Modeling of Nickel Surface State in Electrocatalytic Hypophosphite Oxidation According to On-Line Electrochemical Mass Spectrometry Studies

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Computer simulation of possible distributions of H_{ad} and D_{ad} atoms developed on nickel surface as a result of partial reactions of anodic hypophosphite oxidation and cathodic proton (deuteron) discharge from water respectively was used for modeling of the catalyst surface state according to on-line electrochemical mass spectrometry data. The simpliest lattice-gas model gives a probable qualitative description of the catalyst surface state and allows the genesis of electrocatalytic properties of nickel with the electrode potential to be followed. Location of anodic and cathodic half-reactions at special types of sites was evidenced, leading to formation of non-equilibrium H_2, HD and D_2 mixtures with the lower HD content than that predicted theoretically.

Introduction

Electrochemical Mass Spectrometry (EMS) studies of catalytic hypophosphite oxidation on nickel in D_2O solutions [1] suggest the overall process

$$H_2PO_2^- + D_2O \xrightarrow{Ni} HDPO_3^- + HD\ (H_2,\ HD,\ D_2) \quad (1)$$

to proceed via coupling of anodic (2) and cathodic (3) half-reactions at the catalyst surface

$$H_2PO_2^- + D_2O \xrightarrow{Ni} HDPO_3^- + D^+ + H_{ad} + e \quad (2)$$

$$D^+ + e \xrightarrow{Ni} D_{ad} \quad (3)$$

The classical electrochemical theory of heterogeneous catalytic processes [2–4] presupposes all of the catalyst surface to be equally accessible for both anodic (2) and cathodic (3) half-reactions. Equilibrium mixtures of H_2, HD and D_2 should be formed in this case due to statistical recombination of H_{ad} and D_{ad} atoms randomly developed in half-reactions (2) and (3): e.g., catalytic oxidation of hypophosphite on nickel in D_2O solution under open-circuit conditions should lead to the formation of gas containing equal amounts of hydrogen and deuterium (H/D = 1) with the distribution $H_2:HD:D_2 = 1:2:1$ (the probability of HD molecule formation is twice as high as either H_2 or D_2 [5, 6]). However, location of reactions (2) and (3) at less or more stable sites – microanodes and microcathodes – seems to be probable, taking into account a heterogeneity (both structural and energetic) of the real catalyst surface.

Non-equilibrium mixtures with the ratio $H_2:HD:D_2 = 5:6:7$ were found to be formed in reaction (1) under open-circuit conditions [7]. A spatial separation of anodic (2) and cathodic (3) half-reactions occurring on microanodes and microcathodes respectively was suggested to be responsible for such a composition of the evolving gas. The surface concentration gradient of H_{ad} and D_{ad} atoms along the distance between microanode and microcathode (the model of the linear source) allowed to explain formation of the gas mixtures with $H_2:HD:D_2 = 1:1:1$ similar to that obtained experimentally [7].

Only the final product of the process (1), i.e. molecular hydrogen (H_2, HD and D_2), can be detected by EMS. However, the catalyst microstructure can be reconstructed by the computer simulation since the gas evolved "remembers" it: H_{ad} and D_{ad} atoms serve as peculiar markers of reactions (2) and (3) and thereby define on which site – either anodic or cathodic – they appear. A simplified lattice-gas model [8] has been used in the present study for simulation the microstructure of the nickel catalyst in a wide range of electrode potentials.

Methods

Equipment and Chemicals

The experiments were carried out in the D_2O (D content 99.8 mol%) solution containing (mol l^{-1}): NaH_2PO_2 (anhydrous prepared according to [7]) –0.19; CH_3COONa (anhydrous, p.a.) –0.15; $T = 353 \pm 1$ K; pH = 4.5 was adjusted by adding CD_3COOD (D content 98 mol%). Deuterated chemicals were received from "Isotope" (Russia).

The experimental EMS set-up has been described elsewhere [1]. It consisted of the mass spectrometer MI-1201, a programming potentiostat PI-50-1 and a digital voltmeter Φ-30 (all the equipment from Russia). A 5 µm thick gas permeable Teflon film supported by a glass frit, to withstand the difference in pressure between high vacuum in mass spectrometer and the electrolyte, was used as an inlet system. A teflon membrane has been sputtered in vacuum by metal nickel layer of ca. 0.1 µm thick and geometric area of 1 cm^2 which served as a working electrode. Hydrogen evolving at the electrode could penetrate through the membrane due to the pressure gradient and was analysed mass spectrometrically on-line. Water vapour and other volatiles were trapped by the liquid nitrogen before the gases reached the ion source of the mass spectrometer. Two platinum counter electrodes and $Ag/AgCl/KCl_{sat}$ reference electrode were used (all potentials are referred to the Standard Hydrogen Electrode (SHE)).

