Electrochemical Dinitrogen Fixation

Investigators
Matthew W. Kanan, Assistant Professor, Department of Chemistry, Stanford University
Thomas Veltman, Graduate Researcher, Department of Chemistry, Stanford University

Project Period: 9/1/11—8/31/12

Abstract
Materials that catalyze efficient electrochemical N\textsubscript{2} fixation would open up the possibility of using an N\textsubscript{2}/NH\textsubscript{3} cycle to store and utilize energy from diffuse renewable sources. In such a cycle, N\textsubscript{2} and H\textsubscript{2}O would be electrolysily transformed to NH\textsubscript{3} and O\textsubscript{2} in an electrolyzer powered by a renewable electricity source. With existing technologies, NH\textsubscript{3} can be utilized in solid oxide fuel cells or combustion engines to generate electricity or work and regenerate N\textsubscript{2} and H\textsubscript{2}O. In contrast to H\textsubscript{2}, which has received the most attention for fuel-based renewable energy storage, NH\textsubscript{3} is easy to store in solid form by complexation with earth-abundant salts. Despite the attraction of an N\textsubscript{2}/NH\textsubscript{3} cycle, to date no suitable electrocatalysts have been developed for this reaction. Moreover, there is no reliable dataset available that characterizes the activities of common electrode materials under any set of conditions. A principal obstacle to studying electrochemical N\textsubscript{2} fixation and progressing towards a useful catalyst has been the lack of a sensitive and rapid method for NH\textsubscript{3} quantification. Conventional spectrophotometric methods are cumbersome and prone to false positives from the presence of metal ions or other sample impurities. We have addressed this analytical problem by developing a device that quantifies NH\textsubscript{3} liberated from an aqueous solution. This device accurately quantifies NH\textsubscript{3} content in solutions with as little as a few hundred ppb of NH\textsubscript{3} and reaches a saturation response within minutes. Because NH\textsubscript{3} is removed from a solution prior to detection, this method is completely immune to interference from metal ions or other electrolyte impurities that impair spectrophotometric methods. Using this unique analytical tool, we have begun determining the N\textsubscript{2} reduction activity of a large collection of metal electrodes in both acidic and alkaline electrolytes. We have also constructed electrolysis cells suitable for evaluating catalysts in gas diffusion electrodes that provide much higher concentrations of N\textsubscript{2} at the catalyst surface. The information available from these studies will provide the foundation for the subsequent discovery and development of catalysts that are suitable for use in an electrolytic device.

Introduction
Transitioning from a fossil fuel economy to a renewable energy economy will require energy storage technologies that are capable of reaching the terawatt (TW) scale. Fuels are particularly attractive energy storage media because of the high energy density of chemical bonds. Robust technologies are available for converting renewable sources such as sunlight or wind into electric potential energy. Fuel-based renewable energy storage requires efficient conversion of electric potential energy to chemical energy via electrolytic devices. Current electrolyzer technology enables efficient (90%) water electrolysis to H\textsubscript{2} and O\textsubscript{2}, albeit at significant cost.[1] However, the scalability of H\textsubscript{2}-based renewable energy cycles is limited by the difficulty of storing H\textsubscript{2} in large
quantities. An electrolyzer that produces NH$_3$ via electroreduction of N$_2$ is a very attractive alternative target that avoids the shortcomings of H$_2$.[2] Ammonia is easily stored by forming a solid, bench-stable complex with alkaline earth salts (e.g. Mg(NH$_3$)$_6$Cl$_2$).[3] Gaseous NH$_3$ can be liberated from these complexes on demand by heating and combined with O$_2$ in medium-temperature fuel cells to produce electricity and N$_2$ and H$_2$O as byproducts.[4] An NH$_3$-producing electrolyzer would therefore enable an N$_2$/NH$_3$ renewable energy cycle (Figure 1). The abundance and ease of purification of N$_2$, combined with the energy density of NH$_3$, make this cycle a viable candidate for TW-scale energy storage.

The key technological hurdle for an NH$_3$/N$_2$ cycle is the development of an efficient electrocatalyst for the N$_2$ reduction reaction: N$_2$ + 6 e$^- + 6$ H$^+$ $\rightarrow$ 2 NH$_3$. In contrast to H$^+$ or CO$_2$ reduction, very few electrocatalysts have been reported to exhibit any activity for N$_2$ reduction.[5] Moreover, these few reports[6,7] have not been subsequently verified and extended. Consequently, little is known about the requirements or possible mechanisms for this reaction. The goals of our research project are to determine the electrocatalytic activities of metal electrodes in both solution-phase and gas-phase N$_2$ reduction electrolyses. We hypothesize that metals that exhibit activity for multi-electron CO$_2$ reduction[8-10] will also be active for the 6 e$^-$ reduction of N$_2$ to NH$_3$. While this activity is expected to be minor relative to H$_2$O reduction in aqueous solution-phase electrolyses, we anticipate that increased N$_2$ concentration at the electrode surface in gas-phase electrolyses will enable N$_2$ reduction with higher efficiency. These efforts will provide the foundation for subsequent catalyst design and discovery efforts.

**Figure 1**: Renewable energy cycle using NH$_3$-based storage. Available technology enables storage and utilization of NH$_3$ fuel (solid lines). Electrochemical N$_2$ fixation would enable re-generation of NH$_3$ using sun or wind (dashed lines).

