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## Rhodium-molybdenum oxide electrocatalyst with dual active sites for electrochemical ammonia synthesis under neutral pH condition

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## ABSTRACT

Electrochemical nitrogen reduction reaction (NRR) process has attracted significant attention recently as an alternative route for green ammonia (NH<sub>3</sub>) production to replace conventional, energy intensive Haber-Bosch process. However, a major challenge in NRR process is the relatively poor selectivity of NRR process over its competing hydrogen evolution reaction (HER) process. Herein, we report the synthesis of molybdenum oxide decorated on the rhodium (Rh<sub>MoOx</sub>/C) catalyst for an efficient NRR with high selectivity. Rh<sub>MoOx</sub>/C catalyst exhibits an outstanding NH<sub>3</sub> yield rate of 57.2 μg h<sup>-1</sup> mg<sub>cat</sub><sup>-1</sup> at -0.6 V vs. RHE and a high faradaic efficiency of 22% at -0.2 V vs. RHE in 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte. This study reveals the interdependent relationship between the catalyst structure, operating conditions, and the reaction selectivity in the electrochemical NH<sub>3</sub> synthesis. Moreover, this study also demonstrates the effectiveness of the bimetallic materials in enhancing the NRR process which is an important finding for designing a future electrocatalyst for electrochemical NH<sub>3</sub> production.

## 1. Introduction

Ammonia (NH<sub>3</sub>) plays an essential role in the global economy and is mostly used for the production of fertilizers, explosives, refrigerants and other chemical feedstocks [1,2]. NH<sub>3</sub> is also being considered as a green and effective hydrogen carrier due to its high volumetric and storage densities of hydrogen (~120 kg m<sup>-3</sup> and 17.7 wt%) and being carbon-free in nature [3,4]. Haber-Bosch process which is the most widely used NH<sub>3</sub> production method, requires high energy consumption arising from its harsh reaction conditions (400–500 °C and ~200 bar) and high purity H<sub>2</sub> feedstock which is extracted from the carbon rich fossil fuels [5]. In order to overcome such limitations of conventional NH<sub>3</sub> production process, electrochemical synthesis route has been gaining significant attention as a promising alternative approach due to single step process, potentially low energy

consumption arising from its mild reaction condition (ambient pressure and low temperature) and the required feedstocks being water and air which are abundant in nature [6,7]. Moreover, the dropping prices of electricity from renewable sources of energy such as solar photovoltaics and wind power are making the electrochemical ammonia production process to be more viable in near future [8–15]. However, the low kinetics of the nitrogen reduction reaction (NRR) process and poor yield of ammonia arising from the low reaction selectivity over its competing hydrogen evolution reaction (HER) have been main challenges hindering its progress for adoption in industry. As a result, in the electrochemical NH<sub>3</sub> synthesis process, development of effective electrocatalyst materials which provide high yield and high selectivity of NRR over HER is essential.

According to the Sabatier volcano curve, amongst many NRR catalyst candidates, rhodium (Rh) is found to be a thermodynamically

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