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Term-Paper 2
SEE607:HYDROGEN ENERGY:PRODUCTION, STORAGE AND UTILIZATION

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Electrochemical synthesis of ammonia as a potential alternative to the Haber-Bosch process.

As we all know that the foremost Haber-Bosch process has been feeding humankind for more than one hundred years. In early Nineties (1909) Fritz Haber invented a process converting nitrogen and hydrogen to ammonia(1). Later in 1913, with amazing speed his bench reactor was converted by Carl Bosch into the first commercial ammonia plant in Oppau, Germany, making twenty tonnes of ammonia per day.

$$3H_2 + N_2 \rightarrow 2NH_3 \qquad (1)$$

Currently, ammonia is produced at global scale is about 240 million tonnes per year. The conventional method of ammonia production consume the energy more than 110 kWh kg^{-1} (2) . After hundred years of development there has been a great decrease in production cost and energy consumption to 7.7 – 10.1 kWh kg^{-1}. Apart from nitrogen separation from air, ammonia plant uses two major fossil fuels as feedstocks. Firstly the natural gas which is quite economical and least polluting. Secondly, coal which is primarily used to produce hydrogen from steam reforming (2) (3), and these fossil fuels also used to run the Haber- Bosch process as it require high temperature and pressure as operating conditions. Eventually leads to high emissions of CO_2 by coal based plants. The following reaction takes place in coal based plants:

$$3CH_4 + 6H_2O + 4N_2 \rightarrow 8NH_3 + 3CO_2 \qquad (2)$$

$$3C + 6H_2O + 2N_2 \rightarrow 4NH_3 + 3CO_2 \qquad (3)$$

Constrains of Haber-Bosch Process:
Requires high purity hydrogen. High energy demand process.

1.44% of overall global CO_2 emission is contributed by ammonia synthesis which is a concerning data. According to literature the global average emission od CO_2 is 2.86 tons per ton of amonia synthesis(1) .

The current huge bottleneck that the major part of the researchers are working on this field is that the Haber-Bosch process plants require billions of dollars of capital. Which makes is highly capital intensive process.

Another major problem of the conventional process is that it takes several years to build. Though due to thorough engineering and invovation this can be addressed.

In order to address the above challenges and as the global trend is shifting towards the net zero carbon emission till 2050. A potential alternative is under development , so that the synthesis of ammonia process could brought towards more sustainable and economical.

Renewable ammonia: It has becomes very important that one really needs to focus on completely eliminating the carbon emission from ammonia synthesis process. Basically there are two major steps for ammonia synthesis, one is the hydrogen production and another is the power needed to run the process. If we try to address the above two major problem by making it from renewable sources and one can possible able to make renewable ammonia synthesis in future.

As one of trending and important field of research that majorly the globle is working on is the production of hydrogen by water electrolysis. In this case, the hydrogen can be produced by the commercially available water electrolysis such as Proton exchange membrane(PEM) or emerging Anion exchange membrane(AEM) or Solid oxides electrolyser cells(SOEC).

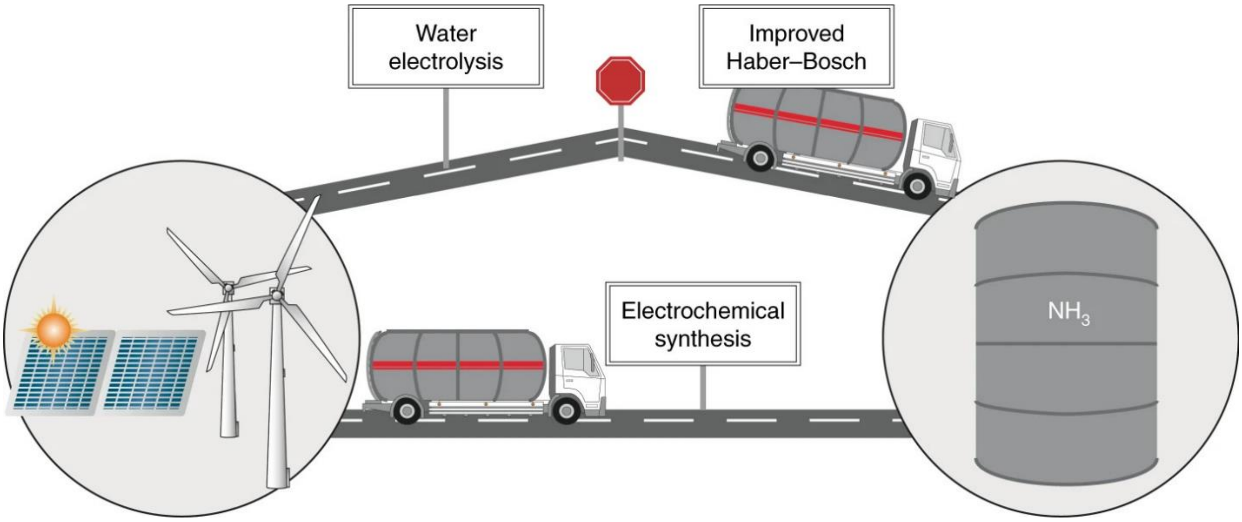

Fig.1 Pathways to renewable ammonia.

