



# 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 LiClO<sub>4</sub> + 0.001 M HClO<sub>4</sub> + x mM KNO<sub>3</sub>; 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 NO<sub>2</sub>, NH<sub>2</sub>OH, N<sub>2</sub>, NH<sub>3</sub>, NO and N<sub>2</sub> occur on Cu electrode in

alkaline electrolytes [6–10]. However, in acidic milieu, NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> 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 N<sub>2</sub>-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 N<sub>2</sub> and CO<sub>2</sub> 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 N<sub>2</sub> and CO<sub>2</sub> 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 LiClO<sub>4</sub> + 0.001 M HClO<sub>4</sub> + x mM KNO<sub>3</sub> (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 cm<sup>2</sup>) 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 (KNaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>) 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 KNaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>).

### 2.2. Quantitative analysis

The analytical results of preparative electrolysis were yielded only ammonia and nitrite ions in the solution. Concentrations of NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> 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 sulfanylamine 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 spectroscopy (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 LiClO<sub>4</sub> + 0.001 M HClO<sub>4</sub> (pH = 3) where the small peaks at -0.6 V belong to Cu [26,34]. However, if NO<sub>3</sub><sup>-</sup> 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 NO<sub>3</sub><sup>-</sup> ion concentration causes remarkable changes in the current densities on blank Cu in 0.1 M LiClO<sub>4</sub> + 0.001 M HClO<sub>4</sub> + x mM KNO<sub>3</sub> (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 KNaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> solution between -0.8 V and +0.65 V.

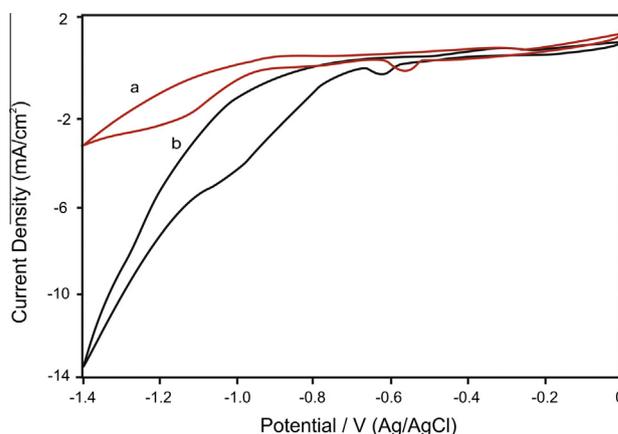


Fig. 1. Electrochemical behaviours of blank copper in (a) 0.1 M LiClO<sub>4</sub> + 0.001 M HClO<sub>4</sub> and (b) 0.1 M LiClO<sub>4</sub> + 0.001 M HClO<sub>4</sub> + 50 mM KNO<sub>3</sub>.  $\nu = 20 \text{ mV s}^{-1}$ .

