



Progress in the Electrochemical Synthesis of Ammonia



V. Kyriakou, I. Garagounis, E. Vasileiou, A. Vourros, M. Stoukides*

Department of Chemical Engineering, Aristotle University, Thessaloniki, 54124 & Chemical Processes & Energy Resources Institute, CERTH, Thessaloniki, 56071, Greece

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ABSTRACT

Ammonia is one of the most important and widely produced chemicals worldwide with a key role in the growth of human population. Nowadays, the main route for ammonia synthesis is the Haber–Bosch process, developed a century ago. In this process, Fe-based catalysts are usually employed at temperatures between 400 and 500 °C and pressures between 130 and 170 bar. As opposed to the industrial process, in nature, plants and bacteria have been producing ammonia for millions of years at mild conditions. Atmospheric nitrogen is reduced by solvated protons on the FeMo cofactor of the metalloenzyme nitrogenase. The natural method of nitrogen fixation has motivated several research groups to explore the electrochemical synthesis of ammonia at ambient pressure. Since it was first demonstrated in 1998, the electrochemical synthesis has been studied in a variety of experimental configurations over a wide temperature range (25–800 °C). In the present review, the progress of this method in both solid and liquid electrolyte cells is reported. The experimental studies are divided into high ($T > 500$ °C), intermediate (500 °C $> T > 100$ °C) and low ($T < 100$ °C) temperatures. The experimental observations are comparatively discussed with theoretical predictions based on DFT calculations. The techno-economic advantages and disadvantages of the electrochemical approach, as well as the requirements to be met in order to enable practical applications are also analyzed.

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1. Introduction

Ammonia is one of the most important chemicals with an annual production exceeding 200 million tons [1]. Nearly 80% of the produced ammonia is used in the fertilizer industry and has played a key role in maintaining the growth of human population [2]. The dominant industrial route for its synthesis is the Haber–Bosch process, according to which ammonia is produced from the reaction of dinitrogen with dihydrogen:



The Haber–Bosch process was developed one hundred years ago [3] and employs Fe-based catalysts in the temperature range of 400–500 °C and at pressures of 130–170 bar [3–5]. The newer KAAP (Kellogg Advanced Ammonia Process) process uses a Ru-based catalyst at relatively lower pressures (<100 bar) [6]. The high operating pressures are dictated by the reaction stoichiometry and the Le Chatelier principle. The operating temperature is a trade-off solution. The need for fast reaction rates dictates operation at high

temperatures. On the other hand, the need for high equilibrium conversion dictates operation at low temperatures [4]. Although the reaction is exothermic, a significant energy input is required. Today, the energy consumption for ammonia synthesis is about 1.4% of all energy consumed worldwide [7]. This high energy need is due to the production of hydrogen, the thorough purification of the reactant gases and the compression of the reacting mixture.

Because of its importance, the Haber–Bosch process is one of the most thoroughly studied catalytic reactions. Most of these theoretical and experimental studies suggest that the rate determining step is the dissociation of dinitrogen on the catalyst surface [2,8]. Since the first industrial application, numerous researchers have contributed to the discovery and development of more efficient ammonia synthesis catalysts, which would allow operation at lower temperatures and, consequently, at lower pressures [1–5].

As opposed to the industrial process, which requires elevated pressures and temperatures, plants and bacteria can convert gaseous nitrogen into ammonia at ambient conditions [2,7–10]. This is achieved with the use of metalloenzymes, called nitrogenases. These enzymes are formed by the combination of two proteins [11]. The first of these proteins mediates the electron transfer for the reduction of dinitrogen via an iron sulfur complex (Fe_4S_4). The other contains two iron–molybdenum cofactors

* Corresponding author.

E-mail address: stoukidi@cperi.certh.gr (M. Stoukides).

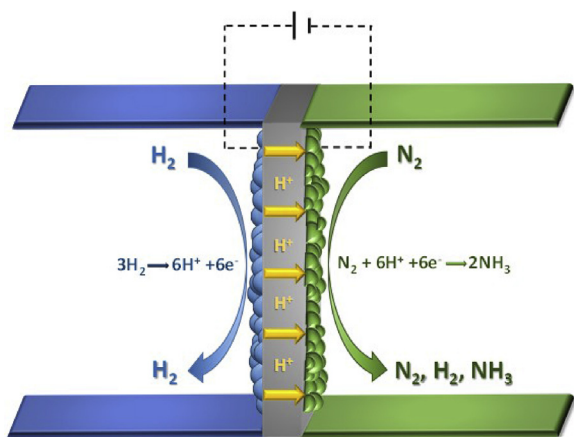
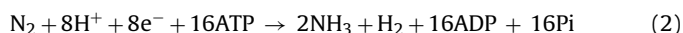


Fig. 1. Schematic diagram of the solid state ammonia synthesis (SSAS) process in a double chamber proton conducting reactor cell.

(molybdenum may be substituted by vanadium or iron) on which the actual nitrogen fixation takes place according to the following overall reaction scheme [7,11]:



Despite the use of enzymes and the reaction's exothermicity, a significant amount of energy equivalent to 8 ATP moles per mol of ammonia produced is consumed, i.e. 244 kJ/mol NH_3 , which is still better than the industrial method [7]. Contrary to the Haber-Bosch synthesis, however, most of the studies of the enzyme-catalyzed synthesis propose an associative mechanism, wherein the $\text{N}\equiv\text{N}$ bond breaks after partial hydrogenation of the N_2 molecule [2,7–9].

