



The electrochemical reduction of nitrate ion on polypyrrole coated copper electrode



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ABSTRACT

Reduction of nitrate ion was investigated on copper and polypyrrole coated copper electrode (PPy-Cu) in acidic aqueous medium. The nitrate concentration was increased, from 5 to 200 mM (0.1 M LiClO₄ + 0.001 M HClO₄ + x mM KNO₃; x = 5, 20, 50, 100 and 200 mM). The applied potentials were -0.4, -0.6, -0.8, -1.0 and -1.2 V [Ag/AgCl]. Depending on these parameters, nitrate reduction gave the same products with different concentrations on blank Cu and on PPy-Cu. On blank Cu, nitrite ion was formed under almost any condition whereby on PPy-Cu, ammonia was the main product. Especially at low overpotentials, such as -0.4, -0.6 and -0.8 V no nitrite was detected on PPy-Cu which leads to the conclusion that the coating of the surface changes the reaction mechanism.

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1. Introduction

Nitrate ion is produced at nitrification state in the nitrogen-cycle and is a common ground source of water pollutant resulting from overfertilization and animal wastes. Although nitrate ion itself is a nontoxic ion, but it can be reduced to nitrite ion by bacteria and nitrite is the precursor of many carcinogens. Different techniques were applied to remove nitrate from ground water; i.e. biological removal, ion exchange, reverse osmosis, chemical and electrochemical reduction, for example can be mentioned under effectively tested methods [1–3]. Nevertheless, all these techniques are not economically feasible and universally applicable in every situation [4,5]. Additionally, none of them appears as efficient as electrochemical reduction.

Depending on electrode material used, the product distribution of nitrate reduction varies from nitrite to ammonia. Metals, such as Pb, Ni, Zn, Rh, Ru, Ir, Pd, Cu, Ag and Au were tested as electrode material in different electrolytic medium [6]. It was experimentally found that among these materials, Cu has a special place due to its affinity to produce more hydrogenated-products such as hydrazine (in alkaline solution) and ammonia as end-product [6].

It was reported that depending on applied potential, the formation of NO₂, NH₂OH, N₂, NH₃, NO and N₂ occur on Cu electrode in

alkaline electrolytes [6–10]. However, in acidic milieu, NO₂⁻ and NH₄⁺ were formed as main products [5,11–16]. The investigation of nitrate reduction and its mechanism became an important part of our subject, since it is an interstage of N₂-cycle which we are still studying electrochemically. By near consideration of nitrate reduction, the choice of right electrode material plays a primary role for achieving only ammonia (without nitrite). In that manner, we attempted to combine the nitrate reduction with our previous experiences gained on polymer coated metal electrodes by N₂ and CO₂ reduction in acidic media [17–28].

Beside bulk phase materials, the metals modified with conducting polymers, appear to be an alternative and can be employed for reduction as well. Polypyrrole coated metal electrodes were appropriate materials for N₂ and CO₂ reduction ([26,27]) and could be employed also for nitrate reduction. In fact, it was previously reported about polypyrrole coated Cu electrodes which were electro-active to nitrate ions [29].

From the ecological view of point, denitrification of ground water is surely a worthy aspect of treatment. On the other hand, the electro-reduction of nitrate ion to usable substances, such as ammonia, is another way need to be explored where the understanding of the mechanism of this process attains exceeding observance. So, we focussed our attention on the conversion of nitrate directly into ammonia keeping applied potentials as low as possible. In that manner, we present our results in relation to nitrate reduction on a polypyrrole-modified Cu electrode between -0.4 V and -0.8 V [Ag/AgCl] in 0.1 M LiClO₄ + 0.001 M HClO₄ + x mM KNO₃ (x = 5, 20, 50, 100 and 200 mM), for the first time.

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2. Experimental

A three-compartment H-type cell was used in the experiments. As working electrode, a copper disk (99.9%) with a diameter of 1 cm was embedded into a cylindrical polyester body. Prior to polypyrrole coating, the Cu-surface was cleaned mechanically from oxides and other impurities, washed with water and acetone. A Pt-plate (7.5 cm²) as counter electrode and Ag/AgCl (3.5 M KCl), as reference electrode were employed.

The electrochemical measurements were performed with an electrochemical workstation (CHI 660B). All preparative electrolysis were carried out potential-controlled (Wenking Potentiostat, POS 73). The current passing through electrolysis cell was determined with a coulombmeter (Denko, HF-201). Qualitative and quantitative product analyses were realized with spectrophotometer (Shimadzu, 1700 model). Electrochemical Impedance Spectra (EIS) were recorded with electrochemical workstation. The spectra were simulated by using a software programme (Z-view 1.2). The morphological images of electrode surface were recorded with a scanning electron microscope (Zeiss, Supra 55).

2.1. Coating procedure of Cu surface

The surface of the prepared Cu electrode was coated with polypyrrole for voltammetric studies and preparative electrolysis. For the coating process, aqueous 0.2 M potassium-sodium tartarate (KNaC₄H₄O₆) solution was used as electrolyte. 0.5 M of pyrrole was dissolved in this electrolyte and freshly cleaned Cu disc was immersed for coating in the electrolyte.

For initiation of the polymerization, the first cycle was kept between -0.80 V and 1.60 V [Ag/AgCl]. The following next 5 cycles were recorded between -0.80 V and +0.8 V [Ag/AgCl] in order to grow the polymer film on the Cu surface. After accomplishment of the coating process, the electrode was removed from the cell, washed with methanol and distilled water. Afterwards, it was employed for electrochemical studies. Electro-activity of the film was studied in a pyrrole-free ground electrolyte (0.2 M KNaC₄H₄O₆).