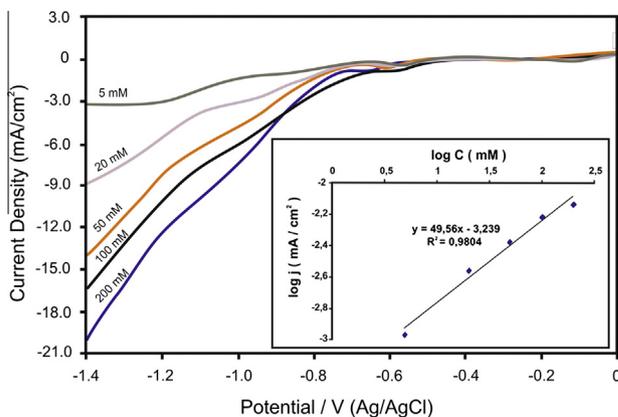
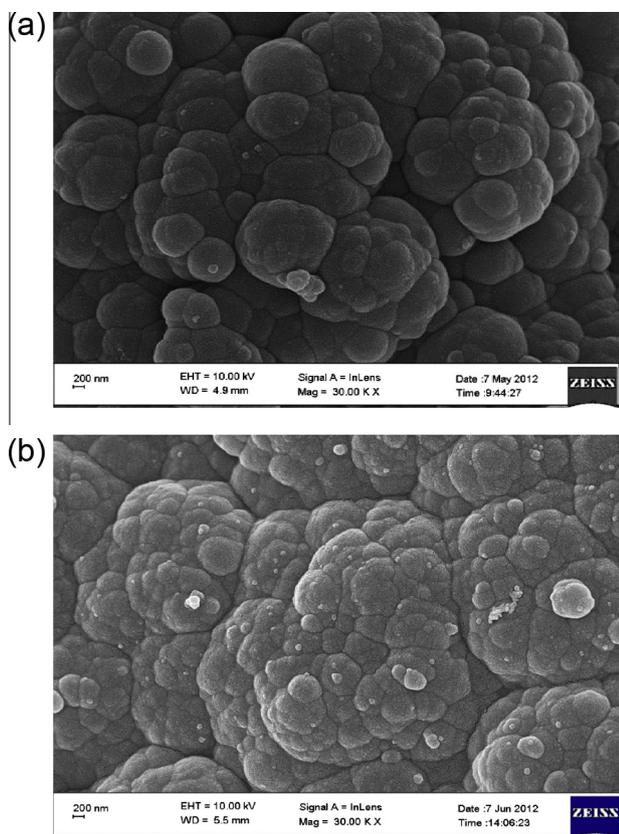
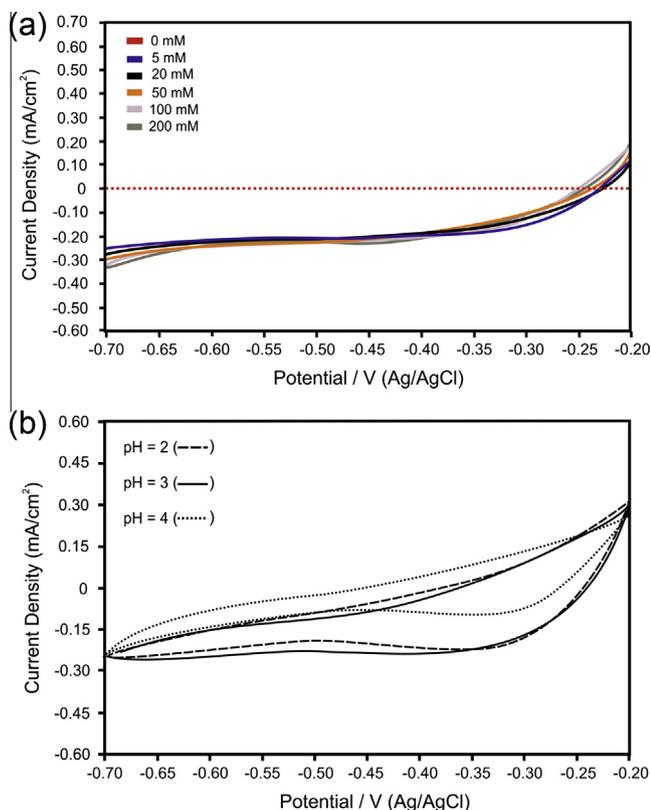


Fig. 2. Changes of current density with increasing NO<sub>3</sub><sup>-</sup> concentration on blank Cu in 0.1 M LiClO<sub>4</sub> + 0.001 M HClO<sub>4</sub> + x mM KNO<sub>3</sub> (x = 5, 20, 50, 100 and 200 mM). Inset diagram: log C vs. log j;  $\nu = 20 \text{ mV s}^{-1}$ .



