

RAPID COMMUNICATION

Electrochemical synthesis of ammonia from water and nitrogen catalyzed by nano- Fe_2O_3 and CoFe_2O_4 suspended in a molten LiCl-KCl-CsCl electrolyte

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(Received 28 December 2015 • accepted 19 March 2016)

Abstract—Nano- Fe_2O_3 and CoFe_2O_4 were suspended in molten salt of alkali-metal chloride (LiCl-KCl-CsCl) and their catalytic activity in electrochemical ammonia synthesis was evaluated from potentiostatic electrolysis at 600 K. The presence of nanoparticle suspension in the molten chloride resulted in improved production of NH_3 , recording NH_3 synthesis rate of $1.78 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$ and $3.00 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$ with CoFe_2O_4 and Fe_2O_3 , which are 102% and 240% higher than that without the use of a nanocatalyst, respectively. We speculated that the nanoparticles triggered both the electrochemical reduction of nitrogen and also chemical reaction between nitrogen and hydrogen that was produced from water electro-reduction on cathode. The use of nanocatalysts in the form of suspension offers an effective way to overcome the sluggish nature of nitrogen reduction in the molten chloride electrolyte.

Keywords: Ammonia, Electrochemical Reduction, Molten Salt, Nano-catalysts

INTRODUCTION

Ammonia (NH_3) is an important fertilizer and nitrogen precursor. This essential substance, currently the second most produced chemical on this planet [1], has also been regarded as a green energy carrier; when compared to the conventional energy carrier, hydrogen, storage and transportation are far cheaper and easier [1]. Its production is primarily done by a process termed the Haber-Bosch (H.B.) process, which converts more than 120 million tons of nitrogen (N_2) to NH_3 every year [2]. This old and mature technology, however, is energy-intensive *per se*: very high temperature ($\sim 500^\circ\text{C}$) and pressure (~ 200 bar) are required even in the presence of potent catalysts, resulting in the consumption of over 30 GJ per ton of NH_3 produced [3-5]. Besides, one of reactants hydrogen is prepared via the steam reforming of natural gas, and as a result a massive amount of CO_2 is emitted: 1.87 ton CO_2 is released per ton of NH_3 produced [6], suggesting the product is not at all a green carrier after all. Accordingly, it is of great importance to develop an alternative with the nature of true sustainability.

Electrochemical NH_3 synthesis is one such candidate: it is estimated to be able to reduce the total energy consumption (over 20% compared to the H.B. process) and yet allows to avoid immediate carbon emission [1,6]. If electricity is provided from renewable sources especially on a commercial scale, in particular, this electrochemical way has a great potential to position NH_3 to act as a workable green energy carrier [6].

Among electrochemical platforms explored thus far, molten alkali-metal chloride (i.e., LiCl-KCl-CsCl)-based electrolyte has drawn

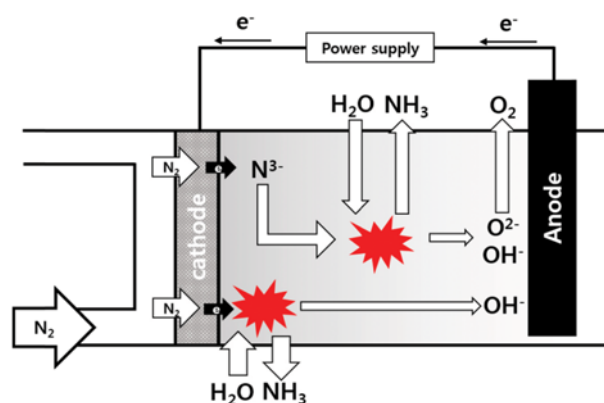


Fig. 1. The principle of electrochemical synthesis of NH_3 from water and N_2 in LiCl-KCl-CsCl molten salt (Ref. [8]). Reactions that are likely to happen are stated.

