

Available online at www.sciencedirect.com



ELECTROCHIMICA

Electrochimica Acta 52 (2007) 6237-6247

www.elsevier.com/locate/electacta

Nitrate and nitrite electrocatalytic reduction on Rh-modified pyrolytic graphite electrodes

Oleg Brylev^{a,b}, Mathieu Sarrazin^{a,b}, Lionel Roué^b, Daniel Bélanger^{a,*}

^a Département de Chimie, Université du Québec à Montréal, C.P. 8888, Succursale Centre-Ville, Montréal, Québec, Canada H3C 3P8 ^b INRS-Energie, Matériaux et Télécommunications, 1650 Blvd Lionel Boulet, C.P. 1020, Varennes, Québec, Canada J3X 1S2

> Received 15 November 2006; received in revised form 20 March 2007; accepted 31 March 2007 Available online 5 April 2007

Abstract

The electrochemical reduction of nitrate and nitrite anions was investigated on Rh-modified pyrolytic graphite electrodes prepared by potentiostatic electrodeposition with the use of a double-pulse technique. Several important parameters (pH, temperature and composition of electrolytic medium, electrolysis potential) were varied. Only ammonia and nitrite ions were detected among NO_3^- reduction products, while NO_2^- ions are straightforwardly reduced to ammonia. The experimental data (CV measurements and the results of electrolyses) clearly show that Rh/graphite electrodes are much more efficient for NO_2^- reduction than for that of NO_3^- at room temperature which was confirmed by the determination of rate constants of corresponding reactions and the activation energy of NO_2^- reduction. The influence of carboxylate anions and tetraalkylammonium cations on the electrocatalytic activity of Rh/graphite electrodes was investigated and the inhibiting effect of HCOO⁻ anions on hydrogen evolution reaction and nitrate reduction was demonstrated.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Rhodium; Double-pulse electrodeposition; Nitrate reduction; Nitrite reduction; Electrocatalysis

1. Introduction

Intensive use of fertilizers in agriculture and nitrates in some industrial sectors causes a severe nitrate pollution of water sources and industrial sites [1]. Such a contamination can result in a high risk for public health causing bladder and ovary cancers [2–5]. Various methods such as biological, physicochemical and chemical have been proposed so far for the removal of nitrates from potable water and wastewaters [6–11]. However, they possess various disadvantages, such as a low NO_3^- destruction rate, the formation of toxic byproducts and the production of secondary brine wastes [12].

The electrochemical methods of nitrate removal have been intensively studied for the last three decades [13–16]. Several ways of NO_3^- electrocatalytic reduction are known (for example, the addition of electrocatalytically active ions to the treated solution [17], immobilization of the catalyst at the cathode

surface [18] and electrocatalytic reduction on solid electrodes [19–21]). Concerning the last case, numerous materials have been tested including Cu [22], Pt [23], Pd [24], Ru [20], Ir [25] and Rh [26–28]. The last one demonstrates the highest activity for NO_3^- reduction among transition and coinage metals [20].

In our previous works, we have reported the properties of Rh-modified pyrolytic graphite electrodes obtained by potentiostatic electrodeposition and their catalytic activity towards nitrate reduction in neutral medium [29,30]. It was shown that the highest specific catalytic activity can be achieved using the double-pulse electrodeposition technique, which is based on the application of a short nucleation potential pulse (typically <200 ms) and a subsequent growth pulse at much more positive potential [31]. The application of nucleation potential pulse allows to obtain an enhanced surface coverage in comparison with usual potentiostatic deposition and to decrease both the mean Rh particle size from 70 to 40 nm and the surfaceto-volume ratio $(4.0 \times 10^6 \text{ cm}^2 \text{ cm}^{-3})$, which is beneficial for catalytic applications [30]. Then, the optimal conditions (i.e. the potential and duration of both pulses) providing the highest values of specific catalytic activity were determined [30]. Potentiostatic and galvanostatic electrolyses were performed

^{*} Corresponding author. Tel.: +1 514 987 3000x3909; fax: +1 514 987 4054. *E-mail addresses:* brylev@inorg.chem.msu.ru (O. Brylev),

roue@emt.inrs.ca (L. Roué), belanger.daniel@uqam.ca (D. Bélanger).

^{0013-4686/\$ –} see front matter © 2007 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2007.03.072

at Rh-modified graphite electrodes to determine the qualitative and quantitative composition of nitrate electrochemical reduction products in neutral medium. In all the cases, only NO_2^- , NH_3 and H_2 were detected [30]. It was shown that the Rh electrodeposition parameters (i.e. growth pulse potential, duration of nucleation and growth pulses) did not influence the composition of formed products, indicating the absence of preferential Rh crystallographic orientation [30].

It is known that different factors such as pH and temperature of electrolytic medium, electrolysis parameters (applied current or potential) can affect the products of nitrate electrocatalytic reduction [26]. The influence of co-existing species in electrolytic medium is also crucial, especially for industrial applications [32–34]. Accordingly, the nitrate electroreduction is an extremely complex process that can be partially described by the reactions listed below (E_0 = potential versus normal hydrogen electrode (NHE)):

• In acid medium [35]:

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O, \quad E_0 = 0.83 V$$
 (1)
 $NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O, \quad E_0 = 0.87 V$ (2)

In alkaline medium the same reactions can be written as follows [35]:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-, \quad E_0 = 0.01 V$$
(3)

$$NO_2^- + H_2O + e^- \rightarrow NO + 2OH^-, \quad E_0 = 0.46 V$$
 (4)

$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^-, \quad E_0 = -0.12 V$$
(5)

The hydrogen evolution reaction (HER) competes with the above-mentioned reactions:

• In acid medium:

$$2\mathrm{H}^+ + 2\mathrm{e}^- \to \mathrm{H}_2, \quad E_0 = 0 \,\mathrm{V} \tag{6}$$

• In alkaline medium:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-, \quad E_0 = -0.83 V$$
 (7)

Although the HER (Eqs. (6)–(7)) occurs at potentials more negative than those of nitrate and nitrite reductions (Eqs. (1)–(5)), the slow kinetics of NO_3^- and NO_2^- reductions may result in the partial charge consumption for gaseous hydrogen formation [36]. It should be noted that the hydrogen adsorption blocks the one of NO_3^- at the electrode surface hindering the nitrate reduction [19]. Concerning the adsorption of different species on Rh electrode, the value of potential of zero charge (PZC) should be taken into account. In 0.01N Na₂SO₄ (pH 2.5) the PZC is 0.02 V versus NHE and linearly decreases to -0.52 V at pH 12.7 [37].

