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Electrolytic decomposition of ammonia to nitrogen in a multi-cell-stacked electrolyzer with a self-pH-adjustment function

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Abstract

This paper describes a study of continuous decomposition characteristics of ammonia to nitrogen in a multi-cell-stacked electrolyzer with an anion exchange membrane. The pH change of ammonia solution in both the anodic and cathodic chambers of a divided cell due to the water splitting reactions was studied together with the electrolytic decomposition of ammonia. The electrolytic decomposition efficiency of ammonia was considerably affected by the pH change of ammonia solution caused by the water splitting reactions. In the anodic chamber with the ammonia solution, the water splitting reaction which produced protons occurred at a pH of less than 8, and in the cathodic chamber, that producing hydroxyl ions occurred at a pH of more than 11. By using the characteristics of the electrolytic water splitting reactions in a divided cell, a continuous electrolyzer with a self-pH-adjustment function was devised, wherein a portion of the ammonia solution from a pH-adjustment reservoir was circulated through the cathodic chambers of the electrolyzer. This enhanced the pH of the ammonia solution being fed from a pH-adjustment reservoir into the anodic chambers of the electrolyzer, which caused a higher ammonia decomposition yield. Based on this electrolyzer, a salt-free ammonia decomposition process was suggested. In this process, ammonia in the solution was continuously and effectively decomposed into environmentally harmless nitrogen gas.

1. Introduction

NH_3-nitrogen compounds in wastewaters being released to the environment are detrimental in several respects. They can cause eutrophication which is fatal to aquatic life and a hindrance to the disinfection of water supplies as well as giving offensive odours and being a carcinogen [1–5]. Ammonia can be removed or decomposed by several methods such as air-stripping, biological denitrification, breakpoint chlorination, electrolysis and so on. Recently, the electrochemical method has attracted a lot of attention for the advanced treatment of wastewater because of its advantages such as a minimal generation of a secondary waste, easy operation, remote control, and sometimes competitive operation costs. In our previous work [5–8], ammonia of the lowest oxidation state among the nitrogen compounds was found to be able to be electrochemically decomposed to harmless nitrogen species through complex electrolytic reaction paths and even to be converted partially to nitrate ions of the highest oxidation state among the nitrogen compounds. The electrolytic decomposition of ammonia to nitrogen is known to be more effective in basic conditions where the ammonia exists in a non-ionic form than in acidic or neutral conditions where it exists in an ionic form of ammonia, i.e. ammonium ion [5, 8, 9]. Ammonia in a basic solution is oxidized to nitrogen through a direct electrolytic reaction accompanying its adsorption at the electrode. On the other hand, the ammonium ion in a neutral or an acid solution is partially decomposed to nitrogen through oxidation by the OH radicals generated at the electrode during oxygen evolution [5, 6]. Also, the electrolytic decomposition yield of ammonia is known to be better in the anodic chamber of a cell with a membrane than in a cell without a membrane, because the re-reduction and the re-oxidation of the intermediate species generated during an electrolysis at the cathode and at the anode are prevented in a divided cell [7, 8]. When a divided cell is used for electrolysis, the pH in the anodic and cathodic chambers changes due to the electrolytic water splitting actions occurring as side reactions, which result in a considerable affect on the decomposition of the ammonia. However, there is scant data on the effect of the pH change during the electrolytic decomposition of ammonia.

In this work, pH changes of ammonia solution in the anodic and cathodic chambers of divided cells with an ion exchange membrane were studied initially. On the basis of the results, the characteristics of the electrolytic decomposition of ammonia by a continuous multi-cell-stacked electrolyzer with an ion exchange membrane were evaluated, and finally a new electrolytic process for ammonia decomposition to nitrogen gas was suggested by using the multi-cell-stacked electrolyzer with a self-pH-adjustment function to boost the alkalinity in the anodic chambers without adding any chemicals. The performance characteristics of the electrolytic system were also evaluated.

2. Experimental

In order to observe the pH change of the ammonia solution in the anodic and cathodic chamber of a divided-cell during ammonia electrolysis, a cell with an anode of IrO_2 and a cathode of Ti, of the same dimensions (2 × 4 × 0.2 cm) of a plate type, was used with an anion exchange membrane (AEM) (Electrolytica, A7001) or a cation exchange membrane (CEM) (Nafion 424). The details on the experimental apparatus used were described previously [8]. The volumes of the anodic and cathodic chambers of the cell were 16.5 ml. The IrO_2 electrode was prepared by coating multi-iridium oxide layers onto a Ti plate in the same way as that used in our previous work to fabricate some catalytic oxide electrodes [10–12]. In this experiment, an electrolyte solution of 65 ml of 0.5 M $(NH_4)_2SO_4$ in 0.1 M Na_2SO_4, of which the initial pH was adjusted before each electrolytic run, was circulated into the respective reservoirs for the anolyte and catholyte solutions through the anodic and cathodic chambers. The pH of the anodic and cathodic chambers was measured by on-line pH-sensors by using a data-logger system (Almemo 5990-2, Ahlborn Co.).

For evaluation of the continuous electrolytic decomposition characteristics of ammonia to nitrogen gas, a 4 cell-stacked electrolyzer with an AEM was used, where the anolyte and catholyte solutions flowed independently in series through the respective anodic and cathodic chambers of the stack. The dimensions of each half cell consisting of the stack were 3.5 × 8 × 0.7 cm. The solution volume in the half cell was 16.5 ml. All the cell frames were made of polyethylene. Each half cell of the stack had designed flow-paths of 4 mm in diameter within its frame in order for the electrolytes to flow through the respective cathodic or anodic half cells of the stack in series, as shown in Figure 1. Because of the gas generation problem during electrolysis, the flow-path directions within the frames were configured so that the electrolyte could flow into the cell from the bottom and left the cell from the top. The electrode-membrane gap was 5 mm. For the anodes of the stack electrolyzer, IrO_2 electrodes with the dimensions of 2 × 4 × 0.1 cm and with a mesh form of 6 mm × 12 mm were used. For the cathodes of the stack, Ti electrodes of the same dimensions and form as the anodes were used. In all experiments, the flow rate of each electrolyte solution was fixed at 5 ml min^{-1}. A current density of 80 mA cm^{-2} was chosen on the basis of our previous work [8], where the ammonia in the solution was electrochemically converted to nitrogen gas with a minimal loss of ammonia due to an air-stripping by oxygen evolution. In this system, the measured anodic voltage vs. SSE (Ag/AgCl electrode) was 1.5 V, and the cell voltage between the anode and cathode was 4.9 V. All the experiments were performed at a room temperature of 25 ± 2 °C. During electrolysis, each electrolyte solution at the outlet of the electrolyzer was sampled at regular intervals for an analysis of the Total Nitrogen (TN) by a TN analyzer (Shimadzu TOC-V CSH/TNM-1). The pH of the anodic and cathodic effluent solutions was monitored by on-line pH-sensors by using a data-logger system. After the electrolyzer had reached a steady state, the pH of each anodic and cathodic half cell was measured by a pH test paper (Schleicher & Schuell, Panpeha Plus).

