



Electrochemical conversion of dinitrogen to ammonia induced by a metal complex–supported ionic liquid



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ABSTRACT

Electrochemical synthesis of NH₃ from dinitrogen and protons from water by using Cp₂TiCl₂ supported in a hydrophobic ionic liquid, 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ([C₉H₂₀N]⁺[(C₂F₅)₃PF₃]⁻), was achieved in a solid polymer electrolyte (SPE) cell under ambient conditions. The yield of NH₃ per Cp₂TiCl₂ and current efficiency are 27% and 0.2%, respectively, which are improved in comparison with those reported previously.

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1. Introduction

A number of researchers in various chemical fields have investigated conversion of N₂ to NH₃ under mild conditions [1–14]. Transition metal complexes have been found to promote electrochemical generation of NH₃ as catalysts. For example, Pickett and Talarmin reported the electrochemical synthesis of NH₃ through protonation of *cis*-[W(N₂)₂(PMe₂Ph)₄] under ambient conditions [15], with the reaction carried out in THF–0.2 M [NBu₄][BF₄] using a toxic Hg–pool cathode as the working electrode at –2.6 V (vs. Fc/Fc⁺). Furuya and co-workers demonstrated electrochemical reduction of N₂ to NH₃ using a gas diffusion electrode modified by Fe–phthalocyanine, but the current efficiency of NH₃ production was found to be less than 0.1% after controlled-potential electrolysis for 10 min [16]. Becker and co-workers reported that titanocene dichloride, Cp₂TiCl₂, could reduce N₂ to NH₃ when the controlled-potential electrolysis (CPE) is carried out at –2.2 V (vs. Ag wire) in MeOH solution containing 0.3 M LiClO₄ and 0.25 M catechol [17]. This reaction proceeds at room temperature under 1 atm using hydrogen atoms from catechol and/or MeOH, but the yield of NH₃ per Cp₂TiCl₂ and the current efficiency were both found to be quite low (1.45% and 0.28%, respectively). In order to improve this reaction, we decided to carry out CPE using a solid polymer electrolyte cell (SPE cell), which is composed of a working electrode (W.E.) and a counter electrode C.E. separated by a proton

exchange membrane. Electrochemical synthesis of NH₃ in an SPE cell using a Ru cathode as the W.E. was previously reported [18]. In this case, a proton was generated by oxidation of H₂O at C.E., which was transferred to the W.E. to react with N₂. It is advantageous that the proton originating from H₂O oxidation is employed and the generated O₂ is separated from the W.E. by proton exchange membrane. Thus, it is possible to use H₂O as the hydrogen source. Furthermore, in order to use Cp₂TiCl₂ as the metal complex in the SPE cell, we investigated an ionic liquid as the supporting material.

An ionic liquid, which is a salt in a liquid state under ambient conditions, has recently been employed in a number of different research efforts, because it has several unique properties such as low volatility, an electrochemical window, high thermal and chemical stability, and electric conductivity [19]. In particular, 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluoro-phosphate, [C₉H₂₀N]⁺[(C₂F₅)₃PF₃]⁻, is appropriate for use as a supporting material because of its high stability [20]. The W.E. is conveniently fabricated by coating the ionic liquid [C₉H₂₀N]⁺[(C₂F₅)₃PF₃]⁻ supported with a transition-metal complex.

Here, we report the electrochemical reduction of N₂ to NH₃ using a W.E. coated with Cp₂TiCl₂-supported ionic liquid in an SPE cell (Fig. 1) under ambient conditions.

2. Experimental

2.1. Reagents and instrumentation

Cp₂TiCl₂ and 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate, [C₉H₂₀N]⁺[(C₂F₅)₃PF₃]⁻, were purchased from

