Quantified platinum nanoparticles decorating carbon nanotubes for a hydrogen evolution reaction

by

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Abstract

Scientists are constantly searching for a viable replacement for fossil fuels. A commonly discussed option is hydrogen. However, hydrogen availability and production cost continue to be a problem for those promoting it as an alternative. This study proposed that the amount of the expensive catalyst platinum (Pt) needed as a water-splitting catalyst may be drastically reduced by using it to decorate carbon nanotubes (CNTs) on a nanoscale, which would then be used to for the electrochemical deposition of water. In this way, hydrogen could be efficiently and cheaply produced while simultaneously stretching the efficacy of Pt, increasing the availability of hydrogen and promoting its use. *Unfortunately, due to COVID-19, this research could not be completed, and no results were produced to answer the research question. *

Keywords: nanotube, catalyst platinum, water-splitting

Introduction

With the rise in global warming and increasing environmental concerns about the use of fossil fuels, scientists are turning to environmentally friendly "green" energy alternatives. Several prominent options include solar and wind energy, and hydrogen fuel. Hydrogen, the lightest element on the periodic table, has a high-energy content and emits no harmful greenhouse gases when used (Zhang et al., 2016). It is useful as a sustainable fuel not only because it is a plentiful element in the environment, but also because it is relatively inexpensive to produce. However, despite hydrogen's abundance, it is not an easy fuel to obtain and store because no source of unbound hydrogen molecules exists in nature (Li & Zheng, 2017). Instead, existing substances that include hydrogen must be separated to free their hydrogen components; usually this substance is water. Water is comprised of two hydrogen and a single oxygen molecule, as shown by its chemical formula H_2O. As a non-toxic and easily obtainable substance, water is an ideal source for hydrogen production. The process for separating water into its atomic components is known as water-splitting. A recent, popular development related to water-splitting hydrogen production is the use of photocells and photocatalysts thus, sunlight driven operations. This illustrates the potential for green fuels not only as a replacement for fossil fuels in the energy sector, but also fossil fuel free energy production. The splitting of water can be accomplished multiple ways, including dividing the gases in steam or using electrolysis—the application of an electrical current—which is the method used in this study. Water-splitting through electrolysis needs several parts. First, it requires a source of electricity and a pathway for electricity to reach the water. Second, some type of cell must act as a center for the reaction. Finally, a catalyst is needed to initiate the reaction (Vineesh et al., 2016; Yamada & Domen,

2018). Sources of electricity and ways to deliver it can be found using any electrical device; however, centers and catalysts are not so common.

For this study, carbon nanotubes (CNT), a model of which is depicted in Figure 1 (Boyes, n.d.), will be used as a center for the reaction. CNTs are microscopic, hollowed cylinders made of atom-thick carbon walls (Akbari & Buntat, 2017). They are available in simple form, called single wall carbon nanotubes (SWCNT), or in complex, multilayered form known as multiwall carbon nanotubes (MWCNT), modeled in Figure 2 below (Nanoelectronics Laboratory of..., 2019), which involve different sizes of tubes "nesting" together.

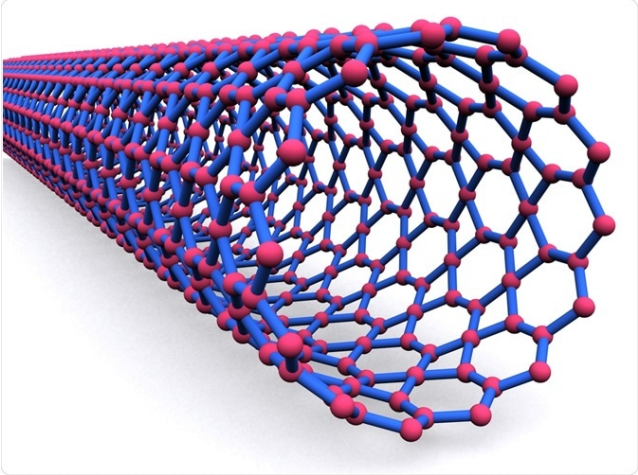

Figure 1: A single nanotube isolated on white (Boyles, n.d.)

CNTs are excellent candidates for water-splitting reactions for several reasons: Not only carbon, the cylinders' base unit, is an inherently stable atom, CNTs also boast large surface areas and can conduct electricity (Uzundurukan & Devrim, 2019). In a study that described them as "bamboo-like," CNTs were found to aid precise control of the experiment because of their uniform, predictable structure. The researchers used nitrogen-decorated CNTs to break down formic acid, finding that CNTs functioned best as catalyst bases and performed excellent reduction reactions (Podyacheva