**Fig. 3.** SEM micrographs of a Cu-PPy electrode (a) before electrolysis and (b) after electrolysis.



**Fig. 4.** Cyclic voltammograms on PPY-Cu electrode (a) at various nitrate concentrations in 0.1 M LiClO<sub>4</sub> + 0.001 M HClO<sub>4</sub> + x mM KNO<sub>3</sub> (x = 0, 5, 20, 50, 100 and 200 mM) and (b) at various acid concentrations (pH) in 0.1 M LiClO<sub>4</sub> + y M HClO<sub>4</sub> (y = 0.01 M; 0.001 M; 0.0001 M) + 50 mM KNO<sub>3</sub>.  $\nu = 20 \text{ mV s}^{-1}$ .

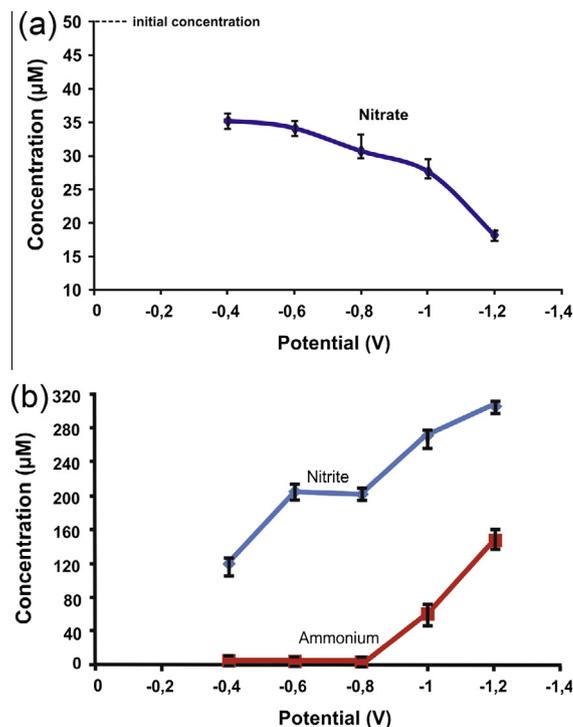
The cauliflower appearance is typical for polypyrrole films [32]. Freshly prepared film keeps its structure also after electrolysis at low overpotentials and no degradation of the film is observable (Fig. 3a and b). At more negative potentials than  $-0.8 \text{ V}$  however, the degradation of the film begins due to hydrogen evolution and it crumbles from the metal surface to the cell-bottom, which is why we stop the potential preventive below  $-0.8 \text{ V}$  during analytical measurements and preparative electrolysis as well. Cyclic voltammograms of polymer coated Cu electrode have been presented at various nitrate concentrations in 0.1 M LiClO<sub>4</sub> + 0.001 M HClO<sub>4</sub> + x mM KNO<sub>3</sub> (x = 5–200 mM) solution (Fig. 4a).

In case of an electron transfer onto nitrate, the current should depend on the substrate concentration. But, as can be seen in Fig. 4a, there is no relation between nitrate concentration, applied-potential values and current densities (Fig. 4a). On the other side, the current varies depending on proton concentration (pH) visibly (Fig. 4b). These results indicate that polymer coating may support the atomic hydrogen ( $\text{H}_{\text{ads}}$ ) formation and no electron transfer occurs onto nitrate at these low overpotentials.

### 3.2. Product analysis

All preparative electrolysis on blank Cu were performed in 0.1 M LiClO<sub>4</sub> + 0.001 M HClO<sub>4</sub> + 50 mM KNO<sub>3</sub> solution, potential controlled. To compare the blank Cu and PPY-Cu to each other, preparative electrolysis were carried out under the same conditions. Results of analytical investigation revealed that nitrate ions were converted into nitrite and ammonia depending on the applied potential only.

Potential influence on the reduction was tested at five different potential values ( $-0.4, -0.6, -0.8, -1.0$  and  $-1.2 \text{ V}$  [Ag/AgCl]) on a blank Cu electrode in aqueous 0.1 M LiClO<sub>4</sub> + 0.001 M HClO<sub>4</sub> + 50 mM KNO<sub>3</sub>. The product analysis after 3 h of electrolysis time gave the results, presented in Fig. 5.