continuous attention owing to its high ionic conductivity, thermodynamic stability, wide electrochemical window, and low vapor pressure [7,8]. Using this electrolyte, Murakami and others investigated NH_3 synthesis from N_2 and various hydrogen sources (H_2 , H_2O , CH_4 , H_2S , and HCl) at ambient pressure, and the underlying principles are rather well stated in the previous publications as well as in Fig. 1 [9-14]. This molten chloride-based NH_3 electro-synthesis, however, is still far from being commercially viable. One critical barrier is the sluggish reduction of N_2 due to the extremely strong triple bond between N atoms (941 kJ mol^{-1}) [6,15]. Our aim, therefore, was to speed up this rate-limited step, especially by including mediators in the form of nanoparticles suspended in the molten liquid electrolyte.

Licht et al. attempted to use iron oxide (Fe_2O_3) nanoparticles as a suspended catalyst for NH_3 synthesis in their molten hydroxide

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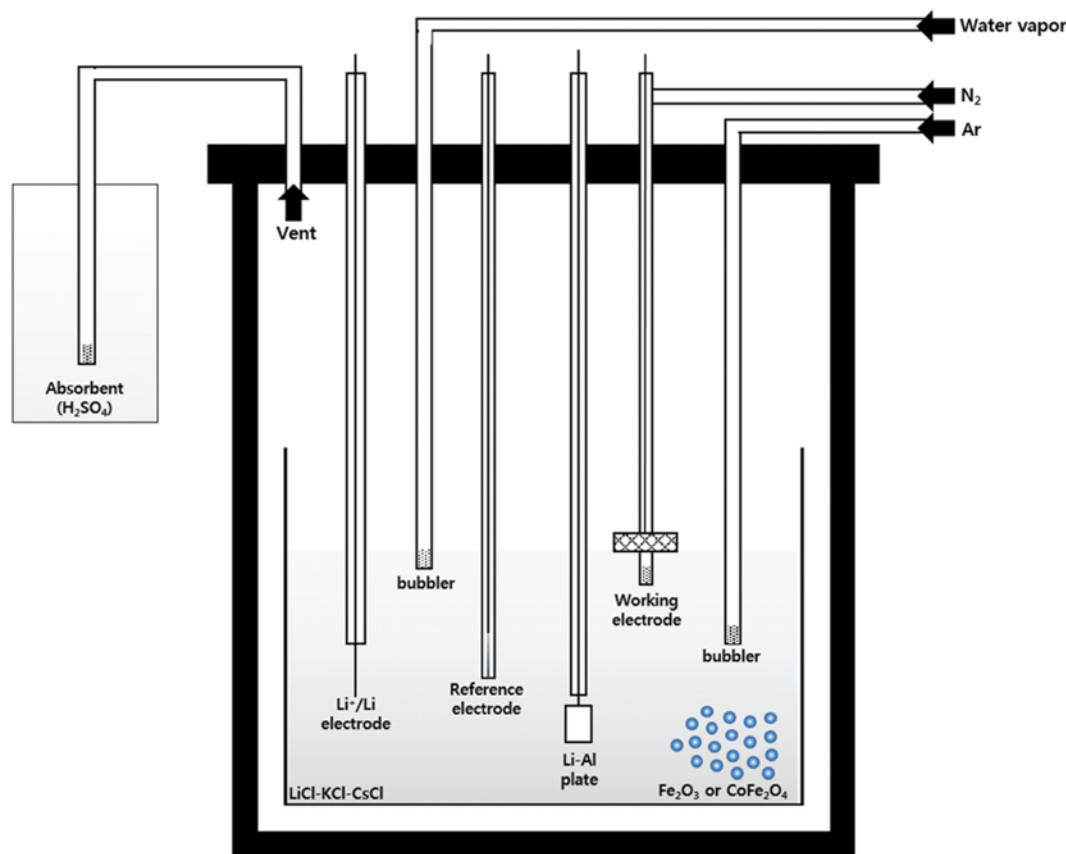


Fig. 2. A schematic representation of experimental apparatus.

electrolyte (NaOH-KOH) [2], and in an ensuing study, detailed mechanisms were speculated [16]. In this study, CoFe_2O_4 as well as Fe_2O_3 nanoparticles were suspended in the molten LiCl-KCl-CsCl electrolyte and employed as nanocatalysts for electrochemical NH_3 synthesis.