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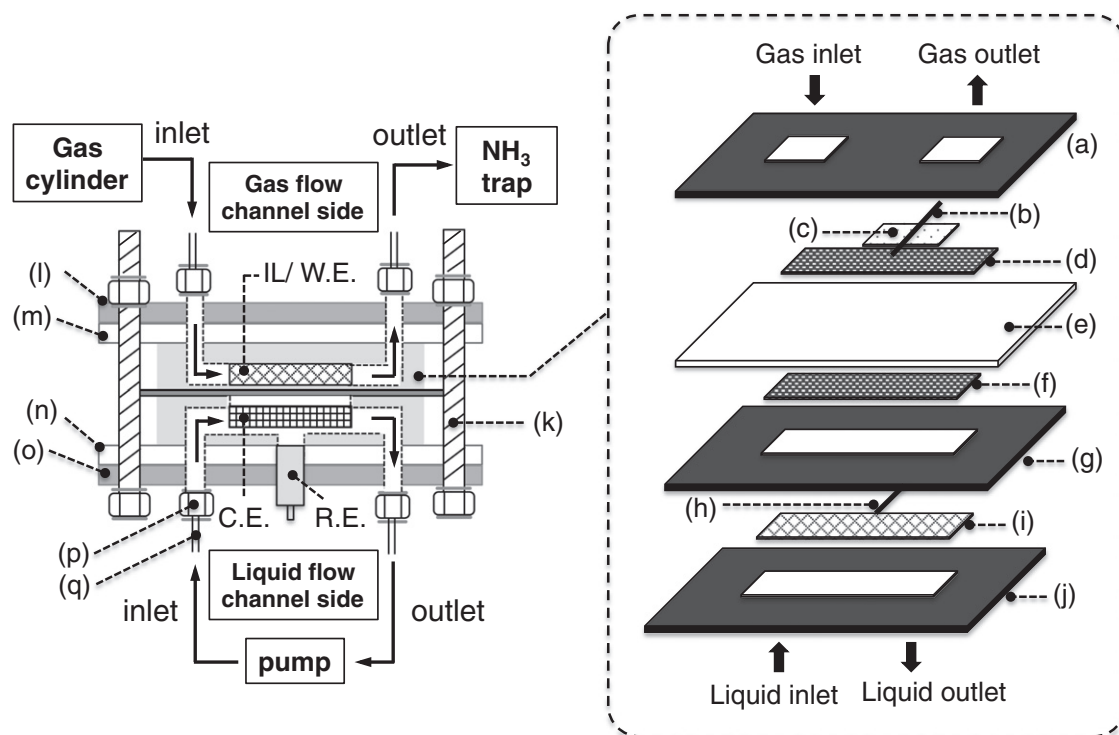


Fig. 1. A schematic diagram of the constructed SPE cell (left) and the internal structure of electrolysis cell (right); (a) gasket (30 mm (D) × 55 mm (W) × 1 mm (H)), (b) Cu wire, (c) parafilm (10 mm (D) × 10 mm (W)), (d) carbon paper (TORAY, TGP-H-120) as the working electrode (10 mm (D) × 20 mm (W) × 0.37 mm (H)) coated with 50 μL of IL containing 10 mM Cp_2TiCl_2 , (e) Nafion[®]212 membrane, (f) carbon paper (10 mm (D) × 20 mm (W) × 0.37 mm (H)) that is used as support to bind membrane, (g) gasket, (h) Pt mesh as the counter electrode, (i) gasket, (j) bolt, (k) bolt, (l) aluminum plate (70 mm (D) × 50 mm (W) × 5 mm (H)), (m) polytetrafluoroethylene (PTFE) plate (70 mm (D) × 50 mm (W) × 5 mm (H)), (n) PTFE plate that has a hole (1/4 28UNF) at the center to screw the reference electrode, (o) aluminum plate that has a hole (1.2 cm diameter) at the center, (p) teflon connector, and (q) silicon tube (1 mm diameter). The reference electrode is Ag/AgCl one (3 M NaCl aq.) that is a screw type to attach in teflon body. The inlet of gas channel is connected by gas cylinder and the outlet is connected to 10 mM HCl aqueous solution as NH_3 trap. The flow rate of gas was kept at 5 mL/min. The inlet and outlet of liquid channels are connected by pump, and the 0.2 M H_2SO_4 aqueous solution is circulated.

Tokyo Chemical Industry Co., Ltd. and Merck Ltd., respectively, and used without further purification. All treatments of these reagents were performed in MBRAUN MB 150B – G glovebox under Ar atmosphere (<1 ppm $\text{O}_2/\text{H}_2\text{O}$). Electrospray ionization time-of-flight mass spectra, ESI-TOF/MS, were obtained with a Micromass LCT spectrometer. Electrochemistry was performed using a potentiostat (BAS, ALS/600).

