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# Quantification of Metallic Copper and Nickel in Their Binary Mixtures by Voltammetry of Immobilized Microparticles

*Wenjuan Liu*[1,2,3]*, Farzin Arjmand*[3]*, Fehe Cao*[2] *and Annemie Adriaens*[3,*]

[1] College of Materials Science and Engineering, Nanjing University of Technology, Nanjing 210009, PR China
[2] Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China
[3] Department of Analytical Chemistry, Ghent University, Krijgslaan 281-S12, 9000 Ghent, Belgium
[*]E-mail: annemie.adriaens@ugent.be

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We report the use of voltammetry of immobilized microparticles for the quantification of metallic copper and nickel in their binary mixtures. Twenty-two electrolytes were investigated in order to obtain well-separated oxidation peaks. An experimental design strategy was employed to study the effect of the electrolyte concentration and the scan rate on the resolution of the oxidation peaks. With the optimum experimental parameters, a quantification was performed and the linear results of percentage of anodic currents in term of their relative amount in the binary mixture were obtained. Finally, the prediction of two mixture samples was performed and gave satisfactory results.

**Keywords:** Voltammetry of immobilized microparticles, Carbon paste electrode, Differential pulse voltammetry, Copper, Nickel.

## 1. INTRODUCTION

As an alloy of copper, bronze has been widely used in various fields for centuries. As with brass, bronze exists in a variety of formulations, which may be selected depending on the application. Aluminium bronze, tin bronze, phosphor bronze, nickel bronze, and silicon bronze are all examples of this alloy. Nickel bronze, also known as copper-nickel alloy, is usually used in piping, heat exchanging systems, and condensers in seawater systems as well as marine hardware [1]. It is also commonly used in silver-coloured circulation coins with a typical composition of 75% copper and 25% nickel [1]. Additionally, a mixture of 55% copper and 45% nickel is used in thermocouples to make resistors whose resistance is stable across changes in temperature [1].

Abrasive stripping voltammetry as a non-destructive electroanalysis method receives considerable attention for the determination of alloys or other electroactive compounds. Also called voltammetry of immobilized microparticles (VMP), it was first introduced by Scholz in 1989 [2-3]. Since then, it has been proven a useful tool in the identification, speciation, and quantification of electroactive components in electroactive solids [4-5]. The transfer of the sample can be simply achieved by abrasion from the solid substance onto the surface of the suitable solid electrodes, such as a paraffin impregnated graphite electrode or a carbon paste electrode.

Analytical efforts are mainly focused on the identification and quantification of as many components as possible. In the last years, several methods have been introduced for the quantification of materials using VMP. Coulometric data were recorded by Scholz for the first time in 1990 [6-7]. Other methods, such as the measurement of peak areas in voltammograms [7-9], peak potential shifts [4, 10-11], internal standard addition [12-15] and Tafel plots [16] have also been reported to quantify different insoluble solid compounds.

Recent VMP research on copper-based alloys has been reported, where four metallic elements, Zn, Sn, Pb and Cu, were quantified in a 0.01 M $NH_4Cl$ solution with differential pulse voltammetry [17]. Also the identification or quantification of copper alloyed with Fe [18] and Bi [19] has been reported.

The aim of this work is to introduce VMP as a helpful technique to identify and quantify copper and nickel in their binary alloy. Several electrolytes were investigated in order to obtain well-separated peaks of these two metals. Optimization of the experimental parameters was achieved by an experimental design strategy called central composite design. Finally, the calibration curve of each metal was made based on the optimum electrochemical responses.

## 2. EXPERIMENTAL

### *2.1. Reagents, apparatus and electrodes*

Solid paraffin, sodium acetate, sodium hydroxide, sodium nitrate, sodium chloride, sodium sulphate, sodium carbonate, sodium hydrogen carbonate, oxalic acid, potassium sulphate, potassium chloride, potassium dihydrogen phosphate, and calcium chloride were purchased from Merck (Darmstadt, Germany). Ammonium carbonates, ammonium chloride, ammonium acetate, ammonium persulphate, ammonium hydrogen carbonate, ammonium sulphate, hydrochloric acid, ethylene diamine tetra acetic acid and a $Na_2HPO_4$/ NaOH buffer (pH 12) were purchased from Sigma-Aldrich (St. Louis, USA). Graphite powder ($\leq$ 0.1 mm) was purchased from Fluka (St. Louis, USA). All reagents were of analytical grade.

