

# 39<sup>th</sup> Topical Meeting

of the **International Society of Electrochemistry**

23 - 26 March 2025

***Natal, Brazil***

The Role of Electrochemistry  
in Sustainable Energy  
and the Environment



## PROGRAM

<https://topical39.ise-online.org>

e-mail: [events@ise-online.org](mailto:events@ise-online.org)

# Rh-Cu Bimetallic Catalysts for Nitrate Electroreduction: Insights from Online Electrochemical Mass Spectrometry

Beatriz Bridi Schiavo, Rodrigo Gomes de Araujo and Joelma Perez

*Chemistry Institute of São Carlos -USP  
Ave. Trabalhador São-carlense, 400  
CEP 13566-590 - São Carlos - SP – Brazil  
rodrigogomesaraujo@usp.br*

The nitrate ion ( $\text{NO}_3^-$ ) is one of the most abundant ionic forms of nitrogen in nature, due to its high solubility and stability in aqueous environments. This compound is naturally formed from certain types of rocks and through the decomposition of organic matter. Nitrate is widely used in various applications, such as food preservation within the food industry, ammunition for the defense industry, and agriculture.<sup>1</sup> However, inadequate management of industrial waste, particularly in intensive agricultural activities, has led to the contamination of soils and water resources with nitrate. The presence of nitrate in water bodies can cause eutrophication and, when ingested, pose health risks to living organisms.<sup>2</sup> Therefore, sustainable and efficient methods for removing nitrate from water have been extensively studied.<sup>1-2</sup> One promising alternative to mitigate this problem is the electro-reduction reaction of nitrate ( $\text{NO}_3\text{RR}$ ) to ammonia ( $\text{NH}_3$ ), a compound widely utilized in agriculture, promoting the recycling of nitrate-containing waste.<sup>3</sup> In this study, RhCu electrocatalysts supported on Vulcan carbon were synthesized to evaluate the electro-reduction reaction of nitrate and to assess the distribution of products generated during the reaction. The RhCu nanocatalyst was prepared in a 70:30 (at.%) ratio. The physical characterization of the electrocatalyst was performed using thermogravimetry (TG), energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD). The catalytic activity of the synthesized material was evaluated through electrochemical tests conducted in  $1.0 \text{ mol L}^{-1}$  NaOH in the presence of  $0.5 \text{ mol L}^{-1}$   $\text{NaNO}_3$ . The electrochemical measurements were performed in a one-compartment Teflon cell, utilizing a gas diffusion electrode as the working electrode, with the catalyst deposited on carbon cloth, a platinum electrode as the counter electrode, and a  $\text{Hg|HgO}$  ( $1 \text{ mol L}^{-1}$  NaOH) reference electrode. Electrochemical analyses were accompanied by Online Electrochemical Mass Spectrometry (OLEMS), recording mass signals of  $m/z$  2 ( $\text{H}_2$ ),  $m/z$  17 ( $\text{NH}_3$ ),  $m/z$  28 ( $\text{N}_2$ ),  $m/z$  30 ( $\text{NO}$ ),  $m/z$  44 ( $\text{N}_2\text{O}$ ), and  $m/z$  46 ( $\text{NO}_2$ ). The literature indicates that the  $\text{NO}_3\text{RR}$  mechanism can produce a series of products, such as  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_2^-$ , which can subsequently form  $\text{N}_2$  and/or  $\text{NH}_3$ .<sup>4</sup> In our results, the hydrogen production detected by the mass signal  $m/z$  2 was identified starting from a potential of 0.0 V vs. RHE. The signal  $m/z$  17, associated with ammonia production, was observed from 0.2 V vs. RHE. The mass signals  $m/z$  30 ( $\text{NO}$ ) and  $m/z$  46 ( $\text{N}_2\text{O}$ ) were detected starting from 0.3 V vs. RHE, while the mass signal  $m/z$  46 ( $\text{NO}_2$ ) was identified in small quantities from a potential of -0.3 V vs. RHE. The mass signal  $m/z$  28 ( $\text{N}_2$ ) was not detected at any evaluated potential. Ge Zi-Xin et al.<sup>5</sup> quantified  $\text{NH}_3$  using UV-Vis spectroscopy, employing bimetallic RhCu nanocubes as catalysts in  $0.1 \text{ mol L}^{-1}$   $\text{HClO}_4$  in the presence of  $0.05 \text{ mol L}^{-1}$   $\text{KNO}_3$ , and observed  $\text{NH}_3$  production at a potential of 0.05 V vs. RHE. The results obtained from this study indicate that, for the bimetallic RhCu catalyst in an alkaline medium, OLEMS analyses revealed a favorable low potential window of 0.2 – 0.1 V vs. RHE, in which the nitrate reduction reaction occurs efficiently on the catalytic surface, without interference from the hydrogen evolution reaction. This observation suggests a higher Faradaic efficiency when operating within these potential ranges.

## References

- 1 ULLAH, S. et al. Recent developments in designing Cu-based electrocatalysts and advanced strategies for electrochemical nitrate reduction to ammonia. **Journal of Environmental Chemical Engineering**, v. 11, n. 5, p. 110927, 2023/10/01/ 2023. ISSN 2213-3437.
- 2 CAO, Y. et al. Recent Advances in Electrocatalytic Nitrate Reduction to Ammonia: Mechanism Insight and Catalyst Design. **ACS Sustainable Chemistry & Engineering**, v. 11, n. 21, p. 7965-7985, 2023/05/29 2023.
- 3 XU, H. et al. Electrocatalytic reduction of nitrate – a step towards a sustainable nitrogen cycle. **Chemical Society Reviews**, v. 51, n. 7, p. 2710-2758, 2022. ISSN 0306-0012.
- 4 NIU, S. Recent progress and challenges in structural construction strategy of metal-based catalysts for nitrate electroreduction to ammonia. **Journal of Energy Chemistry**, v. 86, p. 69-83, 2023/11/01/ 2023. ISSN 2095-4956.
- 5 GE, Z.-X. et al. Interfacial Engineering Enhances the Electroactivity of Frame-Like Concave RhCu Bimetallic Nanocubes for Nitrate Reduction. **Advanced Energy Materials**, v. 12, n. 15, p. 2103916, 2022/04/01 2022. ISSN 1614-6832.