Electrochemical synthesis of ammonia from water and nitrogen: A Fe-mediated approach

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Abstract−Operation at mild conditions is essential for electrochemical processes enough to replace the Haber-Bosch process. Current electrochemical methods mainly rely on the synthesis of novel electro-catalysts before the operation of an electrochemical system, which burdens with extra cost, time, and the use of toxic non-green organic solvents. In this study, the zero-valent iron(Fe^0)-mediated synthesis of NH_3 was achieved at room temperature, with the active iron prepared in an on-site and continuous way. This on-site approach enabled us to remove the step of cumbersome synthesis of nano-sized electrocatalysts, thereby providing the active surface Fe for nitrogen reduction in eco-friendlier way. When a cell voltage of 4.5 was applied in the two-electrode water-based system, NH_3 was found to be synthesized, which was accompanied by the deposition of Fe on the cathode surface. Considering that iron is among the most abundant and cheapest metals, this room-temperature synthesis proof of the concept with solvent-free, in-situ deposition and its utilization as an electrochemical catalyst, once optimized, may offer an economically advantageous option.

Keywords: Ammonia, Electro-synthesis, Nitrogen, Iron Deposition

INTRODUCTION

Ammonia (NH_3), one of the most important man-made chemicals, is used mostly as a nitrogen fertilizer (about 85%) [1,2] at present; and because of the nature of high energy density and convenience of storage and transportation, it is considered as an energy or hydrogen carrier as well [3]. The current synthesis route of NH_3 is via the famous Haber-Bosch process [4]. This process entails reacting nitrogen gas with hydrogen gas at very harsh conditions of 400-600 °C and around 200 bar using costly catalysts, inevitably ending up with exceedingly high energy consumption and global house gases (GHG) emissions [5-7].

To synthesize the essential chemical in a more sustainable manner, electrochemical methods were proposed recently using molecular nitrogen and water (or molecular hydrogen), now being actively studied [8,9]. When this route is backed by renewable energy sources like solar or wind power, it can become an environmentally friendly method for NH_3 production in a true sense. In addition, there is a possibility that energy input can be getting smaller and process design easier, all of which helps to render NH_3 production economically competitive [8].

Despite this enormous potential, however, this electrochemically-mediated approach has as yet succeeded in substantiating it, mainly owing to kinetically limited slow conversion [10]. It is, of course,

possible to raise the kinetics via temperature control in a dramatic fashion; however, it does so at the expense of faraday efficiency (FE), which is an equally important parameter. At elevated temperature (e.g., T>500 °C), FE is very low, and it is so because of rapid thermal decomposition of produced NH_3. Even if an acceptable temperature range is identified, it is less likely that long-term stability of catalysts at such a harsh condition is ascertained [11]. It is this reason that an ambient temperature-based technology is needed.

Iron is a key catalyst component in the Haber-Bosch process [12-14]. Interestingly, its ionic species is a cofactor of the ammonia-synthesizing enzyme nitrogenases, indicating the possibility that it has a certain affinity towards molecular ammonia and/or molecular nitrogen. Its elemental form, or Fe^0, when present in a catalyst, has a great tendency to donate electrons [13]. The zero-valent iron, an environmentally benign material, has a property of being easily converted to ferric/ferrous ion forms due to its low standard reduction potential ($Fe^{2+}+2e^-{\rightarrow}Fe^0$, $E^0=-0.44$ V); because of its ability to easily give up electrons, iron species (mostly zero-valent) is being used to reduce and remove contaminants in ground/wastewater or chemical wastes [15-18]. In this study, therefore, the zero-valent iron, particularly prepared via electrochemical reductive deposition from ferrous ion, was explored for its potential as an electron donor and/or a catalyst for the electrochemical NH_3 synthesis (Fig. 1).

While many environmentally harmful organic solvents are used to enhance the reactivity and selectivity of nitrogen and to make catalysts with good surface morphology, the proposed water-based in-situ deposition and catalysis process in this study can eliminate the use of such harmful solvents [8,19].

