



Electrochemical Removal of Nitrite Using an Activated Copper Rotating Cylinder Electrode

Omar González Pérez^z and José M. Bisang

Universidad Nacional del Litoral, CONICET, Programa de Electroquímica Aplicada e Ingeniería Electroquímica (PRELINE), Facultad de Ingeniería Química, S3000AOM Santa Fe, Argentina

An undivided electrochemical reactor with a rotating cylinder electrode was examined for the removal of nitrite from a synthetic effluent, 30 mmol dm⁻³ NaNO₂ in 0.1 mol dm⁻³ Na₂SO₄ as supporting electrolyte. Nitrite was reduced to ammonia at a copper cathode activated by a film of copper oxides, which was anodically produced at a potential of 18 mV against saturated calomel electrode, SCE, in the supporting electrolyte. The deactivation of the cathode was avoided by application of a periodic potential reversal, PPR, technique making the rotating electrode work 5 min as a cathode and 5 min in reactivation. The reactor performance was improved applying both strategies, cathode activation and use of a PPR procedure. The best results were obtained at a cathodic potential of -1.3 V vs. SCE, ammonia being the main product of the reduction of nitrite, obtaining a molar yield of 94% and a current efficiency of 59% with a nitrite conversion of 92% in an experiment of 1 h.

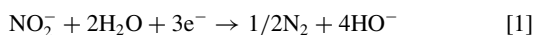
© 2017 The Electrochemical Society. [DOI: 10.1149/2.0521712jes] All rights reserved.

Manuscript submitted May 30, 2017; revised manuscript received July 26, 2017. Published August 5, 2017.

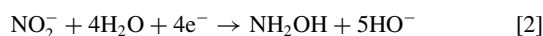
Nitrite is present in industrial effluents such as low level nuclear waste¹ and aquaculture wastewaters from fish factories.² Fortunately, drinking water rarely contains nitrite. The presence of nitrite in water bodies at concentrations greater than the guideline values causes health problems in humans and animals.³ For industrial wastewaters, the WHO-recommended treatment technique is disinfection/chlorination in order to oxidize nitrite to the less toxic nitrate.⁴ Nitrite removal methods include ion exchange⁵ and biological denitrification.⁶ However, there are disadvantages associated with both approaches, including the need for regeneration and disposal of spent regenerant with ion exchange, as well as the potential for microbial and carbon feed contamination of the final water with biological denitrification.⁴ Thus, electrochemical processes can compete favorably with these technologies.⁷ Furthermore, the importance of studying the reduction of nitrite lies in the fact that it is the main intermediate of nitrate electro-reduction.

A useful graphical representation of the thermodynamics of electrochemical systems are so-called oxidation state diagrams, or Frost-Ebsworth diagrams, which plot the change of free energy, expressed as the exchanged electron number multiplied by the equilibrium potential for the half-reaction of a particular nitrogen compound with respect to nitrogen gas, versus its oxidation state.⁸ Fig. 1 shows such a diagram for the most important compounds in the nitrogen system in neutral or alkaline solution at 30°C. This graph illustrates that the preferred end products in the reduction of nitrite are nitrous oxide, nitrogen gas and in less extension also azide. Moreover, a straight line, represented in dashed shape in Fig. 1, from the zero oxidation state to the point at +3 oxidation state shows that the point at +1 oxidation state lies above this line. This means that N₂O is thermodynamically unstable and it decomposes into NO₂⁻ and N₂. Thus, nitrogen can be recognized as the main product expected by the nitrite reduction. Furthermore, according to Fig. 1 the nitrite oxidation to nitrate is favored.

In water treatment applications the common goal is to convert nitrite to N₂ as shown below:



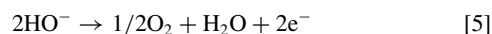
but hydroxylamine and ammonia are usually formed and the electrolyte gradually becomes alkaline.



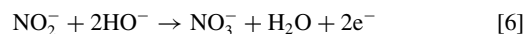
Main parasitic reaction at cathode is hydrogen evolution:



Electrochemical reactions at anode are oxygen generation:



and re-oxidation of nitrite to nitrate:



Nitrite can be electrochemically oxidized or reduced. The preferred material for oxidation is Pt⁸ although copper oxides have also been used.⁹ Nitrite reduction has been extensively studied on Pt, other metals or functionalized electrodes in acid, neutral and basic solutions.⁸ From the above review it is inferred that despite the large number of fundamental contributions devoted to this subject, the cathodic reduction of NO₂⁻ has not been well understood. Thus, the type of product depends on the concentration of nitrite as well as on cathode material, electrode potential and charge passed. In general, the cathodic behavior of nitrite is similar to nitrate, hence materials for NO₃⁻ removal could be used for NO₂⁻ abatement. Of the coinage metals, copper is the most active surface for nitrate reduction and it has been widely investigated as a catalyst for these reaction.⁸ Ammonia was reported to be the final product. However, the electrocatalytic reduction of NO₃⁻ at Cu is strongly hindered by the presence of specifically adsorbing anions as well as nitrate-reduction products. Besides, the decrease of the electrocatalytic activity of the Cu electrode may be due to its poisoning by adsorbed hydrogen, blocking the electrode surface for further reduction of N-containing molecules. Methods that activate copper for nitrate reduction comprised high-energy ball milling and alkaline pre-treatment. For the latter approach, by applying a less negative potential at the cathode than that required for nitrate reduction it is possible to reactivate the copper electrode by means of desorbing the poisoning species.¹⁰

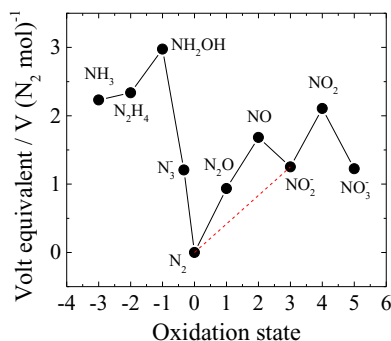


Figure 1. Oxidation state diagram of inorganic nitrogen compounds in neutral or alkaline solution at 30°C.