Carbon paste electrodes (CPE's) containing milligrams of metal particles were used as working electrodes. A total amount of 100 mg carbon paste containing 40 mg of the metal/alloy particles was transferred into a plastic tube with a length of 2 cm and a diameter of 0.5 cm. A copper rod was inserted into the plastic tube to make an electrical contact with the mixture. The working surface of the electrode was renewed by removing the copper rod and polishing it on a sheet of clean paper to remove the reacted analyte after each measurement [24].

The VMP measurements were carried out using an Autolab Eco Chemie potentiosat (PGSTAT 10) with a three-electrode electrochemical cell. The reference electrode was a saturated Ag/AgCl/KCl electrode, the counter electrode a graphite rod, and the CPEs with different ratios of the metal particles were used as working electrodes. Differential pulse voltammograms of the samples were recorded in a potential range of -1.5 V to 0.5 V with different scan rates. The latter was done by changing the interval time (scan rate = step potential × 1 / pulse period).

### *2.2. Experimental design*

In order to optimize the experimental conditions, a central composite design (CCD) was used to obtain the maximum separation between copper and nickel oxidation peaks [25]. The response surface method was used to investigate the response of one variable to changes in a set of design or explanatory variables, and to find the optimal conditions for that response. The variables (and ranges) considered in the current optimization process were the scan rate (0.1–10 mV/s) and the concentration of the electrolyte (0.1–4 M).

The polynomial equations, response surface, and central design for a particular response were obtained using the statistical software package Essential Regression 97 [26]. For an experimental design with two factors, the model includes linear, quadratic and cross terms and can be expressed as Equation 1:

$$\text{Response}= b_0+b_1\times F_1+b_2\times F_2+b_3\times F_1\times F_1+b_4\times F_2\times F_2+b_5\times F_1\times F_2 \qquad [1]$$

where $F_1$ and $F_2$ are the variables and $b_0$ through $b_5$ are the coefficient values obtained through a multivariate linear regression; $b_0$ indicates the intercept and is used in the error calculation. The statistical significance of the predicted model was evaluated by an analysis of variance (ANOVA) and the method of least squares. Replicates (n = 4) of the central points were performed to estimate the experimental error.

## 3. RESULTS AND DISCUSSION

### *3.1. Identification*

The electrochemical behaviour of copper and nickel in their mixture electrodes in different electrolytes was investigated with differential pulse voltammetry. As shown in Table 1, the only suitable electrolyte for the analysis of a copper and nickel mixture is potassium chloride. In all the other electrolytes, at least one oxidation peak of copper overlapped with that of nickel. In potassium chloride solution, two oxidation peaks for copper and only one wide peak for nickel oxidation are detectable and distinct.

**Table 1.** Different electrolytes used to identify Ni and Cu in their binary mixtures (√ means identifiable, × means not identifiable).

| Electrolyte (0.1 M) | Ni | Cu |
|---|---|---|
| Buffer solution (pH = 12) | × | √ |
| Oxalic acid | × | × |
| Hydrogen chloride | × | × |
| Sodium hydroxide | × | √ |
| Sodium chloride | × | × |
| Sodium nitrate | × | × |
| Sodium sulphate | × | × |
| Sodium carbonate | × | × |
| Sodium acetate | × | × |
| Sodium hydrogen carbonate | × | √ |
| Disodiumhydrogen orthophosphate | × | × |
| ammonium hydrogen carbonate | × | × |
| Ammonium carbonate | × | × |
| Ammonium persulfate | × | × |
| Ammonium chloride | × | × |
| Ammonium sulphate | × | × |
| Ammonium acetate | × | × |
| Calcium chloride | × | × |
| Potassium chloride | √ | √ |
| Potassium sulphate | × | × |
| Potassium dihydrogen phosphate | × | × |
| Ethylene diamine tetra acetic acid | × | √ |

In the next step, CCD was used to optimize the experimental parameters: the potassium chloride concentration and the scan rate were varied in order to obtain the maximum separation between the oxidation current peaks, and to overcome any interference between copper and nickel oxidation peaks. With CCD, the number of experiments required is greatly decreased. Table 2 shows the list of the experiments and the levels of the coded values, including the corresponding response of each experiment. Twelve experiments were carried out, and the peak potential differences ($\Delta E_p$) between the nickel peak and the first oxidation peak of copper were recorded to obtain the response surface plots.