The reaction products of nitrate reduction on Rh electrode in $3 \text{ M HNO}_3 + 0.5 \text{ M H}_2 \text{SO}_4$ were followed by differential electrochemical mass spectroscopy and in situ FTIR measurements [26]. It has been proposed that the nitrate reduction starts with partial N-O bond dissociation and partial N-H bond formation generating NO and N₂O. At potentials lower than 0.2 V versus reversible hydrogen electrode (RHE) the reaction proceeds forming dissolved NH4⁺. For potentials lower than 0 V, the reduction continues via a multiple pathway reaction leading to the production of N₂, NH₂OH and N₂H₂. The catalytic activity of Rh electrode was also investigated in acidic 0.1 M nitrate solution [20]. No gaseous products were found, indicating that only NH₂OH and NH₄⁺ were formed. Hayden and coworkers have shown that the prolonged activation of Rh surface in $0.3 \text{ M KNO}_3 + 0.2 \text{ M KOH} + 2 \text{ M KCl}$ aqueous solution at 70 °C resulted in the decrease in the activation energy of nitrate reduction and the preferential formation of N_2 [38]. The activated Rh electrode demonstrated a later onset of HER with respect to the non-activated ones, thus facilitating the nitrogen formation. However, no details concerning the changes in surface composition and morphology were reported to explain such a result [38].

In the present study, we report the detailed analysis of nitrate and nitrite reduction on Rh/graphite electrodes investigated by cycling voltammetry (CV), galvanostatic and potentiostatic electrolyses performed under variable operating conditions (i.e. pH, temperature and composition of the electrolytic solution) with the use of various analytical techniques.

2. Experimental

2.1. Preparation of Rh-modified pyrolytic graphite electrodes

The Rh electrodeposition on pyrolytic graphite substrate was performed at room temperature under quiescent conditions in a three-electrode, one-compartment electrochemical cell consisting of pyrolytic graphite (working electrode), Pt mesh (counter electrode) and Ag/AgCl (3 M KCl) as a reference electrode. An aqueous solution containing 10 mM Na₃RhCl₆ was used as a rhodium source. In the case of double-pulse electrodeposition, a short potential nucleation pulse of -800 mV versus Ag/AgCl was applied for 20 or 100 ms, followed by a growth pulse of different duration. A more detailed description of Rh/graphite electrode preparation can be found elsewhere [29,30]. Further in the text, all the nucleation and growth pulse potentials will be referred to the Ag/AgCl electrode.

2.2. Investigation of NO_3^- and NO_2^- reduction on *Rh/graphite electrodes*

The electrochemical reduction of NO_x^- (x = 2 or 3) was studied employing the electrochemical cell configuration used for Rh electrodeposition. All the aqueous solutions were prepared using ultrapure water (18 M Ω , obtained from a Sybron/Barnstead Nanopure II system). Firstly, Rh/graphite electrodes were tested by cycling voltammetry for the HER in 1 M NaCl solution and then subsequently in the presence of NO₃⁻ and NO₂⁻ anions, so

the contributions from hydrogen evolution and nitrite or nitrate reduction can be qualitatively split up. The solutions were not preliminary deaerated and this fact did not alter the shape of obtained CV curves (data not shown) as it has been observed before [38]. The potential limits for the CV characterization were from -0.7 to -1.5 V versus SCE. We noted that upon cycling the current slightly increased in the NO_x⁻ reduction region and stabilized after the fifth cycle. All charge and current densities are quoted in terms of apparent geometrical area of the substrate graphite electrode, unless otherwise stated.

In order to establish and to quantify the products of NO_x^{-1} reduction on Rh/graphite electrodes, the electrolyses were performed in a two-compartment cell either in potentiostatic or galvanostatic mode under mechanical stirring. A detailed scheme of the experimental setup is given elsewhere [30]. The compartments of the cell are separated by a Nafion[®] 117 membrane. The cathodic compartment contains a working Rh/graphite electrode and a reference electrode immersed in nitrite or nitrate-containing solutions having various pH values. As reference electrodes, either SCE (pH<8) or Hg/HgO (pH 14) mounted in a Luggin capillary were used. The anodic compartment includes a Pt grid (counter electrode) plunged into 1 M Na₂SO₄ or 1 M NaOH, when the initial pH value of the cathodic compartment solution is inferior to 8 or equal to 14, respectively. In this case, all the solutions were purged with argon for 30 min. A Solartron 1470 potentiostat/galvanostat interfaced with a PC and the Corrware 2 and CorrView 2 software (Scribner Associates) was employed for the electrochemical experiments. For the galvanostatic electrolyses the current was normalized to the Rh deposit surface area measured by well-known procedures [39], and the current density was adjusted to 4 mA cm^{-2} . Further in the text, all the potentials recorded in course of CV measurements and electrolysis experiments will be referred to SCE.

Solution samples were regularly taken for the quantitative determination of NO₃⁻, NO₂⁻, NH₂OH and NH₄⁺/NH₃(aq). The NO₃⁻ concentration was evaluated by UV-vis spectroscopy (Hewlett Packard 8452A) by measuring the absorbance at 220 nm [40], while NH₂OH was quantified by the absorbance at 710 nm [41]. The content of nitrite anions was evaluated from the absorbance at 544 nm, due to the diazonium complex formed by reaction involving NO2⁻, sulfanilamide (Aldrich) and N-(1-naphtyl)-ethylenediamine dihydrochloride (98%, Aldrich) [40]. NH_4^+/NH_3 concentration in solution was evaluated by Nessler's classic method described elsewhere [40]. Gas samples were regularly taken during the electrolysis and injected into a gas chromatograph (Varian 3000, molecular sieve 5 Å and $200 \text{ cm} \times 0.3 \text{ cm}$). Calibrating curves were recorded using gas mixtures with known composition (Praxair) to quantify the formation of H₂, N₂ and N₂O [42]. Then the Rh/graphite electrode performance for nitrate reduction was quantitatively estimated using the following criteria:

• nitrate destruction degree (%) corresponding to the duration *t* of the electrolysis and defined as $([NO_3^-]_0 - [NO_3^-]_t) \times 100/[NO_3^-]_0$, where $[NO_3^-]_0$ and $[NO_3^-]_t$ are the NO₃⁻ molar concentrations at the beginning and at the instant *t* of the electrolysis, respectively;

- current efficiency (or faradaic yield) CE(*i*) (%) for the formation of product *i* defined as (n_i × m_i × F) × 100/q, where n_i is the number of electrons involved in the reaction giving a product *i* (*i*=NH₃, NO₂⁻, N₂O and H₂), m_i is the quantity of the formed species *i* (mol), *q* is the total electrical charge consumed in course of the electrolysis and *F* is the Faraday constant (96,485 C mol⁻¹);
- selectivity S(j) (%) of nitrate reduction to a nitrogencontaining product *j* defined as $(n_j \times m_j \times F) \times 100/(q - q_{H_2})$, where q_{H_2} is the charge consumed for hydrogen formation.

