# Design of an Ammonia Electrolyzer for Hydrogen Production

Rosanna Viscardi<sup>#1</sup>, Pecoraro Matteo<sup>\*2</sup> <sup>#</sup>ENEA, Rome, Italy <sup>\*</sup>Bi Strategy, Salerno, Italy

# ABSTRACT

The design and performance of an alkaline ammonia electrolyzer for hydrogen production and its feasibility for fuel cell applications are presented in this work. By comparison of the energy consumption and power for the ammonia electrolytic and water electrolyzers at different hydrogen production rates, the total energy consumption by the water electrolyzer as well as the power required is much higher than for the ammonia electrolytic cell (up to 65% higher). For this reason, the ammonia electrolytic cell has the potential to operate by stealing part of the energy of a PEM hydrogen fuel cell. Furthermore, the lower energy consumption when compared to a water electrolyzer indicates that renewable energy sources can operate the ammonia electrolytic cell to produce hydrogen on demand. In this paper, we suggest an electrochemical study on a Pt-based ammonia oxidation and hydrogen evolution electrocatalysts. These materials are exciting; significantly, Pt-Ir supported on carbon improves the performance of Platinum on Carbon, reference commercial, so that the energy consumed by the ammonia electrolytic cell is lower.

**Keywords** — Ammonia, Ammonia Electrolyzer, H<sub>2</sub> production, Platinum catalyst, Platinum-Iridium catalyst

# I. INTRODUCTION

One of the most critical challenges limiting the commercialization of fuel cells is not the intricate design of the cell or the cost of that design, but rather the source of fuel and its cost [1]. Part of the promise of fuel cells is that they can be powered by hydrogen, which is a non-polluting fuel source. However, hydrogen can be too costly to produce [2]. Ammonia electro-oxidation could solve the problems associated with the production, storage, and transportation of hydrogen (as well as its cost) [3]. Although toxic, liquid ammonia contains 1.7 times more hydrogen than liquid hydrogen for a given volume. Ammonia is also easily condensed at ambient temperature (under 8 bar of pressure), which makes it a right choice for transportation and storage. Furthermore, decomposition of ammonia by electro-oxidation in alkaline media at low over potentials is NO<sub>x</sub> and CO<sub>x</sub> free with nitrogen and water as reaction products. The most massive current problem with the production of hydrogen from the electro-oxidation of ammonia involves the kinetics of the reaction. While the

reaction is thermodynamically favourable, slow kinetics prove to make the process financially infeasible. Though expensive, platinum is commonly used to improve the kinetics of the ammonia electro-oxidation reaction [4]. This work intends to optimize the ammonia electrolysis process. The objective is to find a suitable catalytic material that increases nitrogen and hydrogen production rate, enhance the current efficiency and decrease the oxidation and reduction potentials. The criteria for choosing electrode materials for industrial applications are based mostly on a compromise between electrocatalytic activity, long-term stability and cost [5].

The main goal of the present study is to investigate a Pt-based ammonia oxidation and hydrogen evolution electrocatalysts for exploitation in electrochemical devices. Notably, we want to demonstrate how an ammonia electrolyzer can generate hydrogen for a fuel cell using so little electrical input that the fuel cell can power both its electrolyzer and an end application - thereby generating a "power profit" (Fig.1).

A schematic of how it works is shown below: there is an ammonia electrolyzer linked to a conventional PEM hydrogen fuel cell. The latter generates sufficient electricity to run the electrolyzer and, in this case, a fan.



Fig 1: Ammonia Electrolyser and Fuel Cell for a "power profit"

### II. EXPERIMENTAL CONDITIONS AND METHODOLOGY

A standard methodology for the electrode preparation was followed throughout this work. This procedure is described in detail in this paragraph.

