

## Co/Co oxide Foam Catalysts for Sustainable Nitrate to Ammonia Electroreduction

N. Ashtaman Pillai Syamaladevi<sup>1,3</sup>, A. Dutta<sup>1,3</sup>, J. Drnec<sup>2</sup>, P. Broekmann<sup>1,3\*</sup>

<sup>1</sup>Department of Chemistry, Biochemistry and Pharmaceutical Science, University of Bern, <sup>2</sup>European Synchrotron Radiation Facility (ESRF), Grenoble, France, <sup>3</sup>National Centre of Competence in Research (NCCR) Catalysis, University of Bern

Electrochemical nitrate reduction (NO<sub>3</sub>RR) is an energy-efficient method to remove harmful nitrate from wastewater while producing valuable ammonia. Catalyst selection is crucial for accelerating NO<sub>3</sub>RR and directing the process towards the target product. This process addresses environmental concerns by reducing nitrate through electrochemical reactions, generating ammonia with high added value.<sup>1</sup> By utilizing electrochemical nitrate reduction and suitable catalysts, simultaneous nitrate removal and ammonia synthesis can be achieved, promoting sustainable wastewater treatment and resource utilization. **Ongoing research aims** to optimize this promising approach for efficient and environmentally friendly nitrate valorization.

In this study, we synthesize novel Co foam catalysts using additive-assisted electrodeposition in combination with the dynamic hydrogen bubble template method and followed by thermal annealing at 300 °C for 6 h. The resulting three-dimensional foam morphology significantly influences the catalyst's overall process performance. The foam structure provides a high active surface area, an improved mass transport, and enhanced utilization of active sites, leading to enhanced catalytic activity.

Oxidized Co foams exhibit a remarkable selectivity in the electroreduction of nitrate. Within the specific low potential range of -0.1 to -0.3 V vs. RHE, the Faradaic efficiency (FE<sub>NH<sub>3</sub></sub>) for ammonia production exceeds 95%. Notably, this efficient conversion process from nitrate to ammonia occurs with hydrogen as a minor by-product, and no other nitrogen-containing products (e.g., NO, N<sub>2</sub>O, or N<sub>2</sub>) are formed during electrolysis. These findings underscore the exceptional selectivity and efficiency of Co based foam catalysts in driving the conversion of nitrate to the targeted ammonia.

To elucidate the active chemical states/species contributing to the superior efficiency of ammonia production, we employed *operando* Raman spectroscopy and synchrotron-based *operando* X-ray diffraction (XRD) techniques. These analytical approaches enabled us to investigate the potential-dependent alterations in the chemical states of Co species prior to and during the nitrate reduction reaction (NO<sub>3</sub>RR). Intriguingly, **our findings reveal that** the active phase responsible for the reduction of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub> is not metallic Co or Co<sub>3</sub>O<sub>4</sub>. Instead, **it comprises a composite of Co(OH)<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub>**, which forms only during the nitrate to ammonia conversion. These results underline the importance of oxidized Co<sup>2+</sup> and Co<sup>3+</sup> ions as active catalyst species for the efficient transformation of nitrate into ammonia.

[1] Duca, M.; Koper, M. T. M. Powering denitrification: the perspectives of electrocatalytic nitrate reduction. *Energy Environ. Sci.* **2012**, *5*, 9726– 9742