



# Suitable Catalysts for Electrosynthesis of Ammonia as Green Hydrogen Storage

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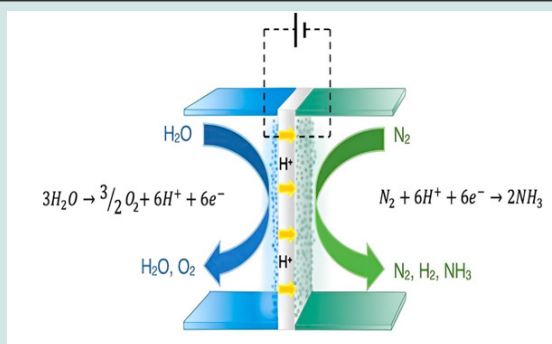
## Abstract

Designing, synthesizing, and applying electrochemical catalysts for the generation of ammonia ( $\text{NH}_3$ ) from electro-reduction nitrogen gas ( $\text{N}_2$ ) in the presence of water ( $\text{H}_2\text{O}$ ) is a very attractive research topic due to the extremal trend for green hydrogen utilization in the energy production sector. It became vital to be energy-free of  $\text{CO}_2$  in order to avoid elevating the earth's temperature and the subsequent impacts. Therefore, generating ammonia via a direct electrochemical process under ambient conditions is the most promising and scalable green hydrogen storage technique. In this review, the challenges that face commercializing experimental results are reported, and the performance of new electrochemical catalysts is described. The conclusion discusses the most important technical issues which must be considered in future research.

## Introduction

Ammonia ( $\text{NH}_3$ ) is one of the high-potential chemical storage for green hydrogen, its usual synthesis process from nitrogen ( $\text{N}_2$ ) and hydrogen ( $\text{H}_2$ ) depends intensively on the energy from non-renewable sources. Ammonia plays an essential role in the evolution of the human population as nitrogen-based fertilizer creates. The Haber-Bosch procedure allows the production of nearly 150 million metric tons of  $\text{NH}_3$  [1], which is responsible for consuming about 1–2% of the average global energy [2,3]. Another process is the steam-methane re-forming method which consumes about 5% of pure methane as a hydrogen source [4]. Consequently, this process alone is accountable for about 1.4% of  $\text{CO}_2$  emissions [5]. Hydrogen is considered as a future green energy resource; recently, many worldwide projects have been announced, and some of them have reached the production phase. There are many challenges and barriers in the generation of green hydrogen, including renewable

electricity price, storage, and hydrogen transportation. Liquid ammonia is considered a possible high-density energy carrier (22.5 MJ kg<sup>-1</sup>), at 8 bar and 22°C. However, synthesizing ammonia with available technology is unsustainable, and new technologies must be developed to overcome environmental concerns [6]. Electrochemical synthesis of ammonia is a promising solution as it can produce green  $\text{NH}_3$  in a flexible and scalable approach to take advantage of an intermittent overflow of electricity generated by renewables [7]. Figure 1 describes the general process of electrochemical syntheses of ammonia from  $\text{N}_2$  and  $\text{H}_2\text{O}$ . The electrochemical creation of ammonia at room temperature and in low-pressure situations remains unreasonable at a scalable level, and various challenges should be tackled to further empower immediate electrolytic ammonia synthesis. These challenges can be summarized as follows [8–12] (Figure 1).



**Figure 1:** Illustrated diagram of a solid-state  $H^+$  conducting cell where  $NH_3$  is generated from  $H_2O$  (steam) and  $N_2$ . Reprinted with permission [12].

