



Influence of Rh on electrocatalytic reduction of NO_3^- and NO_2^- over Pt and Pd films

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ABSTRACT

Electrocatalytic reduction of NO_3^- and NO_2^- were performed using Rh-modified Pt and Pd electrodes supported on H^+ conducting Nafion-117 polymer electrolyte. Cathodic electrolysis experiments showed that Pt–Rh and Pd–Rh cathodes could efficiently reduce nitrate and nitrite ions. The nitrate reduction followed first-order kinetics. The value of constant k_1 was increased in the second experiment from $30.1 \times 10^{-3} \text{ min}^{-1}$ to $39.0 \times 10^{-3} \text{ min}^{-1}$ but in the 6th experiment; the rate constant was decreased to $10.42 \times 10^{-3} \text{ min}^{-1}$. The surface corrosion identified as the main reason of surface deactivation. The activity of the Pt–Rh surface was maximum at acidic pH (3.0), which was lost at basic pH (11.0). At potentials, negative than NO_3^- reduction peak potential, NO_2^- reduction currents, exceeded that of NO_3^- currents. This feature eliminated the intermediate NO_2^- during cathodic electrolysis of NO_3^- at potentials negative than -1.2 V . The Pd–Rh assembly was proved to have better catalytic ability to reduce NO_3^- and NO_2^- over that of Pt–Rh assembly.

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1. Introduction

The existence of NO_3^- in the surface and groundwater is mainly due to industrial waste and intensive agriculture practices that causes acute environmental problems. The reduction of nitrate is recognized as one of the few means to get nitrate free drinking water. The catalytic or electrochemical treatment of nitrate containing water yields a wide spectrum of products, where the most common products are nitrite and ammonia, which also pose great environmental threats. The permissible level of these hazardous species are as $50 \text{ mg L}^{-1} \text{ NO}_3^-$ [1], $0.5 \text{ mg L}^{-1} \text{ NO}_2^-$ [1,2] and NH_3 , higher than 0.5 mg L^{-1} is inadmissible for drinking water [3]. One of the most promising methods of NO_3^- removal from drinking water is electrocatalytic reduction because of its relevance to attaining fast reaction rate, which included plenty of papers [4–27]. Meanwhile, NH_3 , NO , N_2 , N_2O can be synthesized by reducing nitrate/nitrite ions. The product selectivity during the electrochemical reduction of nitrate ions can be regulated by choosing pH of the medium, the concentration of nitrate ions and types of the reactor and electrode used [6–9,12,22,27]. In relation to nitrate reduction, single metal electrodes have been widely used [4–13].

Recently, bimetallic electrodes either in the form of alloys or co-deposited films or ad-atoms on the surface of a core metal have been explored in order to maximize the reduction performance and to control product selectivity [14–27]. The electrode materials can play very important catalytic role in deciding product selectivity while nitrate ions are reduced electrochemically. It has been reported that Cu, Zn and Al cathodes are highly ammonia selective [19] on the other hand, Sn cathodes can produce molecular nitrogen only during the course cathodic electrolysis of nitrate containing water [20].

In order to promote cathodic nitrate/nitrite reduction, recently, we have unveiled a sandwiched-type membrane reactor, where electrode materials are deposited on the each side of H^+ conducting Nafion membrane having a configuration like Pt|Nafion|Pt–Cu, for example [21]. Though the Cu modified electrodes can reduce NO_3^- efficiently but they are not efficient NO_2^- remover. It has been observed that, in the electrolyte reactor, bimetallic Pt–Cu and Pd–Cu cathodes can reduce nitrate ions having first-order rate constant of $17.8 \times 10^{-3} \text{ min}^{-1}$ and $49.0 \times 10^{-3} \text{ min}^{-1}$, respectively, with NO_2^- selectivity of 40% and 13% when 0.05 M NaNO_3 solution is electrolyzed for 3 h by passing 100 mA DC [22]. The cyclic voltammetric investigations of Rh-modified pyrolytic graphite electrodes in the neutral medium have been reported to show higher nitrite reduction currents than that of nitrate reduction [23]. In connection to this observation, in this study, we applied Rh-modified Pt and Pd cathodes in our electrolyte reactor system in order minimize nitrite selectivity during the course of bulk electrolysis. In another report [24], we have shown that the Pt–Cu and Pt–Ag cath-

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odes can reduce nitrate and nitrite ions with different reaction pathways in the membrane reactor. In this reactor, the thickness of the Nafion membrane is 180 μm , which corresponds to the distance between anode and cathode. In case of Pt–Cu, the H^+ , generated on the anode surface (Pt) under applied potential, is migrated to the cathode surface through the H^+ conducting polymer to be converted into atomic and or molecular hydrogen, which promoted $\text{NO}_3^-/\text{NO}_2^-$ reduction. But in case of Pt–Ag cathode, heterogeneous electron transfer was identified as the major route of nitrate reduction. Recently, we have reported that Pd–Rh electrode does not reduce $\text{NO}_3^-/\text{NO}_2^-$ due to chemical hydrogenation reactions [25].

The present work mainly concerns the comparative efficiencies of Pt–Rh and Pd–Rh electrodes in reducing nitrate ions. We will discuss the mechanistic pathways of nitrate/nitrite reduction from the view of cyclic voltammetry and bulk electrolysis experiments.

