Title Page

The title page concisely provides the project title and committee member contact information

Control of Platinum Surface Structure and Environment for Electrochemical Ammonia Oxidation

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Specific Aims

I. Specific Aims

As our society shifts toward renewable energy sources and away from traditional fossil fuels, the intermittency of common renewable sources such as solar and wind becomes problematic. We believe the use of ammonia as a carbon neutral liquid fuel for energy storage can address this issue. Not only does ammonia have a high energy density, but it is also currently produced at scale. Accordingly, safe transportation procedures are already in place despite its inherent chemical dangers. Additionally, ammonia is carbon free and its use can help the energy industry move beyond the carbon cycle. The two primary engineering issues facing wide deployment of ammonia as a liquid fuel are carbon neutral production and effective conversion to electricity. Although current production routes use carbon-based feedstocks to produce the necessary hydrogen gas, there is precedent for ammonia production from renewable sources with proper economic motivation. We therefore will focus on developing methods to convert ammonia to electricity efficiently.

Presently, the best method for converting ammonia to energy is through a fuel cell. The key process involved is the conversion of ammonia to nitrogen, and the best catalysts to date for such a process are platinum and platinum alloys. Unfortunately, platinum is expensive, prohibiting its effectiveness as a mass-produced catalyst. Additionally, platinum has a large electrochemical overpotential, and the platinum surface quickly poisons during the ammonia oxidation process. My thesis will thus address the following questions:

How does the surface structure and coordination environment of platinum, particularly on a E nanometer and sub-nanometer scale, affect its overpotential and activity for ammonia is electrooxidation?

Current reports indicate that ammonia oxidation occurs primarily on the (100) surface of platinum, inspiring synthesis of particles with preferential (100) surfaces. We aim to build on this result, using previously reported procedures to synthesize platinum nanocubes with side lengths ranging from 5 nm to 10 nm and primarily composed of the (100) surface (Figure 1b). We also plan to synthesize sub-nanometer platinum particles, exploring the phase space from single platinum atoms up to clusters of diameter one nanometer that do not exhibit specific crystal faces and thus could have fundamentally different catalytic properties (Figure 1a). These subnanometer clusters have been shown to have high catalytic activity for other systems and give us an opportunity to tune the electronic structure of the catalyst via cluster size and support material. Because sub-nanometer particles are strongly influenced by the environment, we will explore metal sulfides as a support material (Figure 1a). Specifically, due to their surface morphology and ability to break scaling relationships in other systems, we hope that metal sulfides will be able to work in concert with platinum particles to lower the activation energy and avoid the poisoning of platinum surfaces that deactivates the catalyst. Through these studies, we aim to tune the electronic structure of the catalytic platinum and not only decrease the overpotential and reduce surface poisoning, but also significantly decrease the platinum loading, making platinum catalysts more tractable as a commercial ammonia electrooxidation catalyst.

The aims begin with a brief introductio n to the topic

Each aim is set apart from the rest of the text (in this case by italics). A numbered list can also be useful What adsorbates are responsible for the poisoning of the platinum surface and can this poisoning be avoided through use of non-aqueous electrolytes?

Although the poisoning mechanism has been widely accepted, and we do not dispute it, recent research has shown that platinum in a non-aqueous environment does not experience poisoning. We want to probe this reaction and determine if the hydroxide anion is partially responsible for the poisoning or if different electrolyte environments can prevent the poisoning through modification of adsorption energy of the poisoning species.

In addition to addressing the above questions, we will apply our catalysts to a standard fuel cell geometry that can maximize energy efficiency and demonstrate the practicality of converting ammonia into electrical energy.



Figure 1: Schematic of proposed catalysts

Shown is a metal sulfide support with sub-nanometer Pt clusters on top (a) and a Pt cube with (100) faces (b). Atoms shown are Pt (silver), S (yellow), and Fe (purple). Note that these are not to scale and the platinum clusters are visually placed on top of the metal sulfide surface, intentionally ignoring any surface interactions or lattice incorporation.