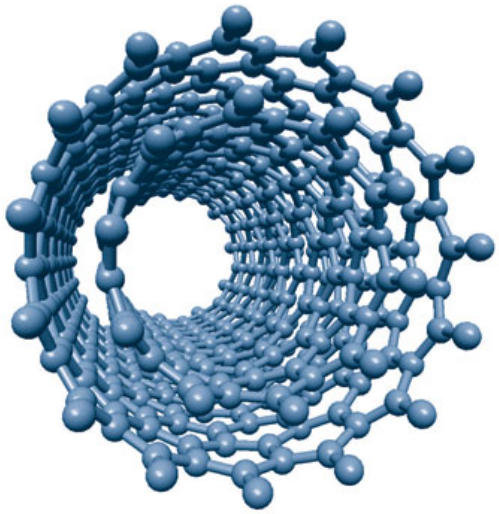

Figure 2: Representation of a multi-walled carbon nanotube (Nanoelectronics Laboratory of..., 2019)

et al., 2019). Another study that surveyed and summarized the use of CNTs in fuel production illustrated their capabilities as catalytic enhancers and stabilizers (Akbari & Buntat, 2017). CNTs slowed the corrosion of fuel cells, preventing surface oxidation and remaining intact while other materials broke down. They also served as electrodes, centers for electrical and/or chemical reactions. Due to their high surface area, which provided much more room for reactions to occur, and lightweight composition, which allowed for a higher volume ratio, electron transmission was increased, especially when combined with platinum (Akbari & Buntat, 2017).

Research Question

Can the amount of the catalyst platinum used in water-splitting be reduced without compromising the efficiency of hydrogen production by using it to decorate CNTs on a nanoscale?

Theoretical Framework – Bond Enthalpy

The relevant theory is called Bond Enthalpy. This refers to both the theory itself and the energy exchange it describes. Heike Kamerlingh Onnes formulated it in the very early 1900s, eventually publishing it in 1909. The formal definition of bond enthalpy is given in terms of the mathematical equation:

$$H=U+pV$$

H=enthalpy, U=internal energy, p=pressure, V=volume

From this equation, several foundational concepts about energy and the efficiency of its production can be drawn. Since enthalpy cannot be directly measured, a system's *change* of enthalpy is measured instead. This refers to either the energy released or consumed by a chemical reaction and can also be expressed as the change in energy caused by a reaction. Bond Enthalpy describes energy transfer in forming chemical bonds between atoms. It is always positive. In other words, forming a bond will always release energy. It is also a measure of thermodynamic potential. Changes in temperature and pressure (if the system is not closed) directly affect enthalpy. In order to answer this project's research question, the question of experiment efficiency must also be answered. Bond Enthalpy helps explain this question because it provides a measure for the efficiency of hydrogen production. Catalysts, like a CNT-Pt electrode, reduce the input energy needed to break an atomic bond (negative enthalpy), but the positive enthalpy (output energy from creating an atomic bond) remains the same. So, reaction efficiency (input energy divided by output energy) could be calculated using the Bond Enthalpy equation.

Literature Review

As public attention increasingly shifts to the issue of global warming, the scientific community's attention has followed. In order to contextualize this project's research in its larger field and give the reader a thorough understanding of its parameters, a review of relevant, recent literature follows. Recently, this shift has surfaced in the form of green energy research, in the hopes of inventing sustainable alternatives to fossil fuels and designing alternative fuel cells. Researchers have barely begun to scratch the surface of possibilities in green energy production. For example, a Japanese study proposing a sunlight powered hydrogen-production facility highlighted the efficiency and potential of this alternate source of power. Fascinatingly, the

entire proposed system was nearly self-sustaining. Excluding routine maintenance, the hydrogen factory drew all energy and other necessary inputs from its surroundings (Yamada & Domen, 2018). This study, which is fully described later, illustrates the exciting and important ideas currently circulating in the field of clean energy production, specifically regarding hydrogen. Two main developments in these areas are the use of CNTs to enhance catalytic properties of platinum in hydrogen-producing reactions and the fine-tuning of variables such as temperature to enhance the performance of hydrogen fuel cells.

CNTs

CNTs have enormous potential in the field of energy production. This is demonstrated by the multitude of literature overviews and research projects devoted to the topic in recent years. A study titled *Carbon Nanotube-Enzyme Biohybrids in a Green Hydrogen Economy* reviewed literature on using CNTs as catalysts for producing hydrogen, specifically when combined with enzymes. The great majority of the paper's sources used were less than ten years old and originated from a scientific journal. The study mainly articulated the high potential for CNTs to be used in the energy due to their inherent chemical characteristics. As a further incentive to incorporate such materials, the authors found that they are extremely cost-effective alternatives to precious metals previously used, such as platinum. The potential for use of CNTs in all stages of hydrogen consumption, from production to storage to conversion, was also highlighted. Special emphasis was placed on their use in hydroxide fuel cells (De Poulpiquet et al., 2019).

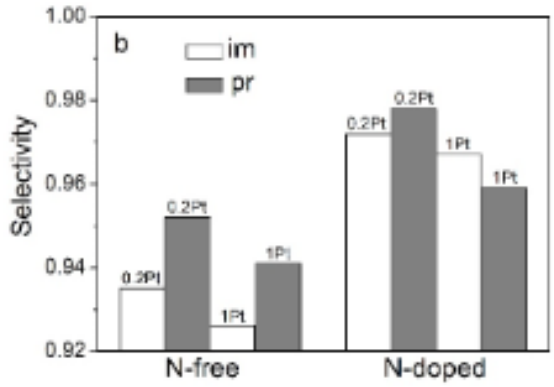

Figure 3: Selectivity of CNT catalyst versus N-CNT catalyst (Podyacheva et al., 2019)