3. Results and discussion

3.1. Nitrate and nitrite reduction on Rh/graphite electrodes

CV curves recorded for the same Rh/graphite electrode in 1 M NaCl, 1 M NaCl+0.1 M NaNO₃ and 1 M NaCl+0.1 M NaNO₂ aqueous solutions are represented in Fig. 1. Concerning a 1 M NaCl solution, a slight increase in current density at -0.75 V for the sweep in the negative potential direction is due to the formation of H_{ads} layer as it has been previously reported for alkaline solution [43] and the hydrogen evolution begins at approximately -1.0 V. In the case of 1 M NaCl + 0.1 M NaNO₃ solution, the onset of the increase in current density occurs at more positive potentials pointing to the beginning of NO_3^- reduction whose peak maximum is observed at -0.90 V as previously reported [30] (Fig. 1, dotted curve). Concerning the nitrite containing solution, an ill-defined peak or a shoulder on the cathodic wave corresponding to the NO2⁻ reduction is observed at -1.25 V (Fig. 1, dashed curve). At more negative potentials, the following increase in current density is related to the competitive HER occurring at Rh surface.

To compare the catalytic efficiency of Rh/graphite electrode for nitrite and nitrate reduction, the difference between the corresponding current values and 1 M NaCl at the same potential (e.g. at -1.25 and -0.90 V) might be taken and it is higher for



Fig. 1. CV curves (fifth cycle) of Rh/graphite electrode (no nucleation pulse, growth pulse potential of -352 mV, growth pulse duration of 480 s) in 1 M NaCl, 1 M NaCl+0.1 M NaNO₃ and 1 M NaCl+0.1 M NaNO₂ solutions. Scan rate 20 mV s⁻¹.

the 1 M NaCl + 0.1 M NaNO₂ solution (20.7 and 12.9 mA cm⁻², respectively). In addition, for nitrite-containing solution a significant increase in current density is observed from -0.9 V on the cathodic scan with respect to 1 M NaCl and 1 M NaCl + 0.1 M NaNO₃ (Fig. 1). These facts point to a higher catalytic activity of the Rh/graphite electrodes towards nitrite reduction than for the nitrate one.

The CV results allow a mechanism for the NO_x^- reduction on Rh/graphite electrodes to be suggested. It is known that on a Pt electrode a competitive adsorption between H₂O (resulting in H_{ads}), NO₃⁻ and its reduction intermediate products takes place [19]. Hence, a similar behavior might be also found in the case of Rh/graphite electrodes. However, the PZC for Rh is more negative than for Pt suggesting a stronger anion adsorption [37]. When H_{ads} and NO₃⁻_{ads} begin to be formed at -0.75 V, a large part of the surface is covered by adsorbed hydrogen since H is more easily adsorbed [19]. Then the NO₃⁻ reduction starts at -0.75 V and a competition between H and NO₃⁻ takes place to occupy free adsorption sites. At more negative potentials when H is more strongly adsorbed (as all the measurements were performed below the PZC of Rh), it occupies a more significant fraction of liberated sites thus blocking nitrate adsorption. This results in a decrease of the current density (from -0.9 to -1.04 V) since the nitrate reduction (even to nitrite) requires more electrons than the formation of H_{ads} (Eqs. (1) and (3)). At more negative potentials, the electrochemical NO₃⁻ reduction might be suppressed because the current densities for 1 M NaCl and 1 M NaCl + 0.1 M NaNO₃ are the same and only gaseous hydrogen is electrochemically produced. Concerning 1 M NaCl+0.1 M NaNO₂ solution, the onsets of nitrite and nitrate adsorption occur at the same potential but nitrite anions are more strongly adsorbed on Rh surface, thus from -0.9 to -1.4 V the current density values are higher (Fig. 1) implying that more electrons are necessary for nitrite reduction (e.g. nitrite reduction to ammonia requires six electrons) and the NO₂⁻ reduction rate is higher. At potentials more negative than -1.4 V the current densities are the same for all the three solutions. This might mean that only H₂ is electrochemically generated in this potential range and since nitrate and nitrite anions are reduced during electrolyses at this potential, NO₃⁻ and NO₂⁻ would be chemically reduced by hydrogen in statu nascendi.

The activation energy (ΔE_a) of NO_x⁻ reduction, might give a hint about the reaction mechanism. In order to determine ΔE_a value for NO₂⁻ reduction reaction, the current densities at the potentials of -0.89 and -1.04 V were measured as a function of temperature in the range from 3 to 70 °C. At -0.89 V, the impact of the competitive reaction (i.e. HER) is negligible, while at -1.04 V it is more important (Fig. 1, dashed curve). For both cases, the variation of current density versus reciprocal absolute temperature is represented in Fig. 2 and ΔE_a is calculated using the following equation:

$$j = j_{\infty} \exp\left(-\frac{\Delta E_a}{RT}\right) \tag{8}$$

where j is the current density at a given potential, j_{∞} the preexponential term (i.e. j limit when T tends to the infinity), R



Fig. 2. Arrhenius plots for nitrite reduction current density at -0.89 (**I**) and -1.04 V (**O**) vs. SCE on a Rh/graphite electrode (nucleation pulse of 20 ms, growth pulse potential of -232 mV, growth pulse duration of 120 s) in 1 M NaCl + 1 M NaNO₂ solution.

the ideal gas constant $(8.314 \text{ J mol}^{-1} \text{ K}^{-1})$ and *T* is the absolute temperature.

Concerning the NO₃⁻ reduction on Rh/graphite electrodes, at -0.89 and -1.04 V, ΔE_a was found to be equal to 32 kJ mol⁻¹ in the same temperature range [30]. The competitive HER does not influence the activation energy of the nitrate reduction reaction significantly in this potential range as it has been already observed [38]. But in the case of NO_2^- reduction, one can observe two straight lines for the above-mentioned potential values (Fig. 2). Above 45 °C, the activation energy increases from 18 to 70 kJ mol⁻¹, while ΔE_a of nitrate reduction remains 32 kJ mol⁻¹ [30]. The j_{∞} value for NO₂⁻ reduction increases from 2.5×10^4 (T < 45 °C) to 2×10^{13} mA cm⁻² (T > 45 °C), which corresponds to a general trend of simultaneous enhancement of j_{∞} and ΔE_a [38]. It has been reported that activation energies greater than 80 kJ mol⁻¹ are considered typical of chemical reaction steps, such as bond breaking, whereas ΔE_a values lower than 20 kJ mol⁻¹ point to diffusion controlled reaction [44]. Hence, indeed the observed temperature dependence is likely to be associated with the rate-determining step of NO₂⁻ reduction reaction at Rh surface. The measurements were performed for the Rh/graphite electrodes obtained under different conditions (i.e. nucleation and growth pulse potentials and durations), and similar results are obtained. To the best of our knowledge, there is no report of the temperature dependence of nitrite reduction on Rh in any medium. Lower ΔE_a values at room temperature confirm that Rh is a more efficient catalyst for nitrite reduction than for the nitrate one.

