Feasibility of Electrolyzing Ammonia Effluents for the Production of Hydrogen

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Abstract

The overall objective of the project is to study the technical feasibility of electrolyzing ammonia found in municipal waste waters influents and, industrial and agricultural effluents for the removal of ammonia and the production of hydrogen to be used in fuel cells. The electrolysis of ammonia for the production of hydrogen requires less energy than the electrolysis for water for the production of hydrogen. Theoretically, the hydrogen produced from the ammonia would be able to provide enough energy to power the electrolysis system. This system not only removes ammonia from the waste streams, but also creates a non-fossil-fuel based source of hydrogen.

The specific objectives of the project were to study the electrode substrate and catalyst behavior in low ammonia concentration streams, and to find the minimum ammonia operating concentration for the system studied.

The concentration range of ammonia studied is 0.5 mM to 50 mM. A previous study in the Electrochemical Engineering Research Laboratory at Ohio University used high concentrations (1M) of ammonia in alkaline media at low temperatures (25-60°C) to electrolyze ammonia.[1]

Carbon fiber electrodes plated with noble metals were tested in the low concentrations of ammonia with potassium hydroxide to determine the optimum electrode design for the conditions. Raney nickel electrodes plated with noble metals were also tested for preliminary results.

The results of the specific objectives and limitations of the system are reported.

[1] G. G. Botte, F. Vitse, and M. Cooper, *Electro-catalyst for Oxidation of Ammonia in Alkaline Media and Its Application to Hydrogen production, Ammonia Fuel Cells, Ammonia Electrochemical Sensors, and Purification Process for Ammonia-contained Effluents*. October 10, 2003. [Provisional Patent].

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Introduction

Proton exchange membrane (PEM) fuel cells are being promoted by the government and other agencies as part of the energy plan for the future. There are several problems behind the fuel source, hydrogen, that will need to be remedied before fuel cells, no matter how operable they are themselves, are a viable part of the energy plan. Hydrogen is expensive to produce. It is also difficult to transport and store due to its gaseous state and high rate of diffusivity. Currently, hydrogen produced commercially is derived from fossil fuels. These problems with hydrogen promote alternatives to the commercially produced hydrogen.

One such replacement for the commercial hydrogen, is a hydrogen-containing liquid. This liquid could be electrolyzed immediately before use in a PEM fuel cell. The liquid source of hydrogen thought of most commonly is water. Water can be electrolyzed to form elemental oxygen at the anode and elemental hydrogen at the cathode.

Anode: Water Oxidation $H_2O(l) \rightarrow \frac{1}{2}O_2(g) + 2H+(aq) + 2e-$, E°=1.229 V vs. SHE
Cathode: Water Reduction $2H^+(aq) + 2e- \rightarrow H_2(g)$, E°=0.0 V vs. SHE

The hydrogen can be directly fed to the fuel cell, where energy and more water are derived. The overall reaction potential against the standard hydrogen electrode (SHE) is 1.23 V. The positive value means that energy must be input into the system for the reaction to occur. Theoretically, more energy will be put into the electrolysis of water than what will be generated by the fuel cell.

The initial clean water and high energy requirements of water electrolysis allow for economical alternatives to be sought. The focus of the research is one such alternative. Ammonia containing waste streams from agriculture, industry, and municipal waste treatment facilities may be used in an ammonia electrolysis system very similar to the water electrolysis system described above. In the electrolysis of ammonia, elemental nitrogen is formed at the anode and elemental hydrogen is formed at the cathode.

Anode: Ammonia Oxidation $2NH_3(g) + 6OH^-(aq) \rightarrow N_2(g) + 2H_2O(l) + 6e^-$
E°= -0.77V vs. SHE
Cathode: Water Reduction $2H_2O(l) + 2e- \rightarrow H_2(g) + 2OH^-(aq)$
E°=0.82 V vs. SHE

The overall theoretical energy requirement for the reaction is 0.059 V. In an ammonia electrolysis system, less energy is required to form the hydrogen than what will be produced using the fuel cell. The other incentive for the ammonia electrolysis is the dual purpose of the reaction. The ammonia will be reacted out of the streams, replacing the need for other ammonia removal treatments.