A study by Podyacheva et al. (2019) explored the use of nitrogen-doped CNTs in conjunction with platinum as a hydrogen-production catalyst in the breakdown of formic acid, focusing mainly on reducing the temperature threshold for an energy-producing reaction. The samples were synthesized from the decomposition of two materials, ethylene or ethylene-ammonia, in a flow reactor. Platinum was deposited on the CNT and N-CNT surface using incipient wetness impregnation and homogenous precipitation. Twenty milligrams of each sample were then used in separate formic acid decomposition experiments performed in a 6mm-inner-diameter quartz reactor. Figure 3 shown also provides a graphical representation of the samples' selectivity, with "im" bars representing impregnated samples and "pr" bars representing homogenously precipitated samples (Podyacheva *et al.*, 2019). The turnover frequency was measured and then compared to the performance of 1%Pt/N-CNF (carbon nanofibers). Each sample (1%Pt/CNTs-pr and 1%Pt/N-CNTs-pr) was used in a formic acid decomposition trial. The 1%Pt/N-CNTs performed best in the trials, with the reaction almost completed before the reactor reached 200 degrees Celsius. The conclusion stated that the N-CNTs surpassed their nitrogen-free counterparts by a factor of three to four. Akbari & Buntat (2016) wrote in *Benefits of using carbon nanotubes in fuel cells: a review* about the use of CNTs in fuel cells. Their purpose was to determine different applications for CNTs and discover if they improved cell performance. The paper contains five topics related to CNTs and fuel cells. Topics were the effect of CNTs on fuel cells, decreasing the use of platinum with CNTs, contact between catalyst and CNT support, utilizing CNTs to enhance catalyst function, and CNTs catalyst synthetic

conditions. The authors systematically summarized current research in each category and drew applicable conclusions. Practical take-aways of this case study include findings that the addition of graphene to catalysts supplemented CNT effectiveness and mixing in alloyed CNTs improved the electrocatalytic behavior of platinum (Akbari & Buntat, 2016).

Another research project, completed in 2009, fabricated an electrode detector of hydrogen-peroxide, specifically as a biosensor and medical diagnostic tool. Researchers decorated CNTs with platinum and deposited them onto a waxed-graphite surface, as shown in Figure 4 (Shi *et al*., 2009), to produce an electrode. This was accomplished by dispersing CNTs in distilled water, adding a chemical containing platinum, and drying the mixture at 500 degrees Celsius. To form an electrode, graphite was polished and sonicated, then dipped into the CNT-Pt powder. Hydrogen peroxide, the substance of interest, was diluted 30% with distilled water for electrode testing. The primary testing occurred in four hours; 80 cycles were completed in that time frame. Continuous testing over the next two months confirmed electrode stability. On average, the CNT-Pt electrodes responded to the presence of hydrogen peroxide in five seconds, and final detection performance deteriorated to 97% of initial efficiency. Researchers concluded that CNT-Pt waxed graphite electrodes performed as excellent catalysts and retained hydrogen peroxide detection abilities well (Shi, Q., Zeng, W., & Zhu, Y, 2009). In another research project by Yeon et al. (2019), long-lasting, highly durable, corrosion-resistant carbon nano-onions (CNOs), which can be substituted for

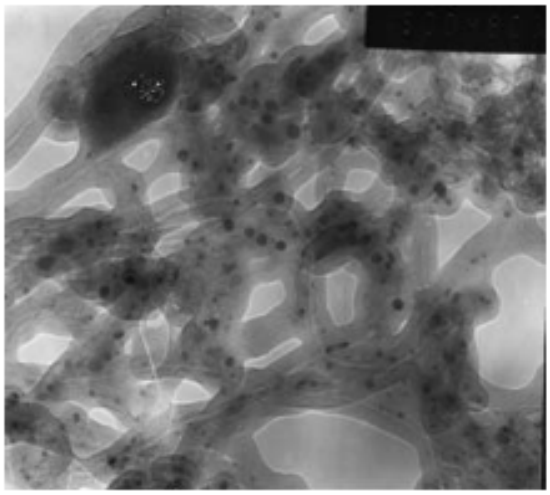

Figure 4: Transmission electphotos of CNT-Pt x150 000 (Shi et al., 2009)

