Electrocatalytic Reduction of Nitrate Using Cu–Pd and Cu–Pt Cathodes/H$^+$-Conducting Solid Polymer Electrolyte Membrane Assemblies

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Electrocatalytic reduction of nitrate ions (NO_3^-) was carried out over Cu–Pd and Cu–Pt bimetallic cathodes, which were deposited on a Nafion-117 H$^+$-conducting polymer membrane. By applying DC current to the membrane–electrode assembly (MEA), H_2 evolved on the cathode caused monotonic degradation of NO_3^- in the cathode compartment. The NO_3^- reduction proceeded in a consecutive manner and copper increased significantly the catalytic activity for the first step from NO_3^- to NO_2^-. The Cu–Pd and Cu–Pt cathodes, with 38 and 20 mol % Cu, respectively, exhibited the highest reduction rate. The product selectivity was also dependent on the content of Cu. The Cu–Pd cathode showed a lower selectivity to NO_2^- and a higher selectivity to NH_4^+, because the catalytic activity for NO_2^- reduction is high. The rate of nitrate reduction was increased by supplying CO_2, which plays a role of a buffer to keep pH lower than 7 and promotes the reaction, $2NO_3^- + 5H_2 \rightarrow N_2 + 2OH^- + 4H_2O$.

Increasing concentration of nitrates in groundwater has been caused by overfertilization in agriculture. Water containing more than 50 ppm NO_3^- is harmful to health and the environment.[1–3] In the last couple of decades, this environmental issue has led to acute attention to research of nitrate mitigation. In this regard, electrochemistry and catalysis have been components of many research papers for the reduction of nitrate ions.[4–29] Electrochemical nitrate conversion uses cathodic reactions.[4–18] At acidic pH, hydrogen atoms adsorbed on the cathode surface inhibits the reduction of nitrate, whereas the reaction in alkaline solutions produces ammonia. Catalytic hydrogenation for the removal of nitrate from water has been studied using various supported metallic or bimetallic catalysts.[19–28] In many catalytic systems reported so far however, it is difficult to avoid the formation of nitrite and ammonia, which cause higher toxicity and intolerable smell, respectively. In this aspect, the validity of these processes has sometimes been controversial[24] and is critically dependent on the development of catalytic as well as electrocatalytic materials with excellent activity and selectivity. Recently, we have reported electrocatalytic reduction of nitrate in water using membrane/electrode assemblies (MEAs), which were prepared by chemical plating on an H$^+$-conducting solid polymer electrolyte.[29] The reduction performance is strongly dependent on the metallic composition of cathode and the addition of Cu to Pt exhibited a significant promoting effect.

In the present study, the electrocatalytic reduction of nitrate as well as nitrite was studied for Pt as well as Pd cathodes modified with Cu. The aim of this work is to explore the effects of cathode compositions on nitrate/nitrite conversion and product selectivity under different experimental conditions using batch and flow microreactors. The effects of initial concentration of nitrate and bubbling CO_2 on the rate of nitrate reduction and product selectivity are also discussed.

Experimental

Preparation of Electrode. In order to prepare MEAs, platinum or palladium was chemically deposited on a Nafion-117 membrane (DuPont, Inc.) from $PtCl_6$ or $PdCl_4$. The Nafion membrane was first sand blasted and dried at 110 °C then was immersed into 200 mL of water containing a suitable amount of $PtCl_6$. 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 °C at a rate of 5 °C h^{-1}. The Pt or Pd plating with an area of 2×3 cm^2 per side of the Nafion membrane was completed within 12 h, which was followed by the second plating of Cu metal only on the cathode. Various amounts of copper metal were deposited onto Pt or Pd cathodes using a $CuSO_4$ solution. MEAs thus prepared were first washed with dilute HCl and then sonicated for 0.5 min to remove unreacted $NaBH_4$ and NaOH from the surface and finally dried at 110 °C in air. The metallic composition of each MEA was determined by X-ray fluorescence analysis (Horiba MESA500). The crystal structure of the electrode was determined by X-ray diffraction, which was recorded using a Rigaku Multiflex diffractometer (Cu Kα, 30 kV, 20 mA).

