Final Report

Project Title

Low temperature, ambient pressure electrochemical ammonia synthesis in alkaline media — Mechanistic studies and catalyst design

Project Period

09/15/2016 – 09/14/2019

Award Information

Recipient Award Identification Number: DE-SC0016537

Institution Information

Name: University of Delaware

Address: 150 Academy Street, Newark, DE 19716

DUNS: 059007500

Principal Investigator Information

Name: Bingjun Xu

Position/Title of PI: Associate Professor

Phone Number: 302-831-6725

Email Address: bxu@udel.edu

Address: 150 Academy Street, Newark, DE 19716

Abstract

Ammonia synthesis via the Haber-Bosch process is a pillar of modern agriculture, which converts the abundant but inert dinitrogen in the atmosphere to nitrogen-based fertilizers. Despite more than a century of optimization, the Haber-Bosch process remains energy intensive and reliant on fossil fuels and produces large amounts of CO_2. Distributed and modular ammonia synthesis via the electrochemical nitrogen reduction reaction (ENRR) at or close to ambient conditions, powered by renewable electricity is an attractive alternative because it allows as needed production of ammonia, and in turn fertilizers. However, selective ENRR catalysts remain lacking. In this project, we systematically investigated two categories of catalytic materials, i.e., precious metals and transition metal nitrides, in the ENRR. Precious metals exhibit low activity and selectivity in the ENRR, which is in agreement with recent computational studies. Transition metal nitrides, especially VN, has been demonstrated as active and selective ENRR catalysts. We developed the first quantitative method to determine the amount of ammonia produced in the ENRR on N-containing containing catalysts in the membrane electrode assembly configuration. An initial ammonia production rate of 6.6×10^{-10} mol s^{-1} mg^{-1} and a Faradaic efficiency of 6.0% at −0.1 V were reached on VN. After the initial deactivation, VN was shown to be stable in the ENRR for 116 hours with a steady state ammonia production rate of 1.1×10^{-10} mol s^{-1} cm^{-2}. A vanadium oxynitride species was identified as the active phase in the ENRR via a combination of operando and ex situ characterization techniques. In addition, we established that the ENRR proceeded on transition metal nitrides via the Mars van Krevelen mechanism and determined the initial and steady state active site densities by developing a quantitative isotopic exchange method.

Objectives of the project

The overarching goal of the proposed research is to **obtain fundamental insights in developing selective electrochemical nitrogen reduction reaction (ENRR) catalysts** at low temperature (<100 °C). Specific objectives include:

1) Establish analytical procedures to quantify ammonia production rates and columbic efficiencies on representative metals, e.g., Ru, Pd, Pt, and Ni, and metal nitrides with the membrane electrode assembly (MEA) configuration at well-defined potentials.

2) Identify and determine the density of active sites for ENRR by employing and developing in-situ/operando and ex-situ characterization techniques.

3) Design, synthesize and evaluate nitride ENRR catalysts based on the mechanistic insights gained.

Accomplishments

We have established reliable reactivity testing procedure in a membrane electrode assembly (MEA) configuration for both proton exchange membranes (PEMs) and hydroxide exchange membranes (HEMs), as well as sensitive analytical techniques to quantify the amount of ammonia in the effluent of the from the MEA-based electrolysis unit. Ammonia evolved is captured in a dilute sulfuric acid solution (1 mM), and the ammonia content is quantified by the Nessler's reaction with a detection limit of 3×10^{-6} M. We have investigated ENRR using Nafion, the prototypical PEM, for the platinum group metals (PGMs) at 80 °C at two different potentials (-0.2 and -0.4 V vs. reversible hydrogen electrode, RHE) to establish reliable baselines against which other systems can compare. While the cathode catalyst varies from experiment to experiment in the N_2 atmosphere, Pt (0.4 mg/cm^2) is used as the anodic electrocatalyst in all testing in a hydrogen atmosphere so that the anode side could serve as a reference electrode, i.e., RHE. This configuration enables accurate control of cathodic potential, which is the ENRR potential. Ammonia production rates on PGMs are on the order of $10^{-12} – 10^{-11}$ mol/cm^{2}s. The order of the ammonia production rate is Ir > Pt > Pd > Ru. Among PGMs, Ru shows the highest FE at 0.15%. Pd, Ir, and Pt all show a FE of ~0.05%. Decreasing the cathode potential to -0.4 V decreases the Faradaic efficiency for all catalysts, which is expected because PGMs are excellent catalysts for the competing hydrogen evolution reaction (HER). This is the first systematic study of ENRR rates on monometallic PGM catalysts with PEMs. Although the measured rates and FEs are low, they will serve as important benchmarks for future studies.

