Inorganic Materials & catalysis Electrocatalysis

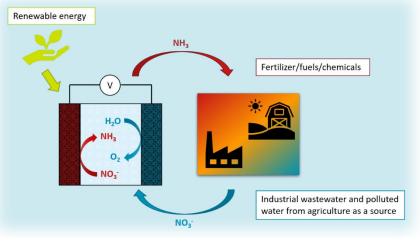
Research Project - Emiel Hensen/Marta Costa Figueiredo/Yvette van Beek



Electrochemical reduction of nitrate/nitrite for ammonia production

Background

Ammonia is widely considered to be an important building block for many chemical processes, e.g. fertilizers, fuels, and fine chemicals [1]-[3]. Until now the Haber-Bosch process has been considered as the major source for industrial ammonia production. It requires harsh conditions (200-300 bar and 400-500 °C) and demands ~1.4% of the world energy supply, resulting in a carbon footprint of 1.5 ton CO₂ per ton of ammonia produced [4]. The electrochemical synthesis of ammonia recently gained interest because it allows a more sustainable and local production of



ammonia, eliminating the large costs that come from inflexible Haber-Bosch plants and reducing environmental hazards associated with runoff and the use of hydrogen that leads to increasing CO_2 emissions [5]. A possible route towards NH₃ is the electroreduction of nitrates and nitrites (NO_{3⁻}/NO_{2⁻}) via an eight (1) and six (2) electron transfer process:

 $NO_3^- + 6 H_2O + 8 e^- \rightarrow NH_3 + 9 OH^-$ (1)

 $NO_2^- + 5 H_2O + 6 e^- \rightarrow NH_3 + 7 OH^-$ (2)

An increasing number of studies focusses on the electrochemical route towards ammonia [6]–[13]. Interest lies in NO_3^{-}/NO_2^{-} reduction since it is kinetically more accessible than breaking the triple bond in N_2 . Additionally, electrochemical reduction of NO_3^{-}/NO_2^{-} seems a feasible route to reduce water pollution that jeopardizes our environment and health [14]. In line with this, the electrochemical reduction of $NO_3^ /NO_2^{-1}$ for ammonia synthesis is a promising route to restore the nitrogen cycle and creates an attractive route where ammonia production can be decentralized fuelled by renewable energy [15].

Techniques used:

- Preparation and characterization (e.g. SEM, XRD, XPS) of novel catalyst materials for the electroreduction of NO₃⁻/NO₂⁻ to NH₃;
- Electrochemical techniques (e.g. CV, LSV) to study the reaction mechanism;
- Analytical techniques (e.g. NMR, GC-MS, HPLC, DEMS) to study obtained reaction products; .
- Optimization of catalyst and reaction conditions for electrochemical cell configuration.

For further information:

Emiel Hensen (Helix, STW 3.33), Tel 5178, e.j.m.hensen@tue.nl Marta Costa Figueiredo (Helix, STW 3.43), Tel 6310, m.c.costa.figueiredo@tue.nl Yvette van Beek (Helix, STW 3.37), y.v.beek@tue.nl

P. H. van Langevelde, I. Katsounaros, and M. T. M. Koper, "Electrocatalytic Nitrate Reduction for Sustainable Ammonia Production," Joule, no. 2020, pp. 1–5, 2021, doi: 10.1016/j.joule.2020.12.025.
J. M. McEnaney et al., "Electrolyte engineering for efficient electrochemical nitrate reduction to ammonia an a titanium electrode," ACS Sustain. Chem. Eng., vol. 8, no. 7, pp. 2672–2681, 2020, doi: 10.1021/acssuschemeng.9b05983.
J. Lu, D. Richards, M. Singl, and B. R. Goldsmith, "Activity and Selectivity Trends in Electrocatalytic Nitrate Reduction on Transition Metals," 2019, doi: 10.1021/acssu3020179.
M. Appl, "Ammonia," in Ultiman's Encyclopedia of Industrial Chemistry, Weinheim, Germany: Wiley-VCI Veraig GmbH & Co. KGaA, 2006.
Z. W. She, J. Kobagaard, C. F. Dickens, I. Chorkendorff, J. K. Nørskov, and T. F. Jaramillo, "Combining theory and experiment in electrocatalysis: Insights into materials design," Science (80-,), vol. 355, no. 6321, 2017, doi: [1] [2] [3] [4] [5]

^[6] [7] [8]

Let al., "Endspaced by C. F. Dickerison", J. K. Noiskov and T.F. Janamino, Combining usery and experiment in electrotacitysis. Insights into materials design," Science (80-7), vol. 335, no. 0321, 2017, doi: 10.1126/science.aad4998.
 M. Mecnaney et al., "Reduction to Ammonia on a Titanium Electrode," 2020, doi: 10.1021/acssuschemeng.9b05983.
 Let al., "Efficient Ammonia Electrosynthesis from Nitrate on Strained Ruthenium Manoclusters," 2020, doi: 10.1021/jacs.0c00418.
 G. E. Dima, A. C. A. De Vooys, and M. T. M. Koper, "Electrocatalytic reduction of mitrate at low concentration on coinage and transition-metal electrodes in acid solutions," J. Electroanal. Chem., vol. 554-555, no. 1, pp. 15–23, 2003, doi: 10.1016/s0022-07280(2)01443-2. E. Pérez-Gallent, M. C. Figueiredo, I. Katsounaros, and M. T. M. Koper, "Electrocatalytic reduction of Nitrate on Copper single crystals in acidic and alkaline solutions.," *Electrochim. Acta*, vol. 227, pp. 77–84, 2017, doi: 10.1016/j.lectracta.2016.12.147. [9]

^[10] [11] [12] [13]

^[14] [15]