

Electrolytic Ammonia Synthesis Directly from Various Hydrogen Sources under Atmospheric Pressure

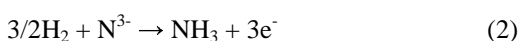
T. Murakami, T. Nohira, Y. H. Ogata* and Y. Ito
Graduate School of Energy Science, Kyoto University

*Institute of Advanced Energy, Kyoto University
Sakyo-ku, Kyoto, 606-8501, Japan

*Uji, 611-0011, Japan

murakami@fchem.nucleng.kyoto-u.ac.jp

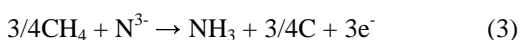
The fixation of nitrogen to ammonia is of great importance since ammonia is used in various fields of the present social activities. For example, ammonia is an essential ingredient in the manufacture of fertilizers and various important chemicals. Moreover, the distributed use of ammonia will increase in near 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) at high pressures (~ 10 MPa). When the forthcoming various demands of ammonia described above are taken into account, it is required to reduce the synthetic temperature and pressure. From this background, the authors have proposed the novel ammonia synthesis method by using electrochemical reactions (reaction (1) and (2)) in molten salts under atmospheric pressure at lower temperature than that of the Haber-Bosch process.¹



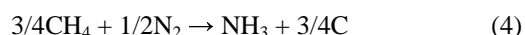
However, hydrogen gas, which is supplied to the anode gas electrode, should be prepared by steam reforming, water electrolysis, and so on. If ammonia can be synthesized directly from various hydrogen sources, a new route of ammonia synthesis, such as from sewage gas, would be established. Therefore, in this work, various hydrogen sources such as methane, water, hydrogen chloride and hydrogen sulfide were examined.

The eutectic mixture of LiCl-KCl-CsCl (LiCl : KCl : CsCl = 57.5 : 13.3 : 29.2 mol%) was used as an electrolyte. The nitride ion source is Li_3N . The working electrode was a hydrogen gas electrode: Porous Ni ($6 \text{ mm}\phi \times 1.6 \text{ mm}^t$, specific surface area: $7500 \text{ m}^2 \text{ m}^{-3}$) was attached to the bottom of an alumina tube (inside diameter: $5.0 \text{ mm}\phi$). The counter electrode was an aluminum plate. The reference electrode was an Al-Li alloy in ($\alpha+\beta$) coexisting phase state. Potential of the reference electrode was calibrated with reference to that of the Li^+/Li electrode. The sampled gases (~ 900 ml) after the electrolysis were analyzed by IR spectroscopy qualitatively and quantitatively.

At first, methane was examined as the hydrogen source. The principle of the electrolytic ammonia synthesis from methane and nitrogen is shown in Figure 1. On the cathode, nitrogen gas is reduced to nitride ion according to reaction (1). On the anode, it is expected that ammonia is synthesized according the following reaction.



As the overall reaction, ammonia is synthesized from methane and nitrogen.



The theoretical standard electrolysis voltage is estimated as about 0.11 V at 600 K from the standard Gibbs energy change of the total reaction.

In order to confirm the feasibility of reaction (3), potentiostatic electrolysis was conducted at 2.1 V at 773 K. Figure 2 shows IR spectra obtained after (a) methane gas bubbling for 2 hours without electrolysis and (b) potentiostatic electrolysis for 1 hour at 773 K. In both spectra, peaks corresponding to unreacted methane were observed. Peaks corresponding to ammonia were clearly observed in spectrum (b) but not in spectrum (a). This shows that ammonia was synthesized electrochemically. The current efficiency, which is defined as quantity of electricity corresponding to the yielded ammonia divided by total quantity of flowed electricity, was calculated as 26 %. These results suggest that methane is promising as the hydrogen source in the electrolytic ammonia synthesis in molten salts under atmospheric pressure.

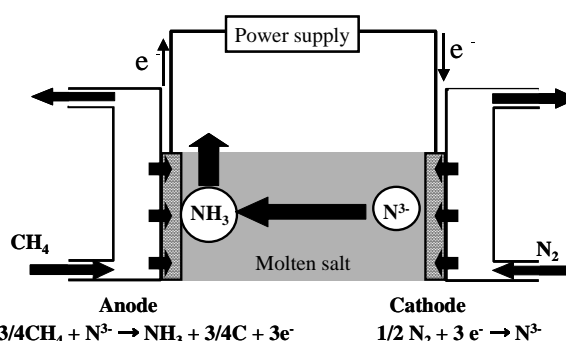


Figure 1. The principle of the electrolytic ammonia synthesis from methane and nitrogen gases in molten salts under atmospheric pressure.

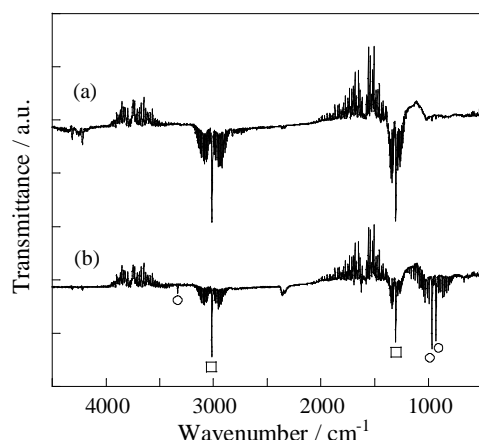


Figure 2. IR spectra obtained after (a) methane gas bubbling for 2 hours without electrolysis and (b) potentiostatic electrolysis at 2.1 V for 1 hour at 773 K in LiCl-KCl-CsCl- Li_3N (0.5 mol% Li_3N added). ○: ammonia, □: methane.

Acknowledgment

One of the authors T. Murakami thanks JSPS Research Fellowships for Young Scientists for the financial support.

References

- [1] T. Murakami, T. Nishikiori, T. Nohira and Y. Ito, *J. Am. Chem. Soc.*, **125**, 2, 334 (2003).