2.2. Quantitative analysis

The analytical results of preparative electrolysis were yielded only ammonia and nitrite ions in the solution. Concentrations of NO₂⁻ and NH₄⁺ were determined spectrophotometrically. Prior to spectrophotometric analysis, nitrite ion was converted into diazo-compound in the presence of N-(1-naphthyl) ethylene diamine (NEDA) and sulfanylamide and then, analysis were done with UV-VIS spectrophotometer at 540 nm. Determination of ammonia concentration was carried out according to Indophenol method [30,31]. The remaining amount of nitrate ion in electrolyte was also established by using Cu/Cd column as described in literatures [32,33]. For mechanistically investigations, electrochemical impedance spectroscopy (EIS) was employed and the EIS-spectra were simulated through a computer using the software (Z-view 1.2).

3. Results and discussion

Nitrate ions were reduced to nitrite and to ammonia on blank copper and polypyrrole-coated copper electrodes at low overpotentials in acidic medium. Nitrate concentration and applied potential play an important role for the electro-reduction. The influence of these parameters on the reaction was studied in detail via electrochemical techniques. Subsequently to analytical proceedings, the preparative electrolysis were carried out and for comprehension of reaction mechanism, electrochemical impedance spectroscopic (EIS) data were used.

3.1. Voltammetric investigations

3.1.1. On blank copper electrode

In the absence of nitrate ions, the cyclic voltammogram of blank copper shows no significant electrochemical activity up to ca. -1.2 V (Fig. 1a) in 0.1 M LiClO₄ + 0.001 M HClO₄ (pH = 3) where the small peaks at -0.6 V belong to Cu [26,34]. However, if NO₃⁻ ions do exist in the solution, an intensive cathodic wave is apparent up ca. -0.7 V, which may have its source from reduction of nitrate to nitrite and ammonia. Finally, hydrogen evolution starts up to -1.2 V (Fig. 1b).

Variation of NO₃⁻ ion concentration causes remarkable changes in the current densities on blank Cu in 0.1 M LiClO₄ + 0.001 M HClO₄ + x mM KNO₃ (x = 5, 20, 50, 100 and 200 mM) solution (Fig. 2). A comparison of increasing nitrate concentration, log C vs. log J, leads to a linear arising of the current, indicating a non-diffusion controlled reaction (Fig. 2, inset diagram).

As shown in Fig. 2, there was almost no electrochemical activity in the region between -0.2 V and -0.7 V on blank Cu. Up ca. -0.7 V the current increases depending on increasing substrate concentration.

3.1.2. Polypyrrole coated copper electrode

Polypyrrole was deposited potentiodynamically on Cu from 0.5 M pyrrole + 0.2 M KNaC₄H₄O₆ solution between -0.8 V and +0.65 V.

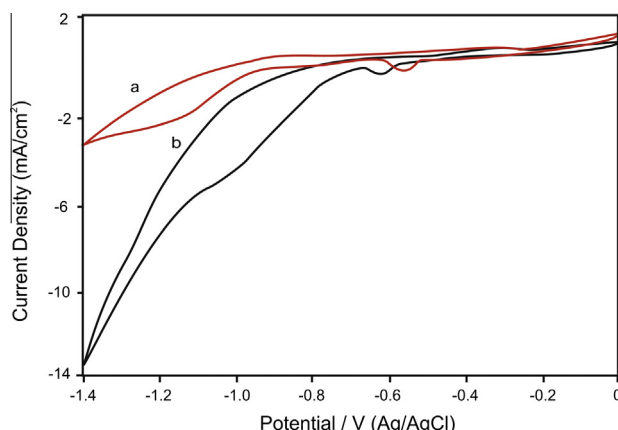


Fig. 1. Electrochemical behaviours of blank copper in (a) 0.1 M LiClO₄ + 0.001 M HClO₄ and (b) 0.1 M LiClO₄ + 0.001 M HClO₄ + 50 mM KNO₃. $\nu = 20 \text{ mV s}^{-1}$.

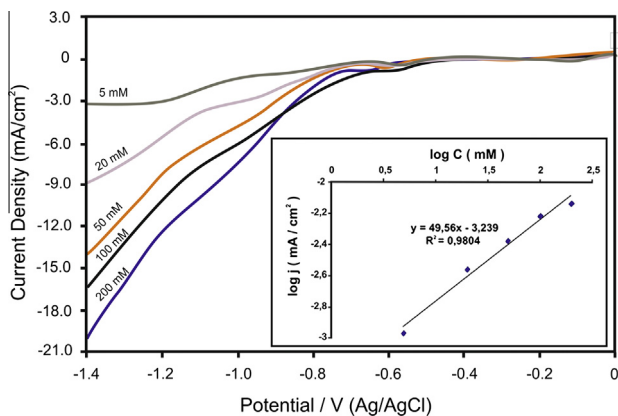


Fig. 2. Changes of current density with increasing NO₃⁻ concentration on blank Cu in 0.1 M LiClO₄ + 0.001 M HClO₄ + x mM KNO₃ (x = 5, 20, 50, 100 and 200 mM). Inset diagram: log C vs. log j; $\nu = 20 \text{ mV s}^{-1}$.

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