All the reagents ($(NH_4)_2SO_4$, NaCl, Na_2SO_4) used to prepare ammonia solutions were reagent grade (Showa, Japan), and they were dissolved, as received, in demineralized water of 18.2 MΩ prepared by a double distillation and one ion-exchange (Mill-Q plus).

3. Results and discussion

3.1. *pH behavior of ammonia solution in the electrolytic cell*

It is known that the anodic decomposition of ammonia depends on the pH of the ammonia solution and it has a better yield when a divided cell with a membrane is used, in comparison to using an undivided cell without a membrane [5–8]. When a divided cell is used, the pH of the anodic chamber decreases and that of the cathodic chamber increases, because water splitting occurs as electrolytic side reactions which are the anodic evolution of oxygen and the cathodic evolution of hydrogen. As mentioned previously [5, 8, 13], for the electrolytic decomposition of ammonia, basic conditions are more favorable than acidic ones. Accordingly, without controlling the pH of the ammonia solution in the anodic chamber, the electrolytic decomposition yield of ammonia decreases with time, because the pH in the anodic chamber eventually becomes acidic, even though the initial pH of the ammonia solution is sufficiently basic. The water splitting reactions at the anode and cathode are generally known to change, depending on the solution pH. The evolution of oxygen and hydrogen are expressed by Equations (1) and (2) in acidic conditions and by Equations (3) and (4) in basic conditions.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad \text{at anode in acid} \qquad (1)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad \text{at cathode in acid} \qquad (2)$$

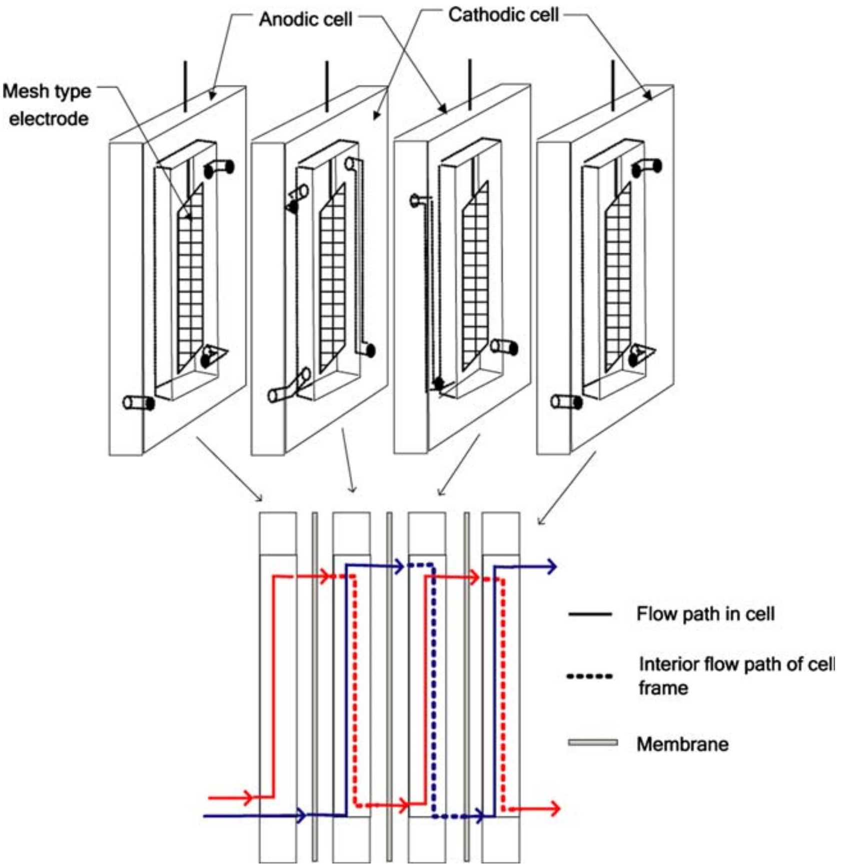


Fig. 1. Schematic repetitive half-cell configuration of the stack electrolyzer.

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad \text{at anode in base} \qquad (3)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad \text{at cathode in base} \qquad (4)$$

From the above equations, if such reactions occur as side reactions, the pH of the ammonia solution is thought to be considerably affected by the water splitting reaction changes according to the solution pH during electrolysis. In the electrolytic decomposition of ammonia, the pH values at which Equations (1) and (2) or Equations (3) and (4) can occur in an ammonia solution are not known as yet. Accordingly, in order to elucidate the pH changes of ammonia solutions in the anodic and cathodic chambers and in order to find a way to maintain the pH of ammonia solution in the anodic chamber sufficiently high during the electrolytic decomposition of ammonia, an experiment to investigate the anodic and cathodic pH changes was carried out before the main experiments to study the characteristics of the continuous electrolytic ammonia decomposition by using a multi-cell-stacked electrolyzer with a function to boost the alkalinity in the anodic chambers of the stack without adding chemicals.