- The reduction of nitrogen to ammonia competes with the hydrogen evolution reaction (HER), which requires lower energy than the nitrogen reaction because of stable tertiary covalent bonds in ( $N\equiv N$ ) molecules.
- The activation energy for HER is lower due to the polar nature of water molecules.
- Hydrogen adsorption on the catalyst's active sites easily occurs at a negative potential over nitrogen adsorption. Therefore, recombining adsorbed H on the catalyst surface is easy to generate  $H_2$  instead of ammonia production.
- The major issue of electrosynthesis ammonia in an aqueous medium is that the very weak solubility of nitrogen gas in an aqueous medium.
- Finally, most catalyst surfaces are poisoned by favorably adsorbing oxygen traces, which deactivates active catalyst sites.

Substantial efforts have been recently made to develop new strategies to overcome the mentioned challenges in direct electrochemical nitrogen reduction to ammonia in ambient conditions. In this review, the developments and efficiency of the electrocatalysts for the synthesis of ammonia from  $N_2$ , and  $H_2O$ , using renewable powers will be discussed focusing on the active sites, the rate of  $NH_3$  production and faradaic efficiency (FE).

### NH<sub>3</sub> Electrocatalysts

The metallic catalysts are the most used for generating ammonia. However, heterogeneous structures are critical to enhancing the reaction rate by increasing the selectivity of the surface for  $NH_3$  generation. It has been observed that different electrolytes and electrode surface materials can lower thermodynamic conditions and enhance ammonia creation rate in several studies involving different electrolytes and electrode materials. Several compositional studies have been conducted for ammonia production with different catalysts [13]. The development of an electrochemical cell, for the electrochemical reduction of atmospheric nitrogen and water into ammonia, is a challenging task [14].

### Nobel Metals catalysts

Ruthenium (Ru) based catalysts are one of the most investigat-

ed surfaces for the synthesis of ammonia and they showed higher activity than the common iron catalysts [15]. Most of these investigations were based on the usual method used for ammonia synthesis from  $N_2$  and  $H_2$  under pressure and high temperature, a view studies were done using electrochemical reduction of the  $N_2$  process in the presence of water as a source of hydrogen. In early work, an electrochemical cell for the synthesis of ammonia was developed using Ru as a cathode [16]. Only ammonia detected products from the electrochemical cell from electro-reduction of  $N_2$  at 90 °C and a potential of -1.10 V. The production rate of ammonia was very low ( $1.3 \mu g h^{-1} m^{-1}$ ). The rate of ammonia generation was increased as the reduction potential value was increased until -1.02 V, and then it was decreased to a higher potential value.

Then Ru was used as single-metal sites, where it was distributed on the surface of zeolitic imidazolate framework (ZIF)-8. The formation rate of  $NH_3$  was  $0.12 mg h^{-1} mg cat^{-1}$  and Faradaic efficiency reached 29.6% when loaded mass of Ru was 0.18% [17]. N-doped porous carbon was obtained from the UIO-66 precursor to encapsulate ( $Ru^{3+}$  and  $Ru^0$ ) [18]. The single atom of Ru electrocatalyst  $Ru@ZrO_2/NC$  has enough active sites to reduce  $N_2$  and produce ammonia with a rate of  $3.7 mg h^{-1} mg^{-1} Ru$  when 0.1 wt% of the catalyst is Ru. The created catalyst exhibited high stability for 60 hours as illustrated by Figures 1 & 2. When Pt was supplemented to the Ru, the RuPt alloy improved the performance of composite (RuPt/C) which demonstrated 13.2% of FE at 0.123 V and generation rate of  $NH_3$  was  $3.0 \times 10^{-7} mol h^{-1} cm^{-2}$  [19]. Au-NPs was the matrix for developing CB (7)- $K_2[B_{12}H_{12}]@Au$  [20]. The ability of  $K^+$  ion in limiting and inhibiting the HER lowering the rate determining step. Therefore, the rate of ammonia formation recorded high as  $41.69 \mu g h^{-1} mg_{cat}^{-1}$  and FE 29.53% at -0.4 V (vs. RHE).

