Highly-Selective Electrochemical Reduction of Dinitrogen to Ammonia at Ambient Temperature and Pressure

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1. Background

Heterogeneous catalysts

Haber–Bosch Process:

\[ \text{Holly grail} \]

\[ \text{N}_2 \quad 1 \text{ atm} \quad \rightarrow \quad \text{NH}_3 \]

room temperature

Biological catalysts

Photocatalytic catalysts &
Electrocatalytic catalysts

using water, air and renewable energy

lower energy consumption

Mater. Horiz., 2018, 5, 9  
Energy Environ. Sci., 2018, 11, 45-56  
Science, 2018, 360, eaar6611

Synthetic molecular catalysts

Chem. Rev. 2014, 114, 8, 4041

1. Background

Challenges of heterogeneous nitrogen reduction reaction (NRR)

Limitations of the scaling relations

The competing hydrogen evolution reaction (HER)


2. Review of electrocatalytic NRR

Strategies to enhance heterogeneous NRR under ambient conditions:

- Boosting NRR by rational catalyst design
- Suppressing HER at the catalyst/electrolyte interface
- Avoiding HER by decoupling \( \text{N}_2 \) fixation and \( \text{NH}_3 \) formation

- Review of electrocatalytic NRR
2. Review of electrocatalytic NRR

A summary of electrocatalytic devices for NRR

NH₃ determination methods

1. Colorimetric methods:
   - Indophenol blue method
   - Nessler’s reagent method

2. Ion chromatography

3. Ammonia selective electrode (e.g.: Orion 9512HPBNWP)

4. ¹⁵N₂ isotopic methods
   - Nuclear magnetic resonance spectrometer (NMR)
   - mass spectrometer (MS)
   - Infrared spectroscopy (IR)

3. Hematite catalyst toward NRR

**Hematite (α-Fe₂O₃) nanoparticles**
Motivated by *Science* 2014, 345, 637

**Surface modification to boost NRR**

- Preparation of catalyst ink and deposit onto carbon paper (CP)
  Catalyst loading: 3.4 mg cm⁻²

- Hot-pressing of Nafion 115 membrane and CP at 130°C for 5 min to form an MEA

Using the Nessler’s reagent method for ammonia determination
3. Hematite nanocatalyst toward NRR

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The concentration of the surface oxygen vacancies varied while the crystal phase maintained after annealing.

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3. Hematite catalyst toward NRR

An average $r_{\text{NH}_3}$ of 1.45 $\mu g \cdot h^{-1} \cdot cm^{-2}$ and NH$_3$ FE of 8.28% (1h)

An average $r_{\text{NH}_3}$ of 0.46 $\mu g \cdot h^{-1} \cdot cm^{-2}$ and NH$_3$ FE of 6.04% (4h)

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3. Hematite catalyst toward NRR

An average $r_{\text{NH}_3}$ of 0.183 $\mu\text{g}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ and $\text{NH}_3$ FE of 3.09% (8h)

*Chem. Eur J. 2018, 24, 1*

- Both the $\text{NH}_3$ yield and $\text{NH}_3$ faradaic efficiency of NRR under ambient conditions can be improved by modification of the hematite surface.
- However, the catalytic activity, selectivity and stability toward NRR in aqueous systems are still far from satisfactory.
4. Future directions for NRR

- Rational Design of the Catalysts and the Electrochemical System
- Better Understanding of the NRR Mechanism
- Standard Protocols for the Electrochemical NRR Measurements
- Clarification of the Origin of Nitrogen in the Ammonia Generated
- Advanced Characterization Techniques: in situ and operando studies
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