Background

II. Introduction

a. Energy storage for electrification

The background is divided into sections, which promotes readability

Renewable energy sources, such as solar and wind, have become increasingly prevalent and helped drive progress toward decarbonization of electricity. However, the intermittency of such sources limits their potential as a replacement for traditional fossil fuels. The success of renewable energy sources accordingly requires an energy storage medium that allows the efficient transport and storage of electricity for usage in applications ranging from handheld devices to cars and city grids. Currently, lithium-ion batteries are ubiquitous as solid-state storage for small devices, but they have an energy density an order of magnitude less than that of liquid fuels, hindering their usage for applications with larger energy requirements (**Table 1**). Unsurprisingly, fossil fuels currently act as energy storage carriers for larger energy applications due to their high energy density. In an effort to replace fossil fuels with renewable sources,

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Each aim has a onesentence summary, followed by a 1-2 paragraph descriptio recent research has focused on carbon neutral fuels, such as hydrogen, as an alternative to gasoline. Although hydrogen is less energy dense than gasoline, it is appealing because it can be sourced exclusively from electrochemical water splitting, a process that can be efficiently and modularly operated from renewable sources such as solar. Hydrogen storage and distribution remain issues, however, due to the extreme conditions required for practical transport (**Table 1**). For the reasons outlined below, we support the use of ammonia as an effective carbon neutral fuel and aim to make this a reality through study of ammonia oxidation catalysts for converting ammonia into energy.

Chemical	Energy content (MJ/L)	Transport and Storage Conditions
Liquid H ₂	10	700 bar + ambient T
Gas H ₂	6	20 K + ambient P
Liquid NH ₃	15	~10-15 bars + ambient T
Methanol	18	Ambient T + P
Gasoline	35	Ambient T + P
Lithium-ion Battery	~2	Ambient T + P

Table 1: Comparison of energy storage media energy densities^{1,2}

The primary goal for utilizing a carbon neutral energy storage media is to reduce carbon emissions and rely exclusively on renewable energy sources instead of traditional fossil fuels. In general, we can meet those goals by either closing or moving beyond the carbon cycle.³ One route to decarbonization of energy production and storage could involve converting otherwise emitted carbon dioxide into carbon based liquid fuels such as methanol. The fuel, in turn, would burn or flow through a fuel cell, producing carbon dioxide that would then be captured and converted back into the original fuel using renewable electricity. Thus, the carbon cycle would be closed with no net carbon dioxide produced. A second strategy that results in decarbonization of energy would involve avoiding the generation of carbon dioxide altogether.

Regardless of strategy, a carbon neutral liquid fuel needs to exhibit certain key attributes. First, it must have a high energy density; liquid hydrogen, liquid ammonia, and liquid methanol all exhibit energy densities comparable to gasoline and an order of magnitude larger than lithiumion batteries. Second, a carbon neutral fuel needs to be able to be synthesized and distributed in a manner that is energy efficient, safe, and only relies on renewable energy sources. Hydrogen, although easily produced via water electrolysis, cannot be effectively distributed with the current infrastructure, a significant hurdle to its widespread usage. Methanol and ammonia, in contrast, are attractive due to their high volumetric energy densities and their cost-effective distribution using existing infrastructure; both chemicals are already top five commodity chemicals by production volume and have well-established distribution networks.⁴ Unfortunately, synthesis of ammonia and methanol from renewable sources remains an open challenge, in part due to carbon dioxide emissions from the production of a hydrogen feed stream. Hydrogen gas is generally produced by steam reforming of methane followed by the water gas shift reaction, resulting in large carbon dioxide emissions. In theory, feed hydrogen could be produced through electrochemical water splitting, and there are instances of ammonia production plants dating back to the mid-20th century that rely on electrolysis of water to provide the hydrogen feed. These offer examples for future carbon neutral synthesis routes as the cost of water electrolysis continues to decrease and demonstrate its commercial viability for ammonia production.⁵ The last requirement for a carbon neutral liquid fuel is that it can be easily converted into electrical energy. Hydrogen fuel cells are already well developed and the subject of significant research, but ammonia and methanol fuel cells remain inefficient and impractical.