Faraday's law was utilized to quantify the theoretical amount of hydrogen produced from the Ammonia Electrolyzer at a particular current. The equation is described below,  $\mathbf{m} = (\mathbf{s} \cdot \mathbf{M} \cdot \mathbf{I} \cdot \mathbf{t}) / \mathbf{n} \cdot \mathbf{F}$  (Equation 1) where,

m = mass of hydrogen produced (g)

s = stoichiometric factor = 3 mol

- M = molecular weight of hydrogen gas =  $2 \text{ g mol}^{-1}$
- I = applied current (A)
- t = time (h)
- n = equivalent mole = 6 eq
- $F = Faraday's constant = 26.8 A h eq^{-1}$

The values of s and n in the above equation are for the ammonia electrolysis process described below.

At anode: Oxidation of Ammonia

 $\begin{array}{lll} 2NH_3(g)+6OH^{\text{-}}(aq) & \rightarrow & N_2(g)+6H_2O(l)+6e^{\text{-}}\\ E & = -0.77V \text{ vs SHE} \end{array}$ 

At cathode: Reduction of Water

 $6H_2O(l)+6e^- \rightarrow 3H_2(g)+6OH^-(aq)$ E = -0.82V vs SHE

Overall Reaction:

 $2NH_3(l) \longrightarrow N_2(g) + 3H_2(g)$ 

E =-0.059V vs SHE

The power consumption for an electrolyzer or a fuel cell is given by,

 $P = N \times V \times I$  (Equation 2)

Where,

P = Power consumed/produced (W)

N = number of cells in the electrochemical cell

V = voltage(V)

I = current/load (A)

The Faradaic efficiency was calculated using,

 $\eta = (ActualH_2 / TheoreticalH_2) \cdot 100$  (Equation 3) where.

η	=	Faradaic efficiency of the hydrogen gas produced from the Ammonia Electrolyzer	
ActualH <sub>2</sub>	=	amount of hydrogen gas experimentally collected / measured from the Ammonia Electrolyzer	
TheoreticalH <sub>2</sub> =		amount of hydrogen gas predicted by faraday's law at the operating conditions for the Ammonia Electrolyzer	

To accomplish the research objectives, a specific methodology was followed for all the experiments. The detailed methodology for the preparation of the electrode used for this research project is described in the next paragraph. A Scribner 850C test station equipment (Fig. 2) was used during all the electrochemical testing. All the experiments involved galvanostatic testing for which the current-voltage data was recorded by a computer using the MITS Pro (Multiple Integrated Testing Software) software provided with the Arbin instrument.



Fig 2: Experimental set-up for cell testing

The testing solutions were prepared with chemicals from Sigma-Aldrich. The plates and all the fittings required to construct the AEC (Ammonia Electrolyzer Cell) were purchased from Scrbner. For the testing of the electrodes, 1 M  $NH_4OH + 5$  M KOH solutions were used because these concentrations were considered optimum by previous researches [3].

Throughout the project, the performance criterion for the electrochemical testing was the current response at a voltage of 600 mV versus RHE to avoid high anodic overpotentials. Thus, the current in the design cell was limited to the value mentioned above.

# **III. ELECTRODE PREPARATION**

Based on the literature, the Pt-Ir electrodes have proven to be a suitable catalyst for this reaction [6]. The working electrodes used for the ammonia electrolysis in this experiment were the carbon Vulcan XC-72R based Pt-Ir and Platinum annealed catalysts. 20%Pt-6.7%Ir/Vulcan catalyst was prepared by the polyol method [7]. Pt/C-650°C catalyst was synthesized by annealing at 650°C in the air of 20% Platinum on Vulcan XC-72R purchased by Cabot Corporation (USA).

