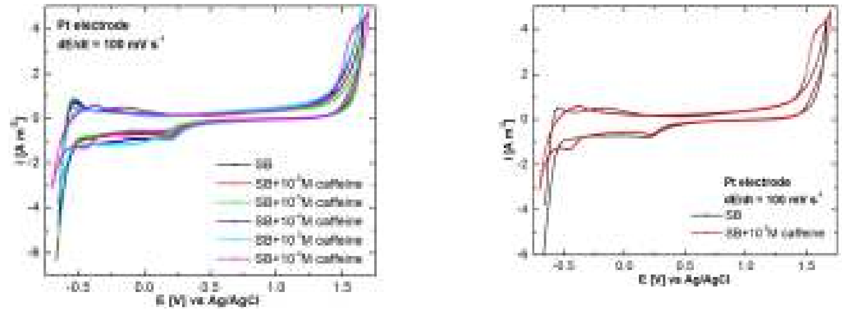
Electrochemical experiments have been carried out using AUTOLAB 302N potentiostat/galvanostat in a 100 mL glass cell consisting of Pt/Cu/Ni (1 cm^2 exposed area) as working electrode and two graphite counter electrodes placed symmetrically to the working electrode. All potentials were referred to the saturated Ag/AgCl reference electrode.

Copper or nickel electrodes was abraded with different grit emery papers, cleaned in ultrasonic bath, washed with distilled water and finally dried.

RESULTS AND DISSCUSION

Electrochemical behavior of caffeine

Preliminary information about the voltammetric behavior of caffeine resulted from cyclic voltammetry. It has been observed its influence on both anodic and cathodic processes. Figure 1 shows cyclic voltammograms recorded with a scan rate of 100 mV s^{-1}, on Pt electrode, in SB solution in the absence/presence of concentrations between 10^{-6} and 10^{-2} mol L^{-1} caffeine.



a) b)

Fig 1. Cyclic voltammograms, on Pt electrode, in SB solution with: a) different concentrantions of caffeine; b) without/with 10^{-2} mol L^{-1} of caffeine, scan rate: 100 mV s^{-1}.

The cyclic curve obtained in SB solution presents the characteristics of polarization voltammograms recorded in acidic solutions (pH=4.5). On the anodic branch of the curve, only the plateau characteristic for oxygen release is observed. On the backward scan one can observe a cathodic peak at +0.25 V/Ag/AgCl, associated with the oxidation of superficial remanent oxygen, also at more negative potentials then -0.5 V/Ag/AgCl, the increasing current can be associated with hydrogen evolution reaction on platinum electrode. In figure 1b only the cyclic voltammogram obtained in SB and SB with 10^{-2} mol L^{-1} of caffeine are shown.

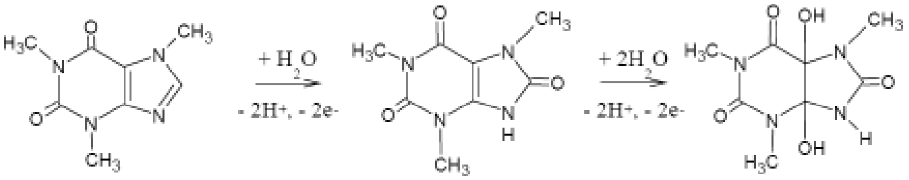


Fig. 2. Caffeine electrochemical oxidation mechanism (Dryhurst G. et al, 1971).

Addition of caffeine in a SB solutions leads to a more visible oxidation plateau, attributed to the oxidation process of the organic compound at a potential above +1.5 V/Ag/AgCl, according to mechanism presented in figure 2. The overall process involves four protons and four electrons as suggested by Dryhurst and Hansen (Dryhurst G. et al, 1971). The first step is a $2H^+$, $2e^-$ oxidation of the C-8 – N-9 bond to give the substituted uric acid. This is followed by a fast $2H^+$, $2e^-$ oxidation to the 4,5-diol analog of uric acid, which rapidly fragments. In weak acidic solution the caffeine oxidation process is reversible, the reduction peak appears around -0.4V/Ag/AgCl.

Also from the analysis of cyclic voltammograms shown in Figure 1, a significant shift toward more negative values of the potential for hydrogen evolution reaction and toward more positive values of the potential for oxygen evolution procces on platinum electrode are observed, which can be correlated in both cases with an increase of overpotentials due to the inhibitory effect of caffeine in the electrolyte solution. The polarization of both processes is due to the absorption/desorption of the caffeine molecules and its oxidation products on platinum electrode. Caffeine as well as its oxidation products have high specific volume and ensuring an optimal concentration in the electrolyte block the active areas of the electrode. Consequently, the overpotentials of both processes mentioned above increase. This influence is significant especially if in the electrolyte solution 10^{-2} mol L^{-1} caffeine is added.