MATERIALS AND METHODS

Fig. 2 shows a schematic illustration of the experimental apparatus. All experiments were carried out in argon (Ar) only atmosphere [17]. Reagent grade LiCl, KCl, and CsCl were purchased from Sigma Aldrich. Their mixture (LiCl:KCl:CsCl=57.5:13.3:29.2 mol%, [9-14]) was prepared in an Ar-filled glove box and then dried under vacuum at least for 24 h at 373 K to remove moisture. The eutectic mixture was melted at around 600 K in a furnace, followed by a treatment with diluted HCl gas (HCl:Ar=1:99) for 8 h to prevent hydrolytic decomposition of molten chloride [18]. The temperature was kept at 600 K throughout the experiment. The working electrode, which acted to reduce N_2 , consisted of porous Ni ($\varnothing 4.5 \text{ cm} \times 1 \text{ cm}$, specific surface area: $1,000 \text{ m}^2 \text{ m}^{-3}$). Before NH_3 synthesis, 0.3 V (vs. Li^+/Li) was applied on the working electrode overnight to reduce oxide films on its surface. The counter electrode was Li-Al alloy in the ($\alpha+\beta$) coexisting phase state [9,19]. Ag^+/Ag was used as the reference electrode in another LiCl-KCl-CsCl eutectic melt. All potentials in this study were referenced to an Li^+/Li electrode.

Fe_2O_3 (Sigma Aldrich, A_{BET} : $35.42 \text{ m}^2 \text{ g}^{-1}$) and CoFe_2O_4 (Sigma Aldrich, A_{BET} : $57.14 \text{ m}^2 \text{ g}^{-1}$), used as nanocatalysts in this study, were suspended in the molten salt. Considering A_{BET} values, an appropriate amount of each nanocatalyst was added to the melt so that the two catalysts had the same total area of 285.7 m^2 .

Potentiostatic electrolysis, with and without each nanocatalyst, was carried performed for 2 h by applying 0.2 V on the working electrode, which was fed with N_2 with a flow rate of 200 sccm. At the same time, water vapor was provided to the melt by flowing 50 sccm of Ar, which passed through a bath of distilled water at 303 K. The vent gas from the reactor was collected in dilute sulfuric acid (0.001 M), and NH_4^+ concentration in the absorbent was determined with an ammonia meter (Palintest 1000, Nessler's method). The current efficiency for synthesized NH_3 was defined as the charge used for NH_3 synthesis divided by total charge passed through the electrolytic cell.

RESULTS AND DISCUSSION

Potentiostatic electrolysis was done for 2 h, with and without each nano-catalyst, by applying 0.2 V on the working electrode. This potential level was expected to ensure a reducing environment enough to form nitride (N^{3-}) [15,20], a highly reduced monoatomic anion that instantaneously and spontaneously reacts with water to form NH_3 [10,11]. The current densities at plateau during the electrolysis were -13 mA cm^{-2} , -17 mA cm^{-2} , and -22 mA cm^{-2} .

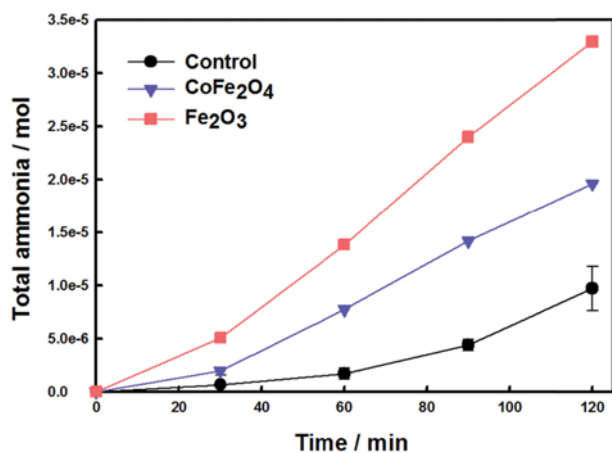


Fig. 3. Cumulative production of NH₃ for 2 h during potentiostatic electrolysis with and without nano-catalysts suspended in the molten salt (working electrode potential: 0.2 V vs. Li⁺/Li, N₂ flow rate: 200 sccm, temperature: 600 K).

