Electrocatalytic nitrate hydrogenation over an H$^+$-conducting solid polymer electrolyte membrane–modified cathode assembly

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Selective electrocatalytic hydrogenation of NO_3^- to N_2 in water has successfully been achieved at room temperature using a membrane–electrode assembly (MEA) consisting of an H$^+$-conducting solid polymer electrolyte (Nafion-117) and a surface-modified Pt cathode.

The increased contamination of water resources by nitrate ions has become a serious environmental problem in recent years. Electrochemical or catalytic processes have been studied as the most common technologies for nitrate removal. Electrochemical nitrate conversion uses cathodic reactions. At acidic pH, hydrogen adsorbed on the cathode surface inhibits the reduction of nitrate, whereas the reaction in alkaline solutions produces ammonia.[1–3] Catalytic hydrogenation for the removal of nitrates from water has been studied using various supported metallic or bimetallic catalysts.[4–7] In many catalytic systems reported so far, however, it is difficult to avoid the formation of nitrite or ammonium ions, which are more toxic than nitrate.[5–8] In this aspect, the validity of these processes has sometimes been controversial[8,9] and is critically dependent on the development of catalytic as well as electro-catalytic materials with excellent activity and selectivity. In this communication, we report a new approach to reduce nitrate to harmless gaseous N_2 very efficiently by hybridizing water electrolysis and catalytic hydrogenation of nitrate using an H$^+$-conducting solid polymer electrolyte membrane–electrode assembly (MEA).

The reduction of nitrate was performed in an electrochemical cell as shown in Fig. 1. On both sides of the polymer electrolyte membrane (Dupont, Inc. Nafion-117), chemical plating using NaBH$_4$ as a reducing agent was applied to form Pt, Pd, Cu, Pd–Cu, and/or Pt–Ni electrodes with an area of 6 cm^2 per side. On the Pt cathode, Cu, Ni and/or Pd were deposited as modifiers by means of electrolytic (EP) and/or chemical plating (CP). Both processes were carried out in an aqueous solution of the corresponding metal sulfates or chlorides. The MEA thus obtained was sandwiched between two chambers, which were filled with 7 mL of water on the anode side and 7 mL aqueous solution of NaNO$_3$ (3000 mg L^{-1} NO_3^-) on the cathode side. The reaction was carried out at room temperature by applying a constant electric current between the anode and the cathode (0–100 mA). The degradation of nitrate ion and formation of nitrite and ammonium ions in the cathode chamber were measured at constant time intervals by ion chromatography (TOA-DKK, ICA-2000). The gas evolved from the cathode was analyzed by on-line mass spectroscopy (Omnistar GSD301, Pfeiffer).

By applying a DC current to the electrochemical cell (Fig. 1), stoichiometric evolution of O_2 and H_2 was observed continuously on the anode and cathode, respectively, suggesting the occurrence of electrolysis of water. This means the oxidation of H_2O on the anode and the H$^+$ thus formed migrated through the Nafion membrane to the cathode, where reduction to molecular hydrogen took place. This was accompanied by a monotonic degradation of nitrate in the cathode chamber, the rate of which was strongly dependent on the cathode materials as summarized in Table 1. Here, the rate constant (k) was calculated on the assumption that the concentration of nitrate (C) can be expressed as a first order reaction, *i.e.*, $C = C_0\exp(-kt)$, where C_0 is the initial concentration of nitrate and t is time (min). When Pt alone was used as the cathode, the degradation was very slow ($k < 10^{-3}$ min^{-1}) and the selectivity to NH_4^+ was considerably high (49%). The rate was
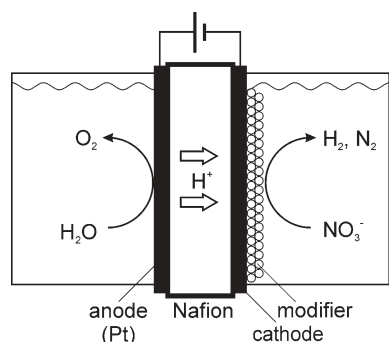

Fig. 1 Schematic illustration of the MEA used for nitrate reduction.

