Supplementary Material (ESI) for Chemical Communications

(Supplementary information)

Hydrogen generation by electrolysis of liquid ammonia

Nobuko Hanada[a], Satoshi Hino[b], Takayuki Ichikawa[b]*, Hiroshi Suzuki[a], Kenichi Takai[a] and Yoshitsugu Kojima[b]

[a] *Department of Engineering and Applied Sciences, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo, 102-8554, Japan*

[b] *Institute for Advanced Materials Research, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, 739-8530, Japan*

The calculation of standard ammonia electrolysis voltage

The standard ammonia electrolysis voltage is calculated here according to reaction (S1),

$$1/2N_2\ (g) + 3/2H_2\ (g) \leftrightarrow NH_3\ (l) \qquad (S1).$$

The voltage difference between anode electrode (E^{N2}) and cathode electrode (E^{H2}) is described by the Nernst's equation as follows,

$$E^{N2} - E^{H2} = -\Delta G^0/3F + RT\ln(p_{N2}{}^{1/2}p_{H2}{}^{3/2})/3F \qquad (S2)$$

where F is the Faraday constant and R is gas constant. Standard Gibbs free energy change (ΔG^0) of reaction (S1) is −10.984 kJ/mol NH_3 from the enthalpy of formation: ΔH_f (liquid NH_3) = −67.2 kJ/mol[1] and the entropies: S^0 (liquid NH_3) = 103.3 J/mol [1], S^0 (H_2) = 130.7 J/mol [2] and S^0 (N_2) = 191.6 J/mol. [2] Hydrogen pressure (p_{N2}) and nitrogen pressure (p_{N2}) should be equivalent to the equilibrium ammonia vapor pressure (p_{NH3}) of liquid ammonia, because the gas is released with working for solution pressure by the ammonia vapor pressure in the closed liquid ammonia system. The p_{NH3} at 298.15 K is 9.9 atm. [3] So the second term of 0.039 V is almost equal to the first term of 0.038 V. It indicates that the pressure change largely affects to the ammonia electrolysis voltage. Finally the standard ammonia electrolysis voltage is determined to be 0.077 V.

Energy consumption of hydrogen generation, storage and supply

Liquid ammonia is comparable to the pressurized hydrogen in point of energy consumption of hydrogen generation, storage and supply to fuel cell or combustion engine. For liquid ammonia the energy consumption of ammonia production from natural gas as a feedstock is 28.5 MJ/kgNH_3 based on a lower heating value (LHV). [4] The energy consumption of hydrogen supply from liquid ammonia by the electrolysis is 7.4 MJ/kgH_2, which is calculated by using the standard voltage of ammonia electrolysis. The total energy consumption is expressed as follows,

$$E_{total}\ [\text{liquid ammonia}] = E\ (\text{ammonia production}) + E\ (\text{ammonia electrolysis})$$
$$= 160.5\ \text{MJ}/5.63\text{kgNH}_3 + 7.4\ \text{MJ/kgH}_2 = 167.9\ \text{MJ/kgH}_2 \qquad (S3)$$

Therefore the total energy efficiency for liquid ammonia is 71 % by using the energy in hydrogen (120 MJ/kgH_2 (LHV)).

For pressurized hydrogen the energy consumption of hydrogen production from natural gas as the feedstock is 183.2 MJ/kgH_2 (LHV) [5] and that of hydrogen compression to 70 MPa is 18 MJ/kgH_2 [6]. The total energy consumption is described as follows,

$$E_{\text{total}}\,[\text{pressurized hydrogen}] = E\,(\text{hydrogen production}) + E\,(\text{hydrogen compression})$$
$$= 183.2\ \text{MJ/kgH}_2 + 18\ \text{MJ/kgH}_2 = 201.2\ \text{MJ/kgH}_2 \quad \text{(S4)}$$

The total energy efficiency for pressurized hydrogen is 60 %.

The current efficiency

The current efficiency of potentiostatic electrolysis for liquid ammonia with 1 M KNH_2 is estimated to 85 % according to equation (S5),

Current efficiency = released hydrogen based on pressure increase (mol)/ released hydrogen based on electric charge (mol)   (S5).

For released hydrogen based on pressure increase, the cell pressure increases 0.523 MPa from 0.963 to 1.486 MPa during the electrolysis at 2 V of cell voltage for 10h as shown in Figure S3. Partial hydrogen pressure is 0.391 MPa from the ratio of H_2 to N_2 (2.960) determined by GC measurement. Therefore the released hydrogen amount is estimated to 4.62×10^{-3} mol by using 298 K of measurement temperature and 29.35 cm^3 of the cell volume subtracted liquid ammonia and KNH_2 volume. For released hydrogen based on electric charge, the total amount of charged electron is 1.09×10^{-2} mol by integrating the chronoamperometry line of Figure 3. Since the mole ratio of released hydrogen to charged electron is half based on reaction (3), released hydrogen amount is estimated to 5.46×10^{-3} mol.