Reduction of Nitrate. The reduction of nitrate/nitrite ions was carried out using MEAs having a Pt anode and four different cathodes, Pt, Pd, Cu–Pt, and Cu–Pd in a batch microreactor as shown in Figure 1a. The cathode and anode compartments were separated by as prepared MEA. The virtual distance between anode and cathode was 180 µm, which corresponds to the thickness of the Nafion membrane. The cathode and anode compartments were filled with 5 mL of aqueous solution of $NaNO_3$ (3–36 g L^{-1}) or $NaNO_2$ (3 g L^{-1}) and with water, respectively. Rela-

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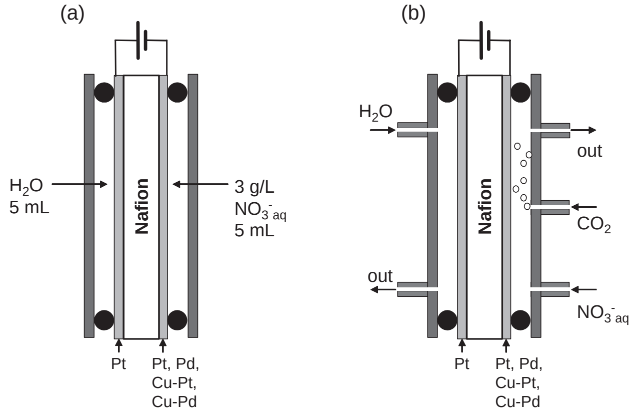

Figure 1. Schematic representation of (a) a batch reactor and (b) a flow reactor.

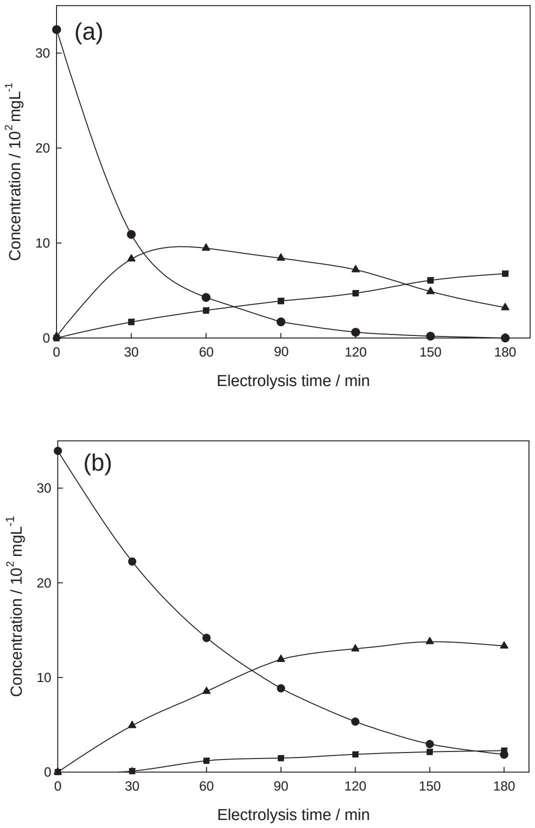

Figure 2. Nitrate reduction for (a) Cu–Pd (38 mol % Cu) and (b) Cu–Pt (15 mol % Cu) cathode using the batch reactor. Applied current: 100 mA, reaction time: 3 h. ● NO_3^-, ▲ NO_2^-, ■ NH_4^+.

tively high concentrations of nitrate/nitrite were used for reliable analyses after dilution of the solution. Each electrode was connected with a DC power supply (100 mA) for electrolysis (3 h). In order to monitor the concentration change of NO_3^-, NO_2^-, and NH_4^+ ions as a function of time, a portion of 20 µL was collected from the solution in the cathode compartment at a constant interval and diluted to 5 mL. The sample was then analyzed by an ion chromatograph (TOA-DKK, ICA-2000). Nitrate/nitrite or other N-containing species was not detected in the anode compartment. The gas evolved from the cathode was analyzed using a quadrupole mass spectrometer (Pfeiffer, OmniStar). Because pH of the solution in the cathode compartment was found to increase with progress of the nitrate reduction, CO_2 was supplied as a buffer by bubbling at the rate of 20 cm^3 min^{-1}.