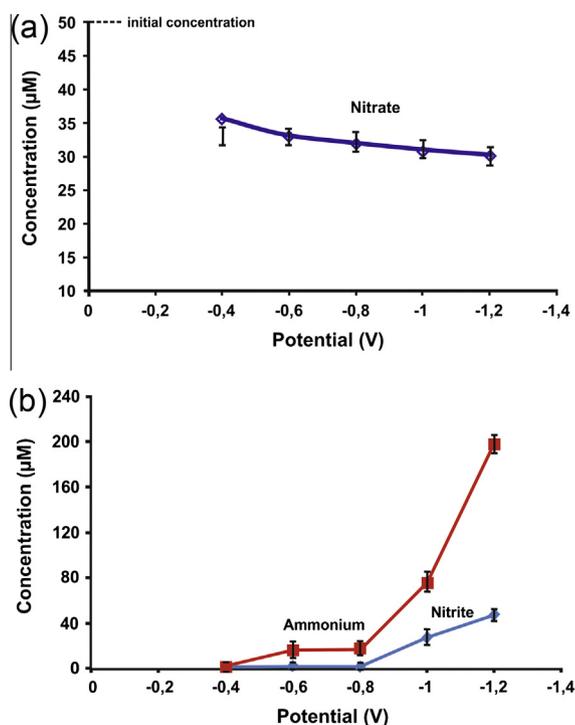


**Fig. 5.** Concentration-potential diagrams on blank Cu electrode (a) changes of nitrate concentration after electrolysis and (b) concentrations profiles of nitrite and ammonium ions in 0.1 M LiClO<sub>4</sub> + 0.001 M HClO<sub>4</sub> + 50 mM KNO<sub>3</sub>. Electrolysis time: 3 h.

The electrolysis time was kept at 3 h to obtain sufficient product concentration for spectroscopic analysis. Near consideration of the reaction mechanism to nitrate reduction might lead to other possible products; theoretically hydrazine and hydroxylamine should have been formed in the solution as well, but these could not be found in the electrolyte.

As shown in Fig. 5, it is noticeable that no ammonia was formed until  $-0.7$  V. The absence of ammonia until ca.  $-0.7$  V was attributed to the fact that on blank Cu the  $H_{ads}$  formation begins theoretically at ca.  $-0.7$  V NHE (depending on pH) [35]. Nitrite was produced on blank Cu throughout the potential scale (between  $-0.4$  V and  $-1.2$  V). This may be explained with a direct electron transfer onto nitrate ion and as the result nitrite was formed. Up  $-0.7$  V the formation of ammonia was accelerated due to initiating of  $H_{ads}$  formation on blank Cu-surface. The accelerated formation of ammonia is an expected result because of the presence of nitrite and nitrate in the solution and both can be reduced to ammonia by H-atoms ( $H_{ads}$ ).

Contrary to blank Cu, in case of PPy-Cu electrode, only ammonia formation was observable between  $-0.4$  V and  $-0.7$  V and no nitrite was available in the electrolyte (Fig. 6b). This is a remarkable point and corresponds with the aim to reduce nitrate to ammonia at lowest possible overpotentials of present study. The absence of nitrite indicates that if Cu surface is coated with polypyrrole,  $H_{ads}$  formation sets earlier than  $-0.7$  V and a direct electron transfer remains secondarily in a competition reaction. We conclude that the coating of a surface with conducting polymer shifts the formation of H-atoms to low overpotentials on Cu and this corresponds with our previous results on other conducting polymer-modified metal electrodes. As reported previously [17–28], coating of a metal surface with conducting polymer causes a controlled formation of H-atoms, which have a great ability to reduce, for example carbondioxide, nitrogen as well as nitrate ions at extremely low overpotentials.