In an economical comparison, ammonia also proves to be better based on the thermodynamic models (see Table 1). Hydrogen from ammonia can be produced at a cost of \$0.90/kg, while hydrogen from water can be produced at a cost of \$7.10/kg (1 kg of H_2 is equivalent to 1 gallon of gasoline).

Table 1. Economic Comparison of Ammonia Electrolysis to Water Electrolysis

	Water Electrolysis	**Ammonia Electrolysis**
Energy ($W\text{-}h/g\ H_2$)	33	1.55
Hydrogen Cost ($\$/kg\ H_2$)	7.10	0.90

While ammonia electrolysis appears to be favorable from what has been presented, there are technological hurdles that must be handled first. Ammonia electrolysis requires expensive noble metal catalysts and has sluggish kinetics. The waste water streams studied as a source of ammonia have low ammonia concentrations and also have stream contaminants that may affect the system.

Objectives

The specific objectives of this work are to evaluate the electrode materials to improve kinetic behavior and to find the optimum stream conditions, particularly the minimum ammonia concentration for favorable operation.

Methodology and Results

The first electrode substrate studied was Raney Nickel. The advantages of Raney Nickel are the large surface area produced and the reduction in the amount of noble metal catalyst required. A previous study in the research group proved that Raney Nickel plated with noble metals provided a favorable reactivity for the electrolysis of ammonia in basic solutions when the ammonia was at high concentrations (1M). When tested at low concentrations (0.5M NH_3 to 50 mM NH_3), using cyclic voltammetry (an electrochemical test that cycles the potential while observing the current response and can be an indication of kinetic behavior), a characteristic peak of ammonia reacting to form hydrogen was recorded (See Figure 1). While the peak was encouraging, further testing at high concentrations showed that the electrodes aged with time. A 40% decrease in reactivity was observed in the span of one month. A poisoning effect was also observed where the peak ended before the cycle began moving in the negative direction.

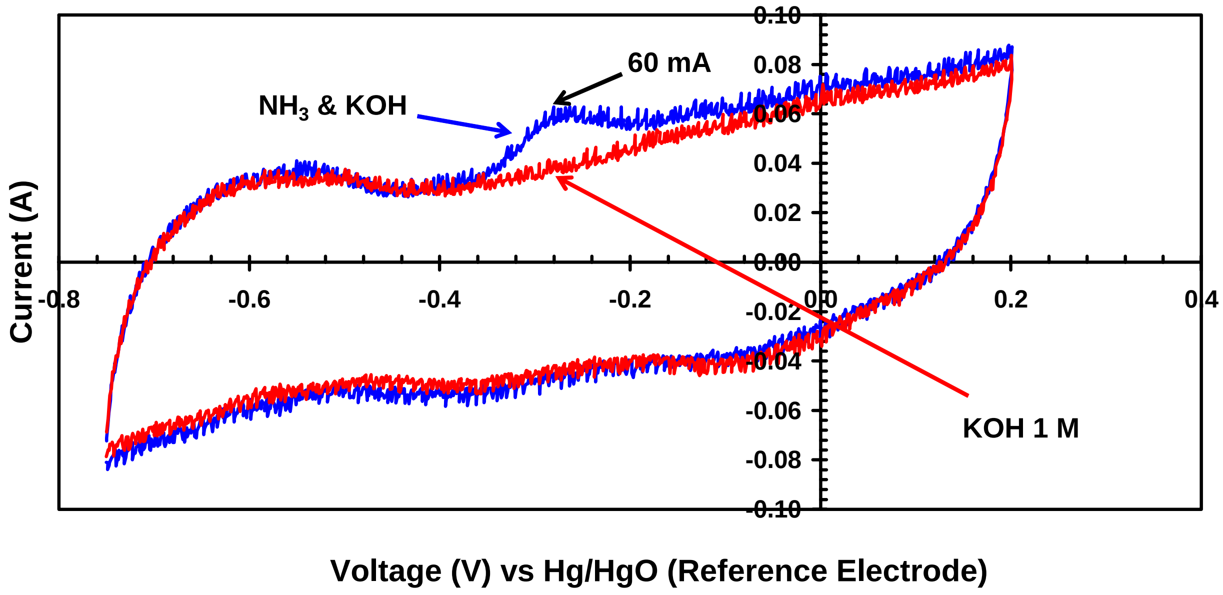

Figure 1. Cyclic Voltammetry for a Raney Nickel-Platinum Electrode in a 2.76 mM NH_3 and 1M KOH Solution.