2. Experimental

2.1. Preparation of electrode

The membrane/electrode assemblies having a Pt anode and a cathode consisting of Pt, Pd and Rh were prepared on Nafion-117 membrane (DuPont, Inc.). The Nafion membrane was first sand blasted and dried at 110 $^\circ\text{C}$ then was immersed into 200 mL water containing suitable amount of PdCl_2 or PtCl_6^{2-} . A mixed solution of 2.0 M NaBH_4 and 4.0 M NaOH was added to the membrane-containing system at a rate of 2.0 mL h^{-1} . Meanwhile, the reaction mixture was heated from 35 $^\circ\text{C}$ at a rate of 5 $^\circ\text{C h}^{-1}$. The Pt or Pd plating with an area of 2 cm \times 3 cm per side of the Nafion membrane was completed within 12 h, which was followed by the second plating of Rh metal only on the cathode surface. Using the Pt or Pd plated Nafion membrane, a sandwiched-type cell was created where the anode chamber was separated from the cathode chamber by the same membrane as shown in Fig. 1. Prior to deposition of Rh particles over Pt/Pd surfaces, electrolysis of 0.01 M H_2SO_4 was performed by passing 60.0C charge. The modifier metal Rh was deposited electrochemically over the cathode surface only. In order to do this, 8 mL of 0.01 M $\text{Rh}(\text{NO}_3)_3$ solution was placed in the cathode after constructing a reactor having configuration of Pt|Nafion|Pt/Pd. Next 9.0C charge was passed through the cell. In this way, deposition of Rh was completed over the cathode surface leading a configuration of Pt|Nafion|Pt–Rh/Pd–Rh. The amount of Rh deposition was controlled by controlling the charge. The scanning electron microscope (SEM) image of the surface was taken with a JEOL model JSM-6060LV instrument. The SEM image of the cross-section of the metal deposited Nafion membrane exhibited that the total thickness of the metallic deposits on both side of Nafion membrane was ca. 2–3 μm .

2.2. Reduction of $\text{NO}_3^-/\text{NO}_2^-$

The electrocatalytic reduction of $\text{NO}_3^-/\text{NO}_2^-$ was carried out in a micro-reactor as shown in Fig. 1. The cathode and anode compartments were separated by the as prepared MEA creating a sandwiched-type reactor. The virtual distance between anode and cathode was 180 μm , which corresponds to the thickness of the Nafion membrane. The cathode and the anode compartments were filled with 8 mL aqueous solution of NaNO_3 (0.05 M) or NaNO_2 (0.05 M), and with water, respectively. Each electrode was connected with a DC power supply (100 mA) for electrolysis (3 h) to be performed. In order to analyze the concentration changes of NO_3^- , NO_2^- and NH_4^+ ions as a function of time, an aliquot of 50 μL was collected from the solution in the cathode compartment

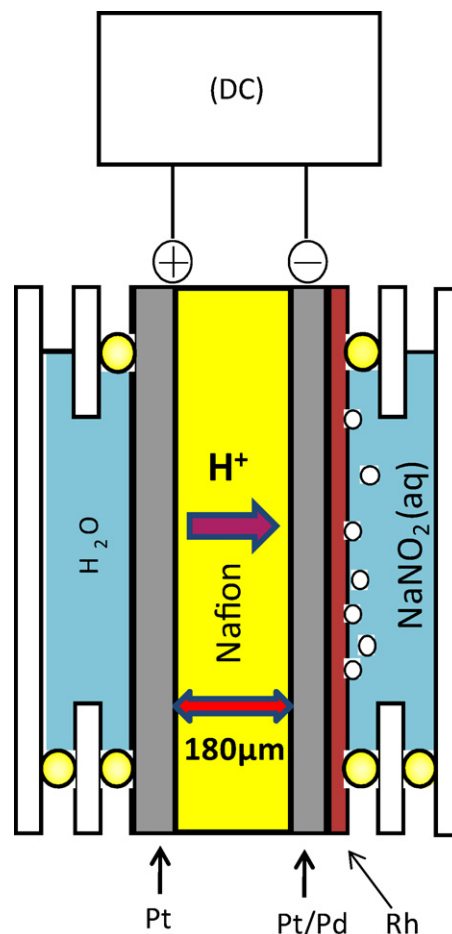


Fig. 1. Schematic illustrations of an electrocatalytic reactor used for the reduction of $\text{NO}_3^-/\text{NO}_2^-$.

at a constant interval and was diluted to 5 mL. The concentration changes of NO_3^- , NO_2^- and NH_4^+ ions as a function of time were evaluated by an ion chromatograph (TOA–DKK, ICA–2000). The gaseous components were detected with a quadrupole mass spectrometer (Pfeiffer, Omnistar). The experiments were carried out under aerated condition. All the glassware was boiled with deionized water and sonicated to remove organic and inorganic contaminants. All of the solutions were prepared with analytical grade chemicals (Wako Pure Chem. Ind. Ltd.) and Millipore Milli-Q water (Resistivity > 18 $\text{M}\Omega \text{cm}^{-1}$ and micro organic concentration ≤ 3 ppb).

The efficiency of nitrate reduction will be discussed in terms of first-order reaction assuming that the concentrations of these ions decayed exponentially as per first-order rate equation (1):

$$C_t = C_0 \exp(-kt) \quad (1)$$

And the $\text{NO}_2^-/\text{NH}_4^+$ selectivity (S) will be evaluated using Eq. (2):

$$\%S = \left(\frac{X_t}{C_0 - C_t} \right) \times 100 \quad (2)$$

where C_0 is the initial molar concentration of reactant NO_3^- , C_t the molar concentration of reactant NO_3^- at time t and X_t the molar concentration of product ($\text{NO}_2^-/\text{NH}_4^+$) formed after time t (180 min). The same equations will also be considered to evaluate the activity and selectivity of NO_2^- reduction assuming C_0 and C_t as the concentrations of reactant (NO_2^-) and X_t the concentration of product (NH_4^+).