^zE-mail: oglezp@fiq.unl.edu.ar

Furthermore, electrochemical reactors for the direct removal of nitrite with different configurations and operating modes have been designed. Electrochemical previous studies on nitrite removal dealt with different configurations: parallel-plate,¹¹ H-cell,^{12,13} batch,^{14–21} PEMFC-type^{22–24} and flow cell.^{25,26} In a series of papers, Shibata et al. studied NO_2^- reduction using gas-diffusion electrodes with various catalysts: Cu,^{27,28} Ag,²⁸ Au,²⁸ Cd,²⁹ Pd²⁹ and metallophthalocyanines.³⁰ In all cases, NO_2^- is reduced to NH_3 with H_2 evolution. They found that copper was the most suitable material. Moreover, NO_2^- -direct reduction in alkaline nuclear waste solutions using FM01 LC and MP Cell devices has been studied.¹² The cathode materials were Pb or Ni and the anodes were Pt, 316 stainless steel, SS, or Ni. They identified lead as the most adequate electrode to transform the effluent into a solution containing ammonia. On the other hand, Sahin and collaborators³¹ analyzed the biofuel production by means of the NO_2^- reduction to produce ammonia in neutral buffered electrolytes using an electrochemical reactor coupled with a bioreactor. Glassy carbon, GC, and Ni porous electrodes were used as cathodes and Ni plate, SS cloth and DSA were used as anodes. Current efficiencies of 80–100% were observed for both cathode materials at $100 \text{ mmol dm}^{-3} \text{ NaNO}_2$. Additionally, Ghazouani and coworkers³² investigated the efficiency of nitrite removal in two types of electrochemical cells containing boron-doped diamond, BDD, anode/cathode or BDD anode and SS cathode. NO_2^- removal was close to 100%, obtaining the best reactor performance when BDD was used as cathode and anode.

As mentioned above, the direct reduction of nitrite generates ammonia and nitrogen oxides along with N_2 . Chloride-salt is widely added to overcome this issue. In this process, chloride is oxidized at the anode and reacts with water to form hypochlorous acid. OCl^- then reacts with NO_2^- and ammonia to produce NO_3^- and N_2 . Thereby, Diaz et al.³³ evaluated the indirect electrochemical removal of nitrite from a recirculating aquaculture system by using the DiaCell 201 PP commercial cell (Adamant Technologies, Switzerland), which was formed by two parallel flow-by compartments separated by a central bipolar BDD electrode placed between two circular terminal electrodes of the same material. It is reported that more than 90% of the initial NO_2^- was removed. An undesirable effect of free Cl_2 is the formation of organochlorinated compounds, which can be more harmful than the original pollutants. This calls for the development of new technologies that eliminate nitrite obtaining products of commercial value or harmless species. In a previous article,³⁴ nitrate removal was carried out using an activated rotating cylinder electrode obtaining a high current efficiency and ammonia as the main product. Hence, the objective of the present paper is to extend the latter methodology to the study of nitrite electrochemical abatement in non-buffered aqueous solutions of sodium sulfate, taking advantage of the versatility and good performance of a reactor with a rotating cylinder electrode.^{35,36}

Experimental

Rotating disk electrode, RDE, experiments.—Electrochemical experiments were performed in a single compartment three-electrode cell. Cu, 316L SS, Ni, Pt and GC rotating disks, all 3 mm in diameter, were employed as working electrodes. A graphite RDE, 5.5 mm diameter, was also employed. The auxiliary electrode was a Pt wire with a large area. A SCE was used as reference and the potentials are referred to this electrode. The preparative work of the disks included polish to a bright mirror finish with slurry of $0.3 \mu\text{m}$ alumina powder, sonication in distilled water and drying with warm air. All solutions were degassed with pure N_2 for 30 min prior to electrochemical experiments, and an inert gas atmosphere was constantly kept over the liquid surface during the experiments. All data concerning current densities are referred to the geometric area.

The experiments were carried out potentiodynamically using a synthetic solution of $30 \text{ mmol dm}^{-3} \text{ NaNO}_2$ in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ as supporting electrolyte with an initial pH of 6.3, a medium that may be considered representative of some polluted neutral wastewaters where the reduction processes, Eqs. 1–3, produce a local alkalization of the solution. The temperature, rotation speed and potential scan rate

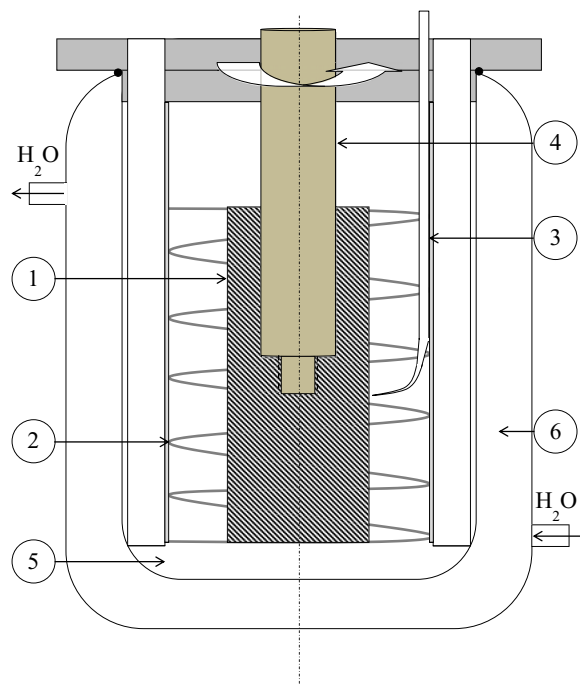


Figure 2. Schematic representation of the electrochemical reactor. 1, Rotating cylinder electrode; 2, counter electrode; 3, Haber-Luggin capillary; 4, electrode shaft; 5, electrolyte container; 6, heating jacket.

were 30°C , 1000 rpm and 0.5 mV s^{-1} , respectively. In some tests, Cu electrode was pre-treated 30 min at the applied potential $E_{\text{SCE}} = 18 \text{ mV}$ into the supporting electrolyte, where an adherent layer of copper oxides is formed.

Rotating cylinder electrode, RCE, experiments.—The electrolysis were performed in an undivided batch reactor, 95 mm internal diameter and 140 mm high, being the reactor thermostated by a heating jacket. Fig. 2 schematically depicts the complete experimental arrangement. The working electrode was a Cu rotating cylinder, 37.6 mm diameter and 90 mm long, with its upper end attached to the motor shaft. A concentric helical Pt wire, 1.0 mm diameter and 500 mm long, was used as anode. The interelectrode gap was 11 mm. The surface of the working electrode was carefully polished with emery paper 2500 grit and it was washed with distilled water.