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EMS set-up allowed:

i) both analogous and digital recording of the intensities of ion currents H_2^+ ($m/z = 2$), HD^+ ($m/z = 3$) and D_2^+ ($m/z = 4$) to be carried out;

ii) deuterium content in the gas (D mol%) to be found according to the equation:

$$\text{D mol\%} = \frac{D_2^+ + 0.5\,HD^+}{H_2^+ + HD^+ + D_2^+} \cdot 100 \ ; \tag{4}$$

iii) the content (in %) of H_2, HD and D_2 to be calculated:

$$H_2\% = \frac{H_2^+}{H_2^+ + HD^+ + D_2^+} \cdot 100 \ , \tag{5}$$

$$HD\% = \frac{HD^+}{H_2^+ + HD^+ + D_2^+} \cdot 100 \tag{6}$$

and

$$D_2\% = 100 - (H_2\% + HD\%) \ . \tag{7}$$

The mass spectrometer was calibrated against equilibrium mixtures of H_2, HD, and D_2 obtained by the reduction of water vapour of different isotopic composition by uranium metal at 873 K [9] assuming the equilibrium constant (K) for reaction

$$H_2 + D_2 \Leftrightarrow 2HD \tag{8}$$

is 4. An accuracy of mass spectrometric analysis of isotopic hydrogen composition was ±0.5 mol%.

Model and Simulation

Possible distributions of H_{ad} and D_{ad} atoms at the catalyst surface were simulated by a PC. For this the following approximate model has been used: reaction (2) and (3) were supposed to occur at two types of the sites – anodic and cathodic respectively. A two dimensional ideal surface fully covered by H_{ad} and D_{ad} atoms (the so-called lattice-gas [8]) was examined. The following assumptions were made: i) the possibility of recombination of any atom with every nearest neighbour (n-n) is equal, i.e. the distance between each atom is the same (hexagonal packing of the elements); ii) interaction forces between H-H, H-D and D-D atoms are equal; iii) the rate of irreversible simultaneous dimerization of the atoms is much higher than their diffusion rate – next nearest neighbour (n-n-n) interactions were not taken into acccount.

For the computer simulation a two dimensional matrix of 60 × 60 with a hexagonal packing of elements was randomly (using a randomize procedure) filled by 1 and 0 (corresponding to D_{ad} and H_{ad} atoms formed at the sites where appropriate reactions took place) with a deuterium content equal to that detected experimentally. A numerical value of the sum of n-n elements (0 to 6) was used to find the bility of H_2, HD, and D_2 formation calculated for e ment. For example, if the element under study was and the numerical value of the sum of n-n elements the probability of HD formation was 1 while for H_2 it was 0. Alternatively, the probability of D_2 formati the same element was 1 if the numerical value of t of n-n elements was 6, etc. The content of H_2, HD, was calculated in the central part of the matrix of elements to avoid edge effects during both simulta irreversible recombination of the elements into dime rearrangements of the matrix. The validity of the ca tion procedure was checked for the matrix randomly by H_{ad} and D_{ad} at D mol% = 50.17: a calculated $H_2\% : HD\% : D_2\%$ was found to be 25.02 : 49.61 : 25.

In the case if calculated H_2, HD, and D_2 compositi not fitted that observed experimentally, the distributi elements in the matrix was rearranged for those ele which had no more than one n-n of the same kind. If was no n-n of the same kind the central element could domly exchange with any of the six n-n with the proba of 0.5. And if the number of the n-n of the same kin equal to one, two rearrangements for the central ele were possible with the same probability. Such rearr ments led to formation of clusters consisting of the ele of the same kind. They were repeated until the calcu $H_2\%$, HD% and $D_2\%$ fitted the experimental values accuracy ±1%.