Figure 2 shows the pH changes in the anodic and cathodic chambers of a cell with an AEM with time, where the ammonia solutions, with different initial pH solutions, were independently circulated into the anodic and cathodic chambers through the respective reservoirs. The total circulating solution volume in each reservoir was 65 ml. The applied cell current density was fixed at 80 mA cm^{-2}. In Figure 2A, in the cases of the ammonia solutions with an initial pH value of more than 9, the anodic solution pH slowly decreased to around 8 within a certain time which changed, depending on the initial pH of the solution. After that, it rapidly decreased to 3 and then slowly went below 1. The pH behavior can be explained as follows. In basic solutions above pH 8, when the ammonia decomposition reaction of Equation (5) occurs at the anode, the adsorption of molecular ammonia at the electrode as in Equation (6) takes place before its oxidation [5, 8, 13–16], and also the adsorption of the hydroxyl ions (OH^-) for the water splitting reaction as in Equation (3) competes with the ammonia [5, 8, 17]. When the initial concentration of ammonia in the solution is sufficiently high, the anode is considerably covered by the ammonia, so a dominant ammonia oxidation occurs at the anode. This results in only nitrogen evolution at the electrode without oxygen evolution. Very little adsorption of the hydroxyl ions onto an anode in a 1.0 M ammonia solution at a pH of 12 was observed by a comparison of the electron spin resonance (ESR) spectra for solutions with and without the ammonia in our previous work [5, 8]. In relation to this phenomena, Botte et al. mentioned that the adsorption of the hydroxyl ions

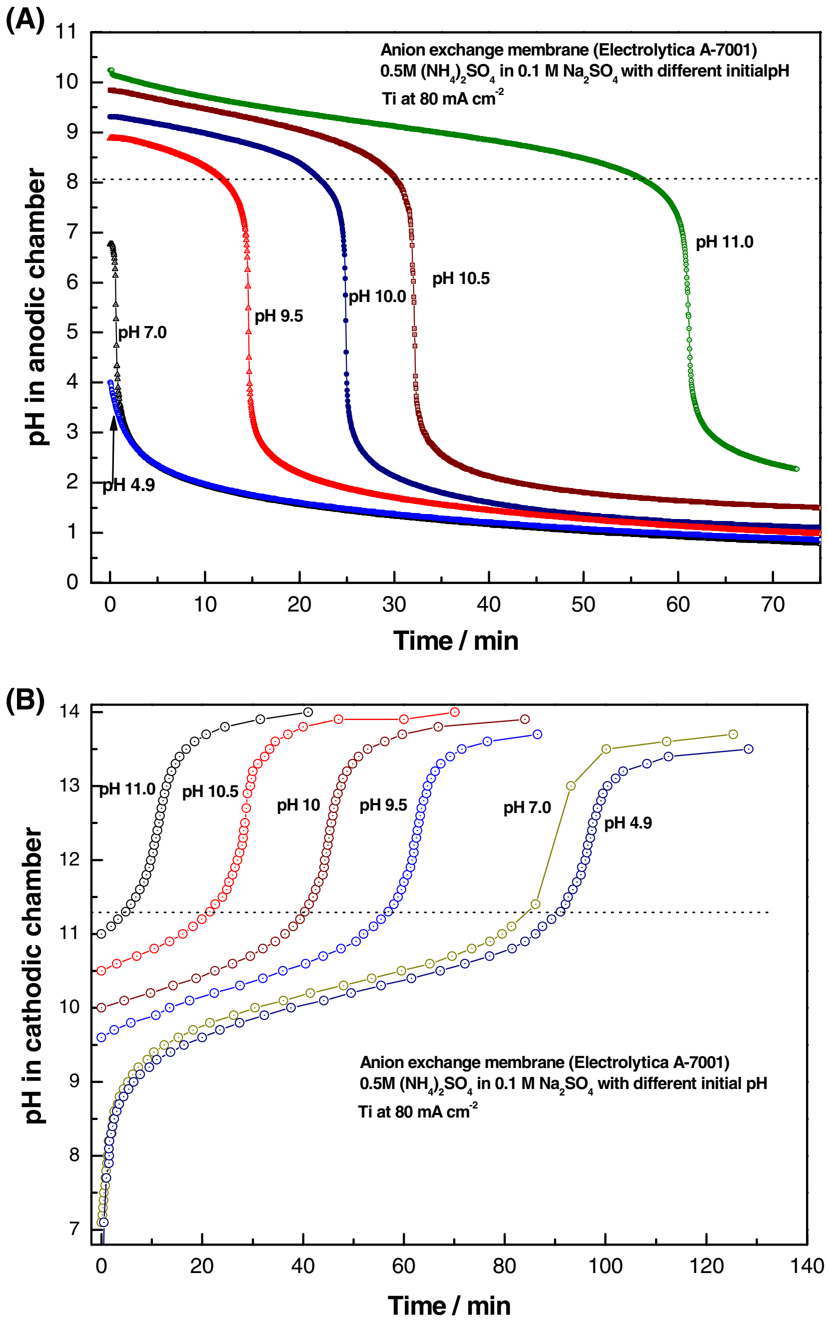


Fig. 2. pH changes in the anodic and cathodic chambers of a divided cell with an AEM with electrolysis time at different initial pH of the ammonia solutions.

onto an anode always take place in low concentration ammonia solution [18]. As the electrolysis elapses, the ammonia concentration in the solution decreases and the adsorption of the hydroxyl ions and consequently the ongoing oxygen evolution begins to increase. At this time, a depletion of the hydroxyl ions in the solution due to oxygen evolution is supplemented by the water self-ionization reaction of Equation (7), which results in leaving the protons in the solution. Therefore, the solution pH gradually falls, as shown in the initial pH change of the anodic chamber in Figure 2A. When the solution pH reaches 8, the water splitting reaction for oxygen evolution changes from Equation (3) to Equation (1), so that protons themselves are directly produced at the anode, which results in a rapid decrease in pH in the anodic chamber to around 3. From a pH of 3, the pH slowly decreases again with time, because considerably more protons are needed in order for the solution pH to become lower.

$$NH_3 + 3OH^- \rightarrow \frac{1}{2}N_2 + 3H_2O + 3e^- \qquad (5)$$

$$\text{M-OH} + NH_3 = \text{M-NH}_2 + H_2O + e^- \qquad (6)$$

where M is adsorption site at the electrode

$$H_2O = H^+ + OH^-, \quad K_w = [H^+][OH^-] = 10^{-14} \quad (7)$$

On the other hand, in Figure 2B, the ammonia solution pH in the cathodic chamber slowly increased to around 11 within a certain time which changed, depending on the initial pH of the solution, similar to Figure 1. It then rapidly went up to 13, and finally slowly approached 14. The pH behavior in the cathodic chamber can be explained in a similar way to that occurring in the anodic chamber. In the cathodic chamber, only hydrogen evolution occurs without any electrolytic change of the ammonia in solution, because ammonia is a nitrogen species of the lowest oxidation state. Before the solution pH reaches 11, the protons in the solution are consumed for the hydrogen evolution reaction of Equation (2), which results in a slow increase in pH because the water self-ionization reaction of Equation (7) occurs to make up for the consumption of the protons in the solution, thus leaving the hydroxyl ions in solution. When the pH reaches 11, the water splitting reaction for hydrogen evolution is considered to change from Equation (2) to Equation (4), so that only hydroxyl ions are generated directly at cathode. This results in a rapid increase in pH in the cathodic chamber to around 13. Then, the pH slowly increases with time because considerably more hydroxyl ions are needed in order for the pH to become higher.