We have also investigated ENRR on PGMs with HEMs at 80 °C at -0.2 and -0.4 V vs. RHE, which show lower ammonia production rates than on PEMs at otherwise similar conditions and comparable FEs. HEMs are alkaline in nature, and are not expected to adsorb much of ammonia. One experimental difficulty we identified with HEMs (for both commercial, i.e., Tokuyama A201, and homemade, i.e., poly(aryl piperidinium) polymers or PAP (US Patent 62/314,008), membranes) is that the slow leaching of the quaternary ammonium cations, which are carriers of hydroxide anions, from HEMs interferes with ammonia quantification. It was confirmed by control experiments in which the MEA is run in a hydrogen pump configuration with Pt in H_2 at both anode and cathode; however, detectable level of ammonium

leaching was only detected in the first hour of control experiments. Thus, we applied a 1 hour break in in all ENRR testing with HEMs. The production rate of ammonia is approximately 2 orders of magnitude lower in HEM compared to PEM (Figure 2a), while FEs are comparable (Figure 2b). Ammonia production rates on Pt, Pd and Ir are comparable, which are more than one order of magnitude higher than that on Ni. Surprisingly, no ammonia was detected on Ru with HEM. Importantly, Ni is not stable with PEM under ENRR conditions, but is modestly active with HEM. Although Ni is much less active than PGMs when normalized by ECSA, comparable ammonia production rate with PGMs could be achieved on Ni at higher loadings. It is known that HOR/HER exchange current density on PGMs in base is 2 orders of magnitude lower than that in acid, which is similar to ENRR. This parallel is consistent with the computational prediction that HBE and NBE are correlated, and the selectivity for ENRR (against HER) should remain relatively constant on monometallic catalysts.

We identified two metal nitride catalysts (VN and Cr_2N) active and selective for ENRR, which possess ammonia production rates and Faradaic efficiencies (FE) 50-200 times higher than precious metals. We established the first reliable reactivity testing procedure in a MEA configuration, as well as sensitive analytical techniques to quantify the amount of ammonia in the effluent of the from the MEA-based electrolysis unit. It is important to recognize that exchange protons in PEM with ammonium cations, as reported in the literature (Lan et al., Synthesis of ammonia directly from air and water at ambient temperature and pressure, Scientific Reports, 3, 2013, 1145) is not a reliable method because the reverse exchange of the ammonium in the membrane with protons produced on the anode could artificially inflate the amount of ammonia produced in ENRR. We also note that MEA-based ENRR activity tests is superior to those conducted in aqueous electrolyte for three main reasons: 1) better contact between N_2 to the electrocatalyst leads to higher ENRR rates; 2) higher overall currents and amounts of ammonia produced (up to 4 mg of ammonia in our experiments) makes the uncertainty resulting from ammonia sources other than ENRR during experiments, much less likely; and 3) catalyst performances measured with an MEA configuration is much closer to those in actually devices than activities determined in aqueous electrolytes (this is a well-known challenge in the catalyst development for both PEM and HEM-based fuel cells).

One of the key challenges in investigating metal nitrides as ENRR catalyst is to determine the origin of N in the produced ammonia because metal nitrides also contain N. We established a reliable procedure to quantify the amount of ammonia detected from ENRR by relying the nitrogen balance:

$$N_{(\mathrm{NH_3,ENRR})} = N_{(\mathrm{NH_3,MEA})} + N_{(\mathrm{NH_3,Effluent})} + N_{(\mathrm{post-ENRR})} - N_{(\mathrm{pre-ENRR})}$$

In which $N_{(\mathrm{NH_3,MEA})}$ and $N_{(\mathrm{NH_3,Effluent})}$, which are the amount of ammonia in the soaking solution of the MEA and the effluent of both the cathode and anode, respectively, are determined by the Nessler's method. The amount of N on the catalyst before and after ENRR, $N_{(\mathrm{pre-ENRR})}$ and $N_{(\mathrm{post-ENRR})}$, respectively, are determined by the elemental analysis.

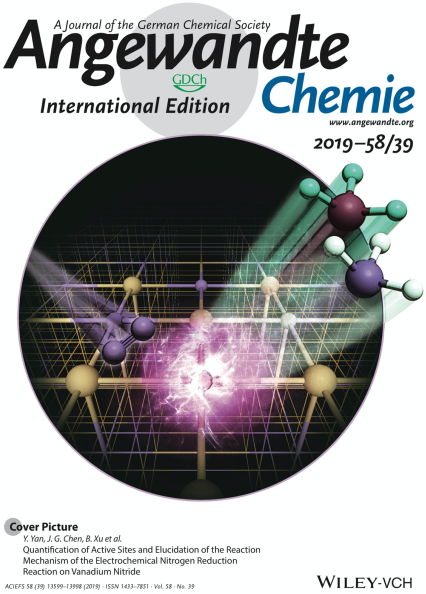
We identified Cr_2N as is an active and selective ENRR catalyst in PEMEL. The specific ENRR rate (1.9×10^{-11} mol·cm^{-2}·s^{-1}) and Faradaic efficiency (0.82%) on Cr_2N are both approximately 50 times higher