**Fig. 6.** Concentration-potential diagrams on PPy-Cu electrode (a) changes of nitrate concentration after electrolysis and (b) concentration profiles of nitrite and ammonium ions in  $0.1$  M  $LiClO_4 + 0.001$  M  $HClO_4 + 50$  mM  $KNO_3$ . Electrolysis time: 3 h.

Preparative electrolysis were carried out up  $-1.2$  V to compare the result to that on blank Cu and as can be seen (Fig. 6b) up ca.  $-0.8$  V through the degradation of polymer layer, Cu character became dominant and the curves proceed a similar course as on blank Cu (Fig. 5b).

### 3.3. Influence of film thickness

Generally, film thickness on a metal surface plays a dominant role concerning reaction pathways. Also in case of polypyrrole modification of Cu surface, the film thickness plays an important role and we found experimentally, the optimum thickness for ammonia formation as 5 cycles ( $0.9$  µm; [26,36]). The results, film thickness in relation to product concentrations, are presented in Table 1.

If the film is too thick, the current drops due to fully covering of metal surface and a preparative electrolysis demands extremely long time. In case of a too thin film, the metallic character becomes dominant. As it was presented in Table 1, the highest ammonia concentration was obtained with the 5-cycle film and all our experiments were carried out at that thickness.

Conclusive to preparative electrolysis, results should be considered in two ranges; below  $-0.7$  V and over  $-0.7$  V. The first range is relevant for PPy-Cu electrode and only ammonia was produced. In the second range, being parallel to nitrite formation, ammonia was also formed on blank Cu. From our point of view, the first range is much more worthwhile, because the  $H_{ads}$  formation was shifted to relative positive overpotentials and the conversion of nitrate to ammonia is executive at these potentials. The preparative results obtained on a PPy-Cu electrode in  $0.1$  M  $LiClO_4 + 0.001$  M  $HClO_4 + 50$  mM  $KNO_3$  presented in Table 2.

### 3.4. Mechanism

#### 3.4.1. On blank Cu electrode

Prior to PPy-Cu experiments, preparative electrolyses were carried out between  $-0.4$  V and  $-0.7$  V potential controlled on blank Cu. No ammonia was detected at  $-0.4$  V and  $-0.5$  V. Also at more negative values, i.e.  $-0.6$  V, nitrite formation became the main reaction (Table 2). In fact; ammonia formation between  $-0.4$  V and  $-0.7$  V could not be the main reaction due to more negative hydrogen overpotential on blank Cu [35] in acidic medium. In this instance, a direct electron transfer onto nitrate ion will be preferred and this leads to nitrite formation consequently. Other

**Table 1**

Product concentrations in relation to film thickness on a PPy-Cu in  $50$  mM  $KNO_3 + 0.001$  M  $HClO_4 + 0.1$  M  $LiClO_4$ . Potential:  $-0.6$  V; electrolysis time: 3 h.

Cycle number	$NO_3^-$ (mM) <sup>a</sup>	$NH_4^+$ (µM)	$NO_2^-$ (µM)
3	15.4	12.27	–
5	16.8	15.16	–
10	14.6	14.61	–
20	13.8	7.88	–

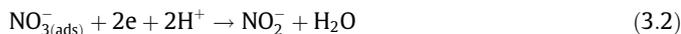
<sup>a</sup> Nitrate concentration remaining in the medium after electrolysis.

**Table 2**

Current efficiencies resulting from the electrolysis in  $0.1$  M  $LiClO_4 + 0.001$  M  $HClO_4 + 50$  mM  $KNO_3$  on Cu and PPy-Cu electrodes. Potential:  $-0.6$  V; electrolysis time: 3 h.

