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An Introduction to Electrochemical Nitrogen Reduction Reaction

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Abstract

The environment friendly electrochemical nitrogen reduction reaction (ENRR) might be an opportunity to replace the Haber–Bosch process for Ammonia (NH_3) production in upcoming future. Large-scale research has been devoted in designing effective electrocatalysts for NH_3 production. According to 'The Royal Society Report 2020', the Haber-Bosch process is the primary method in producing ammonia from Nitrogen and Hydrogen. Ammonia produced, utilized mainly as fertilizers, currently responsible for approximately 1.8% of Carbon Dioxide global emissions. Recently, metal oxides have been widely studied for the electrochemical Nitrogen Reduction Reaction. It is concluded that metal oxides could be used as effective electrocatalysts for nitrogen reduction reaction. Here we discus in brief about Nitrogen Reduction by Electrocatalyst, its process and implication.

Introduction

The Ammonia Production with help of electrochemical synthesis has received huge attention as it could lead the production of ammonia, with creating far less pollution than existing procedures. It will be more effective if done along with generation of electricity from sustainable energy production units including renewable energy sources.

Nitrogen reduction reaction is one of the important reactions driven by electrocatalyst. It could help us in producing Ammonia with less pollution. Ammonia is very important raw material for Agriculture, Pharmaceutical, Chemical and Food industries. It is a fundamental raw material of Nitrogen based fertilizers specially the urea. Urea helps to boost crop yields, now it has become most preferred inorganic source of nitrogen for farmers in the agriculture.

Although it is not ready to implement today but for sake of future, researchers have some vision of NH_3 production with electrocatalysis that will be cheap and more importantly it can help to produce ammonia without promoting greenhouse effect or pollution as traditional procedures.

Background

The reaction of nitrogen and hydrogen gas to produce Ammonia, also known as Haber–Bosch process. The reaction involves the reaction of nitrogen gas (N_2) and hydrogen gas (H_2) at high temperature and pressure to produce ammonia gas (NH_3). It releases carbon dioxide as byproduct and heat, that's an exothermic reaction. The most commonly used catalyst is iron-based i.e., iron with Calcium oxide, Potassium Oxide, etc.

$$N_2 + 3H_2 \xrightarrow[\text{300atm}]{\Delta} 2NH_3$$

The Haber-Bosh is a reliable process of manufacturing ammonia, it is used in about 96% of ammonia manufacturing plants around the world. But it produces carbon dioxide as byproduct, and the setup which creates desired environment of the reaction, consumes lot of energy. The overall conversion yield of the Haber-Bosch process is nearby 97%. The environment friendly electrochemical nitrogen reduction reaction (ENRR) gives an opportunity to replace the Haber–Bosch process for NH_3 production.

Electrochemical Nitrogen Reduction Reaction

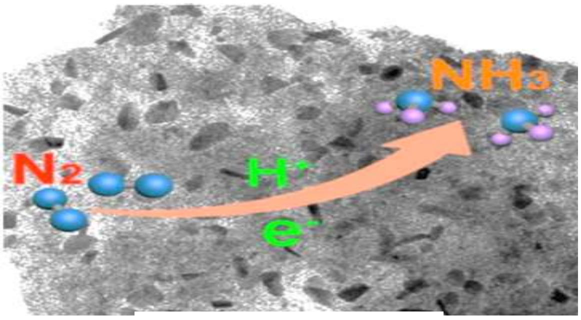
Large-scale research has been devoted in designing effective electrocatalysts for NH_3 production. However, it is still difficult to prevent low selectivity and Faraday efficiency from impeding the development of the electrochemical NRR. Thus, the development of efficient electrocatalysts to improve the selectivity and Faraday efficiency is the foremost issue in enhancing NH_3 production.

Recently, metal oxides have been widely studied for the electrochemical NRR, such as Fe_2O_3, TiO_2, InO_2, NbO_2, SnO_2, etc. It was concluded that metal oxides could be used as effective electrocatalysts for ENRR.

In case of Fe-based oxides, $Fe_2(MoO_4)_3/C$ it is widely recognized as good electrocatalysts for the NRR with overall ammonia yield rate of 51.76%. On the other hands electrocatalysts like $Zr4^+$ co-doped anatase nano TiO_2 shown good electrochemical NRR performance. It showed overall yield around 46.8% which is more than TiO_2(39%), and SnO_2(35%).

Electrocatalytic N_2 fixation is regarded as an essential green road to achieve mild N_2 to NH_3. The basic electrocatalytic NRR process encompasses the following elementary steps:

1) Diffusion of N_2 into the surface



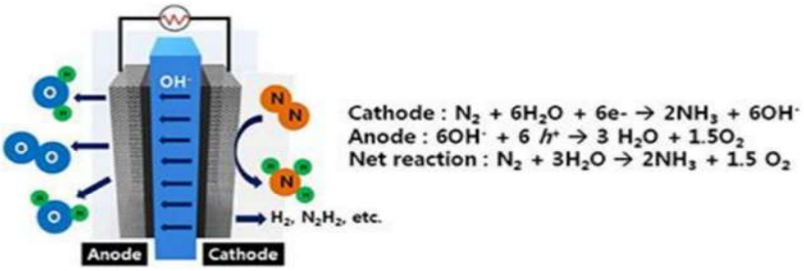
Visualization for ENRR

2) Activation of N_2 molecules to intermediates via the participation
of protons and multiple electron transfer.