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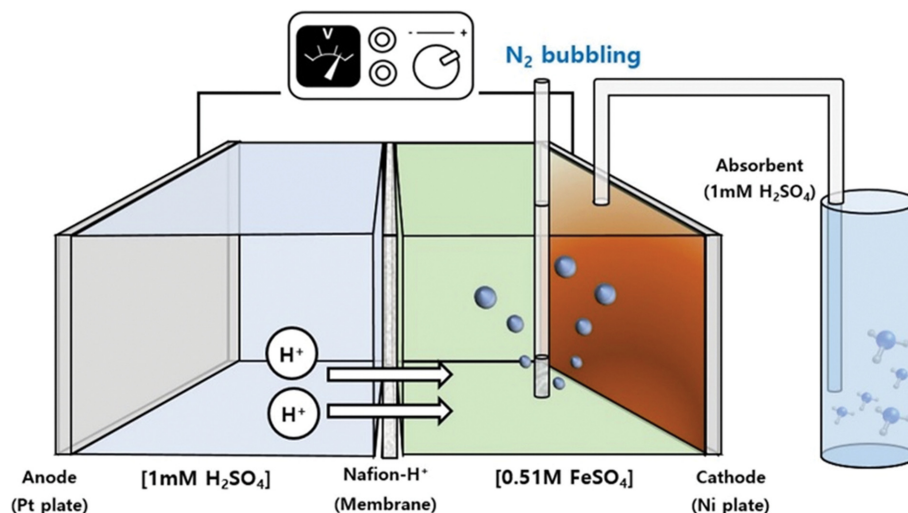E-mail: hyoon@kier.re.kr, hanj2@kaist.ac.kr

Fig. 1. A schematic diagram of iron-mediated electrochemical NH$_3$ synthesis.

MATERIALS AND METHODS

A two-chambered cell, each having a volume of 43 ml, was constructed, as shown in Fig. 1. Nickel (Ni) plate (38×40 mm^2 with thickness of 0.127 mm) was used as a cathode material and platinum (Pt) plate (38×46 mm^2) as an anode. A Nafion membrane (Nafion 117, H$^+$ pre-treated) was placed between the two plates with 1 mm of distance between the electrode and membrane.

H$_2$SO$_4$ was used as an anolyte and a hydrogen ion source (1 mM), and a solution of FeSO$_4$ as a catholyte (0.51 M). Prior to mixing of the FeSO$_4$ solution, Ar gas (pure Ar gas, 99.99%) was purged into de-ionized water at a flow rate of 100 sccm for 20 min to create an oxygen-free environment and to limit the oxidation of iron ions. Potentiostatic experiments with respect to voltage were carried out for 50 minutes using an electrochemical analyzer (CHI604C, CH Instruments).

The cell was designed in such a way that N$_2$ gas was supplied during reaction and all the produced NH$_3$ gas molecules were protonated (NH$_4^+$) and remained in the absorbent (1 mM H$_2$SO$_4$) after leaving the cell. NH$_3$ concentration of the electrolyte and absorbent before and after reaction was measured using the indophenol method, calculating an exact amount of NH$_3$ produced. After a cell operation, the catholyte had to be mixed in a highly basic solution (3% w/w NaOH) and NH$_3$ was recaptured in the absorbent via stripping for accurate assay (Fig. 1), because iron and sulfur in the reaction solution were found to interfere with the NH$_3$ detection method [20]. The surface of the nickel plate was analyzed by FE-SEM (SU5000, Hitachi, Japan) with EDS (Hitachi, Japan). All the experiments were at ambient temperature and pressure.

