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The effect of the hypophosphite ion oxidation on the Ni surface electrode—an XPS study

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Abstract

The effect of the hypophosphite electrooxidation on the Ni surface state was analysed by XPS on electrodes previously submitted to constant-potential polarization in an alkaline solution containing the hypophosphite ion. It was found that Ni surface exhibits the same electronic states than in a hypophosphite-free solution. The XPS spectra of P 2p and P 2s revealed the formation of alloyed phosphorus on the Ni surface. Its dependence on the electrode potential allows concluding that hypophosphite ion participates in competitive surface reactions in the same potential range. The overall results are discussed in the light of the mechanisms proposed in the literature for the phosphorus incorporation process during Ni–P alloy electrodeposition.

Keywords: Electrode materials; Metals and alloys; Electrochemical reactions; Photoelectron spectroscopies

1. Introduction

The hypophosphite ion is a well-known reducing agent for electroless deposition process [1] and electrodeposition of alloys [2] and it is also a promising hydrogen donor in catalytic hydrogenation of organic molecules [3]. The electrooxidation mechanism of the hypophosphite ion on nickel has been the subject of several studies in last 10 years [4–8]. The use of in situ spectroelectrochemical techniques has allowed to characterize adsorbed and solution species involved in this electrode process: (a) hypophosphite ions are adsorbed via its two hydrogen atoms on the nickel surface electrode, from open-circuit potential until the onset of the oxidation potential; (b) at rather negative potentials the adsorption of hypophosphite leads to the cleavage of the P–H bond with the formation of a phosphorus-centred radical, which is subsequently oxidized to the final product, phosphite.

According to the literature, no studies have been undertaken so far with the purpose of evaluating the effect of the hypophosphite oxidation on the nickel surface electrode. The detection and identification of surface species would be important not only to provide more information about hypophosphite oxidation mechanism, but also to better understand the mechanism of phosphorus incorporation during electroless deposition and electrodeposition of Ni–P alloys [9] and to evaluate whether surface species could be responsible for unusual selective organic reactions on Ni in hypophosphite containing solutions [10].

The main purpose of this study is to characterize, by X-ray photoelectron spectroscopy (XPS) technique, Ni surface electrodes previously submitted to constant potential electrolysis in alkaline solutions containing hypophosphite ion. A comparative study was also performed on electrodes prepared in a hypophosphite-free solution.

2. Experimental

2.1. Sample preparation

In the preparation of Ni electrodes for the XPS analysis a 1.5 cm × 1.5 cm Ni foil substrate (99.9%) previously polished with 0.3 μm alumina and electropolished in 57% H_2SO_4 was used. After the electrode surface was rinsed several times with distilled deionised water it was submitted to a constant electrode potential, for 3600 s, in a 0.375 M $H_2PO_2^-$ + 0.10 M NaOH solution. Afterwards it was rinsed again with distilled deionised water and dried on a N_2 flow. Details of the cell set up and polishing procedure were described elsewere [10].

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The electrode potential was controlled by an Autolab potentiostat model 100 and is referred to a saturated calomel electrode (SCE).

2.2. XPS analysis

The spectrometer used was a XSAM800 (KRATOS) operated in the fixed analyser transmission (FAT) mode, with a pass energy of 10 eV, a power of 130 W (10 mA and 13 kV) and the non-monochromatised MgK* X-radiation (h^* = 1253.6 eV). Samples were analysed in a UHV chamber (~10^{-7} Pa) at room temperature, using 0° and 60° analysis angles relative to the normal to the surface. Samples were transferred to the fast introduction chamber under ambient atmosphere. Spectra were recorded by a Sun SPARC Station 4 with Vision software (Kratos) using a step of 0.1 eV. A Shirley background was subtracted and curve fitting for component peaks was carried out with a non-linear least-squares algorithm using pseudo-Voigt profiles. No charge compensation (flood-gun) was used. Binding energies were corrected by using contamination carbon (binding energy = 285 eV) as a reference. X-ray source satellites were also subtracted. For quantification purposes, sensitivity factors were 0.66 for O 1s, 0.25 for C 1s, 4.55 for Ni 2p and 0.26 for P 2s. These factors are included in the Vision software and were checked using several calibrating salts as $NiBr_2$, for instance.