The experiments were carried out potentiostatically at 30°C and 1000 rpm, giving a peripheral velocity of 2 m s^{-1} . The cathodic potential was controlled against a SCE connected to a Haber-Luggin capillary positioned in the middle region of the cathode. During the experiment, the cell voltage and the current were recorded as a function of time. The solution was $30 \text{ mmol dm}^{-3} \text{ NaNO}_2$ in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ as supporting electrolyte with an initial pH of 6.3. The electrolyte volume was 0.825 dm^3 .

Analytical procedures.—The concentrations of nitrate, nitrite, ammonium and hydroxylamine were spectrophotometrically determined. NO_3^- , NO_2^- and NH_3 concentrations were measured following standard methods.³⁷ The determination of hydroxylamine is based on its oxidation to nitrite using sodium arsenate under alkaline condition and the nitrite formed was measured as above.³⁸

Results and Discussion

Preliminary studies with RDEs.—Fig. 3 shows the voltammograms recorded at 1000 rpm on bare copper and pre-treated Cu RDEs in $30 \text{ mmol dm}^{-3} \text{ NaNO}_2 + 0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$, solid curves, and $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$, dashed curves. Only H_2 evolution reaction, curves a' and b', is observed at high negative potentials, $E_{\text{SCE}} \leq \text{ca.}$

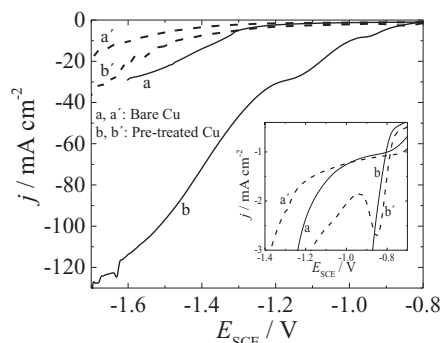


Figure 3. Linear scan voltammograms for RDEs at 0.5 mV s^{-1} , 1000 rpm and 30°C . Solid curves represent experiments in a solution of $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4 + 30 \text{ mmol dm}^{-3} \text{ NaNO}_2$, dashed curves experiments in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$. Inset: electrochemical behavior at lower potentials.

-1.5 V , when the supporting electrolyte is used. It must be observed that the two electrodes display a different ability to perform the nitrite reduction reaction, curves a and b. Also, in the case of modified electrodes into the supporting electrolyte a cathodic peak appears at ca. -0.85 V , as shows the inset in Fig. 3. According to previous studies, this reduction wave has been assigned to $\text{Cu}(\text{OH})_2\text{-CuO/Cu}$ transitions via two-electron transfer reactions.³⁹

In order to compare different electrode materials, Fig. 4 presents the net current densities of nitrite reduction, $j - j_{\text{blank}}$, calculated by subtracting the current density measured at each potential in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ from that measured in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4 + 30 \text{ mmol dm}^{-3} \text{ NaNO}_2$. These corrected curves illustrate that the best performance was achieved with the pre-treated copper electrode, followed by bare Cu and graphite, Fig. 4A. The latter two materials have similar values of current densities, although graphite requires a greater overpotential to carry out the reduction of nitrite. With the three aforementioned electrode materials, nitrite reduction takes place before hydrogen evolution, otherwise at Pt, Ni and 316L SS both reactions are performed simultaneously as shown in Fig. 4B. Furthermore, it is observed that graphite outperforms glassy carbon, and metals or

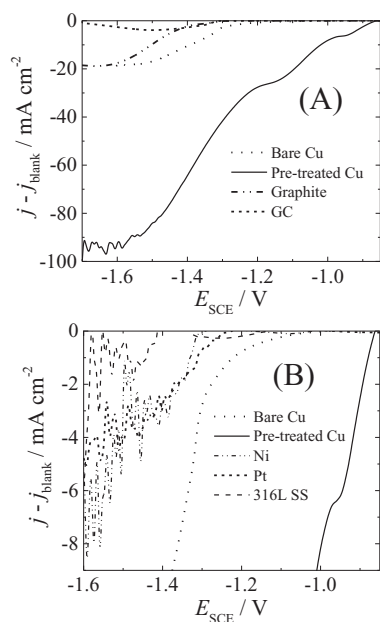


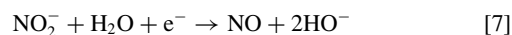
Figure 4. Linear scan voltammograms for RDEs at 0.5 mV s^{-1} , 1000 rpm and 30°C representing the net current densities of nitrite reduction. (A) Copper electrodes and carbonaceous materials. (B) Copper electrodes and metallic materials.

Table I. Physicochemical properties of the electrolyte.

Composition	$[\text{NaNO}_2] \cong 30 \text{ mmol dm}^{-3}$ in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$
Density, kg m^{-3}	1011
Dynamic viscosity, $\text{kg m}^{-1} \text{ s}^{-1}$	8.34×10^{-4}
ν , $\text{m}^2 \text{ s}^{-1}$	8.25×10^{-7}
D , $\text{m}^2 \text{ s}^{-1}$	1.81×10^{-9}
Sc	455

metal alloys here studied have a poor performance for reduction of NO_2^- or its intermediary compounds. This is attributed to poisoning by adsorbed hydrogen blocking the electrode surface for further reduction of N-containing molecules.^{8,40} In the case of bare Cu, graphite and GC, it was observed a decrease in the current of polarization curves when the potential becomes more negative, which is explained by the adsorption of nitrite-reduction products that blocks the electrode surface, as in the case of electrochemical nitrate reduction.⁴¹

