High Compressed Hydrogen Production via
Direct Electrolysis of Liquid Ammonia

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Abstract

In this study, the direct electrolysis of liquid ammonia (NH_3) by using ammonium chloride (NH_4Cl) as an electrolyte to supply ammonium cation (NH_4^+) is performed. As a result, it is confirmed that a certain electric current is observed while voltage below 2.0 V is applied to the electrodes, which indicates that NH_4Cl can work as an electrolyte for the electrolysis of liquid ammonia. Furthermore, generation of high compressed hydrogen by NH_3 electrolysis is successfully demonstrated, where the inner pressure reaches 20 MPa. However, it is confirmed that the electrode corrosion on the anode occur during the electrolysis. Then, the corrosion mechanism of the anode electrode composed of stainless or platinum are investigated by gas chromatography for the generated gas, and powder x-ray diffraction measurement for the electrolyte after the electrolysis. Finally, it is concluded that a metal (M) of an anode electrode is ionized in the ammonia solution to form metal chloride ($M\text{Cl}_x$) instead of the primary oxidation reaction for the electrolysis of ammonia.

Keywords

Hydrogen carrier; Ammonia; electrolysis; high compressed hydrogen production

1 Introduction

To realize a sustainable society by hydrogen H_2 energy, it is essential to develop a high density storage and a transportation method for H_2 . Although H_2 has the high gravimetric energy density, the volumetric energy density is much smaller than that of gasoline even though H_2 is

compressed to high pressure. Thus, it is considered to be difficult to store H₂ compactly. In this view, ammonia NH₃ is regarded as one of the most promising H₂ carrier in the following reasons. The gravimetric H₂ density of NH₃ is as much as 17.8 mass %, which is more than two times higher than those of organic hydrides. Besides, the volumetric H₂ density of NH₃ is 1.5 times higher than that of liquid H₂ because it can be easily liquefied at 20 °C by compressing to 0.87 MPa. However, more than 400 °C is needed for decomposition of NH₃ to generate H₂ even in presence of transition metal catalyst [1-6]. Electrochemical process is one of the promising methods to decompose NH₃ for H₂ generation at moderate temperature. A number of studies for ammonia oxidation reaction with Pt-based electrodes, which are potentially applied to direct ammonia fuel cell, removal of ammonia in wastewater, and generation of H₂, have been reported before [7-12]. Besides, It was reported that NH₃ dissolving in alkaline solution can be decomposed by electrolysis at room temperature [13-16]. However, the gravimetric H₂ density is as low as 6.1 mass % according to its solubility to water, 34.2 mass % at 20 °C. Thus, the direct electrolysis of liquid NH₃ was investigated by Hanada *et al.*, where alkaline metal amide *M*NH₂ (*M*=Li, Na, K) was used as a supporting electrolyte [17, 18]. They predicted that the oxidation-reduction reactions on the anode and the cathode proceed as follows,

Namely, amide anion NH_2^- is electrically oxidized, generating nitrogen N_2 on the anode. Meanwhile, NH_3 is electrically reduced, generating H_2 and NH_2^- on the cathode. Thus, the above redox reactions totally lead to decomposition of NH_3 to generate H_2 and N_2 . In this study, the direct electrolysis of liquid NH_3 with another supporting electrolyte is investigated as a basic research. Thus, ammonium chloride NH_4Cl which is considered to be a more manageable material than MNH_2 is used as an electrolyte to supply ammonium cation NH_4^+ instead of NH_2^- treated in the previous study. Besides, generation of high compressed hydrogen by the NH_3 electrolysis is attempted to demonstrate its feasibility in terms of practical use.

2Experimental section

NH_4Cl (99.5 %, Aldrich) and NH_3 (99.999%) were used for the investigation of NH_3 electrolysis in this work. A pressure-tight and transparent container (Hiper Glass Cylinder HPG-96-1, Taiatsu Techno Co) was used to confirm the solubility of NH_4Cl in liquid NH_3 . NH_3 electrolysis was performed by using a Bi-polar cell composed of a stainless steel container and stainless steel electrodes (H450 mm $\times$ W520 mm $\times$ T1.5 mm) or platinum Pt electrodes (H20 mm $\times$ W20 mm $\times$ T0.2 mm), which was designed to have 30MPa pressure resistance and airtightness. NH_4Cl was introduced into the Bi-polar cell in a glove box (Miwa MFG, MP-P60 W) filled with purified argon Ar (> 99.9999%) to avoid hydration due to water. Then, the inner Ar was preliminarily evacuated by a rotary pump. After that, liquid NH_3 was introduced in the cell to prepare 5 M $\text{NH}_4\text{Cl}/\text{NH}_3$ solution, where lower half part of the electrodes were set to be immersed in the solution (Fig. S1). Electrochemical properties of NH_3 electrolysis were investigated by cyclic voltammetry (CV) (SP-150, Bio-Logic SAS) and chronoamperometry

