# Electrolytic Synthesis of Ammonia in Molten Salts under Atmospheric Pressure

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The fixation of nitrogen to ammonia is of great importance since ammonia is an essential ingredient in the manufacture of fertilizer and many important chemicals. Moreover, the distributed use of ammonia will also increase in the future for the selective catalytic reduction of NO_x emitted from ships and stationary facilities. Large-scale manufacturing of ammonia is conventionally conducted by the Haber–Bosch process, in which hydrogen gas and nitrogen gas directly react under high temperatures (∼750 K) and high pressures (∼10 MPa).[1] For the distributed use of ammonia, it is required to reduce the synthetic temperature and pressure. The electrochemical process is one of the most promising methods. Although ambient pressures or temperatures have been attained in several electro-chemical processes,[2–5] the current efficiencies still remain quite low, 0.1 ∼ 8%. For these electrochemical approaches, hydrogen atoms are generated at the cathode to which nitrogen gas is supplied, and ammonia is produced according to following reaction.

$$1/2 N_2 + 3H^+ + 3e^- \rightarrow NH_3 \tag{1}$$
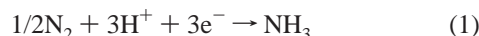
In most cases, however, a competing reaction of hydrogen gas evolution proceeds easily, since recombination among hydrogen atoms themselves is more likely to happen than reaction between hydrogen atoms and nitrogen molecules due to the extremely strong N–N bond. Therefore, it seems to be very difficult to greatly improve the current efficiency as far as utilizing reaction 1. On the other hand, a completely different reaction to synthesize ammonia under atmospheric pressure is expected by the use of anodic reaction in molten salts. The principle is shown in Figure 1. The electrolyte is molten alkali-metal halides containing nitride ion, such as LiCl–KCl–Li$_3$N and LiCl–KCl–CsCl–Li$_3$N. The anode is a hydrogen gas electrode having a porous structure or a hydrogen permeable membrane. On the anode, ammonia is electrochemically synthesized from hydrogen gas and nitride ion according to reaction 2.

$$N^{3-} + 3/2 H_2 \rightarrow NH_3 + 3e^- \tag{2}$$
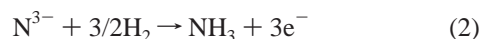
The cathode is a nitrogen gas electrode consisting of a porous structure. The cathode continuously supplies an equal quantity of nitride ion by the reduction of nitrogen to nitride ion.

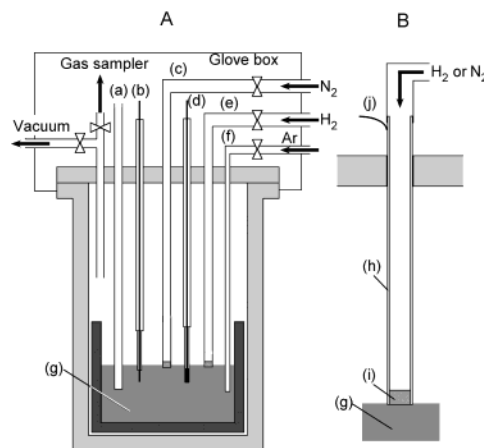$$1/2 N_2 + 3e^- \rightarrow N^{3-} \tag{3}$$
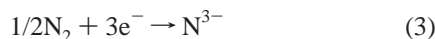
Goto and Ito reported that nitrogen gas was electrochemically reduced to produce nitride ions almost quantitatively according to reaction 3 and that continuous nitride ion supply was achieved for 15 h.[6] As the overall reaction, ammonia is synthesized from its elements.

$$1/2 N_2 + 3/2 H_2 \rightarrow NH_3 \tag{4}$$

Standard electrode potential of N_2/N^{3-} was measured as 0.382 V
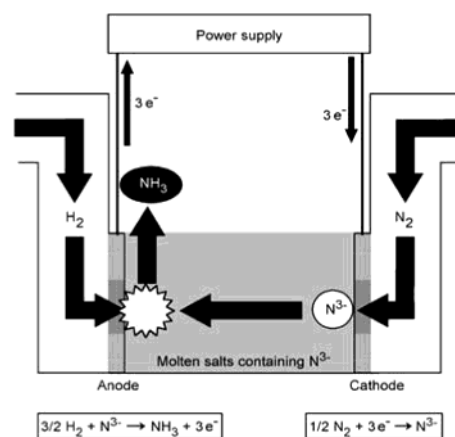
Figure 1. Schematic drawing of the principle of electrolytic synthesis of ammonia. On the anode, ammonia is electrochemically synthesized from hydrogen gas and nitride ion. On the cathode, nitride ion is continuously supplied by the reduction of nitrogen gas to nitride ion on the cathode.

Figure 2. Schematic drawing of experimental apparatus. (a) thermocouple, (b) Li$^+$/Li electrode (Ni wire), (c) nitrogen gas electrode, (d) reference electrode, (e) hydrogen gas electrode, (f) Ar bubbler, (g) electrolyte (LiCl–KCl–CsCl eutectic melt containing 0.5 mol % Li$_3$N), (h) stainless steel tube, (i) porous Ni, and (j) Ni wire lead.

(vs Li$^+$/Li) in LiCl–KCl at 723 K.[7] Since the theoretical standard electrolysis voltage is estimated as about 0.10 V from the standard Gibbs energy change of the total reaction, 30.0 kJ mol^{-1},[8] the standard electrode potential of reaction 2 is estimated to be 0.48 V (vs Li$^+$/Li) in LiCl–KCl at 723 K. In this work, the feasibility of the new electrochemical synthesis method of ammonia has been confirmed.