NO_2^- and NO_3^- reduction display similar voltammetric characteristics at pre-treated Cu, although nitrite reduction starts at a potential of -0.86 V , which is approximately 0.3 V more negative than that for nitrate reduction.³⁴ When the electrode potentials are near -1.16 and -1.7 V , two waves are observed, Fig. 4A. These processes are related to the electrochemical nitrite reduction and the presence of inflection points suggests a combined diffusion and charge-transfer kinetic control for each reaction. The mass-transfer coefficient predicted by the Levich equation, assuming the physicochemical parameters reported on Table I, with D corrected by electrolyte concentration and temperature,⁴² is $9.73 \times 10^{-5} \text{ m s}^{-1}$. Assuming 1 and 4 as the numbers of exchanged electrons per nitrite ion, the limiting current densities are 28 and 113 mA cm^{-2} , which are close to those reported on Fig. 4A. Then, in the first potential region the formation of NO could be proposed as:



and NH_2OH production as Eq. 2 in the second one. Cattarin⁴³ observed a double peak around -1.3 V vs. SCE at cyclic voltammograms for reduction of $1 \text{ mol dm}^{-3} \text{ NaOH} + 50 \text{ mmol dm}^{-3} \text{ NaNO}_2$, which showed a dependence on scan rate close to that expected for a diffusion controlled reaction. Also, constant potential electrolysis of NO_2^- at -1.4 V on Cu cathodes proceeded to a large extent according to Reaction 3, with NH_3 production. No significant amount of NH_2OH was found after electrolysis of NO_2^- .⁴³ This fact may mean that hydroxylamine, formed as an intermediate of Reaction 3, is readily reduced to NH_3 at the applied potential, or that NH_2OH is not formed during the reactions.⁴³ Thus, the pre-treatment of copper emerges as the most promising option to activate the electrode for processing effluents containing nitrite.

Studies with a RCE configuration.—Considering the results obtained with RDEs, previous to each experiment the copper cylinder was pre-treated in a $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution controlling the potential at 8 or 18 mV against SCE at 1000 rpm and 30°C . The copper cylinder was covered with a pale brown adherent layer. In an experiment, after the pre-treatment of the copper rotating cylinder electrode, the film was scraped from the electrode. A sample of this powdery material was collected and analyzed by XPS and Raman spectroscopy, revealing the presence of cuprous oxide and cupric oxide being the first the predominant species. A value of $E_{\text{SCE}} = 8 \text{ mV}$ was experimentally determined as a minimum potential to cover completely the electrode surface area of Cu cylinder with a continuous layer of copper oxides. The pH at the end of the pre-treatment was approximately 10. During this pre-treatment procedure, the solution showed a blue color attributed to the presence of cupric ions, revealing that a portion of the anodic current is used for Cu dissolution.

Fig. 5 shows the current as a function of time for a rotating cylinder electrode at different values of the pre-treatment potential. The

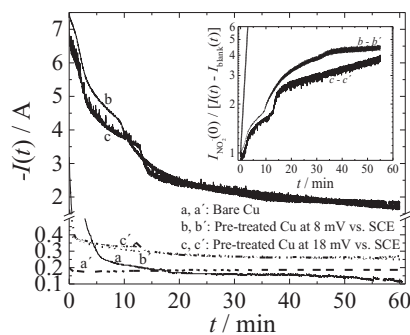


Figure 5. Current as a function of time for a rotating cylinder electrode. Pre-treatment in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ during 30 min. (a, a'): Bare copper. (b, b'): Pre-treated copper at $E_{\text{SCE}} = 8 \text{ mV}$. (c, c'): Pre-treated copper at $E_{\text{SCE}} = 18 \text{ mV}$. Electrolysis potential: -1.2 V against SCE. Electrolysis time: 1 h. Temperature: 30°C . Rotation speed: 1000 rpm. Full lines: total current, dashed lines: blank current. Inset: ratio of initial nitrite current and the value of nitrite current at time t ; straight line: temporal behavior under limiting current conditions.

experiments were made potentiostatically at -1.2 V . At the end of the experiment, the surface of the electrode does not undergo significant changes in morphology, without evidence of corrosion, obtaining a dark-brown color on the outside of Cu cylinder. The results for a not pre-treated copper cylinder are also reported. Moreover, it is observed that the average nitrite current is an order of magnitude higher at pre-treated electrodes than at bare Cu surfaces. Likewise, in the case of bare electrodes at times higher than 17 min the total current for NO_2^- reduction is lower than that of the supporting electrolyte, possibly due to the specific adsorption of the nitrite reduction products. The opposite behavior is observed when using pre-treated electrodes, where NO_2^- reduction current is always higher than the blank ones. Thus, a layer of copper oxides improves electrode performance. Otherwise, the current values become constant after 20 min in the case of the supporting electrolyte for electrodes with and without pre-treatment, while from this time until the end of the electrolysis the electrochemical responses of both pre-treated electrodes are practically the same.

Considering the rotating cylinder electrode as a stirred tank reactor and assuming a first-order reaction for the nitrite removal, the temporal behavior of the NO_2^- reduction current in a batch configuration is given by:⁴⁴

$$I_{\text{NO}_2^-}(t) = I_{\text{NO}_2^-}(0) \exp(-a_c kt) \quad [8]$$

here k is the kinetic constant according to:

$$k = k_t / (1 + Da) \quad [9]$$

being Da the Damköhler number.⁴⁵ The total current, $I(t)$, is:

$$I(t) = I_{\text{NO}_2^-}(t) + I_{\text{blank}}(t) \quad [10]$$

where the second term on the right hand side, $I_{\text{blank}}(t)$, is the background current. This equation assumes that $I_{\text{blank}}(t)$ determined with the supporting electrolyte is maintained in presence of nitrite. Introducing Eq. 8 into Eq. 10 and rearranging yields:

$$\ln \left\{ I_{\text{NO}_2^-}(0) / [I(t) - I_{\text{blank}}(t)] \right\} = a_c kt \quad [11]$$

In the inset of Fig. 5 the data of the experiments with an activation time of 30 min are re-plotted according to Eq. 11. The straight line corresponds to the electrochemical behavior under limiting mass-transfer conditions, which provides the maximum variation of current with time. The mass-transfer coefficient was calculated by using the correlation proposed by Eisenberg et al.⁴⁶

$$Sh = 0.0791 Re^{0.7} Sc^{0.356} \text{ for } 112 < Re < 1.62 \times 10^5 \quad [12]$$

The Sherwood, Reynolds and Schmidt numbers are defined as usual for this electrode geometry.³⁴ By using the physicochemical

