

# Electrochemical synthesis of ammonia at atmospheric pressure and low temperature in a solid polymer electrolyte cell

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The heterogeneous electrocatalytic synthesis of ammonia from nitrogen and water is carried out at Ru cathodes, using a Solid Polymer Electrolyte Cell (SPE), at atmospheric pressure and low temperature; the reduction rate increases with increase of temperature up to 100 °C, while with the increase of the negative potential a maximum is observed at  $-1.02$  V vs. Ag/AgCl and gradually decreases in the hydrogen discharge region.

Industrially the synthesis of ammonia takes place by passing  $N_2$  and  $H_2$  over Fe or Ru surfaces at about 430–480 °C and 100 atm.<sup>1</sup> The synthesis of ammonia over these catalysts at ambient temperatures is a very difficult process because of the high energy barrier for the breaking of the  $N\equiv N$  bond which is about 1000 kJ mol<sup>-1</sup> at 25 °C.

Numerous efforts have been reported so far on the conversion of nitrogen to ammonia at room temperature and atmospheric pressure using, photocatalytic,<sup>2,3</sup> electrochemical<sup>4–11</sup> or catalytic methods.<sup>12</sup> Recently, Marnellos and Stoukides studied the electrochemical synthesis of ammonia at Pd cathodes using a solid proton conductor at 570 °C and atmospheric pressure and pointed out that the thermodynamic demand for high pressure can be compensated by the use of an electrochemical reactor.<sup>13</sup> However, the operation temperature of that cell is high and ammonia undergoes decomposition at this temperature. The high electrical resistance of the electrolyte is an additional disadvantage of this method. The present study deals with the electrochemical synthesis of ammonia in a Solid Polymer Electrolyte (SPE) cell on Ru cathodes at atmospheric pressure and low temperature from nitrogen and water.

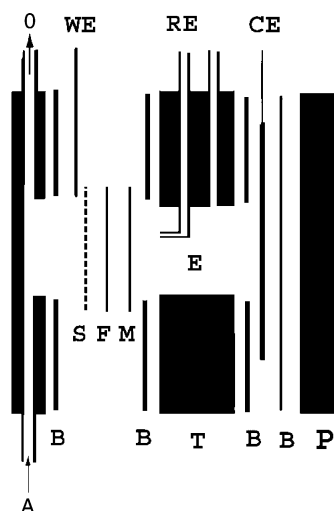
The reduction of nitrogen (99.999%) was performed in a two-compartment cell, as shown in Fig. 1. The cell was placed in a

thermostated bath. Ruthenium was electrochemically deposited on a carbon felt (Electrosynthesis Corporation) from a 0.05 M  $RuCl_3$  solution using a constant current of 25 mA cm<sup>-2</sup> for 60 min. Consequently, it was washed with water to remove the chloride ions and it was finally placed into the electrolytic cell in contact with the Nafion membrane, where it was dried by a nitrogen stream for 24 h. The Nafion membrane was pretreated by heating in  $H_2O_2$  5% solution at 80 °C for 1 h and in ultrapure water for another 1 h. The apparent surface area of the cathode was 2.35 cm<sup>2</sup>. A 2 M KOH solution in ultra pure water was used as electrolyte in all experiments. The anode was in contact with the KOH solution (10 cm<sup>3</sup>) and the anodic reaction was the oxygen evolution. A saturated Ag/AgCl electrode was used as a reference.

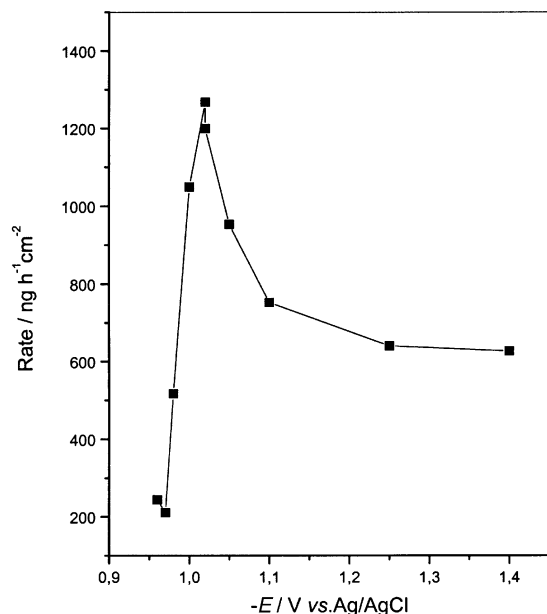
A nitrogen steam with a constant flow rate withdrew the gaseous products from the cell. The  $NH_3$ , which was produced, was stripped by a 15 ml of 0.1 M  $H_3BO_3$  solution. Ammonia was determined by Ion Chromatography using a CS15 column (Dionex Corp.) and a Dionex 4500i Chromatograph, as well as colorimetrically by using the phenate method.<sup>14</sup> Experiments have been conducted for the possible presence of hydrazine colorimetrically at 458 nm using the *p*-dimethylaminobenzaldehyde method.<sup>15</sup> Ammonia was the only product detected in the electrochemical reduction of nitrogen at 90 °C and at potential of  $-1.10$  V, using ruthenium as cathode. Two control experiments were performed at 90 °C and for 24 h, in order to verify that the detected ammonia was a product of nitrogen reduction (i) Nitrogen gas was introduced into the cell at open-circuit ( $I = 0$ ). (ii) Inert gas (Ar) was introduced into both compartments of the cell for 4 h, so that the air trapped within the carbon felt would be expelled. The flow of argon was continued and then a potential of  $-1.10$  V was applied for 24 h. In both cases no ammonia was detected.