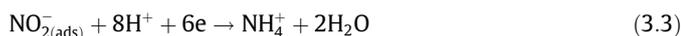
Electrode	$\eta$ /(%) (conversion of $NO_3^-$ )	$\eta$ /(%) amount of $NH_4^+$	$\eta$ /(%) amount of $NO_2^-$
Cu	30.8	2.8	27
Cu/PPy	33.6	28	–

theoretically possible products, especially  $\text{NH}_4\text{OH}$  and  $\text{N}_2\text{H}_4$ , were not found in the solution as well as in the gaseous phase and these results correspond to that in literatures [5,7,11]. The formulation of the reaction mechanism can be as:



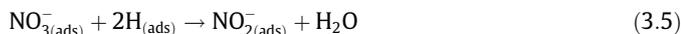
The first step is the adsorption of nitrate ion on the copper surface in acidic aqueous milieu (Eq. (3.1)). Then, an electron transfer onto adsorbed species leads to nitrite primarily (Eq. (3.2)). The formation of ammonia is not the preferred step in that stadium (too low overpotentials). This can be seen also in Table 2, where the amount of nitrite ca. is ten times higher than that of ammonia.

Up ca.  $-0.7$  V, the ammonia formation proceeds to the following reaction (Eq. (3.3)):



### 3.4.2. On polypyrrole coated Cu

Under the same condition, like on blank Cu, the employing of a PPy-coated Cu electrode changes mechanism apparently and the product formation turns over from nitrite to ammonia. The mechanism can be formulated as:



The first step is the adsorption of a proton available in the solution and then it follows an electron transfer onto this species leading to atomic hydrogen ( $\text{H}_{(\text{ads})}$ ). This suggestion is supported through the disappearance of nitrite and formation of ammonia (see Table 2) at low overpotentials. As formulated in the reaction mechanism on PPy-Cu (Eqs. (3.3)–(3.6)), protons in the solution act as a reaction component and the formed atomic hydrogen reduce other species (hydrogenation) available in the electrolyte. This reaction path can be followed easily by Tafel curves. Additionally to Tafel curves, another easy way to investigate this phenomenon can be the electrochemical impedance spectroscopy (EIS), which we employed to clear these points as well [28,37,38].

### 3.5. EIS measurements

Electrochemical impedance spectroscopy is an efficient technique to characterize the interfacial properties of an electrochemical system and it is used to provide clarity to the reaction mechanism.

Polymer films as such contain pores and holes reaching supporting metal surface (Fig. 7) and provide a contact point to the electrolyte. These places are available for electrochemical

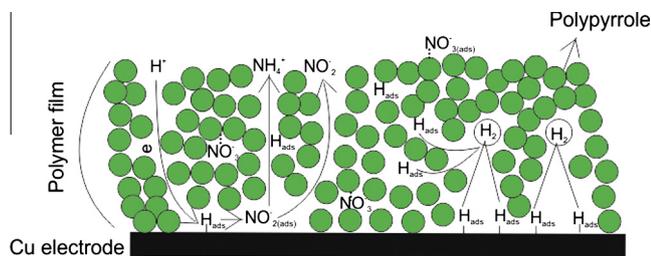


Fig. 7. The possible reactions on PPy-Cu electrode (schematically).

reactions. Protons and nitrate ions, available in the solution, diffuse in these pores/holes and after an electron transfer, protons turn into  $\text{H}_{(\text{ads})}$ , which have two possibilities to react: They can recombine to  $\text{H}_2$  or they react with a nitrate ion to nitrite (Eqs. (3.4) and (3.5)), which can also be converted into ammonia with further H-atoms (Eq. (3.6)). In that case, the role of the polymer film should be the impeding of recombination of  $\text{H}_{(\text{ads})}$  to  $\text{H}_2$  and in other, the film produces H-atoms because of it is self conductance [37–39].

Nyquist curves were recorded between  $-0.2$  V and  $-0.8$  V in 25 mV steps. The presentation of whole spectra and calculated data would go here beyond the scope of the discussion. However as an example, the Nyquist curves recorded at  $-0.6$  V are presented in Fig. 8 for explanation of the events under applied potential.