From the results of Figure 2, the following can be stated. The pH of the anodic chamber which affects the electrolytic decomposition of the ammonia is easily changed to an acidic value by the water splitting reaction occurring at anode. Another thing is that a basic condition can be maintained in the anodic chamber for a certain time during electrolysis, if the initial pH of the ammonia solution is sufficiently high. It was experimentally observed that an AEM could maintain a better alkalinity in the anodic chamber than a CEM, the result of which is not shown in this work.

3.2. *Continuous electrolytic decomposition characteristics of ammonia in a multi-cell-stacked electrolyzer*

In order to compare the characteristics of ammonia decomposition in a continuous electrolyzer with that in a batch electrolyzer observed in our previous work [5, 8], an experiment was carried out with a stack electrolyzer. The stack consisted of four anodic cells, four cathodic cells, and anion exchange membranes with a configuration as shown in Figure 1. An anolyte of an ammonia solution of 0.4 M $(NH_4)_2SO_4$ in 0.1 M Na_2SO_4 with pH 7 or 13 (with or without chloride ions), and a catholyte of 0.1 M Na_2SO_4 with the same pH as the anolyte were fed into the first anodic and cathodic chambers of the stack. Each electrolyte flowed through the respective anodic and cathodic chambers of the stack in series at a flow rate of 5 ml min^{-1}. The current density applied to each cell of the stack was 80 mA cm^{-2}. Figure 3 shows the removal yields of TN from the ammonia solutions at the anodic outlet of the stack electrolyzer at steady state. In the figure, C/Co means the ratios of the TN values measured with time to the initial TN value in the solution. The pH values of the feed and final anodic outlet solutions of the stack and the current efficiency values are marked above the data symbols in Figure 3. The current efficiency was calculated from the moles of total decomposed ammonia divided by total supplied current in view of the three-electron reaction for ammonia decomposition to nitrogen of Equation (5). As in the previous work [5], TN removal yield in the ammonia solution of pH 13 was almost two times higher than that of pH 7. In basic conditions, ammonia is directly oxidized to nitrogen gas with accompanying adsorption of molecular ammonia at the electrode, as mentioned above. On the other hand, in neutral and acidic conditions, ammonia exists in the form of ammonium ion that is not adsorbed at anode and is oxidized by the OH radicals generated at the electrode during oxygen evolution. The ammonia

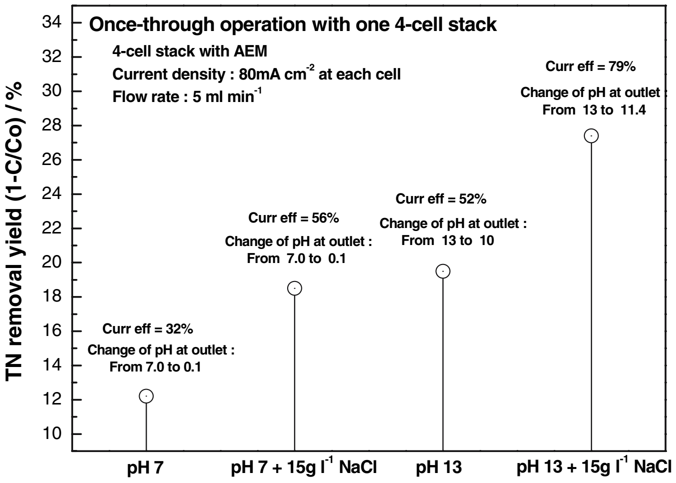


Fig. 3. TN removals in ammonia solutions by a four-cell stack at steady state with feed ammonia solutions of 1 M with and without chloride ions at pH 7 and pH 13.

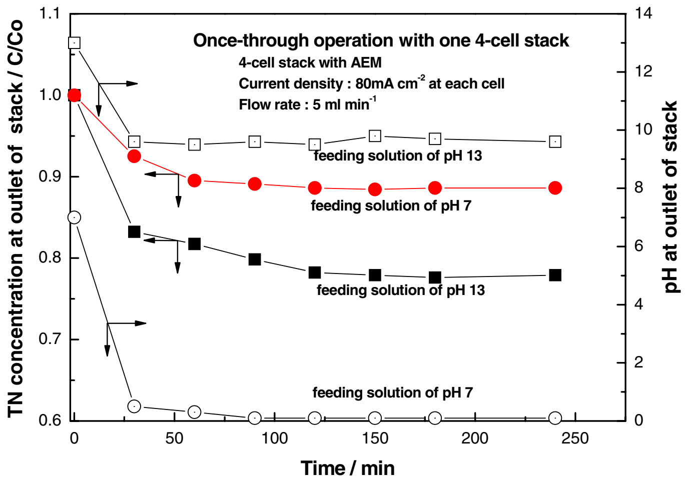
decomposition rate of the later case is considerably lower than that of the former case [5]. In the presence of chloride ions in the ammonia solution, the ammonia decomposition yield was increased further. The chloride ion is oxidized to chlorine at anode with a mechanism similar to that of oxygen evolution [3, 5, 17, 18]. The generated molecular chlorine is hydrolyzed to produce hypochlorous acid (HOCl) which is consecutively changed to hypochlorite ion (OCl^-), depending on the solution pH [3, 5, 12, 19–22]. In the ammonia solution with chloride ions, the increase in ammonia decomposition yield is due to an additional destruction of ammonia or ammonium ion by the hypochlorous acid or the hypochlorite ion, as expressed by Equations (8) and (9). The current efficiency reached about 80% in the case of the ammonia solution of pH 13 with chloride ions.