After considering the above factors, we will focus our efforts on a potential nitrogen economy that relies on ammonia as an energy carrier. We will focus on nitrogen because ammonia has a large energy density, already is the largest commodity chemical produced by volume, and can theoretically be produced commercially using renewably sourced hydrogen. While many of these arguments can be applied to methanol, ammonia is a more ubiquitous and globally significant commodity chemical. Although ammonia is not traditionally associated with energy storage, the practical aspects of using ammonia as a liquid fuel have been studied and the ammonia economy found to be feasible.⁶ The main problem we aim to address is the conversion of ammonia to electrical energy, closing the loop and allowing ammonia to be used as an energy source in applications ranging from transportation to infrastructure.

b. Ammonia oxidation thermodynamics

Converting ammonia into electrical energy is essential for an ammonia economy, but how exactly would such a conversion occur? As our world continues to become more reliant on electricity, the most logical method to convert ammonia to electrical energy is through a fuel cell (**Figure 2**). Such a fuel cell will ideally operate at low temperatures and would need to operate in basic conditions, since ammonia will become the less electrochemically active ammonium at lower pH.⁷ At the anode of the fuel cell, ammonia would be converted to nitrogen gas and water (Equation 1).

$$NH_3(g) + 3OH^-(aq) \to \frac{1}{2}N_2(g) + 3H_2O(\ell)$$
 (1)

At the cathode of the fuel cell, however, we have two options. In the absence of oxygen, we would simply reduce water to hydrogen gas (Equation 2, Case II in **Figure 2**).

$$H_2O(\ell) \to \frac{1}{2}H_2(g) + OH^-(aq)$$
 (2)

In the presence of oxygen gas, we would reduce the oxygen to hydroxide anions (Equation 3, Case I in **Figure 2**).

$$H_2O(\ell) + \frac{1}{2}O_2(g) \to 2OH^-(aq)$$
(3)



Figure 2: Schematic of an ammonia oxidation cell

On the anode (red), ammonia and hydroxide will form water and nitrogen (Equation 1). On the cathode (black), water will form hydroxide ions and hydrogen gas (Equation 2, Case II) or water and oxygen will form only hydroxide ions (Equation 3, Case I).

The thermodynamics of this system reveal the theoretical operating potentials for an ammonia fuel cell (Figure 3). Should the system operate in the presence of oxygen (Equations 1 and 3), power will be output at a voltage of 1.17 V, similar to a hydrogen fuel cell's 1.23 V. Operating a cell in this manner would directly turn ammonia into electricity. Should the system operate in the absence of oxygen (Equations 1 and 2), power will be required as an input at a voltage of 0.06 V. Hydrogen gas will be produced from this cell which can then be used as a fuel for a hydrogen fuel cell, possibly resulting in a more efficient process overall given optimized hydrogen fuel cells. The advantage of operating the cell in the presence of oxygen is that the process is simpler and will directly result in electrical energy as an output. On the other hand, the advantage to running the cell in the absence of oxygen is that hydrogen fuel cells are a more developed technology and the overall process could be more efficient, leading to benefits from the modularity resulting from having hydrogen as an intermediate energy carrier. Hydrogen produced via this route could also be used in synthetic processes which require extremely pure hydrogen feeds. The major disadvantage of producing hydrogen is that the entire process is more complex with potentially more areas for inefficiencies that could result in a lower net power output. Choosing which of these methods is more practical will depend on a multitude of economic and outside factors that cannot be easily predicted *a priori*. Current water and oxygen reduction catalysts that could be used at the cathode are well developed and optimized, so we will primarily focus our investigation on the ammonia oxidation reaction at the anode of the ammonia fuel cell, with the goal of producing nitrogen selectively at the lowest overpotential possible.^{8,9} This goal is independent of the cathode materials that determines whether the electrochemical cell produces hydrogen or electricity.



Figure 3. Thermodynamics of the aqueous ammonia system.

The most important electrochemical reactions are shown on the vertical arrow to the left, with the direction of the oxidative overpotential during operation indicated in red. Undesirable oxygen containing products are shown by the vertical arrow on the right. All voltages are versus the standard hydrogen electrode (SHE)

c. Ammonia oxidation kinetics on platinum

While the thermodynamics are important for understanding the theoretical limits of ammonia oxidation, of primary concern for this process are the reaction kinetics on the catalyst surface. Currently, the best catalyst for ammonia oxidation is platinum metal, although the catalyst can be further optimized by using platinum alloys with other precious metals such as rhodium, ruthenium, or iridium. The widely accepted mechanism for ammonia oxidation was first proposed by Gerischer and Mauerer (Equations 4-9).¹⁰

$$NH_3(aq) \rightarrow NH_{3ads}$$
 (4)

$$NH_{3,ads} + OH^- \rightarrow NH_{2,ads} + H_2O + e^-$$
(5)