Carbon fiber electrodes plated with noble metals replaced the Raney Nickel electrodes. The carbon fiber electrodes have greater surface area per geometric area than Raney Nickel electrodes and have not been proven to age significantly. The amount of catalyst used is also very small. The carbon fibers do not poison (the peak termination seen at low concentrations is due to the diffusion limitations caused by the low concentrations). The reactivity of the carbon fiber electrodes are also much greater than the Raney Nickel electrodes in the electrolysis of ammonia. (See Figure 2 for comparison). Once the carbon fiber substrate was selected, noble metal plating loadings and compositions were studied for optimum performance in the low ammonia concentration systems. In an early comparison of electrode catalyst compositions on the carbon fibers, it was found that 100% platinum catalyst had the most reactivity. Results since the early carbon fiber sets have found that noble metal combinations have better results.

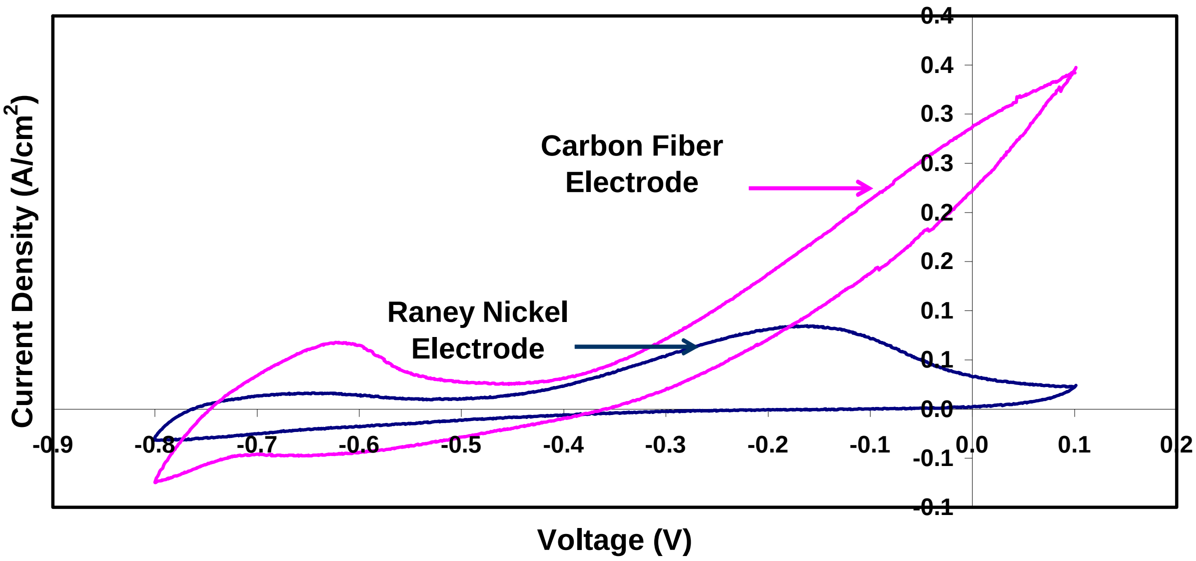

Figure 2. Comparison of carbon fiber electrodes to Raney Nickel electrodes using cyclic voltammetry at 1M NH_3 and 5M KOH. The higher the current, the faster the kinetics.

