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Liquid ammonia electrolysis by platinum electrodes

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ABSTRACT

Liquid ammonia was electrolyzed based on a new concept by using metal amide as the supporting electrolyte for generation of hydrogen. Different metal amides including $LiNH_2$, $NaNH_2$ and KNH_2 were tested, and the influences of the solubility and the concentration of different electrolytes upon the electrolysis current were investigated. Electrolysis efficiency was evaluated on the basis of chronopotentiometry tests at different current densities. Platinized platinum electrodes with fine structure were introduced in order to improve the electrolysis current and reduce the electrolysis potential.

1. Introduction

Hydrogen is regarded as the secondary energy source to generate energy by fuel cells or combustion engines, and it can be produced from renewable energy sources (e.g. solar energy, wind or hydropower energy). However, the lack of practical storage methods has limited its use to such an extent that hydrogen storage is currently a crucial barrier in the development of a hydrogen economy. To be lightweight and compact are the main challenges for hydrogen storing system, particularly for mobile applications [1–3].

Liquid ammonia (NH_3) has a high hydrogen capacity of 17.76 mass% and it is easily liquefied by compression under 1.0 MPa at ambient temperature. In addition, the use of liquid ammonia as a hydrogen provider appears to be a better choice for the generation of CO_x-free hydrogen. Kojima et al. have reported that NH_3 gas reacts with alkali metal hydrides (LiH, NaH and KH) in an exothermic reaction to release hydrogen at room temperature, as a result that alkali metal amides are formed as by-products [4,5]. Mechanochemical decomposition of NH_3 into hydrogen (H_2) and nitrogen (N_2) at room temperature has been reported. However, the reaction yield was still quite low over some active perovskite catalysts ($SrTiO_3$ and $BaTiO_3$) [6]. Furthermore, thermal decomposition of NH_3 into hydrogen and nitrogen has been extensively studied for several decades. However, so far a reaction temperature higher than 673 K was still required for satisfactory activity over some active metal catalysts (Ru, Rh, Pt, Pd, Ni, Fe) [7,8].

Botte et al. have built hydrogen generators using an ammonia alkaline solution electrolytic cell for the production of hydrogen. In their electrolytic cell, ammonia is oxidized in the presence of OH^- at the anode compartment while water is reduced in the alkaline medium at the cathode part [9–11]. Their work got achievement for the treatment of wasted water containing ammonia with power cogeneration. However, the high 'hydrogen density' in ammonia was not exerted completely. Therefore, the development of an actual liquid ammonia electrolytic cell is quite interesting and important to realize the ideal of ammonia to be a hydrogen carrier.

In this study, we present a research on the electrolysis of liquid ammonia based on a new concept by using metal amide as the supporting electrolyte for generation of hydrogen. Different metal amides of $LiNH_2$, $NaNH_2$ and KNH_2 were tested. The influences of the solubility and the concentration of different electrolytes upon the electrolysis current were investigated. Electrolysis efficiency was evaluated on the basis of chronopotentiometry tests at different current densities. In order to improve the electrolysis current and reduce the electrolysis potential, platinized platinum electrodes with fine structure were introduced into the metal amide/liquid NH_3 system.

2. Experimental

2.1. Experimental setup and procedure

A stainless steel two-electrode electrolytic cell (ca. 35 mL) was designed for the purpose of electrolysis of liquid ammonia with shiny Pt-foil acting as normal electrode [12]. The shiny Pt-foil (20 mm × 20 mm) electrodes with very smooth surface were purchased from Nilaco Corporation. About 12 mL of liquid ammonia was imported into the cell with about 0.95 MPa saturated vapor pressure at 298 K. The surfaces of the two-electrodes were set parallel to each other at a gap separation of 10 mm. The immersed part in the liquid ammonia solution was 10 mm × 20 mm.

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A SP-150 potentiostat (Bio-logic, France) was used for the electrochemical studies. Electrolysis current and electrolysis efficiency were evaluated by the characterization of cyclic voltammetry (CV) and chronopotentiometry (CP). Gas chromatography (GC-14B, SHIMADZU) was performed equipped with Shincarbon ST MicroPacked column. Additional characterization of the electrodeposit was obtained with scanning electron microscopy (SEM) (JSM-6380, JEOL DATUM LTD).

2.2. Materials and electrode preparation

Lithium amide ($LiNH_2$, 95%) and sodium amide ($NaNH_2$, 95%) were purchased from Aldrich Co. Ltd. Potassium amide (KNH_2) was synthesized from KH (dispersion in mineral oil, Aldrich) and NH_3 (99.999%). All the samples were handled in a glove box (Miwa MFG, MP-P60W) filled with a purified Ar (>99.9999%) to avoid an oxidation and hydration due to water.