Following were the testing conditions used for building the electrodes for this study:

Anode electrode  $(5 \text{ cm}^2)$ :

Preparation	: electrodes not sintered	
PTFE	: 10%	
Support	: Ni foam 0.8 mm	
Catalyst loading	$: 2.6 \text{mg/cm}^2$	
The solution at the a	anode side: NH <sub>3</sub> 1M in KOH 5M	
Cathode electrode (5ci	m <sup>2</sup> ):	
Preparation	: electrodes not sintered	

Catalyst : 20 wt. % Pt/C (Fuel Cell Scientific) + 10% PTFE Support : E-Tek LT2500W carbon cloth (0.4mm) Platinum loading: 0.2mg/cm<sup>2</sup> The solution at the cathode side: KOH 5M (static)

The mechanically pressing anode fabricated the MEA (Membrane-Electrode Assembly), cathode and anionexchange membrane A-006 (OH-type) obtained from Tokuyama Corporation (Fig. 3 and 4). A dense anode ink was prepared by mixing the powdered catalyst with a 10 wt.% aqueous dispersion of PTFE. The resulting paste was spread onto Ni-foam support. The cathode was carbon cloth with a commercial Pt/C (20 wt.% metal) catalyst (E-TEK) dispersed in the PTFE binder. The catalyst loading at the anode and cathode was 2.6 and 0.2 mg cm<sup>-2</sup>, respectively [8].



Fig 3: Anode and Cathode Electrodes



**Fig 4: Preparation of Electrodes** 

#### **IV. RESULTS AND DISCUSSION**

Fig. 5 shows the performances in the cell of the electrodes at  $1M NH_3 + 5M KOH$  and  $25^{\circ}C$ . 20% Pt-6.7% Ir/Vulcan electrode showed the best behaviour by giving the highest current response of the system

(40mA/cm<sup>2</sup>), and the lowest potential in each of the steps of currents tested. This electrode reported a difference potential of 100mV approximately respects to  $Pt/C-650^{\circ}C$  electrode. This indicated the best catalyst for the ammonia electro-oxidation reaction, due to lower energy consumption and the high current.

This trend confirmed the results of amperometric tests in half-cell (Fig. 6), and it was demonstrated the efficiency of our advanced testing method for chronoamperometry.



Fig 5: Galvanostatic performance of Pt/C-650°C and 20%Pt-6.7%Ir/Vulcan electrodes at 1M NH<sub>3</sub> + 5M KOH at 25°C





Using Eq. 3, it is found that hydrogen is produced from 20%Pt-6.7%Ir/Vulcan catalyst using 2.3 mW/cm<sup>2</sup> of power. Faraday's law can also be used to predict the amount of Gas liberated from a system given a constant applied current. Considering that the electro-oxidation of ammonia has an efficiency of 100%, using Eq. 3 along with faraday's law, it is found that the application of 2.3 mW/cm<sup>2</sup> of power to this electrode liberates a flow of 1.51 X  $10^{-3}$  L H<sub>2</sub>/h per cm<sup>2</sup> of catalyst or equivalently 24.5 Wh/g H<sub>2</sub>. The tests in the cell for the best electrode were also carried out at  $60^{\circ}$ C (Fig. 7).



From Fig. 7, it can be undoubtedly observed that the electrochemical performance for the 20%Pt-6.7%Ir/Vulcan electrode is better at 60°C (0.320 V) as compared to at 25°C (0.460 V) (Fig.6).

The Faradaic Gas Efficiency for ammonia electrooxidation was calculated (Table 1) at different temperatures.

Table 1. Faradaic Gas Efficiency (%) for the<br/>ammonia electrolyzer.

Temperature	H <sub>2</sub> Gas p	Gas		
°C	Faraday's Law	Experimental	Efficiency %	
25	9.3 x 10 <sup>-4</sup>	9.1 x 10 <sup>-4</sup>	96.8	
60	9.3 x 10 <sup>-4</sup>	9.1 x 10 <sup>-4</sup>	96.8	

According to faraday's law, the Gas produced is independent of the operating temperature. This was proved as represented in Table 1. The Gas produced at both 25°C and 60°C was the same (9.1 x  $10^{-4}$  g/hr). An efficiency of 96.8% was achieved on the Ammonia Electrolytic Cell. The power consumption (W) and the energy consumption (Wh) per gram of hydrogen produced are shown in Table 2 at the operating temperatures of 25°C and 60°C.