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Table 1 Rate constant for nitrate reduction and product selectivity for various cathode materials

Cathode[b]	Modifier[b]	$k/10^{-3}$ min^{-1}	Selectivity/%[c]	
			NO_2^-	NH_4^+
Pt (CP)	none	0.9	0	49
	Cu (EP), 17 wt%	22.1	30	0
	Cu (CP), 8 wt%	9.6	44	4
	Cu (CP, CO_2)	45.2	0	5
	Ni (EP), 10 wt%	6.9	0	27
	Pd (EP), 0.4 wt%	3.2	8	9
Pd (CP)	none	1.7	1	9
Cu (CP)	none	1.2	27	6
Pd–Cu (CP)	none	19.8	17	6
Ni–Pd (CP)	none	2.2	0	19

^{a} Applied current: 100 mA, initial NO_3^-: 3000 mg L^{-1}. ^{b} CP: chemical plating using NaBH$_4$, EP: electrolytic plating. ^{c} Selectivity after 180 min reaction.

increased by the deposition of other metals onto the surface of the Pt cathode by CP and/or EP methods. The most effective modifier was Cu, which increased the activity of the Pt cathode more than 25 times (EP). A very low yield of NH_4^+ is another noticeable merit of this modification, which is in contrast to the Ni-modified cathodes. Neither Pd-modified Pt nor Pd alone were active for nitrate reduction. The modification by Cu was also effective for Pd; a bimetallic Pd–Cu cathode (9 wt% Cu), which was prepared by the CP method using a mixed aqueous solution of $CuSO_4$–$PdCl_2$ exhibited a high activity ($k = 19.8 \times 10^{-3}$ min^{-1}). When Cu alone was used as the cathode, however, the activity and stability were too low to use. The low stability should be associated with the ease of oxidation of copper.

In the catalytic hydrogenation by H_2, it is reported that Pd or Pt catalysts can reduce nitrite but are inactive for the reduction of nitrate.[10] We thus suspect that the high activity for the Cu-modified Pt electrode is due to highly-dispersed metallic Cu that is stabilized on Pt. This is compatible with the X-ray diffraction pattern of the Cu-modified Pt electrode, which exhibited a single phase of Pt but the deposition of Cu metal and oxides could not detected. X-Ray photoelectron spectroscopy showed the presence of Cu^{2+}, Cu^0 and Pt^0 on the cathode surface.

The degradation of nitrate did not occur when the applied voltage was not enough for water electrolysis ($<ca.$ 1.2 V). Once water electrolysis began, the rate constant, k, increased monotonically with an increase in current and voltage, but the product selectivity was almost constant. This is quite different from conventional electrochemical nitrate reduction, where the product is dependent on the electrolysis potential; reduction at low negative potentials gives NO_2^-, whereas reduction at high negative potentials gives mainly NH_4^+.[2]
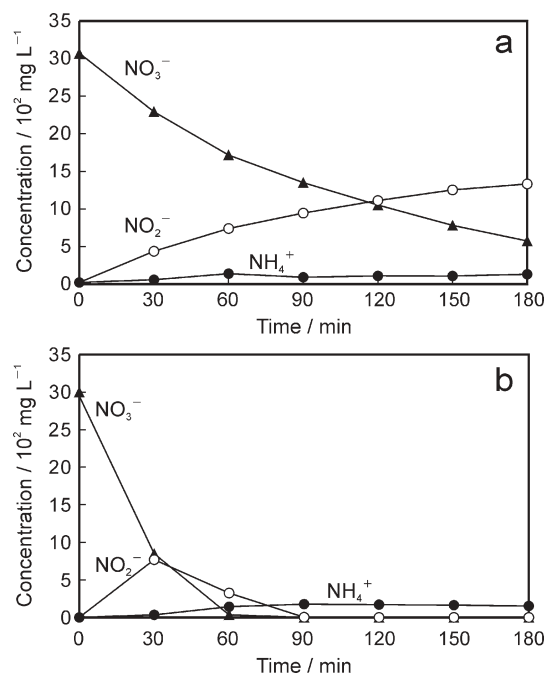
Fig. 2a exhibits the concentration profiles of NO_3^-, NO_2^-, and NH_4^+ for the MEA having a Cu-modified Pt cathode under electrolytic conditions (100 mA). The concentration of nitrate decreased monotonically, although nitrite and ammonium ions were formed. About half of the nitrate reacted in the first 90 min and was mainly converted into nitrite, which would be gradually consumed to N_2 after 180 min. The mass spectrometric analysis of the gas evolved from a cathode chamber detected N_2, but N_2O and NO were negligible. Thus, the reaction seems to take place in a consecutive manner, $NO_3^- \rightarrow NO_2^- \rightarrow$ (NO) $\rightarrow N_2$. The formation of more toxic nitrite as an intermediate causes a serious problem in the catalytic hydrogenation of nitrate. After 180 min of the reaction, the pH of the aqueous solution in the cathode chamber increased from 5.5 to 11.0, indicating that the nitrate reduction yielded OH$^-$ as in the conventional catalytic nitrate reduction. The change of pH is nearly equivalent to the amount of OH$^-$ formed by the reaction shown in eqn (1).