3.2. Kinetics of nitrate reduction on Rh/graphite electrodes

According to above-mentioned issues, in neutral medium the NO_2^- reduction on the investigated electrodes occurs faster than that of NO_3^- . Hence, one can suppose that in this case the



Fig. 3. Variation of the concentration of (\blacksquare) nitrate, (\bigcirc) nitrite and (\blacktriangle) ammonia with time during the galvanostatic electrolysis of 1 M NaCl + 1 M NaNO₃ solution on a Rh/graphite electrode (nucleation pulse of 100 ms, growth pulse potential of -232 mV, growth pulse duration of 60 s). Electrolysis current density is 4 mA cm⁻² (normalized to the Rh deposit surface area).

rate-determining step of nitrate reduction is their transformation into nitrite ions. In order to quantitatively prove this statement, prolonged galvanostatic electrolyses of $1 \text{ M NaCl} + 1 \text{ M NaNO}_3$ solution were performed, and the rate constants of NO₃⁻ reduction steps were determined.

Fig. 3 shows the variations of nitrate, nitrite ions and ammonia concentrations with the electrolysis duration. The concentration of NO_3^- diminishes progressively, while that of NO_2^- increases until 42 h and then decreases. A similar shape of such curves was reported for Pb [14], Cu [45] and bronze [46], which indicate that the nitrate reduction on Rh/graphite electrodes also occurs via a consecutive-reaction mechanism [47]. It can be described as follows:

 $NO_3^{-} \xrightarrow{k_1} NO_2^{-} \xrightarrow{k_2} NH_3$

Thus, the corresponding differential equations are:

$$\frac{d[NO_3^{-}]}{dt} = -k_1[NO_3^{-}]$$
(9)

$$\frac{d[NO_2^{-}]}{dt} = k_1[NO_3^{-}] - k_2[NO_2^{-}]$$
(10)

The solution of Eq. (9) is:

$$[NO_3^-]_t = [NO_3^-]_0 e^{-k_1 t}$$
(11)

Thus, the nitrate concentration follows the first-order exponential decay and in logarithmic coordinates its variation with electrolysis time defines a straight line, whose slope allows $k_1 = 2.6(\pm 0.1) \times 10^{-6} \text{ s}^{-1}$ to be calculated (Fig. 4). The effect of pH value on the nitrate destruction rate will be discussed below.

Eq. (10) is a linear differential equation, whose solution can be written as follows taking account of the initial conditions (i.e.



Fig. 4. Variation of the nitrate concentration with time during the galvanostatic electrolysis of 1 M NaCl + 1 M NaNO₃ solution on a Rh/graphite electrode (nucleation pulse of 100 ms, growth pulse potential of -232 mV, growth pulse duration of 60 s). Electrolysis current density is 4 mA cm⁻² (normalized to the Rh deposit surface area).

when
$$t = 0$$
, $[NO_2^-] = 0$:
 $[NO_2^-]_t = k_1 [NO_3^-]_0 \frac{e^{-k_1 t} - e^{-k_2 t}}{k_2 - k_1}$
(12)

Taking account of previously obtained k_1 value for 1 M NaCl+1 M NaNO₃ solution (Fig. 4), the fitting of the experimental data with Eq. (12) is shown in Fig. 5. The k_2 value is $2(\pm 0.1) \times 10^{-5} \text{ s}^{-1}$, which is eight times higher than k_1 for the reduction of nitrate to nitrite. This confirms a good ability of rhodium for nitrite reduction and validates the CV results and the determination of ΔE_a values. In contrast, the NO₃⁻ reduction on a Sn₈₅Cu₁₅ electrode in 0.1 M K₂SO₄ + 0.05 M KNO₃



Fig. 5. Variation of the nitrite concentration with time during the galvanostatic electrolysis of 1 M NaCl + 1 M NaNO₃ solution on a Rh/graphite electrode (nucleation pulse of 100 ms, growth pulse potential of -232 mV, growth pulse duration of 60 s). Electrolysis current density is 4 mA cm⁻² (normalized to the Rh deposit surface area).



Fig. 6. (a) Current efficiency (CE) of H₂ formation on a Rh/graphite electrode (nucleation pulse duration of 100 ms, growth pulse potential of -232 mV, growth pulse duration of 60 s) in 1 M NaNO₃ solutions as a function of pH value and galvanostatic electrolysis duration. Electrolysis current density is 4 mA cm⁻² (normalized to the Rh deposit surface area). (b) Selectivity of NO₃⁻⁻ reduction to NH₃ on Rh/graphite electrode (nucleation pulse of 100 ms, growth pulse potential of -232 mV, growth pulse duration of 60 s) in 1 M NaNO₃ solution as a function of pH value and galvanostatic electrolysis duration. Electrolysis current density is 4 mA cm⁻² (normalized to the Rh deposit surface area). (c)

solution is characterized by a k_1 value which is about forty times higher than k_2 [46].

3.3. Influence of pH, applied potential and temperature on the nature of NO_3^- reduction products

In course of the electrolysis of nitrate-containing solution, the pH value increases according to Eqs. (3)–(5) and (7) and, as mentioned above, it can significantly alter the composition of nitrate reduction products. Due to this reason buffer solutions were employed to maintain a constant pH throughout the electrolysis duration. The electrolyses were performed in 1 M NaNO₃ within the following pH ranges, ensured by indicated buffer solutions (simultaneously used as support electrolytes):

- (a) 3.7-5.0: acetate buffer ($0.5 \text{ M} \text{ CH}_3\text{COOH}+0.1 \text{ M} \text{ CH}_3\text{COONa}$);
- (b) 5.5–7.2: phosphate buffer $(0.5 \text{ M } \text{ KH}_2\text{PO}_4 + 0.1 \text{ M } \text{ K}_2\text{HPO}_4)$;
- (c) >7: 1 M NaCl (no buffer);
- (d) 14: 1 M NaOH (no buffer).

The anion concentration in buffer solutions did not exceed 0.6 M because higher concentrations can interfere in the nitrate reduction due to the competitive anionic adsorption at the surface of electrodes. In the cases of acetate and phosphate buffers, pH values during the prolonged electrolyses were maintained by periodic dropwise addition of 5 M HCl. During all the galvanostatic electrolyses, the potential progressively decreased and stabilized at -1.4 V after 2–3 h.