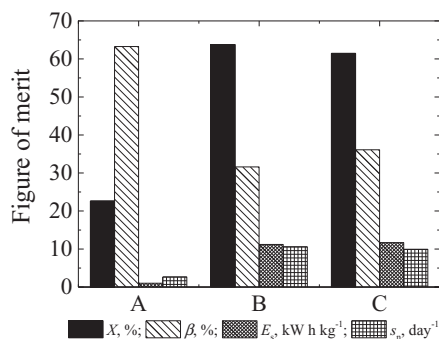


Figure 6. Figures of merit for the nitrite reduction at a rotating copper cylinder for different pre-treatment procedures. $E_{\text{SCE}} = -1.2 \text{ V}$. Electrolysis time: 1 h. Temperature: 30°C . Rotation speed: 1000 rpm. Pre-treatment in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ during 30 min. A: Bare copper. B: Pre-treatment at $E_{\text{SCE}} = 8 \text{ mV}$. C: Pre-treatment at $E_{\text{SCE}} = 18 \text{ mV}$.

properties reported on Table I, the Reynolds number is 89726, being the mass-transfer coefficient $9.87 \times 10^{-5} \text{ m s}^{-1}$ very close to that of the RDE under laminar flow conditions. The kinetic constant can be obtained from the slope of the linear fitting of experimental results at the beginning of the trial. A similar value of the rate constant is obtained with the pre-treated electrodes at 8 or 18 mV against SCE, $1.85 \times 10^{-5} \text{ m s}^{-1}$, giving a Damköhler number of 0.19. This value shows that the nitrite reduction as a global reaction is under a mixed kinetic control and in order to increase the kinetic constant in Eq. 9, it is convenient the use of electrochemical reactors with a good mass-transfer performance as the rotating cylinder electrode. The inset also reveals that immediately after the start of the experiment the slope decreases with time. Thus, the reactor performance declines. Hence, the pre-treatment activates the electrode improving the reactor efficiency during the early stages of the trial, but at longer times the electrode is deactivated probably due to the adsorption of nitrite reduction products, which block the electrode surface.

The nitrite conversion, current efficiency for NH_3 generation, molar yield of P product, specific energy consumption referred to NaNO_2 reacted, and normalized space velocity are respectively defined as follows:

$$X(t) = \left[c_{\text{NO}_2^-}(0) - c_{\text{NO}_2^-}(t) \right] / c_{\text{NO}_2^-}(0) \quad [13]$$

$$\beta(t) = v_e F c_{\text{NH}_3}(t) V / \int_0^t I(t) dt \quad [14]$$

$$Y_P(t) = c_P(t) / \left[c_{\text{NO}_2^-}(0) - c_{\text{NO}_2^-}(t) \right] \quad [15]$$

$$E_s(t) = \int_0^t I(t) U(t) dt / \left[c_{\text{NO}_2^-}(0) M_{\text{NaNO}_2} V X(t) \right] \quad [16]$$

$$s_n(t) = -\ln[1 - X(t)] / [t \ln(10)] \quad [17]$$

Moreover, it will commonly be found that it is not possible to optimize all the figures of merit; a change in reactor design or electrolysis parameters to improve one figure of merit may be detrimental to another. Then, it is necessary to trade-off the importance of the figures of merit to find the overall economic optimum.⁴⁷

The figures of merit for nitrite electro-reduction as a function of the pre-treatment procedure at -1.2 V are depicted in Fig. 6. The concentration of the different species is given in Table II. The data for a not pre-treated Cu cylinder are also displayed. The best results are obtained with a pre-treatment at 18 mV versus SCE, where NH_3 production is maximal. Moreover, in all cases a high NO_3^- generation

Table II. Final composition of the electrolyte, mmol dm^{-3} , after 1 h electrolysis using the rotating cylinder electrode. $E_{\text{SCE}} = -1.2 \text{ V}$. Temperature: 30°C . Rotation speed: 1000 rpm. Supporting electrolyte: $[\text{Na}_2\text{SO}_4] = 0.1 \text{ mol dm}^{-3}$.

Initial composition	Bare copper $[\text{NaNO}_2] = 30.7 \text{ mmol dm}^{-3}$	Pre-treatment, $E_{\text{SCE}} = 8 \text{ mV}$ $[\text{NaNO}_2] = 30.7 \text{ mmol dm}^{-3}$	Pre-treatment, $E_{\text{SCE}} = 18 \text{ mV}$ $[\text{NaNO}_2] = 29.3 \text{ mmol dm}^{-3}$
Nitrite	23.7	11.1	11.3
Nitrate	5.9	12.6	10.7
Ammonia	1.1	6.7	7.3
Hydroxylamine	N D	0.3	N D
pH	11.9	12.6	12.6

N D: no detected.

Table III. Final composition of the electrolyte after 1 h electrolysis using pre-treated electrodes at different cathodic potentials. Temperature: 30°C . Rotation speed: 1000 rpm. Supporting electrolyte: $[\text{Na}_2\text{SO}_4] = 0.1 \text{ mol dm}^{-3}$.

Initial composition, electrolysis at E_{SCE}	Pre-treatment at $E_{\text{SCE}} = 8 \text{ mV}$		
	$[\text{NaNO}_2] = 30.7 \text{ mmol dm}^{-3}$, $E_{\text{SCE}} = -1.2 \text{ V}$	$[\text{NaNO}_2] = 29.3 \text{ mmol dm}^{-3}$, $E_{\text{SCE}} = -1.3 \text{ V}$	$[\text{NaNO}_2] = 29.3 \text{ mmol dm}^{-3}$, $E_{\text{SCE}} = -1.4 \text{ V}$
$Y_{\text{Nitrate}}, \%$	64.5	63.1	75.1
$Y_{\text{Ammonia}}, \%$	34	36.9	24.9
pH	12.6	12.6	12.5
Initial composition, electrolysis at E_{SCE}	Pre-treatment at $E_{\text{SCE}} = 18 \text{ mV}$		
	$[\text{NaNO}_2] = 29.3 \text{ mmol dm}^{-3}$, $E_{\text{SCE}} = -1.2 \text{ V}$	$[\text{NaNO}_2] = 28.4 \text{ mmol dm}^{-3}$, $E_{\text{SCE}} = -1.3 \text{ V}$	$[\text{NaNO}_2] = 28.4 \text{ mmol dm}^{-3}$, $E_{\text{SCE}} = -1.4 \text{ V}$
$Y_{\text{Nitrate}}, \%$	59.3	70.2	78.4
$Y_{\text{Ammonia}}, \%$	40.7	29.8	21.6
pH	12.6	12.5	12.4

and negligible NH_2OH concentration were observed. Further, based on a mass balance for nitrogen, no gases were produced. Likewise, the composition of the final solutions was similar using both pre-treated Cu electrodes, which can be explained considering that the pre-treatment potential is only important up to achieving that the electrode surface area is completely covered with copper oxides. In both cases, NO_2^- conversion was approximately 63%. The current efficiency at 8 mV against SCE pre-treatment was 32% while at 18 mV was 36%.