2.3. Electrochemical measurements

A 0.28 cm² of platinized or pladised Nafion membrane was placed as working electrode in a conventional one-compartment 3-electrode electrochemical cell where, a 1-cm² Pt plate was used as the counter electrode. The Rh metal was deposited over each of Pt/Nafion and Pd/Nafion assembly prior to nitrate/nitrite reduction experiments by cycling the solution (0.05 M Rh(NO₃)₃ + 0.2 M KCl) between –0.2 V and –0.6 V for three times. In this way, layers of Rh metal were formed over Pt and Pd surfaces. The electrochemical measurements were carried out using a Hukoto Denko HZ-5000 automatic electrochemical polarization system. All charges and current densities will be quoted in terms of apparent geometrical surface area. A KCl saturated Ag/AgCl electrode was used as reference electrode; hence all the potentials in this report will be referred to this electrode. The experiments were carried out under thermostatic condition at 25 ± 0.2 °C. Before use, the glassware was purged with deionized water repeatedly. The total volume of the solution taken for each CV experiment was 10 mL. All the solutions were prepared with ultra pure water (18 MΩ). The solutions were not de-gassed because; the deaerated condition did alter the shape of the CVs. In order to attain an equilibrium state, prior to each measurement, the rest potential was maintained at –0.1 V for 30 s.

3. Results and discussions

3.1. Cathodic electrolysis

Fig. 2 shows linear adjustments of exponential decay of NO₃[–] reduction in six different consecutive experiments under same conditions using a Pt–Rh cathode. In order to evaluate the reactivity and selectivity of Rh–Pt/Nafion and Pd–Rh/Nafion assemblies in nitrate reduction, the electrode assemblies were installed in the micro-reactor as shown in Fig. 1. By applying DC current (*j* = 16.67 mA cm^{–2}) to the electrode assemblies, the evolution of H₂ and the reduction of NO₃[–]/NO₂[–] took place simultaneously on the cathode surface. The concentrations of NO₃[–] and NO₂[–] decayed exponentially in the cathode as a function of time consistent with first-order kinetics. Under same considerations, the performance of cathodic NO₃[–]/NO₂[–] reduction process is often explained by estimating the relative first-order rate constant (*k*) [16,19–22]. In this report, in order to compare the relative performance of the cathodes under different conditions, the constant (*k*) was calculated

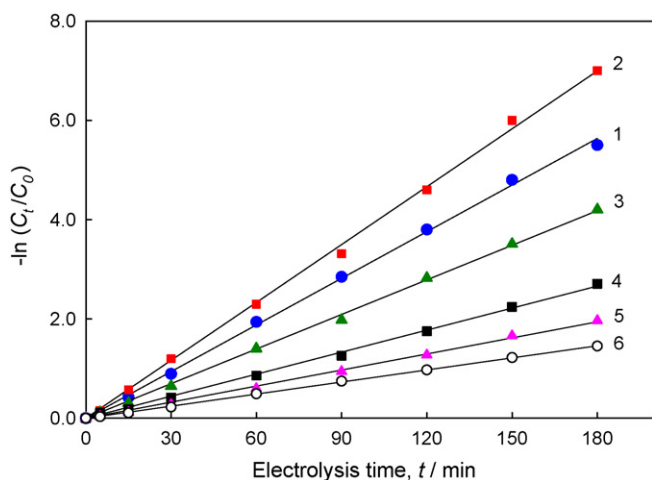


Fig. 2. The first-order fittings of the decays of NO₃[–] concentration with respect to time in the six successive experiments. The number at the right end of each plot indicates the experiment number. Cathode; Pt–Rh, 100 mA, 0.05 M NaNO₃, 8 mL, 180 min, room temperature.

Table 1

Relative catalytic activities and product selectivities of Pt–Rh in three different nitrate reduction experiments.

Experiment	<i>k</i> ₁ (× 10 ^{–3} min ^{–1})	Nitrate removal (%)	Selectivity (%) to	
			NO ₂ [–]	NH ₄ ⁺
First	30.1	99.9	<0.1	75
Second	39.0	99.9	<0.1	72
Third	24.2	98.5	<0.1	76
Fourth	16.8	93.3	1.0	79
Fifth	14.3	86.0	1.2	78
Sixth	10.4	77.1	1.5	80

0.05 M NaNO₃, 8 mL, 100 mA, 180 min, room temperature.

assuming that the change in concentration of NO₃[–]/NO₂[–] (*C*) with time *t* was well matched with Eq. (1). When Pt or Pd alone was used as a cathode, the reaction was very slow (*k* < 2.0 × 10^{–3} min^{–1}). The catalytic effects were obtained when Rh was deposited over Pt and Pd surfaces. The relative first-order rate constant (*k*₁) for NO₃[–] reduction has been evaluated as 18.6 × 10^{–3} min^{–1} for Pt–Rh [24] and 21.1 × 10^{–3} min^{–1} for Pd–Rh [25] cathodes, respectively. It is well known that in the consecutive pathway, nitrate ions are converted into nitrite ions, which are next converted into other products as per the following equation [7,9]:



where P denotes the reduced products NO, NH₄⁺, N₂, etc. According to the previous study [22], after 3 h electrolysis of 0.05 M NaNO₃ solution, Pt–Cu and Pd–Cu electrodes yielded 40% and 13% NO₂[–], respectively, in the electrolyte the electrolyte reactor. Such higher NO₂[–] selectivity has been associated to faster nitrate and slower nitrite reduction rates by these cathodes. In order to eliminate both NO₃[–] and NO₂[–] from water, an efficient cathode should exhibit *k*₁ ≤ *k*₂. It has been reported that when the Pt–Cu cathode is replaced with Pt–Rh, the first-order rate constant for NO₂[–] reduction (*k*₂) could be increased to 23.1 × 10^{–3} min^{–1} from 1.6 × 10^{–3} min^{–1} [24]. Similarly, the Pd–Rh electrode can elevate *k*₂ from 13.9 × 10^{–3} min^{–1} to 25.6 × 10^{–3} min^{–1} when this electrode is used in place of Pd–Cu [25]. Therefore, acceleration of second step (*k*₁ < *k*₂) suggests that Rh metal is indispensable to eliminate NO₂[–] along with NO₃[–] with higher rates. In other words, when Cu atoms are replaced with Rh, sufficient active sites are created over the electrode surface that enables simultaneous reduction of NO₃[–] and NO₂[–]. In the present study, the performance (*k*₁) of Pt–Rh cathode has been re-evaluated as 30.1 × 10^{–3} min^{–1}, which was significantly different from 18.6 × 10^{–3} min^{–1} as reported in Ref. [24]. Hydrogen evolution has the surface cleansing effects [20]. In the present study, prior to the electro deposition of Rh on cathode surface from Rh(NO₃)₃ solution, 0.01 M H₂SO₄ was electrolyzed cathodically by installing a bare Pt|Nafion|Pt assembly into the micro-reactor by passing 60.0C charge. This caused vigorous evolution of H₂ from the bare Pt cathode, which might have removed potential oxides, hydroxides and NaBH₄ adhered to the Pt surface. In addition, some other molecular particles (O₂, micro-organics, etc.) probably were also removed from the Pt surface due to rapid H₂ evolution.

In order to apply an electrode–Nafion assembly for a practical purpose, it is very important to know its longevity. In this regards, six consecutive experiments were carried out under same experimental conditions (0.05 M NaNO₃, 8 mL, 100 mA, 3 h, initial pH 6.8, room temperature) using a Pt–Rh cathode. The linear fittings of exponential decay data with respect to time has been shown in Fig. 2. The reactivity and selectivity have been summarized in Table 1. The extent of reduction was nearly 100% in the first three experiments and in the next subsequent three experiments removal extent was gradually decreased. It was 86% removal in the

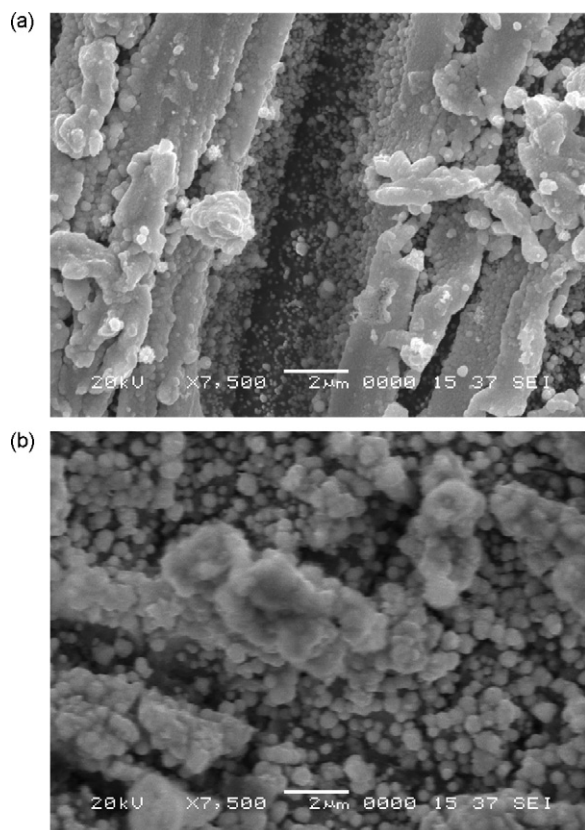


Fig. 3. SEM image of a fresh Pt–Rh surface (a) and after 9-h use (b).

5th and 77% in the 6th experiments, respectively, indicating the gradual deactivation of cathode surface.

The gradual deactivation has been also evaluated in terms of constant k_1 . It was observed that the value of constant k_1 was increased to $39.0 \times 10^{-3} \text{ min}^{-1}$ in the second experiment from $30.1 \times 10^{-3} \text{ min}^{-1}$ but in the third experiment; the rate constant was decreased to $24.2 \times 10^{-3} \text{ min}^{-1}$. In the 4th and 5th experiments, the value of k_1 was evaluated as $16.8 \times 10^{-3} \text{ min}^{-1}$ and $14.3 \times 10^{-3} \text{ min}^{-1}$, respectively. Finally, in the 6th experiment, k_1 was decreased to $10.4 \times 10^{-3} \text{ min}^{-1}$. The increase of rate constant in the second experiment can be explained by the increase of active surface sites. In some instances, long-term electrolysis increases the active surface area [20]. During the first experiment, rigorous hydrogen evolution increased the active surface area enhancing nitrate reduction. The gradual decrease of rate constant from the third experiment can be inferred by examining SEM image of the cathode surface. Fig. 3a and b shows the SEM images of a fresh and 9-h used Pt–Rh surfaces. The damage of the surface is visible in the used surface compared to that of an unused surface indicating corrosion of Rh particles from the cathodic surface. In order to justify the corrosion occurred on Pt–Rh surface, we determined the dissolved Rh species in the catholyte using ICP measurement. After 120 min electrolysis, 4.2 mg L^{-1} Rh was detected while 0.05 M 8 mL NO_3^- solution was electrolyzed supplying 100 mA DC current. These observations implied that the dissolution of Rh particles from the cathode surface due to hydrogen evolution caused the decrease of the surface activity.