The variations of CE(H₂), $S(NH_3)$ and $S(NO_2^-)$ are represented as a function of electrolysis duration in Fig. 6a–c, respectively. As expected, the decrease in the pH of electrolytic solution promotes the hydrogen formation, and thus higher CE(H₂) values are obtained (Fig. 6a). At the end of the electrolysis (i.e. after 12 h), CE(H₂) is 41.0% for pH < 5, while in 1 M NaOH it is decreased down to 8.4% (Fig. 6a). As the hydrogen *in statu nascendi* promotes the ammonia formation, $S(NH_3)$ should increase with the decreasing pH which can be clearly seen in Fig. 6b. It has been already observed that highly reactive hydrogen dissolved in hydrogen storage alloys could participate in the nitrate reduction process and ammonia was found to be a major reduction product [48]. Hence, the variations of $S(NO_2^-)$ follow a reverse trend (Fig. 6c).

In addition, it is known that nitrite anions are not stable in acid medium and can undergo the following transformations [49]:

$$3HNO_2 \rightarrow 2NO + HNO_3 + H_2O \tag{13}$$

$$2HNO_2 \rightarrow NO + NO_2 + H_2O \tag{14}$$

$$3NO_2 + H_2O \rightarrow NO + 2HNO_3 \tag{15}$$

Selectivity of NO_3^- reduction to NO_2^- on Rh/graphite electrode (nucleation pulse of 100 ms, growth pulse potential of -232 mV, growth pulse duration of 60 s) in 1 M NaNO₃ solution as a function of pH value and galvanostatic electrolysis duration. Electrolysis current density is 4 mA cm^{-2} (normalized to the Rh deposit surface area).

This fact justifies low $S(NO_2^-)$ values at pH < 5 (Fig. 6c). It was also proved that desorbed NO was transformed into N₂O in acid medium [50]. That is why the formation of N₂O, with the current efficiency of 4.1%, was detected at the end of the electrolysis performed in acetate buffer solution. Moreover, in this case the sum of faradaic yields for all the detected products was not equal to 100% which can be due to the chemical NO₂⁻ transformation into NO (non-detectable with the analytical techniques used in this work) or into NO₃⁻ (Eqs. (13)–(15)).

The variations of nitrate destruction degree for various electrolytic media are represented in Fig. 7. Along with pH increase, the k_1 value varies from 1.2×10^{-6} (acetate buffer) to 4.0×10^{-6} s⁻¹ (1 M NaOH) which confirms a negative influence of hydrogen evolution on the nitrate removal. Moreover, at low pH values the accuracy of k_1 calculation is poorer. This fact can be explained by the detected N₂O formation in acid medium and hence, a different reduction mechanism and other kinetics equations are involved.

As mentioned above, the selectivity of nitrate electrochemical reduction strongly depends on the applied potential. In order to clarify this issue, potentiostatic electrolyses were performed in 1 M NaCl + 1 M NaNO₃ solution within the potential range where HER and/or nitrate reduction occur (Fig. 1), i.e. between -0.85 and -1.45 V. As expected from the shape of CV curve (Fig. 1), the charge passed at a given electrolysis duration increases with decreasing potential. In general for comparable consumed charge values, CE(H₂) and S(NH₃) increase when the applied potential becomes more negative. At -0.85 V, no hydrogen is detected and the activity towards NO₃⁻ reduction is rather low. Hence, the adsorbed hydrogen inhibits the nitrate adsorption as stated above. When the electrolyses were carried in 1 M NaCl+1 M NaNO₂ at the same potential (i.e. -0.85 V), it was found that the consumed charge is more important than in the case of nitrate-containing solution. At more negative potentials (-1.3 V) after the passage of $30 \text{ C} \text{ cm}^{-2}$,



Fig. 7. Nitrate destruction degree as a function of time and electrolytic solution pH during the galvanostatic electrolysis of 1 M NaNO₃ solution on a Rh/graphite electrode (nucleation pulse of 100 ms, growth pulse potential of -232 mV, growth pulse duration of 60 s). Electrolysis current density is 4 mA cm⁻² (normalized to the Rh deposit surface area).

CE(H₂) for the electrolysis of 1 M NaCl + 1 M NaNO₃ is 9.9% but in 1 M NaCl + 1 M NaNO₂ it drops down to 1.8%. These observations confirm again a better adsorption of nitrite ions in comparison with NO₃⁻ on Rh-modified graphite electrodes which results in a better catalytic efficiency of NO₂⁻ reduction and lower CE(H₂). Concerning the products of NO₂⁻ reduction on Rh/graphite electrodes, only ammonia is detected and for the most negative electrolysis potential (i.e. -1.3 V), hydrogen formation with a current efficiency of about 6% is observed after the passage of 162 C cm⁻².

It was previously reported that a prolonged Rh surface activation at 70 °C in a solution containing OH⁻, Cl⁻ and NO₃⁻ ions allows ΔE_a values to be progressively decreased from 47 to 20 kJ mol^{-1} [38]. That is why the effect of temperature on the nitrate reduction was studied for Rh/graphite electrodes. Concerning the galvanostatic electrolyses performed in 1 M NaCl + 1 M NaNO₃ solution for approximately 3 h, the increase in temperature from 25 to 70 °C causes the decrease in $CE(H_2)$ from 41.2 to 33.7% accompanied by the increase of $CE(NO_2^{-})$ while CE(NH₃) remains constant. However, no products besides those usually observed (e.g. H_2 , NH_3 and NO_2^{-}) were detected. Thus, bearing in mind a high efficiency of Rh/graphite electrodes for nitrite reduction one could suppose that an electrolysis performed in 1 M NaCl+1 M NaNO2 solution would lead to the complete transformation of nitrite to $NH_4^+/NH_3(aq)$. Indeed, potentiostatic electrolyses performed in the range from -0.8 to -1.3 V for 2 h, led to a nearly complete transformation of nitrite to ammonia irrespectively of the electrolysis medium temperature. Finally, one can infer that the increase in temperature does not make a significant effect on the selectivity of nitrate reduction. Perhaps, a longer duration of Rh surface activation and/or some additives to the electrolysis medium would be required to achieve a sufficient Rh surface activation resulting in N₂ formation as earlier reported [38].