The platinization of the Pt-foil was obtained from the following procedure: a solution of 0.072 M (3.5%) chloroplatinic acid plus 1.3×10^{-4} M (0.005%) lead nitrate, at a current density of 30 mA cm^{-2} for up to 10 min.

3. Results and discussion

3.1. The principle of liquid ammonia electrolytic cell

Liquid ammonia dissociates to ammonium ion (NH_4^+) and amide ion (NH_2^-) (Eq. (1)).

$$NH_3(l) \leftrightarrow 1/2NH_4^+ + 1/2NH_2^-,$$

$$K_{eq} = [NH_4^+][NH_2^-] = 10^{-33}(223\,K) \tag{1}$$

By supplying amide ions from metal amide electrolyte, the electrolysis of liquid ammonia is expected to happen. At the cathode, hydrogen molecules are electrochemically generated by the ammonia reduction reaction (Eq. (2)), while at the anode, nitrogen molecules are produced through the oxidation reaction of amide ions (Eq. (3)). As an overall reaction, liquid ammonia is electrochemically decomposed with the generation of hydrogen and nitrogen (Eq. (4)).

$$3NH_3 + 3e^- \rightarrow 3/2H_2 + 3NH_2^- \tag{2}$$

$$3NH_2^- \rightarrow 1/2N_2 + 2NH_3 + 3e^- \tag{3}$$

$$NH_3(l) \rightarrow 1/2N_2(g) + 3/2H_2(g) \tag{4}$$

Theoretically, the electrolysis voltage of liquid ammonia at 298 K corresponding to Eq. (4) is estimated according to Nernst's equation,

$$E = -\frac{\Delta G^0}{3F} + RT\frac{\ln(p_{N_2}{}^{1/2}p_{H_2}{}^{3/2})}{3F} \tag{5}$$

where F is the Faraday constant and R is gas constant. Standard Gibbs free energy change (ΔG^0) of reaction is −10.984 kJ/mol NH_3 [13], leading to 0.038 V. Because ammonia shows much higher saturated pressure at 298 K, being 0.99 MPa [16], hydrogen pressure (p_{H_2}) and nitrogen pressure (p_{N_2}) should be considered in the Nernst's equation. 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. Therefore, the ammonia electrolysis voltage is determined to be 0.077 V. This means that the electrolysis of liquid ammonia requires 94% lower energy than a water electrolysis whose theoretical electrolysis voltage is 1.23 V.

3.2. Influence of different electrolytes and the concentration on the electrolysis current

Fig. 1 shows cyclic voltammetry curves of liquid ammonia (liq. NH_3) containing 1 M MNH_2 (M = Li, Na and K) in the two-electrode system. For liq. NH_3 with 1 M KNH_2, the current density shows ca. 1 mA/cm^2 at 1.1 V and increases to 13 mA/cm^2 with increasing the cell voltage to 2.0 V, which corresponds to the electrolysis of liq. NH_3 as described in Eqs. (2) and (3). The current densities at 2 V for liq. NH_3 with 1 M $LiNH_2$ and $NaNH_2$ are less than one twentieth of that for liq. NH_3 with 1 M KNH_2. As shown in Fig. 1, current density of 1 M $NaNH_2$ shows a little better than that of $LiNH_2$. Therefore, the current density corresponding to a voltage efficiency depends on the cation of metal amides as following tendency, $LiNH_2 < NaNH_2 < KNH_2$. As a matter of fact, the tendency is related to the solubility of metal amide in liq. NH_3, which is insoluble, 0.026 mol/L and very soluble for $LiNH_2$, $NaNH_2$ and KNH_2, respectively [17]. Thus, the voltage efficiency of ammonia electrolysis depends on the concentration of NH_2^- ion in liq. NH_3. In order to increase the concentration of NH_2^- ion, 5 M KNH_2 in liq. NH_3 was tested. As shown in Fig. 1, the current density of 1 mA/cm^2 was observed at lower voltage of 0.7 V compared to that of 1 M KNH_2. Then, it reaches 49 mA/cm^2 at 2.0 V, which is about 4 times larger than that of 1 M KNH_2. This result indicates that the increase of the concentration of NH_2^- ion leads to a high voltage efficiency for the electrolysis of liq. NH_3.