Regarding products, in the aqueous phase, ammonia was identified as only one product irrespective of NO_2^- or NO_3^- employed for reduction. The spectroscopic analysis, after completion of 180 min electrolysis, did not show any signals for other products, especially for NH_2OH implying that the rest of the products were gaseous. The product selectivity was reproducible in all six experiments

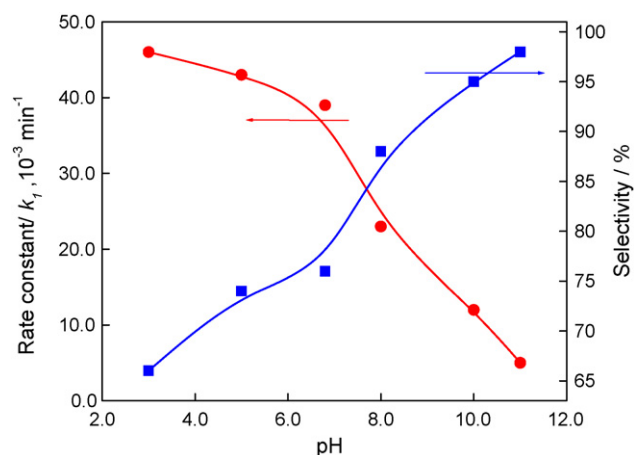


Fig. 4. Influence of pH on the first-order rate constant, k_1 (●) and NH_4^+ selectivity (■) of NaNO_3 reduction over Pt–Rh cathode. Other conditions were same as mentioned in Fig. 2.

showing average ca. 77% ammonia and negligible nitrite selectivity (<0.1–1.5%).

Consequently, the above observations suggest that the Pt–Rh cathode could be effective for 15 h long electrolysis persistently in eliminating $\geq 85\%$ NO_3^- as well as NO_2^- from water.

3.2. Influence of pH

When the assembly Pt|Nafion|Pd–Rh, is installed in the micro-reactor (Fig. 1), NO_3^- and NO_2^- are reduced due to heterogeneous electron transfer reaction only [25]. In the reactor, the rate of NO_3^- reduction and NH_4^+ selectivity was highly pH dependant as shown in Fig. 4. The ambient pH of the 0.05 M NaNO_3 solution was 6.8 but when the electrolysis was commenced, within 30–45 min, pH of the cathodic solution was raised to 12 or more indicating that OH^- was one of the products. Since NO_2^- has been designated as an intermediate in the consecutive mechanism (reaction (3)) and NH_4^+ was identified as a major reduced product in our experiments, it could be assumed that the following reactions ((4) and (5)) might have taken place in priority on the cathode surface during the course of NO_3^- reduction.



In order to evaluate the effects of pH, we performed several experiments under same experimental conditions in the pH range 3.0–11.0. According to the thermodynamic point of view, in the acidic pH, the neutralization reaction could make rooms to favor the reactions (4) and (5) to occur by increasing reaction rates. Meanwhile, reverse effect is seen at basic pH. As the system itself generated OH^- species, the rate of reaction was slowed down when the initial pH of the medium was basic. At the basic pH, excessive negative charges on Pt–Rh surface might have retarded the rate of diffusion of NO_3^- from the bulk to the electrode surface decreasing k_1 . In the other words, the competitive adsorption and diffusion rate of NO_3^- with OH^- was provably determined the relation between the medium pH and the rate constant k_1 ; as the medium pH was increased, k_1 was decreased. Besides reaction rates, ammonia selectivity was also pH dependant. The degree of ammonia generation was increased as the pH was increased. At pH 11.0, almost cent percent product was ammonia, which was 66% at pH 3.0. However, the nitrite selectivity was usually less than 1% throughout the pH range we examined.

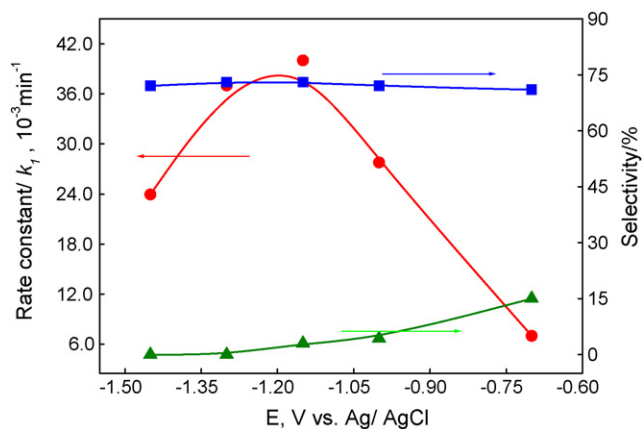


Fig. 5. Influence of potential on the first-order rate constant k_1 (●), NO_2^- selectivity (▲) and NH_4^+ selectivity (■) of NaNO_3 reduction over Pt–Rh cathode. 90 min, 8 mL, 0.05 M NaNO_3 , initial pH 6.8, room temperature.