The nitrate reduction was also carried out using a flow microreactor, which has a similar structure to that of the batch reactor (Figure 1b). The nitrate solution and water were supplied to compartments of the cathode and the anode, respectively, at the constant rate of 0.1 mL min^{-1}. The flow reactor was also operated with bubbling CO_2 only around the cathode at the rate of 10 mL min^{-1}.

Results and Discussion

Reduction Activity of Cu–Pd and Cu–Pt Cathodes. The total thickness of metallic electrodes on both sides of the Nafion membrane was determined to be 2–3 µm from SEM observation of the fracture surface. The X-ray diffraction measurement of the cathode side of the membrane suggested the deposition of crystalline Pt or Pd. As prepared Cu–Pd and Cu–Pt cathodes showed diffraction peaks due to Cu in addition to Pd or Pt, but those ascribable to alloys could not be detected. The composition of Cu–Pt and Cu–Pd can be controlled by the concentration of $CuSO_4$ used in the chemical plating process. The MEAs were used for the electrocatalytic reactions without further treatment.

The reduction activity of MEAs with a Pt anode and four different cathodes (Pt, Pd, Cu–Pt, and Cu–Pd) was tested in a batch microreactor. By applying a DC current to the MEA, the evolution of H_2 and the reduction of nitrate/nitrite took place simultaneously on the cathode surface. Figure 2 exhibits the typical concentration profiles during the nitrate reduction for Cu–Pd (38 mol % Cu) and Cu–Pt (15 mol % Cu) cathodes under the standard electrolytic conditions ($C_0 = 3.0$ g L^{-1}, 100 mA, 3 h). The concentration of NO_3^- decreased monotonically, accompanied by the formation of NO_2^- and NH_4^+. To compare the activity of each cathode, the apparent rate constant (k) was calculated using curve fitting on the assumption that the concentration of NO_3^- (C) expresses as a first-order reaction, i.e., $C = C_0 \exp(-kt)$, where C_0 is the initial concentration and t is time (min). This method was also applied to the reduction of NO_2^-.

Table 1 summarizes the activity and selectivity for the reduction of NO_3^- after 3 h of reaction. When Pt or Pd alone was used as a cathode, the reaction was very slow ($k < 2 \times 10^{-3}$ min^{-1}). The rate was significantly increased by the deposition of Cu onto Pt or Pd. In the case of Cu–Pd (Figure 2), more than half of the NO_3^- reacted in the first 30 min, yielding about half the amount of NO_2^-, which would next be consumed after 60 min to yield about half the amount of NH_4^+. The overall selectivity to NH_4^+ exceeded 15% after 3 h. A similar change was observed for Cu–Pt, but the selectivity to NH_4^+ was only 7%, compared to 40% selectivity to NO_2^-. In all the cases, the mass spectrometric analysis of the gas evolved from a cathode compartment detected mainly N_2, but N_2O and NO were very low (<1% selectivity). Possibly the most toxic by-product in the present reaction system would be hydroxylamine, which can be analyzed by UV–vis absorption at 690 nm after condensation with 8-hydroxyquinoline. However, the concentration of this compound was under the detection limit (<0.1 mg L^{-1}) even at high initial concentra-

Table 1. Apparent Rate Constants and Product Selectivity of Nitrate and Nitrite Reduction[a)]

Cathode	NO_3^- reduction			NO_2^- reduction	
	$k/10^{-3}$ min^{-1}	Selectivity/%		$k/10^{-3}$ min^{-1}	Selectivity/%
		NO_2^-	NH_4^+		NH_4^+
Pd	1.7	12	9	2.9	46
Cu–Pd (38 mol % Cu)	49.0	15	16	13.9	25
Pt	0.9	0	49	1.6	11
Cu–Pt (15 mol % Cu)	17.8	40	7	2.8	26

a) Pt was used as an anode. 3.0 g L^{-1} NO_3^- or NO_2^-, 100 mA, 3 h, room temperature.