$$2NH_3 + 3HOCl \rightarrow N_2 + 3HCl + 3H_2O \qquad (8)$$

$$2NH_3 + 2OCl^- \rightarrow N_2 + 2HCl + 2H_2O \qquad (9)$$

When the pH of the feed ammonia solution was 13, the pH at the outlet in the case with chloride ions was 11.4, which was higher than that in the case without chloride ions, which was 10. This is because the chloride ions take part competitively in the adsorption process at anode together with ammonia and hydroxyl ions, so the consumption of the hydroxyl ions in the anodic chamber decreases [5, 6, 17]. Figure 4 shows the changes of TN and pH in the ammonia solutions at the anodic outlet of the stack with time in the case of the feed solutions of pH 7 and pH 13 without chloride ions shown in Figure 3 together with a table showing the pH at each half cell of the stack in steady state. The steady state was reached in about 70–80 min. In the steady state, in the case of pH 7, all the pH values in the anodic chambers of the stack fell below 1 from the first cell. On the other hand, in the case of pH 13, all the pH values in the anodic chambers were over 10 until the last cell of the stack, although they slowly decreased throughout the cells. These results can be explained by changes in water splitting reactions corresponding to the pH change of ammonia solution during the electrolysis, as explained in Figure 2 and by the total electricity supplied to the cell during the residence time of the electrolyte in the stack. This will be discussed further in Figure 8.

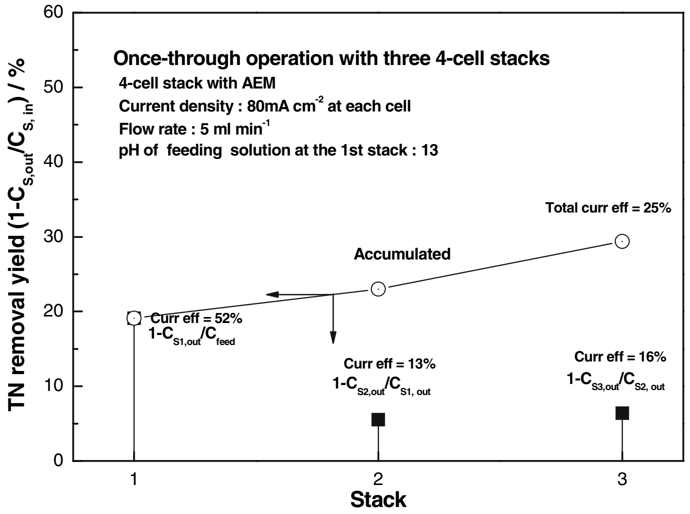
From results of Figures 3 and 4, it is thought that the pH at the outlet anodic chambers of the stack electrolyzer can fall below 8, depending on the residence time of the solution, even when the pH of the feed ammonia solution is sufficiently high. The residence time is proportional to the number of cells in the stack at a fixed feed flow rate. Once the pH in the anodic chambers is below 8, the pH can easily become lower, even as low as 1, as described in Figure 2, because the water splitting reaction directly generating protons occurs, as expressed in Equation (1). In such acidic conditions, the ammonia decomposition yield becomes much low. This means that the ammonia decomposition yield cannot be effectively increased by simply increasing the cells in a stack. In order to confirm this, a once-through experiment for the electrolytic decomposition of ammonia was carried out by using three stacks connected in series where each stack had four cells like the stack used in Figure 4. The feed anolyte and catholyte solutions were 0.4 M $(NH_4)_2SO_4$ in 0.1 M Na_2SO_4 with an initial pH of 13 and 0.1 M Na_2SO_4, respectively. The results are shown in Figure 5



pH of each anodic cell of the stack at steady state

Initial pH	C1	C2	C3	C4
7	0.5	<0.5	0.1	0.1
13	13	12	11	10

Fig. 4. Changes of TN concentrations in ammonia solutions at the anodic outlet of a four-cell stack with electrolysis time with a feed ammonia solution of 1 M at pH 7 and pH 13.



pH of each anodic cell of stacks at steady state

Stack	C1	C2	C3	C4
1	13	12	11	10
2	9.5	8.5	3	2.5
3	0.5	1	~0	~0

Fig. 5. Changes of TN removal yield and total accumulated TN removal yield at the outlets of three 4-cell stacks at steady state with a feed ammonia solution of 1 M at pH 13.

which shows the TN removal yield at each stack, $(1-C_{s,out}/C_{s,in})$ and the total accumulated TN removal yield in the system, $(1-C_{s3,out}/C_{feed})$, together with a table showing the pH values at each half cell of all the stacks at steady state. At the first stack where all the anodic chambers maintained high pH values of more than 10, the TN removal yield was about 20%. However, at the second and third stacks, the pH of the anolyte solution gradually decreased throughout the anodic chambers to about zero at the fourth cell of the third stack. In the second and the third stacks, the ammonia solution became highly acidic. Thus the TN removal yields were reduced to about 7% at each stack. The decomposition yields of the second and third stacks are quite different from that of the first stack where the ammonia solution was basic throughout the anodic cells of the stack. Accordingly, the total accumulated TN removal yield after the third stack became only about 29%. The current efficiency of each stack and the total current efficiency at steady state are noted above the data symbols in Figure 5. The current efficiency of the first stack, where the anodic solution maintained a high alkalinity of more than pH 10, was 52%. At the second and the third stacks, however, they were reduced to 13 and 16%, respectively, because pH and ammonia concentration in the solution were lowered throughput the stacks. As ammonia concentration in solution becomes lower, the current efficiency

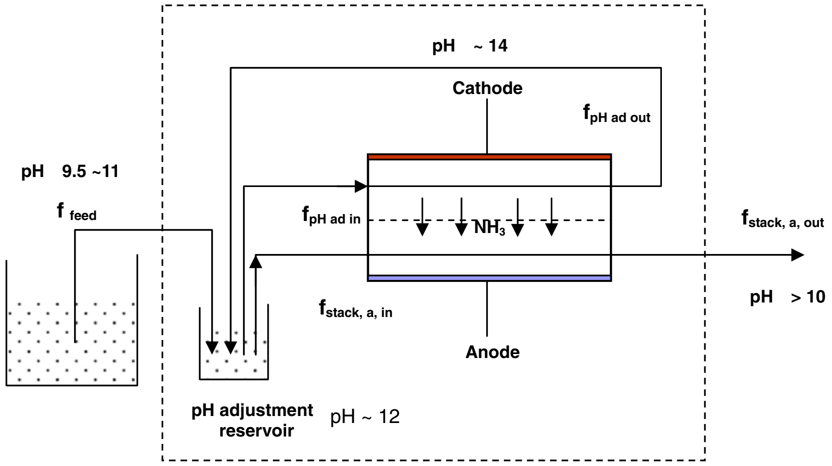


Fig. 6. A schematic diagram of a electrolyzer for the ammonia decomposition with a self-pH adjustment.