References

1. W. L. Jolly, *Chem. Rev.*, 1952, **50**, 351
2. CRC Handbook of Chemistry and Physics, 89th eds., D. R. Lide, Eds.; CRC, Boca raton, FL, 2008
3. NIST chemistry web book http://webbook.nist.gov/chemistry/
4. G. Thomas and G. Parks, *Potential Roles of Ammonia in a Hydrogen Economy*, U. S. Department of Energy, Washington DC, 2006, http://www.hydrogen.energy.gov/pdfs/nh3_paper.pdf
5. P. L. Spath, and M. K. Mann, *Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming*, Report No. NREL/TP-570-27637, National Renewable Energy Laboratory, Golden, CO, February 2001
6. Eberle, U.; Felderhoff, M.; Schüth, F. *Angew. Chem. Int. Ed.* **2009**, *48*, 6608

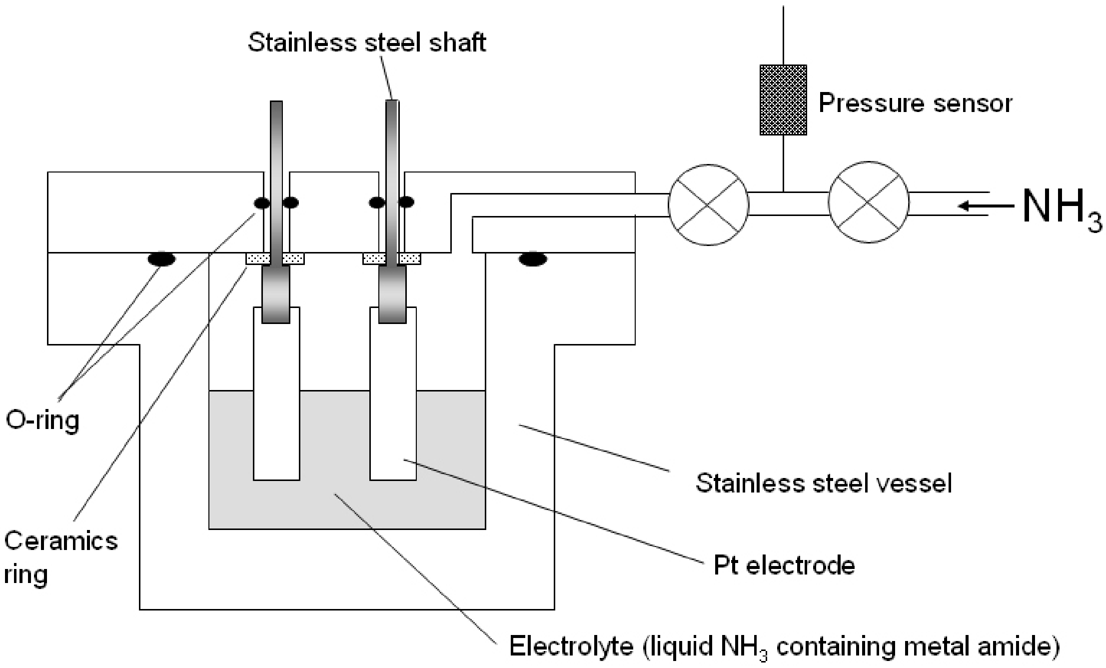

Figure S1. The electrochemical cell for the electrolysis of liquid ammonia

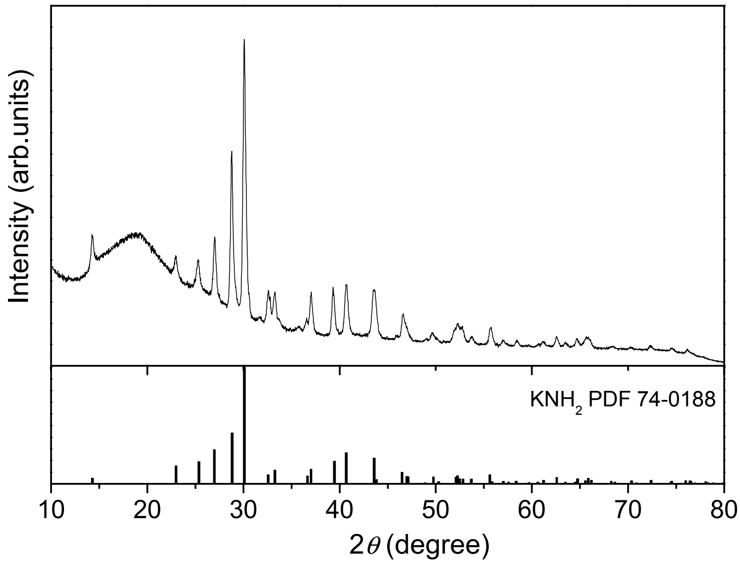

Figure S2. XRD profiles of KNH_2 synthesized from KH and liquid NH_3. As reference, XRD profile of KNH_2 in the database is shown.

Data	H_2 (mol)	N_2 (mol)	Mol ratio of H_2 to N_2
1	9.110×10^{-3}	3.076×10^{-3}	2.962
2	8.462×10^{-3}	2.851×10^{-3}	2.968
3	7.962×10^{-3}	2.683×10^{-3}	2.968
4	7.488×10^{-3}	2.524×10^{-3}	2.967
5	7.018×10^{-3}	2.363×10^{-3}	2.971
6	6.601×10^{-3}	2.228×10^{-3}	2.962
7	6.193×10^{-3}	2.105×10^{-3}	2.941
8	5.814×10^{-3}	1.979×10^{-3}	2.938
Average value	–	–	2.960 ± 0.004

Table S1. Amount of the H_2 gas and N_2 gases in the electrochemical cell of liquid ammonia with 1 M KNH_2 after the chronoamperometry measurement at 2 V of cell voltage for 10 h by using the area of GC peaks. Mole ratio of H_2 to N_2 is calculated from the amount of hydrogen and nitrogen gas.