3.3. Influence of potential

In order to explore the influences of the applied potential on $\text{NO}_3^-/\text{NO}_2^-$ reduction, an electrochemically deposited Pt|Nafion|Pt–Rh assembly was employed in the reactor. The reactor was used to perform for 90 min long electrolysis of 8 mL 0.05 M NO_3^- and NO_2^- solutions separately. In this case, the anodic surface was treated as counter electrode and the reference electrode was placed in catholyte. Fig. 5 shows the dependency of rate constants and product selectivities of NO_3^- reduction on the applied potential (–0.7 V to –1.5 V). The minimum and maximum rate constant (k_1) was at –0.7 V ($7.0 \times 10^{-3} \text{ min}^{-1}$) and –1.15 V ($40.0 \times 10^{-3} \text{ min}^{-1}$), respectively. At more negative potentials, reduction rate was tended to be decreased. At the potentials higher than –1.0 V, the Pt–Rh cathode produced little NO_2^- , which was ca. 15% at –0.7 V. At potentials negative than –1.2 V, no measurable NO_2^- was detected after 90 min electrolysis whereas; the average ammonia formation was ca. 72% in the potential dependant experiments. In order to compare NO_3^- reduction with NO_2^- reduction, potential dependency of NO_2^- reduction was next explored as shown in Fig. 6. The rate constant (k_2) was increased gradually as a function of negative potential. The highest activity was noticed at –1.5 V having rate constant of $49.0 \times 10^{-3} \text{ min}^{-1}$. Throughout the whole potential range, k_2 was higher than k_1 indicating that NO_2^- was reduced quicker than NO_3^- irrespective of potential. The average ammonia selectivity was ca. 71% between –1.0 and –1.4 V, which was

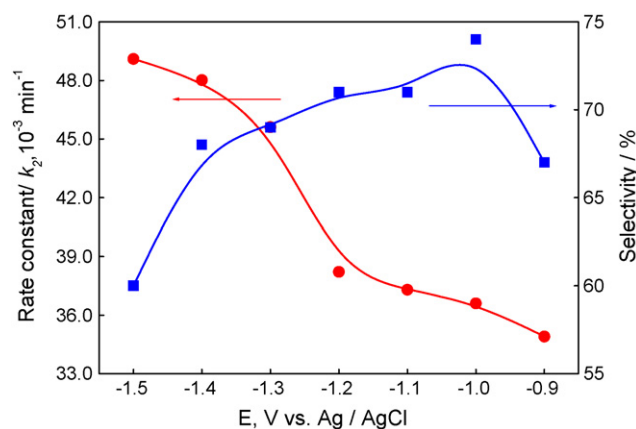


Fig. 6. Influence of potential on the first-order rate constant, k_2 (●) and NH_4^+ selectivity (■) of NaNO_2 reduction over Pt–Rh cathode. 90 min, 8 mL; 0.05 M NaNO_2 , initial pH 6.8, room temperature.

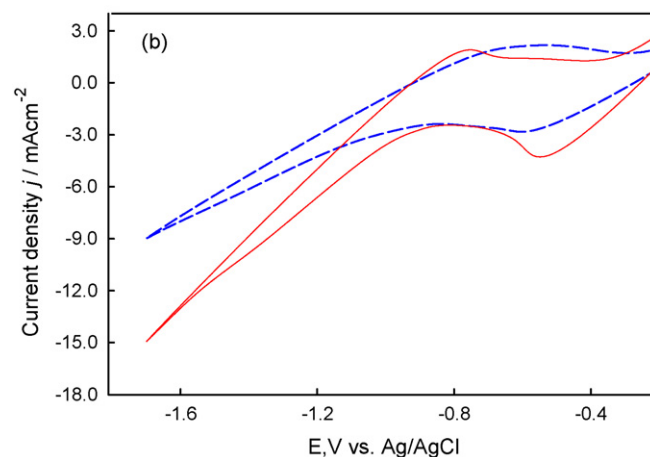
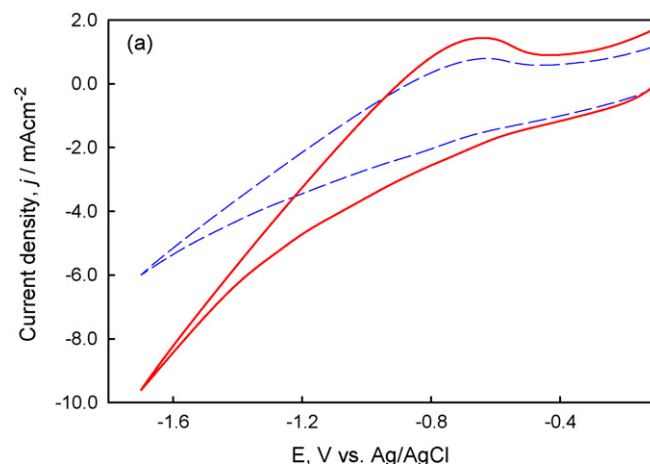


Fig. 7. Cyclic voltammograms (2nd scan) at 25 mVs^{-1} of 0.2 M KCl (dashed line), 0.2 M KCl + 0.10 M KNO_3 (solid line) recorded using (a) Pt/Nafion electrode and (b) Pd/Nafion electrode.

a reflection of the ammonia selectivity as was noticed for NO_3^- reduction. The formation of the similar amount of NH_4^+ from the equivalent amount of NO_3^- and NO_2^- advises the validity of the consecutive reaction (3).

3.4. Electrochemical characterization

Platinum and palladium are two widely used metals in electrochemical studies. In Section 3.1, relative effectiveness of Pt and Pd film based cathodes has been discussed regarding the reduction of NO_3^- and NO_2^- . In this section, some of their electrocatalytic properties will be discussed based on cyclic voltammetric investigations.