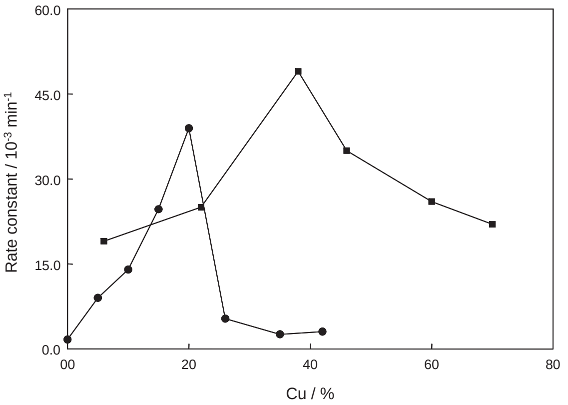

Figure 3. The rate constant of nitrate reduction on the cathodes with different metallic compositions. ● Cu–Pt, ■ Cu–Pd. Other conditions are same as mentioned in Table 1.

tion of NO_3^- (36.1 g L^{-1}). The ICP analysis of the solution in the cathode compartment after 3 h-reaction demonstrated that the dissolution of metallic species (Cu, Pt, and Pd) during electrolysis was negligible.

The reduction of NO_3^- seems to take place on the cathode in a consecutive manner, $NO_3^- \rightarrow NO_2^- \rightarrow N_2$ or NH_4^+, as was pointed out by previous studies.[1–3] In the consecutive pathway of NO_3^- reduction, NO_2^- is recognized as a stable intermediate as noted in Figure 2. In order to explore the relative activity and selectivity of different cathodes, the reduction of NO_2^- was also carried out concomitantly (Table 1). Again, the bare Pt and Pd showed very low activities ($k < 3 \times 10^{-3}$ min^{-1}) for NO_2^- reduction. It should be noted that Pd exhibited a higher selectivity to NH_4^+. Unlike the case of NO_3^- reduction, however, the effect of Cu on these cathodes is so different, i.e., the Cu–Pd exhibited the highest k, 13.9×10^{-3} min^{-1}, in contrast to 2.8×10^{-3} min^{-1} for the Cu–Pt system. The different NO_2^- selectivity in the reduction of NO_3^- can therefore be explained by the relative rate of first and second steps in the consecutive pathway above described. Thanks to the higher activity of Cu–Pd for NO_2^- reduction, NO_3^- reduction yields less NO_2^- but more NH_4^+.

The present results clearly indicate that Cu is indispensable for the first step, i.e., from NO_3^- to NO_2^-. When Cu alone was used as a cathode however, the activity and stability of the reactor was too low to use. The low stability should be associated with the ease of oxidation of copper. The most acceptable explanation for the role of Cu in catalytic hydrogenation of NO_3^- has been proposed by Epron and co-authors.[30] They reported that the role of Cu in the bimetallic Pt–Cu catalyst is to reduce NO_3^- to NO_2^- according to a redox between Cu^0 and Cu^{2+}, where the interaction between Cu and Pt is of major importance to maintain copper in the metallic state by way of hydrogen adsorbed on Pt.