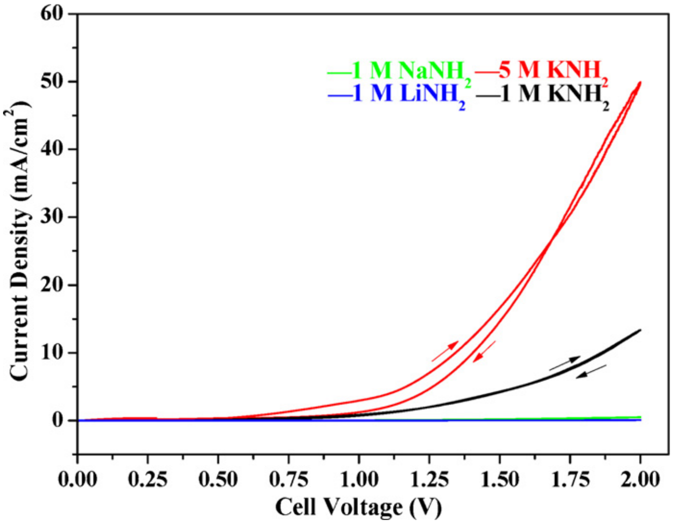

Fig. 1. Cyclic voltammetry (CV) curves of liquid ammonia with 1 M $LiNH_2$ and $NaNH_2$, 1 M and 5 M KNH_2.

3.3. Electrolysis efficiency and gas production analysis

To quantify the averaged current efficiency of the ammonia electrolysis, liq. NH_3 with 1 M KNH_2 and 6 M KNH_2 were kept at constant current densities of 5 mA/cm^2 and 60 mA/cm^2 for 4 h and 1.5 h, respectively. Fig. 2 shows the plots of chronopotentiometry and cell pressure change versus time at corresponding current density. At lower current density of 5 mA/cm^2 (Fig. 2a), the cell potential maintains around 1.3 V and 1.1 V for 1 M and 6 M KNH_2/liq. NH_3, respectively. The cell pressure for both cases starts around 0.945 MPa, which corresponds to the vapor pressure of NH_3 at 25 °C (Fig. 2b). As seen in Fig. 2b, the slopes of the pressure-change plots could represent the extent of pressure change, which show sharp increase in the initial 30 min and a slightly lower increase in the following 3.5 h for both cases. However, cell pressure changes for these two systems are almost the same after four hours electrolysis with $\Delta p = 0.191$ MPa. Supposing the vapor pressure of ammonia gas is not affected by the mixed gases in the cell and it does not change during the electrolysis, as a result, the cell pressure change is only caused by the generated hydrogen and nitrogen. We can calculate the total molar amount of the released hydrogen and nitrogen gases which is 1.77×10^{-3} mol. According to the Faraday's law of electrolysis ($Q = I \times t = n(e) \times F$, Q = quantity of electricity (C), I = current in amps (A), t = time (s), $n(e)$ = moles of electrons, F = Faraday constant = 96,500 C mol^{-1}), the applied electricity of 288 C (0.02 A × 3600 × 4 s) would release 1.4922×10^{-3} mol hydro-