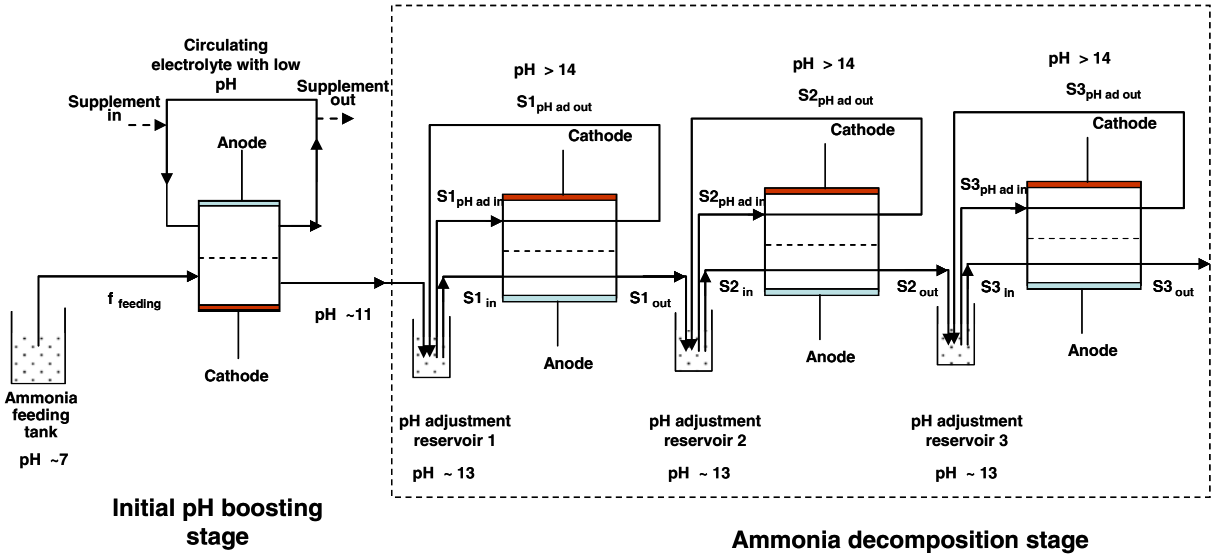
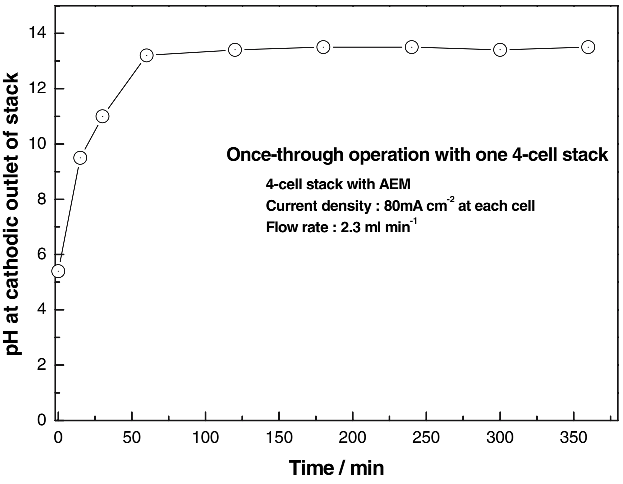


Fig. 7. A schematic diagram of a salt-free electrolytic ammonia decomposition process.

of electrolytic ammonia decomposition is known to become lower, because the competitive adsorption of hydroxyl ions at anode increases [7, 8].

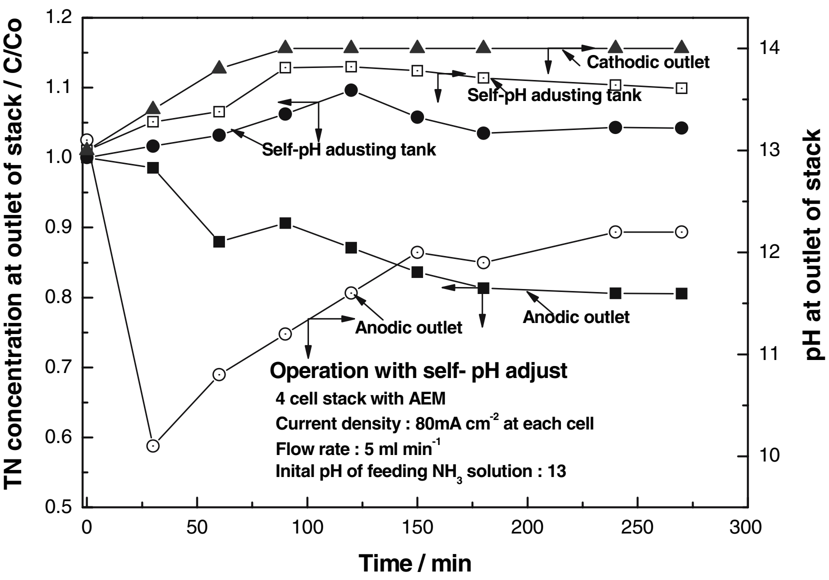
From the above results, maintaining the solution pH high during electrolysis is considered to be necessary to effectively enhance the electrolytic ammonia decomposition. For that, an ammonia solution with a very high initial pH should used, or a chemical such as NaOH should be added into the system to compensate for the decreased pH. However, such methods bring out secondary wastes or increase operation cost for electrolytic ammonia decomposition. In this work, to overcome such problems occurring in the electrolytic ammonia decomposition, a continuous electrolytic system configured like Figure 6 was devised, based on the results of Figures 2–5. The system takes advantage of the facts that ammonia of a nitrogen species with the lowest oxidation state is not changed any more at cathode and that pH in cathodic chamber can become high very easily due to the water splitting. In the electrolytic system, a pH-adjustment reservoir was placed between a feed reservoir and an electrolyzer for ammonia decomposition. The feed ammonia solution and the ammonia solution to be fed into the anodic chamber of electrolyzer were taken into and taken out of the pH-adjustment reservoir at the same flow rates. A portion of solution in the pH-adjustment reservoir was circulated through the cathodic chamber of electrolyzer. The pH of cathodic circulating solution was increased due to the water splitting reaction occurring at cathode, which results in pH increase in the pH-adjustment reservoir. Accordingly, pH in the pH-adjustment reservoir is self-enhanced to be higher than that of the initial feed ammonia solution. Another characteristic of the system shown in Figure 6 is that no waste solution is generated from the system, because catholyte solution is just circulated into the pH-adjustment reservoir of which the solution is to be fed into the anodic chamber for ammonia decomposition. This is different from the conventional electrolytic method where the catholytic solution becomes a waste solution like in the case of Figure 5. In order for the pH-adjustment function to act effectively, the initial pH of the pH-adjustment reservoir needs to be sufficiently high. That ensures that the reaction of Equation (4) occurs easily in the cathodic chambers from the outset. Also, if the pH of the feed ammonia solution going into the pH-adjustment reservoir is too low, the cathodic solution circulating through the pH adjustment reservoir can not reach easily a high pH value, where the hydroxyl ions are generated like Equation (4), within its residence time in the electrolyz-