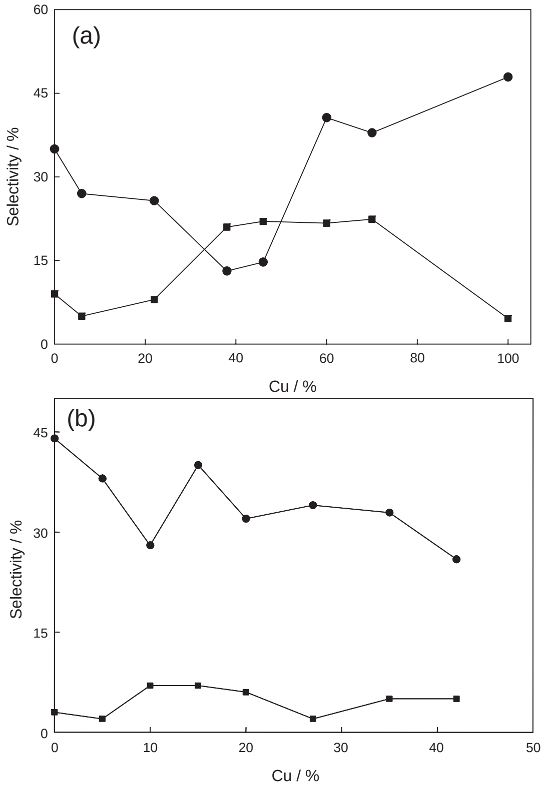

Figure 4. Product selectivity as a function of metallic composition in (a) Cu–Pd and (b) Cu–Pt cathodes. Applied current: 100 mA, reaction time: 3 h. ● NO_2^- selectivity, ■ NH_4^+ selectivity.

Figure 3 shows the dependence of NO_3^- reduction activity on the metallic composition of Cu–Pt and Cu–Pd cathodes. In both cases, the activity increased with increasing amount of Cu deposition onto Pt or Pd surfaces and reached in maxima at 20 and 38 mol %, respectively. Further increase of Cu then steeply reduced the activity. This implies that Cu in combination with Pt or Pd can generate active sites for the reduction of NO_3^- on the cathode. The product selectivity was another important issue. Because the by-products such as NO_2^- and NH_4^+ cause more serious problems, the complete conversion of NO_3^- into N_2 is desired. Figure 4 shows the product selectivity of the two binary cathodes with different metallic compositions. In the

Table 2. Effect of CO_2 on Nitrate Reduction over Cu–Pt Cathode (15 mol % Cu)[a)]

	$k/10^{-3}$ min^{-1}	Selectivity/%		pH_{init}	pH_{fin}
		NO_2^-	NH_4^+		
None	17.8	40	7	5.6	11.6
CO_2 bubbling	49.0	15	16	5.6	5.8

a) Pt was used as an anode. 3.0 g L^{-1} NO_3^-, 100 mA, 3 h, room temperature.

Cu–Pd system, the selectivity to NO_2^- becomes the minimum at around 40 mol % Cu, where the highest activity was attained. The activity for both NO_3^- and NO_2^- is one reason for the higher selectivity to NH_4^+. By contrast, the product selectivity of Cu–Pt cathode was less dependent on the composition. Much higher selectivity to NO_2^- compared to NH_4^+ can be explained by the high reactivity to NO_3^- in contrast to the low reactivity to NO_2^-. The Cu–Pd cathode achieved a higher reduction rate over Cu–Pt cathodes, but its higher selectivity to undesired ammonia may be a problem. The high selectivity to NO_2^- for Cu–Pt would possibly be reduced due to the successive reduction steps in a longer reaction time in a batch reactor.

Effect of CO_2. Table 2 shows pH values of a solution in the Cu–Pt cathode compartment before and after reaction. Clearly, the nitrate reduction increased pH from 5.6 to 11.6 during 3 h-electrolysis, being consistent with the occurrence of the following net reaction.

$$2NO_3^- + 5H_2 \rightarrow N_2 + 2OH^- + 4H_2O \qquad (1)$$

The reduction of NO_3^- produces a base (OH^-) and thus causes an increase of pH. As a result, the NO_3^- reduction becomes unfavorable with an increase of pH. Moreover, basic pH favors the formation of ammonia.[4–6] To keep the pH constant during the catalytic nitrate hydrogenation, bubbling CO_2 gas into the solution is known as an efficient way to facilitate the catalytic hydrogenation of NO_3^-.[25] In the present study, we supplied CO_2 by bubbling (20 mL min^{-1}) into the cathode compartment. The apparent rate constant (k) increased significantly from 17.8 to 49.0 min^{-1} and the selectivity to NO_2^- decreased from 40 to 15%. Because no such effect was observed when bubbling Ar or N_2 was performed, explanation by solution mixing is not valid in this case. CO_2 is considered to facilitate scavenging OH^- ions, which may affect the adsorption of NO_3^- onto the cathode surface. Therefore, the introduction of CO_2 was found to play a role of buffer to keep pH constant and promote the reaction even in the present electrocatalytic nitrate reduction.