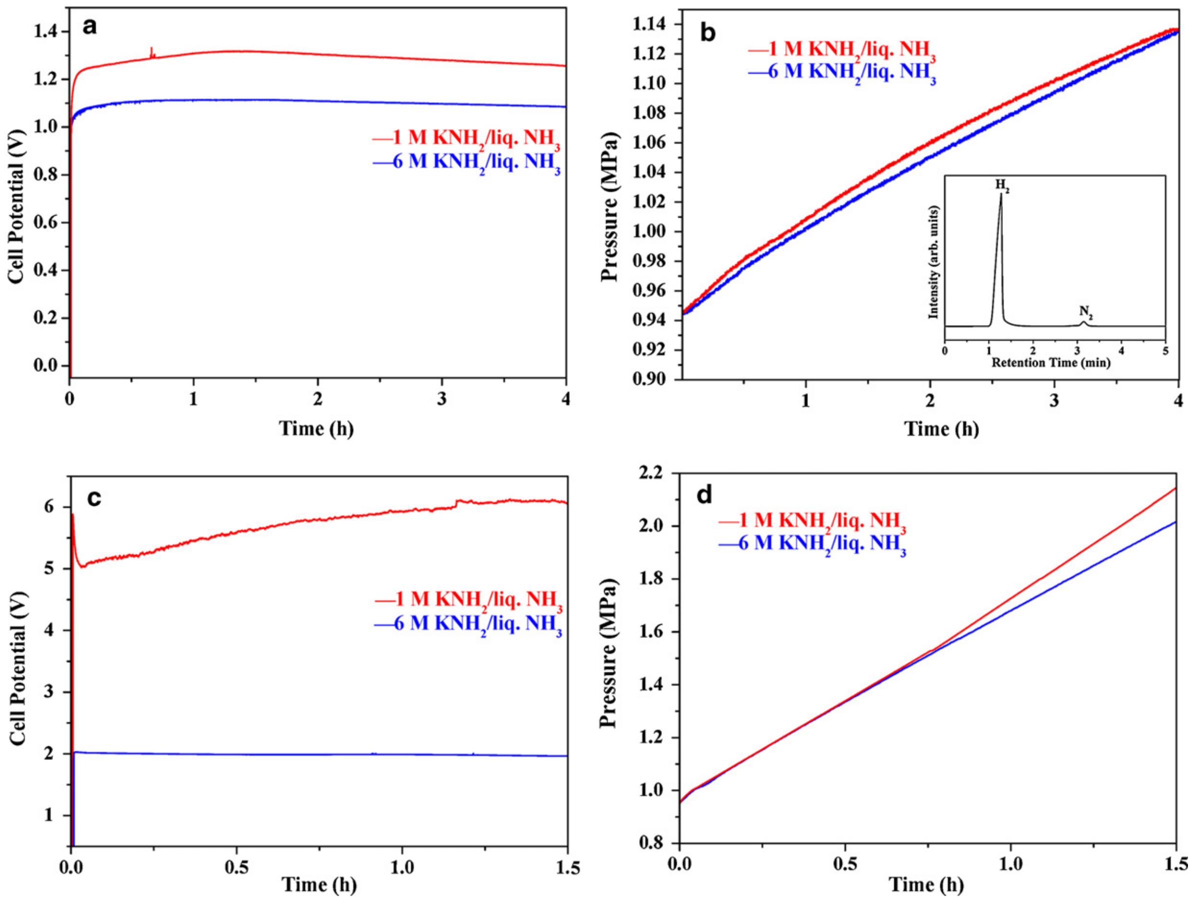

Fig. 2. Illustration of the plots of chronopotentiometry and cell pressure changes versus time at current density of 5 mA/cm^2 for 4 h (a and b) and 60 mA/cm^2 for 1.5 h (c and d) for liquid ammonia with 1 M and 6 M KNH$_2$. The inserted figure shows the GC profile for the generated hydrogen and nitrogen after the CP measurement.

gen and 4.974×10^{-4} mol nitrogen at the ideal condition. Thus, the current efficiency (Faradic efficiency) calculated based on the cell pressure change for both cases are 88.9%. However, as is well known, such result overestimated the real current efficiency as some electric energy will transfer to heat which results in the increase of the pressure of ammonia.

In order to get precise result, after 4 h electrolysis, part of the gas in the cell was analyzed by gas chromatography (GC). The peaks of hydrogen and nitrogen were observed with the retention times around 1.3 min and 3.1 min, respectively, as shown in the inserted figure in Fig. 2b. The molar percentage of hydrogen and nitrogen is 7.31 ± 0.06% and 2.26 ± 0.06% for 1 M KNH$_2$/liq. NH$_3$ and 7.08 ± 0.03% and 2.14 ± 0.07% for 6 M KNH$_2$/liq. NH$_3$ by quantifying the peak areas of hydrogen and nitrogen signals. As a result, the corresponding molar ratios of H$_2$ to N$_2$ are 3.23 ± 0.08% and 3.26 ± 0.05%, which agrees with the decomposition ratio of H_2:N_2 = 3:1 as shown in Eq. (3). Based on the GC results, the current efficiency is 51.95% and 48.60% for 1 M and 6 M KNH$_2$/liq. NH$_3$, respectively.

If keeping the current density at 60 mA/cm^2 for 1.5 h, the cell potential for 1 M KNH$_2$/liq. NH$_3$ shows overshoot at the beginning and then gradually increases from 5.0 V to 6.0 V. While in the case of 6 M KNH$_2$, the potential maintains at 2.0 V constantly during the electrolysis period, as shown in Fig. 2c. The slopes of the pressure-change plots for them keep synchronously in the first 1 h and show obvious difference in the following 30 min (Fig. 2d). The cell pressure changes for 1 M and 6 M are 1.185 MPa and 1.060 MPa, respectively. Since the applied electricity 1296 C (0.24 A × 3600 × 1.5 s) during this period would release 6.715×10^{-3} mol hydrogen and 2.2383×10^{-3} mol nitrogen, on the basis of the pressure change, the current efficiencies were estimated to be 122.2% and 109.3% for 1 M and 6 M, respectively. This overestimation is caused by an increase of the internal temperature of the cell inside as indicated above. However, the GC analyses show the molar percentage of hydrogen and nitrogen are 32.4 ± 0.7% and 11.3 ± 0.3%, respectively, for 1 M KNH$_2$, and 27.0 ± 0.6% and 9.0 ± 0.3%, respectively, for 6 M KNH$_2$. The current efficiencies for these two cases are 96.9% and 84.2%, respectively, with the molar ratio of H$_2$ to N$_2$ are 2.87 ± 0.09% and 2.98 ± 0.06%, respectively.