Concurrently with improvements in the Haber-Bosch process, several research groups studied the “natural” process and used transition metal complexes to develop an “abiological” process and thus, imitate nature [12,13]. Moreover, the need for protons and electrons for the completion of reaction (2) indicated that ammonia could be synthesized *via* an electrochemical process. To this end, various research groups tested the operation of aqueous electrochemical cells in which NH_3 was produced from H_2O and N_2 [1,4,5]. The problem, however, was that these cells had to operate at low temperatures at which the reaction kinetics were slow. In 1981, Iwahara and coworkers [14] discovered solid state materials that exhibited substantially high proton (H^+) conductivity at elevated temperatures (500–1000 °C). By using such a high-temperature solid electrolyte cell (Fig. 1), the electrochemical synthesis of ammonia from its elements was experimentally demonstrated in 1998 [15]. The process was simple. Gaseous hydrogen passed over the anodic electrode of the proton-conducting cell and was converted to H^+ . By imposition of the proper voltage, the produced protons were electrochemically transported to the cathode where they reacted with gaseous nitrogen to produce ammonia. The cell operated at an atmospheric pressure because the high pressure requirement was counterbalanced by the consumption of electrical energy. In fact, when the cell of Fig. 1 is used and the reactant hydrogen is supplied in the form of protons, one reactant volume produces two volumes of product. Thus, the high pressure requirement is essentially reversed [16].

In the past two decades, several research groups have studied the Solid State Ammonia Synthesis (SSAS) in an effort to improve reaction rates and minimize the electric energy consumption. The main findings from studies published before 2013, have been reviewed recently by Amar et al. [5], Giddey et al. [1] and Garagounis et al. [4]. The present review reports on the progress in the electrochemical synthesis of ammonia in both solid electrolyte and liquid electrolyte cells. Depending on the operating

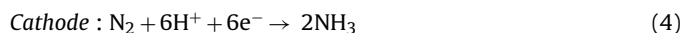
temperature range, the experimental studies are divided into three groups: a) high temperature ($T > 500^\circ\text{C}$), b) intermediate temperature ($500^\circ\text{C} > T > 100^\circ\text{C}$) and c) low temperature ($T < 100^\circ\text{C}$). The presentation of the experimental findings is followed by a summary of the results obtained from theoretical studies, primarily DFT calculations. Theoretical predictions and experimental observations are then comparatively discussed, together with the similarities and differences between the catalytic and the electrochemical process. The techno-economic advantages and disadvantages of the electrochemical approach as well as the requirements to be met in order to enable promotion into industrial practice are also analyzed.

2. Experimental Studies

2.1. High Temperature SSAS

Table 1 summarizes the reported results on the electrochemical synthesis of ammonia at high temperatures ($T > 500^\circ\text{C}$) until the end of 2015. This table shows the electrolytes and electrodes used by various research groups, along with the maximum ammonia synthesis (and current density at which they were obtained) and Faradaic Efficiency (FE) values achieved when using these materials. Certain values of FE or current density are marked with an asterisk. These values were not reported in the cited reference, but have been calculated from data presented therein. Also, in a number of cases no specific value is given, because these works did not provide enough information to permit its calculation. Similar tables have been compiled for works conducted at intermediate and low temperatures (Tables 2 and 3, respectively).

Most of the studies presented in Table 1 employed solid electrolytes, in a reactor-cell design like that depicted in Fig. 1. In the majority of these cases, the electrolyte material was a perovskite. Materials with fluorite or pyrochlore structures have also been reported as possible electrolytes. One group [32,33] reported quite high ammonia rates with a composite electrolyte consisting of YDC combined with calcium-potassium phosphate. When, as in Fig. 1, the electrolyte is a proton conductor the electrochemical reactions at the two electrodes can be written as:



Reactions (3) and (4) combined give us an overall reaction which is the same as reaction (1). As can be seen in Table 1, the most common reactants at the anode and cathode were gaseous H_2 and N_2 , respectively. The highest rates have been observed over Pd-containing catalysts. In the earliest SSAS work, the cathodic electrode (catalyst) was Pd and the highest reaction rate was $4.5 \times 10^{-9} \text{ mol s}^{-1} \text{ cm}^{-2}$, while the highest FE was 78% [15]. In the past decade, many researchers have tested the activity of Ag-Pd. Li et al. used barium cerates (BCS, BCGS) as electrolytes and reported reaction rates as high as $5.82 \times 10^{-9} \text{ mol s}^{-1} \text{ cm}^{-2}$ [18]. Using a lanthanum-doped cerium oxide electrolyte (LDC), Liu et al. obtained a reaction rate of $8.2 \times 10^{-9} \text{ mol s}^{-1} \text{ cm}^{-2}$ [35]. In addition to the high reaction rates, Ag-Pd electrodes have also given the highest Faradaic Efficiencies. The FEs attained by Zhang et al. [20], Chen et al. [36] and Xie et al. [25] were 70%, 73% and 80%, respectively, when using lanthanum gallate and lanthanum zirconate electrolytes.

The presence of water vapor (steam) has been reported to increase the protonic conductivity of perovskite electrolytes [5]. To this end, the introduction of humidified, rather than dry, hydrogen has also been examined on various materials [28,30,31,34,39–42]. It can be seen from Table 1 that, in the case of barium cerate-based electrolytes operating with wet hydrogen over the anode, higher reaction rates and FEs are obtained [31,39,42].

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