RESULTS AND DISCUSSION

The actual amount of NH$_3$ produced was calculated to be generated during purging of N$_2$ gas and it was confirmed that NH$_3$ was electrically synthesized from N$_2$ through Ar purging. The amount of produced NH$_3$ (Fig. 2) decreased up to 3.0 V, probably because the unwanted reaction of hydrogen production was dominant in
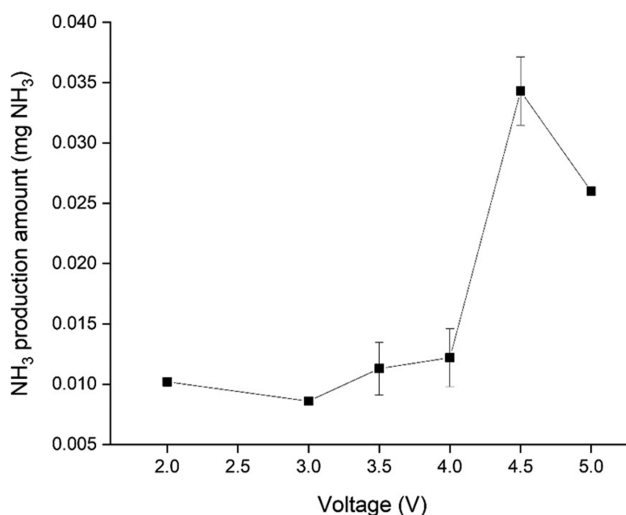

Fig. 2. NH$_3$ synthesis amount by voltage.

this voltage range [21,22]. From 3.5 V, it started to increase and at 4.5 V it suddenly rose to the highest point. The highest synthesis rate was 4.537*10^{-11} mol cm^{-2} sec^{-1} at 4.5 V, which might have to do with reactions other than nitrogen reduction. The electrodeposition of iron in solution can be seen from this voltage onward, which is different from the lower range [23,24].

Interestingly, the trend in NH$_3$ formation – decrease up to 3.0 V followed by increase afterward – turned to out to be closely related to the surface characteristic of cathode, that is, the deposition behavior of Fe. After operation of the electrochemical system, the cathode (nickel plate) was examined for its surface characteristics through SEM and compared with a pristine one. When operated at 3.0 V, there was virtually no visual change on the surface (Fig. 3(a)-(b)).

At 3.5 V, on the other hand, spore-like structures on the long line-shaped deposits were formed as a cluster, as shown in Fig. 3(c). SEM-EDS analysis revealed that Fe and O components were non-existent up to 3.0 V, meaning that the iron reduction occurred
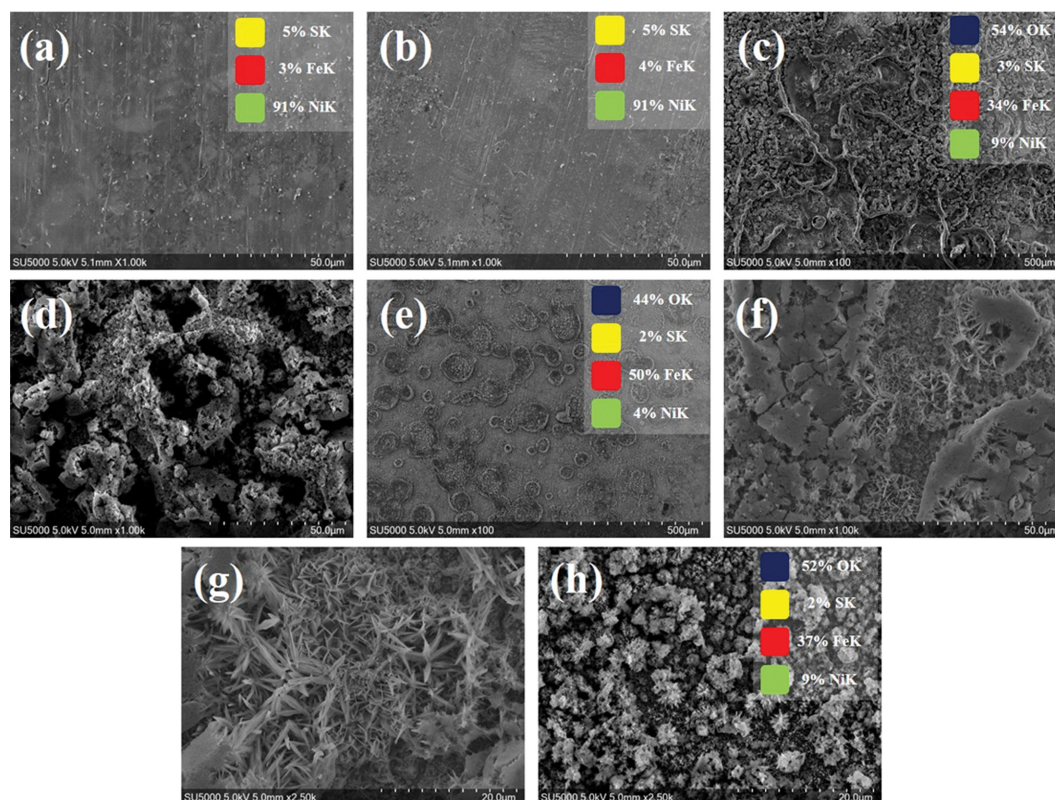
Fig. 3. SEM Image& SEM-EDS analysis for nickel electrode surface on voltage. (a) 0 V, (b) 3.0 V, (c) 3.5 V (×100), (d) 3.5 V (×1,000), (e) 4.0 V (×100), (f) 4.0 V (×1,000), (g) 4.0 V (×2,500), (h) 4.5 V (×2,500).

