Recent Advances on Nitrogen Activation and Conversion · (N2X) · 31st March - 1st April, 2021
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Author: Ifan E.L. Stephens

Title: Towards efficient electrosynthesis of ammonia on solid electrodes

Abstract:

Current ammonia production via the Haber Bosch process requires high pressures, high temperatures and consumes >1% of our current fossil fuel production. To the contrary, nitrogenase in nature catalyses N2 reduction at room temperature and atmospheric pressures. At present, sold electrodes are rather inactive and unselective. The translation of the activity and selectivity of nitrogenase to a solid inorganic surface would enable the efficient on-site on demand synthesis of ammonia, powered by renewable electricity.

We recently used quantitative isotopic labelling experiments to provide unequivocal proof that Li-based electrodes are able to reduce N2 to NH3 in non-aqueous electrolytes.1 Conversely, transition metals in aqueous electrolytes yield so little ammonia that it is indistinguishable from background contamination. In this talk, I will review why the lithium mediated system is unique amongst solid electrodes in its ability to reduce N2 to NH3. I will draw from concepts from enzymes, homogeneous catalysis and battery science. On that basis, I will discuss different avenues towards more efficient N2 reduction.

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Author: Nicolas Mézailles

Title: Dinitrogen functionalization at Mo centers: mechanistic studies and catalysis

Abstract:

Nature is able to reduce N2 into NH3 under mild conditions, using transition metal clusters (active sites of enzymes nitrogenases). Despite intense researches during the past decades, metal complexes capable of reducing N2 into either NH3 or amines are rare. As early as 1989, Hidai has shown that a Mo(0) complex could catalyze the formation of silylamine from N2.

Further developments toward ever more efficient catalysts rely on a precise mechanistic understanding of the process. We have developed the use of a tri and tetradentate phosphine ligand/Mo system which not only allow catalytic functionalization of N2, but also the isolation of several intermediates.[1,2]. We have moreover shown that the direct splitting of N2 can be achieved at the (PP2)Mo fragment to form the corresponding Mo-nitrido. This complex can be functionalized under mild conditions (room temperature to mild heating) by E-H (E = Si, B) bonds to generate the corresponding amine NE3 and/or NE2H, that is liberated from the Mo center.[3-5] These results and recent developments in catalysis will be presented.

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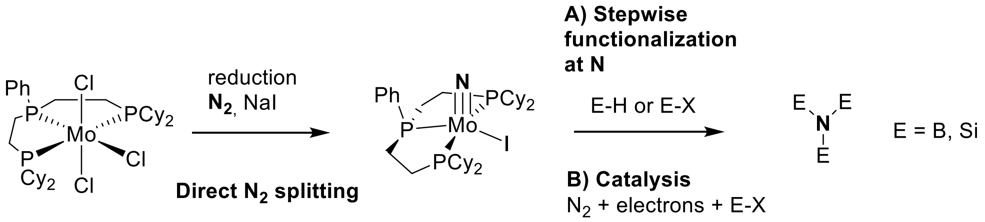

Authors: Qing Qin, Martin Oschat & Wolfgang Schuhmann

Title: Rational design of porous carbon-based electrocatalysts for N2 fixation through understanding of structure-property relationships

Abstract:

As expressed by its annual worldwide production exceeding 145 million tons, NH3 plays an extremely important role in agricultural fertilizers, fuels, as hydrogen carrier and in many other fields.1 The industrially applied Haber-Bosch process suffers from the need for high temperature and pressure. Even more important, the production of H2 as reactant by steam reforming contributes significantly to the world energy consumption and the overall cost of the process. Hence, electrochemical N2 reduction reaction (NRR) at ambient conditions by using renewable electricity is emerging as an alternative technology towards a more sustainable NH3 production.2 Considering the extremely challenging 6 electron transfer process, rational design of efficient catalysts is required.3

In order to explore a new mode for activation of N2 and thus to achieve more efficient catalysts for NRR, a Titanium-based metal-organic framework (MOF) is used as the precursor and pyrolyzed at high temperature (800-1100 °C) to obtain noble metal-free C-doped TiO2/C (C-TixOy/C) material with porous structure and abundant oxygen vacancies (OVs).4 At the potential of -0.4 V vs. RHE, the highest FE of 17.8 % can be achieved with a remarkable NH3 yield of 9.2 µg h-1 mg-1. No decay in the current and NH3 yields is observed during the long-time stability test. On the basis of the experimental results and theoretical calculations, the remarkable properties of the MOF-derived catalysts can be attributed to the doping of carbon atoms into OVs and the formation of (O-)Ti-C bonds, which are found to be the active sites for N2 activation.

To minimize the amount of metal and create more active sites, a novel catalyst construction composed of Au single ions decorated on N-doped porous carbons (NDPCs) was synthesized successfully.5 The introduction of Au single sites which are stabilized by N species in NDPCs leads to catalytic activity for N2 activation. Thus, the interaction within as-prepared Au single atoms modified NDPCs catalysts enabled promising performance for electrochemical NRR. At a potential of -0.2 V vs. RHE, a stable NH3 yield of 2.32 µg h-1 cm-2 is produced at a FE of 12.3%. Besides, there is no notable fluctuation of Faradaic efficiency and NH3 yield in 6-cycle test, which indicates good stability.

