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## Review

# Review of electrochemical ammonia production technologies and materials



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## ARTICLE INFO

## Article history:

Received 20 June 2013

Received in revised form

5 September 2013

Accepted 12 September 2013

Available online 5 October 2013

## Keywords:

Ammonia

Electrochemical ammonia synthesis

Haber–Bosch process

Energy storage

Hydrogen

Fuel cells

## ABSTRACT

Ammonia, being a good source of hydrogen, has the potential to play a significant role in a future hydrogen economy. The hydrogen content in liquid ammonia is 17.6 wt% compared with 12.5 wt% in methanol. Although a large percentage of ammonia, produced globally, is currently used in fertiliser production, it has been used as a fuel for transport vehicles and for space heating. Ammonia is an excellent energy storage media with infrastructure for its transportation and distribution already in place in many countries. Ammonia is produced at present through the well known Haber–Bosch process which is known to be very energy and capital intensive. In search for more efficient and economical process and in view of the potential ammonia production growth forecast, a number of new processes are under development. Amongst these, the electrochemical routes have the potential to substantially reduce the energy input (by more than 20%), simplify the reactor design and reduce the complexity and cost of balance of plant when compared to the conventional ammonia production route. Several electrochemical routes based on liquid, molten salt, solid or composite electrolytes consisting of a molten salt and a solid phase are currently under investigation. In this paper these electrochemical methods of ammonia synthesis have been reviewed with a discussion on materials of construction, operating temperature and pressure regimes, major technical challenges and materials issues.

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## 1. Introduction

Ammonia (NH<sub>3</sub>) is an alkaline, colourless and lighter than air gas with pungent and penetrating odour. The boiling point for liquefied anhydrous ammonia is –33.3 °C at atmospheric pressure [1]. It is the second most commonly produced chemical in the world. Ammonia stays in liquid form above about 9–10 bar pressure at ambient temperature [1,2], thus it can be stored in low pressure vessels similar to those used for LPG. The conventional route of producing ammonia is by the

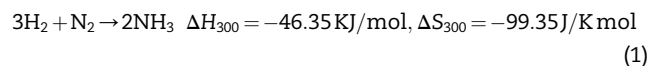
Haber–Bosch process named after two Scientists Fritz Haber and Carl Bosch (both winning Noble prize for their contribution to the discovery and industrial process development respectively) [1,4–6]. The process requires reaction of hydrogen and nitrogen over an iron based catalyst at temperatures in the vicinity of 500 °C and pressures up to 300 bar. Over 200 million metric tons of ammonia per annum is produced by this process worldwide [7,8]. About 80% of the ammonia produced globally is used for nitrogen based fertiliser production [8]. The remaining 20% of the ammonia

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production is used in explosives, pharmaceuticals, refrigeration, cleaning products and many other industrial processes [1,8–10]. For ammonia synthesis, the source of hydrogen is mostly natural gas (NG) and involves desulphurisation, methane steam reforming followed by water gas shift reaction to convert CO to hydrogen and CO<sub>2</sub>. The residual CO is removed by methanation reaction and CO<sub>2</sub> is removed by pressure swing adsorption process [1,11]. Nitrogen is typically sourced from atmospheric air by using cryogenic air separation units.

Ammonia synthesis reaction in the Haber–Bosch process is given as:



The negative entropy of the reaction dictates that the reaction is favoured at lower temperatures, however, the high dissociation energy of triply bonded nitrogen molecule (911 kJ mol<sup>-1</sup>) presents a significant activation barrier [1]. While from thermodynamic standpoint, the reaction is favoured by high pressures and low temperatures, the kinetics demands high operating temperatures to achieve reasonable ammonia production rates. The kinetic rate of Reaction (1) increases with increasing temperature, reaching maxima at a certain temperature and then decreasing if the temperature is increased further due to lower equilibrium ammonia concentration stemming from its decomposition. The temperature at which the reaction rate is maximum, obviously varies with the process pressure. For example, at a pressure of 100 bar (1 bar = 0.1 MPa), for a stoichiometric H<sub>2</sub>/N<sub>2</sub> mixture, the reaction rate reaches a maximum of 0.01 kmol h<sup>-1</sup> kg<sup>-1</sup> at about 432 °C while increasing the pressure to 300 bar pushes the maxima to 537 °C with a reaction rate of 0.18 kmol h<sup>-1</sup> kg<sup>-1</sup> [1,2]. Clearly there is a need for balance between the operating temperature, pressure and the ammonia yield. Also to facilitate the activation under practically feasible pressures, the use of catalysts such as iron oxides is virtually mandatory for industrial production. Typically in industrial processes, the reaction is carried out at temperatures between 300 and 550 °C and pressures between 100 and 300 bar in the presence of reduced Fe<sub>3</sub>O<sub>4</sub> based catalyst bed for reaction to proceed at reasonable rates. Since conversion rates are very low for a single pass (only 10–15% conversion of reactants), the overall plant has several catalytic beds with gases cooled after each bed, ammonia separated and unreacted gases fed to the next bed to increase overall yield. Alternatively the unreacted gases can be recycled over the same bed. The total energy consumption by this route is around 9500 kWh/ton of ammonia and increases to 12,000 kWh/ton if H<sub>2</sub> is produced via electrolysis of water rather than by the steam reforming of methane [9].