2.2. Electrochemical measurements and experimental conditions

Solid polymer electrolyte (SPE) cell (Fig. 1) was designed according to the previous report² [18]. A gas (N_2 or Ar) was flowed through the respective channels in a rate of 5 mL/min. In the case of using $^{15}\text{N}_2$ gas (99.9%), it was flowed through the channels in a rate of <1 mL/min. The outlet of gas was introduced to 10 mM HCl aqueous solution as NH_3 trap.

3. Results and discussion

3.1. The redox behavior of Cp_2TiCl_2 in $[\text{C}_9\text{H}_{20}\text{N}]^+[(\text{C}_2\text{F}_5)_3\text{PF}_3]^-$ and the linear sweep voltammetry in the SPE cell

Cyclic voltammogram of Cp_2TiCl_2 in $[\text{C}_9\text{H}_{20}\text{N}]^+[(\text{C}_2\text{F}_5)_3\text{PF}_3]^-$ is shown in Fig. 2 (A). The $E_{1/2}$ value of $\text{Cp}_2\text{TiCl}_2(\text{IV}/\text{III})$ was -1.10 V (vs.Fc/Fc⁺), which is good agreement with previous report, where

² The SPE cell is composed of metallic plate, polytetrafluoroethylene (PTFE) plate, gasket made of Viton (fluoropolymer elastomer), Nafion[®]212 membrane, carbon paper (TORAY, TGP-H-120) as a working electrode, Pt mesh as a counter electrode, and Ag/AgCl (3 M NaCl aq., ALS Co., Ltd., RE-3VP) as a reference electrode. The gas and liquid channels were made of Viton gaskets. Cu wire was used as the current collector of working electrode that was coated by 50 μL of ionic liquid, $[\text{C}_9\text{H}_{20}\text{N}]^+[(\text{C}_2\text{F}_5)_3\text{PF}_3]^-$, containing 10 mM Cp_2TiCl_2 .

measurements were made in MeOH [17,21–23]. In more negative potential regions, two reduction waves were observed at -2.31 V and -2.54 V (vs.Fc/Fc⁺), which might be assigned to the reduction of $\text{Cp}_2\text{TiCl}_2^-$ or Cp_2TiCl [24,25]. These waves were slightly different compared with that in THF [24,25]. This is because the polarity of ionic liquid affected the redox of Cp_2TiCl_2 or the equilibrium of anion exchange between Cl anion and $[(\text{C}_2\text{F}_5)_3\text{PF}_3]^-$ anion affected.

The linear sweep voltammograms of Cp_2TiCl_2 in the SPE cell were investigated and the results are shown in Fig. 2(B) together with the results of control experiments: The linear sweep voltammograms (a) and (b) were carried out under N_2 and Ar atmospheres, respectively, and (c) is the result obtained without Cp_2TiCl_2 under N_2 . Under both N_2 and Ar, broadened peaks were observed at -1.13 V (vs. Ag/AgCl), but no peaks were observed without Cp_2TiCl_2 . Thus, it is clear that the observed peaks originate from the oxidation of Ti(IV) to Ti(III) in Cp_2TiCl_2 . The current under N_2 is considerably greater than that under Ar. The noisy pattern in the peak is due to the generation of H_2 gas. These findings indicate that the reduced Ti(III) species reacts with N_2 , accompanied by an H_2 evolution reaction. This appears to be the first time a difference between Cp_2TiCl_2 reactions conducted under N_2 and Ar has been observed. Hence, CPE in the range of -1.0 to -1.5 V was performed to evaluate the yield of NH_3 per Cp_2TiCl_2 and its current efficiency.

3.2. Electrochemical synthesis of ammonia

In the CPE in the range of -1.0 to -1.4 V, NH_3 was not detected, but it was detected at -1.5 V. The quantification of produced NH_3 was evaluated using the indophenol method [26]. In order to prove that the generated NH_3 was derived from N_2 gas, we performed the controlled experiments under $^{15}\text{N}_2$ atmosphere and Ar atmosphere. The

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