Results and Discussion

The data of Fig. 1 indicate the content of H_2, HD, D_2 in equilibrium gas mixtures obtained by the reduc

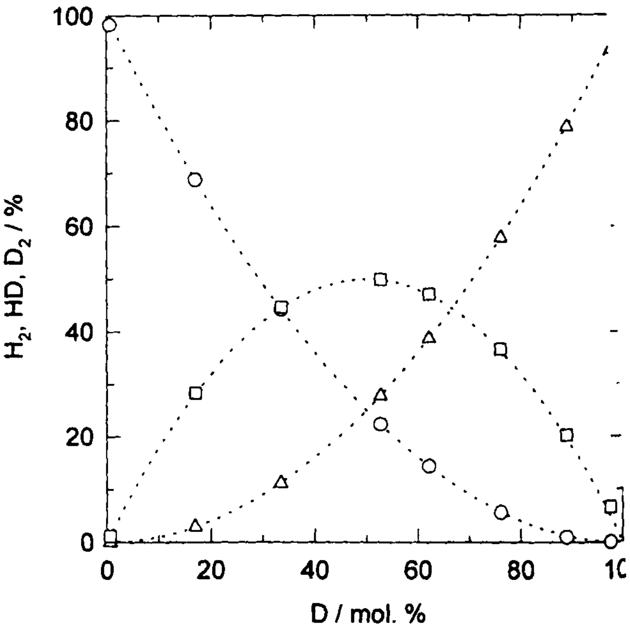

Fig. 1
Dependence of H_2 (○), HD (□) and D_2 (△) distribution on isotopic composition of the gas obtained by reduction of water spe mens on uranium at 873 K according to mass spectrometric da Dotted lines – equilibrium values

of water vapour with different deuterium content on uranium metal to be in a good agreement with that calculated according to the equation

$$K = \frac{[HD]^2}{[H_2]\,[D_2]} = 4 \qquad (9)$$

Non-equilibrium mixtures of H_2, HD, and D_2 with a lower HD content than that predicted by the Eq. (9) were found by EMS in the course of catalytic hypophosphite oxidation on nickel in D_2O solutions under open-circuit conditions (Figs. 2 and 3) as well as in a wide range of electrode potentials (Figs. 4 and 5).

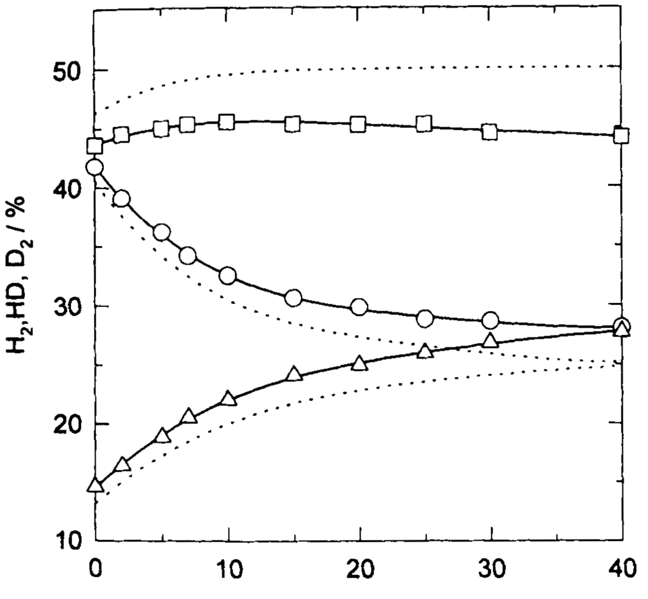

Fig. 2
Dependence of H_2 (○), HD (□) and D_2 (△) distribution in the gas evolving during catalytic hypophosphite oxidation on nickel under open-circuit conditions on reaction time according to EMS data. Dotted lines – equilibrium values. The solution contained (mol l^{-1}): NaH_2PO_2 – 0.19; CH_3COONa – 0.15. Solvent – D_2O; pH = 4.5 (adjusted by adding CD_3COOD); $T = 353$ K

The deviations of H_2%, HD% and D_2% from equilibrium values increase with time in the absence of the external current (Fig. 2), though deuterium content in the evolving gas reaches 50 mol% after ca. 40 min of catalytic hypophosphite oxidation on nickel (Fig. 3) in accordance with reaction (1). The reason of a lower deuterium content at the early stages of the reaction under open-circuit conditions could be explained by reduction of nickel oxy-species at the surface by hypophosphite as discussed in [1].