At all potential values examined, the amount of the produced ammonia is in an almost linear relationship with time, which confirms that ammonia was produced by an electrochemical reaction. The rate of ammonia formation remained constant even when the electrolysis was continued for another 100 h at a potential of  $-1.10$  V. This implies that the electrode is not deactivated with time. Given this fact, the same electrode was used for all experiments.

The standard potential for the  $N_2$  reduction to  $NH_3$ , as calculated from the Nernst equation, was found to be  $-0.67$  V vs. NHE or  $-0.88$  V vs. Ag/AgCl. The calculations were performed assuming that  $P_{N_2} = 0.99$  atm,  $P_{NH_3} = 0.01$  atm and pH = 14. The reduction of nitrogen in our experiments on Ru began at  $-0.96$  V; a value which is slightly higher (0.08 V) than that anticipated from the thermodynamic calculations. The rate of ammonia formation, as is shown in Fig. 2, was increased with the negative potential until  $-1.02$  V, where a maximum value was displayed and afterwards it was decreased. A similar behaviour was reported by Sclafani *et al.*,<sup>11</sup> in the electrochemical reduction of nitrogen at iron cathodes in the region of hydrogen discharge, which was attributed to the competitive adsorption of nitrogen and hydrogen species on the electrode surface. An explanation similar to this might be proposed for the observed behaviour at our ruthenium electrode.



**Fig. 1** Exploded view of the electrolysis cell: (A) gas inlet, (O) gas outlet, (T) polytetrafluoroethylene plate, (B) silicone gasket, (M) Nafion membrane, (F) carbon felt, (S) stainless steel screen 150 mesh, (E) electrolyte chamber, (P) stainless steel plate, (WE) working electrode, (RE) reference electrode, (CE) Pt anode.



**Fig. 2** The rate of formation of ammonia against negative cathodic potential, at 90 °C and an electrolysis time of 24 h.

**Table 1** Rate and CE of ammonia formation at the Ru cathode at various experimental conditions

Potential/V	N <sub>2</sub> flow rate/ cm <sup>3</sup> min <sup>-1</sup>	T/°C	Current <sup>a</sup> /mA	CE(%)	Rate of NH <sub>3</sub> /μg h <sup>-1</sup> cm <sup>-2</sup>
-1.02	1	90	6.1	0.24	1.30
-1.02	10	90	5.8	0.23	1.20
-1.02	15	90	6.8	0.20	1.25
-0.96	25	90	0.3	0.92	0.25
-1.10	25	90	16.2	0.17	0.90
-1.10	25	20	8.2	0.28	0.21

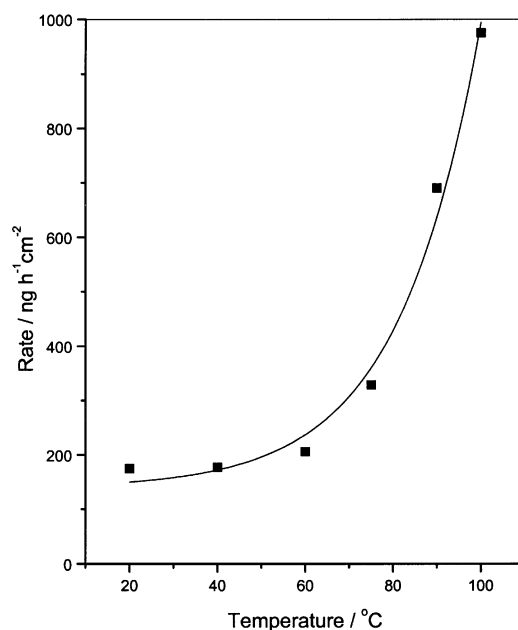
<sup>a</sup> Average current.