Fig. 7 shows the cyclic voltammograms of 0.10 M KNO_3 solution at neutral pH over Pt and Pd films chemically deposited on Nafion membrane. In both cases, NO_3^- was adsorbed in the double layer region and in the kinetic region (ca. –0.8 V to –1.7 V), this ions were reduced along with H_2 evolution without showing any clear reduction waves. The reduction waves were observed when Rh was deposited over Pt and Pd films. In the kinetic region, nitrate reduction took place along with hydrogen evolution reaction (HER). Fig. 8 shows that the deposited Pt–Rh and Pd–Rh films reduced NO_3^- showing defined peak potentials, i.e. –1.14 V for Pt–Rh and –1.31 V for Pd–Rh at neutral pH. The corresponding normalized currents have been reported in Table 2 as -2.59 mAcm^{-2} and -3.13 mAcm^{-2} , respectively. The features of Fig. 8a may explain why the value of k_1 was atop at ca. –1.2 V as shown in Fig. 5. The rate of electron transfer was highest around this potential for

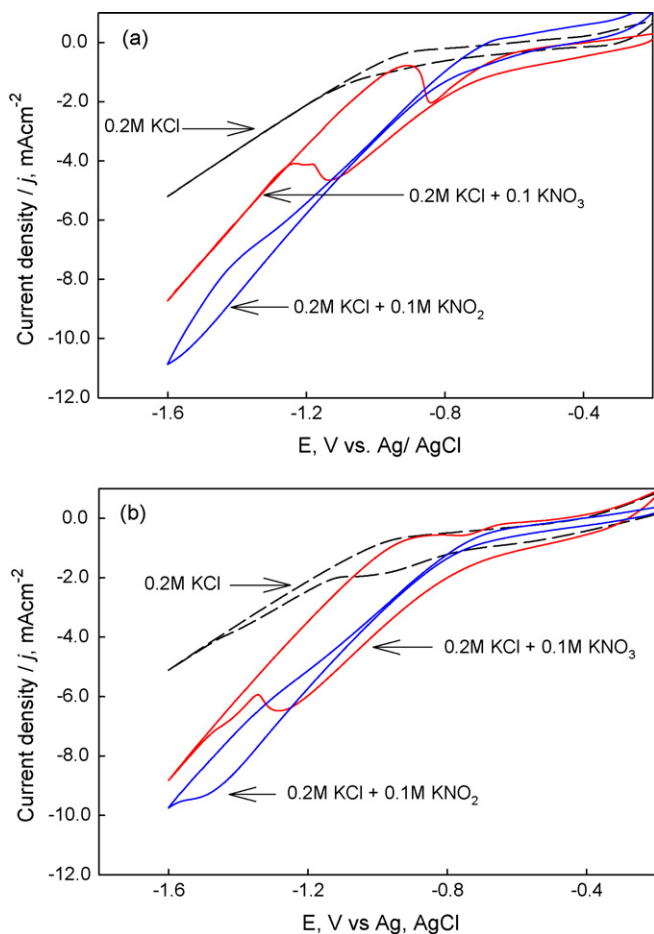


Fig. 8. Cyclic voltammograms (2nd scan) of 0.2 M KCl, 0.2 M KCl + 0.1 M KNO_3 and 0.2 M KCl + 0.1 M KNO_2 solutions recorded using (a) Pt–Rh electrode and (b) Pd–Rh electrode (The NO_2^- fraction over Pd–Rh/Nafion electrode was cited in Ref. [25]). Scan rate 5 mV s^{-1} .

NO_3^- reduction exhibiting maximum decay rate of nitrate ions. Meanwhile, the current due to NO_2^- reduction was increased as a function of negative potential without showing any characteristic reduction waves in both cases. Up to NO_3^- peak maximum, NO_2^- was reduced exhibiting almost similar electron transfer rate as was shown by NO_3^- reduction. However, at potentials negative than NO_3^- peak, NO_2^- currents in both cases exceeded that of NO_3^- currents. This feature is also consistent Figs. 5 and 6 exhibited by Pt–Rh cathode. At highly negative potentials ($< -1.2 \text{ V}$), k_2 exceeded significantly that of k_1 and this was the reason why we did not observe any NO_2^- formation during NO_3^- reduction as shown in Fig. 5.

Fig. 9 shows the voltammograms (CVs) of 0.05–0.20 M KNO_3 recorded using the bimetallic Pt–Rh and Pd–Rh electrodes in 0.2 M KCl solution at a potential sweep rate of 5 mV s^{-1} . However, the peak potentials were appeared rather independent of the initial nitrate concentrations for these electrode systems. Such a behavior

Table 2
Kinetic properties of 0.1 M NO_3^- reduction observed for the Pt–Rh and Pd–Rh electrodes in 0.2 M KCl solution.

MEA	j_p (mA cm^{-2})	j_o (mA cm^{-2})	α
Pt–Rh	2.59 (–1.14V)	0.042	1.02
Pd–Rh	3.13 (–1.31V)	0.134	0.98

α : order of reaction; j_o was calculated in the potential region -0.43 V to -0.5 V ; scan rate: 5 mV s^{-1} .