Once an optimum electrode was found, tests were performed to find the minimum ammonia concentration for favorable operation. It was calculated that an operating potential of 0.6 V would be most economically favorable. The minimum ammonia concentration was found by running galvanostatic stair tests (constant current for twenty minute intervals before the next current increase occurs, observing the potential response) in decreasing amounts of ammonia in solutions of 5M potassium hydroxide. The minimum ammonia concentration was found to be 50 mM. At 50 mM ammonia, 0.6 V was reached when the current was holding steady at 200 mA, while at a concentration of 10 mM ammonia was unable to reach 0.6 V before becoming unstable. The higher the current reached for the same potential, the more optimal the system is operating (see Figure 3).

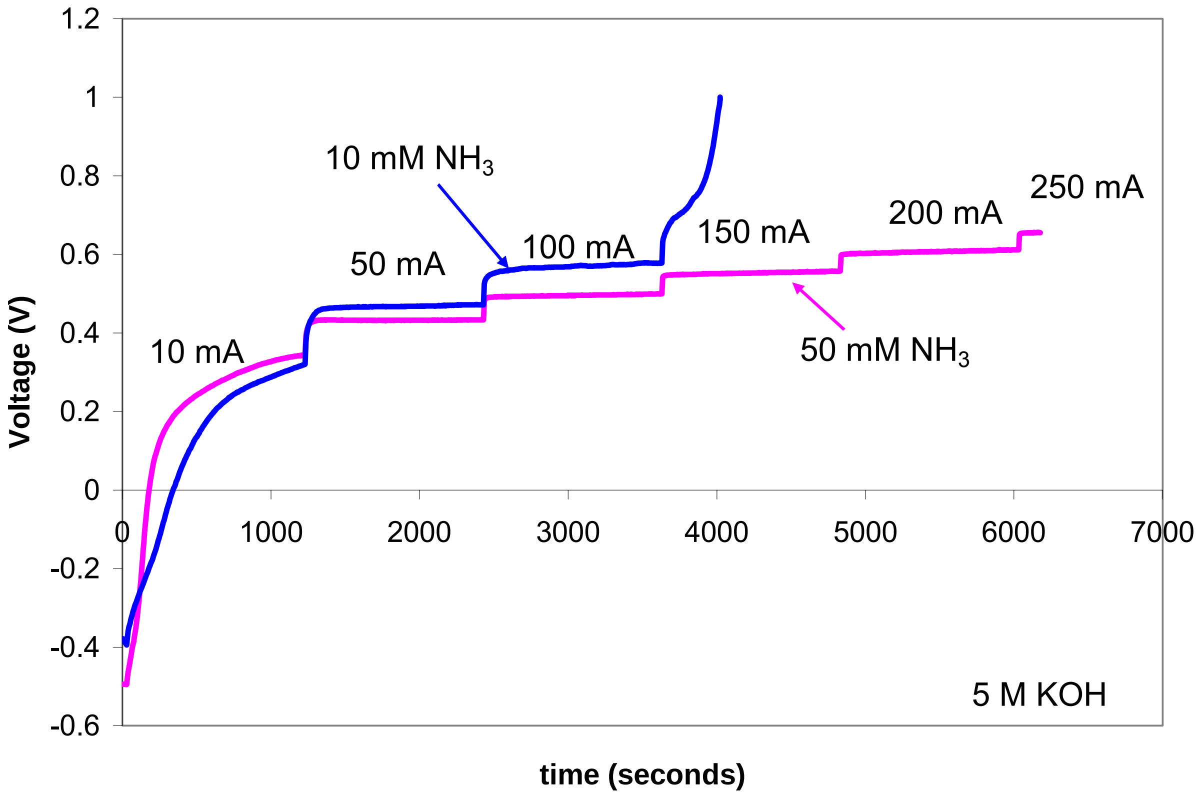

Figure 3. Galvanostatic test for the determination of minimum ammonia concentration to maintain 0.6V.

Comparison to Literature

In 1978, Marincic and Leitz reported on the electrolysis of ammonia for waste removal. The electrodes designed in this study were compared to the 1978 results using cyclic voltammetery. The results showed that the carbon fiber electrodes have much greater reactivity per geometric area than that of the Marincic and Leitz study. The carbon fibers were also closer to the thermodynamic estimate on potential than that of the Marincic and Leitz study (See Figure 4).