3. Results and discussion

On the preparation of the sample electrodes, the negative potential that was applied (−1.1 V) was selected on account of previous work [3,4,11]. It is known that at this potential the electrode exhibits the highest activity to oxidize the hypophosphite ion. Despite the rather long electrode polarization time, 3600 s, the current evolution recorded during the electrode polarization, Fig. 1, reveals that the oxidation of hypophosphite persists all along. In the present experimental conditions no gas evolution was detected, contrasting to what was observed in other experimental conditions [1,5]. Surface characterization of the Ni electrodes prepared at −1.1 V for 3600 s was performed by XPS by analysing the electronic states of nickel and phosphorus. For comparison, the spectrum obtained in the Ni 2p region for the Ni electrode prepared in a hypopohosphite-free solution was also examined.

In Fig. 2, the XPS Ni 2p region is shown for electrodes submitted to polarization in 0.375 M $H_2PO_2^-$ + 0.10 M NaOH and 0.10 M NaOH solutions. For both samples, the Ni 2p exhibits its doublet—Ni $2p_{1/2}$ and Ni $2p_{3/2}$ with a distance around 17.6 eV. Analysis of the Ni $2p_{3/2}$ region in both electrodes show three main components centred at 852.2 ± 0.1 eV, 855.7 ± 0.1 eV and 861.5 ± 0.1 eV. The first one is assignable to metallic nickel and has a full width at medium height (fwmh) of 1.37 eV. Its relative importance is larger in the electrode submitted to potentiostatic polarization in the hypophosphite solution showing that it is the less oxidized sample. In the literature (see Table 1) a large dispersion of values for Ni $2p_{3/2}$ biding energy (BE) is found ranging from 852.6 to 858.3 eV. The source of the lowest value dates from 1983 [13] whereas the source of the highest one dates from 1972 [14a] when XPS spectrometers were far from reliable. Recent data from a French group gives a value of 852.6 eV [14b]. Concerning the second component, the assignment is much more difficult: this value may be assigned to NiO, Ni_2O_3 or $Ni(OH)_2$ (see Table 1). Given its width (fwmh ~3 eV) it may be a mixture of them. Since its position and shape are the same for both electrodes and taking into account the fact that the modified electrodes were prepared at rather negative potentials and in a solution containing a reducing agent (hypophosphite), Ni_2O_3 is

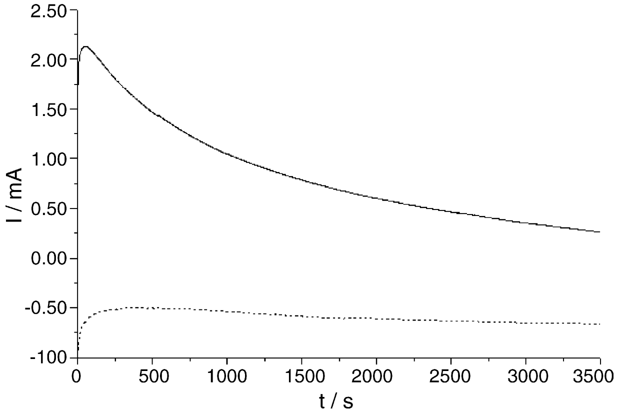

Fig. 1. Current–time profile for the Ni electrode at −1.1 V in 0.375 M $H_2PO_2^-$ + 0.10 M NaOH solution (solid line) and in 0.10 M NaOH solution (dashed line).

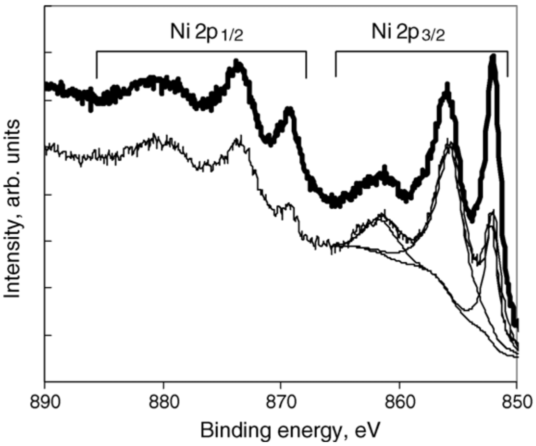

Fig. 2. XPS Ni 2p for nickel electrodes submitted to constant potential polarization in NaOH (bottom line) and $H_2PO_2^-$ + NaOH (top line) solutions by constant potential electrolysis at −1.1 V. Curve fitting with three peaks for the Ni $2p_{3/2}$ regions is shown in the lower spectrum. For the sake of clarity, just the curve fitting for the NaOH treated electrode is shown.