$$NH_{2ads} + OH^{-} \rightarrow NH_{ads} + H_{2}O + e^{-}$$
(6)

$$NH_{x,ads} + NH_{y,ads} \rightarrow N_2 H_{x+y,ads} \qquad (x, y = 1, 2)$$
(7)

$$N_2 H_{x+y,ads} + (x+y)OH^- \rightarrow N_2 + (x+y)H_2O + (x+y)e^-$$
 (8)

$$NH_{ads} + OH^{-} \rightarrow N_{ads} + H_2O + e^{-}$$
⁽⁹⁾

Perhaps not intuitively, the key step in this mechanism is the recombination of adsorbed amide and imide species to form an N_2H_{x+y} compound (Equation 7). Another important aspect

of this mechanism is that when the adsorbed ammonia is deprotonated enough to become a nitrogen atom, the nitrogen atom will bind tightly to the surface and poison the catalyst (Equation 9). Notably, other researchers have disputed this poisoning mechanism and have suggested that deactivation of the catalyst is due to hydroxide adsorption to the surface.¹¹⁻¹⁴ Overall, Gerischer and Mauerer's mechanism is supported by careful electrochemical and Differential Electrochemical Mass Spectroscopy (DEMS) experiments.¹⁵⁻¹⁷ Additionally, multiple experiments have reported a Tafel slope of around 40 mV/dec, demonstrating that the rate determining step is the second deprotonation (Equation 6). Although work done to date does not conclusively prove that Gerischer and Mauerer's mechanism is the sole reaction pathway, the experiments support the mechanism and provide evidence of nitrogen poisoning. Other research using FTIR found evidence of N_2H_{x+y} on a platinum catalyst surface, further supporting the above mechanism.¹⁸



Some preliminary data supports the suspected mechanism

Figure 4. Example CV of ammonia oxidation on a platinum anode.

A platinum cathode was used with a 1 M KOH and 1 M NH₃ electrolyte. Additional experimental details provided in Appendix A.

This mechanism is best visualized with a typical cyclic voltammagram (CV) of a platinum electrode (**Figure 4**). This CV was conducted with an aqueous electrolyte of 1 M ammonia and 1 M KOH solution using a sputtered platinum electrode on a gas diffusion layer (GDL). The resulting CV is prototypical of such ammonia oxidation CVs on platinum found in the literature. Essentially, at around 0.5 V vs the reversible hydrogen electrode (RHE), corresponding to an overpotential of 400 to 500 mV, oxidation of ammonia to nitrogen gas begins to occur. The products have been consistently determined in the literature with DEMS. As the voltage increases, so does the current, until poisoning occurs around 0.6 V vs RHE. The poisoning is evidenced by the current peaking well below the diffusion limiting current and then decreasing as voltage increases to around 0.8 V vs RHE. At potentials above 0.8 V vs RHE, the current will again increase, and previous research using DEMS has observed nitrous oxides such as NO and N₂O as the products at such potentials.^{15,16} These nitrous oxides typically occur when the catalyst surface becomes

oxidized, providing easy access to oxygen. The formation of such nitrous oxides at these potentials is expected thermodynamically (Figure 3).

d. Ammonia oxidation on non-platinum catalysts

So far, we have only discussed platinum catalysts. Work by De Vooys et al. explored a range of pure metals and resulted in a so-called volcano plot of activity versus nitrogen adsorption energy (Figure 5). De Vooys et al. discovered that platinum is by far the most active catalyst for ammonia oxidation and explained this via the binding energy and the mechanism provided above. Essentially, for metals that bind molecules tighter than platinum, the surface will quickly become poisoned with tightly bound nitrogen atoms and not produce any nitrogen gas. For metals that bind molecules loosely, the ammonia will have difficulty binding in the first place and the rate determining step will be the adsorption or the first deprotonation of the ammonia (Equations 4 or 5, respectively).¹⁹ Qualitative determination of nitrogen binding strength to metal surfaces can be determined using d-band theory and the d-band center relative to the fermi level as a descriptor.²⁰ The coinage metals have additional difficulty acting as catalysts because they will form metal ammonia ions and dissolve in solution at sufficiently oxidative potentials. Other than platinum, iridium is the only metal that exhibits significant activity and selectivity towards nitrogen production; although iridium binds nitrogen tightly, it has a lower equilibrium coverage The author of nitrogen and thus can function catalytically.¹⁶ uses



