



Electrochemical reduction of nitrate on bismuth cathodes

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ABSTRACT

The electrochemical reduction of nitrate was studied on bismuth cathodes in a 0.4 M NaHCO₃/0.4 M Na₂CO₃ solution containing 0.05 M NaNO₃. The main product of the electrolysis was nitrogen having selectivity (%S) between 58% and 65%. The other products were nitrous oxide (7–22%), ammonia (3.8–19%) and nitrite (1.8–2.6%). The total Faradaic Efficiency (%FE) was ranged from 80% at –1.8 to 20% at –2.6 V vs. Ag/AgCl. The reduction of nitrate takes place through two paths; the first is electrochemical and the second one is autocatalytic, which involves an intermediate having an oxidation number lower than +2. The rate of the autocatalytic path at –1.8 V vs. Ag/AgCl was up to 48 times higher than that of the electrochemical one. The bismuth cathode undergoes slow cathodic corrosion during the electrolysis the rate of which increases with the increase of the negative potential. Bismuth is a promising cathode for the treatment of wastewaters containing nitrate, such as the low level nuclear wastes, since both the rate of the reduction and the selectivity to nitrogen are high.

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1. Introduction

The electrochemical reduction of nitrate has a long history since 1834, when the first attempt was made by Faraday [1]. The work done until 1926 has been reviewed by Bancroft [2] and Joss [3]. The main purpose of these early works was either the study of the action of nitric acid on metals or the production of useful chemicals such as metal nitrates and hydroxylamine [4]. In the studies performed during the last 30 years [5–28] the interest has been mainly focused on the treatment of wastewaters, such as the low level nuclear wastes and the brine resulting from the removal of nitrate from potable water by physicochemical methods (e.g. ion exchange, reverse osmosis and electrodialysis), as well as on the production of useful chemicals, such as hydroxylamine nitrate [29]. The electrochemical treatment of the above mentioned wastewaters aims to the conversion of nitrate to the non toxic nitrogen gas.

Given that nitrogen has oxidation states from +5 to –3, the transition from nitrate to nitrogen can give a large number of by-products such as NO₂, NO₂⁻, NO, N₂O, NH₂OH, NH₃, NH₂NH₂. In addition, some intermediates such as: H₂N₂O₃, HNO (or its dimer H₂N₂O₂) and NH₂NO₂, whose stability depends on the solution pH and the temperature [30–33], may be involved in the reduction mechanism. The intermediates of the reduction of nitrate have not been fully clarified yet because reliable analytical methods are not available.

The conversion of nitrate to nitrogen is a difficult reaction since both the selectivity to nitrogen and the rate of the reduction are usually low. In recent works from our laboratory [28,34,35] the electrochemical conversion of nitrate was carried out on Sn with both high rate and high selectivity (%S) (85–92%) towards nitrogen. Other researchers have recently reported a high selectivity to nitrogen on Pt–Sn (85%) [36] and on Pd–Cu (60%) [16]. It was found that on tin cathode the rate of the reduction increases as the potential becomes more negative and as the concentration of the supporting electrolyte and the crystallographic radius of its cation increases in the order Li⁺ < Na⁺ < K⁺ < Cs⁺ and that of the anion in the order F⁻ < Cl⁻ < Br⁻ < I⁻ [34].

Even though the reduction of nitrate on tin proceeds with both high rate and selectivity to nitrogen it requires a high negative potential (~ –2.8 V vs. Ag/AgCl), where tin undergoes cathodic corrosion, which leads to a final solution with a non acceptable concentration of tin. The present work deals with the reduction of nitrate on bismuth which was found to be also an efficient cathode for the conversion of nitrate to nitrogen and nitrous oxide at less negative potentials, where the cathodic corrosion is limited. Moreover, the work shows that the mechanism of the reduction includes an autocatalytic path, the rate of which is much higher than that of the electrochemical one.

2. Experimental

A Teflon electrochemical cell equally divided into two volumes by a Nafion 117 (H⁺ form) cation exchange membrane was used in all experiments. The geometrical area of the bismuth cathode (Sigma–Aldrich, 99.9%) was 2 cm² and the anode was a platinized Pt

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foil (Alpha Metal) of 6 cm². The bismuth cathode was prepared by melting granulated bismuth (99%, BDH Laboratory reagents) followed by cooling at ambient temperature and finally by polishing it with a #1200 paper before each use. All chemicals were reagent grade (Sigma–Aldrich) and sodium hyponitrate (Angeli’s salt) was provided from Cayman Chemicals. Ultra-pure water from a Sation 9000 apparatus were used for the preparation of the solutions.

The potential was controlled by a Wenking POS73 (Bank Elektronik) potentiostat and the reference was a saturated Ag/AgCl electrode. A helium stream (high purity, Air Metal) having a constant flow rate of 12 mL min⁻¹ withdrew the gaseous products of the electrolysis from the catholyte. The dilution of the gaseous stream mainly due to the hydrogen evolution as well as to the nitrogen production was taken into account in the calculations. The total volume of the produced gases was calculated by integrating the instant concentration curve of each product.

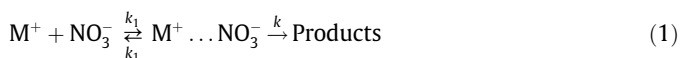
The analytical methods have been described previously [28,34,35]. More information about Section 2 and the calculation of the %S can be found in Refs. [28,34].