Studies on hydrogen evolution reaction

Linear voltammetry curves were recorded on platinum, copper and nickel electrodes, in SB solution, without and with different concentration of caffeine (10^{-6} - 10^{-2} mol L^{-1}) in order to determine the influence of caffeine on hydrogen evolution reaction. In figure 3 linear voltammetry curves recorded with 10 mV s^{-1}, from -0.25 to -1.2 V vs Ag/AgCl, on platinum electrode are presented.

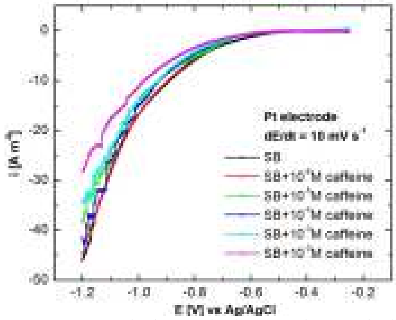
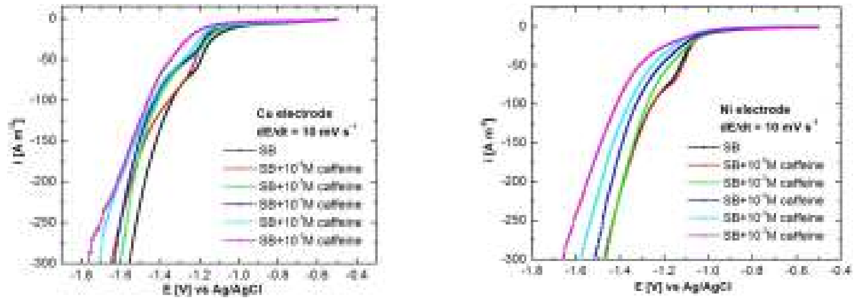


Fig 3. Linear voltammograms recorded on platinum electrode in SB solution and in the presence of different concentrations of caffeine, scan rate: 10 mV s^{-1}.

Figure 4 shows linear curves obtained on copper and nickel electrodes, in the absence and presence of different caffeine concentrations.

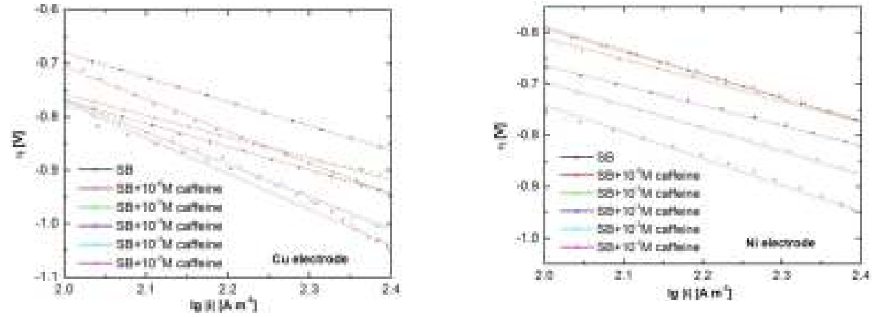


a) b)

Fig 4. Linear voltammograms recorded on a) copper and b) nickel electrode, in SB solution and in the presence of different concentrations of caffeine, scan rate: 10 mV s^{-1}.

Above presented figures reveal an increase of the hydrogen evolution overpotential with the increase of caffeine concentration. This effect becomes more visible at high concentration of additive in the electrolyte solution.

In order to obtain more information about the inhibitor effect of caffeine on hydrogen evolution reaction, kinetic parameters were determined from Tafel polarization plots, as shown in figure 5.



a) b)

Fig 5. Tafel plots recorded for hydrogen evolution reaction in SB solution without and with different concentrations of caffeine on a) copper and b) nickel electrode.

Kinetic data corresponding to the Tafel plots, presented in table 1, reveal lower values of the exchange current density with the increase of the caffeine concentration in electrolyte solution on both copper and nickel electrodes. Based on presented data, it can be conclude that the presence of caffeine in the electrolyte leads to its adsorption onto the electrode surface, blocking the active areas of the electrode.

Table 1

Kinetic parameters (i_o - exchange current density and (1-α) - cathodic transfer coefficient) for hydrogen evolution:

Electrolyte	**Cu electrode**			**Ni electrode**		
	-b [mV dec^{-1}]	***1-α***	**$i_o \cdot 10^5$ [A m^{-2}]**	**-b [mV dec^{-1}]**	***1-α***	**$i_o \cdot 10^5$ [A m^{-2}]**
SB	670	0.09	3.18	551	0.11	3.78
SB + 10^{-6}M caffeine	622	0.11	3.69	499	0.12	3.64
SB + 10^{-5}M caffeine	535	0.13	4.27	485	0.13	2.51
SB + 10^{-4}M caffeine	499	0.14	4.71	474	0.15	2.23
SB + 10^{-3}M caffeine	462	0.15	5.22	461	0.17	2.07
SB + 10^{-2}M caffeine	454	0.06	7.56	448	0.18	1.77

Studies on nickel deposition process

Linear voltammograms on copper (figure 6) and nickel (figure 7) electrodes, in SB + 5 g L^{-1} Ni^{2+} solutions were recorded with a scan rate of 1 mV s^{-1}.

