

Electrochemical Dinitrogen Fixation

Investigators

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Abstract

Materials that catalyze efficient electrochemical N_2 fixation would open up the possibility of using an N_2/NH_3 cycle to store and utilize energy from diffuse renewable sources. In such a cycle, N_2 and H_2O would be electrolytically transformed to NH_3 and O_2 in an electrolyzer powered by a renewable electricity source. With existing technologies, NH_3 can be utilized in solid oxide fuel cells or combustion engines to generate electricity or work and regenerate N_2 and H_2O . In contrast to H_2 , which has received the most attention for fuel-based renewable energy storage, NH_3 is easy to store in solid form by complexation with earth-abundant salts. Despite the attraction of an N_2/NH_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_2 fixation and progressing towards a useful catalyst has been the lack of a sensitive and rapid method for NH_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_3 liberated from an aqueous solution. This device accurately quantifies NH_3 content in solutions with as little as a few hundred ppb of NH_3 and reaches a saturation response within minutes. Because NH_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_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_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_2 and O_2 , albeit at significant cost.[1] However, the scalability of H_2 -based renewable energy cycles is limited by the difficulty of storing H_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 H₂. [2] Ammonia is easily stored by forming a solid, bench-stable complex with alkaline earth salts (e.g. Mg(NH₃)₆Cl₂). [3] Gaseous NH₃ can be liberated from these complexes on demand by heating and combined with O₂ in medium-temperature fuel cells to produce electricity and N₂ and H₂O as byproducts. [4] An NH₃-producing electrolyzer would therefore enable an N₂/NH₃ renewable energy cycle (**Figure 1**). The abundance and ease of purification of N₂, combined with the energy density of NH₃, make this cycle a viable candidate for TW-scale energy storage.

The key technological hurdle for an NH₃/N₂ cycle is the development of an efficient electrocatalyst for the N₂ reduction reaction: $\text{N}_2 + 6 \text{e}^- + 6 \text{H}^+ \rightarrow 2 \text{NH}_3$. In contrast to H⁺ or CO₂ reduction, very few electrocatalysts have been reported to exhibit any activity for N₂ 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 N₂ reduction electrolyses. We hypothesize that metals that exhibit activity for multi-electron CO₂ reduction [8-10] will also be active for the 6 e⁻ reduction of N₂ to NH₃. While this activity is expected to be minor relative to H₂O reduction in aqueous solution-phase electrolyses, we anticipate that increased N₂ concentration at the electrode surface in gas-phase electrolyses will enable N₂ reduction with higher efficiency. These efforts will provide the foundation for subsequent catalyst design and discovery efforts.

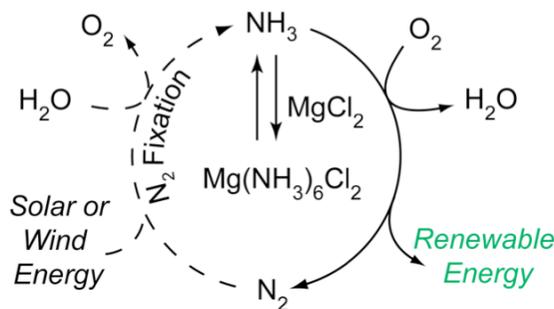


Figure 1: Renewable energy cycle using NH₃-based storage. Available technology enables storage and utilization of NH₃ fuel (solid lines). Electrochemical N₂ fixation would enable re-generation of NH₃ using sun or wind (dashed lines).

Background

Developments in N₂ reduction in the past year

There have been no recent reports of electrochemical N₂ reduction with heterogeneous electrocatalysts. However, a recent computational study by Nørskov and coworkers examined electrochemical reduction of N₂ 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 N₂ 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 N_2 reduction electrolyses. Solution-phase electrolyses are experimentally convenient because electrode preparation and characterization are greatly simplified relative to gas-phase experiments. Unfortunately, N_2 is only sparingly soluble in aqueous solutions (600 μM saturation at 1 atm), limiting the substrate concentration and greatly favoring competitive H^+ or H_2O reduction. N_2 reductions in aqueous solutions are expected to yield only small amounts of NH_3 relative to the amount of H_2 produced. A highly sensitive NH_3 detection method is therefore required to accurately determine catalytic activity. The conventional method for detecting and quantifying NH_3 is discrete analysis, a spectrophotometric method based on the formation of a dye from reaction of NH_3 in solution with a dye precursor. We began our studies of N_2 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 NH_3 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 NH_3 detector with sub-ppm sensitivity

To avoid the sensitivity limitations and false positives of conventional NH_3 analysis methods, we constructed a device that detects gaseous NH_3 liberated from an aqueous solution (**Figure 2**). The device is designed to quantify the amount of NH_4^+ in an acidic solution, which would be produced from N_2 reduction in an acidic electrolyte or from acidic trapping of the NH_3 produced from N_2 reduction in a basic electrolyte. The sample containing NH_4^+ is treated with strong base and moderate heating to release NH_3 into the gas phase whereupon it is detected electrochemically. The detector reaches a saturation response to an NH_3 concentration within minutes and we have interfaced it with an autosampler to enable automated NH_3 quantification of many samples in an overnight run. A standard curve for NH_3 detection from samples containing 1.5 ppm, 1.0 ppm, 0.5 ppm and 0.25 ppm NH_4^+ is shown in **Figure 3**.