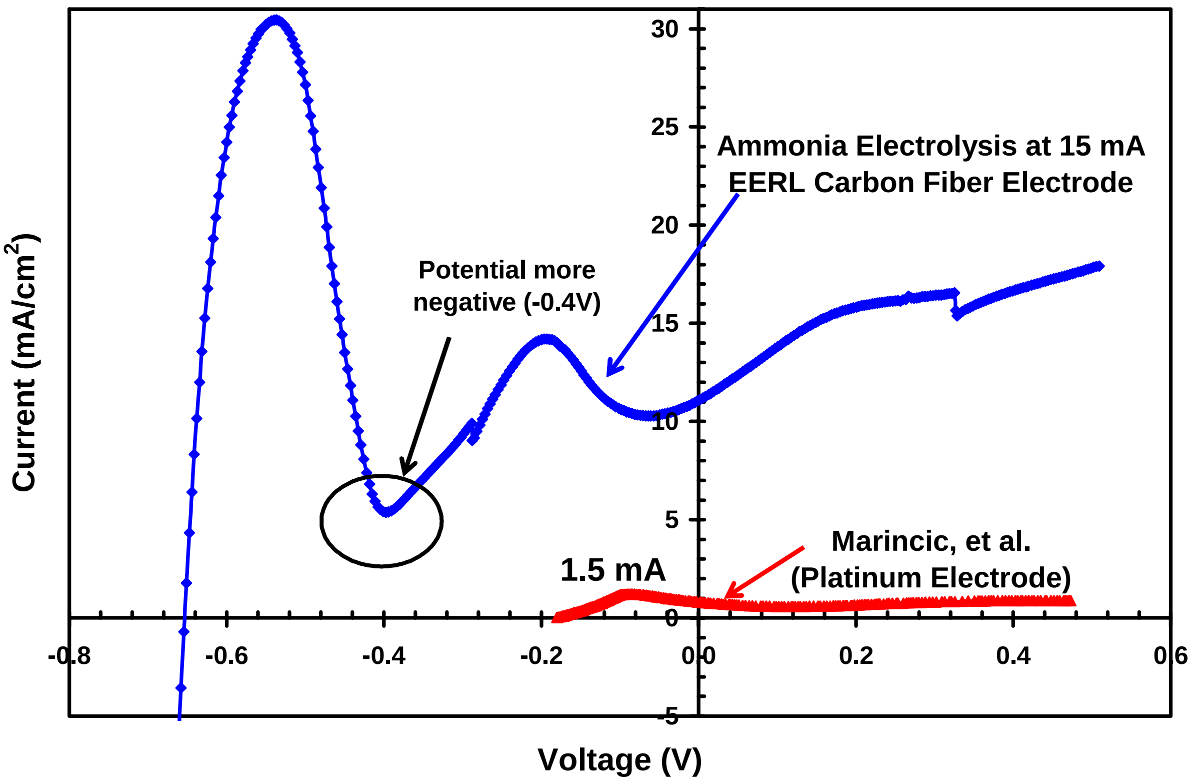

Figure 4. Current technology compared to literature.

Conclusions

Two substrates were studied in the ammonia electrolysis at low concentrations study. The Raney Nickel, while reactive, had problems with poisoning and aging. The carbon fiber electrodes were more reactive, more thermodynamically efficient and did not show any aging. The carbon fiber substrate was selected as the better electrode. A minimum ammonia concentration of 50 mM was found to operate at 0.6 V.

Further research on the topic will continue in the laboratory. Currently, a continuous-injection bench-scale setup for low concentrations is being developed. This continuous process will limit the diffusion problems that are associated with low concentrations. The minimum potassium hydroxide concentration required to operate using 50 mM ammonia at 0.6 V is also being studied. Temperature effects on the system will be tested. Tests for the affects of phosphates and suspended solids on the electrolysis system are also being planned.

Current challenges with the technology are the reproducibility of the electrodes and the current density of the electrodes. If more consistent catalyst reactivity on the electrodes can be established and current density of the electrodes continues to increase, the technology will be more marketable.

Acknowledgments

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