Table 3 shows the p-values of each term in Equation 1 obtained from the ANOVA. In statistical significance testing, the p-value is the probability of obtaining a test statistic at least as extreme as the one that was actually observed, assuming that the null hypothesis is true. One often rejects the null hypothesis when the p-value is less than the significance level $\alpha$, which is often 0.05 or 0.01. When the null hypothesis is rejected, the result is said to be statistically significant [25]. Therefore, a smaller p-value means the null hypothesis rejection more valid. As shown in Table 3, $b_2$ has a smaller value than $b_1$, indicating that the potassium chloride concentration ($F_2$) is the more significant factor. This can be explained through the kinetics of the electrochemical reactions as well. Anodic oxidation/dissolution of metals can be controlled either by charge transfer (e.g. iron [27]), mass transfer or in some cases such as copper [28] by mixed charge transfer-mass transfer reactions. Furthermore, the cathodic reduction of oxygen, which occurs simultaneously at the metal-electrolyte interface, is also know in the literature as a mixed charge transfer-mass transfer controlled reaction [29]. Therefore, it is obvious that in these reactions the role of the electrolyte concentration becomes dominant, especially in chloride containing solutions.

**Table 2.** Design matrix and relative |ΔE| values in central composite design for two factors: the scan rate in mV/s ($F_1$) and the KCl concentration in M ($F_2$). The factors are expressed in coded values.

| Exp. # | $F_1$ (scan rate in mV/s) | $F_2$ (concentration in M) | \|ΔE\| (V) [$Cu_1$ - Ni] |
|---|---|---|---|
| 1 | 1.6 | 3.42 | 0.284 |
| 2 | 8.5 | 3.42 | 0.263 |
| 3 | 10 | 2.05 | 0.225 |
| 4 | 8.5 | 0.68 | 0.237 |
| 5 | 5.05 | 4.0 | 0.231 |
| 6[a] | 5.05 | 2.05 | 0.264 |
| 7 | 5.05 | 0.1 | 0.142 |
| 8 | 1.6 | 0.68 | 0.214 |
| 9[a] | 5.05 | 2.05 | 0.234 |
| 10 | 0.1 | 2.05 | 0.231 |
| 11[a] | 5.05 | 2.05 | 0.265 |
| 12[a] | 5.05 | 2.05 | 0.265 |
| coded value (-2) | 0.1 | 0.1 | |
| coded value (-1.41) | 1.6 | 0.68 | |
| coded value (0) | 5.05 | 2.05 | |
| coded value (1.41) | 8.5 | 3.42 | |
| coded value (2) | 10 | 4.0 | |

a: replicate experiments

**Table 3.** Obtained p-values.

| Coefficient | p-value |
|---|---|
| $b_0$ | 0.0259 |
| $b_1$ | 0.4850 |
| $b_2$ | 0.0220 |
| $b_3$ | 0.6990 |
| $b_4$ | 0.0577 |
| $b_5$ | 0.4430 |

The corresponding 3D response surface plot is shown in Figure 1. This plot represents the variation of the $|\Delta E_p|$ of copper and nickel oxidation peaks versus the scan rate ($F_1$) and the potassium chloride concentration ($F_2$). It is obvious that the separation between the copper and nickel oxidation peaks is greatest when the scan rate is between 0.1–6.7 mV/s and the potassium chloride concentration is about 1.8–4.0 M. In general, long-time voltammetric experiments are preferred because solid state electrochemical processes involve diffusion and surface reactions whose rates typically are lower than those involved in solution phase electrochemistry. As mentioned above, the scan rate is the less significant of the two factors in the optimization. A 0.5 mV/s scan rate was chosen to ensure sufficient reaction time between solid particles and the electrolyte. For the electrolyte, a 3 M potassium chloride solution was chosen according to the obtained optimum area in Figure 2.