Figure 5. Volcano plot of peak data when current (a proxy for activity) and relevant and nitrogen adsorption energy cites it

literature

Squares indicate nitrogen gas was observed via DEMS. Circles indicate no nitrogen gas observed (current was from deprotonation or formation of nitrous oxides). Data replotted from De Vooys et al.¹⁶

Research Plan

III. Research Plan Initial paragraph provides overview of research plan, before breaking into sections

Based on the current state of the literature, our goals are twofold: to reduce the overpotential required to oxidize ammonia to nitrogen and to prevent catalyst poisoning that currently is hindering the field. Specifically, we will focus on four major thrusts: reduction of catalyst mass loading, surface facet optimization, support effects on the electronic structure of platinum, and non-aqueous electrolyte stabilization of adsorbates. At the conclusion of our work, we hope to apply our catalyst design to an optimized fuel cell geometry and evaluate parameters such as power density.

a. Platinum optimization

Platinum is an expensive material, and in order for platinum catalysts to be commercially viable, a minimal amount of platinum must be used for the electrode. This means that a relevant parameter for judging the quality of the catalyst will be activity per mass platinum, or mA/mg Pt. Current state-of-the-art research on ammonia oxidation catalysts typically explore metal surface coatings (e.g., through electrodeposition) or nanoparticles down to a mean particle size of 2-5 nm.^{21–23} We are interested in reducing the platinum loading even further by exploring sub-nanometer platinum clusters ranging from a single platinum atom, to dimers and trimers, up to clusters that approach 1 nm diameter. Platinum single-atom catalysts have been shown to be effective catalysts for reactions such as hydrogen evolution and CO oxidation.^{24–28} Due to their low coordination environment compared to nanoparticles or surfaces, single atoms have been found to be more selective and active for some of the previously mentioned reactions. For ammonia oxidation, in particular, single atoms or dimers provide a unique opportunity to probe or change the oxidation mechanism, since the recombination step (Equation 7) in the mechanism requires two adsorbed molecules to be near each other, an infeasible occurrence with single atoms (see Appendix B for experimental details). Single atoms are also the ideal minimal loading of precious metals. Because some works have found success of platinum alloys, we will also explore subatomic clusters of Pt + M, for a metal M, of sizes down to the subnanometer scale.



Figure 6. Comparison of Pt surface morphology for ammonia oxidation.

Comparison of Pt(100), Pt(110), Pt(111), and polyoriented Pt single crystal in 0.1 M NaOH and 1 mM ammonia. Figure reproduced from Vidal-Iglesias et al.²⁹

In addition to reduction of catalyst loading, facet optimization of the catalyst surface can drastically improve catalytic activity. Vidal-Iglesias et al. demonstrated the effect of the platinum surface on ammonia oxidation activity (**Figure 6**).²⁹ Using Pt single crystals, they determined that the (100) surface was the most active, likely due to optimal coordination and nitrogen binding energy of surface platinum atoms. By looking at other surfaces with higher indices, Vidal-Iglesias et al. also correlated ammonia oxidation activity with the amount of (100) surface exposed using a terrace-step decomposition of surface indices.

While this has led researchers to focus on creating particles with preferential (100) surfaces,^{30,31} we hope to build on this previous research and synthesize nanocubes with primarily (100) surfaces, as described by Chia-Kuang Tsung et al. (**Figure 7**).³² Not only did Chia-Kuang Tsung et al. create monodisperse cubes made up entirely of (100) surfaces, but they also synthesized cubes of side lengths varying from 5-9 nm. While platinum nanocubes have been synthesized to demonstrate surface structure effects on ammonia oxidation,^{33,34} we will use size control to minimize catalyst loading and tune the electronic structure of the platinum surface, and we will also investigate the mechanism of ammonia oxidation as it relates to surface structure.



Figure 7. TEM images of Pt nanocubes

TEM images of 9 nm nanocubes (a), 7 nm nanocubes (c), and 6 nm nanocubes (e). HRTEM images of a single 9 nm nanocube (b), 7 nm nanocube (d), and a 6 nm nanocube (f). Scale bars are 20 nm in TEM images and 1 nm in HRTEM images. Image reproduced from Chia-Kuang Tsung et al.³² TEM images of 5 nm and 6 nm cubes synthesized in our lab are given in Appendix B.