In order to reduce the concentration of nitrite to minimum values and to maximize the NH_3 production, electrolysis were carried out potentiostatically at different cathodic potentials using pre-treated electrodes. The results are illustrated in Fig. 7 and Table III. The best performance is obtained at a potential of -1.3 V and pre-treatment at a potential of 18 mV against SCE, where the specific energy consumption is minimal. This figure of merit is crucial because it is closely related to the electrolytic energy costs. Likewise, in all cases no gases and a negligible hydroxylamine formation were observed. Thus, as a relevant consequence of the above studies, henceforth Cu electrode will be treated in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ at 18 mV versus SCE during 30 min previous each run.

The application of a periodic potential reversal, PPR, approach has been shown to be useful in the formation of ammonia from synthetic effluents containing nitrate in a sulfate medium at neutral pH.³⁴ Then, Fig. 8 reports on the temporal behavior of the current using a PPR procedure at 1000 rpm and 30°C in a non-buffered nitrite electrolyte. Thus, the cylinder electrode was controlled at a fixed cathodic potential during five minutes, and immediately reactivated by applying a potential of 18 mV with respect to SCE during the same time, passing an anodic current. The results for experiments without use of PPR are also reported as a comparison. At the beginning, the runs with and without PPR show a similar behavior, but at times higher than 15 min the electrode reactivation allows obtaining a higher current.

Fig. 9 shows the figures of merit for electrolysis when the PPR approach is applied at different cathodic potentials with a pre-treated Cu cylinder into a $30 \text{ mmol dm}^{-3} \text{ NaNO}_2 + 0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution. The concentration of the different species is given in

Table IV. It can be emphasized that at each cathodic potential here analyzed the use of PPR increases not only the nitrite conversion, but also the current efficiency and the normalized space velocity. Also, the ammonia molar yield is enhanced, diminishing that of nitrate.

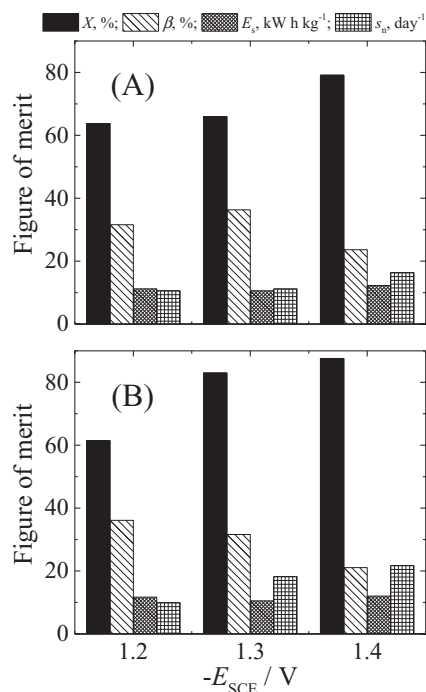
**Figure 7.** Figures of merit for the nitrite reduction at a rotating copper cylinder for different cathodic potentials. Electrolysis time: 1 h. Temperature: 30°C . Rotation speed: 1000 rpm. Pre-treatment in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ during 30 min. (A) Pre-treatment at $E_{\text{SCE}} = 8 \text{ mV}$. (B) Pre-treatment at $E_{\text{SCE}} = 18 \text{ mV}$.

Table IV. Final composition of the electrolyte, mmol dm^{-3} , after 1 h electrolysis using the rotating cylinder electrode. Pre-treatment at a potential of $E_{\text{SCE}} = 18 \text{ mV}$ in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ during 30 min. Temperature: 30°C . Rotation speed: 1000 rpm. Supporting electrolyte: $[\text{Na}_2\text{SO}_4] = 0.1 \text{ mol dm}^{-3}$.

Initial composition	$[\text{NaNO}_2] = 29.2 \text{ mmol dm}^{-3}$, $E_{\text{SCE}} = -1.2 \text{ V}$	$[\text{NaNO}_2] = 29.2 \text{ mmol dm}^{-3}$, $E_{\text{SCE}} = -1.3 \text{ V}$	$[\text{NaNO}_2] = 30 \text{ mmol dm}^{-3}$, $E_{\text{SCE}} = -1.4 \text{ V}$
Nitrite	3.5	2.2	2.3
Nitrate	2.9	1.6	3.2
Ammonia	22.8	25.3	24.6
pH	13.2	13	13

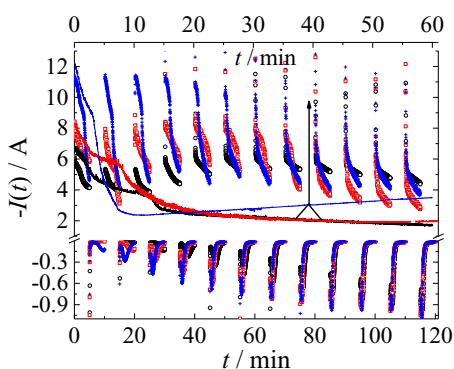


Figure 8. Current as a function of time for a rotating cylinder electrode applying a potential periodic reversal, PPR, procedure. Pre-treatment in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ during 30 min at a potential of $E_{\text{SCE}} = 18 \text{ mV}$. Temperature: 30°C . Rotation speed: 1000 rpm. Continuous line: experiments under the same working conditions without PPR. Scattered line: trials with PPR. Applied cathodic potentials: (o) $E_{\text{SCE}} = -1.2 \text{ V}$, (□) $E_{\text{SCE}} = -1.3 \text{ V}$, (+) $E_{\text{SCE}} = -1.4 \text{ V}$.