Table 1
Binding energies of P_{2p}, P_{2s} and $Ni_{2p3/2}$ core-level lines of standard substances

Standard compounds	BE (eV)			Ref.
	P 2p	P 2s	Ni $2p_{3/2}$	
Ni			852.6–853.8	[12–14]
NiO			853.6–857.2	[12,15,16]
Ni_2O_3			855.8–856.0	[12]
$Ni(OH)_2$			855.1	[12]
NiOOH			856.1–861.7	[12,14]
NaH_2PO_2	132.5	190.1		[17,19]
Na_3PO_3	134.1			[18]
Na_2HPO_3	132.9			[12]
Na_2HPO_4	133.0	190.8		[17–19]
P	130.0	187.7–188.05		[19,20]
PH_3	129.8			[20,21]

not expectable. The distance between peaks is less sensitive to spectrometer energy calibration and, in reference 13 differences around 3.5 eV between metallic and Ni^{2+} can be found confirming that the oxidation state must be the 2+. For very well defined NiO (1 0 0) surfaces, cleaved under vacuum, two components are detected at 854.1 and 855.6 eV [15,16], which is not the case of our sample, pointing to an amorphous oxide or a mixture of oxides and/or hydroxides. The third component, centred around 861.7 ± 0.1 eV and approximately 6 eV wide, is assigned to the complex multiplet structure existing in nickel [15]. In fact, both Ni and Ni^{2+} have unpaired electrons in 3d orbitals which may couple differently with the unpaired electron left in the 2p orbital after the photoelectron ejection giving rise to a complex series of multiplet peaks spreading over 10 eV [15].

The comparative analysis of these spectra lead us to conclude that despite the extent of Ni oxidation is higher in the hypophosphite-free solution, the nickel exhibits the same oxidation states in an solution containing the hypophosphite ion.

Although some authors endorse the formation of nickel hydride upon the hypophosphite oxidation [22], evidence for its formation was not given yet. Hydrogen-metal bonds can be indirectly detected by XPS, via a chemical shift in the photoelectron energies of the metal atom and via line shape changes, but it requires very clean sample surfaces and a rather high amount of hydrogen on the surface. Surface contamination by elements like oxygen, carbon or chloride would have to be avoided, which was not feasible in the present experimental conditions.

Concerning phosphorus, two XPS regions were studied: P 2p and P 2s. The most commonly studied region is the P 2p one and extensive data are found in the literature [17,20,23]. However, in this system, P 2p is not an adequate region to properly study the amount and the nature of phosphorus at the surface because the P 2p overlaps with a very broad shake-up (most probably, a plasmon) of the Ni 3s peak. Although it was also found that the P 2s peak overlaps with Cl 2p satellites (centred around 190 eV), it was possible to subtract the satellites and to obtain the neat P 2s peak from it. Quantification was thus performed with the P 2s region and the binding energies were evaluated either from P 2s or the P 2p region. No attempt was made to eliminate contaminating chloride ions from the surface because we wanted to maintain the same experimental methodology that was previously used [10].

It was found that the P 2s region could be fitted with two components: one centred at 190.3 eV and another one (absent in the −1.10 V treated electrode) centred at 188.4 eV, Fig. 3. The first component is assigned to hypophosphite (Table 1). Albeit the same binding energy is also characteristic of phosphate, previous studies have revealed that only phosphite is formed upon the oxidation of hypophosphite and that it does not remain adsorbed on the electrode surface. The detection of hypophosphite on the surface is consistent with data obtained by SNIFTIRS that revealed that hypophosphite adsorbs on the nickel surface, even at open circuit potential [3,4].