other carbon-based underlying catalytic material, were produced using laser pyrolysis. An infrared CO_2 laser was used to form CNOs from ethylene. Using beam distance, gas flowrate and other variables, researchers were able to control CNO size, shape, and crystallinity. Finally, the substance was heated on a hotplate, stirred, and baked in a furnace at 290 degrees Celsius for five hours. Through thermogravimetric analysis, researchers determined that 40% of the liquid's mass was Pt/CNOs. Using a spray-gun, the liquid was applied to a membrane electrode. The membrane electrode served as an anode while the control sample, platinum, and carbon black, served as the cathode. During trials, researchers varied humidity levels, performed cyclic voltammetry, and measured cell impedance and stress resistance. Humidity was varied 100%. Cyclic voltammetry voltage ranged from 0.1-1.2V. Cell stress-tests were performed by simulating power-on and off procedures. Researchers concluded that not only do CNOs display impressive corrosion and damage resistance that lengthens fuel cell life, their production process is also highly manipulable, allowing producers to mold output CNO characteristics. In 2019, Uzundurukan & Devrim investigated the performance of a Pt/MWCNT catalyst as opposed to a Pt/C catalyst (amorphous carbon only). Using two catalyst types, Pt/MWCNT and Pt/C, they produced hydrogen from sodium borohydride. Platinum was deposited on the different carbon types via microwave-polyol synthesis. The Pt/MWCNT catalyst was found to be 30% Pt by weight, while the Pt/C catalyst was 20% Pt. The catalysts were studied and their surface structures mapped using transmission electron microscopy, high-resolution transmission electron microscopy and x-ray diffraction. A thermal analyzer was also used, in the temperature range of 100-900 degrees Celsius, to detect Pt loading. For testing, each catalyst was placed in a heart-shaped flask in a water bath for even heating. A meter connected to the flask neck was used to collect and measure hydrogen production. For the experiment, researchers varied the amount of

Pt on the catalyst, the concentration of sodium borohydride and the outside temperature. Each test, with its set of variables, was performed at least three times to verify experimental reproducibility. Researchers concluded that an increase in temperature and electrolyte concentration increased hydrogen generation for both types of catalyst. However, the Pt/MWCNT catalyst's performance was marginally superior to the Pt/C catalyst, which was attributed to its low activation energy requirement. The purpose of this research is to create a highly efficient nonmetal hydrogen evolution catalyst by doping graphene microtubes (GMT) with nitrogen. Researchers combined glycin and dicyandiamide, heating the mixture to 1,100 degrees Celsius and applying a gaseous nitrogen stream. Tubes with a one to two micrometer diameter were formed. The tubes were analyzed using high-resolution transmission electron microscopy, x-ray diffraction spectra and x-ray photoelectron spectroscopy. A hydrogen evolution reaction was then performed using a 6M potassium hydroxide solution on a rotating disc electrode. The N-GMTs completed over one thousand voltammetric cycles with negligible performance deterioration. Researchers found that the larger diameter of GMT allowed the tubes' outer and inner surfaces to act as catalytic sites. Furthermore, they stated that N-GMTs exhibited impressive durability, and maintained electrochemical stability and current density better than other carbon products. Another research project by Zhang et al. (2016), examined novel MWCNT configurations and test their effect on catalytic capability in proton exchange membrane fuel cells (PEMFC). MWCNTs grown using chemical vapor deposition were exfoliated in a furnace at 200 degrees Celsius. The tubes were then mixed with ethylene glycol, water and hexa-chloroplatinic acid, and stirred for twenty-four hours. After this, the mixture was refluxed, washed with distilled water, and dried. Researchers deposited the resulting powder, dissolved in ethanol and Nafion on a glassy carbon electrode. The traditional three-electrode

setup was used to electrochemically characterize the Pt-MWCNT catalyst in oxygen and nitrogen infused sulfuric acid, before transitioning the catalyst to a membrane electrode fuel cell. A graphite plate was placed on either side of the membrane electrode with minimal space between them to form the fuel cell, which was supplied with hydrogen and oxygen in gaseous form at ninety percent humidity. Results showed that the Pt-MWCNTs exceeded Pt-C performance, which researchers attributed to the "unraveled graphene layers" that more effectively exposed tube surface area to the gasses and provided a larger catalytic space (Sahoo, Scott & Ramaprabhu, 2018). Another article analyzed the catalytic performance of Pt-CNTs alongside cesium dihydrogen phosphate as an electrolyte, as compared to Pt-C catalysts with the same electrolyte. Researchers formulated the cesium dihydrogen phosphate in-lab. A unique deposition technique was followed decorate the nanotubes with platinum, before being dried into powder. The MWCNTs were then electro-sprayed onto the carbon paper electrodes by dispersing them in water together with cesium dihydrogen phosphate; two batches of this mixture were prepared and a small amount of a commercial dispersant solution, two separate varieties, were added to each. Electrodes were then sandwiched between stainless steel, which were screwed together. Gaseous hydrogen was bubbled through water to humidify it before sending it to the electrode catalyst. Three sets of each catalyst were prepared and tested, differentiated by platinum content and dispersant solution. The types were plain Pt-CNTs (30% Pt by weight) as a control group, the same with a cesium dihydrogen phosphate added, then 40% Pt and 46% Pt, also with cesium dihydrogen phosphate. Researchers concluded that even with minimal Platinum content, the Pt-CNTs successfully reduced protons and oxidized hydrogen in solid fuel cells. They also noted that the electro-spray technique could be easily modified based on research demand (Thoi, Usiskin & Haile 2015). Rather (2019) wrote in *Preparation, characterization and*

hydrogen storage studies of carbon nanotubes and their composites: A review about projects involving CNTs, specifically relating to hydrogen storage. Rather divided the topic into three sections: preparation of nanocomposites, characterization, and hydrogen storage. In the first section, CNTs, metal compounds and a combination of the two are discussed. The CNT formation method chemical vapor deposition (CVD), which enables manufacturers to control tube diameter and scale, was described; this was followed by an explanation of CNT metallic composites. Metals are ball-milled, a process that reduces their size to the nanometer scale, then incorporated into CNT structure through various methods like ultrasonication and sputtering deposition.