Effect of Nitrate Concentration. Nitrate reduction experiment was also carried out using various initial NO_3^- concentrations in the range 3.4–36.1 g L^{-1} over the Cu–Pt cathode (15 mol % Cu). As shown in Figure 5, the concentration of NO_3^- decreased almost linearly with time on stream, when the initial concentration is high (>16 g L^{-1}). The slope of each line should reflect the rate of nitrate reduction, which is almost constant at around 0.1 g-NO_3 L^{-1} min^{-1}. Figure 6 shows the dependence of product selectivity on the initial NO_3^- concentration. With an increase of the concentration, the selectivity to NO_2^- decreases monotonically, whereas the selectivity to NH_4^+ tends to increase. A similar dependence was also confirmed for the Cu–Pd cathode. Using a high initial concentration (29 g L^{-1}) of NO_3^-, the effect of supplied current was also examined. The reaction rate was found to increase almost linearly as the current was increased from 50 to 200 mA, but further increase did not improve the rate. Under various current supplies, the Cu–Pt composition did not produce significant NH_4^+ after 180 min electrolysis of nitrate solution.

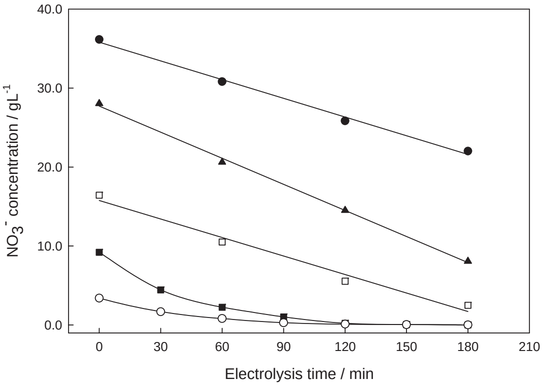

Figure 5. Nitrate reduction by the Cu–Pt cathode (15 mol % Cu) with different initial nitrate concentration. Applied current: 100 mA. ● 36.1 g L^{-1}, ▲ 28.0 g L^{-1}, □ 16.4 g L^{-1}, ■ 9.2 g L^{-1}, and ○ 3.4 g L^{-1}.

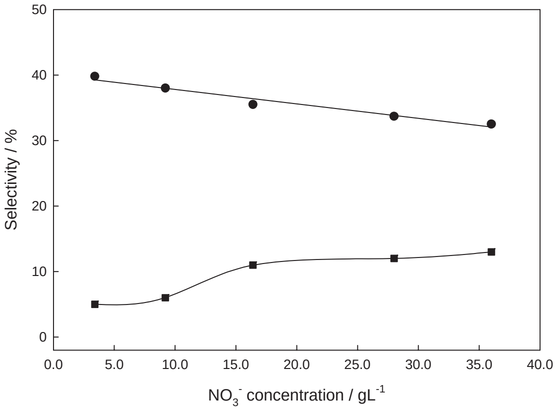

Figure 6. The product selectivity for nitrate reduction by the Cu–Pt cathode (15 mol % Cu) with different initial nitrate concentration. Applied current: 100 mA, reaction time: 3 h. ● NO_2^-, ■ NH_4^+.

Nitrate Reduction in a Flow Reactor. The electrocatalytic reduction of nitrate was finally carried out using a flow microreactor (Figure 1b), in which Cu–Pt (15 mol % Cu) or Cu–Pd (33 mol % Cu) cathodes were installed. Figure 7 shows concentration profiles in the effluent from the cathode compartment, when a solution containing a low concentration of 30 mg L^{-1} NO_3^- was supplied at a slow rate of 0.1 mL min^{-1}. The reactions reached steady states after 60 min, where each concentration was almost constant. The Cu–Pt cathode showed 33% conversion of NO_3^-, about half of it remained in the form of NO_2^- in the effluent. By contrast, the Cu–Pd cathode could convert 85% of NO_3^- without forming noticeable amounts of NO_2^- and/or NH_4^+ (<1 mg L^{-1}). As shown in Figure 2a, the Cu–Pd cathode yielded a significant amount of NH_4^+ (16% se-