than those on Pt at -0.2 V. Similar to the results on precious metals, electrode potential does not impact the rate of ENRR much within the range of -0.2 to -0.8 V. Meanwhile, FE drops precipitously as the electrode potential becomes more negative, to 0.01% at -0.8 V, indicating that the competing hydrogen evolution reaction (HER) is a favored at lower potentials. The bulk composition of the catalyst remains unchanged after ENRR as confirmed by ex-situ X-ray diffraction (XRD) and operando X-ray absorption spectroscopy (XAS). X-ray photoelectron spectroscopy (XPS) results indicate that Cr_2N, CrN and CrO_x species are present on the surface of the catalyst. CrN was synthesized and showed very poor ENRR performance. The fraction of CrN_xO_y increased after ENRR at -0.8 V for 4 h, and longer ENRR test (24 h) showed that catalyst was severely deactivated after 4h (ammonia production rate dropped by 2/3). Thus, we conclude Cr_2N is the active phase for ENRR. At -0.2V, no appreciable catalyst deactivation was observed over 24 h. We attribute the catalyst deactivation of the Cr_2N catalyst at <-0.4 V to the slow conversion of surface Cr2N phase to CrO_x and CrN_xO_y species.

In addition, we discovered that VN nanoparticles are more active and selective ENRR catalysts than Cr_2N, with an average ENRR rate and FE of 3.3×10^{-10} mol s^{-1} cm^{-2} (6.6×10^{-10} mol s^{-1} mg^{-1}) and 6.0% at −0.1 V within 1 h, respectively. The catalysts show that the ENRR rate and FE, measured in a PEMEL configuration, are more than two orders of magnitude higher than those of noble metal catalysts. *Ex situ* XPS and *operando* XAS characterizations revealed that vanadium oxynitride (determined to be $VN_{0.7}O_{0.45}$) is the active phase for ENRR. Conversion of $VN_{0.7}O_{0.45}$ to VN deactivates the catalyst, which was accelerated at lower potentials. While the catalyst became mostly inactive after 2 h at potentials at or below −0.2 V, it was able to maintain an ammonia production rate of 1.1×10^{-10} mol s^{-1} cm^{-2} for 116 h at −0.1 V. This is consistent with the observation that the amount of the vanadium oxynitride at -0.1 V decreased within the first hour but stabilized afterwards with *operando* XAS. It is important to point out that the total amount of ammonia produced within 116 h is 5 times of the amount of N in the VN catalyst, thus ruling out the possibility that the produced ammonia is impacted by the leaching of VN. The turnover number of the VN catalysts for nitrogen reduction is determined to be ~50 at −0.1 V over 120 h. This is the first time that reliable turnover number of ENRR on metal nitride catalysts is determined. We further developed a quantitative $^{15}N/^{14}N$ exchange method to determine the density of initial and steady state active surface N sites, which allow accurate turnover frequency (TOF) and turnover number (TON) to be determined.

Publications

1. X. Yang, S. Kattel, J. Nash, X. Chang, J. Lee, Y. Yan*, J. Chen* and B. Xu*, "Quantification of Active Sites and Elucidation of Reaction Mechanism of Electrochemical Nitrogen Reduction Reaction on Vanadium Nitride", *Angew. Chem. In. Ed.*, 131, **2019**, 13906. **(Cover Story)**



2. X. Yang, J. Nash, N. Oliveira, Y. Yan*, and B. Xu*, "Understanding the pH Dependence of Underpotential Deposited Hydrogen on Platinum", *Angew. Chem. Int. Ed.*, **2019**, 58, 17718.
3. J. Nash, X. Yang, M. Dunwell, J. Anibal, S. Yao, K. Attenkofer, J. Chen, Y. Yan*, B. Xu*, "Elucidation of the Active Phase and Deactivation Mechanisms of Chromium Nitride in the Electrochemical Nitrogen Reduction Reaction", *J. Phys. Chem. C*, 123, **2019**, 23967.
4. X. Yang, J. Nash, J. Anibal, M. Dunwell, S. Kattel, E. Stavitski, K. Attenkofer, J. Chen*, Y. Yan*, B. Xu*, "Mechanistic Insights into Electrochemical Nitrogen Reduction Reaction on Vanadium Nitride Nanoparticles", *J. Am. Chem. Soc.*, 140, **2018**, 13387.
5. J. Nash, X. Yang, J. Anibal, J. Wang, Y. Yan*, B. Xu*, "Electrochemical Nitrogen Reduction Reaction on Noble Metal Catalysts in Proton and Hydroxide Exchange Membrane Electrolyzers", *J. Electrochem. Soc.*, 164, **2017**, F1712.

Participants

Bingjun Xu, Jared Nash, Xuan Yang

Partners

Yushan Yan, Jingguang Chen

Impact

From a chemical engineering perspective, we established a reliable approach to evaluate ENRR catalysts, especially metal nitrides, in an MEA configuration. This is significant because future ENRR devices will likely be membrane based, and catalysts' performance determined in liquid electrolytes often does not translate into device performance.

We conclusively confirmed the computational predictions that precious metals are not active or selective ENRR catalysts in the MEA configuration. Since a significant fraction of literature on ENRR focused on metal catalysts, our work indicates this may not be a fruitful direction for future research efforts. Meanwhile, the discovery that metal nitrides are promising ENRR catalysts opened up a new category of materials for this reaction. The novel analytical and characterization methods developed in this project will be informative in electrocatalytic investigations in general.