Following examples from the literature, we have begun and will continue to synthesize single atoms of platinum on metal sulfide supports, as well as 5 to 10 nm platinum cubes.^{32,28} A significant difficulty will be characterizing such materials and confirming we have the correct catalysts; for example, imaging of a single-atom of platinum will require a HAADF-STEM, an instrument not found on MIT's campus but available at other institutions, such as Harvard. Additionally, although the activity of the catalyst may increase when measured per unit mass of platinum, with extremely small loadings it will be challenging to calculate the activity due to the

potentiostat's sensitivity at such low currents. Accordingly, careful cell design and use of gas diffusion electrodes will be necessary to achieve the high dispersion necessary per unit area, making the measurements more difficult and time intensive than tests on simple flat substrates such as ITO or glassy carbon. Currently, we have had some success with decreasing platinum loading and retaining activity for ammonia oxidation (**Figure 8**). We have compared a sputtered platinum electrode on carbon paper with 5 nm platinum cubes dispersed on carbon paper. The sputtered Pt has a coating of Pt 50 nm thick and a relatively large surface area. The cubes have a nominal dispersion of 0.025 mg Pt/cm². ICP analysis will be used to determine how much less platinum was used for the cubes compared to the sputtered layer. Regardless, the magnitude of the oxidation peak is similar for both materials, suggesting that we have improved the oxidative capabilities per mass of catalyst significantly. We will need to explore multiple sizes ranging from a single atom to a nanoparticle to create a complete picture of the effect of mass loading on catalytic activity.



Figure 8. CV comparison of Pt cubes with sputtered Pt on a GDE

5 nm cubes (red) and platinum sputtered electrodes (black) in 1 M KOH and 1 M NH_3 solution. CV taken at 20 mV/s.

b. Platinum coordination environment

One important factor mentioned previously that affects catalytic activity and must be considered with sub-nanometer clusters is the support material. Because a significant fraction of the platinum in a sub-nanometer platinum cluster is in direct contact with the support, the support effects will become more important than they are for larger particles. Although platinum is the current state-of-the-art catalyst, it is plagued by the poisoning effects of adsorbed nitrogen atoms. Thus far, the phase space of pure metals and metal alloys has been well explored throughout the literature. However, with our exploration of sub-nanometer platinum clusters, we gain the ability to adjust the support material and further tune the

electronic structure of the platinum catalyst. One could imagine a support that donates electrons to edge platinum atoms, raising the fermi level of the platinum clusters relative to its d-center and loosening the binding of nitrogen at the particle-support interface. This would allow tightly bound nitrogen atoms to be released, ideally as nitrogen gas, preventing surface poisoning. One could also imagine a support that binds nitrogen tightly, acting as a sink and allowing the poisoning nitrogen to move off the active platinum onto the support, which facilitates slow recombination and prevents poisoning of the platinum. By changing the support and altering the binding energy of the active catalyst, it is also possible that small clusters of other metals such as iridium or palladium could become effective catalysts with the aid of a support even if they do not function well on their own. Support effects on ammonia oxidation have been touched upon in past work, such as when Ntais et al. found that Pt/NiO performed better than Pt/MnO_2 and Pt/C for ammonia oxidation, but the full extent of support influence remains unexplored.³⁵ In a related reaction, the support effects on sub-nanometer clusters were reported for the electrooxidation of CO on platinum.³⁶ In their research, Siburian et al. found lower onset potentials with smaller platinum clusters on a graphene support (Figure 9).³⁶ Their analysis revealed that the graphene support was essential for stabilizing the small clusters and enabling them to function as active catalysts. One of our aims is to follow the same synthesis route as Siburian et al. to test sub-nanometer to 3 nm platinum clusters on graphene support.



Figure 9. Demonstration of Pt loading reduction and overpotential decrease

Reproduction of data from Siburian et al. demonstrating the effectiveness of small platinum nano-clusters on a graphene support.³⁶ The overpotential for CO oxidation increases with particle size (a) on graphene (\Box) and remains constant on carbon black (\bullet). Note that the average particle size (b) decreases to below a nanometer according to ECSA measurements with hydrogen (\bullet) and CO (\circ).