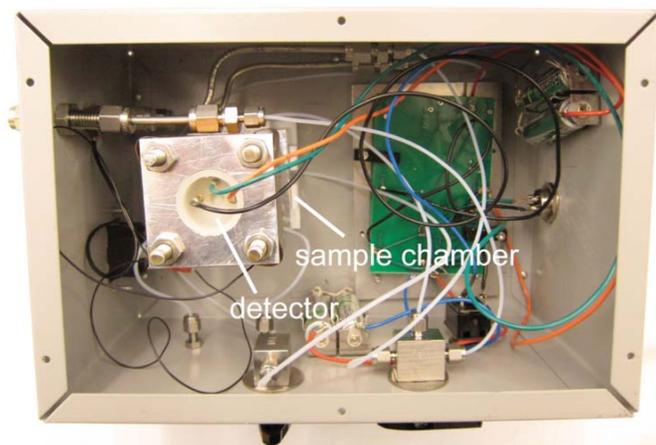


Figure 2: Top-view of the home-built NH_3 detector with sub-ppm sensitivity.

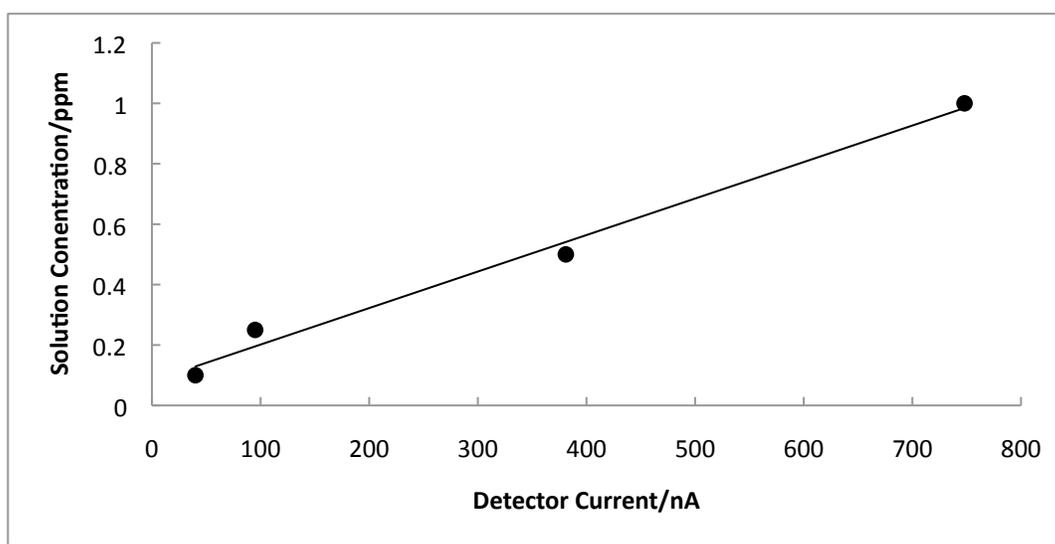


Figure 3: Instrument response vs sample concentration for NH_4^+ samples in pH 6.5 aqueous electrolyte.

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 a solution-phase electrolysis. Our cell design borrows many of the standard features used for H_2 fuel cells. We have performed preliminary electrolyses 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 electrolyses alongside our solution-phase work and aim to complete both datasets in parallel.

Progress

N₂ electroreduction studies have previously been hampered by the lack of a sensitive, reliable and rapid NH₃ quantification method. We have addressed this problem in a novel way by developing a device that detects gaseous NH₃ 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 N₂ reduction in the near future and illuminate materials that are promising for subsequent development.

Future Plans

The remainder of the research project will focus on catalyst evaluation. Utilizing the unique analytical capabilities that we have developed, we are in the process of evaluating a large set of metal electrodes in acidic (HClO₄) and alkaline (KOH) electrolytes. In addition, we will evaluate the most active metals in a gas diffusion electrode configuration to determine whether increased N₂ concentration at the catalyst surface improves the Faradaic efficiency of N₂ reduction vs H⁺ (H₂O) reduction as expected.

Publications and Patents

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

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