(Potentiostats/ Galvanostats HA151, Hokuto Denko Co). The generated gas after the electrolysis in the gas sampling container was analyzed by gas chromatography (GC) (GC-14B, Shimadzu Co.), where an activated carbon column (SHINCARBON ST, Shinwa Chemical Industries Ltd, 2.0 m×3.0 mm) was used to separate N₂ and H₂. Liquid NH₃ in the container was transferred to the NH₃ trap part cooled by liquid N₂(Fig. S1). Then, the remaining solid materials in the container after the electrolysis were identified by x-ray diffraction measurement (XRD) (Rigaku, RINT-2100, CuK α radiation).

3 Results and Discussion

3.1 Electrolysis of NH₄Cl/NH₃ solution with stainless steel electrodes

The theoretical electrolysis voltage of liquid NH₃ at 25 °C is estimated from Nernst's equation as follows,

$$E = -\Delta G^o/3F + RT \ln(P_{\text{N}_2}^{1/2}P_{\text{H}_2}^{3/2})/3F.(4)$$

In the equation (eq. 4), F, R, ΔG^o , T, P_{H_2} , and P_{N_2} represent the Faraday constant, the gas constant, the standard Gibbs free energy change of reaction, temperature, partial pressure of H₂,

and partial pressure of N₂, respectively. Besides, ΔG^o is expressed by the standard enthalpy change of reaction ΔH^o , the standard entropy change of reaction ΔS^o , and temperature T as follows,

$$\Delta G^o = \Delta H^o - T\Delta S^o. (5)$$

From the above equation (eq. 4, 5), the theoretical electrolysis voltage E for liquid NH₃ is estimated to be 0.077 V, where the ΔH^o and ΔS^o are calculated by combining the reported standard enthalpy change of formation $\Delta_f H^o$ and the standard entropy S^o [-67.2 kJ/mol for $\Delta_f H^o$ (liquid NH₃), 103.3 J/mol for S^o (liquid NH₃) [19], 130.7 J/mol for S^o (H₂), 191.6 J/mol for S^o (N₂) [20]].

Liquid NH₃ dissociates to NH₄⁺ and NH₂⁻ according to its ionization constant K_{eq} as follows [21, 22],

$$K_{eq} = [\text{NH}_4^+][\text{NH}_2^-] = 10^{-33} (223 \text{ K}). (7)$$

It is considered that such ions serve an important role on electrodes for NH₃ electrolysis. In this work, NH₄Cl was used as an electrolyte for NH₃ electrolysis to supply NH₄⁺ ion in liquid NH₃. Herein, NH₄Cl was chosen for a baseline study, while there are a number of ammonium compounds as a candidate to supply NH₄⁺ ion in liquid NH₃, e.g. NH₄F, (NH₄)₂CO₃, NH₄NO₃, and so on. Namely, it is considered that NH₄Cl is the simplest and well-known material to supply NH₄⁺, which is expected to facilitate the analysis and understanding of the side reactions possibly caused during the NH₃ electrolysis. Besides, it was pre-experimentally confirmed that more than 5 M of solid NH₄Cl can dissolve in liquid NH₃, which was visually examined by using the pressure-tight and transparent container. Then, the expected oxidation-reduction reaction on the electrodes for NH₄Cl/NH₃ solution are expressed as follows,

Namely, NH₄⁺ is reduced on cathode to generate H₂ gas. Meanwhile, NH₃ is oxidized on anode to generate N₂ gas. Thus, it follows that NH₃ is decomposed to N₂ and H₂ with a molar ratio of H₂/N₂ = 3 in totally as follows,

Thus, CV measurement for $\text{NH}_4\text{Cl}/\text{NH}_3$ solution was performed by using stainless steel electrodes which is chosen as a common metal. Fig.1 shows the CV profile of 5 M $\text{NH}_4\text{Cl}/\text{NH}_3$ solution at 25 °C, where the voltage was applied in the range from 0 V to 1.5 V at scan rate of 10 mV/s. As shown in the CV profile, a certain electric current of 7.5 mA /cm² was observed while 1.5 V was applied to the electrodes, which would indicate that NH_4Cl can work as an electrolyte for the electrolysis of liquid NH_3 . However, unexpected current peak around 0.4 to 1.1 V was observed, which is possibly attributed to an electrochemical reaction such as electrode corrosion.

Fig. 1 CV profile of 5M $\text{NH}_4\text{Cl}/\text{NH}_3$ solution at 25°C with stainless steel electrodes. The voltage was applied in the range from 0 V to 1.5 V at scan rate of 10 mV/s.

