Nitrogen Electrochemical Reduction Reaction on Noble Metals

By

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Abstract

Nitrogen electrochemical reduction reaction has become a hot research topic in recent years, since it allows the direct conversion of renewable electric energy into chemical energy stored in ammonia, thus streamlining the procedures and enhancing the process efficiency with zero CO₂ emission. However, the achievements in this area are still far from meeting the requirements for its commercial application, majorly owing to the serious competing of the hydrogen evolution reaction on the cathodic electrocatalysts surfaces. Furthermore, the mechanism study is significantly limited for this reason, even though understanding the reaction mechanism on the electrocatalysts surface is vital for the rational design of more advanced electrocatalysts.

In this thesis, the nitrogen electrochemical reduction mechanism on noble metals surfaces (Au, Pt, Ru, Rh) is studied first time by the in situ electrochemical techniques, including the surface enhanced infrared absorption spectroscopy (SEIRAS) and differential electrochemical mass spectrometry (DEMS). On Au surface, the N-N stretching band at 1109 cm⁻¹ was detected during the nitrogen reduction reaction in an alkaline electrolyte, indicating that the N₂H₃ (3≤y≤4) is a reaction intermediate on Au surface and that the nitrogen electrochemical reduction on Au surface follows an alternative pathway. While on Ru and Rh surface, the N=N stretching band at ~2000 cm⁻¹ is detected in acidic and alkaline electrolytes, respectively. N₂Hₓ (0≤x≤2) is a reaction intermediate on Ru and Rh surface, which could be oxidized on Ru surface at potential below 0 V. Additionally, the differential electrochemical mass spectrometry signal of N₂H₂ (m/e=29) further confirmed it, and also indicated that the N₂H₂ could be desorbed from the Rh surface and decomposed into nitrogen and ammonia in the electrolyte. Besides, a series chromium oxynitrides were synthesized as the electrocatalysts for nitrogen electrochemical reduction, which were evaluated in a home-made proton exchange membrane electrolyzer (PEMEL). High ammonia formation rate of 8.9×10⁻¹¹ mol s⁻¹ cm⁻² and 15.56 μg h⁻¹ mg⁻¹cat was achieved, demonstrating that metal nitride-based materials could be promising electrocatalysts toward nitrogen electrochemical reduction.