



Recent progress towards the electrosynthesis of ammonia from sustainable resources



Michael A. Shipman, Mark D. Symes*

WestCHEM, School of Chemistry, University of Glasgow, Glasgow G12 8QQ, United Kingdom

ARTICLE INFO

Article history:

Received 31 March 2016
Received in revised form 29 April 2016
Accepted 3 May 2016
Available online 7 June 2016

Keywords:

Nitrogen reduction
Ammonia synthesis
Electrocatalysis
Electrosynthesis
Sustainable chemistry

ABSTRACT

Ammonia (NH₃) is a key commodity chemical of vital importance for fertilisers. It is made on an industrial scale via the Haber Bosch process, which requires significant infrastructure to be in place such that ammonia is generally made in large, centralized facilities. If ammonia could be produced under less demanding conditions, then there would be the potential for smaller devices to be used to generate ammonia in a decentralized manner for local consumption. Electrochemistry has been proposed as an enabling technology for this purpose as it is relatively simple to scale electrolytic devices to meet almost any level of demand. Moreover, it is possible to envisage electrosynthetic cells where water could be oxidised to produce protons and electrons at the anode which could then be used to reduce and protonate nitrogen to give ammonia at the cathode. If this nitrogen were sourced from the air, then the only required infrastructure for this process would be supplies of water, air and electricity, the latter of which could be provided by renewables. Hence an electrosynthetic cell for ammonia production could allow NH₃ to be generated sustainably in small, low-cost devices requiring only minimal facilities. In this review, we describe recent progress towards such electrosynthetic ammonia production devices, summarizing also some of the seminal literature in the field. Comparison is made between the various different approaches that have been taken, and the key remaining challenges in the electrosynthesis of ammonia are highlighted.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Ammonia is essential for fertilisers in order to feed the World's growing population. Indeed, it is estimated that between a third and half of us would starve to death if ammonia-based fertilisers were not available, and ammonia's industrial-scale synthesis from its elements is arguably the single biggest scientific discovery of the 20th century [1]. In 2014, total worldwide NH₃ production exceeded 140 million tons, and demand for ammonia continues to grow [2].

Industrially, ammonia is produced almost exclusively via the Haber Bosch process. This process reacts high purity streams of N₂ and H₂ together at high temperatures and pressures (300–500 °C and 200–300 atm) over iron or ruthenium-based catalysts, as in Eq. (1):



High temperatures are needed in order to off-set the sluggish kinetics of this reaction, however, the thermodynamics of this process favour ammonia decomposition to nitrogen and hydrogen at elevated temperatures and hence the need for high pressure. Including the energy required to obtain the pure feed gases, pressurization and so forth, ammonia synthesis by the Haber Bosch process typically requires an energy input of around 485 kJ mol⁻¹ [3]. Whilst this is indeed a large amount of energy (especially in comparison to the Natural systems, see below), and therefore methods that reduce this requirement would be welcome, we shall see that this is in fact a very challenging target. Much is made of the inefficiencies of the Haber Bosch process and its requirement for pure H₂ (often obtained from fossil fuels), but currently there is no scalable ammonia synthesis technology that comes close to matching its performance.

Nitrogen reduction to ammonia on a heterogeneous surface can proceed by two broad classes of mechanism: *Associative* and *Dissociative* (see Fig. 1). In an associative mechanism, the two nitrogen centres in N₂ remain bound to each other as the molecule is hydrogenated, with NH₃ being released only once the final N–N bond is broken. Hydrogenation in an associative mechanism can then itself be envisaged to occur through two possible pathways.

* Corresponding author.

E-mail address: mark.symes@glasgow.ac.uk (M.D. Symes).

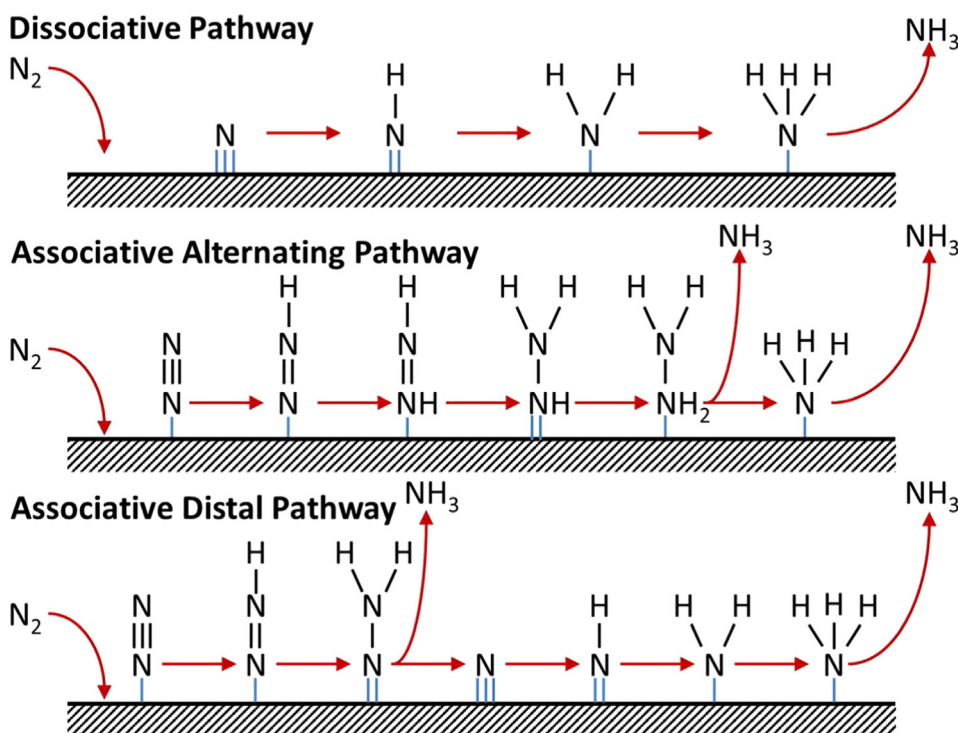
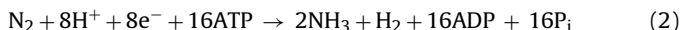