On account of Table 1 data, the second component could be assigned to elemental phosphorus; however this species is not expected to be detected because it is very unstable in aqueous solutions. Two other hypotheses are proposed for its assignment: alloyed phosphorus (normally represented as Ni–P, independently of its stoichiometry) and phosphine. The formation of phosphorus bound to nickel is the most plausible hypothesis to be considered. Literature data on the characterization of Ni–P alloys by XPS reveal the formation of a reduced form of phosphorus which is bound to nickel [17,20,24–27], however such analysis concerns exclusively the P 2p region. According to literature data, the binding energy of alloyed phosphorus lies within 129.0–129.7 eV in the P 2p region, depending on the phosphorus content and sample preparation method. The qualitative analysis of the present electrodes in the P 2p region also reveals a peak in that energy range, which is indicative of alloyed phosphorus formation. In order to confirm this assignment the P 2s and 2p regions of a Ni–P sample prepared by electroless deposition on a Ni foil were also analysed. The obtained values, 190.4 and 187.0 eV for the P 2s region, 132.7 and 129.2 eV for the P 2p region, are consistent with the binding energies reported on the sample electrodes, which supports our hypothesis that alloyed phosphorus is formed upon polarization of the Ni electrode in a solution containing hypophosphite. Data obtained on the analysis of the P 2s region in a $Fe_{40}Ni_{40}P_{14}B_8$ glass sample, further corroborates the assignment of 187.95 eV peak to phosphorus bound to nickel [24]. Phosphine presents a binding energy at 129.9 eV (there are no published results on the P 2s region) [20] but its detection by an ex situ technique (XPS) is unlikely because phosphine, like phosphorus, is very unstable in aqueous solution.

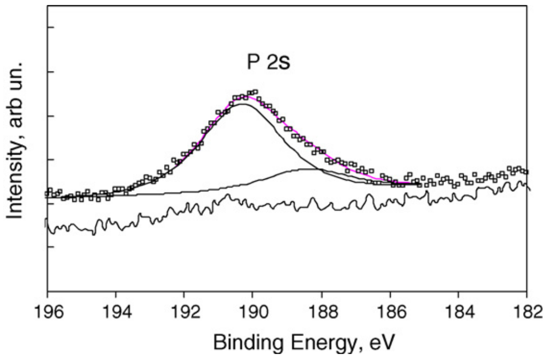

Fig. 3. XPS P 2s region for the Ni electrode after electropolishing (bottom line) and potentiostatic polarization at −1.2 V in 0.375 M $H_2PO_2^-$ + 0.10 M NaOH solution (top dashed line). P 2s was fitted with two peaks (top continuous line).

The amount of each phosphorus component on the surface (measured as P/Ni atomic ratio) as a function of the applied potential is shown in Fig. 4. The fact that the atomic ratio P/Ni increases for an analysis angle of 60° is a clear evidence that phosphorus, in both forms, is on the top layers of the surface electrode, as expected. From the figure it is also evident that the dependence of each phosphorus component on the applied potential follows opposite routes. The amount of hypophosphite on the surface electrode, highly dependent on the electrode potential, reaches its maximum value at −1.10 V. This result is consistent with the potential dependence of the electrode activity to oxidize the hypophosphite ion [3,6,11]. In contrast, the amount of alloyed phosphorus is approximately constant in the −1.00 to −1.30 V potential range, except at −1.10 V where it

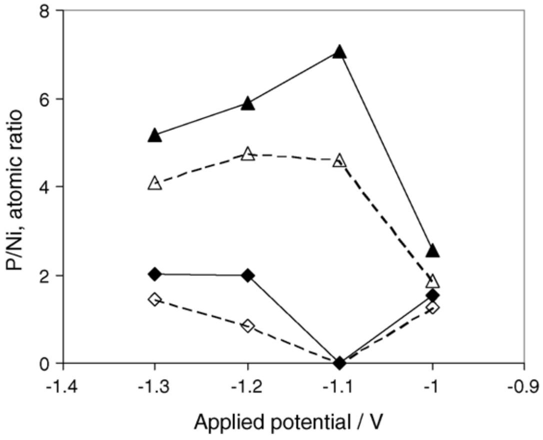

Fig. 4. Diamonds correspond to the lower binding energy P 2s component (188.4 eV) and triangles to the higher binding energy P 2s component (190.3 eV). Results for 0° (relative to the normal to the surface) are represented by empty symbols and for 60° by full symbols.