While Siburian et al. provide a method for exploring support effects on sub nanometer clusters to clusters of diameter 3 nm, we plan to also study metal sulfide nanoparticles for support for our single atom and sub-nanometer clusters. We will use metal sulfides that are stable under the oxidative potentials, and we chose metal sulfides in particular because they will not facilitate easy oxide formation that could provide oxygen for nitrous oxide products to form instead of the desired nitrogen. We can vary the metal using a solvothermal method, and we will thus aim to control the adsorbate binding energy on the cluster.³⁷

Metal sulfides offer many advantages as a support material. Not only do metal sulfides contain earth abundant metals that should be cheap, they also have a very different surface morphology and electronic structure than metals and metal alloys. Unlike pure metals, metal sulfides have sulfur atoms on their surface, which could attract the hydrogen atoms, weakening the NH bond and reducing the overpotential required to oxidize ammonia, since the rate-limiting step is known to be a deprotonation step. Doped MoS₂ has been theoretically shown to break the traditional volcano scaling relationship with CO₂ reduction due to different types of binding sites for the adsorbates: sulfur and metal.³⁸ Additionally, DFT studies show that NH₂ and N₂H bind to metal atoms but OH and H bind to sulfur atoms, with adsorbates bound to the metal exhibiting a different scaling relationship than those bound to the sulfur (Figure 10).³⁹ In fact, not only do the scaling relationships have different slopes, the sign of the slope for adsorption energy as a function of d-band center is different for adsorbates bound to a metal atom (negative slope) than those to a sulfur atom (positive slope) in a metal sulfide. The different scaling relationships caused by different binding sites could allow a metal sulfide to function as a unique support environment that could prevent poisoning and lower the activation barrier for the oxidation reaction. There is the additional chance, for the above reasons, that metal sulfides will function as ammonia oxidation catalysts on their own without platinum and could offer a radically different solution to the ammonia oxidation problem. So far, we have successfully synthesized nanoparticles of iron sulfide, nickel sulfide, copper sulfide, zinc sulfide, and tin sulfide using a solvothermal method and will be screening them for support effects as we develop procedures for single atom catalysts.





Note the different scaling for nitrogen compounds compared to OH and H. Figure reproduced from the work of Tsai et al.³⁹

Throughout all of our work, we will need an understanding of the adsorbates on the surface of our catalysts. To probe the adsorbates, we will be using ATR-FTIR to determine the presence of nitrogen-containing species on the electrode surface and see if we are binding ammonia too tightly or too loosely. This will be applicable for all of the above-mentioned catalyst systems.

c. Non-aqueous studies and mechanism determination

So far, we have discussed tuning platinum and its environment to become more active. However, while the current mechanism for ammonia oxidation is widely supported, there is some evidence that it does not describe the complete picture. Katsounaros et al. suggest that the mechanism actually involves decoupled electron and proton transfer steps, instead of the coupled ones assumed by Gerisher and Mauerer.⁴⁰ Zöllig et al. suggest that ammonia oxidation is not inhibited by nitrogen poisoning, but instead by local changes in pH that prevent the ammonia from approaching the electrode surface.⁴¹ While these theories remain unproven, there is some evidence that hydroxide adsorption on the surface can inhibit ammonia oxidation.^{11–14,42} While De Vooys et al. and others have strong evidence that nitrogen is adsorbed on the surface, they do not conclusively prove that the inhibition is *not* due to some other mechanism.^{16,17} In one particularly compelling study, Peng et al. use DEMS with a platinum electrode in aqueous electrolyte and in an acetonitrile electrolyte (**Figure 11**).¹¹ They find the characteristic CV peak in aqueous solution caused by surface poisoning. In acetonitrile, though, they find no such poisoning. Although there is a larger overpotentnial in acetonitrile, they find that instead of a peak, the current increases with increasing potential.





CV tests of platinum electrodes in NH₃-saturated acetonitrile solution (a) and 0.1 M NH₃ and 1 M KOH (b). Note that the acetonitrile tests used a Ag/Ag+ reference electrode.