Fig. 1. Generic mechanisms for nitrogen reduction to ammonia on heterogeneous catalysts.

Hydrogenation might occur preferentially on the nitrogen furthest away from the surface (assuming an end-on coordination mode for the N_2 molecule), leading to the release of one equivalent of NH_3 and leaving behind a metal nitrido ($M\equiv N$) unit which will itself be hydrogenated to give a second equivalent of ammonia. This is known as a *distal* associative pathway. The second type of associative mechanism (the *alternating* pathway) calls for each of the two nitrogen centres to undergo single hydrogenation events in turn, until such time as one of the nitrogens is converted into NH_3 and the $N-N$ bond is broken. In a *dissociative* mechanism on the other hand, the $N\equiv N$ bond is broken before any hydrogenation takes place, leaving individual N -atoms on the surface which are converted into NH_3 independently. Current evidence suggests that the Haber Bosch process operates through a dissociative mechanism.

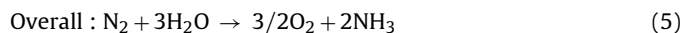
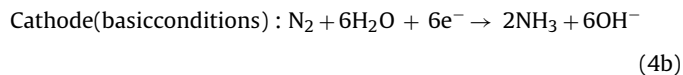
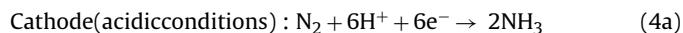
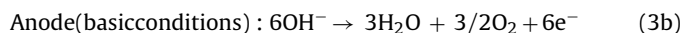
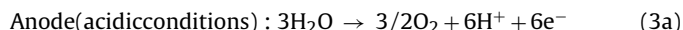
In Nature, nitrogen reduction to ammonia is achieved by a class of enzymes called the nitrogenases and presents a very different picture to the Haber Bosch process. The most effective nitrogenases are the FeMo nitrogenases, which consist of two fused iron-sulfur clusters with a carbon atom at their junction and a molybdenum atom in one of the apical positions [4,5]. It appears that a minimum of 16 equivalents of ATP (adenosine triphosphate) are required in order to reduce one N_2 molecule Eq. (2), meaning that 244 kJ are required per mole of NH_3 produced [6]:



where ADP is adenosine diphosphate and P_i denotes “inorganic phosphate” (a mixture of HPO_4^{2-} and $H_2PO_4^-$ ions). The formation of H_2 as a side-product may well be obligatory, and indeed more H_2 than suggested by Eq. (2) may be formed, rendering the energetic requirements for ammonia synthesis somewhat greater (depending on how much H_2 is actually produced). In contrast to the Haber Bosch process, the mechanism of formation is believed to be associative (with the N_2 molecule coordinating to a metal centre in the FeMo nitrogenase end-on), although whether hydrogenation proceeds by a distal or an associative pathway is still open to debate [7]. Regardless of the details of the mechanism operating, however, it is

clear that nitrogenase enzymes are able to catalyse the production of ammonia from air and water under very mild conditions (room temperature and pressure, aqueous media) with impressive energy efficiency. Reproducing similar chemistry in a format applicable to industrial-scale production is in many respects the ultimate goal of all nitrogen reduction studies.

Against this backdrop, electrochemistry has emerged as an alternative technology by which to reduce nitrogen to ammonia [8]. In particular, an electrochemical system that oxidises water in order to obtain protons and electrons for the reduction of nitrogen would be very attractive, as the only inputs required would be N_2 (which could conceivably come from the air), water and electricity (which could conceivably come from renewable sources). The basic equations for such a process can be expressed as:



Hence no fossil fuels would need to be consumed to generate ammonia. Furthermore, by exploiting the inherent flexibility of electrochemical systems, NH_3 production could be carried out at either a small or a large scale as required. It has been estimated that such a system could be up to 20% more energy-efficient than a Haber Bosch process using coal as the hydrogen source, although with today's technology it would remain 30% less efficient than a Haber Bosch process using natural gas as its hydrogen source [9].

In this review, we shall examine recent progress towards electrochemical systems that produce ammonia by the reduction of

Download English Version:

<https://daneshyari.com/en/article/6455297>

Download Persian Version:

<https://daneshyari.com/article/6455297>

[Daneshyari.com](https://daneshyari.com)