Then, the electrolysis reaction was further investigated by performing a chronoamperometry and an analysis of its reaction product to clarify the actual electrochemical process. Fig.2 shows the chronoamperometry profile of 5 M $\text{NH}_4\text{Cl}/\text{NH}_3$ solution at 25 °C and the variation of the inner pressure, where constant voltage of 2 V was applied for 8 h. The inner pressure constantly increased to 5 MPa, indicating that an electrolysis reaction proceeded to generate a certain amount of gas component. Meanwhile, the current reached a maximum in the early region and then gradually decreased as time proceeded. Such a variation of the current would be caused by the change in the condition of the electrode surface, for example, removal of oxide layer as an activation in the early region and then corrosion of the electrodes. Thus, the inner gas and the electrolyte powder in the container after the electrolysis were analyzed by GC and XRD, respectively. As a result, the observed two peaks in the GC profiles of the inner gas corresponded to those of reference gases of pure H_2 and pure N_2 as shown in the inset in Fig. 2, which indicates that the expected NH_3 electrolysis reaction could proceed to generate H_2 and N_2 . However, the molar ratio of H_2/N_2 was estimated to be 3/0.6 from the peak areas of the GC profile, which is inconsistent with the theoretical value of 3/1 and means that some unexpected oxidation reaction proceeded instead of the NH_3 oxidation reaction to generate N_2 as in the equation (eq. 9).

Fig. 2 Chronoamperometry profile of 5M $\text{NH}_4\text{Cl}/\text{NH}_3$ solution at 25°C with stainless steel electrodes and the variation of the inner pressure during the electrolysis. Constant voltage of 2V was applied between the electrodes. The inset shows the GC profile of the generated gas during the chronoamperometry.

Besides, for the XRD measurement of the electrolyte powder after the electrolysis, it was confirmed that the diffraction pattern observed with that of NH_4Cl corresponded to that of iron chloride hexa-ammine complex $(\text{Fe}(\text{NH}_3)_6)\text{Cl}_2$ (Fig. S2). From these GC and XRD results, it is considered that Fe in the anode electrode ionized to form iron cation Fe^{2+} , which combined with chloride anion Cl^- to form iron chloride FeCl_2 and then to form $(\text{Fe}(\text{NH}_3)_6)\text{Cl}_2$ spontaneously[23]. In fact, it was visually confirmed that the immersed part of the anode electrode dissolved and

thinned down in obvious. The predicted oxidation-reduction reactions and the total reaction associated with the anode corrosion are expressed as follows,

Thus, the events observed in the CV and the chronoamperometry for the electrolysis of $\text{NH}_4\text{Cl}/\text{NH}_3$ solution with stainless steel electrodes can be explained by the above corrosion reaction. In the CV, the corrosion current increased in the voltage range from approximately 0.4 V and then **decreased**, showing the peak shape of the current. As the reason for this, it is considered that the concentration of the generated Fe^{2+} around the anode became higher and reached its saturation point, resulting the **decrease** of the corrosion current. **This discussion is also applied to the cause that the current of the chronoamperometry drastically decreased in the early region in Fig. 2.** Meanwhile, the gradual decrease of the current in the chronoamperometry is considered to be due to the decrease of the NH_4Cl concentration in liquid NH_3 because NH_4Cl was consumed by the corrosion reaction.

3.2 Electrolysis of $\text{NH}_4\text{Cl}/\text{NH}_3$ solution with Pt electrodes for high compressed H_2 production

It was clarified that stainless steel electrode as the anode for electrolysis of $\text{NH}_4\text{Cl}/\text{NH}_3$ solution was corroded even below 0.5 V. Thus, the electrolysis of $\text{NH}_4\text{Cl}/\text{NH}_3$ solution was performed with Pt electrodes whose ionization tendency is typically known to be low, which could result in the inhibition of the electrode corrosion. Fig.3 shows the CV profile of 5 M $\text{NH}_4\text{Cl}/\text{NH}_3$ solution at 25 °C, where the voltage was applied between Pt electrodes in the range from 0 V to 1.5 V at scan rate of 10 mV/s. The current increased from approximately 1.2 V according to the voltage increase and then reached 13.3 mA/cm^2 at 1.5 V without such a corrosion current peak observed in the case of CV with stainless steel electrodes, which indicates that the voltage to cause the corrosion of Pt electrode is higher than that of the stainless steel electrode.

Fig. 3 CV profile of 5M $\text{NH}_4\text{Cl}/\text{NH}_3$ solution at 25°C with Pt electrodes. The voltage was applied in the range from 0 V to 1.5 V range at scan rate of 10 mV/s.