The aforementioned shows clearly that current density has a great effect on the current efficiency in our system. The lower current efficiency at low current density might be caused by a current loss during the electrolysis, which could be ascribed to the conductive metallic cell. Moreover, it further proves that the concentration of the electrolyte plays a crucial role in the voltage efficiency. Obviously, higher concentration of the electrolyte helps to decrease and stabilize the cell potential. On the other hand, the decrease of the voltage plays a negative role in the current efficiency which shows the dependence of the current efficiency on the cell voltage.

3.4. Influence of electrode surface area on the electrolysis current

As is well known, the platinum group metals are effective catalysts for some gas-involved electrochemical reactions. Clearly, the rate at which the reaction happens will be proportional to the area of the electrode. However, the geometrical surface area (length × width) of the electrode is not the only issue because the geometrical surface area cannot be increased unlimitedly. Platinum black is widely used as a thin film covering solid platinum metal, forming platinum electrodes for applications in electrochemistry.

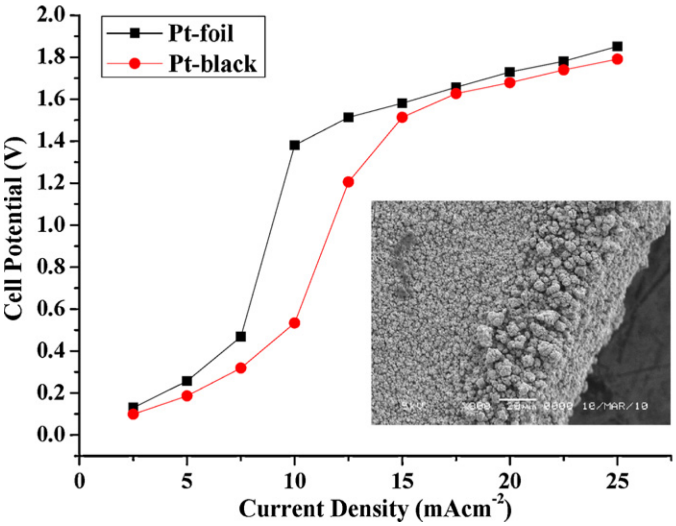

Fig. 3. Polarization curves for the electrolytic cell in 1 M KNH_2/liq. NH_3 using shiny platinum electrodes and Pt-black electrodes. The inserted figure shows the SEM image of the Pt-black electrode.

The process of covering platinum electrodes with such a layer of platinum black is called “platinization of platinum” [18]. The platinized platinum has a true surface area much higher than the geometrical surface area of the electrode and, therefore, exhibits catalytic action superior to that of shiny platinum. In context, Pt-black was introduced into the 1 M KNH_2/liq. NH_3 system. SEM image of the Pt-black electrode (as shown in the inserted figure in Fig. 3) confirmed that uniform Pt clusters with fine structure are attached on the Pt-foil with the size of the cluster lower than 5 μm. The polarization curves for the electrolytic cell in 1 M KNH_2/liq. NH_3 using shiny platinum electrodes and Pt-black electrodes are shown in Fig. 3. The result displays that with the employment of Pt-black electrode, the cell potential could be reduced.

4. Summary

The electrolysis of liquid ammonia has been performed successfully by using metal amides as the supporting electrolytes. The voltage efficiency which is related to the energy utilization shows great dependence on the solubility and the concentration of the metal amide in liquid ammonia. The current density affects the current efficiency, and thus the voltage efficiency. The introduction of platinized platinum electrodes proves that it is possible to reduce the cell voltage by improving the surface area of the electrode. Although progress has been made toward the electrolysis of liquid ammonia, there still has been a long way to go for this promising subject, which is based on the following considerations: (i) large overpotentials of more than 0.5 V exist for the electrolysis of liquid ammonia in spite of low theoretical electrolysis voltage, 0.077 V; (ii) the negative effect of ammonia on the performance of the electrode catalyst was recognized for at least PEMFC [19–21]. Taking these problems into account, the choice of catalyst, which should further decrease the overpotentials and withstand the attack of ammonia as far as possible, therefore becomes a critical issue. Further works for the performance of composite alloy catalysts such as Pt–Ru, Pt–Ir, Pt–Rh on the electrolysis of liquid ammonia are necessary.

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