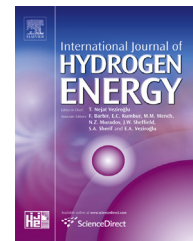




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Short Communication

High compressed hydrogen production via direct electrolysis of liquid ammonia

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ARTICLE INFO

Article history:

Received 1 April 2016

Received in revised form

9 June 2016

Accepted 13 June 2016

Available online 14 July 2016

Keywords:

Hydrogen carrier

Ammonia

Electrolysis

High compressed hydrogen production

ABSTRACT

In this study, the direct electrolysis of liquid ammonia (NH₃) by using ammonium chloride (NH₄Cl) as an electrolyte to supply ammonium cation (NH₄⁺) 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 NH₄Cl can work as an electrolyte for the electrolysis of liquid ammonia. Furthermore, generation of high compressed hydrogen by NH₃ 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 (MCl_x) instead of the primary oxidation reaction for the electrolysis of ammonia.

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Introduction

To realize a sustainable society by hydrogen H₂ energy, it is essential to develop a high density storage and a

transportation method for H₂. Although H₂ has the high gravimetric energy density, the volumetric energy density is much smaller than that of gasoline even though H₂ is compressed to high pressure. Thus, it is considered to be difficult

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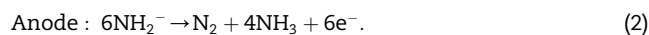
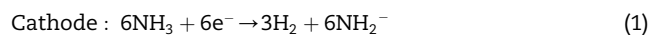
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<http://dx.doi.org/10.1016/j.ijhydene.2016.06.137>

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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 MNH₂ (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 NH₂[−] is electrically oxidized, generating nitrogen N₂ on the anode. Meanwhile, NH₃ is electrically reduced, generating H₂ and NH₂[−] on the cathode. Thus, the above redox reactions totally lead to decomposition of NH₃ to generate H₂ and N₂. In this study, the direct electrolysis of liquid NH₃ with another supporting electrolyte is investigated as a basic research. Thus, ammonium chloride NH₄Cl which is considered to be a more manageable material than MNH₂ is used as an electrolyte to supply ammonium cation NH₄⁺ instead of NH₂[−] treated in the previous study. Besides, generation of high compressed hydrogen by the NH₃ electrolysis is attempted to demonstrate its feasibility in terms of practical use.

Experimental section

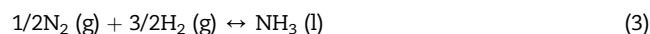
NH₄Cl (99.5%, Aldrich) and NH₃ (99.999%) were used for the investigation of NH₃ electrolysis in this work. A pressure-tight and transparent container (Hiper Glass Cylinder HPG-96-1, Taiatsu Techno Co) was used to confirm the solubility of NH₄Cl in liquid NH₃. NH₃ electrolysis was performed by using a Bi-polar cell composed of a stainless steel container and stainless steel electrodes (H450 mm × W520 mm × T1.5 mm) or platinum Pt electrodes (H20 mm × W20 mm × T0.2 mm), which was designed to have 30 MPa pressure resistance and airtightness. NH₄Cl 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 NH₃ was introduced in the cell to prepare 5 M NH₄Cl/

NH₃ solution, where lower half part of the electrodes were set to be immersed in the solution (Fig. S1). Electrochemical properties of NH₃ 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, CuKα radiation).

Results and discussion

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,



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

In the equation (Eq. (4)), F, R, ΔG°, T, P_{H₂}, and P_{N₂} 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° is expressed by the standard enthalpy change of reaction ΔH°, the standard entropy change of reaction ΔS°, and temperature T as follows,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

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

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



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

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

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