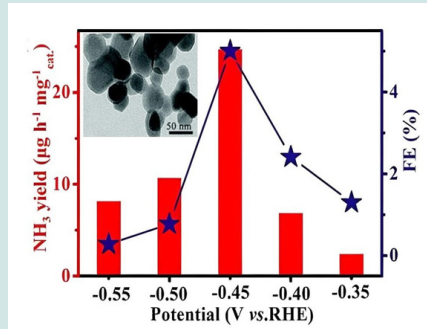
### Transition Metals catalysts

Transition metals have been investigated as active electrocatalysts. Molybdenum is another promising metal for electrochemical reduction of  $N_2$  and it forms many compounds with different nonmetallic elements. New nanodots were prepared from molybdenum carbide and then inserted in ultrathin carbon nanosheets [21]. This catalyst shows very low FE (7.8%), and the production yield was only  $11.3 \mu g h^{-1} mg^{-1} cat$ . Furthermore,  $MoS_2$  was utilized as electrochemical catalyst for generation  $NH_3$  from 0.1 M  $Na_2SO_4$

where generation rate recorded ( $8.08 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-1}$ ) at  $-0.5 \text{ V}$  (vs. RHE). The developed catalyst shows good activity even in acidic solution [22].  $\text{MoS}_2$  nanoflowers show higher FE compared with the previous work (8.34%) and higher  $\text{NH}_3$  yield of  $29.28 \mu\text{g h}^{-1} \text{ mg}^{-1} \text{ cat}$  at  $-0.40 \text{ V}$  under same conditions [23].  $\text{MoN}_3$  was immobilized at N-doped black phosphorus and applied to the electrochemical reduction of  $\text{N}_2$  under ambient conditions at  $0.02 \text{ V}$  [24].

The fabricated surface shown desorption free energy of  $\text{NH}_3$  is  $0.56 \text{ eV}$ , Quantum dots (QD) were prepared from black phosphorus and the  $\text{MnO}_2$  nanosheets were immobilized at the surface of

QD [25]. The performance of this catalyst demonstrated a formation rate of  $25.3 \mu\text{g h}^{-1} \text{ mgcat.}^{-1}$  with 6.7% FE at  $-0.5 \text{ V}$  (vs RHE) in  $0.1 \text{ M Na}_2\text{SO}_4$  solution. Moreover,  $\text{ZrO}_2$  nanoparticles were examined for electrochemical reduction of  $\text{N}_2$  in water at ambient conditions [26]. The proposed catalyst enabled producing  $\text{NH}_3$  at a rate of  $24.74 \mu\text{g h}^{-1} \text{ mg}^{-1} \text{ cat}$ .  $0.1 \text{ M HCl}$  with 5.0% FE at  $-0.45 \text{ V}$  (vs RHE). Figure 2 illustrates the effect of applied potential on the production yield of  $\text{NH}_3$  and FE using  $\text{ZrO}_2$  nanoparticles as catalysts. Likewise, a perovskite oxide of ( $\text{La}_{0.8}\text{Cs}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3.8}$ ) was prepared to be applied as an electrochemical catalyst for producing ammonia from wet air [27].



**Figure 2:** Average  $\text{NH}_3$  yields and FEs for  $\text{ZrO}_2/\text{CP}$  at each given potential in  $0.1 \text{ M HCl}$  and inset TEM image of  $\text{ZrO}_2$  nanoparticles. Reprinted with permission [26].