Generally, if a polymer coated electrode was immersed in electrolyte, the electrolyte resistance  $R_e$ , metal/polymer double layer behaviours ( $\text{CPE}_1$ ), metal/electrolyte double layer capacitance in the pores ( $\text{CPE}_2$ ) and Warburg impedance (a resistance due to non-ideal capacitive behaviours and transport phenomena in porous film) can be captured via impedance spectroscopic measurements. As the consequence of these thoughts, an equivalent circuit can be proposed to simulate the whole system. The numerical data were obtained through the simulation of Nyquist diagrams with equivalent circuit used for Cu and PPy-Cu electrode (Fig. 9).

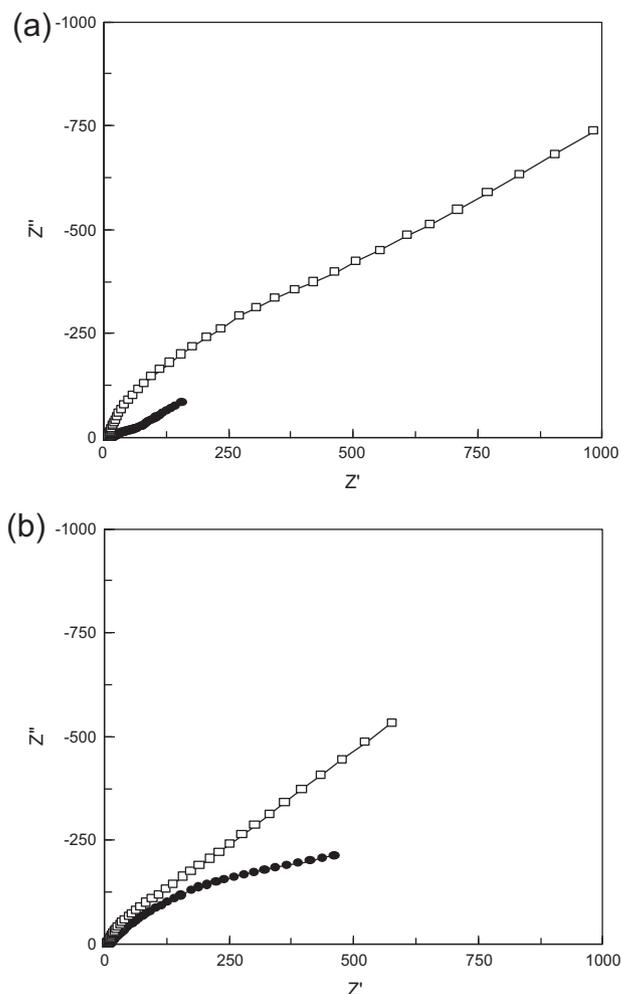


Fig. 8. Impedance plots and Bode diagrams of Cu and Cu-PPy electrodes at  $-0.6$  V (Ag/AgCl) from 100 kHz to 0.1 Hz in 0.1 M  $\text{LiClO}_4 + 0.001$  M  $\text{HClO}_4$  (a) without  $\text{NO}_3^-$ ; and (b) added 50 mM  $\text{KNO}_3$ , (white: Cu; black: PPy-Cu). The solid lines represent the best fitting results according to the equivalent circuits.

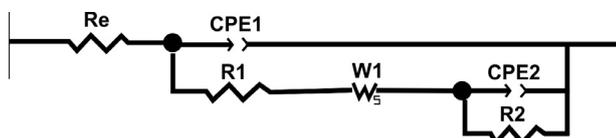


Fig. 9. Equivalent circuits for Cu and Cu-PPy electrodes.