from 3.5 V (Fig. 3). The Fe originated from the deposition of dissolved ferrous cations onto the cathode – which is a way of providing an active surface area of nitrogen reduction in a continuous way [23].

According to the Pourbaix diagram of iron, iron exists in a zero-valence state above a certain potential, regardless of pH and ions in solution [25]. In the present system, zero-valent iron started to be generated above 3.0 V, and at higher voltages the entire surface of the nickel electrode was covered with active zero-valent iron. This surface, which was very likely unstable due to the great ten-dency of iron to donate electrons, exhibits a strong reducing power to decompose or weaken other substances [16-18]. This electrically deposited iron is believed to promote NH_3 synthesis by relaxing nitrogen triple bond, which is a rate-limiting step in the whole reaction [12,13,26].

When a higher overpotential of 4.0 V was applied, a large lump of deposits of small spores was observed instead of the long line-shaped deposits; the surface of the electrode was less clear and the surface iron content higher than that of 3.5 V (Fig. 3(e)). According to this, the surface deposition of iron could be predicted to be
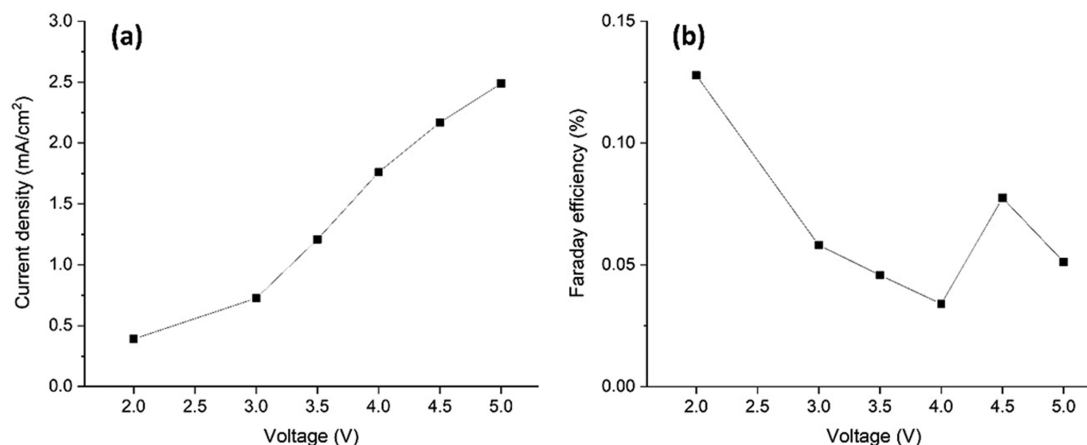