Taking into account the results with the PPR procedure, the best reactor performance was achieved at a potential of -1.3 V , being the NO_2^- conversion, the molar yield and the current efficiency for NH_3 generation of 92%, 94% and 59%, respectively. Under these working conditions, the mean values of the cell voltage and the cathodic current were 6 V and 5.7 A, respectively. Otherwise, similar values for X and s_n were obtained at the most cathodic potential. However, at -1.4 V the high value of E_s , $26.1 \text{ kW h kg}^{-1}$, becomes unsuitable this cathodic potential.

Comparing the electrolysis in the presence and absence of PPR, it is observed that the reversion of potential causes the reduction of the nitrate generated by the undesired anodic oxidation of nitrite. Initially part of NO_2^- is reduced at the cathode to NH_3 , while another portion of nitrite is oxidized at the platinum anode to NO_3^- , which accumulates in

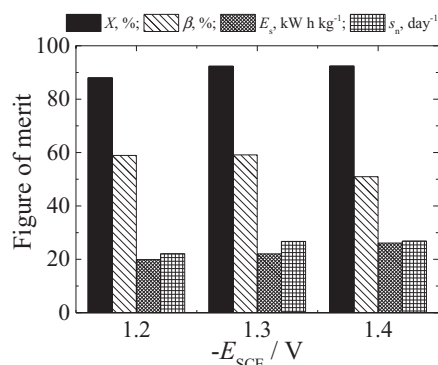


Figure 9. Figures of merit for the nitrite reduction at a rotating copper cylinder for different cathodic potentials applying a potential periodic reversal, PPR, procedure. Electrolysis time: 1 h. Temperature: 30°C . Rotation speed: 1000 rpm. Pre-treatment in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ during 30 min at a potential of $E_{\text{SCE}} = 18 \text{ mV}$.

the electrolyte. In addition, NO_2^- reduction products can be adsorbed onto the surface of Cu cylinder. These adsorbed products decrease the reactor performance, obtaining a concentrated solution of nitrate and nitrite. When PPR is applied, the products of the NO_2^- reduction are desorbed due to the formation of a new copper oxides layer, favoring the reduction of NO_3^- to NH_3 . The electrochemical behavior of the present reactor is similar to that obtained with nitrate solutions.³⁴ The figures of merit at -1.3 V and -1.4 V with solutions containing $30 \text{ mmol dm}^{-3} \text{ NaNO}_2 + 0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ are approximately equal to those presented at -1.2 V and -1.3 V in nitrate electrolytes, $30 \text{ mmol dm}^{-3} \text{ KNO}_3 + 0.1 \text{ mol dm}^{-3} \text{ K}_2\text{SO}_4$, respectively.

Conclusions

Copper electrodes showed a good performance for the reduction of nitrite to ammonia from a specific synthetic effluent, $30 \text{ mmol dm}^{-3} \text{ NaNO}_2$ in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ as supporting electrolyte, when they are activated at a potential of 18 mV against SCE in a $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ aqueous solution forming a film of cuprous oxide and cupric oxide being the first the predominant species.

The high conversion of NO_2^- to NH_3 with no gases and NH_2OH production reveals that an undivided electrochemical reactor with an activated rotating cylinder cathode of copper is promising as a first step for the transformation of this synthetic effluent containing nitrite in fertilizers.

The application of a periodic potential reversal technique, 5 min as cathode and 5 min in reactivation mode as anode, permits the maintenance of the activation of the cathode and the achievement of a high conversion of nitrite to ammonia. Also, the PPR procedure enables the electro-reduction of the accumulated nitrate to NH_3 , improving NO_2^- conversion, the current efficiency and the normalized space velocity.

An electrochemical reactor with an activated rotating cylinder electrode applying a PPR procedure showed a good performance for the abatement of nitrite. This reactor can be easily scale up using a horizontal cylinder and dividing the electrolyte volume into several compartments with annular baffles in order to approach the plug flow model, as it was employed for the removal of metal ions.⁴⁸

Acknowledgments

This work was supported by the Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and Universidad Nacional del Litoral (UNL) of Argentina.

List of Symbols

a_e	specific surface area, m^{-1}
c_i	molar concentration of i species, mg dm^{-3} or mol dm^{-3}
d	cylinder diameter, mm or m
D	diffusion coefficient, $\text{m}^2 \text{ s}^{-1}$
Da	Damköhler number = k_f/k_m
E_s	specific energy consumption, kW h kg^{-1}
E_{SCE}	electrode potential referred to Saturated Calomel Electrode, V
F	Faraday constant, $96484.56 \text{ C mol}^{-1}$

I	current, A
j	current density, mA cm ⁻² or A m ⁻²
k	kinetic constant, m s ⁻¹
k_f	rate constant, m s ⁻¹
k_m	mass-transfer coefficient, m s ⁻¹
M	molar mass, g mol ⁻¹
Re	Reynolds number = $\omega d^2/(2\nu)$
s_n	normalized space velocity, h ⁻¹ or day ⁻¹
Sc	Schmidt number = ν/D
Sh	Sherwood number = $k_m d/D$
t	time, min or h
U	cell voltage, V
V	electrolyte volume, dm ³
ν_e	number of exchanged electrons per nitrite molecule
X	nitrite conversion, %
Y_P	molar yield of P product, %

Greek

β	current efficiency for NH ₃ generation, %
ν	kinematic viscosity, m ² s ⁻¹
ω	rotation speed, rad s ⁻¹ or rpm