Table 2.Power and Energy consumption comparison at 25°C and 55°C for the ammonia electrolyzer.

T	Power and Energy consumption for Ammonia Cell		
Temperature	Power (mW/cm <sup>2</sup> )	Energy (Wh g <sup>-1</sup> H <sub>2</sub> )	
25	2.3	24.5	
60	1.6	17	

It was observed that the energy required per gram of hydrogen at  $60^{\circ}$ C is approximately 31% less than that at

 $25^{\circ}$ C. The reasons for better performance at higher temperatures could be attributed to increased reaction rate due to better ionic conduction at  $60^{\circ}$ C, and improved catalytic activity. Secondly, the ease of gas evolution at higher temperature is better because, at the higher temperature, the density of the hydrogen gas decreases.

#### **V. CONCLUSIONS**

An ammonia alkaline electrolyzer for the production of hydrogen is presented. The electrochemical study about two catalysts is proposed for the feasibility of this process for low-cost, low-temperature, high-purity hydrogen production. The efficiency of ammonia electrolyzer was improved by using 20%Pt-6.7%Ir/Vulcan catalyst. This electrode reported a difference potential of 100mV approximately respects to Pt/C-650°C electrode. This indicated the best catalyst for the ammonia electro-oxidation reaction, due to lower energy consumption and the high current. Remarkably, at higher temperatures, the energy required per gram of hydrogen was approximately 31% less than that at 25°C on this catalyst.

#### REFERENCES

- D. Akinyele, E. Olabode and A. Amole, Review of Fuel Cell Technologies and Applications for Sustainable Microgrid Systems, Inventions, 5(3) (2020) 1-35.
- [2] R. Viscardi, V. Barbarossa, R. Maggi and F. Pancrazzi, Development of Sulfonic Supported Acids and Their Application in Power to Gas Systems, International Journal of Mechanical Engineering and Robotics Research, 9(9) (2020) 1271-1274.
- [3] F. Vitse, M. Cooper and G. G. Botte, On the Use of Ammonia Electrolysis for Hydrogen Production, Journal of Power Sources, 142 (1-2) (2005) 18-26.
- [4] J. Huang, J. Cai and J. Wang, Nanostructured Wire-in-Plate Electrocatalyst for High-Durability Production of Hydrogen and Nitrogen from Alkaline Ammonia Solution, ACS Appl. Energy Mater, 3(5) (2020) 4108–4113.
- [5] N. Hanada, Y. Kohase, K. Hori, H. Sugime and S. Noda, Electrolysis of ammonia in aqueous solution by platinum nanoparticles supported on carbon nanotube film electrode, Electrochimica Acta, (341) (2020) 136027.
- [6] S. Morita, E. Kudo, R. Shirasaka, M. Yonekawa, K. Negai, H. Ota, M. N-Gamo and H. Shiroishi, Electrochemical oxidation of ammonia by multi-wall-carbon-nanotube-supported Pt shell–Ir core nanoparticles synthesized by an improved Cu short circuit deposition method, Journal of Electroanalytical Chemistry. (762) (2016) 29-36.
- [7] F. Fievet, S. Ammar-Merah, R. Brayner, F. Chau, M. Giraud, F. Mammeri, J, Peron, J.-Y. Piquemal, L. Sicard and G. Viau, The polyol process: a unique method for easy access to metal nanoparticles with tailored sizes, shapes and compositions, Chemical Society Reviews, (47) (2018) 5187-5233.
- [8] E. Antolini, Glycerol Electro-Oxidation in Alkaline Media and Alkaline Direct Glycerol Fuel Cells, Catalysts, 9(12) (2019) 980.
- [9] K. Sruthi Udayakumar, A.Rengaraj, V. Manojkumar, Electrochemical Production Of Hydrogen From Rice Mill Wastewater, SSRG International Journal of Chemical Engineering Research. 4(1) (2017) 1-5.