The rate and the current efficiency (CE) of the process, as shown in Table 1, were quite low and in the best case they reached about 1.3 μg h<sup>-1</sup> cm<sup>-2</sup> at -1.02 V and 0.92% at -0.96 V respectively. This rate is about fifty times lower than that previously reported at 570 °C.<sup>13</sup>

Experiments were also conducted at -1.02 V and 90 °C and at various flow rates of 1, 10 and 15 cm<sup>3</sup> min<sup>-1</sup>. Within the experimental error, no measurable effect was observed in the (CE) and at the rate of the reaction. This indicates that diffusion was not the rate determining step. Furthermore, the chemical yield (CY) of the reaction was 0.003% when the flow rate of nitrogen was 1 cm<sup>3</sup> min<sup>-1</sup> and it was about inversely proportional to the flow rate of nitrogen. The chemical yield (CY) of the reaction can be increased with a different planning of the cell so that the retention time of N<sub>2</sub> will be increased. The rate displayed an exponential growth with temperature in accordance to the Arrhenius equation, as is shown in Fig. 3, and it was about 5 times higher at 100 than that at 20 °C. A corresponding increase of the reduction rate with temperature was previously observed in the reduction of nitrogen with hydrogen on Ru catalyst at ambient temperature.<sup>12</sup>

These results are in agreement with the recent work of Rod *et al.*,<sup>16</sup> who showed that it could be possible to produce ammonia at ambient temperature on Ru from nitrogen and hydrogen *via* a dissociative mechanism, by using density functional theory (DFT) calculations. Furthermore, the fact that hydrazine was not detected in any of our experiments, suggests the ammonia was produced *via* a dissociative mechanism, in a similar way to that in the gas phase.<sup>17,18</sup>

Examination of the crystal structure of the electrode (after electrolysis) by XRD indicated that the main reflections (101) and (100) of Ru had a ratio 100:10. It is known that the



**Fig. 3** Rate of formation of ammonia against temperature at -1.10 V and at an electrolysis time of 24 h.

ammonia synthesis reaction is extremely structure sensitive and that the energy barrier for the dissociation of nitrogen depends strongly on the particle size and the crystal structure of Ru.<sup>16,19</sup> The Ru, which was used in our experiments, had planes with different activities and this fact led to the decrease of the number of active catalytic sites and therefore to a low reaction rate. Moreover, the competitive adsorption of hydrogen to that of nitrogen and the low number of sites, where a contact N<sub>2</sub>/Ru/membrane exists, are two additional reasons.

This is the first report regarding ammonia production at atmospheric pressure and low temperature. The main problems that exist at the present are the low rate of ammonia formation and the hydrogen evolution at the cathode. Further work to optimize these factors is in progress.

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## Notes and references

- 1 F. M. Herman, D. F. Othmer, C. G. Overberger and G. T. Seaborg, *Encyclopedia of Chemical Technology*, Wiley and Sons, New York, 1978, vol. 2, p. 494.
- 2 G. N. Schrauzer and T. D. Guth, *J. Am. Chem. Soc.*, 1977, **99**, 7189.
- 3 M. M. Taqui Khan, R. C. Bhardwaj and C. Bhardwaj, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 923.
- 4 E. E. van Tamelen and D. A. Seeley, *J. Am. Chem. Soc.*, 1969, **91**, 5194.
- 5 M. E. Vol'pin, *J. Organomet. Chem.*, 1980, **200**, 319.
- 6 J. Y. Becker, S. Avraham and B. Posin, *J. Electroanal. Chem.*, 1987, **230**, 143.
- 7 J. Y. Becker and B. Posin, *J. Electroanal. Chem.*, 1988, **250**, 385.
- 8 J. Y. Becker and S. Avraham, *J. Electroanal. Chem.*, 1990, **280**, 119.
- 9 C. J. Pickett, K. S. Ryder and J. Talarmin, *J. Chem. Soc., Dalton Trans.*, 1986, 1453.
- 10 C. J. Pickett and J. Talarmin, *Nature*, 1985, **317**, 652.
- 11 A. Sclafani, V. Augugliaro and M. Schiavello, *J. Electrochem. Soc.*, 1983, **130**, 734.
- 12 K. Aika, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 558.
- 13 G. Marnellos and M. Stoukides, *Science*, 1998, **282**, 95.
- 14 L. S. Clesceri, A. E. Greenberg and R. Trussell Rhodes, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, 1989, pp. 120–121.
- 15 G. W. Watt and J. D. Chrisp, *Anal. Chem.*, 1952, **24**, 2006.
- 16 T. H. Rod, A. Logadottir and J. K. Nørskov, *J. Chem. Phys.*, 2000, **112**, 5343.
- 17 O. Hinrichsen, F. Rosowski, A. Hornung, M. Mihler and G. Ertl, *J. Catal.*, 1997, **165**, 33.
- 18 W. Liu and T. T. Tsong, *Surf. Sci.*, 1986, **165**, L26.
- 19 S. Dahl, A. Logadottir, R. C. Egeberg, J. H. Larsen, J. Chorkendorff, E. Tornqvist and J. K. Nørskov, *Phys. Rev. Lett.*, 1999, **83**, 1814.