Sample Name	Hydrogen Storage (wt.%)	Temperature (K)	Pressure (MPa)	Reference
SWCNT (lo purity)	5–10	273	–	[97]
GNFs (Herring bone)	67.55	RT	11.35	[99]
GNF (platelet)	53.68	RT	11.35	[99]
GNFs (tubular)	11.26	RT	11.35	[99]
CNF	~10.0	RT	10.10	[30]
SWCNT (hi purity)	8.2 5	80	7.18	[98]
SWCNTs (50% purity)	4.25	RT	10.1	[104]
MWCNTs	~5.0	RT	~10	[32]
SWCNTs	~0.1	300	0.1	[7]
CNT bundles	~1.0	RT	12	[105]
CNT	3.7	300	14	[106]
CNT & CNF	10	RT	–	[44]
CNT	0.5	RT	10	[33]
CNT	<0.2	RT	11.5	[107]
AC	5.7	77	3.0	[32]
MWCNTs	3.5	143	75	[108]
Air-oxidized MWCNTs	0.9	293.1	12.05	[30,104]
CO_2-oxidized MWCNTs	1.0	293.1	12.02	[30,104]
Acti-MWCNTs	0.78	298	100	[109]
MWCNTs-99%	2.00	77	0.1	[103]
CNTs	0.27	298	–	[110]
Pristine MWCNTs	0.15	553	–	[111]
SWCNTs	1.73	77	10	[112]

CNT -Carbon nanotube, GNF - Graphite nanofibre, AC - activated carbon, CNF - Carbon nanofibre, SWNTs - Single walled carbon nanotube, MWNTs - Multiwalled carbon nanotube, Acti – Activated.

Figure 5: Summary of experimental results of hydrogen uptake measurement in CNTs performed at different temperatures and pressure (Rather, 2019)

Secondly, the characterization portion explained analytical procedures for CNT samples. Frequently, researchers use X-ray diffraction (XRD), thermogravimetric analysis (TGA), energy

dispersive X-ray spectroscopy (EDS) and the Brunauer-Emmett-Teller (BET) surface area method, among others. Lastly, the author examines methods of hydrogen storage using CNTs, using a chemisorptive formation of reversible carbon-hydrogen bonding. As shown in Figure 5 (Rather, 2019), carbon-based materials in various forms could store as much as 67% of their weight in hydrogen. Researchers concluded that metal oxides and platinum increase CNT storage capacity, as did activation via potassium hydroxide.

Platinum Catalyst

Platinum is a common catalyst, especially in hydrogen production reactions. High cost is an obvious limitation of its use, but rather than eliminate it researchers are exploring methods to reduce the amount of platinum needed for effective catalyzation. The following reviews explore this and various other problems relating to platinum use. Korchagin et al. (2017) looked at the possibility of reducing the amount of platinum by 30% by adding CNTs and using a rotating disk electrode in a fuel cell. Researchers used two catalyst types, 60 Pt 9100 and 40 Pt/CNT, for the fuel cell tests. To synthesize the 40 Pt/CNT, CNTs were combined with a chloroplatinate in glycerol. The catalyst solids were then separated using a centrifuge and dried using a desiccator. The resulting powder was dispersed on rotating disk electrodes for use in the hydrogen-air fuel cell. One hundred and thirty-five millivolts were applied to the cell and the resulting current was measured in several forms: Researchers looked at the current divided by surface area as a whole and for area of platinum, then at current per milligram of catalyst and per milligram of platinum. Two sets of the 40 Pt/CNT catalyst were used and one set of the 60 Pt 9100 catalyst. Six tests were done using the three sets, first with H_2SO_4 as the electrolyte and KOH second. Results showed that the current for both CNT samples was equal, and in some cases greater, than the current of the purely platinum sample. Researchers concluded that the 40 Pt/CNT catalyst

showed “high activity,” performing well alongside the platinum. However, they also stated that the model equation used to measure results behaved questionably. Similar to the previous study, the purpose of the following study was to reduce the use of platinum as a catalyst for electrolysis. Microbial electrolysis cells sourced from renewable biomass to produce hydrogen were also studied. A cathodic catalyst was formed using polyaniline with CNTs. In a plexiglass chamber, researchers raised each group to maximum voltage in three cycles, then sealed the chamber and ran the electrolysis reaction until the voltage deteriorated to 25% of the maximum. Checks for material quality and breakdown were carried out at the beginning and end of testing. The group composed of 75% PANI and 25% MWCNTs performed the most comparably to the platinum and carbon catalyst. At least four sets of each catalyst group were tested at every voltage level. The tests occurred over a period of six months. Researchers concluded that a co-supportive structure greatly enhanced platinum’s catalytic ability during methanol reformation reactions, specifically by accelerating water activation (Yang et al., 2019). Research performed in 2018 attempted to design a method for performing oxidation with less precious metal by electrically oxidizing methanol by combining platinum and iron deposits on graphene. Only one batch of the solution, described as ink, was made. First, the graphene oxide was synthesized from natural graphite and add to distilled water. Compounds containing iron and platinum were subsequently dispersed in the distilled water along with chloroplatinic acid as a pH balancer. The mixture was then dried into a powder, which was added to the methanol fuel cell. Scanning electron microscopy was used to examine the powdered catalysts, one with only platinum added to the graphene, one with platinum and iron added. The sample with iron showed spherical specks relatively evenly dispersed throughout the graphene (the platinum to iron ratio was 2.6:1 atomically). It was found that that sample performed better in the methanol cell than both the