The above Figure demonstrate the pathways to renewable ammonia. As we discussed above the production of hydrogen by water electrolysis. In order to address the high operating cost as Haber-Bosch process requires high temperature and pressure, also catalyst to increase the kinetices of the reactions. It increases the catalyst replacement cost and overall capital cost.

A alternative process which has been discussed in various literature is to use different types of plasma to accelerate the reactions. However, it is an emerging process and people are yet to discover how much energy is wasted for non-productive plasma generation and the ammonia production rate is far slow by plasma.Which leaves two possible scenarios for potential production of renewable ammonia.

generation of hydrogen by water electrolysis

$$H_2O \leftrightarrow H_2 + 0.5O_2 \qquad (4)$$

direct electrochemical reduction of dinitrogen in the presence of water

$$N_2 + 3H_2O \leftrightarrow 2NH_3 + 1.5O_2 \qquad (5)$$

Electrochemical synthesis of ammonia: Electrochemical synthesis of ammonia was first demonstrated by Humphrey in 1807, while the relevant patent was provided in 1908 (2) . Electrochemical N_2 reduction reaction offers a renewable and distributed route for ammonia production. Various researchs has been carried out and many are still ongoing have focused on design and develiopment of advanced electrocatalysts to make electrochemical dinitrogen reduction as one of most promising and potential alternative against conventional Haber-Bosch process from the economic and ecological viewpoint.

The electrochemical ammonia synthesis reaction of dinitrogen in presence of water and a proton source under the power conditions by renewable electricity (solar and wind energy), which offers a promising carbon-neutral and sustainable strategy.

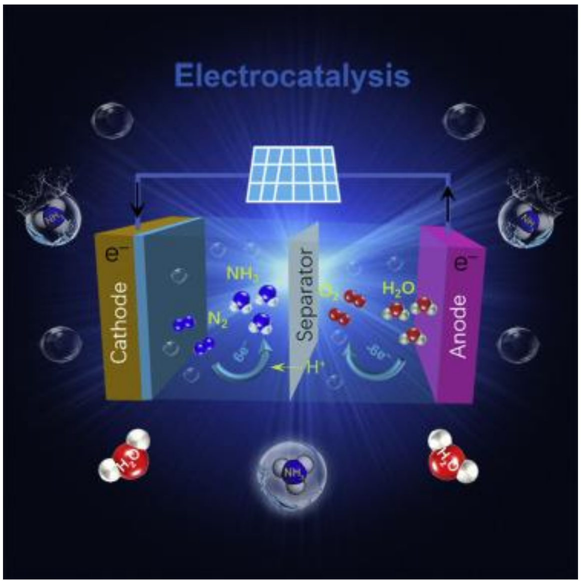

Fig:2 Electrochemical ammonia process

Why Electrochemical synthesis of ammonia via dinitrogen reduction is attractive process compared to other process such as Biocatalysis, Photocatalysis, Haber-Bosch process? (2) (3)

1) Potentially higher energy efficiency than the Haber-Bosch process
2) Environment compatibility through coupling with carbon-free renewable energy resources like, solar, wind, tidal.
3) Elimination of fossile fuels as H_2 sources where by the required protons(H^+) are generated in situ from water oxidation.
4) Flexible control of the reaction by adjusting external parameters(such as electrochemical voltage), being conductive to modular and small-scale operation
5) Scalability and on-demand, on site ammonia production.

However, there many factors that on needs to look after: (3) (4) (2)

1) N_2 has remarkable thermodynamic stability and requires high energy to be activated.
2) Impementation of this “clean” ammonia synthesis route therefore still requires significant enhancement in energy efficiency.
3) It has slow conversion rate.
4) The durability of the process is less.
5) High overpotentials are usually demanded to overcome the kinetic barrier of N-N bond.

The design of efficient electrocatalysts and development of novel electrocatalysys would make huge beneficial change in the above contraints.