3) As electrical charges are exchanged and protons are injected to break bonds and hydrogenate N_2 (bond dissociation energy = 941 $kJmol^{-1}$) and NH_3 released.

The corresponding reactions are shown in Alkaline condition as follows.

*Anode: $6OH^{-} \rightarrow 3/2O2 + 3H_2O + 6e-$
*Cathode: $6H_2O + N_2 + 6e^{-} \rightarrow 2NH_3 + 6OH^{-}$
Overall reaction: $N_2 + 3H_2O \rightarrow 3/2O_2 + 2NH_3$



ENRR reaction in Alkaline

Mechanism

The Electrochemical nitrogen reduction happens primarily by Direct or Indirect pathway. The direct pathway can be classified into two categories based on the nature of the electrolyte, viz., nonaqueous and aqueous. The aqueous pathway is the most feasible approach to produce ammonia from atmospheric Nitrogen and protons from water. Ammonia production in nonaqueous electrolytes uses sacrificial proton donors, such as alcohols or cationic complexes, to protonate the adsorbed N_2 into ammonia.

The indirect pathway is mediated through nonaqueous aprotic electrolytes (electrolytes which do not donate protons or undergo hydrogen bonding), and involves forming intermediates. These intermediates are usually the corresponding metal nitrides that can be hydrolysed to produce ammonia. Because of the instability, recyclability, and scalability of nonaqueous electrolytes, indirect ammonia synthesis does not compete with the industrial demands.

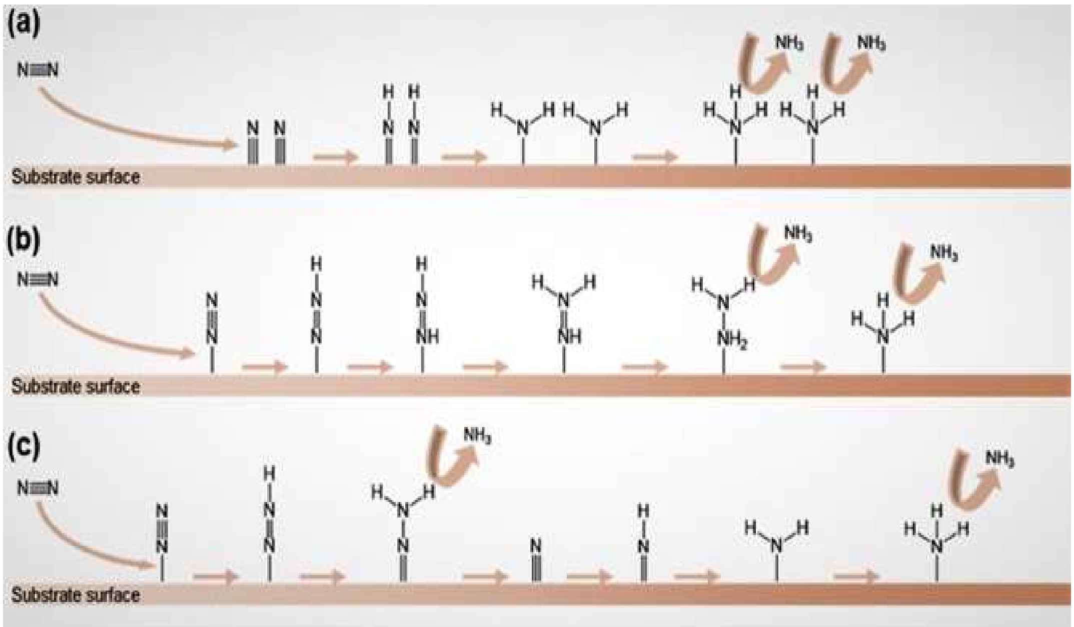
Different pathways of the NRR: (a) dissociative pathway, (b) associative alternating pathway, (c) associative distal pathway

Direct ammonia synthesis occurs under several process, of which dissociative and associative pathways are primarily followed. The dissociative and associative mechanisms are differed by either direct dissociation of the N_2 triple bond or by protonation of the adsorbed N2 molecule. The hydrogenation of the dissociative adsorbed N_2 usually occurs with the H_2 produced from natural gas, producing CO2 as the byproduct. The associative pathway reduces the nitrogen molecule into ammonia in six proton-coupled electron transfer stages. The reduction of nitrogen molecule in associative pathway takes place in six proton-coupled electron transfer stages.

In the associative alternating pathway, hydrogenation occurs at the same time on both nitrogen atoms, and the ammonia molecule released. In the associative distal pathway, the hydrogenation series appeared only on the first nitrogen atom, and only after the release of the first ammonia molecule does protonation of the other nitrogen.

Conclusion

- The electrochemical nitrogen reduction reaction (ENRR) is environment friendly; it gives an opportunity to replace the Haber–Bosch process for NH_3 production in upcoming future.
- Electrochemical nitrogen reduction reaction basically consists of three important steps,
    1) The electrode surface approached by N_2 molecules
    2) Electrical charges introduced to break bonds and hydrogenate N_2
    3) Ammonia releases
- Metal oxides have the potential to act as electrocatalysts for NRR. Electrocatalysts like, $Fe_2(MoO_4)_3/C$ and $Zr4^+$ co-doped anatase nano TiO_2 shown good electrochemical NRR performance.
- However, some loopholes are still there to need more research in designing the ideal electrocatalysts in improving NH_3 production rate.



Different pathways of the NRR: (a) dissociative pathway, (b) associative alternating pathway, (c) associative distal

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