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Assessment of an integrated solar hydrogen system for electrochemical synthesis of ammonia

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ABSTRACT

In this paper, a solar based electrochemical system is designed, built and tested to synthesize ammonia and hydrogen from nitrogen and saturated steam. Ammonia can serve as a sustainable fuel and is in heavy demand by the fertilizer industry. However, the conventional methods rely on hydrogen produced from fossil fuels. Hydrogen can be supplied back by implementing fuel cells and feeding electricity back to the system, directed to the conventional ammonia production methods as a reactant, or sold as a fuel. A simple and direct system is studied to pose a sustainable option for ammonia and hydrogen production. Very high concentrations of Nano iron catalyst are used to promote the concentration of ammonia at the output. The reactor is designed for continuous flow and can be disassembled for varying tests and scenarios. The maximum concentration of ammonia is found to be 950 ppm measured with excess reactant supply. Increasing nitrogen flow rates along with decreasing steam flow rates render increasing concentration results. The system at optimum conditions consumes 650 mA at 1.7 V. The low power requirements and valuable products of the system encourage further studies. Additionally, a solar energy based system is proposed as a renewable approach to ammonia synthesis with a fuel cell component to increase the efficiency by reducing the power consumption to 60% of its original value.

Introduction

Ammonia is considered a renewable fuel due to its cleaner combustion relative to fossil fuels. It has also been the focus in fuel cell development as a fuel similar to hydrogen. The high potential for ammonia to become a candidate as a future fuel is based on continuous development. Ammonia production is presently increasing at a steep rate and its source is mainly fossil fuels. As the world increases its attention to pollution and conservation as well as the development of renewable energy technologies, it is of importance to find suitable methods to produce ammonia based on carbon-free sources.

Electrochemical synthesis of ammonia is the main method that connects renewable sources to the final delivery of ammonia. This is because most renewable energy technologies produce electricity which is the main driving force behind the ammonia synthesis. This paper studies a particular method which is electrochemical synthesis of ammonia from nitrogen and water. It is important to note that hydrogen is not a reactant which is preferred since hydrogen in the present day is produced from fossil fuels. The electrochemical

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methods are predicted to decrease the energy input by more than 20% which, if partnered with cost effective materials, could shift industrial ammonia production from the conventional thermochemical method to a new electrochemical method as mentioned by Giddey et al. [4].

The three fundamental components involved in electrochemical synthesis include an ionic conducing electrolyte, a cathode, and an anode. The reversible potential of the reaction is defined by the reactants being used and the characteristics of the activation, ohmic, and concentration over potentials. The goal of such a system is to efficiently consume the energy supplied to synthesise ammonia at high rates. Catalysts have a very important role in chemical reactions. The requirement for complex and varying catalysts used on electrodes as well as suspended in electrolytes has led to a large spectrum of experimental results in the ammonia synthesis field. The methods can be divided based on the electrolytes used; there are solid state electrolytes, liquid electrolytes, molten salt electrolytes, and composite electrolytes.

Solid state electrolytes have rendered the highest production rates with the use of nafion membranes and complex anode and cathode compositions. The value rendered by Xu et al. [9]; is 1.13×10^{-8} mol s^{-1} cm^{-2} with an efficiency of 90.4%. It was found by Amar et al. [1] that solid polymers render the highest rate of ammonia formation while pyrochlores render the least. However, they note that catalysts in the electrodes also have an impactful role in these results.

Liquid electrolyte systems are based on materials such as lithium perchlorate in tetrahydrofuran, $Li(CF_3SO_3)$ in tetrahydrofuran and ethanol, $LiBF_4$, and a combination of methanol and $LiClO_4$ given by Giddey et al. [4]. Other materials tested without Li resulted in unrecognizable production rates and thus Li was found to be the mediating material. The current efficiencies from this method were 5–59.8% and the production rates were calculated from 3.68×10^{-10} mol s^{-1} cm^{-2} to 4.0×10^{-9} mol s^{-1} cm^{-2} of ammonia.