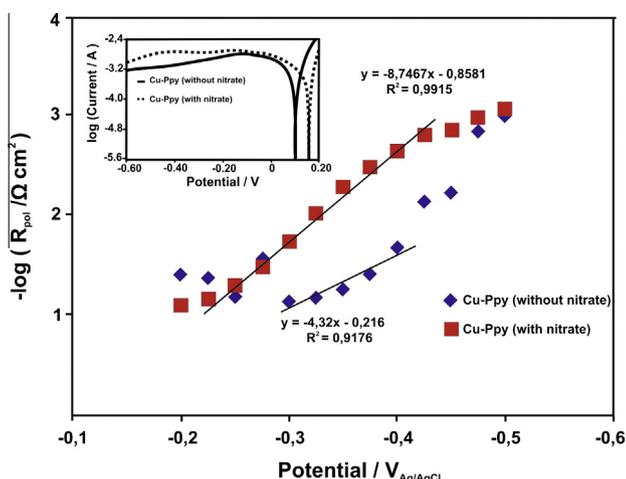


Fig. 10.  $\log R_{\text{pol}}$ -Potential curves of Cu-PPy electrode in 0.1 M  $\text{LiClO}_4 + 0.001 \text{ M HClO}_4$ . Inset diagram: Tafel diagrams.

The Nyquist diagrams have two semi-circles in high and in middle frequencies and a straight line (diffusion part) in low frequency region (Fig. 8). The first unclosed semicircle describes metal-film double layer. This double layer represents the sum of  $R_e$ , film resistance  $R_1$  and metal/polymer double layer capacitance  $\text{CPE}_1$  in the equivalent circuit. The second semicircle characterises the charge transfer reactions and contains charge transfer resistance for intermediates  $R_2$  and capacitance of metal/electrolyte double layer  $\text{CPE}_2$  (Fig. 9). The sum of  $R_1$  and  $R_2$  can be considered as a polarisation resistance  $R_{\text{pol}}$  and used for creating an EIS-Tafel diagram (Fig. 10) [37,38].

In acidic solution, the formation of a  $\text{H}_{\text{ads}}$  needs theoretically 118 mV (Volmer reaction) for one electron in the Tafel slope [19,39]. At low overpotential regions, being near to equilibrium potential, the slope of the Tafel equation turns into  $2RT/F$  and over 200 mV, the recombination of H-atoms proceeds to  $\text{H}_2$  [18,19,26–28,39].

The analysis of Tafel diagram (Fig. 10, inset diagram) and the EIS-Tafel obtained from simulations data provide nearly closed values, 116 mV and 120 mV, in the presence of nitrate ions in the solution, respectively. These values lead us to the conclusion that the main reaction should be a Volmer reaction, which means primarily that a  $\text{H}_{\text{ads}}$  was formed and this species reduce nitrate ion to the end-product. In the absence of nitrate ion in the solution, the calculated Tafel and EIS-Tafel values are 235 mV and 230 mV, respectively. That means, if no consumer (nitrate and/or nitrite) is available in the solution, the H-atoms recombine to  $\text{H}_2$ .

#### 4. Conclusion

Reduction of nitrate ion was investigated on a blank copper and on a polypyrrole coated copper electrode (PPy-Cu) in acidic aqueous medium. The nitrate concentration was varied from 5 to

200 mM (0.1 M  $\text{LiClO}_4 + 0.001 \text{ M HClO}_4 + x \text{ mM KNO}_3$ ;  $x = 5, 20, 50, 100$  and 200 mM). The applied potentials were  $-0.4, -0.6, -0.8, -1.0$  and  $-1.2 \text{ V [Ag/AgCl]}$ . The variation of the electrode material led to same products with different concentrations. On blank Cu, nitrite ion was formed at almost all potential values, applied. On PPy-Cu, the low overpotential region between  $-0.4 \text{ V}$  and  $-0.8 \text{ V}$  was very interesting, due to ammonia formation only why we focused our interest on this potential region. Approximately 33% of employed nitrate was converted only into ammonia and no nitrite was found in case of PPy-Cu as electro-catalyst. From mechanistic point of view, the reaction in low overpotential region obeys to a simple electrochemical hydrogenation, which could be verified with Tafel and EIS-Tafel values of ca. 120 mV.

#### Conflict of interest

The authors declare that there is no conflict of interest.

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