Subscripts

blank	supporting electrolyte
-------	------------------------

References

- J. O'M. Bockris and J. Kim, *J. Appl. Electrochem.*, **27**, 623 (1997).
- C. O. Akinbile and M. S. Yusoff, *Int. J. Phytorem.*, **14**, 201 (2012).
- A. Cockburn, G. Brambilla, M.-L. Fernández, D. Arcella, L. R. Bordajandi, B. Cottrill, C. van Peteghem, and J.-L. Dorne, *Toxicol. Appl. Pharm.*, **270**, 209 (2013).
- World Health Organization, *Nitrate and nitrite in drinking-water*, WHO Press, Geneva (2011).
- R. Ansari, N. Khoshbakht Fahim, and A. Fallah Delavar, *Open Process Chem. J.*, **2**, 1 (2009).
- G. Zhu, Y. Peng, B. Li, J. Guo, Q. Yang, and S. Wang, *Rev. Environ. Contam. Toxicol.*, **192**, 159 (2008).
- S. Pulkka, M. Martikainen, A. Bhatnagar, and M. Sillanpää, *Sep. Purif. Technol.*, **132**, 252 (2014).
- V. Rosca, M. Duca, M. T. de Groot, and M. T. M. Koper, *Chem. Rev.*, **109**, 2209 (2009).
- C. Xia, C. Xiaolan, W. Ning, and G. Lin, *Anal. Chim. Acta*, **691**, 43 (2011).
- D. Reyter, D. Bélanger, and L. Roué, *Electrochim. Acta*, **53**, 5977 (2008).
- S. Prasad, J. W. Weidner, and A. E. Farrell, *J. Electrochem. Soc.*, **142**, 3815 (1995).
- J. D. Genders, D. Hartsough, and D. T. Hobbs, *J. Appl. Electrochem.*, **26**, 1 (1996).
- S. Kondaveeti, S.-H. Lee, H.-D. Park, and B. Min, *Water Res.*, **51**, 25 (2014).
- S. H. Lin and C. L. Wu, *J. Environ. Sci. Health*, **A32**, 2125 (1997).
- H. A. Duarte, K. Jha, and J. W. Weidner, *J. Appl. Electrochem.*, **28**, 811 (1998).
- N. S. Abuzaid, Z. Al-Hamouz, A. A. Bukhari, and M. H. Essa, *Water, Air, Soil Pollut.*, **109**, 429 (1999).
- K. Jha and J. W. Weidner, *J. Appl. Electrochem.*, **29**, 1305 (1999).
- J. L. Ginner, P. J. J. Alvarez, S. L. Smith, and M. M. Scherer, *Environ. Eng. Sci.*, **21**, 219 (2004).
- D. De, E. E. Kalu, P. P. Tarjan, and J. D. Englehardt, *Chem. Eng. Technol.*, **27**, 1 (2004).
- L. Szpyrkowicz, S. Daniele, M. Radaelli, and S. Specchia, *Appl. Catal., B: Environ.*, **66**, 40 (2006).
- A. Fernandes, D. Santos, M. J. Pacheco, L. Ciriaco, and A. Lopes, *Appl. Catal., B: Environ.*, **148-149**, 288 (2014).
- M. A. Hasnat, R. Agui, S. Hinokuma, T. Yamaguchi, and M. Machida, *Catal. Commun.*, **10**, 1132 (2009).
- I. Katsounaros, M. Dortsiou, and G. Kyriacou, *J. Hazard. Mater.*, **171**, 323 (2009).
- M. Saiful Alam, M. A. Hasnat, M. A. Rashed, Md. Rezwan Miah, and I. S. M. Saiful, *Electrochim. Acta*, **76**, 102 (2012).
- G. Pérez, R. Ibáñez, A. M. Urtiaga, and I. Ortiz, *Chem. Eng. J.*, **197**, 475 (2012).
- E. Lacasa, P. Cañizares, J. Llanos, and M. A. Rodrigo, *Sep. Purif. Technol.*, **80**, 592 (2011).
- M. Shibata, K. Yoshida, and N. Furuya, *J. Electroanal. Chem.*, **387**, 143 (1995).
- M. Shibata, K. Yoshida, and N. Furuya, *J. Electroanal. Chem.*, **442**, 67 (1998).
- M. Shibata, K. Yoshida, and N. Furuya, *J. Electrochem. Soc.*, **145**, 595 (1998).
- M. Shibata and N. Furuya, *J. Electroanal. Chem.*, **507**, 177 (2001).
- A. Sahin, W.-T. Lin, W. O. Khunjar, K. Chandran, S. Banta, and A. C. West, *J. Electrochem. Soc.*, **160**, G19 (2013).
- M. Ghazouani, H. Akrou, and L. Bousselmi, *Desalination Water Treat.*, **53**, 1107 (2015).
- V. Díaz, R. Ibáñez, P. Gómez, A. M. Urtiaga, and I. Ortiz, *Water Res.*, **45**, 125 (2011).
- O. González Pérez and J. M. Bisang, *Electrochim. Acta*, **194**, 448 (2016).
- C. T. John Low, C. Ponce de León, and F. C. Walsh, *Aust. J. Chem.*, **58**, 246 (2005).
- F. C. Walsh, G. Kear, A. H. Nahlé, J. A. Wharton, and L. F. Arenas, *Corros. Sci.*, (2017).
- L. S. Clesceri, A. E. Greenberg, and A. D. Eaton, *Standard Methods for the Examination of Water and Wastewater*, 20th ed., Public Health Association, Washington (1999).
- B. Deepa, N. Balasubramanian, and K. S. Nagaraja, *Chem. Pharm. Bull.*, **52**, 1473 (2004).
- Y.-H. Wang and J.-B. He, *Electrochim. Acta*, **66**, 45 (2012).
- O. A. Petrii and T. Y. Safonova, *J. Electroanal. Chem.*, **331**, 897 (1992).
- D. Reyter, D. Bélanger, and L. Roué, *Electrochim. Acta*, **53**, 5977 (2008).
- P. Vanýšek, in *CRC Handbook of Chemistry and Physics*, D. R. Lide, Editor, pp. 5, CRC Press/Taylor and Francis, Boca Raton (2010).
- S. Cattarin, *J. Appl. Electrochem.*, **22**, 1077 (1992).
- F. C. Walsh, *A first course in Electrochemical Engineering*, Electrochemical Consultancy, Hants (1993).
- K. Scott, *Electrochemical Reaction Engineering*, Academic Press Inc., London (1991).
- M. Eisenberg, C. W. Tobias, and C. R. Wilke, *J. Electrochem. Soc.*, **101**, 306 (1954).
- D. Pletcher and F. C. Walsh, *Industrial Electrochemistry*, Chapman and Hall, London (1993).
- F. S. Holland, *Chem. Ind. (London)*, **7**, 453 (1978).