pH of each cell at steady state

Cell	C1	C2	C3	C4
Anodic	2	1	<1	<1
Cathodic	9	10	13	14

Fig. 8. pH change of ammonia solution at the outlet of a 4-cell stack with electrolysis time with a feed ammonia solution of 1 M at pH 5.5.



pH of each cell of stack at steady state

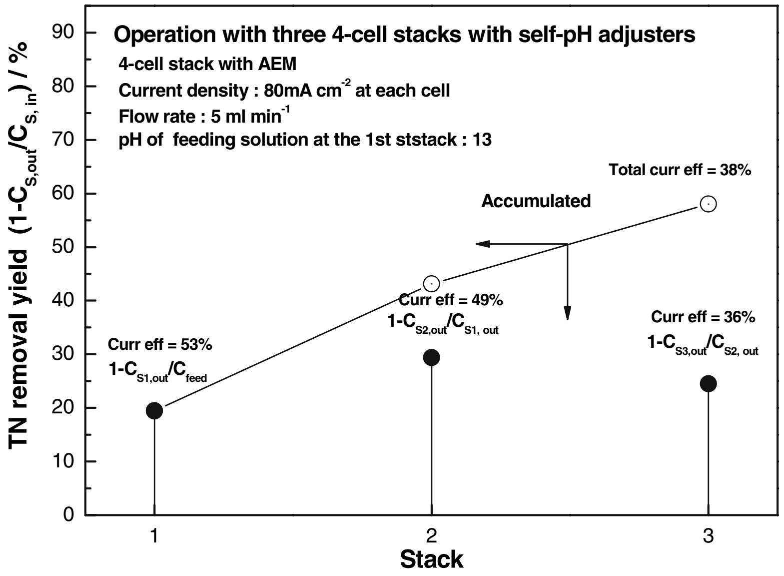
Self pH-adjustment reservoir	Cell	C1	C2	C3	C4
~ 13.5	Anodic	14	14	13	12.5
	Cathodic	14	14	>14	>14

Fig. 9. Changes of TN concentration and pH in ammonia solution at the outlet of a 4-cell stack with a self-pH adjuster with electrolysis time with a feed ammonia solution of 1 M at pH 13.

er, as explained in Figure 2B. On the basis of these facts together with the above results, the feed ammonia solution needs to have a pH of about 10–11 at least. In this condition, the cathodic circulating solution could readily increase to pH 14 and the pH of pH-adjustment reservoir could exceed 12, which would help the ammonia solution of anodic chamber maintain its alkalinity longer and higher during the time the anodic solution passed through the electrolyzer. (See Figures 9 and 10) Without adding any chemicals in the system, the feed ammonia solution could achieve a pH value of above 10 by introducing a pH-boosting stage ahead of the ammonia decomposition system of Figure 6. This is to say that the ammonia solution is passed through the cathodic chambers of another electrolyzer first so that the solution can become sufficiently basic by hydroxyl ions generated at cathode. By using such pH-boosting stage and ammonia decomposition stage using the electrolyzers equipped with the pH-adjustment reservoirs, a salt-free electrolytic ammonia decomposition system can be configured like that shown in Figure 7.

In order to confirm the necessity of the electrolytic pH-boosting stage like that of Figure 7, a once-through electrolysis experiment was carried out with using a stack which consisting of 4 cells using an AEM. The feed catholyte was 0.4 M $(NH_4)_2SO_4$ in 0.1 M Na_2SO_4 with an initial pH of 5.5 and the feed anolyte solution was 0.1 M Na_2SO_4. The solution flow rates were fixed at 2.3 ml min^{-1} and the current density applied to all the cells of the stack was 80 mA cm^{-2}. The result is shown in Figure 8 together with a table showing the pH at each cathodic and anodic chamber of the stack at steady state. The steady state was reached in 50 min, and the pH value at each cathodic chamber increased throughout the cells and became almost 14 at the fourth chamber of the stack. Also the anodic pH in the stack decreased easily to about 1. About 4% ammonia of the catholyte solution was experimentally observed to move into the anodic solution by diffusion through membrane. In the batch electrolysis of Figure 2B, the time required for a circulating ammonia solution of 65 ml with an initial pH of 4.9 to reach pH 13 was about 90 min. For that time, the total electricity supplied to the circulating cathodic system was 152 C ml^{-1}. In Figure 8 where the flow rate was 2.3 ml min^{-1}, the volume of each cell of the stack was 16.5 ml, and the applied current was 1.84 A per each cell, the pH of the ammonia solution reached 13 at the third cell of the stack. The total electricity supplied to the solution until the third cell was 144 C ml^{-1}, which was similar to that of Figure 2B. This result means that pH change in solution is proportional to the electricity supplied into the solution. From Figure 8, it can be said that the initial pH of the ammonia solution to be electrolyzed can be readily adjusted to a high basic condition before the electrolytic decomposition step of Figure 7.