iron-less sample and a platinum-carbon sample. It also held a constant resistance longer than the other catalysts (Eshghi, Kheirmand & Sabzehmeidani, 2018). The next paper researched the expansion of low-cost catalysts in fuel-cells. The authors performed a minireview of research involving various metals, polymers and carbonites used as catalysts in fuel cells and batteries. Their four areas of focus were Organic Molecules (Phthalocyanines and Related)-CNT Catalysts for Oxygen Reduction Reaction (ORR); Spinel Oxide-CNT-based Bi(tri)functional Catalysts for ORR and OER; Group 4 and 5 Oxide-based Oxygen Reduction Catalysts Using Carbon Nanotubes as Support in Acidic Media; and Nanocarbon-based Catalysts for Zn-Air Battery, Hydrogen Evolution Reaction (HER) and Water Splitting. Experimental procedures from multiple studies were outlined in each section as well as author conclusions. Several main conclusions drawn were the superior performance of MWCNTs over other variants, the necessity of using wet binding methods to best functionalize CNTs, and the promising possibility of oxide materials outperforming precious metal catalysts if used in conjunction with CNTs. The article closed by recommending MWCNTs over other types of nanotubes in order to decrease the cost of fuel cells as well as improve performance (Yang et al., 2019). Another project endeavored to detect minute levels of hydrogen gas in nitrogen using MWCNTs overlaid with platinum. Pristine and functionalized MWCNTs were drop-casted onto separate interdigitated electrodes, with platinum applied to both using a metal sputtering system. The electrodes were then heat to 550 degrees Celsius and cooled to anneal them. Pre-test, researchers used X-ray diffraction to analyze platinum dispersion across the electrodes. In the sealed, room-temperature testing chamber, valves controlled the flow of nitrogen and hydrogen to the electrode and resistance values were recorded by a multimeter.

Researchers stated that the sputtering process successfully deposited platinum onto the CNT electrodes and concluded that the functionalized MWCNTs/Pt exhibited higher sensitivity to hydrogen and a faster response time than their pristine counterparts, as clearly shown in Figure 6 (Dhall & Jaggi, 2019). Another project fabricated a self-supporting CNT membrane with Pt nanoparticles for hydrogen adsorption and storage. Researchers formulated a platinic salt which they applied to a free-standing MWCNT membrane through chronoamperometric electrosynthesis. Average membrane thickness was found via scanning electron microscopy to be about 1.8 micrometers. Three forms of the MWCNT-Pt membrane were formulated by maintaining voltage potential for the following time periods: 25 seconds, 50 seconds, and 100 seconds. These time intervals resulted in the deposition of 7, 11.5 and 25.4 micrograms per cm^2 on the three different membrane forms. Multiple spectra and X-ray techniques were used to analyze MWCNT membrane structure before and after the application of platinum. Using quartz crystal microbalance (QCM) characterization, researchers were able to estimate the membrane's projected hydrogen uptake as a percentage of weight. Researchers used four membrane forms, from plain MWCNTs to the membrane with 100 seconds of platinum deposition, finding that hydrogen capacity increased in order of least to most platinum-containing membrane, with the 100-second MWCNT-Pt membrane holding 0.22% of its own weight in hydrogen. From this data and analysis, researchers concluded that the MWCNT-Pt

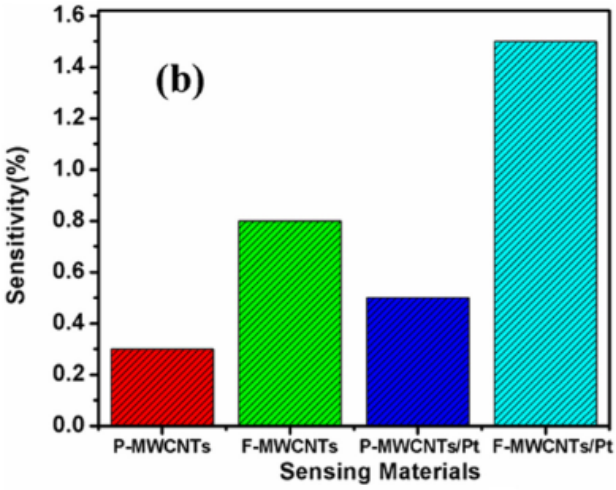

Figure 6: Comparison of sensitivity of different materials for 0.05% H2 concentration (Dhall & Jaggi, 2019)