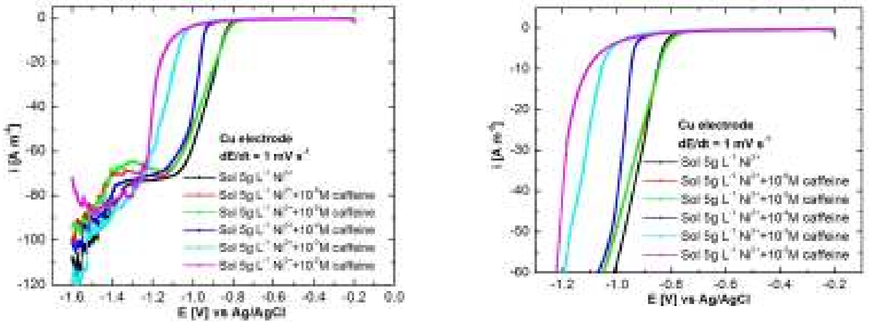


Fig 6. Linear voltammograms recorded on copper electrode in SB + 5 g L^{-1} Ni^{2+} solution in the presence of different concentrations of caffeine, scan rate: 1 mV s^{-1}.

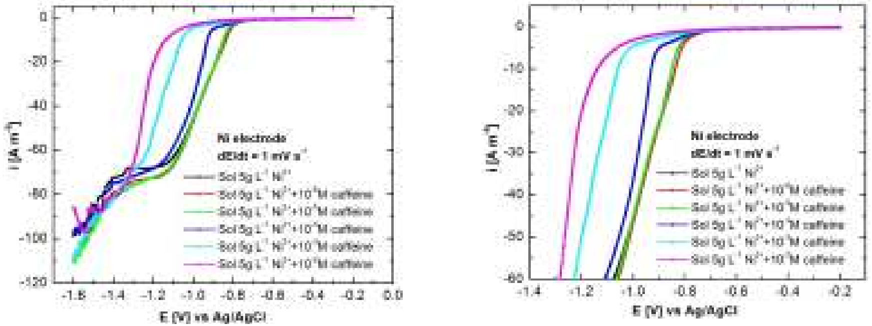
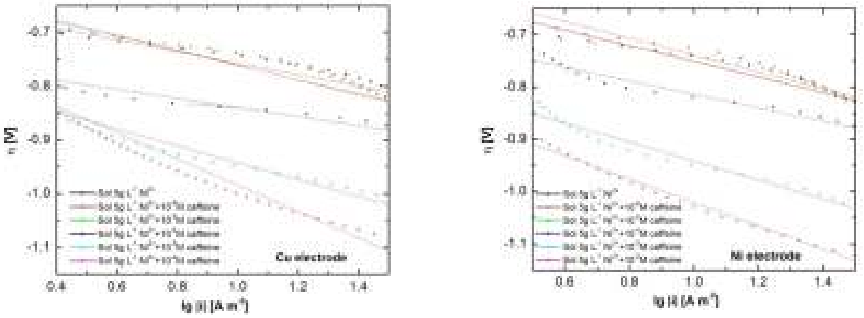


Fig 7. Linear voltammograms recorded on nickel electrode in SB + 5 g L^{-1} Ni^{2+} solution in the presence of different concentrations of caffeine, scan rate: 1 mV s^{-1}.

From the analysis of above linear voltammograms it can be observed that nickel deposition process is accompanied by cathodic polarization in the presence of caffeine. Increasing the caffeine concentration in the electrolyte solution entails an increase of nickel deposition overpotential. Kinetic data of nickel deposition process are presented in table 2.



a) b)

Fig 8. Tafel plots for nickel electrodeposition process in SB + 5 g L^{-1} Ni^{2+} solution without/with different concentrations of caffeine on a) copper and b) nickel electrode.

Table 2

Kinetic parameters (i_o - exchange current density and (1-α) - cathodic transfer coefficient) for nickel deposition process:

Caffeine concentration [mol L^{-1}]	Cu electrode			Ni electrode		
	-b [mV dec^{-1}]	*1-α*	$i_o \cdot 10^5$ [A m^{-2}]	-b [mV dec^{-1}]	*1-α*	$i_o \cdot 10^5$ [A m^{-2}]
0	245	0.24	31.5	223	0.26	26.6
10^{-6}	168	0.27	28.1	185	0.32	16.7
10^{-5}	151	0.30	21.1	175	0.36	10.5
10^{-4}	139	0.43	12.1	167	0.39	9.2
10^{-3}	133	0.46	3.9	159	0.42	7.5
10^{-2}	106	0.55	0.1	148	0.44	6.6

Inspection of obtained data emphasises a decrease of exchange current density in the presence of caffeine due to the adsorbtion onto electrode surface.

CONCLUSIONS

Experimental data presented in this paper confirm the possibility of using caffeine as additive in a Watts-type elctrodeposition bath.

Kinetic data reveal caffeine inhibitory effect, acting by differential adsorption onto the electrode surface, like most of additives.

Acknowledgement

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