Fig. 4. Effect of voltage on (a) current density and (b) faraday efficiency.

made smaller in nanoscale at 4.5 V (Fig. 3(g), (h)), and NH_3 be synthesized all the more efficiently by way of supplying additional electric energy. As the size of the deposited iron gets smaller, it has a relatively high surface area and the reduction appears to become more active [27]. Unfortunately, the reducing power of the deposited iron would be used to promote the hydrogen evolution [21], if overpotential exceeded a required value for both iron reduction NH_3 synthesis (Fig. 4(b), 5.0 V). As a result, the energy intended to produce NH_3 was instead directed to the unintended side reaction of hydrogen generation.

A change in current density with respect to overvoltage is shown in Fig. 4(a). There was a faster rise around 3.5 V where the iron reduction reaction supposedly occurred. Current density started at 0.39 mA*cm^{-2} at 2.0 V, but kept rising around the range of iron reduction reaction, reaching 2.49 mA*cm^{-2} at 5.0 V. The effect of voltage on FE is illustrated in Fig. 4(b). FE decreased from 0.13% at 2.0 V to 0.03% at 4.0 V in a gradual way, likely due to low reaction rate at ambient temperature and competitive H_2 evolution, which is in fact, a frequently haunted issue of this kind of system [28,29].

There have been some efforts to electrochemically synthesize NH_3 on the basis of Fe, Cui et al. obtained FE of 6.04% at −0.9 V vs. Ag/AgCl in 0.1 M KOH electrolyte using Fe oxide catalyst, and Zhao et al. showed FE of 6.45% at −0.4 V vs. RHE using a nanostructured Fe_3S_4 catalyst [30,31]. Also, Chen et al. made a catalyst containing Fe and Mo and showed an FE of about 1% at −0.7 V vs. RHE at room temperature [32]. There are, however, some meaningful difference in experimental conditions: they used a three-electrode cell and also a high temperature of at least 160 °C (up to 450 °C) to fabricate the catalyst used [30-35]. Also, there are several more studies showing higher FEs, but they employed a high reactive electrolyte such as ionic liquid analogue [31] rather than the aqueous electrolyte. This study, though its low Faraday efficiency, is advantageous in terms of industrial applicability, as it is a water-based two-electrode cell and the catalyst is electrically produced in-situ from the electrolyte continuously with the NRR. Besides, this study was carried out in a rather wide electrode area of at least 15 cm^2 from the point of view of proof-of-concept studies and did not employ cost-intensive conditions for catalyst fabrication (i.e., reducing agents and high temperature).

CONCLUSION

We have demonstrated the possibility of NH_3 production at ambient temperature and pressure through an electrochemically deposited iron deposition. SEM-EDS analyses showed that iron deposited on a nickel electrode indeed increased nitrogen reduction, whose mechanism warrants further studies. The electrochemical generation and immediate use of zero-valent iron has the advantage of being able to be stronger than the conventional method without a reducing agent or high temperature, It can offer a new process avenue of achieving higher NH_3 efficiency, of course, through intensive system optimization.

ACKNOWLEDGEMENTS

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Electrochemical synthesis of ammonia from water and nitrogen: A Fe-mediated approach