Figure 9 is a performance test result of an electrolytic system configured like that in Figure 6. In the system, a stack electrolyzer same as that used in Figure 4 with a pH-adjustment reservoir of 30 ml was used. An ammo-



pH of each cell of stacks at steady state

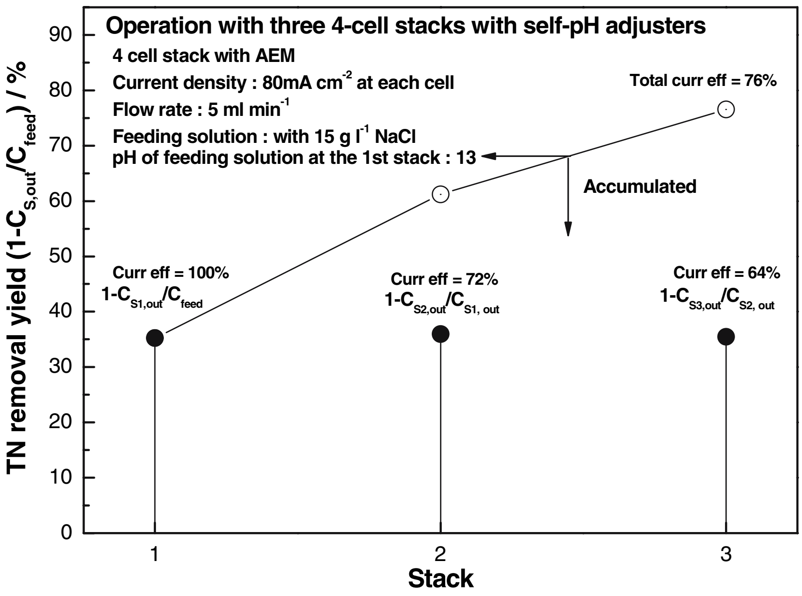
Stack	Self pH-adjustment reservoir	Cell	C1	C2	C3	C4
1	13.8	Anodic	14	14	13	12.5
		Cathodic	14	14	>14	>14
2	13.8	Anodic	13	13	12	11
		Cathodic	14	14	14	14
3	13.7	Anodic	13	12	11	10
		Cathodic	14	14	14	14

Fig. 10. Changes of TN removal yield and total accumulated TN removal yield at three 4-cell stacks with self-pH adjusters at steady state with a feed ammonia solution of 1 M at pH 13.

nia solution of 0.4 M $(NH_4)_2SO_4$ in 0.1 M Na_2SO_4 with pH 13 was fed into the pH-adjustment reservoir at 5 ml min^{-1}, and a portion of solution in the pH-adjustment reservoir was circulated through the cathodic chambers of the stack with a flow rate of 10 ml min^{-1}. The initial pH of feed ammonia solution was adjusted in advance by using another electrolyzer like that used in Figure 8. Figure 9 shows the changes of pH and TN at the catholytic and anolytic outlets of the stack and those at the pH-adjustment reservoir with time together with a table showing the pH value at each half cell of the stack at steady state. The pH in the catholytic chambers of the stack reached almost 14, and the pH in the pH-adjustment reservoir also gradually increased to 13.5. Before the pH at cathodic outlet became sufficiently high, the pH at anolytic outlet decreased at the beginning of electrolysis, but it finally increased to 12.5 at steady state. The TN removal yield was about 20%. These results show that the electrolytic system with the self-pH-adjustment reservoir like that in Figure 6 can effectively decompose ammonia in solution without falling pH of the solution.

Figure 10 shows a performance test result of an electrolytic system configured like that in Figure 7. For the test, three stacks connected in series were used for the ammonia decomposition stage. Each stack consisted of four cells with a pH-adjustment reservoir like that used in Figure 9. All the experimental condition was the same as Figure 5 except for use of the pH-adjustment reservoir. The ammonia solution at each stack could sustain a high alkalinity of more than pH 10. The TN removal yields at all the stacks, $(1 - C_{s,out}/C_{s,in})$, were about 20% or over. The total accumulated TN removal yield increased almost linearly with the number of stacks, which became about 60% after the third stack. These results are different from those of Figure 5 where the TN removal yield did not increase with stacks, because there was no the function of the pH-adjustment reservoirs in the system used in Figure 5 so that the ammonia solution pH decreased a lot along with stacks. The current efficiency at the first stack was similar to that of Figure 5. However, the current efficiencies of the second and the third stacks had much higher than those of Figure 5 because of the high alkalinity of ammonia solution in the stacks due to the function of the pH-adjustment reservoir.

As mentioned in Figure 3, the electrolytic ammonia decomposition yield can be enhanced when chloride ions are present in ammonia solution. Accordingly, when an ammonia solution with chloride ions is used in an electrolytic system like that in Figure 7, the electrolytic decomposition yield of the ammonia is expected to



pH of each cell of stack at steady state

Stack	Self pH-adjustment reservoir	Cell	C1	C2	C3	C4
1	13.9	Anodic	14	14	14	13.5
		Cathodic	14	14	>14	>14
2	13.9	Anodic	14	14	14	11.5
		Cathodic	14	14	~14	14
3	13.4	Anodic	14	14	12	10.5
		Cathodic	14	14	14	14

Fig. 11. Changes of the TN removal yield and the accumulated TN removal yield at three 4-cell stacks with self-pH adjusters at steady state with feed ammonia solutions of 1 M with and without chloride ions at pH 13.

increase further [1–5, 20, 21]. To confirm this, an experiment was performed, in which the experimental conditions were the same as those used in Figure 10 except for the fact that the ammonia solution contained 15 g l^{-1} NaCl. The results are shown in Figure 11. The TN removal yield at each stack was about 35% with an increase of about 15%, compared with the case in absence of chloride ions in Figure 10. Accordingly, the total accumulated TN removal yield reached about 80% at the third stack. At this time, the gas at the final anodic outlet was analyzed by a gas chromatograph. It consisted of about 90% N_2 and 10% O_2. Also, the current efficiency at the first stack was almost 100% and those at the second and third stacks were much higher than those in Figure 10 as well.

4. Conclusions

The pH in the ammonia solution was considerably affected by the water splitting reactions occurring in a divided cell. The water splitting reaction which produced protons began to occur at a pH of less than 8 in the anodic chamber, and that producing the hydroxyl ions did so at a pH of more than 11 in the cathodic chamber. A continuous electrolyzer with a self-pH-adjustment function devised in this work enhanced the ammonia decomposition yield. The electrolytic process with a pH-adjustment function suggested in this work was able to continuously and effectively decompose ammonia into environmentally harmless nitrogen gas in a salt-free way.

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