for control (no nano-catalyst), CoFe₂O₄, and Fe₂O₃, respectively. The increase in the overall current density in the presence of nano-catalysts was attributable partially to marginal yet discernible dendritic deposition of Fe or Co on the working electrode [21–23]. In addition, enhanced electrochemical N₂ reduction catalyzed by nano-catalysts seemed to be another important cause of the increase, as discussed later.

Fig. 3 shows cumulative NH₃ production during the potentiostatic electrolysis with and without nanocatalysts. Clearly, the presence of nano-catalysts did enhance NH₃ synthesis all the time; and Fe₂O₃ was more active than CoFe₂O₄. The total NH₃ production for 2 h was 9.71×10^{-6} mol, 1.96×10^{-5} mol, and 3.30×10^{-5} mol for control, CoFe₂O₄, and Fe₂O₃, which corresponded to NH₃ synthesis rates of 8.83×10^{-11} mol s⁻¹ cm⁻², 1.78×10^{-10} mol s⁻¹ cm⁻², and 3.00×10^{-10} mol s⁻¹ cm⁻², respectively. This NH₃ yield in the order of Fe₂O₃ > CoFe₂O₄ > control accorded with the trend in the magnitude of the current densities. This suggested that the increase in current density, which in turn indicated enhanced electrochemical reaction, was the major contributor of improved NH₃ production in the presence of nanoparticles. Unfortunately, however, the corresponding current efficiencies were rather poor: 0.18%, 0.14%, and 0.17% for control, CoFe₂O₄, and Fe₂O₃, respectively, mainly owing to H₂ evolution from water electro-reduction. Slightly lower current efficiencies in the presence of nanocatalyst suspensions were observed, presumably because some of electrons were diverted to dendritic Fe or Co deposition on the working electrode [21–23].

Fig. 4 illustrates the schematic cross-sections of the reaction sites on the working electrode. In the absence of nanocatalysts, the surface of Ni working electrode (a) is the only available site where any reaction occurs. In the presence of nanoparticles suspended in molten chloride, two more sites become available to account for the catalytic role of nanocatalysts: a junction between the electrode and nanoparticles (b) and the surface of nanoparticles (c).

The junction between the electrode and nanocatalysts (b) is thought to provide excellent reaction sites where electrical conductivity and catalytic activity are both ensured [24]. In our experiment,

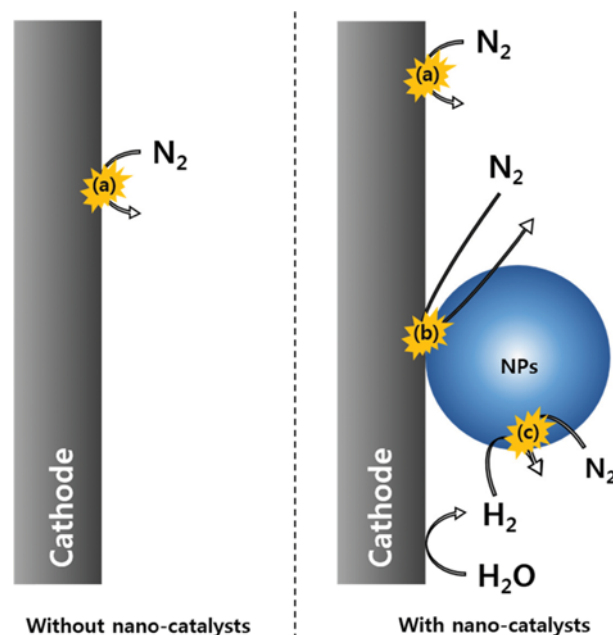


Fig. 4. Schematic cross-sections of the reaction sites on the working electrode with and without nano-catalysts.

