MSc thesis topic: Manganese and its different oxide phases as promising catalyst for electrochemical nitrogen reduction to ammonia

Daily supervisor: Boaz Izelaar
Supervisors: Prof. Dr. Wiebren de Jong, Dr. Ruud Kortlever

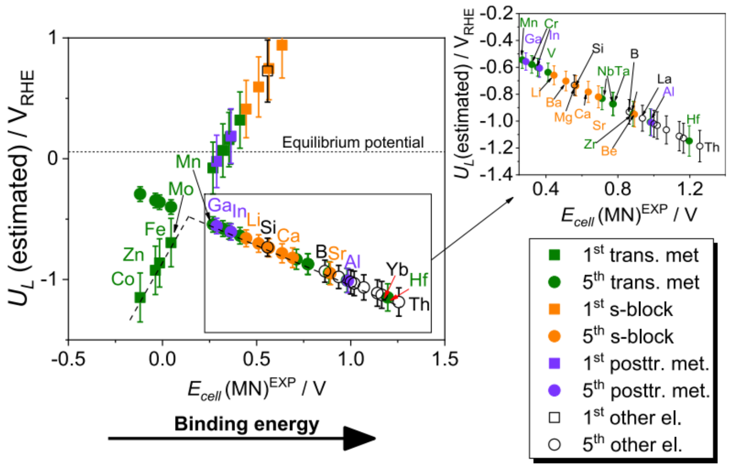

Figure 1 Nitrogen reduction vulcano plot for 31 different elements [6]

The world market size for ammonia is estimated to be 171 million tonnes in 2020 with an expected annual growth rate of 3-5%[1]. Therefore, it belongs to the group of highest produced synthetic chemicals. It is mainly used as fertilizer and contributes to the nitrogen nutrition demand of agriculture. Ammonia is for 90% produced by the energy intensive Haber-Bosch process[2], which is responsible for 1.8% of the global CO_2 emissions and contributes highly towards climate change.

Recently, a lot of research interest focusses on finding sustainable alternatives for ammonia production. Ammonia can potentially be produced by an electrolyser, where the conversion of nitrogen, water and electrons (Nitrogen reduction) into ammonia[4], seems a promising alternative since no emissions are involved and it could be produced on small scale in a decentralized manner.

However, heterogeneous electrocatalytic conversion of nitrogen into ammonia is very difficult due to the inert nature of the nitrogen molecule and its competition with the hydrogen evolution reaction (HER) which occurs at similar reducing potentials. It is therefore key to select and design electrocatalysts that can activate the nitrogen molecule and at the same time inhibits HER. Many transition metals, such as Fe and Ru (H-B catalysts) were tried and only low selectivities were reported[5].

A recently published theoretical study by Dražević & Skúlason proposed manganese as an overlooked effective nitrogen reduction electrocatalysts[6]. According to their DFT results, manganese tend to be a better NRR promotor as Fe and Mo. At the same time, it is less selective towards the HER at both neutral and alkaline pH, which makes it even more promising. Up till now, the experimental NRR performance of Mn in the literature is somewhat precarious. A comprehensive comparison between the NRR activity and different Mn-oxide phases has not been published yet, which makes this MSc thesis a true pioneering project.

This thesis will mainly involve experimental work executing fundamental electrochemical tests, such as cyclic voltammetry, electrochemical impedance spectroscopy and chronoamperometry measurements. Ammonia, nitrite and nitrate quantification will be performed by UV-Vis, Nuclear Magnetic Resonance spectroscopy (NMR) and ion chromatography. **The main deliverables at the end of this project enclose:**

- An extensive literature screening and documentation of related electrochemical ammonia articles.
- Create an understanding of experimental electrochemistry principles with the focus on nitrogen reduction.
- Finalize if manganese is a suitable nitrogen reduction catalyst.

We are looking for: Motivated MSc. Students with affinity towards experimental work who are able and willing to work in a consistent, controlled and precise manner. Understanding electrochemistry fundamentals is a pre, but not required.

What's in it for you? Gaining research experience in a multidisciplinary group, become an expert in electrocatalysis and nitrogen reduction, contributing to a significant knowledge gap in the ammonia research field.

For more information, please contact: Boaz Izelaar (b.izelaar@tudelft.nl)

[1] The Catalyst Group, "Ammonia Production: Recent Advances in Catalyst and Process Technology and Impacts on the Competetive Lanscape," 04 2018.

[2] M. Appl, "Ammonia," in *Encyclopedia for industrial chemistry*, Wiley-VCH, 2006, p. 155.

[3] A. Kapałka, A. Cally, S. Neodo, C. Comninellis, M. Wächter, K. M. Udert, *Electrochemistry Communications* **2010**, *12*, 18–21.

[4] MacFarlane et al. Joule, **2020**, 4, 1–20

[5] S.Z. Andersen, V. Čolić, S. Yang, J.A. Schwalbe, A.C. Nielander, J.M. McEnaney, K. Enemark, Rasmussen, J.G. Baker, A.R. Singh, B.A. Rohr et al., *Nature,* **2019**, 570, 504-508.

[6] Dražević & Skúlason, iScience, **2020**, 23, 101803