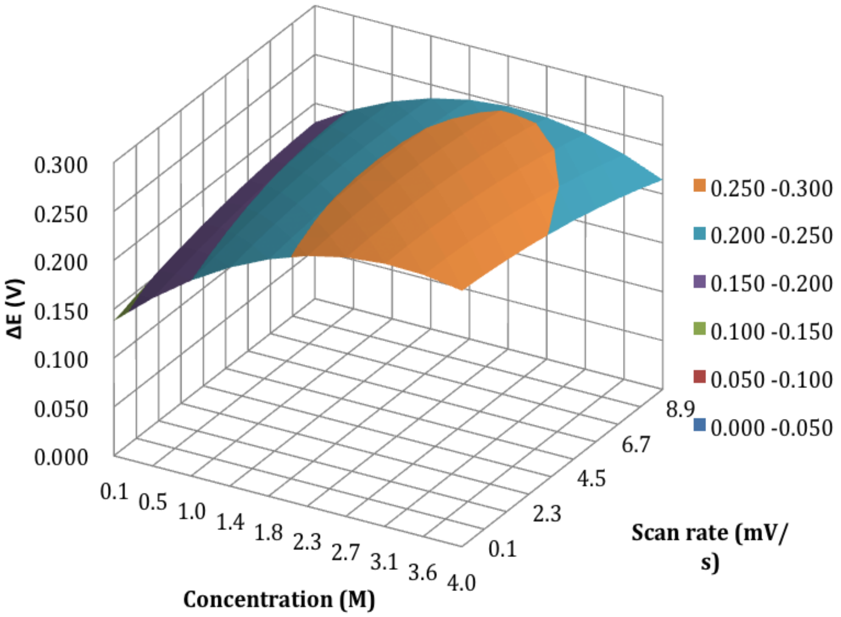

**Figure 1.** Response surface estimated from the central composite design by plotting scan rate as a function of potassium chloride concentration.

Figure 2 shows a good separation between the copper and nickel oxidation peaks with the optimal scan rate and potassium chloride concentration. There are two oxidation peaks for copper, located at -0.05 V and 0.35 V vs. Ag/AgCl, respectively, and one wide oxidation peak at 0.19 V vs. Ag/AgCl for the nickel single electrode. Changing the optimal experimental conditions obtained above results in a slight fluctuation of the peak potentials (more so for copper than for nickel). When [KCl] = 0.68 M and the scan rate is 8.5 mV/s, the potential of the first oxidation peak of copper shifts toward more positive values. For the rest of the experimental conditions, the oxidation peaks of copper and nickel are not well shaped: the oxidation peak of nickel and the second oxidation peak of copper are wide.

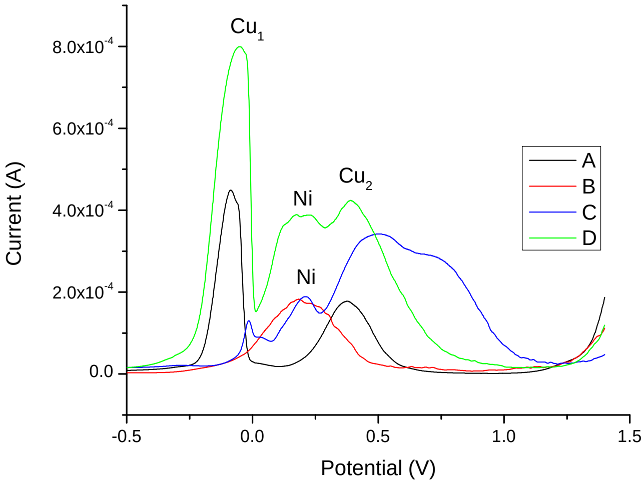

**Figure 2.** Differential pulse voltammograms of copper and nickel in potassium chloride solutions. (A and B) copper and nickel single electrodes, [KCl] = 3 M, scan rate 0.5 mV/s (optimum conditions). (C) copper and nickel mixture electrode, [KCl] = 0.68 M, scan rate 8.5 mV/s. (D) copper and nickel mixture electrode, in optimum conditions.

### *3.2. Quantification*

CPEs of copper and nickel mixture, with a total amount of 40 mg, were made in different compositions. Differential pulse voltammogram of each electrode was recorded using the optimized parameters ([KCl] = 3 M and scan rate = 0.5 mV/s). Each experiment was repeated at least five times.