The formation rate of ammonia attained  $1.23 \times 10^{-6} \text{ mol s}^{-1} \text{ m}^{-2}$  in  $400 \text{ }^\circ\text{C}$  cell when wet  $\text{N}_2$  (3 mol%  $\text{H}_2\text{O}$ ) was introduced at  $1.4 \text{ V}$ . Another, Hematite nanostructure surface was developed and used for the electrochemical synthesis of ammonia at room temperature and low pressure [28]. The generation rate of  $\text{NH}_3$  reached  $0.46 \mu\text{g h}^{-1} \text{ cm}^{-2}$  and FE of 6.04 % at  $-0.9 \text{ V}$  (vs.  $\text{Ag}/\text{AgCl}$ ) in  $0.10 \text{ M KOH}$ . The rate increased slightly after one hour and dropped by 63%, and FE was only 2.74 %. Indium-tin oxide glass (ITO/G) was used as electrochemical catalyst for formation  $\text{NH}_3$ . The yield records  $1.06 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$  and FE 6.17% at  $-0.40 \text{ V}$  (vs, RHE) in  $0.5 \text{ M LiClO}_4$  [29] (Figure 2). Recently, the Density functional theory (DFT) calculation for the catalytic activity of  $\text{Fe}(100)$  was done to explore the ability and effect of dopant elements (Ru, Rh, Pd, Os, Ir, Pt) on the electronic properties of  $\text{Fe}(100)$  [30]. The results demonstrated that the hydrogenation step at  $\text{Ir@Fe}(100)$  was initiated at  $0.342 \text{ eV}$  with remarkably inhibited the  $\text{H}_2$  evolution.

### Free metal catalysts

Synthesized black phosphorus nanosheets in zigzag and diff-zigzag edges assist selective electrochemical reduction of  $\text{N}_2$  and the greatest  $\text{NH}_3$  producing rate was  $31.37 \mu\text{g h}^{-1} \text{ mg}^{-1} \text{ cat}$  at  $-0.7 \text{ V}$  [31]. A free metal, electrochemical carbon catalyst was doped by nitrogen, and the carbon microstructure was optimized. The developed catalyst exhibited excellent activity to the electrochemical reduction of  $\text{N}_2$  in  $0.1 \text{ M KOH}$  under ambient pressure [32]. The ammonia yield rate of  $3.4 \times 10^{-6} \text{ mol cm}^{-2} \text{ h}^{-1}$  and an FE as maximum as 10.2% at  $-0.3 \text{ V}$  vs. RHE at room temperature. The formation rate reached  $7.3 \times 10^{-6} \text{ mol cm}^{-2} \text{ h}^{-1}$  when the temperature increased to

$60 \text{ }^\circ\text{C}$ .  $\text{FeN}_4$  moiety was inserted in the carbon framework, but it showed a decrease in the ammonia production rate at same conditions. black phosphorus quantum dots (BPQDs) with the support of a conductive polymer nanofibrous membrane were tested for electrosynthesis of ammonia [33]. The yield of production in  $0.1 \text{ M Na}_2\text{SO}_4$  reached  $1.91 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$  and FE 11.9%.

### Conclusion

As a conclusion, the developed electrochemical catalysts for generation of ammonia and intensive research enlighten the role for upscale and commercialized the electrosynthesis  $\text{NH}_3$  in closed future. However, the electrochemical catalysts developed for this purpose still fall short of expectations in terms of durability and Faradaic efficiency. Also, the production rate of ammonia is still very low, and the ability to suppress hydrogen reduction utilizing the same catalyst remains a real challenge. The impressive results are recorded via free metal catalysts as they reached more than 10% FE and rate order in level  $10^{-6} \text{ mol cm}^{-2} \text{ h}^{-1}$ . This demonstrates the ability of creating catalysts from low prices precursors and safe the un abundant noble metals. Also, single atom- based catalysts improve the FE and production rate but the stability and reducing posing surface rate need more creative technic. Ru remains a desirable electrocatalyst for electrochemical generation of  $\text{NH}_3$  even its high price as it offers more than 29.6% FE and excellent production rate. More research work can be done to improve and develop electrochemical catalysts for green hydrogen storage in the form of ammonia.

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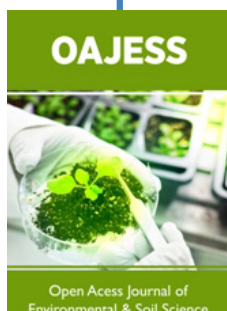


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