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Efficient Electrochemical Reduction of N_2 to NH_3 Catalyzed by Lithium

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A novel electrochemical N_2 reduction system is reported. Ammonia was formed with a significant current efficiency (up to 8%) by a simple electrolysis, which was conducted under N_2 flow (1 atm) in a solution of $LiClO_4$ (0.2 M) in tetrahydrofuran / ethanol (99:1 v/v) on some metal electrodes. Higher current efficiency (48.7%) for NH_3 formation was achieved when the electrolysis was conducted under high pressure of N_2 (50 atm). Lithium seemed to act as a catalyst (mediator) in this electrochemical system.

So far, many chemists have been engaged in the electrochemical reduction of dinitrogen, and several reduction systems have been developed.[1—10] Most of these systems employ the complexes of transition metals, such as Ti or Mo, as catalysts. Here we report our findings of a novel electrochemical N_2 reduction system.

The cell used in this system was a single-compartment type. Wires (1.5 or 3.0 cm^2) of Al (99.999%), Ti (99.9%), Mo (99.95%), Fe (99.5%), Co (99.99%), Ni (99.9%), Cu (99.9%), Ag (99.99%), Zn (99.99%), and Pb (99.9%) were used as working electrodes. Most of the electrodes were polished with alumina powder (0.05 μm) before use, while a Cu wire was electropolished in H_3PO_4 (85%). A Pt wire served as an anode, and the electrolysis medium was a solution of $LiClO_4$ (3.2 g, 0.2 M) in THF/ethanol (99:1 v/v, 150 mL). The electrolysis was carried out at ambient temperature (24—26 °C) at a constant current (2.0 mA cm^{-2}). The product ammonia contained in the resulting homogeneous colorless solution was analyzed using an indophenol method and an ammonia gas sensing electrode; the values obtained from these two analytical methods agreed well with each other. No ammonia was detected in the effluent gas which was trapped by 0.1 M H_3BO_3. Hydrazine was determined colorimetrically with *p*-dimethylaminobenzaldehyde reagent.

Table 1. Electrochemical reduction of N_2 in nonaqueous solutions under 1 atm of N_2[a)]

Run	Cathode	Solvent	NH_3 / μmol[b)]	Current efficiency / %
1	Al	THF/ethanol (99:1)	0.9	0.5
2	Ti	THF/ethanol (99:1)	14.1	8.2
3	Mo	THF/ethanol (99:1)	12.6	7.3
4	Fe	THF/ethanol (99:1)	10.3	6.0
5	Co	THF/ethanol (99:1)	10.6	6.1
6	Ni	THF/ethanol (99:1)	11.2	6.5
7	Cu	THF/ethanol (99:1)	9.1	5.3
8	Ag	THF/ethanol (99:1)	14.5	8.4
9	Zn	THF/ethanol (99:1)	8.6	4.5
10	Pb	THF/ethanol (99:1)	0.4	0.3
11	Mo	THF	0.5	0.3
12	Mo	THF/H_2O (99.8:0.2)	0.4	0.3
13[c)]	Mo	THF/ethanol (99:1)	0.5	0.3

a) Passed charge: 50 C.

b) Determined by an indophenol method.

c) Under Ar.

We first carried out the electrolysis under atmospheric pressure of N_2 by bubbling N_2 gas (flow rate: 4—8 mL min^{-1}) through the cell during the electrolysis. As shown in Table 1, ammonia was formed on several metal electrodes. Among the various electrodes, Ti (run 2) and Ag (run 8) showed high activities (current efficiencies for NH_3 formation were up to 8%), while only a small amount of ammonia was formed on Al (run 1) and Pb (run 10) electrodes. A small amount of ammonia was detected in the control experiment carried out under argon (run 13), which would be due to some impurities contained in the electrolyte. No hydrazine was detected in all reactions. Hydrogen evolution seemed to be a major side reaction.

In Fig. 1, the amount of NH_3 produced on a Mo electrode under 1 atm of N_2 was plotted against the charge passed. Apparently the amount of NH_3 increased linearly with the charge. This result confirms that N_2 is electrochemically reduced into NH_3 on the Mo electrode. It is notable that the activity of the electrode was not diminished through this period.

The yield of NH_3 was strongly affected by the composition of the electrolyte solution. When ethanol was not added to the electrolyte solution, only a small amount of NH_3 was formed (run 11). Thus, in this NH_3 formation reaction, ethanol should play an important role, probably acting as a proton source. When a mixture of THF (149.7 mL) and H_2O (0.3 mL) was used as a solvent, the yield of NH_3 was negligible (run 12). This

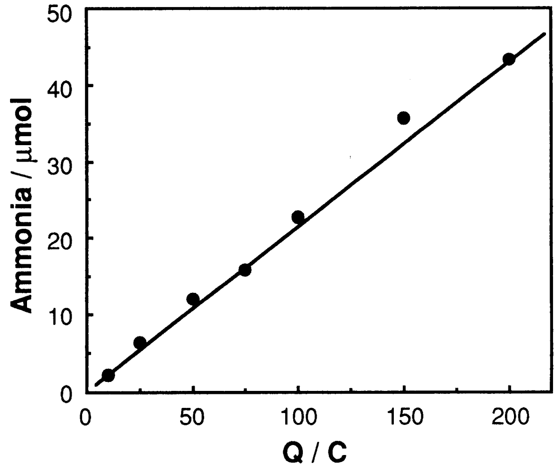

Fig. 1. Ammonia formation on a Mo electrode under 1 atm of N_2 (flow rate: 4—8 mL min^{-1}). Electrolysis medium: $LiClO_4$ (0.2 M) in THF / ethanol (99:1 v/v, 150 mL).

