Electro-oxidation of Ammonia by Raney Nickel and Platinum

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Introduction
The use of hydrogen as a source of fuel for fuel cells as well as the emergence of legislation promoting a hydrogen economy has made the production of hydrogen a very important topic in engineering. At this time, hydrogen production costs for distributed power cannot compete with more traditional power generation methods, however, and the storage and transportation of hydrogen are both inefficient and dangerous. The discovery of a feasible hydrogen production process is very important to the future of energy and therefore life on Earth, given that natural gas and oil reserves are quickly diminishing.

Ammonia is one of the most highly-used commodity chemicals in the U.S.; its storage, transportation, and handling procedures are well-known and documented. The use of ammonia as a feedstock for hydrogen production via catalytic cracking has been researched as early as the 1960’s, due to the high hydrogen density of the molecule. However, the catalytic cracking process requires high temperatures, proves to have a low efficiency in practice [1], and requires purification of the product gases. The electro-oxidation of ammonia, conversely, can be carried out at ambient temperature, has an efficiency of 99.7% on platinum [2], and produces pure streams of nitrogen and hydrogen gases at the anode and cathode, respectively. Applying this method to the production of hydrogen is a relatively new development; little research has been performed on the subject.

Simons, et al. report that the reversible thermodynamic potential of the oxidation of ammonia is 0.77 V [3], while the overall reaction of

\[ 2 \text{NH}_3 \rightarrow \text{N}_2 + 3 \text{H}_2 \]  

realizes a thermodynamic potential of -0.058 V. These thermodynamics compare favorably to conventional water electrolysis, which has a reversible thermodynamic potential of -1.23 V. While the reaction mechanism is not completely understood, a recent study by De Vooy, et al. [4] as well as an earlier study by Despic [5] agree on a mechanism which includes adsorbed nitrogen (N_ads). De Vooy, et al. further found that the activity of a catalyst for the reaction is related directly to the nature of the species at the surface: the electrode is active if adsorbed nitrogen hydrides (NH_ads or NH_2_ads) are present, and inactive when nitrogen atoms (N_ads) are adsorbed onto the catalyst surface. The same study further deduced that platinum is the best catalyst for the reaction due to its ability to stabilize NH_ads rather well.

The work of McKee, et al. [6] shows a substantial improvement in the performance of ammonia fuel cells when using a platinum-iridium alloy rather than a platinum-only catalyst. Lopez de Mishima, et al. [7], corroborated these results by studying the electrochemical oxidation of ammonia on each of platinum-only, iridium-only, and platinum-iridium catalysts. It was also found that iridium alone showed little catalytic activity on the reaction, but produced a synergistic effect when paired with platinum for use as a catalyst [7].

Similar to the results reported for iridium by Lopez de Mishima, et al. [7], a catalyst known as activated Raney nickel also shows little to no activity when used to catalyze the ammonia electro-oxidation reaction [5]. However, the combination of Raney nickel and platinum has yet to be studied as an electrocatalyst for the oxidation of ammonia, and it is possible that a synergistic effect exists similar to that found by combining platinum and iridium for use as a catalyst for the reaction. The objective of this paper is to study the electro-oxidation of ammonia on a Raney nickel-platinum electrode.

Methodology
The electro-oxidation of ammonia was studied on a catalyst comprised of an activated Raney nickel substrate along with an outer layer of platinum. The electrochemical measurements were made using a potentiostatic monitoring system from ARBIN. The working electrodes were produced by electrodeposition and were characterized by SEM and BET analysis. Gases generated during the experiments were analyzed using an SRI Gas Chromatograph.

Results
Figure 1 shows the cyclic voltammetry (CV) performance of a 1 M NH₃ / 1 M KOH solution using the Raney nickel / platinum catalyst. The large peak near -0.2 V on the plot confirms activity of the catalyst on the reaction. The curves shown on the plot are actually the final 5 cycles out of 50 performed by the CV test; this shows the staying activity of the catalyst after many cycles, and the fact that the curves are so close together may indicate that deactivation by N_ads on the catalyst is at a minimum. Further analysis and results will be presented.

![Figure 1: Cyclic voltammetry performance of 1 M NH₃ / 5 M KOH at a scan rate of 10 mV/s on a Raney nickel-Pt electrode at 25 °C](image-url)

References