3.4. Effect of additives to the electrolytic medium on the selectivity of NO_3^- reduction

The desirable dinitrogen formation in course of nitrate reduction on Rh electrodes has been already reported and explained by the fact that the prolonged Rh surface activation at elevated temperatures allowed the HER onset to be shifted towards more negative potentials [38]. Indeed, the absence of hydrogen in statu nascendi stops the chemical NO3⁻ reduction to ammonia. Another way of inhibiting the HER is the use of various additives, which are adsorbed onto the electrode surface, thus blocking hydrogen adsorption. In fact, it was shown that the presence of bulky hydrophobic cations such as tetrabutylammonium $(C_4H_9)_4N^+$ hindered the HER during the electrochemical synthesis of ethylene glycol [51]. It was also observed that formate anions HCOO⁻ are adsorbed at Rh surface and suppress the HER [52]. Hence, in the present study the electrochemical measurements were performed on Rh/graphite electrodes in NO3and NO₂⁻-containing solutions in the presence of various ions (tetraalkylammonium cations (CH₃)₄N⁺, (C₂H₅)₄N⁺ and carboxylate anions, namely acetate CH_3COO^- , tartrate $C_4H_4O_6^{2-}$ and formate HCOO⁻).



Fig. 8. CV curves (fifth cycle) of Rh/graphite electrode (nucleation pulse of 100 ms, growth pulse potential of -232 mV, growth pulse duration of 60 s) in 1 M NaNO₃ solutions containing 0.1 M NaX (X = Cl⁻, HCOO⁻, C₄H₄O₆²⁻, CH₃COO⁻). Current density is normalized to the Rh deposit surface area. Scan rate 20 mV s⁻¹.

CV curves recorded in 1 M NaNO₃ solutions containing 0.1 M NaX ($X = Cl^-$, HCOO⁻, $C_4H_4O_6^{2-}$, CH_3COO^-) are shown in Fig. 8. The current density values at the most negative potential (i.e. -1.5 V) are almost the same for all the anions except HCOO⁻ for which they are about 15% lower. Moreover, only in the presence of formate ions the nitrate reduction peak is not observed. These results point out a stronger HCOO⁻ adsorption on the investigated electrodes comparing with that of $C_4H_4O_6^{2-}$, CH_3COO^- , H_3O^+ and NO_3^- . Regarding the nitrite reduction, the addition of carboxylate anions alter neither the shape of CV curves nor the current density values (not shown).

It should be noted that for all the investigated carboxylate anions the oxygen atoms are responsible for their adsorption at the metallic surface [53]. A lower intensity of NO_3^- reduction peak for tartrate comparing with that for acetate can be due to a more favorable tartrate adsorption onto Rh/graphite electrodes which is explained by the presence of two -COO and two -OH groups. The absence of the cathodic wave at about -1.05 V suggests that the formate ions are much more efficiently adsorbed onto Rh/graphite electrode than the above-mentioned anions blocking the nitrate adsorption. Moreover at the beginning of an electrolysis for the same carboxylate anion concentration, the pH value is the lowest for HCOO⁻-containing solutions and a priori one could expect a higher activity for HER, which is not the case. In fact in the hydrogen evolution region, interactions between adsorbed hydrogen and adsorbed formate may lead either to bridge-bonded or to linear bonded CO according to the following reactions [52,54]:

 $Rh-COOH + Rh-H \rightarrow Rh_2C=O + H_2O$ (16)

$$Rh-COOH + Rh-H \rightarrow Rh-CO + Rh-H_2O$$
 (17)

Both forms of CO can interconvert to each other and in this case a positively charged carbon atom is bonded to the Rh surface. Presumably this is not the case for the other carboxylate anions investigated in this work and that is why the formate anions are



Fig. 9. (a) CV curves (fifth cycle) of Rh/graphite electrode (nucleation pulse of 100 ms, growth pulse potential of -232 mV, growth pulse duration of 60 s) in 1 M NaCl + 0.1 M NaNO₃ solutions containing *x* M HCOONa (*x*=0.1, 0.01, 0.001). Current density is normalized to the Rh deposit surface area. Scan rate 20 mV s⁻¹. (b) CV curves (fifth cycle) of Rh/graphite electrode (nucleation pulse of 100 ms, growth pulse potential of -232 mV, growth pulse duration of 60 s) in 1 M NaCl solutions containing *x* M HCOONa (*x*=0.1, 0.01, 0.001). Current density is normalized to the Rh deposit surface area. Scan rate 20 mV s⁻¹.

readily adsorbed onto negatively charged Rh electrode surface blocking the nitrate and hydrogen adsorption in the potential region where their reduction takes place.

To study the effect of formate anions on NO₃⁻ reduction in more details, CV curves were recorded in 1 M NaCl + 1 M NaNO₃ and 1 M NaCl solutions containing different amounts of formate anions. A progressive increase in HCOO⁻ concentration results in a decrease of the NO₃⁻ reduction peak and in its final disappearance, which confirms the HCOO⁻ effectiveness for blocking the NO₃⁻ adsorption and reduction (Fig. 9a). Concerning the 1 M NaCl solution (Fig. 9b), the decrease in the current density within HER potential range clearly manifests that HCOO⁻ ions inhibit hydrogen adsorption as previously shown [52]. The differences between current densities in different solutions could be used as a comparison criterion and are summarized in Table 1. In the case of NO_x⁻ presence, the current values are corrected with respect to 1 M NaCl solution. One



Fig. 10. (a) Current efficiency (CE) of H_2 formation on a Rh/graphite electrode (nucleation pulse duration of 100 ms, growth pulse potential of -232 mV, growth pulse duration of 60 s) in 1 M NaNO₃ solutions as a function of HCOO⁻ concentration and galvanostatic electrolysis duration. Electrolysis current density is 4 mA cm⁻² (normalized to the Rh deposit surface area). (b) Selectivity (S) of NO₃⁻ reduction to NH₃ on a Rh/graphite electrode (nucleation pulse duration of 100 ms, growth pulse potential -232 mV, growth pulse duration 60 s)

Table 1

Influence of formate anions addition on the current density values (fifth cycle) for Rh/graphite electrode (nucleation pulse of 100 ms, growth pulse potential of -232 mV, growth pulse duration of 60 s) in different solutions

HCOO ⁻ concentration (M)	Solution composition		
	1 M NaCl ^a	1 M NaCl+0.1 M NaNO3 ^b	1 M NaCl+0.1 M NaNO ₂ ^a
0 10 ⁻³	2.6 2.2	0.6 0.3	0.9 1.3

The current density is normalized to the Rh deposit surface area.

^a At -1.25 V vs. Ag/AgCl.

^b At -0.9 V vs. Ag/AgCl.

can infer that the effectiveness of NO_2^- reduction increases with formate addition contrary to the NO_3^- one. This fact confirms again a more favorable adsorption of NO_2^- on Rh with respect to that of NO_3^- , so the addition of HCOO⁻ does not hinder the NO_2^- adsorption and reduction.