**Background**

*Developments in N$_2$ reduction in the past year*

There have been no recent reports of electrochemical N$_2$ reduction with heterogeneous electrocatalysts. However, a recent computational study by Nørskov and coworkers examined electrochemical reduction of N$_2$ adsorbed on metal surfaces for the transition metal series.[11] This study predicted that Mo, Fe, Rh and Ru are optimally energetically efficient for this reaction, but this activity cannot be realized because H$^+$ reduction dominates on these metals. Viable N$_2$ reduction, albeit with relatively low energetic efficiency, was predicted for early transition metals such as Zr and Ti. These
recent results underscore the importance of establishing a reliable experimental dataset for metal electrodes.

Results
Our efforts to date have focused on solution-phase N₂ reduction electrolyses. Solution-phase electrolyses are experimentally convenient because electrode preparation and characterization are greatly simplified relative to gas-phase experiments. Unfortunately, N₂ is only sparingly soluble in aqueous solutions (600 µM saturation at 1 atm), limiting the substrate concentration and greatly favoring competitive H⁺ or H₂O reduction. N₂ reductions in aqueous solutions are expected to yield only small amounts of NH₃ relative to the amount of H₂ produced. A highly sensitive NH₃ detection method is therefore required to accurately determine catalytic activity. The conventional method for detecting and quantifying NH₃ is discrete analysis, a spectrophotometric method based on the formation of a dye from reaction of NH₃ in solution with a dye precursor. We began our studies of N₂ reduction relying on discrete analysis but eventually determined that this method was too slow and not sufficiently sensitive for our needs. Moreover, we discovered that discrete analysis is prone to false positives due to trace metal ions in solution that can leach from an electrode at open circuit or during catalysis. Faced with this limitation, we designed and developed a new quantitative NH₃ detector with sub-ppm sensitivity and immunity from metal ion interference. We have begun collecting our target dataset with this detector and, in parallel, have assembled the infrastructure to initiate gas-phase studies.

Quantitative NH₃ detector with sub-ppm sensitivity
To avoid the sensitivity limitations and false positives of conventional NH₃ analysis methods, we constructed a device that detects gaseous NH₃ liberated from an aqueous solution (Figure 2). The device is designed to quantify the amount of NH₄⁺ in an acidic solution, which would be produced from N₂ reduction in an acidic electrolyte or from acidic trapping of the NH₃ produced from N₂ reduction in a basic electrolyte. The sample containing NH₄⁺ is treated with strong base and moderate heating to release NH₃ into the gas phase whereupon it is detected electrochemically. The detector reaches a saturation response to an NH₃ concentration within minutes and we have interfaced it with an autosampler to enable automated NH₃ quantification of many samples in an overnight run. A standard curve for NH₃ detection from samples containing 1.5 ppm, 1.0 ppm, 0.5 ppm and 0.25 ppm NH₄⁺ is shown in Figure 3.

Solution-phase electrolyses
A survey of metal electrodes for N₂ reduction in 0.1 M HClO₄ electrolyte did not uncover an electrode with appreciable activity within our detection limits. Small amounts of NH₄⁺ were produced in a number of electrolyses but were identified as the product of reduction of NO₃⁻ contaminants in the electrolyte. Operating in alkaline conditions offers two advantages: the competitive reaction is H₂O reduction instead of H⁺ reduction and the electrode potential is much more negative at the same value vs RHE. Our work in alkaline electrolytes is ongoing.
Figure 2: Top-view of the home-built NH$_3$ detector with sub-ppm sensitivity.

Figure 3: Instrument response vs sample concentration for NH$_4^+$ samples in pH 6.5 aqueous electrolyte.

Gas-phase reactor for N$_2$ reduction studies

In parallel with our detector development, we have constructed an electrolysis cell suitable for the use of gas diffusion electrodes. These electrodes enable catalysis to take place at a gas-solid-liquid triple phase boundary and provide much higher concentrations of a gaseous reactant at the electrode surface than is possible for solution-phase electrolysis. Our cell design borrows many of the standard features used for H$_2$ fuel cells. We have performed preliminary electrolys en in this cell using catalysts dispersed on Nafion membranes. We have also developed a method for trapping NH$_3$ off of a outgas stream from a gas diffusion electrode and verified a trapping efficiency of >80%. With this set up, we are equipped to evaluate N$_2$ reduction in gas-phase electrolys es alongside our solution-phase work and aim to complete both datasets in parallel.
Progress

$N_2$ electroreduction studies have previously been hampered by the lack of a sensitive, reliable and rapid NH$_3$ quantification method. We have addressed this problem in a novel way by developing a device that detects gaseous NH$_3$ liberated from an aqueous solution. This unique analytical tool positions us to survey the activity of metal electrodes in both aqueous solutions and triple-phase boundaries of gas diffusion electrodes. We anticipate that the results from this effort will illuminate several materials that exhibit electrocatalytic activity. This information will be valuable for assessing the viability of electrochemical $N_2$ reduction in the near future and illuminate materials that are promising for subsequent development.

Publications and Patents

No manuscripts have been submitted thus far related to this project.

References


Contacts

Matthew Kanan: mkanan@stanford.edu
Thomas Veltman: tveltman@stanford.edu