N₂ might undergo enhanced electronation processes with the aid of nanocatalyst at this site (b), as can be inferred from the increased magnitude of current densities in the presence of nanoparticles. Recent similar studies, in fact, demonstrated the electro-catalytic activity of metal oxide suspension (especially Fe₂O₃) on the electrochemical N₂ reduction in molten hydroxide [2,16].

Another feasible mechanism is NH₃ synthesis via a chemical reaction between N₂ and H₂, which originated from the electro-reduction of water, namely H₂ evolution [2]. This route is indeed plausible in that Fe₂O₃ is a commonly used catalyst in the traditional H.B. process and its composites amended with Co have also been attempted for the improvement of catalytic activity and/or stability [25–27].

The catalytic activity of Fe₂O₃ was found to be higher than CoFe₂O₄ in terms of both current density and NH₃ yield. Their activities could also be translated into the nanoparticle-induced increment in NH₃ yield, that is, the difference in NH₃ yield with and without nanocatalysts, normalized with mass of catalyst used: 1.98×10^{-6} mol g⁻¹ and 2.89×10^{-6} mol g⁻¹ for CoFe₂O₄ and Fe₂O₃, respectively. Among a great many factors affecting catalytic performance, the Fe-Co alloy seemed to be critically dependent upon the ratio of Co to Fe for its NH₃ synthesis activity [25–27]. The incorporation of an appropriate amount of Co, e.g., a molar ratio of Co:Fe=5:95 according to Ref. [26], led to enhanced performance [26,27], and therefore the poorer performance of CoFe₂O₄ arose from the use of a suboptimal content of basically inactive component Co, as reported in previous studies [26,27].

This study, though without rigorous optimization for reactor configuration and catalyst preparation, revealed that metal oxide nanoparticles, as either primary cocatalysts or mere catalysis enhancers, can be included to increase yield and speed of electrochemical synthesis of NH₃ in molten chloride. The maximum NH₃ syn-

thesis rate in this study ($3.00 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$) using Fe_2O_3 is lower than previously reported data obtained on the basis of molten salt, LiCl-KCl-CsCl ($2.00 \times 10^{-8} \text{ mol s}^{-1} \text{ cm}^{-2}$ at 573 K) and NaOH-KOH ($1.00 \times 10^{-8} \text{ mol s}^{-1} \text{ cm}^{-2}$ at 473 K) [2,10]; and of solid electrolyte, namely, Nafion ($1.13 \times 10^{-8} \text{ mol s}^{-1} \text{ cm}^{-2}$ at 353 K) [1]. The issue of low performance of this molten-typed system is expected to further be resolved by way of not only the addition of more appropriate additives but also the continuous optimization of reactor configuration, enabling to avoid H_2 evolution and NH_3 back-oxidation on the anode. Over time, some of nanoparticles might coagulate or decompose in the form of ion, leading to dendritic deposition on the cathode [21-23], and these are related to the catalyst stability and thus must be investigated in the future.

CONCLUSIONS

Nano- Fe_2O_3 and CoFe_2O_4 were suspended in molten salt of LiCl-KCl-CsCl and their potential applicability as nanocatalysts in this molten chloride-based NH_3 electro-synthesis was investigated. Overall performance, evaluated in terms of current density and NH_3 yield during potentiostatic electrolysis, was improved in the presence of nanocatalysts, with better performance observed using Fe_2O_3 than CoFe_2O_4 . The nanocatalysts were speculated to catalyze both the electrochemical N_2 reduction and chemical reaction between N_2 and water-derived H_2 , thereby resulting in enhanced NH_3 synthesis.

ACKNOWLEDGEMENTS

This work was conducted under the framework of Research and Development Program of the Korea Institute of Energy Research (KIER) (B6-2442).

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