It should be noted that the ratio in the evolving gas obtained after 40 min of hypophosphite catalytic oxidation on nickel under open-circuit conditions differs from that found in [7]: larger deviations from equilibrium values were found in the latter case (H_2:HD:D_2≈5:6:7). Apparently, this might be caused by the difference in catalyst preparation in

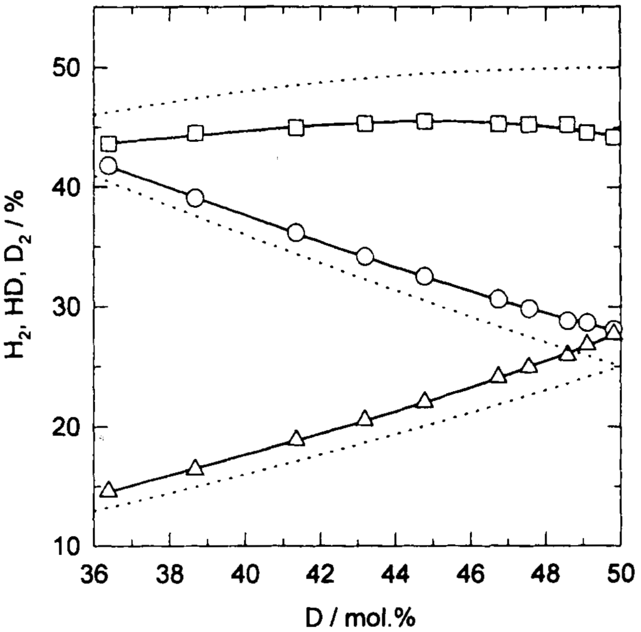

Fig. 3
Dependence of H_2 (○), HD (□) and D_2 (△) distribution in the gas evolving during catalytic hypophosphite oxidation on nickel under open-circuit conditions on the isotopic composition of the gas according to EMS data. Dotted lines – equilibrium values. Solution composition the same as for Fig. 2

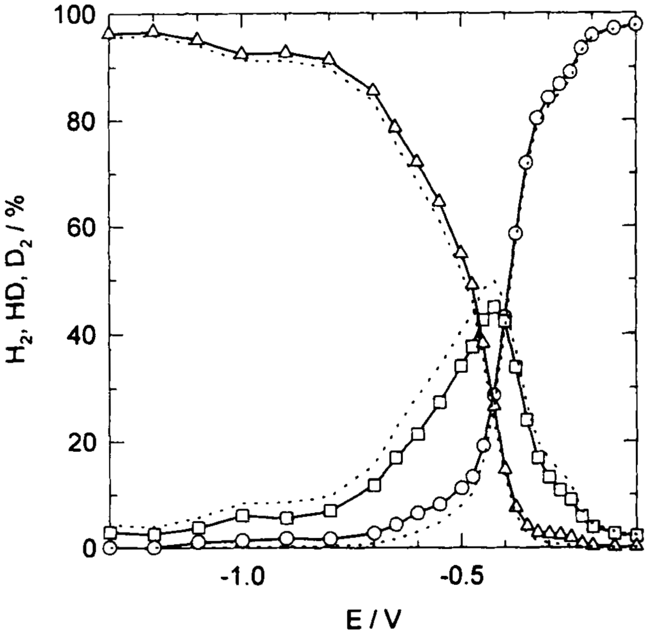

Fig. 4
Dependence of H_2 (○), HD (□) and D_2 (△) distribution in the evolving gas on nickel electrode potential according to EMS data. Dotted lines – equilibrium values. Solution composition the same as for Fig. 2

the present work and in [7] – recent electrochemical studies on nickel single crystals demonstrated anodic oxidation of hypophosphite to be structure-sensitive [10, 11]. On the other hand, on-line EMS analysis of the evolving gas used in the present study differs from the mass spectrometric analysis of the evolved gas samples in [7] – nickel is known