membranes were not effective hydrogen storage devices, but that the carbon membranes decorated with platinum might be useful supports for catalytic Pt structures. They also noted that the platinate salt performed well as a tool for the electrosynthesis of platinum (Tamburri et al., 2019). Further research by Shanmugam et al. (2014) explored the competence of various co-supports for platinum catalysts in a methanol steam-reforming reaction performed at different temperatures. The platinum was primarily supported by indium oxide. Three porous metal-oxides, (CeO_2, Al_2O_3 and ZrO_2) were used with indium oxide for the co-supported samples. Researchers calcined the oxide-mixture was at 350 degrees Celsius for four hours, added the platinum and calcined the mixture again at 450 degrees Celsius for six hours. The resulting catalytic powder was analyzed using x-ray diffraction. Polyvinyl alcohol was then mixed with water, to which the catalyst powder was added, and used to wash-coat the microreactors. These reactors were heated to a range of 300-375 degrees Celsius at atmospheric pressure and stabilized before water and methanol were passed through sealed catalytically coated chambers within them. Methanol conversion rate was calculated using the inlet and outlet methanol readings in moles. Lastly, the microreactors were subjected to a 100-hour stability test. Researchers determined that CeO_2 best supported indium oxide in the platinum catalyst and also outperformed the other metal-oxides in the stability test. They also stated that indium oxide drastically reduced carbon monoxide biproduct formation when used as catalytic support in methanol steam-forming reactions.

Electrochemical Deposition

Electrochemical deposition is the use of both electricity and some form of chemical, whether solid or liquid, to deposit one substance on another. As an example, one research project formed microscopic copper columns using pulse current localized electrochemical deposition, in

order to understand the effect of varying voltages and duty cycles on deposition output and copper ionization. A platinum wire welded to copper wire formed the micro anode and a copper square formed the plate cathode. A glass cylinder feeding silicon tubing and connected to a potentiostat served as the microelectrode to record deposition potential. The system was submerged in copper sulfate mixed with sulfuric acid and a stepping motor managed experimental timing. When the motor was engaged, copper would be deposited on the cathode plate, and when it stopped so would the deposition. Deposition duty cycle ranged from 0.1-1 while voltage ranged from 2.8-3.2V. This formed cylindrical columns on the copper base plate, whose morphologies were analyzed using scanning electron microscopy. Three voltage levels and four duty cycles produced a range of twelve columns. The lower values of both variables produced regular, smooth cylindrical columns, while the higher values produced irregular, powdery columns (Lin et al., 2010).

Hydrogen Production and Water-splitting

Water-splitting is a promising source of hydrogen. Two thirds of the molecule (by atom number) is composed of hydrogen, and the process to split water is relatively easy and non-hazardous. The studies that follow have explored the subject. One such project synthesized a cheap and long-lasting catalytic alternative to precious metals in oxygen and hydrogen producing reactions. Their solution is nickel and cobalt alloys. Researchers created a Ni sponge by sonicating a combination of nitrogen-rich solutions for one hour and then placing the blend on a 300-degree Celsius hotplate. An identical process was followed to form the Ni-Co sponge with slightly different compounds. The sponges were analyzed using various techniques such as powder X-ray diffraction, X-ray photoelectron spectroscopy and X-ray fluorescence. Then, using linear sweep voltammograms, researchers completed the oxygen reduction experiment.

Secondly, the hydrogen evolution reaction was completed in an alkaline substrate. Finally, a water-splitting cell was created using the Ni-Co sponge and a separate Ni-NG sponge, which served as the anode. Researchers stated that the sponges remained stable for more than ten hours in the water-splitting reaction. Four versions of the nitrogen sponge were manufactured. The first contained nitrogen as the only catalytic substance. The three remaining sponges contained Ni-Co in differing ratios. The evolution reactions ran at 1.6 volts. Researchers concluded that their method for sponge formation (the sonication and transfer to a hotplate) produced well-formed samples and could be scaled to an industrial level. They also cited their sponges' long-term durability in the water-splitting reactions as evidence that they may be viable option for fuel-cell catalysts (Vineesh et al., 2016). Another paper, as previously mentioned, explored the idea of a closed-loop H_2 production plant planned by the Japan Technological Research Association of Artificial Photosynthetic Chemical Process (ARPChem), a scientific organization working towards energy sustainability. Researchers have written a review and summary, both of the H_2 plant system and exploratory research in water-splitting, a current major focus of ARPChem. Four components form the self-sustaining plant, depicted in Figure 7 (Yamada & Domen, 2018).

The core concept on which ARPChem bases its hydrogen producing plant is photoelectrodes. A dual-purpose solar-powered cell will gather energy necessary for water-splitting, which will also occur at the cell using the photoelectrodes. A dual network of pipes will supply the solar farm: Half will transport water to the cells while the other half will carry away the gaseous byproduct. The pipe system will carry these byproducts to a gas

