



## Review

# Lowering reaction temperature: Electrochemical ammonia synthesis by coupling various electrolytes and catalysts

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## ABSTRACT

Ammonia is a vital emerging energy carrier and storage medium in the future hydrogen economy, even presenting relevant advantages compared with methanol due to the higher hydrogen content (17.6 wt% for ammonia versus 12.5 wt% for methanol). The rapidly growing demand for ammonia is still dependent on the conventional high-temperature and high-pressure Haber–Bosch process, which can deliver a conversion rate of about 10%–15%. However, the overall process requires a large amount of fossil fuels, resulting in serious environmental problems. Alternatively, electrochemical routes show the potential to greatly reduce the energy consumption, including sustainable energy sources and simplify the reactor design. Electrolytes perform as indispensable reaction medium during electrochemical processes, which can be further classified into solid oxide electrolytes, molten salt electrolytes, polymer electrolytes, and liquid electrolytes. In this review, recent developments and advances of the electrocatalytic ammonia synthesis catalyzed by a series of functional materials on the basis of aforementioned electrolytes have been summarized and discussed, along with the presentation and evaluation of catalyst preparation, reaction parameters and equipment.

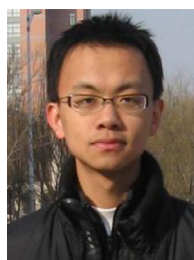
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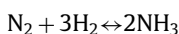
**Table 1.** Electrocatalytic ammonia production employing different catalysts and electrolytes.

Working electrodes	Electrolytes		Temperature (°C)	Ammonia production rate	References
Ag	Solid oxide	BaZr <sub>0.8</sub> Y <sub>0.2</sub> O <sub>3-δ</sub>	550	2.9 × 10 <sup>-14</sup> mol·s <sup>-1</sup> ·cm <sup>-2</sup>	[19]
Ru/Y <sub>5</sub> Si <sub>3</sub>	electrolytes	Electride	400	5.3 × 10 <sup>-7</sup> mol·g <sup>-1</sup> ·s <sup>-1</sup>	[20]
Pd		SrCe <sub>0.95</sub> Yb <sub>0.05</sub> O <sub>3</sub>	570	4.5 × 10 <sup>-9</sup> mol·s <sup>-1</sup>	[21]
La <sub>0.75</sub> Sr <sub>0.25</sub> Cr <sub>0.5</sub> Fe <sub>0.5</sub> O <sub>3-δ</sub>		Ce <sub>0.8</sub> Gd <sub>0.18</sub> Ca <sub>0.02</sub> O <sub>2-δ</sub> –((Li/Na/K) <sub>2</sub> CO <sub>3</sub> )	375	3.9 × 10 <sup>-10</sup> mol·s <sup>-1</sup> ·cm <sup>-2</sup>	[22]
Glassy carbon rod	Molten salt	LiCl–KCl–CsCl molten salts	300	2.0 × 10 <sup>-8</sup> mol·s <sup>-1</sup> ·cm <sup>-2</sup>	[23]
Ni (catalyzed by nano-Fe <sub>2</sub> O <sub>3</sub> )	electrolytes	Molten hydroxide	250	N.A.	[24]
Sm <sub>1.5</sub> Sr <sub>0.5</sub> FeO <sub>4</sub>	Polymer-type	Nafion	80	9.2 × 10 <sup>-9</sup> mol·s <sup>-1</sup> ·cm <sup>-2</sup>	[25]
SmBaCuNiO <sub>5+δ</sub>	electrolytes	Nafion	80	8.7 × 10 <sup>-9</sup> mol·s <sup>-1</sup> ·cm <sup>-2</sup>	[26]
Pt/C	Liquid electrolytes	0.1 M Li <sub>2</sub> SO <sub>4</sub> solution	80	9.4 × 10 <sup>-10</sup> mol·s <sup>-1</sup> ·cm <sup>-2</sup>	[27]
Au nanorods		0.1 M KOH aqueous solution	25	2.7 × 10 <sup>-11</sup> mol·s <sup>-1</sup> ·cm <sup>-2</sup>	[28]
Au/TiO <sub>2</sub>		0.1 M HCl aqueous solution	25	3.5 × 10 <sup>-7</sup> mol·s <sup>-1</sup> ·g <sup>-1</sup>	[29]
Fe <sub>2</sub> O <sub>3</sub> –CNT		Diluted KHCO <sub>3</sub> aqueous solution	20	3.6 × 10 <sup>-12</sup> mol·s <sup>-1</sup> ·cm <sup>-2</sup>	[30]
PEBCD/C		0.5 M Li <sub>2</sub> SO <sub>4</sub>	25	2.6 × 10 <sup>-11</sup> mol·s <sup>-1</sup> ·cm <sup>-2</sup>	[31]
Ru/Ti		0.5 M H <sub>2</sub> SO <sub>4</sub> aqueous solution	30	1.2 × 10 <sup>-10</sup> mol·s <sup>-1</sup> ·cm <sup>-2</sup>	[32]

## 1. Introduction

Ammonia (NH<sub>3</sub>) is a unique pungent gas with a lighter density compared with air at room temperature and atmospheric pressure and can be widely used in the fields of textile industry, plastic, energy conversion and fertilizer production, making it one of the most common industrial chemicals produced nowadays [1–3]. Compared with methanol, liquid ammonia, with 17.6 wt% hydrogen, is a very promising emerging energy carrier and storage medium for the future hydrogen economy [4,5]. Obviously, the rapidly growing demand for ammonia has led to a huge consumption with 150 million tons per year as a result of the aforementioned applications.