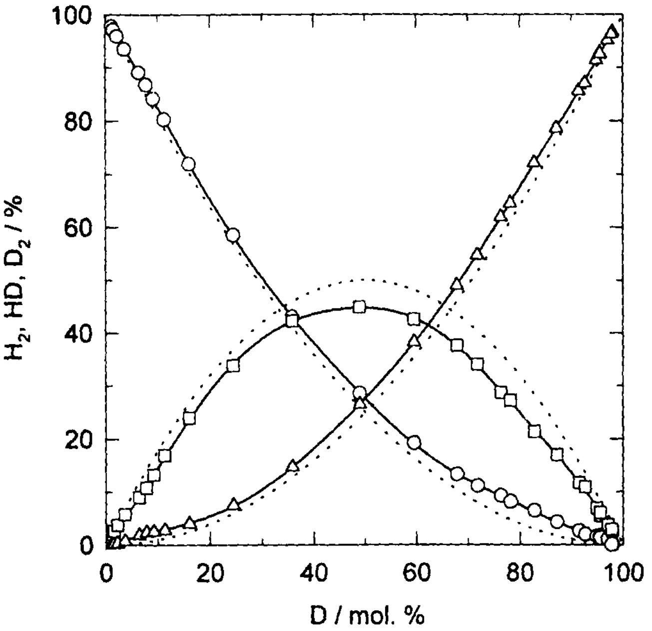

Fig. 5
Dependence of H_2 (○), HD (□) and D_2 (△) distribution on the isotopic composition of the evolving gas on nickel electrode in the potential range from -0.1 to -1.3 V according to EMS data. Dotted lines – equilibrium values. Solution composition the same as for Fig. 2

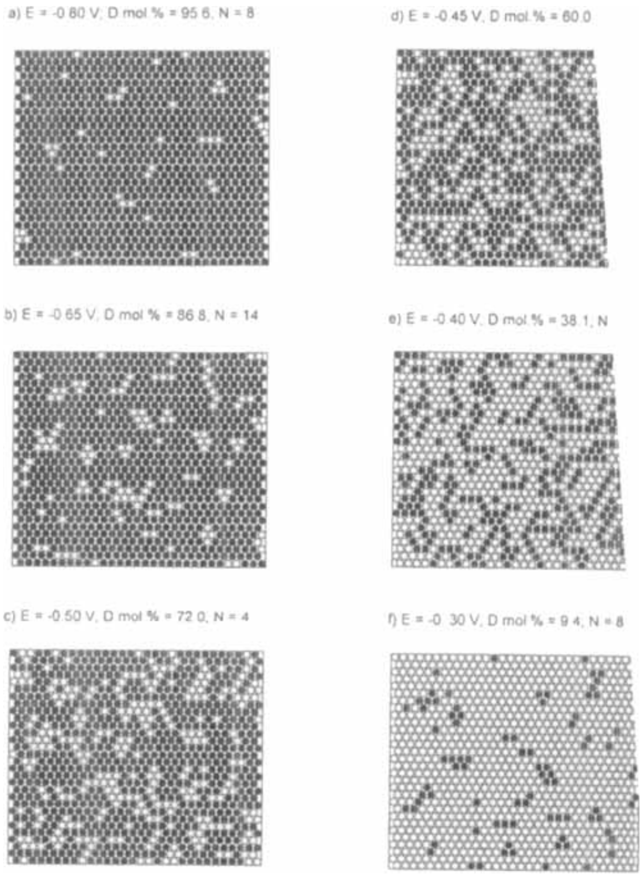

Fig. 6
Some possible distributions of H_{ad} (○) and D_{ad} (●) atoms in the lattice-gas on the nickel surface developed in reactions (2) and (3) respectively leading to formation of gas mixtures with H_2, HD, and D_2 content equal to that detected by EMS (Figs. 4 and 5). *N* – number of transformations of the matrix starting from random distribution

to catalyse equilibration according to reaction (8) [5, 6]. Nevertheless, formation of gaseous mixtures with the lower HD content than that predicted by the Eq. (9) is found under open-circuit conditions in both cases.

The change of D mol% in the evolving gas on nickel electrode potential in hypophosphite solution using D_2O as a solvent (from 90–95 mol% at -0.8 V and more negative potentials to about 5 mol% at -0.1 V) is caused mostly by the exponential potential dependence of the rate of partial reaction (3) as evidenced quantitatively by EMS [1]. Plots of H_2%, HD% and D_2% content in the evolving gas vs. the electrode potential (Fig. 4) or D mol% (Fig. 5) give a qualitative description of the system and demonstrate clearly deviations from equilibrium values.

The greatest deviations of H_2%, HD% and D_2% from equilibrium values occur at the potentials more negative than an open-circuit potential (-0.4 V) up to ca. -1.0 V and at more positive potentials of some -0.3 V (Fig. 4). At the negative limit of -1.3 V as well as at the positive limit of -0.1 V the composition of H_2-HD-D_2 mixtures reaches the equilibrium values. Fig. 5 demonstrates corresponding deviations of H_2%, HD% and D_2% from equilibrium values in the whole range of deuterium content in the evolving gas.