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

One may consider that the following electrochemical reactions of nitrate are also possible.

$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O \qquad (2)$$

$$2NO_3^- + 6H_2O + 10e^- \rightarrow N_2 + 12OH^- \qquad (3)$$
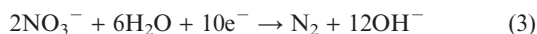
However, eqn (2) cannot explain the pH increase. According to eqn (3), the final pH of the cathode solution should exceed 13,

Fig. 2 Concentration profiles of NO_3^-, NO_2^-, and NH_4^+ during application of a DC current (100 mA) (a) without a CO_2 supply and (b) with a CO_2 supply to the Cu-modified Pt cathode (CP) at room temperature.

which is not in accord with the experimental value, 11. Actually, the cyclic voltammetry measurement exhibited no obvious signals ascribable to these cathodic processes.

These considerations suggest that the reaction is probably due to catalytic hydrogenation of NO_3^- by H_2, which is evolved electrochemically on the surface of the cathode. To confirm this point, the catalytic nitrate hydrogenation was carried out by supplying H_2 by bubbling onto the cathode surface without applying an external potential. The rate of H_2 supply, 20 cm^3 min^{-1}, corresponds to 26 times more than Faradic H_2 evolution at the cathodic current of 100 mA. Nevertheless, the degradation of nitrate was negligible ($k < 0.1 \times 10^{-3}$ min^{-1}). The result implies that the reduction of nitrate should basically be catalytic but promoted significantly by applying a cathodic potential.

To keep the pH constant during the catalytic nitrate hydrogenation, bubbling CO_2 gas into the reaction solution is known as an useful buffer.[11] Fig. 2b displays the result of electrocatalytic nitrate reduction when CO_2 was supplied into the cathode chamber at a rate of 20 cm^3 min^{-1}. The pH in this case became almost constant at ca. 6. Clearly, the nitrate reduction became about 5-times higher compared to the reaction without a CO_2 feed (Fig. 2a). Moreover, the amount of NO_2^- released intermediately during the reaction course was significantly suppressed and totally disappeared after 90 min without increasing NH_4^+. The final selectivity to NH_4^+ after 180 min of the reaction was less than 5%, which is lower than those reported so far for catalytic and electrocatalytic hydrogenation of nitrate.[4–7] The maximum Faradaic efficiency for the hydrogenation of nitrate to N_2 on the Cu–Pt cathode reached more than 25%, which is extremely larger than the efficiency reported for conventional catalytic reduction of nitrate by H_2 ($\leqslant 1\%$).[4–7,12]

The solid electrolyte membrane reactors are of significant interest not only as fuel cells but also as reduction–oxidation converters. However, application of polymeric proton exchange membranes in chemical reactors at low temperature is not common.[13] We previously reported the NO–H_2–O_2 reactions over Pt/Nafion MEA,[14] where electrolytic H_2 evolution of the Pt cathode exhibited high activities towards NO reduction at $\leqslant 80$ °C. As the present result suggested, this type of MEA reactor is very efficient not only for NO reduction at the cathode/gas interface, but also for NO_3^- reduction at the cathode/water interface. A common knowledge of these studies is that the electrochemically generated hydrogen on the MEA cathode possesses a higher reactivity compared to molecular H_2. The electrochemical promotion effect is known as the NEMCA effect,[15] but its contribution to the present process is now under investigation.

Consequently, the present study demonstrates that the electrocatalytic nitrate reduction using polymer solid electrolytes is promising as an efficient and selective process to reduce nitrate to N_2 in aqueous solutions at room temperature. Another important feature is that, unlike the catalytic hydrogenation of nitrate, a serious safety hazard due to a large H_2 reservoir can be eliminated. The combination between the solid polymer electrolyte and electrode catalysts can broadly be applied to novel nitrate reduction processes required for water purification technology.

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