To investigate the selectivity of NO_3^- reduction in the presence of formate anions, the galvanostatic electrolyses were performed for Rh/graphite electrodes in 1 M NaNO₃ + *x* M HCOONa (*x* = 0, 0.001, 0.1) solutions. The variation of CE(H₂), *S*(NH₃) and *S*(NO₂⁻) are shown in Fig. 10a–c, respectively. The following conclusions can be derived from these data:

- (i) it can be clearly seen that CE(H₂) diminishes with the increase in HCOO⁻ concentration and the electrolysis duration which confirms CV results (Fig. 10a);
- (ii) in the absence of formate anions at the initial stages of the electrolysis, S(NH₃) decreases following the CE(H₂) variation but then increases because of the easy reduction of accumulated NO₂⁻ to NH₃ (Fig. 10b). In the presence of HCOO⁻, S(NH₃) increases during the electrolysis though the decrease in CE(H₂) would favor the ammonia formation. This is explained by the easier adsorption of nitrite ions at Rh/graphite electrodes where they are readily reduced to NH₃. It is also confirmed by the increase in S(NH₃) with HCOO⁻ concentration (Fig. 10b);
- (iii) in the absence of HCOO⁻, $S(NO_2^-)$ dependence (represented in Fig. 10c) passes through a maximum as it has been observed before [30]. In the presence of HCOO⁻, $S(NO_2^-)$ decreases as formed NO₂⁻ ions are efficiently adsorbed at Rh surface and rapidly reduced to NH₃, as stated above. Decrease in $S(NO_2^-)$ with increasing $c(HCOO^-)$ is due to a poorer NO₃⁻ adsorption and hence, slow nitrite formation.

in 1 M NaNO₃ solutions as a function of HCOO⁻ concentration and galvanostatic electrolysis duration. Electrolysis current density is 4 mA cm⁻² (normalized to the Rh deposit surface area). (c) Selectivity (S) of NO₃⁻ reduction to NO₂⁻ on a Rh/graphite electrode (nucleation pulse duration of 100 ms, growth pulse potential of -232 mV, growth pulse duration of 60 s) in 1 M NaNO₃ solutions as a function of HCOO⁻ concentration and galvanostatic electrolysis duration. Electrolysis current density is 4 mA cm⁻² (normalized to the Rh deposit surface area).

Concerning the influence of tetraalkylammonium cations on the activity of Rh/graphite electrodes towards nitrate reduction, CV measurements (not shown) revealed that the addition of 0.1 M (CH₃)₄N⁺ to 1 M NaNO₃ solution does not change the shape of CV curve but the addition of 0.1 M (C₂H₅)₄N⁺ results in decreasing the intensity of NO₃⁻ reduction peak. The galvanostatic electrolyses performed for the same series of solutions showed that the addition of $(CH_3)_4N^+$ does not affect the selectivity of NO₃⁻ reduction while the addition of (C₂H₅)₄N⁺ results in increasing $CE(H_2)$. However, a proper choice of potentiostatic electrolysis parameters results in diminishing CE(H₂). A 24 h electrolysis was performed at -1.1 V on a Rh/graphite electrode in 1 M NaNO3 solution with and without the addition of 0.1 M (CH₃)₄N⁺. These conditions allow CE(H₂) to be decreased from 6.9 to 0% and hence, $CE(NO_2^{-})$ to be increased from 26.7 to 57.0%. It means that $(CH_3)_4N^+$ ions hinder the hydrogen adsorption at Rh surface which results in the decrease of CE(NH₃) and accumulation of NO₂⁻ anions. Nevertheless, the addition of tetraalkylammonium cations does not permit to achieve the dinitrogen formation on Rh/graphite electrodes.

4. Conclusions and summary

The data presented above clearly demonstrate that $NO_2^$ ions are more strongly adsorbed on Rh/graphite electrodes than NO_3^- . During the initial stages of the electrolysis of a nitrate solution, the NO_2^- concentration increases but remains low. When a certain nitrite concentration is reached (ca. 0.1 M), NO_2^- ions occupy a significant part of electrode surface (the decrease in nitrate concentration promotes this process) and are readily reduced to NH₃. Afterwards the selectivity for the formation of NO_2^- and hence, NO_2^- concentration in solution become lower (Figs. 5 and 10c).

Finally, one can suppose that the reaction mechanism involves nitrite ions and adsorbed hydrogen resulting in the ammonia formation and the decrease in CE(H₂). The mechanism involving a chemical reaction between adsorbed hydrogen and adsorbed nitrite ion has been already proposed for mesoporous palladium in alkaline medium [55]. On the other hand, a very tiny fraction of N₂O (0.2%) was detected after a 96 h electrolysis. This allows us to represent schematically the nitrate reduction mechanism on Rh-modified graphite electrodes (Scheme 1). Surely, there are some intermediate species formed between NO_{2(ads)}⁻ and NH₃ [20] but their quantitative determination requires more complicated analytical methods than those used in our investigation [20,26].



Scheme 1. Nitrate reduction mechanism on Rh/graphite electrodes.

Our main conclusions about the reduction of nitrate and nitrite ions on Rh/graphite electrodes can be summarized as follows:

- (i) All our experimental results (CV measurements, calculation of reaction rate constants and activation energy, effect of anion addition) demonstrate unambiguously that at room temperature Rh/graphite electrodes possess a high affinity for NO_2^- anions thus facilitating their adsorption. These electrodes are much more efficient for nitrite reduction than for that of nitrate. Ammonia proves to be the only product of nitrite reduction.
- (ii) The rate of nitrate destruction increases along with pH value. Indeed, in acid medium $CE(H_2)$ is higher and mainly chemical reduction of NO_3^- to NH_4^+ occurs. In alkaline medium, the adsorption of NO_3^- is favored, hence they are electrochemically reduced to NO_2^- .
- (iii) The electrolysis performed at elevated temperatures does not allow the selectivity of nitrate reduction to dinitrogen to be improved.
- (iv) The inhibiting influence of formate anions on HER and nitrate reduction was demonstrated. Other carboxylate anions and tetraalkylammonium cations do not significantly influence the nitrate reduction and HER on Rh/graphite electrodes.

Acknowledgements

The authors are grateful to NanoQuébec, Natural Sciences and Engineering Research Council of Canada (NSERC) and ENPAR Technologies Inc. (Guelph, ON, Canada) for the financial support.