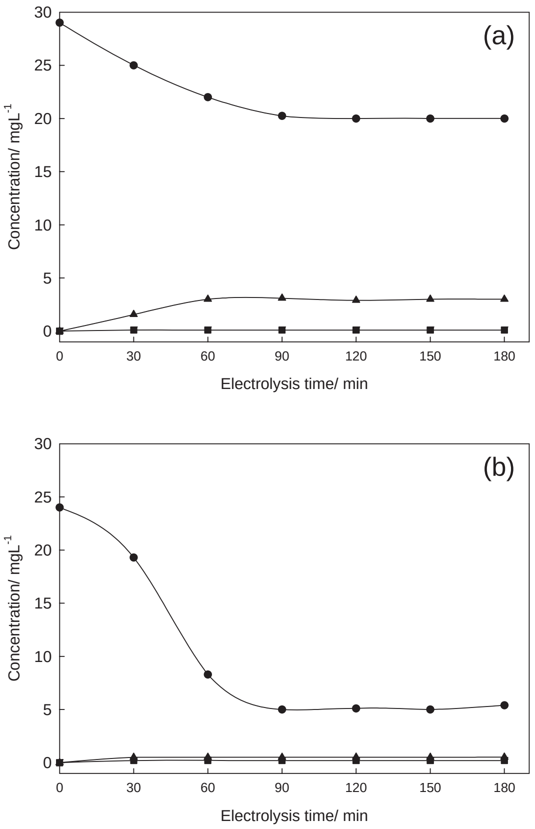

Figure 7. The reduction of NO_3^- in a flow reactor using (a) Cu–Pt (15 mol % Cu) and (b) Cu–Pd (33 mol % Cu) cathodes. 30 mg L^{-1} NO_3^-, flow rate; 0.1 mL min^{-1}, DC current; 100 mA. ● NO_3^-, ▲ NO_2^-, ■ NH_4^+.

lectivity) in a batch microreactor. This is not the case for a flow microreactor, because of its NO_3^- concentration in the feed two orders of magnitude lower than that in a batch microreactor. Under such conditions, the diffusion of N-containing species (NO_3^- and NO_2^-) to the bulk solution would suppress the formation of NH_4^+, the final product in the consecutive reaction. On the contrary, a high concentration N-containing species becomes abundant around the cathode surface, being favorable for the formation of NH_4^+. The nitrate reduction over the Cu–Pd cathode in a flow microreactor was also carried out with introduction of CO_2 into the cathode compartment. The reaction achieved a steady state in a short time of about 30 min, compared to more than 60 min required in the absence of CO_2. However, NO_3^- conversion in the steady state was almost the same with the results in Figure 7b, indicating that the reaction is under mass-transfer limitation. To achieve an efficient nitrate conversion at higher flow rates, further study is now directed to the preparation of electrodes having a larger surface and/or porous structure.

Conclusion

Electrocatalytic reduction of NO_3^- in water has been achieved successfully at room temperature using MEAs consisting of an H^+-conducting Nafion membrane, a Pt anode and Cu–Pd or Cu–Pt cathodes. In contrast to Pt, Pd, or Cu alone, the bimetallic cathode exhibited high activity and stability. Although copper in the cathode plays a key role in the first step from NO_3^- to NO_2^- in the consecutive reaction pathway, further steps would rather be accelerated by the combination of Cu and Pd. Because the reaction produces OH^- to increase pH, introducing CO_2 as a buffer to the cathode compartment not only accelerates the NO_3^- reduction, but also suppresses the amount of NO_2^- released intermediately during the reaction course without increasing NH_4^+. The formation of NO_2^- and NH_4^+ could further be suppressed by using a flow microreactor, which was operated at low concentration (30 mg L^{-1}) of NO_3^-.

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