The lattice-gas model allows the catalyst microstructure to be simulated under open-circuit conditions as well as at various potentials from EMS data (Fig. 6). The deviations from equilibrium values (Figs. 3 and 5) suggest the areas covered by atoms of a certain kind to exist at the catalyst surface. Such catalytically active regions as microanodes (white sections), where reaction (2) occurs, and microcathodes (black sections), where reaction (3) proceeds, can be seen on the transformed matrix at -0.4 V (Fig. 6e) which corresponds to the "snapshot" of the catalyst surface at the initial stages of hypophosphite oxidation under open-circuit conditions (Figs. 2 and 3).

A potential shift to more negative values leads to a gradual increase in the number and the area of microcathodes due to increase in the number of electrons arriving from the external circuit and participating in reaction (3), and causes fragmentation and diminishing of catalytically active regions (Figs. 6a–d). This corresponds to the increase in the rate of reaction (3) and some decrease in the rate of reaction (2) at more negative potentials as found by EMS [1]. The catalytically active areas (microanodes) are particularly distinct on the electrode surface at cathodic potentials from -0.65 to -0.8 V (Figs. 6a and b) where deviations of H_2%, HD% and D_2% from equilibrium values are the greatest (Figs. 4 and 5). At potentials more negative as -1.2 V equilibriums H_2-HD-D_2 mixtures are formed and the corresponding distribution of H_{ad} and D_{ad} atoms in the matrix becomes random. The shift of the electrode potential to more positive values than the open-circuit potential suppresses reaction (3) and causes the number as well as the size of microcathodes to reduce (Fig. 6f) – the external circuit captures a part of electrons generated in anodic half-reaction (2) (a corresponding anodic current as well as decrease in the rate of reaction (3) and some increase in the rate of reaction (2) is found at more positive potentials [1]). Finally, this results in formation of equilibrium H_2-HD-D_2 mixtures and random distribution of H_{ad} and D_{ad} atoms at -0.2 V.

Conclusions

Formation of non equilibrium mixtures of H_2, HD, and D_2, with a lower HD content than that predicted theoretically by the Eq. (9), in the course of catalytic oxidation of hypophosphite under open-circuit conditions and in the wide range of electrode potentials (-0.2 to -1.2 V) detected by EMS, suggests such sites, covered by atoms of a certain kind (H_{ad} and D_{ad} respectively), as microanodes and microcathodes to exist at the catalyst surface.

The simpliest lattice-gas model approach gives a probable qualitative description of the catalyst surface state (quantitative EMS data in the same system are discussed elsewhere [1]). It confirms the catalytically active areas to exist on the nickel surface and allows the genesis of the catalyst microstructure with the electrode potential to be followed. The data obtained support the electrochemical mechanism of catalytic hypophosphite oxidation on nickel – the key reaction of electroless nickel plating [12].

References

[1] Z. Jusys, J. Liaukonis, and A. Vaškelis, J. Electroanal. Chem. *307*, 87 (1991).
[2] C. Wagner and W. Traud, Z. Electrochem. *44*, 391 (1938).
[3] M. Spiro, J. Chem. Soc. Faraday Trans. 1 *75*, 1507 (1979).
[4] J.E.A.M. van den Meerakker, J. Appl. Electrochem. *11*, 395 (1981).
[5] K. Christmann, Surf. Sci. Rep. *9*, 33 (1988).
[6] G.C. Bond, in: Catalysis by Metals, pp. 1567–1568, Academic Press, London New York, 1962.
[7] J.H. Marshall, J. Electrochem. Soc. *130*, 369 (1983).
[8] H. Stettin, H.-J. Mögel, and C.M. Care, Ber. Bunsenges. Phys. Chem. *100*, 20 (1996).
[9] G. Nief and R. Botter, in: Advances in Mass Spectroscopy, Chap. 37, ed. by J.D. Waldron, Pergamon Press, London, 1959.
[10] L.M. Abrantes, M.C. Oliveira, J.P. Belier, and J. Lecoeur, Electrochim. Acta *39*, 1915 (1994).
[11] L.M. Abrantes and M.C. Oliveira, Electrochim. Acta *41*, 1703 (1996).
[12] Z. Jusys, J. Liaukonis, and A. Vaškelis, J. Electroanal. Chem. *325*, 247 (1992).

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