It is well known that only part of the sample undergoes an electrochemical reaction in VMP measurement, and the actual current does not indicate the real amount of the solid sample [24, 30]. In the present work, quantification was done using the percentage of the oxidation current for each metal. The correlation between the oxidation current of copper ($I_{Cu}$) and nickel ($I_{Ni}$) and the percentage of the current for these metals in their binary mixtures (I) is as follow:

$$I_{Cu}(\%) = \frac{I_{Cu}}{I_{Cu} + I_{Ni}} \times 100$$

$$I_{Pb}(\%) = \frac{I_{Ni}}{I_{Cu} + I_{Ni}} \times 100$$

[2]

Different ratios of the anodic signals for copper and nickel are plotted in Figure 3. Good linear fitting of the curves in the range of 10% to 90% was obtained, with $R^2$ = 0.9837 for copper and $R^2$ = 0.9818 for nickel. However, at low and high percentages of copper (with either low amounts of copper or nickel, respectively), an unavoidable variety of effects will dominate the measurement. This results in a low signal-to-noise ratio and thus greater uncertainly. Therefore, in the quantification process, the alloys in which the copper amount is higher than 90% and lower than 10% are removed.

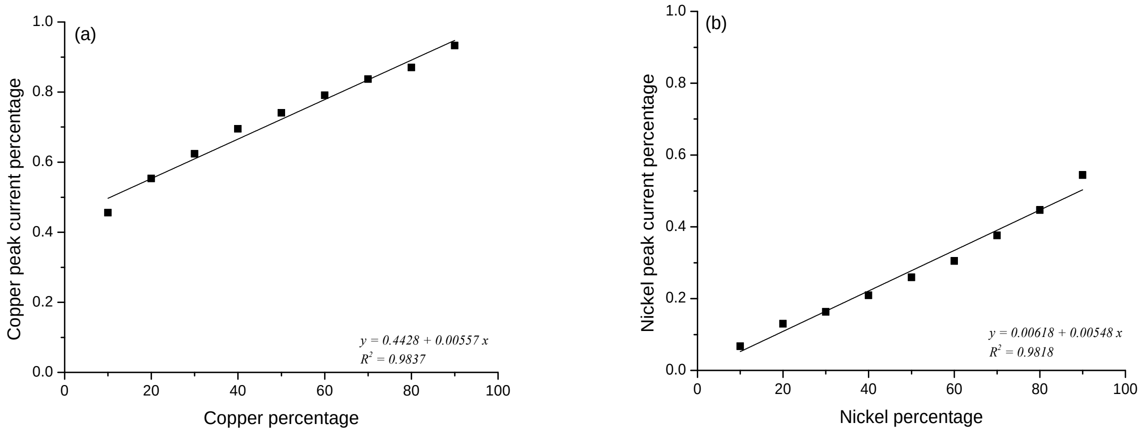

**Figure 3.** Dependence of copper and nickel oxidation peak current percentages on the composition of the copper-nickel alloy (total amount of the sample is 40 mg).

### *3.3. Prediction*

The calibration curves obtained above were tested using two samples of copper and nickel mixtures. The mixture electrodes were made using the same procedure, and the total amount of the mixture was also 40 mg. The amount of each metal in their mixtures was calculated by the calibration curves and compared with the real values. Each prediction was repeated three times. Then the relative errors were calculated. As shown in Table 4, the relative errors were small, which indicates that the calibration curves may be used to determine the concentration of copper and nickel in binary alloys.

**Table 4.** The predicted amounts of copper and nickel and their relative standard deviations.

| Metal | Sample 1 | | | Sample 2 | | |
|---|---|---|---|---|---|---|
| | Added | Found | Relative error | Added | Found | Relative error |
| Copper (mg) | 10 | 9.92 | 0.8% | 27 | 27.73 | 2.7% |
| Nickel (mg) | 30 | 30.13 | 0.4% | 13 | 12.03 | 7.4% |

## 4. CONCLUSIONS

The quantification of copper and nickel in their binary mixture by VMP using CPEs has been studied. Two relevant chemical and instrumental parameters, the concentration of the electrolyte and the scan rate, were investigated. These parameters enabled the selection of the most appropriate conditions for the quantification procedure based on the clearly resolved oxidation peaks of copper and nickel in their binary mixture. The correlation of the percentage of the anodic currents in terms of their relative amount was used to make the calibration plots, which were used to predict compositions of binary mixtures with satisfactory results. Thus, voltammetry of immobilized particles, as an easily performed and non-destructive method, is a suitable technique for the quantification of components in copper-nickel binary mixtures.