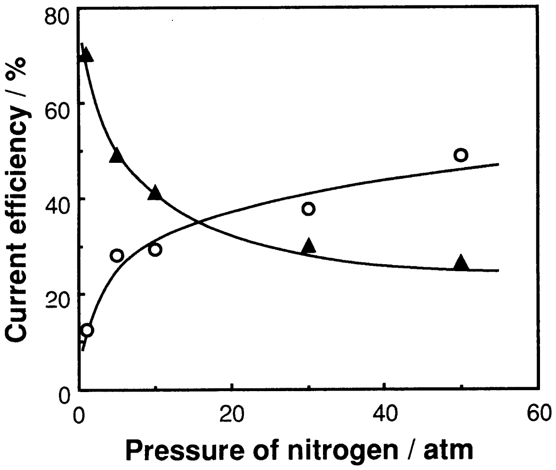

Fig. 2. Effect of N_2 pressure on the electrochemical reduction of N_2 to NH_3 on a Cu electrode: (○) NH_3, (▲) H_2. Electrolysis medium: $LiClO_4$ (0.2 M) in THF/ethanol (99:1 v/v, 150 mL).

indicates H_2O is not favorable as a proton source. It should be also noted that complete removal of water from THF, ethanol, and $LiClO_4$ was indispensable for the formation of NH_3 with a good yield.

In order to improve the ammonia formation efficiency, we tried to increase the concentration of N_2 in the reaction medium by increasing N_2 pressure. Using a gas-tight stainless autoclave, we carried out the electrolysis under 1, 5, 10, 30, and 50 atm of N_2 on a Cu electrode (1.0 mA cm^{-2}, 50 C). Results are shown in Fig. 2; current efficiencies for NH_3 and H_2 are plotted as functions of N_2 pressure. As expected, with increasing the N_2 pressure, the current efficiency for NH_3 formation increases accompanied by the decrease in H_2 evolution. Under 50 atm of N_2, 48.7% of the current efficiency for ammonia formation was achieved.

The potential of the working electrode (cathode) was monitored with respect to a Ag / AgCl / AgCl (saturated), LiCl (0.01 M), $LiClO_4$ (0.2 M) / THF reference electrode which was connected electrically to the electrolyte through a glass frit. In most cases, the uncorrected electrode potential was initially about -4 V and shifted gradually in the negative direction during the electrolysis, whereas it was difficult to measure the electrode potential precisely because of IR drop.

By our preliminary study, it was found that ammonia was formed only when a lithium salt was employed as an electrolyte. When $NaClO_4$ or Bu_4NClO_4 was used, only a negligible amount of NH_3 was formed on a Cu electrode even under 50 atm of N_2. This observation suggests that lithium act as a catalyst (mediator). Considering the fact that Li reacts with N_2 to form Li_3N even at room temperature,[11] the following mechanism is plausible; Li^+ is reduced on the electrode to deposit metallic Li, which reacts with N_2 to form Li_3N, and then subsequent ethanolysis occurs to afford NH_3. As described above, the electrode potential seemed to be negative enough to reduce Li^+ to Li. The result that no hydrazine was formed on any metal electrode in contrast to the ammonia formation would also provide the evidence for this mechanism. The low activities of Al and Pb electrodes for ammonia formation can be well explained by the fact that Al and Pb readily form alloys with lithium electrochemically.[12)] The lithium metal deposited on the electrode surface, not incorporated in the alloy, should be active toward N_2. Further investigation on this N_2 fixation reaction is now in progress and will be reported in due course.

References

1) O. N. Efimov and V. V. Strelets, *Coord. Chem. Rev.*, **99**, 15 (1990).
2) E. E. Van Tamelen, *Acc. Chem. Res.*, **3**, 361 (1970).
3) A. E. Shilov, *J. Mol. Cat.*, **41**, 221 (1987).
4) M. Koizumi, H. Yoneyama, and H. Tamura, *Bull. Chem. Soc. Jpn.*, **54**, 1682 (1981).
5) K. Tanaka, Y. Hozumi, and T. Tanaka, *Chem. Lett.*, **1982**, 1203.
6) C. J. Picket, K. S. Ryder, and J. Talarmin, *J. Chem. Soc., Dalton Trans.*, **1986**, 1453.
7) J. Y. Becker, S. Avraham (Tsarfaty), and B. Posin, *J. Electroanal. Chem.*, **230**, 143 (1987).
8) M. M. T. Kahn, R. C. Bhardwaj, and C. Bhadwaj, *Angew. Chem.*, **100**, 1000 (1988); *Angew. Chem., Int. Ed. Engl.*, **27**, 923 (1988).
9) N. Furuya and H. Yoshida, *J. Electroanal. Chem.*, **272**, 263 (1989).
10) W. Yefan, W. Shuiju, H. Liang, L. Guodong, Y. Youzhu, and C. Qirui, *Gaodeng Xuexiao Huaxue Xuebao*, **12**, 1251 (1991); *Chem. Abstr.*, **116**, 138545b (1992).
11) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York (1972), p. 190.
12) A. N. Dey, *J. Electrochem. Soc.*, **118**, 1547 (1971).

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