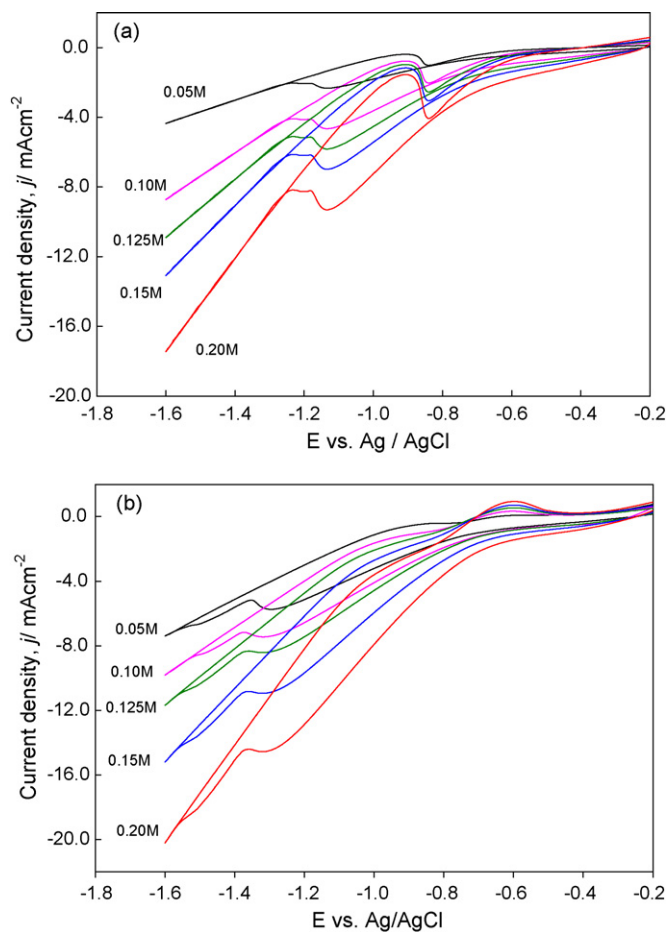


Fig. 9. Cyclic voltammograms of variable KNO_3 concentrations over (a) Pt–Rh electrode and (b) Pd–Rh electrode at 5 mV s^{-1} scan rate in 0.2 M KCl.

of the electrodes was indicative of rapid NO_3^- reduction process occurring at the Pt–Rh and Pd–Rh interfaces.

In order to evaluate the order of NO_3^- reduction (α) at peak potentials (-1.14 V for Pt–Rh and -1.31 V for Pd–Rh), $\log j$ was plotted against $\log[\text{NO}_3^-]$ in the concentration range as mentioned above. The slopes of the regression lines ascribed the respective order (α) of reaction, which was 1.02 for Pt–Rh and 0.98 for Pd–Rh as is tabulated in Table 2. The estimated values were noticeably lower than 1.25 (Pd–Cu) [16] but 2–3 times higher than 0.51 (Pt) and 0.34 (Rh) [7] those were obtained previously for nitrate electroreduction in the acidic medium. Recently, nitrate reduction on Pt (1 1 1) electrode in acidic medium has been reported as zero order [10]. The reason/s for such a difference with respect to reaction order is not clear from our study. However, the order of reaction in the present study suggests that the NO_3^- reduction followed first-order kinetics over Pd–Rh and Pt–Rh electrodes, where the rate constant and half-life of reduction should be independent of initial nitrate concentration.

The areas under cathodic peak as well as estimation of relative k_1 suggest that Pd–Rh combination was more efficient in reducing nitrate ions. In order to justify this relative efficiency, exchange current density (j_o) was next evaluated. At the equilibrium potential, the electrode/solution interface still has electron transfer processes going on in both directions. The anodic current balances the cathodic current. When the potential is set more negative, the cathodic current is greater than the anodic current. This ongoing current in both directions is known as the exchange current density (j_o). The net current density is the difference between the cathodic and anodic current density. A system having high exchange cur-

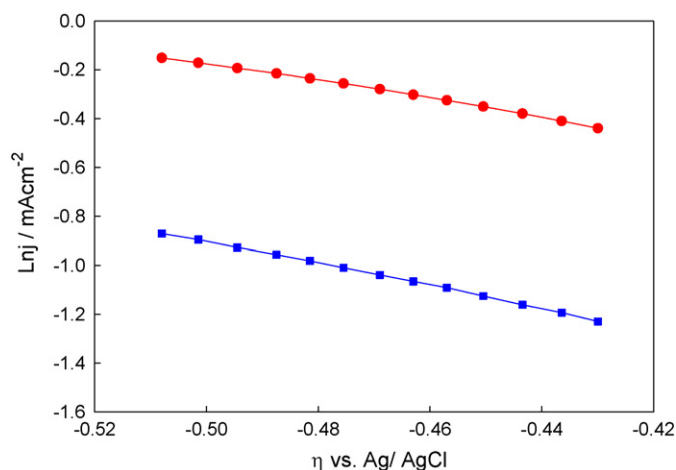


Fig. 10. $\ln j$ versus over potential (η) curves of Pt–Rh (○) and Pd–Rh (●) electrodes in presence of 0.2 M KCl + 0.1 M KNO₃ solution. Scan rate 5 mV s⁻¹.

rent density has the fast kinetics and often can respond rapidly to a potential change [27].

The exchange current density (j_0) at equilibrium state for a cathodic process is related to the overpotential (η) as per Eq. (6) [28]:

$$j = j_0 \exp\left(-\frac{\eta}{b}\right) \quad (6)$$

here j is the current density and b is an electro-kinetics related constant. The intercept of semi-logarithmic plot ($\ln j$ vs. η , Fig. 10) determined the exchange current for the electrocatalytic NO₃⁻ reduction process, took place over Pt–Rh and Pd–Rh electrodes. The ratio of exchange currents ($j_{0,\text{Pd-Rh}}/j_{0,\text{Pt-Rh}} = 3.2$, Table 2), determined with respect double layer region between -0.43 V and -0.51 V, indicates that Pd–Rh electrode had better catalytic activity over Pt–Rh in reducing nitrate ions.

4. Conclusion

In this study, electrocatalytic reduction of nitrate and nitrite ions was explored using Pt–Rh and Pd–Rh electrodes supported on H⁺ conducting Nafion polymer. Both of the electrodes were active in reducing nitrate and nitrite ions electrochemically. The Pt–Rh cathode could be effective for 15 h persistently in eliminating $\geq 85\%$ NO₃⁻ as well as NO₂⁻ from water by passing 100 mA DC. The efficiency as well product selectivity was influenced by the pH and potential. In the aqueous phase, ammonia was identified as only one product during cathodic electrolysis.

Measurements of rate constants, exchange current densities fairly supported that Pd–Rh/Nafion had better electrocatalytic properties over Pt–Rh/Nafion in reducing nitrate and nitrite ions.

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