is not formed. These observations suggest that hypophosphite ion participates in two competitive surface reactions in the same potential range: its reduction to alloyed P and its oxidation to phosphite. The latter is known to occur through an intermediate, $HPO_2{}^-$ [7,11]:

$$H_2PO_{2(ads)}{}^- \rightarrow H_{(ads)} + HPO_{2(ads)}{}^-$$

$$H_2O + HPO_{2(ads)}{}^- \rightarrow HPO_3{}^{2-} + e + 2H^+$$

$$H_{(ads)} \rightarrow H^+ + e.$$

At this stage it seems pertinent to analyse these results in the light of the mechanisms that are proposed in the literature for the incorporation of phosphorus during the Ni–P electrodeposition. According to the literature, two different mechanisms are proposed: the direct and the indirect mechanism. The former supports that phosphorous acid, or phosphite (depending on the pH), is electrochemically reduced to elemental phosphorus, which would react with Ni giving rise to Ni–P alloy [25]:

$$H_3PO_3 + 3H^+ + 3e \rightarrow P + 3H_2O$$

$$n\mathrm{Ni} + \mathrm{P} \rightarrow \mathrm{Ni}_n\mathrm{P}.$$

The latter is based on the assumption that phosphine (PH_3), itself formed by hypophosphite or phosphite ion reduction (or their respective acids), reacts with Ni^{2+} ions present in the solution to produce the Ni–P alloy [7,9,26–28]:

$$H_3PO_3 + 6H^+ + 6e \rightarrow PH_3 + 3H_2O$$

$$\mathrm{w}PH_3 + \mathrm{y}Ni^{2+} \rightarrow Ni_yP_w + \mathrm{z}H^+.$$

This mechanism has been more widely accepted than the direct mechanism.

Based on the above results it can be concluded that, independently of the type of mechanism (direct or indirect), phosphite ion does not seem to be the species that is reduced to alloyed P, otherwise, it would have been expected that alloyed P was formed at the potential corresponding to the highest electrode activity to oxidize hypophosphite to phosphite (−1.1 V). This conclusion is in agreement with the Zeller and Landau [27] and Harris and Dang [9] results in Ni–P electrodeposition experiments: the phosphorus content of the alloy is null or very low when H_3PO_3 is used instead of H_3PO_2.

It is also important to note that the detection of alloyed phosphorus, on sample electrodes that were prepared in the absence of Ni^{2+}, reveals that the presence of this metallic cation is not a constraint for the incorporation of phosphorus (in very small amounts) on nickel. This result is indicative that probably different reaction pathways (supported by both direct and indirect mechanisms) will be responsible for the Ni–P alloy formation. To our knowledge this is the first time that alloyed phosphorus is detected on a nickel electrode in a Ni^{2+}-free solution in an alkaline medium. Although Kurowski et al. have reported its detection by XPS in an acidic solution [28], in such medium the dissolution of the Ni may occur, contributing to the presence of the Ni^{2+} ions in the solution. Zeng and Zhou have shown by in situ surface enhanced Ramam spectroscopy, that a Ni–phosphine compound is formed in a solution without Ni^{2+} in a neutral medium [8], but no evidence for the formation of alloyed P was given.

Although it is not the aim of this work to study the phosphorus incorporation mechanism during Ni–P electrodeposition, these peculiar results reveal that this matter should be subjected to further investigation in the future.

4. Conclusions

In this work it was concluded that the Ni surface electrode is modified upon polarization in a hypophosphite containing solution. It was revealed by XPS that alloyed phosphorus is the responsible species for the surface electrode modification. Its dependence on the electrode potential reveals that hypophosphite ion participates in two surface competitive reactions in the same potential range: its oxidation to phosphite and its reduction to alloyed phosphorus.

The analysis of these results suggest that the mechanism for the incorporation of phosphorus in the Ni–P electrodeposition process involves the hypophosphite ion, and not phosphite, and that alloyed P can be formed even in the absence of Ni^{2+} ions.

References

[1] L.M. Abrantes, J.P. Correia, J. Electrochem. Soc. 141 (1994) 2356.
[2] (a) B. Popov, Plat. Surf. Finish. 91 (2004) 40;
(b) A. Brenner, Electrodeposition of Alloys, vol. II, Academic Press, New York, 1963.
[3] (a) R. Johnstone, A. Wilby, I. Endtwistle, Chem. Rev. 85 (1995) 129;
(b) M.C. Oliveira, Proceedings of the VIII Iberic Meeting of Electrochemistry and XIII Meeting of the Portuguese Electrochemical Society, Covilhã, Portugal, 2005.
[4] (a) L.M. Abrantes, A. Bewick, M. Kalaji, M.C. Oliveira, J. Chem. Soc. Faraday Trans. 92 (1996) 4663;
(b) L.M. Abrantes, M.C. Oliveira, J. Correia, M. Kalaji, A. Bewick, J. Chem. Soc. Faraday Trans. 93 (1997) 1119.
[5] L.M. Abrantes, M.C. Oliveira, J. Electrochem. Soc. 147 (2000) 2981.
[6] L.M. Abrantes, E. Vieil, M.C. Oliveira, Electrochim. Acta 41 (1996) 1515.

