



Selective conversion of N₂ to NH₃ on highly dispersed RuO₂ using amphiphilic ionic liquid-anchored fibrous carbon structure

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ARTICLE INFO

Article history:

Received 8 May 2021

Revised 25 August 2021

Accepted 2 September 2021

Available online 10 September 2021

Keywords:

Ammonia synthesis

Nitrogen reduction reaction

Imidazolium-based ionic liquid

Ruthenium oxide

ABSTRACT

Ammonia (NH₃) plays a key role in the agricultural fertilizer and commodity chemical industries and is useful for exploring hydrogen storage carriers. The electrochemical nitrogen reduction reaction (NRR) is receiving attention as an environmentally sustainable NH₃ synthesis replacement for the traditional Haber–Bosch process owing to its near ambient reaction conditions (<100 °C and 1 atm). However, its NH₃ yield and faradaic efficiency are extremely low because of the sluggish kinetics of N≡N bond dissociation and the hindrance from competitive hydrogen evolution. To overcome these challenges, we herein introduce a dual-functionalized ionic liquid (1-(4-hydroxybutyl)-3-methylimidazolium hydroxide [HOBIM][OH]) for a highly dispersed ruthenium oxide electrocatalyst to achieve a biased NRR. The observed uniform distribution of RuO₂ on the carbon fiber and increase in the surface area for N₂ adsorption by limiting proton access can be attributed to the presence of imidazolium ions. Moreover, extensive N₂ adsorption contributes to enhanced NRR selectivity with an NH₃ yield of 3.0 × 10^{−10} mol cm^{−2} s^{−1} (91.8 μg h^{−1} mg^{−1}) and a faradaic efficiency of 2.2% at −0.20 V_{RHE}. We expect our observations to provide new insights into the design of effective electrode structures for electrochemical NH₃ synthesis.

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1. Introduction

The electrochemical nitrogen (N₂) reduction reaction (NRR) as a green ammonia (NH₃) production route has garnered attention in recent years. This has led to significant research interest in the development of highly active and selective electrocatalyst materials. NH₃ has the potential for widespread application as a hydrogen-storage medium, renewable-energy carrier, and carbon-free fuel owing to its high energy density (4.32 kW h L^{−1} for liquid NH₃) and high H₂ content (17.8 wt%) as well as easy handling and storage exploiting existing infrastructure [1–3].

For over 100 years, NH₃ has been majorly produced via the traditional Haber–Bosch process [4]. This technology, however, consumes approximately 2% of the global energy output [5] and generates around 2% of all CO₂ greenhouse gas emissions worldwide. The increased production coupled with the widespread use of NH₃ as a key feedstock for fertilizers played a significant role in the growth of the world's population [6,7]. To overcome challenges such as the high activation barrier of the robust triple covalent bond (N≡N, ~941 kJ mol^{−1}) and thermodynamic limitations as exemplified using Le Chatelier's principle [8], industrial NH₃ production via the Haber–Bosch process involving an iron- or ruthenium-based heterogeneous catalytic reaction (via an exothermic process) is desired. The conversion is typically conducted at high temperatures (350–600 °C) and under high pressures (150–300 bar) owing to the use of highly pure N₂ and H₂ and is therefore considered an energy-intensive process [9–11]. In order to achieve a desirable NH₃ yield, this thermodynamically unfavorable NH₃ production process (N₂ + 3H₂ ↔ 2NH₃, ΔH = −46 kJ mol^{−1}) is required to expedite the alternative technology [12].

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