Molten salt electrolyte systems operate at higher temperatures from 200 to 500 °C due to the melting point of the salts. However, the ionic conductivity is improved significantly as well. Most systems use nitrogen, hydrogen, and methane as the reactants and the highest achieved efficiency rate was 72% with a corresponding formation rate of 3.3×10^{-9} mol s^{-1} cm^{-2} by Murakami et al. [8]. The reactants were hydrogen gas and nitride ions within the molten salts consisting of a LiCl-KCL-CsCL eutectic mixture. Licht et al. [6]; investigated the synthesis of ammonia from air and steam producing rates from 2.9×10^{-9} mol s^{-1} cm^{-2} to 6.7×10^{-9} mol s^{-1} cm^{-2} with efficiencies up to 35%. The system, although currently inefficient, has addressed the necessity to use easily available reactants instead of hydrogen which itself requires energy that is not generally accounted for. Furthermore, the system produces hydrogen at 30% efficiency which could be used to supply other reactors that do require it by using integrated systems. The investigation uses a KOH-NaOH eutectic mixture with Nano-iron oxide catalysts suspended in the mixture working as low as 200 °C in atmospheric pressure. Cui et al. [3] used the same method but added an active carbon component to the catalyst. They found the highest production rate of ammonia to be 8.27×10^{-9} mol s^{-1} cm^{-2} with the highest efficiency being 13.7%.

Composite electrolytes use a combination of ion conducting phases. The combination improves electrical, thermal, or mechanical properties and is concurrently being studied for applications in intermediate temperature fuel cells. The use of these electrolytes have rendered production rates up to 6.95×10^{-9} mol s^{-1} cm^{-2} and an efficiency up to 2.95% was found by Amar et al. [2].

Some key reviews in this field were provided by Kyriakou et al. [5] who summarized electrochemical ammonia synthesis from work during the past 20 years by temperature and provided the corresponding half reactions for key processes. Needed progress in the areas of materials science, solid state ionics, and heterogeneous catalysis were identified as the most important. In another review performed by Montoya et al. [7]; they summarized the challenges of electrochemical ammonia synthesis while also proposing methods to select new catalysts when considering the mechanisms taking place in the reduction of nitrogen to ammonia.

The methods for the electrochemical synthesis of ammonia offer a variety of advantages and disadvantages in terms of efficiency and formation rate. These are balanced where one needs to be sacrificed to maximise the other. For example, in the Haber Bosch process low temperatures render high efficiencies but low reaction rates. High efficiencies have been found up to 90.4% which leaves the area of focus on increasing the amount of ammonia formed. This can be done in three ways: by altering the characteristic of the materials to decrease losses, by increasing the presence of known catalysts, or by simply increasing the size of the systems to scale up the production with current rates. Due to the low cost of materials, the latter method may be best choice. Since there are limited studies in the open literature, the present paper focuses on a novel method which presents promising results with simple procedures that could potentially be scaled up with a new system, depending on financial factors and viability of alternative methods. This paper aims to experimentally validate the process of electrochemical synthesis of ammonia while also proposing improvements and finally to present a solar based system which uses PV technology and solar thermal collectors in combination with a fuel cell component to decrease the power consumption to 60% of the consumption without the improvement.

Analysis

The reaction of steam and nitrogen to form ammonia, hydrogen, and oxygen is one that can be analysed thermodynamically in order to find the Gibbs free energy of the reaction.

$$\begin{aligned}\Delta G = \big(&X \times (\Delta_f H^\circ NH_3 - T \times S^\circ NH_3) + Y \times (\Delta_f H^\circ O_2 - T \times S^\circ O_2) \\ &+ W \times (\Delta_f H^\circ H_2 - T \times S^\circ H_2)\big) - \big(Z \times (\Delta_f H^\circ N_2 - T \times S^\circ N_2) \\ &+ B \times (\Delta_f H^\circ H_2O - T \times S^\circ H_2O)\big)\end{aligned} \tag{1}$$

From this, the reversible voltage of the reaction can be found from:

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