Then, chronoamperometry of $\text{NH}_4\text{Cl}/\text{NH}_3$ solution with Pt electrodes was performed to demonstrate the feasibility of high compressed H_2 production by NH_3 electrolysis. According to Nernst's equation (eq. 4), the maximum pressure of produced H_2 can basically reach to more than 80 MPa even if only 0.153 V is applied for the electrolysis (the calculation details are described in the supporting information). In practice, however, much higher voltage than that is needed to perform the electrolysis at certain reaction rate due to its overpotential. In this experiment, the electrolysis voltage was set to 2 V with consideration for the result of the CV as shown in Fig. 3 to produce high compressed hydrogen in realistic time scale. Fig.4 shows the chronoamperometry profile of 5 M $\text{NH}_4\text{Cl}/\text{NH}_3$ solution at 25 °C and the variation of the inner pressure, where constant voltage of 2 V was applied for 48 h. The inner pressure increased almost constantly and successfully reached 20 MPa. Besides, the generated gas was analyzed by GC and turned out to be a mixture gas of H_2 and N_2 as shown in the inset in Fig.4. Thus, it was experimentally indicated that compressed hydrogen can be produced by NH_3 electrolysis without a mechanical compressor apparatus. Nevertheless, electrode corrosion seemed to occur despite the use of Pt electrode given from the chronoamperometry profile. Namely, the current decreased gradually from 20 h and was not observed at the end of the experiment, which would be attributed to both of a consumption of NH_4Cl and a decrease of the electrode material. In fact, mole ratio of generated H_2 and N_2 was estimated to be not 3/1 but 3/0.85 from the peak areas of the GC profiles, indicating that the immersed part of anode electrode was corroded as similarly shown in the case of the NH_3 electrolysis with stainless electrodes, and therefore NH_4^+ was consumed due to the electrode corrosion.

Fig. 4 Chronoamperometry profile of 5M $\text{NH}_4\text{Cl}/\text{NH}_3$ solution at 25°C with Pt electrodes and the variation of the inner pressure during the electrolysis. Constant voltage of 2 V was applied between the electrodes. The inset shows GC profile of the generated gas during the chronoamperometry.

Thus, XRD measurement for the electrolyte powder after the electrolysis was performed. As a result, a diffraction pattern of unknown phase was observed with that of NH_4Cl and corresponded to that of product after the reaction of commercial PtCl_4 with liquid NH_3 (Fig. S3). Besides, as the most decisive evidence, it was confirmed that immersed part of anode electrode entirely disappeared (Fig. S4). It is therefore considered that Pt electrode is corroded during the NH_3 electrolysis with NH_4Cl electrolyte even if Pt shows low ionization tendency. The

oxidation-reduction reaction and the total reaction associated with the anode corrosion are expressed as follows,

Herein, it was reported that NH_3 electrolysis with MNH_2 electrolyte and Pt electrodes proceeded without such an electrode corrosion, where the mole ratio of generated H_2/N_2 was estimated to be 3/1 from the GC profile, that is, the electrode corrosion proceeds more heavily by using NH_4Cl than MNH_2 [18]. This behavior would be analogous to a metal corrosion in an aqueous solution, where it is well known that the corrosion is promoted by increasing the concentration of proton H^+ . Thus, it is considered that $\text{NH}_4^+/\text{NH}_3$ solution would act like as an acid solution, resulting the heavy electrode corrosion.

4 Conclusions

In this work, NH_3 electrolysis with NH_4Cl as an electrolyte to give NH_4^+ was investigated. As a result, a certain current density of 70 mA/cm^2 at 2.0 V and generation of mixture gas of H_2/N_2 was confirmed, indicating that NH_4Cl can work as an electrolyte for NH_3 electrolysis. Besides, high compressed hydrogen production of 20 MPa by NH_3 electrolysis was successfully demonstrated. Recently, the hydrogen pressure supplied to a fuel cell vehicle is required to be more than 80 MPa , therefore, an efficient way to produce high compressed hydrogen should be developed. It is considered that NH_3 electrolysis is one of the most promising way, because high compressed hydrogen can be produced electrochemically without mechanical drive which make the system high cost due to the hydrogen embrittlement. However, there are still several problems to resolve for NH_3 electrolysis from the perspective of the practical use. For example, the overpotential of the NH_3 electrolysis was still significant. Therefore, a novel electrolyte and electrode should be developed to decrease the overpotential. Besides, the electrode corrosion should be taken into the consideration. Namely, it was indicated that a metal on the anode is oxidized and combine with the counter anion of the electrolyte in liquid NH_3 , resulting the electrode corrosion on anode as shown in this work. Therefore, an appropriate combination of the elements in an electrolyte and an electrode should be chosen not to produce such a stable product like MCl_x in liquid NH_3 to avoid the electrode corrosion.

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