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## References

1. *Copper-Nickel Alloys - Properties and Applications (12007)*, Copper Development Association, New York (1982).
2. F. Scholz, L. Nitschke, G. Henrion, *Naturwiss.* 76 (1989) 71.
3. F. Scholz, L. Nitschke, G. Henrion, F. Damschun, *Naturwiss.* 76 (1989) 167.
4. F. Scholz, B. Meyer, in *Electroanalytical Chemistry, A Series of Advances* Vol. 20 (Eds: A.J. Bard) Marcel Dekker, New York (1998) pp. 1.
5. T. Grygar, F. Marken, U. Schröder, F. Scholz, *Collection of Czechoslovak Chemical Communications* 67 (2002) 163.
6. F. Scholz, L. Nitschke, G. Henrion, *Electroanalysis* 2 (1990) 85.
7. F. Scholz, B. Lange, *Fresenius' J. Anal. Chem.* 338 (1990), 338, 293.
8. M. Lamache, D. Bauer, *Anal. Chem.* 51 (1979) 1320.
9. A. Doménech, S. Sánchez, D.J. Yusá, M. Moyá, J.V. Gimeno, F. Bosch, *Electroanalysis* 16 (2004) 1814.
10. S. Zhang, B. Meyer, G.H. Moh, F. Scholz, *Electroanalysis* 7 (1995) 319.
11. B. Meyer, S. Zhang, F. Scholz, *Fresenius' J. Anal. Chem.* 356 (1996) 267.
12. A. Doménech, S. Sánchez, D.J. Yusá, M. Moyá, J.V. Gimeno, F. Bosch, *Anal. Chim. Acta* 201 (2004) 103.
13. A. Doménech, M. Moyá, M.T. Doménech, *Anal. Bioanal. Chem.* 380 (2004) 146.
14. A. Doménech, M.T. Doménech, J.V. Gimeno, F. Bosch, *Anal. and Bioanal. Chem.* 385 (2006) 1552.
15. F. Bosch, A. Doménech, M.T. Doménech, J.V. Gimeno, *Electroanalysis* 19 (2007) 1575.
16. A. Doménech, M.T. Doménech, H.G.M. Edwards, *Anal. Chem.* 80 (2008) 2704.
17. F. Arjmand, A. Adriaens, *J. Solid State Electrochem.* 16 (2012) 535.
18. A.B.A. Sedano, M.L.T. García, M.D.V. Barbado, P.S. Batanero, *J. Electroanal. Chem.* 566 (2004) 433.
19. A.B.A. Sedano, M.L.T. García, M.D.V. Barbado, P.S. Batanero, *J. Solid State Electrochem.* 7 (2003) 301.
20. M.M. Ghoneim, A.M. Hassanein, E. Hammam, A.M. Beltagi, *Fresenius' J. Anal. Chem.* 367 (2000) 378.
21. A. Doménech M.T. Doménech-Carbó, L. Osete-Cortina, J.V. Gimeno-Adelantado, F. Bosch-Reig, R. Mateo-Castro, *Talanta* 561 (2002) 161.
22. M. Nimmo, G. Fones, *Anal. Chim. Acta* 291 (1994) 321.
23. G. Gillain, G. Duyckaerts, *Anal. Chim. Acta* 106 (1979) 23.
24. F. Arjmand, A. Adriaens, *Electroanalysis* 23 (2011) 1941.
25. G.E.P. Box, W.G. Hunter, J. S. Hunter, *Statistics for Experimenters,* Wiley, New York (1978).
26. http://www.jowerner.homepage.t-online.de/download.htm.
27. J. O. M. Bockris, D. Drazic, *Electrochim. Acta* 7 (1962) 293.
28. G. Kear, B. D. Barker, F. C. Walsh, *Corros. Sci.* 46 (2004) 109.

29. L. Caseres, T. Vargas, L. Herrera, *Corros. Sci.* 49 (2007) 3168.
30. A. Doménech, M.T. Doménech-Carbó, L. Osete-Cortina, J.V. Gimeno-Adelantado, *Electroanalysis* 15 (2002) 1465-1475.