References

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[4] Q. Qin, T. Heil, M. Antonietti, M. Oschatz, Small Methods, 2018, 2, 1800202.

Authors: A. Shoji Hall

Title: Reorganization of Interfacial Water by an Amphiphilic Cationic Surfactant Promotes Electrocatalysis

Abstract:

The presence of cetyltrimethylammonium bromide (CTAB) near the surface of a Cu electrode promotes the electrochemical reduction of CO2-to-fuels. The presence of CTAB increases the CO2 reduction rate by as much as 10x and decreased the HER rate by 4x, leading to ~75% selectivity towards the reduction of CO2. We utilized Surface Enhanced Infrared Absorption Spectroscopy (SEIRAS) to probe the dynamics of CTAB adsorption on the structure of interfacial water and CO2 reduction intermediates. HER suppression was found to arise from the displacement of interfacial water molecules from the presence of CTAB in the double layer. The enhanced CO2 reduction rate can be correlated to an increased population of atop bound CO and the emergence of a low frequency atop CO band. These results unravel the role of additives in improving CO2-to-fuels electrocatalysis and establishing this as a powerful methodology for directing product selectivity.

Authors: Núria López

Title: Modeling Ammonia synthesis from N2

Abstract:

Nitrogen conversion to ammonia at ambient pressures and temperatures is one of the major challenges to reach sustainable process. The present Haber-Bosch process produces 1.5 % of the total CO2 and thus an electrochemical route has been much searched for. However, the lack of truly active materials that could serve as a benchmark for the calculations and the fact that most simulations only work with simple model systems has limited our advances in the field. In my talk I will address the main challenges and how developing an alternative process will require breaking linear-scaling relationships indicating that complexity in the models and in the catalyst is needed.

Authors: Karthish Manthiram

Title: Non-aqueous gas diffusion electrodes for ammonia synthesis at ambient conditions

Abstract:

Chemical synthesis is responsible for significant emissions of carbon dioxide worldwide. These emissions arise not only due to the energy requirements of chemical synthesis, but since hydrocarbon feedstocks can be overoxidized or used as hydrogen sources. Using renewable electricity to drive chemical synthesis may provide a route to overcoming these challenges, enabling synthetic routes which operate at benign conditions and utilize sustainable inputs. We are developing an electrosynthetic toolkit in which distributed feedstocks, including carbon dioxide, dinitrogen, water, and renewable electricity, can be converted into diverse fuels, chemicals, and materials.

In this presentation, we will share recent advances made in our laboratory on nitrogen fixation to synthesize ammonia at ambient conditions. Specifically, our lab is pursuing a lithium-mediated approach to ammonia synthesis and understood the reaction network that controls the reductive chemistry. The coupling of kinetics and transport has a significant influence on the rates of ammonia synthesis, providing a means to improve selectivity of nitrogen fixation. We have developed non-aqueous gas-diffusion electrodes which lead to high rates of ammonia synthesis at ambient conditions. These findings will be discussed in the context of a broader range of electrosynthetic transformations which could lead to local and on-demand production of critical chemicals and materials.

Biography

Karthish Manthiram is the Theodore T. Miller Career Development Chair and Assistant Professor in Chemical Engineering at MIT. The Manthiram Lab at MIT is focused on the molecular engineering of electrocatalysts for the synthesis of organic molecules, including pharmaceuticals, fuels, and commodity chemicals, using renewable feedstocks. Karthish received his bachelor's degree in Chemical Engineering from Stanford University in 2010 and his Ph.D. in Chemical Engineering from UC Berkeley in 2015. After a one-year postdoc at the California Institute of Technology, he joined the faculty at MIT in 2017. Karthish's research has been recognized with several awards, including the NSF CAREER Award, DOE Early Career Award, 3M Nontenured Faculty Award, American Institute of Chemical Engineers 35 Under 35, American Chemical Society PRF New Investigator Award, Dan Cubicciotti Award of the Electrochemical Society, and Forbes 30 Under 30 in Science. Karthish's teaching has been recognized with the C. Michael Mohr Outstanding Undergraduate Teaching Award, the MIT ChemE Outstanding Graduate Teaching Award, and the MIT Teaching with Digital Technology Award. He serves on the Early Career Advisory Board for ACS Catalysis and on the Advisory Board for both Trends in Chemistry and the MIT Science Policy Review.

Authors: Alexander J. M. Miller

Title: Mechanistic Lessons from Rhenium-Mediated Dinitrogen Reduction to Ammonia

Abstract:

The direct cleavage of dinitrogen between two metal centers could serve as the key step in ammonia synthesis, but examples of splitting N2-bridged complexes into terminal nitride complexes that can be reduced to release ammonia remain rare. This presentation describes rhenium pincer complexes that reductively bind N2, photochemically cleave the bridging ligand into terminal nitrides, and undergo proton-coupled electron transfer reduction to furnish ammonia. Comparisons across rhenium complexes provides a framework for understanding the factors that influence the barrier height and free energy of N2 cleavage. Design principles and prospects for catalysis are considered.