While this does not prove that hydroxide anions are the cause of surface poisoning, it reveals that the oxidation process is different in non-aqueous solutions. This could be due to lack of hydroxide poisoning, or it could be due to solvent stabilization or destabilization of intermediates. Ammonia oxidation in non-aqueous solvents appears to avoid surface poisoning, an important step towards making ammonia fuel cells a reality. Unfortunately, working with non-aqueous solvents brings challenges, such as solvent compatibility and non-aqueous reference electrodes. We plan to explore this non-aqueous phenomenon and use ATR-FTIR to determine the root of this non-aqueous effect by characterizing the surface species in the absence of hydroxides. Should the effect be the result of adsorbed hydroxide, this would fundamentally change the mechanistic understanding and guide us towards preventing the poisoning even in

aqueous solution. Should the effect be due to the solvent, we can explore other solvents with a range of pK_a values and polarizability.

d. Fuel cell development

Up to this point, we have discussed the development of an anode for electrochemical ammonia oxidation, but eventually, the goal is to develop a complete fuel cell that takes ammonia as a feed and produces nitrogen and energy (or hydrogen). Unfortunately, the poisoning of the anode has prevented the development of effective ammonia fuel cells. There is a small body of work on ammonia fuel cells examining power density over time with nanoparticles of platinum alloys as the catalyst.^{22,23,43–46} Should our research yield an effective catalyst, the next step would be to apply such a catalyst to a gas diffusion electrode and put it into a fuel cell to measure its power density and study its failure mechanisms. Stability is an important metric for catalyst design and one we should use when judging our catalysts. Studying how the catalyst works in a real fuel cell is not a near-term goal but is definitely a priority for the future.

Safety

IV. Safety

The majority of the work described above involves standard general laboratory safety concerns. The synthesis routes involve mostly common solvents and precursors and when high temperatures are used, they are used in an oven or furnace without much danger. Strong acids and bases are used, and these require awareness of one's surroundings. Additionally, there are some dangerous compressed gases required, such as ammonia and hydrogen. We have spent time building our experimental setups that require ammonia such that they will be safe to use, and we have borrowed an ammonia sensor to use while flowing the ammonia gas to prevent any leaks from compromising the safety of the laboratory. All compressed gases will be handled with care, and they will be used infrequently and only in a fume hood. Waste materials will be disposed via regular channels.

Timeline

V. Timeline

A timeline of the above proposed research is essential for organization and effective progress (**Table 2**). However, all timelines remain in flux and will likely be altered as we gain more knowledge and improve our understanding of ammonia oxidation.



Table 2: Proposed Timeline for research

VI. Acknowledgements

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VIII. Appendices

a. Appendix A: Cell design and parameters for platinum tests

The cell we are using is a two compartment cell as shown in Figure A1. There is a counter electrode (left compartment) and a working compartment (middle). A reference electrode is inserted into the working compartment. The third compartment shown is used for Ar to purge the electrolyte, but the flow of Ar is turned off during cell operation.





The flow of Ar is used to purge the electrolyte but is turned off during electrochemical tests.

The sputtered platinum electrodes were synthesized by sputtering Pt onto a Sigracet 39BC GDL using MIT MTL's Ajax sputtering machine. The deposition was performed at 15 mTorr in an Ar atmosphere at 510 K.

The Pt cubes were dispersed in ethanol, and 50 microliters of dispersion were deposited on a hydrophilic Toray H-060 carbon paper. The original hydrophobic carbon paper was treated under stagnant ambient atmosphere at 800 °C for 20 minutes to functionalize the carbon and make the paper hydrophilic.

b. Appendix B: TEM images of our synthesized platinum nano-cubes TEM images using the Koch Institute's JEOL 2100F TEM are shown for 6 nm cubes (**Figure B1**) and 5 nm cubes (**Figure B2**).



Figure B1: TEM images of 6 nm cubes.

Images are of the cubes zoomed out (a) and zoomed in (b).



Figure B2: TEM images of 5 nm cubes.

Images are of the cubes zoomed out (a) and zoomed in (b).

c. Appendix C: Deposition procedure of single atoms as well as dimers/trimers

Although we have not successfully tested single atoms deposited onto a metal sulfide for ammonia oxidation, our research group has been working on single atom deposition by placing the metal sulfide coated electrode into a 0.75 mM K₂PtCl₆ solution for 1 to 6 hours at 50 °C. We have had success with the single atoms for nitrate and nitrite reduction. We will be exploring and expanding on this procedure in the near future. For dimers and trimers, we intend to increase the temperature and the time in solution, using TEM images to inform us of the success of our procedure.