Techno-economis analysis of electrochemical: Many studies claims the cradle of Gate Life Cycle Assessment for ammonia by Haber-Bosch and Electrochemical Method, The Greenhouse Gases, Regulated Emission, and the energy use in transportation and the environmental impact of the ammonia production process by Haber-Bosch and electrochemical method. (3) (4) (5)

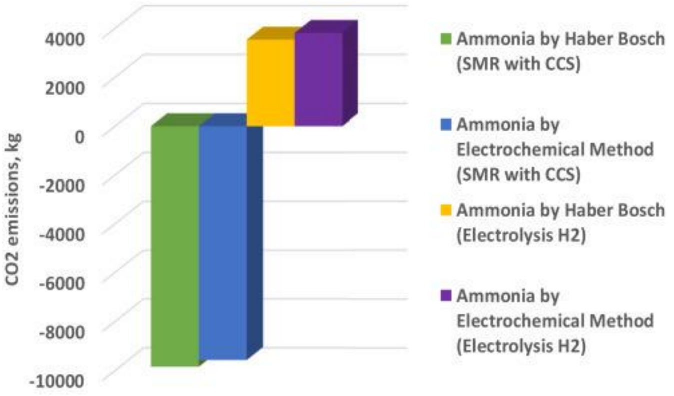

Fig:3 Varition in CO2 emission of ammonia processes

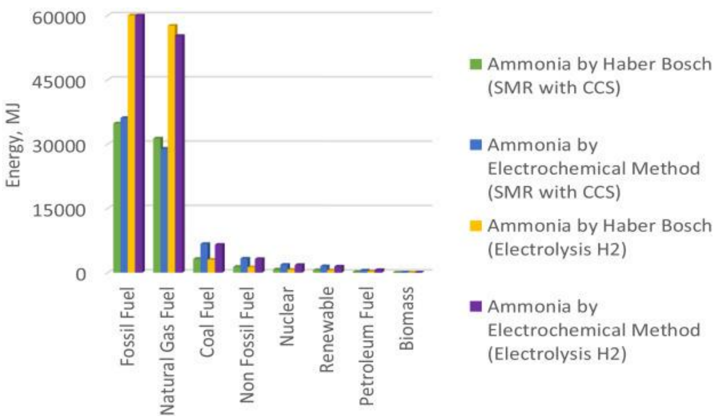

Fig:4 Resource consumption of ammonia processes

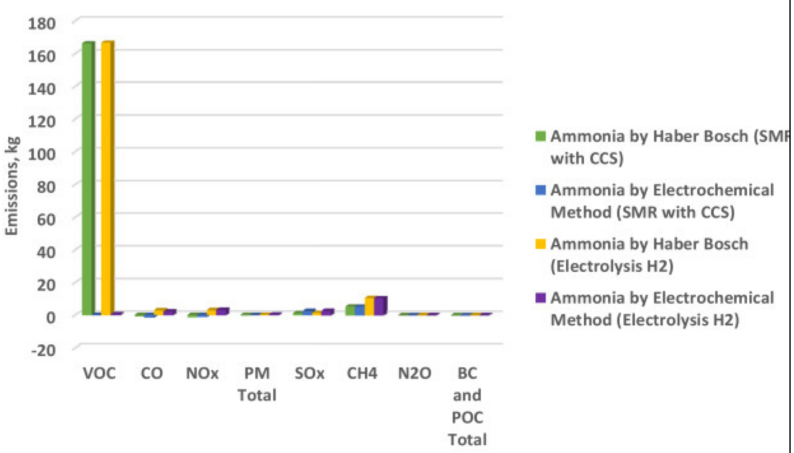

Fig:5 Emission contribution of ammonia processes

- Hydrogen production by water electrolysis produces 70% less CO2 emmision when compared to SMR.

- Ammonia by celectrochemical method powered by renewable electricity throughout will bring us closer to having a carbon neutral process.

- Fig:4 shows the consumption of renewable and non renewable energy resources which is a major component of Life Cycle Assessment.

- Hydrogen production by Steam Methane Reformation results in a higher resources consumption.

- Volatile organic compounds(VOCs) is shown as the second large major emissions sources largely(>99%) produced by Haber-Bosch process followed by methane, nitrogen oxides, sulfur oxides, carbon monoxide etc.

- Emission of other greenhouse gases and air pollutant from ammonia production has shown if Fig:5

Conclusion

The conventional method of ammonia synthesis has two major drawbacks the feedstocks cost and the energy consumption which makes it highly cost intensive process. However if water electrolysis combined with improved Haber-Bosch process can reduction the major cost of the hydrogen production and can improve the energy efficiency of the process. The major research focus on reducing the ammonia synthesis reaction pressure and temperature. Also, integrating electrochemical ammonia systems with renewable sources has scalability advantages in order to meet the increasing demand of ammonia around the global (5).

Over past 9 years, significant and encouraging advances have been achieved for electrochemical nitrogen reduction reaction to synthesize ammonia. Coupling different strategies of design of electrocatalysts and current techno advancement will lead electrochemical process as one of most emerging and promising process economically and ecologically sustainable innovation.

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