[7] Y. Zeng, S. Zhou, J. Electroanal. Chem. 79 (1999) 469.
[8] Y. Zeng, S. Zhou, Electrochem. Commun. 1 (1999) 217.
[9] T. Harris, Q. Dang, J. Electrochem. Soc. 140 (1993) 81.
[10] M.C. Oliveira, Electrochim. Acta 48 (2003) 1829.
[11] M.C. Oliveira, PhD Thesis, University of Lisbon, 1996.
[12] C. Wagner, A. Naumkin, A. Kraut-Vass, J. Allison, C. Powell, J. Rumble, NIST X-ray Photoelectron Spectroscopy Database, NIST Standard Reference Database 20, Version 3.4 Version, 2003.
[13] V. Nemoshalenko, V. Didyk, V. Krivitskii, A. Senekevich, Zh. Neorg. Khimi. 28 (1983) 218.
[14] (a) S. Grim, L. Matienzo, W. Swartz, J. Am. Chem. Soc. 94 (1972) 5116;
(b) F. Basile, J. Bergner, C. Bombart, B. Rondot, P. Guevel, G. Lorang, Surf. Interface Anal. 30 (2000) 154;
(c) M. Schulze, R. Reissner, M. Lorenz, U. Radke, W. Schnurnberge, Electrochim. Acta 44 (1999) 3969.
[15] H. Kuhlenbeck, G. Odörfer, R. Jaeger, G. Illing, M. Menges, T. Mull, H. Freund, M. Pöhlchen, V. Staemmler, S. Witzel, C. Scharfschwerdt, K. Wennemann, T. Liedtke, M. Neumann, Phys. Rev. B 43 (1999) 1969.
[16] F. Parmigiani, L. Sangaletti, J. Electron Spectrosc. Relat. Phenom. 62 (1993) 141.
[17] P. Lo, W. Tsai, J. Lee, M. Hung, J. Electrochem. Soc. 142 (1995) 91.
[18] P. Swift, Surf. Interface Anal. 4 (1982) 47.
[19] R. Franke, T. Chasse, P. Streubel, A. Meisel, J. Electron. Spectrosc. Relat. Phenom. 56 (1991) 381.
[20] H. Li, W. Wang, H. Chen, J. Deng, J. Non-cryst. Solids 281 (2001) 31.
[21] M. Yu, D. Vitkavage, B. Meyerson, J. Appl. Phys. 59 (1986) 4032.
[22] (a) N. Feldstein, T. Lancsek, J. Electrochem. Soc. 118 (1971) 869;
(b) R. Lukes, Plating 51 (1964) 96.
[23] (a) P. Peeters, G. Hoorn, T. Daenen, A. Kurowski, G. Staikov, Electrochim. Acta 47 (2001) 161;
(b) S. Splinter, R. Rofagha, N. McIntyre, U. Erb, Surf. Interface Anal. 24 (1996) 181;
(c) M. Thube, S. Kulkarni, D. Huerta, A. Nigavekar, Phys. Rev. B 34 (1986) 6874;
(d) S. Lee, Y. Chen, J. Mol. Catal. A: Chem. 152 (2000) 213.
[24] R. Franke, T. Chasse, P. Streubel, A. Meisel, Electron. Spectrosc. Relat. Phenom. J 56 (1991) 381.
[25] T. Morikawa, T. Nakade, M. Yokoi, Y. Fukumoto, C. Iwakura, Electrochim. Acta 42 (1997) 115.
[26] M. Saitou, Y. Okudaira, W. Oshikawa, J. Electrochem. Soc. 150 (2003) C140.
[27] R. Zeller, U. Landau, J. Electrochem. Soc. 139 (1999) 2464.
[28] A. Kurowski, J. Schultze, G. Staikov, Electrochem. Commun. 4 (2002) 565.