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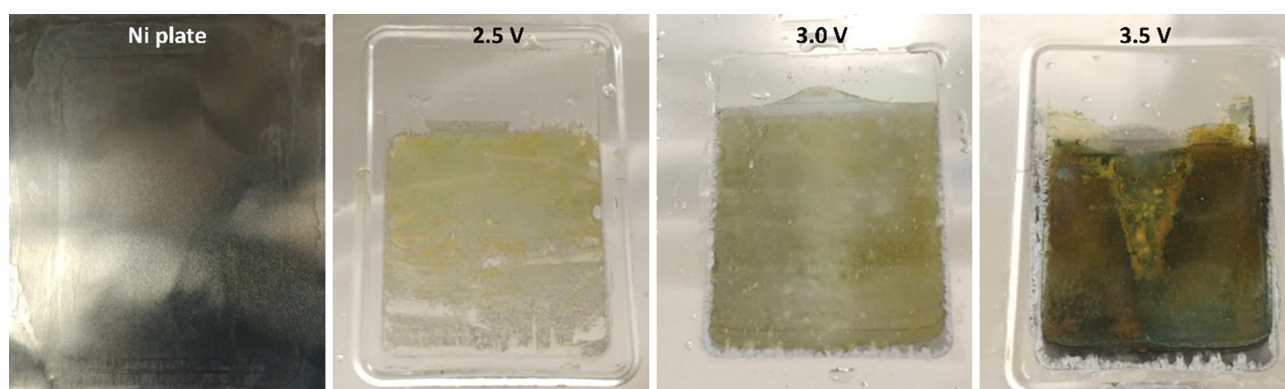***Clean Fuel Laboratory, Korea Institute of Energy Research, Daejeon 34101, Korea

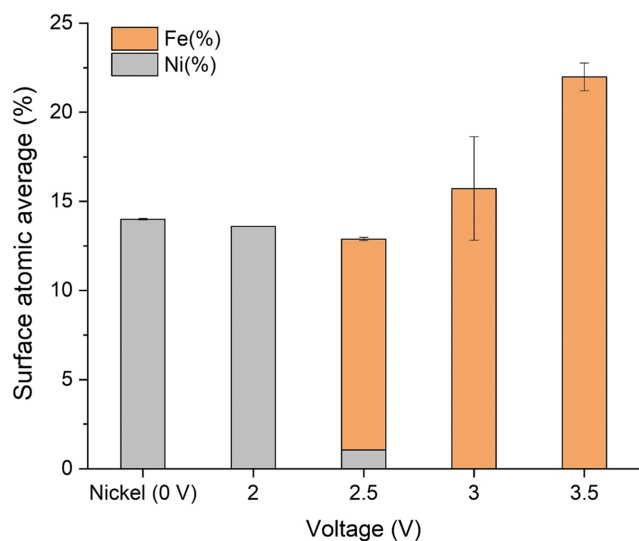Fig. S1. Fe deposition on Ni electrodes by voltage.

Fig. S2. X-ray photoelectron spectroscopy (XPS) results for Fe deposition on Ni plate (Left: Ni electrode immersed in FeSO$_4$ solution without applying voltage).
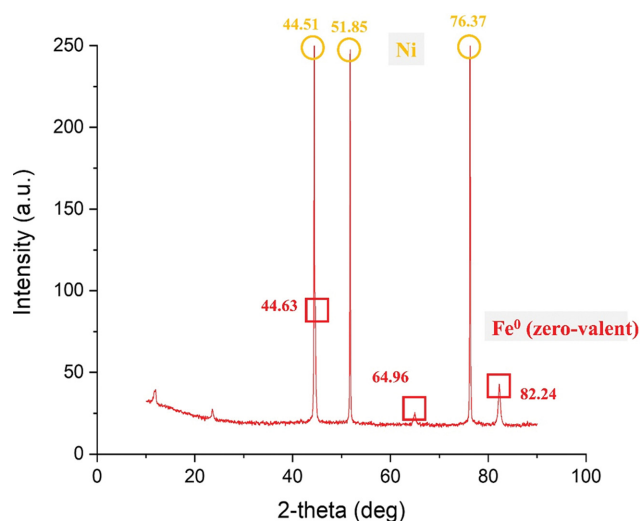

Fig. S3. X-ray diffraction (XRD) patterns for zero-valent iron deposition on nickel plate (applied voltage: 3.5 V).