



# Selective conversion of N<sub>2</sub> to NH<sub>3</sub> on highly dispersed RuO<sub>2</sub> using amphiphilic ionic liquid-anchored fibrous carbon structure

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## ABSTRACT

Ammonia (NH<sub>3</sub>) 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 NH<sub>3</sub> synthesis replacement for the traditional Haber–Bosch process owing to its near ambient reaction conditions (<100 °C and 1 atm). However, its NH<sub>3</sub> 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 RuO<sub>2</sub> on the carbon fiber and increase in the surface area for N<sub>2</sub> adsorption by limiting proton access can be attributed to the presence of imidazolium ions. Moreover, extensive N<sub>2</sub> adsorption contributes to enhanced NRR selectivity with an NH<sub>3</sub> yield of 3.0 × 10<sup>−10</sup> mol cm<sup>−2</sup> s<sup>−1</sup> (91.8 μg h<sup>−1</sup> mg<sup>−1</sup>) and a faradaic efficiency of 2.2% at −0.20 V<sub>RHE</sub>. We expect our observations to provide new insights into the design of effective electrode structures for electrochemical NH<sub>3</sub> synthesis.

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## 1. Introduction

The electrochemical nitrogen (N<sub>2</sub>) reduction reaction (NRR) as a green ammonia (NH<sub>3</sub>) 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. NH<sub>3</sub> 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<sup>−1</sup> for liquid NH<sub>3</sub>) and high H<sub>2</sub> content (17.8 wt%) as well as easy handling and storage exploiting existing infrastructure [1–3].

For over 100 years, NH<sub>3</sub> 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 CO<sub>2</sub> greenhouse gas emissions worldwide. The increased production coupled with the widespread use of NH<sub>3</sub> 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<sup>−1</sup>) and thermodynamic limitations as exemplified using Le Chatelier's principle [8], industrial NH<sub>3</sub> 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 N<sub>2</sub> and H<sub>2</sub> and is therefore considered an energy-intensive process [9–11]. In order to achieve a desirable NH<sub>3</sub> yield, this thermodynamically unfavorable NH<sub>3</sub> production process (N<sub>2</sub> + 3H<sub>2</sub> ↔ 2NH<sub>3</sub>, ΔH = −46 kJ mol<sup>−1</sup>) is required to expedite the alternative technology [12].

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