References

- World Health Organization, Rolling Revision of the WHO Guidelines for Drinking-Waters Quality, Nitrates and Nitrites in Drinking-Waters, World Health Organization, 2004.
- [2] A. Kapoor, T. Viraraghavan, J. Environ. Eng. 123 (1997) 371.
- [3] G.C.C. Yang, H.-L. Lee, Water Res. 39 (2005) 884.
- [4] P.E. Hartman, Environ. Mutagen. 5 (1983) 111.
- [5] P. Fraser, C. Chivers, Sci. Total Environ. 18 (1981) 103.
- [6] B.H. Gu, Y.K. Ku, P.M. Jardine, Environ. Sci. Technol. 38 (2004) 3184.
- [7] R. Molinari, P. Argurio, L. Romeo, Desalination 138 (2001) 271.
- [8] A. Elmidaoui, F. Elhannouni, M.A. Menkouchi Sahli, L. Chay, H. Elabbassi, M. Hafsi, D. Largeteau, Desalination 136 (2001) 325.
- [9] Ş. Aslan, A. Türkmann, Process Biochem. 40 (2005) 935.
- [10] B.U. Bae, C.H. Kim, Y.I. Kim, Water Sci. Technol. 49 (2004) 413.
- [11] S. Kerkeni, E. Lamy-Pitara, J. Barbier, Catal. Today 75 (2002) 35.
- [12] X. Zhang, J. Wang, Z. Wang, S. Wang, Synth. Met. 155 (2005) 95.
- [13] M. Paidar, I. Rousar, K. Bouzek, J. Appl. Electrochem. 29 (1999) 611.
 - [14] J. O'M. Bockris, J. Kim, J. Appl. Electrochem. 27 (1997) 623.
 - [15] J. Gootzen, P. Peeters, J. Dukers, L. Lefferts, W. Visscher, J. van Veen, J. Electroanal. Chem. 434 (1997) 171.
 - [16] L.J.J. Janseen, M.M.J. Pieterse, E. Barendrecht, Electrochim. Acta 22 (1977) 27.
 - [17] Y. Xiang, D. Zhou, J.F. Rushling, J. Electroanal. Chem. 424 (1997) 1.
 - [18] N. Chebotareva, T. Hyokong, J. Appl. Electrochem. 27 (1997) 975.
 - [19] O.A. Petrii, T.Ya. Safonova, J. Electroanal. Chem. 331 (1992) 897.
 - [20] G.E. Dima, A.C.A. de Vooys, M.T.M. Koper, J. Electroanal. Chem. 554/555 (2003) 15.
 - [21] M.T. de Groot, M.T.M. Kooper, J. Electroanal. Chem. 562 (2004) 81.

- [22] A.C.A. de Vooys, R.A. Santenvan, J.A.R. van Veen, J. Mol. Catal. A 154 (2000) 203.
- [23] G. Horányi, E.M. Rizmayer, J. Electroanal. Chem. 143 (1983) 323.
- [24] J.F.E. Gootzen, L. Lefferts, J.A.R. van Veen, Appl. Catal. A 188 (1999) 127.
- [25] D. De, J.D. Englehardt, E.E. Kalu, J. Electrochem. Soc. 147 (2000) 4224.
- [26] M.C.P.M. da Cunha, J.P.I. De Souza, F.C. Nart, Langmuir 16 (2000) 771.
- [27] K.J. Reddy, J. Lin, Water Res. 34 (2000) 995.
- [28] J.W. Peel, K.J. Reddy, B.P. Sullivan, J.M. Bowen, Water Res. 37 (2003) 2512.
- [29] O. Brylev, L. Roué, D. Bélanger, J. Electroanal. Chem. 581 (2005) 22.
- [30] O. Brylev, M. Sarrazin, D. Bélanger, L. Roué, Appl. Catal. B 64 (2006) 243.
- [31] M. Ueda, H. Dietz, A. Anders, H. Kneppe, A. Meixner, W. Plieth, Electrochim. Acta 48 (2002) 377.
- [32] T.Ya. Safonova, O.A. Petrii, J. Electroanal. Chem. 448 (1998) 211.
- [33] T. Omori, M.S. El-Deab, M. Osawa, J. Electroanal. Chem. 470 (1999) 46.
- [34] S.J. Hsieh, A.A. Gewirth, Langmuir 16 (2000) 9501.
- [35] A.J. Bard, R. Parsons, J. Jordan (Eds.), Standard Potentials in Aqueous Solutions, Marcel Dekker, New York, 1985.
- [36] D. Coleman, R.E. White, D.T. Hobbs, J. Electrochem. Soc. 142 (1995) 1152.
- [37] E. Lazarova, Elektrokhimiya 18 (1982) 1654 (in Russian).
- [38] Ph.M. Tucker, M.J. Waite, B.E. Hayden, J. Appl. Electrochem. 34 (2004) 781.

- [39] G. Jerkiewicz, J.J. Borodzinski, Langmuir 9 (1993) 2202.
- [40] A.E. Greenberg, L.S. Clesceri, A.D. Eaton, M.A.H. Franson (Eds.), Standard Methods for the Examination of Water and Waste Water, 18th ed., American Public Health Association, Washington, DC, 1992, p. 4.
- [41] D.S. Frear, R.C. Burell, Anal. Chem. 27 (1955) 1664.
- [42] R.N. Dietz, Anal. Chem. 40 (1968) 1576.
- [43] P.N. Bartlett, J. Marwan, Micropor. Mesopor. Mater. 62 (2003) 73.
- [44] J.L. Ginner, P.J.J. Alvarez, S.L. Smith, M.M. Scherer, Environ. Eng. Sci. 21 (2004) 219 (and references therein).
- [45] K. Bouzek, M. Paidar, A. Sadlikova, H. Bergmann, J. Appl. Electrochem. 31 (2001) 1185.
- [46] C. Polatides, G. Kyriacou, J. Appl. Electrochem. 35 (2005) 421.
- [47] G.P. Sakellaropoulos, AlChE J. 25 (1979) 781.
- [48] Ch. Lu, Sh. Lu, W. Qiu, Q. Liu, Electrochim. Acta 44 (1999) 2193.
- [49] Q. Cai, W. Zhang, Z. Yang, Anal. Sci. 17 (2001) i917.
- [50] A.C.A. de Vooys, G.L. Beltramo, B. van Riet, J.A.R. van Veen, M.T.M. Koper, Electrochim. Acta 49 (2004) 1307.
- [51] N.L. Weinberg, D.J. Mazur, J. Appl. Electrochem. 21 (1991) 895.
- [52] F. Hahn, B. Beden, C. Lamy, J. Electroanal. Chem. 204 (1986) 315.
- [53] J.M. Philips, F.M. Leibsle, A.J. Holder, T. Keith, Surf. Sci. 545 (2003) 1.
- [54] B.B. Damaskin, O.A. Petrii, V.V. Batrakov, Adsorption of Organic Compounds on Electrodes, Plenum Press, New York, NY, 1971.
- [55] G. Denuault, Cl. Milhano, D. Pletcher, Phys. Chem. Chem. Phys. 7 (2005) 3545.