3. Results

3.1. Study by voltammetry

Cyclic voltammograms of Bi electrodes in 0.4 M NaHCO₃/0.4 M Na₂CO₃ buffer solution containing various concentrations of nitrate are shown in Fig. 1a. Given that the rate of the reduction of nitrate depends on the ionic strength [34], the latter was kept constant (1.6 M) in all solutions.

The reduction is irreversible and the form of the voltammetric curves was independent of the scan rate in the range of 25–100 mV s⁻¹, which is usually related to a chemical equilibrium which takes place before the electron transfer. Furthermore, the current in the presence of nitrate continuously increases as the potential increases from -1.3 to -2.25 V vs. Ag/AgCl. Similar phenomena have been also observed on tin cathodes [19,35] and have been explained by assuming that the reduced nitrate and the cation of the supporting electrolyte form a virtual ion pair, which is located at the outer Helmholtz plane according to the equilibrium:



Based on this hypothesis the equation which gives the rate of the reduction is [35]:

$$-\frac{d[NO_3^-]}{dt} = k[M^+] \frac{K[NO_3^-]}{1 + K[NO_3^-]} \quad (2)$$

where $K = \frac{k_1}{k_{-1}}$, k is the rate constant and $[M^+]$ is the concentration of the cation of the supporting electrolyte. If it is assumed that the reaction (1) is fast, the rate of the reduction (Eq. (2)) depends upon the $[NO_3^-]$ and $[M^+]$ at the outer Helmholtz plane and the values of k and K . The formation of the ion pair $M^+NO_3^-$ can additionally explain why nitrate is not repelled by the likely charged electrode at so negative potentials.

Eq. (2) can also predict the form of the curve of the net current density (cd) vs. the concentration of nitrate (Fig. 1b) at -1.6 V vs. Ag/AgCl, where the background current due to the hydrogen evolution reaction is negligible. The cd at low concentrations (0.05–0.2 M) increases almost linearly, while at higher concentrations the effect is less pronounced.

3.2. Steady state electrolytic experiments

Fig. 2 shows the concentration profile of nitrate and its concentration which was converted to each product vs. time at -2.1 V vs. Ag/AgCl, in a 0.4 M NaHCO₃/0.4 M Na₂CO₃ buffer containing 0.05 M NaNO₃. The main products were nitrogen and nitrous oxide with %S 65% and 16%, respectively. The by-products were ammonia (12%) and nitrite (1%). The deviation of the sum of the nitrogen containing species from 100% was attributed to the experimental error which was about ±10%. It should be mentioned that traces of hydroxylamine were also detected during the electrolysis but it was not detectable in the final solution.

3.3. Influence of the potential

The rate of the reduction increases as the potential becomes more negative (Fig. 3) which is in agreement with the voltammetric measurements. At potentials more negative than -2.0 V vs. Ag/AgCl the concentration of nitrate drops rapidly from the beginning of the electrolysis, while at -1.8 V vs. Ag/AgCl there is an induction period where the reaction is slow (90 min) followed by a stage where the concentration of nitrate decreases rapidly. However, the pH of the bulk solution changes during the electrolysis from 9.65 at the beginning to 11.3 at the end, despite the high capacity of the buffer, while the increase in the local pH is expected to be higher. In order to verify if the S-shaped profile of the concentration of nitrate was due to the gradual increase of the pH during the electrolysis an additional experiment was performed in which the pH of a solution containing 0.65 M Na₂CO₃ and 0.05 M NaNO₃

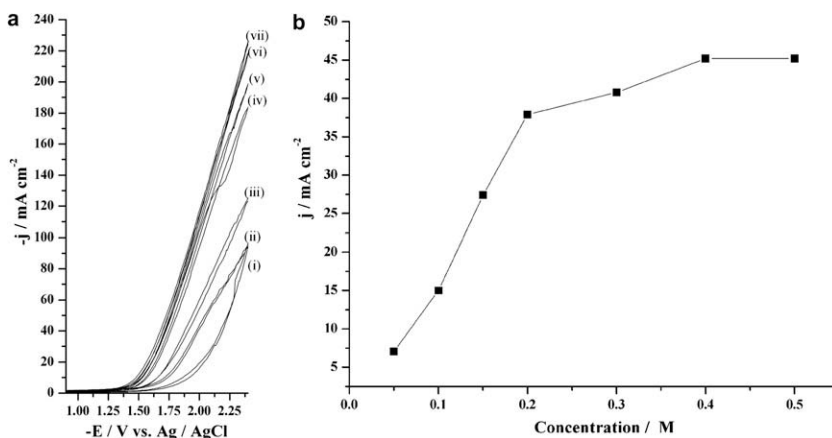


Fig. 1. (a) Cyclic voltammograms in 0.4 M NaHCO₃/0.4 M Na₂CO₃ electrolyte solution containing various concentrations of nitrate (i) 0 M, (ii) 0.05 M, (iii) 0.1 M, (iv) 0.2 M, (v) 0.3 M, (vi) 0.4 M and (vii) 0.5 M. Scan Rate: 25 mV s⁻¹ (b) Current density (cd) vs. the concentration of nitrate at -1.6 V vs. Ag/AgCl.

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