The industrial synthesis process of ammonia simply follows the reaction as shown below:



in which the N<sub>2</sub> molecule comprises the highly stable N≡N structure with a considerably large binding energy of 962 kJ·mol<sup>-1</sup> [6–9]. Moreover, the N<sub>2</sub> gas volume decreases when converted into NH<sub>3</sub>, and accordingly, at high temperature N≡N triple binding can be broken and the N<sub>2</sub> kinetic energy overcomes the inert synthesis reaction of ammonia. High pressure is used to promote the equilibrium toward the product direction, thus increasing the reaction conversion and reducing the reverse decomposition of NH<sub>3</sub> to N<sub>2</sub>. Based on the above principles, the Haber–Bosch NH<sub>3</sub> production technology, relying on Fe-based catalysts, is one of the most popular processes operating at high temperature (350–550 °C) and high pressure (150–350 atm) [6–9]. The process is associated with high energy consumption of about 485 kJ·mol<sup>-1</sup> of NH<sub>3</sub> and a relatively low equilibrium conversion of 10%–15%. In addition, in order to convert 120 million tons of N<sub>2</sub> from the air, the process results in 200 million tons of CO<sub>2</sub> emission to provide required H<sub>2</sub> from fossil fuels (e.g., natural gas, coal and oil) [10–12]. Alternative environmental-friendly method of biological N<sub>2</sub> fixation takes place primarily in microbial organisms with nitrogenases, which catalyze the reduction of H<sup>+</sup> and N<sub>2</sub> to finally generate H<sub>2</sub> and NH<sub>3</sub> [13–15]. However, this process is associated with relatively slow reaction rate, which is not compatible with industrial requirements. Therefore, it is urgent to explore energy-saving, environmental-friendly and highly efficient processes for large-scale production of ammonia.

Electrocatalytic N<sub>2</sub> reduction process is a promising candidate which would save over 20% of the total energy consumption compared to the Haber–Bosch technology. Additionally, the electrochemical reduction can also be powered in conjunction with renewable solar and wind energy, which provides a great potential for commercial applications. Several electrocatalytic routes [16–32] for the ammonia synthesis have been demonstrated in

Table 1, the reaction temperature varies depending on the utilized electrocatalysts and electrolytes. More specifically, in the high-temperature range beyond 500 °C, solid oxide electrolytes, most commonly reported electrolytes so far, are based on proton-conducting perovskites of strontium zirconate [21,33–35] and barium cerate [36–39]. Noble metals such as Ag–Pd are usually used as catalytic electrodes. In the medium-temperature range between 200 and 500 °C, molten salt electrolytes such as LiCl–KCl–Li<sub>3</sub>N and LiCl–KCl–CsCl alkali-metal halides are the common choice to synthesize ammonia [23,40–44]. Recently, an electrocatalytic cell based on molten hydroxide (NaOH/KOH) electrolyte operated at 200 °C, was reported with porous Ni mixed with high-surface-area nano-Fe<sub>2</sub>O<sub>3</sub> catalysts [24,45]. However, limited reports can be found on the electro-synthesis of ammonia at low temperature (i.e., below 100 °C) or even at room temperature. At this temperature range, the Nafion membrane with a good proton conductivity of 4.5 × 10<sup>-2</sup> S·cm<sup>-1</sup> at 80 °C was most adopted [25–27,46]. Very recently, intense research has been devoted to identifying special electrocatalysts for ammonia production using liquid electrolytes at room temperature [28–32]. The ammonia electro-reduction reaction with liquid electrolytes allows the room temperature synthesis and hardly involves complex and expensive electrolytes. Therefore, an updated summary is urgent and beneficial for understanding the recent progress of electrocatalytic ammonia production. In this review, we will explore the developments of electrocatalytic ammonia synthesis based on various electrolytes operating at different temperature ranges, with emphasis on new material preparation, ammonia production rates and reaction instruments.

## 2. Solid oxide electrolytes at high temperature (>500 °C)

Solid oxide based cells for N<sub>2</sub> reduction can overcome limitations of conventional catalytic reactors, e.g., limited conversion and high energy consumption [16–18]. The typical cell mainly consists of two porous electrodes (i.e., anode and cathode) and a dense solid oxide electrolyte. The solid oxide electrolyte separates the anode from the cathode, allows ion transport of either protons or oxide ions and serves as a barrier to gas diffusion [47,48]. The typical schematics of solid oxide based cells using proton conducting electrolytes for N<sub>2</sub> reduction are shown in Fig. 1.

The solid oxide can be a perovskite-type, pyrochlore-type or fluorite-type oxide. Fig. 2(a) represents the typical structure of a perovskite-type oxide (barium cerate-based oxides, BaCeO<sub>3</sub>), which can be generally expressed as ABO<sub>3</sub>, where the A site is occupied by a rare earth cation and the B site is occupied by a transition metal [49], such as strontium zirconate (SrZrO<sub>3</sub> or SrCeO<sub>3</sub>), barium cerate (BaCeO<sub>3</sub>) and Lanthanum gallate (LaGaO<sub>3</sub>). These compound formulas can also be expressed as AB<sub>1-x</sub>M<sub>x</sub>O<sub>3-δ</sub>, while M is a divalent cation (Ca<sup>2+</sup>) or a trivalent cation (Y<sup>3+</sup>, Gd<sup>3+</sup>, Yb<sup>3+</sup>, Nd<sup>3+</sup>,

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