Ammonia is also being considered an energy storage media and a source of hydrogen as the hydrogen content in liquid ammonia is 17.6 wt% compared with 12.5 wt% in methanol [3,12–14]. Ammonia has been used as a fuel for transport vehicles as it can be combusted in an internal combustion engine, and also for space heating [3,9]. Ammonia, being a good source of hydrogen, has the potential to play a significant role in a future hydrogen economy [3,12–15]. Ammonia can be easily cracked to produce hydrogen for use in fuel cells or

**Table 1 – Energy content of various fuels.<sup>b</sup>**

Chemical	Energy content (HHV) <sup>a</sup>		Energy content (LHV) <sup>a</sup>	
	MJ/kg	MJ/L	MJ/kg	MJ/L
Liquid H <sub>2</sub>	141.9	10.1	119.9	8.5
Liq NH <sub>3</sub>	22.5	15.3	18.6	12.7
CH <sub>3</sub> OH	22.9	18.2	20.1	15.8
C <sub>2</sub> H <sub>5</sub> OH	29.9	23.6	26.9	21.2
CH <sub>4</sub> (LNG)	56.2	23.6	50.0	20.9
LPG	47.2	25.5	43.5	23.5
Gasoline	46.5	34.6	43.1	32.1
Diesel	45.7	38.3	42.8	35.8

<sup>a</sup> HHV: High Heating Value, LHV: Low Heating Value.

<sup>b</sup> [http://www1.eere.energy.gov/hydrogenandfuelcells/tech\\_validation/pdfs/fcm01r0.pdf](http://www1.eere.energy.gov/hydrogenandfuelcells/tech_validation/pdfs/fcm01r0.pdf), [http://www.afdc.energy.gov/fuels/fuel\\_comparison\\_chart.pdf](http://www.afdc.energy.gov/fuels/fuel_comparison_chart.pdf), [http://www.engineeringtoolbox.com/combustion-values-d\\_411.html](http://www.engineeringtoolbox.com/combustion-values-d_411.html), <http://www.dtic.mil/dtic/tr/fulltext/u2/638360.pdf>.

other hydrogen applications at end user sites. The by-products of direct ammonia combustion are water and nitrogen. Table 1 compares total volumetric and gravimetric energy content of various liquid fuels with ammonia. However, the main advantage of using ammonia as a source of hydrogen is that the volumetric hydrogen energy density in liquid anhydrous ammonia is significantly higher than that of liquid hydrogen [3,9,12,14,15]. In fact, the volumetric hydrogen energy density of ammonia is the highest amongst many common liquid fuels (methanol, ethanol, gasoline, LPG, etc.) after reforming to produce hydrogen. Ammonia can be used directly as a fuel in alkaline or high temperature fuel cells [16–19] which have good tolerance for residual ammonia levels. However, low temperature fuel cells based on acidic membranes such as Nafion are incompatible and degrade easily by ammonia concentration as low as 0.1 ppm [14].

Liquid ammonia storage, transportation and distribution is relatively easy due to the low pressure (~9–10 bar) at which it stays in the liquid form at room temperature and its high gravimetric density of 0.68 g ml<sup>-1</sup> (at boiling point and 1 bar) compared to 0.071 g ml<sup>-1</sup> for liquid hydrogen at -253 °C. From safety point of view, ammonia gas is lighter than air (just under 60% of the density of air) and if a leak does occur, ammonia dissipates into upper atmosphere quickly. Furthermore, ammonia has a strong pungent smell and can be detected by most humans in very low concentrations (20–50 ppm) [14], well below its harmful limits. The Immediately “Dangerous to Life or Health” (IDLH) concentration level is 300 ppm. Procedures for safe handling of large quantities of ammonia are well established and documented and the infrastructure for its transportation by rail, road or pipelines exists in many countries.

Due to the large number of applications and products where ammonia is utilised and increasing interest in using it as an energy storage media, a rapid growth in ammonia production capacity is expected globally. This is encouraging the development of alternative routes for ammonia production which are less energy intensive and economically more viable. Ammonia can be synthesised with a number of electrochemical routes and many different electrolytic systems are currently under development. A short review of solid state

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