Figure 2 shows a schematic drawing of the experimental apparatus for electrochemical investigations. Reagent grade LiCl (Wako Pure Chemical Co., Ltd., 99.0%), KCl (Wako Pure Chemical
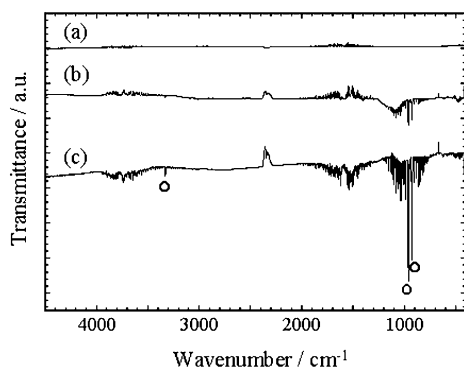
Figure 3. IR spectra of the gas samples obtained after flowing (a) argon gas and (b) hydrogen gas for 2 h, and (c) after potentiostatic anodic electrolysis at 0.7 V for 40 min in LiCl−KCl−CsCl−Li$_3$N (0.5 mol % Li$_3$N added) melts at 673 K. Peaks with open circle symbols correspond to ammonia.

Co., Ltd., 99.5%), and CsCl (Wako Pure Chemical Co., Ltd., 99.0%) were dried under vacuum for more than 24 h at 473 K to remove residual water. The eutectic mixture of LiCl−KCl−CsCl (LiCl: KCl:CsCl = 57.5:13.3:29.2 mol %)[9] was used as an electrolyte and was melted in a high-purity alumina crucible (Nikkato Co., Ltd., SSA-A, 99.5% Al$_2$O$_3$) under pure argon (99.998%) atmosphere. The nitride ion source was Li$_3$N (Wako Pure Chemical Co., Ltd.). The working electrode was a hydrogen gas electrode, and the counter electrode was a nitrogen gas electrode. These gas electrodes consisted of porous Ni (Figure 1(B)). The porous Ni (i.d. 6 mm × 1.6 mm, specific surface area: 7500 m^2 m^{-3}) was attached to the bottom of the alumina tube (i.d. 5.0 mm). The average flow rate of hydrogen and nitrogen gases was set to 5 and 45 mL min^{-1}, respectively. The reference electrode was an Al−Li alloy in ($\alpha + \beta$) coexisting phase state.[10] The potential of the reference electrode was calibrated with reference to that of the Li$^+$/Li electrode, which was prepared by electrodepositing lithium metal on a nickel wire. Measured electrode potentials are given with reference to this Li$^+$/Li electrode potential. The sampled gases (∼900 mL) after the electrolysis were analyzed by IR spectroscopy. Lambert−Beer's law was used to estimate the concentration of ammonia after constructing the calibration curve. The quantitative analysis of ammonia was also conducted by a titration with HCl solution. After passing the synthesized ammonia through pure water, a pH titration curve with a HCl solution (initial pH was 3.2) was measured by an electronic pH meter.

A gas was sampled after potentiostatic anodic electrolysis at 0.7 V for 40 min at the hydrogen gas electrode in LiCl−KCl−CsCl containing 0.5 mol % Li$_3$N at 673 K. For comparison, sample gases were also prepared by only flowing argon gas or hydrogen gas through the electrode into the melt for 2 h without electrolysis. Figure 3 shows the IR spectra of the gas samples for (a) only argon gas, (b) only hydrogen gas, and (c) hydrogen gas obtained by electrolysis. The peaks corresponding to ammonia are clearly observed in spectrum (c). On the other hand, no peaks are found in spectrum (a), which shows that formation of ammonia by the

reaction of nitride ion with contaminating water can be excluded in this experiment. Although very small peaks of ammonia are observed in spectrum (b), the concentration of (c) is estimated to be about 20 times higher than that of (b). Therefore, it was confirmed that ammonia was synthesized by electrolysis according to reaction 2. Since the quantity of synthesized ammonia was 8.0 × 10^{-5} mol, the current efficiency, (defined as the quantity of electricity corresponding to the yielded ammonia divided by the total flow of electricity) was calculated as 72% that corresponds to 2.5 × 10^{-6} mol F^{-1}. The quantitative analysis of the synthesized ammonia was also conducted by a titration with HCl. This result agreed well with that of the IR spectrum within the experimental error. The synthesis rate of ammonia was calculated as 0.12 mol h^{-1} m^{-2}. During the electrolysis, the potential of the nitrogen gas cathode stayed around 0.3 V (vs Li$^+$/Li). This potential is sufficiently more positive than that of the electrodeposition of lithium metal, which shows nitride ion was continuously supplied to the melt by the reduction of nitrogen gas according to reaction 3.

Electrolysis under the present conditions has been conducted several times, and ammonia was formed successfully in all experiments with similar current efficiency. The longest time for the cell operation was 1 h, and increase of voltage between the anode and the cathode was not observed.

The remaining current efficiency, 28%, is explained by residual ammonia in the molten salts and a competing reaction of nitrogen gas evolution according to the following reaction.

$$N^{3-} \rightarrow 1/2N_2 + 3e^- \qquad (5)$$
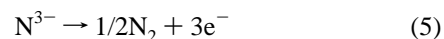
The obtained current efficiency, 72%, is expected to become higher by improving the structure of the gas electrodes and optimizing the electrolysis conditions.

In conclusion, the obtained results confirm the feasibility of the new electrolytic synthesis method of ammonia from its elements under atmospheric pressure.

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