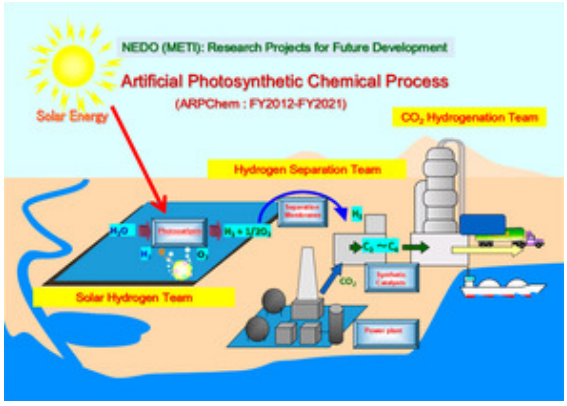

Figure 7: Schematic Diagram of ARPChem (Yamada & Domen, 2018)

separation plant, the second component, which will remove all water vapor and divide the gas into oxygen and hydrogen. Thirdly, an independent solar plant, solely generating electricity, will provide power for gas transportation and to the separation plant. Finally, the hydrogen will be fed to an unrelated system that, with the additional input of CO_2, will produce light olefins (core petrochemical components). Ideally, this green-energy plant will exist alongside a conventional, carbon-based power plant whose waste products will directly supply the CO_2. The authors next turn to development of technology. On the practical level, photoelectrodes and photocatalysts that would make this self-sufficient system possible do not exist yet. So, the article includes a lengthy discussion of potential materials and combinations of materials yielding satisfactory catalytic and reductive results, as well as photocell design and filtration techniques. Although most of the article followed the format of a literature review and relied on external sources, authors did perform one novel experiment testing a 1-square-meter water photo-splitting panel. The panel, made of hydrophilized acrylic, was exposed to sunlight for a day and the gas bubbles collected using plastic tubing, with actual reaction efficiency results determined by gas collection. The authors concluded with a recap of ARPChem's water-splitting plant goal of a self-sufficient closed system and outlook for future materials that might serve as effective catalysts and electrodes (Yamada & Domen, 2018). Shi et al. (2015) overviewed photoelectrochemical (PEC) cells and different arrangements for them, as well as pros and cons of performance based on their structure. Figure 8 depicts an example of a hydrogen fuel cell (Liu, 2018).

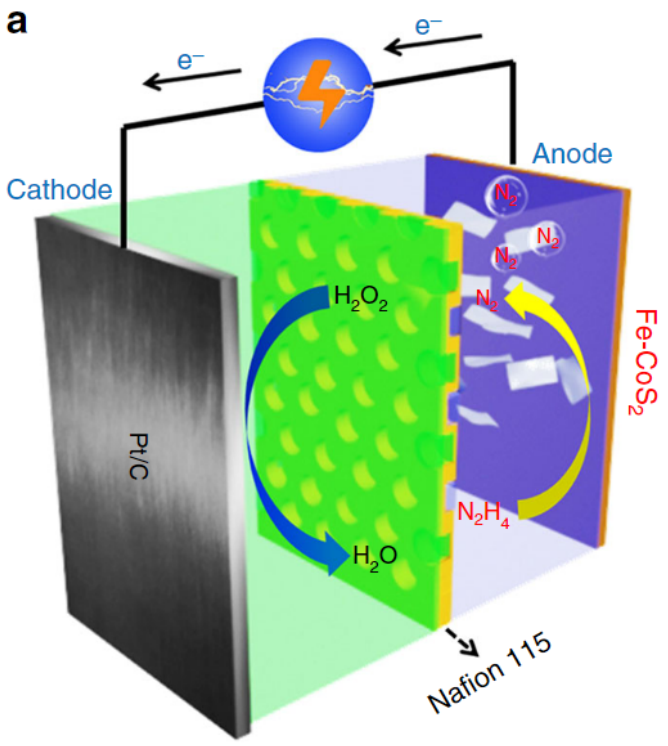

Figure 8: Schematic image of a hydrogen evolution reaction cell (Liu, 2018)

The minireview is divided into four sections entitled, respectively, Methods for the Evaluation of Overall PEC Performance, Methods for the Characterization of Optical Properties, Methods for the Characterization of Charge-Transport Properties and Methods for the Characterization of the Surface Charge-Transfer Property. The first section describes the common three-electrode setup, comprised of working, counter and reference electrodes. A source of light, potentiostat connection and inert gas circulation system are also included in the basic PEC cell. Authors describe configurations for space-limited cells, cell sealing, different liquid mixtures used and gas product collection methods. The second section discusses photo efficiency measures, including reflectance and absorption. The third section focuses on the effectiveness and transport of electron charge, known as potential. Finally, the charge transfer, similar to the charge transport, is examined. The charge transfer efficiency is a measure of energy loss between the electrode and the water molecule being split. The authors state that transfer efficiency can greatly alters cell performance since it affects the electrode's ability to function. They referred to specific processes and ideas found in the studies, citing nearly eighty reference articles. In their summary, the researchers noted that the main measure for a PEC cell's performance is its ratio of

solar power use to hydrogen produced. The importance of precise light intake measurement of a cell was also stressed, since poorly measured or quantified photo exposure would spoil research results. Another study overviewed and assessed current developments in one-dimensional catalysts for hydrogen and oxygen production. Researchers performed a literature review of recent advances in nanomaterials for electrolytic reactions. The review is broken into three sectional categories: hydrogen evolution reaction, oxygen evolution reaction and bifunctional catalysts. These sections were broken into subsections based on catalytic metal content or lack thereof. In the first section, novel metal catalyst systems such as cobalt nanowire groupings grown on carbon cloth and iron phosphate nanowires supported by titanium plates. Two subsections explaining CNT research, with and without the addition of metal components, followed, focusing on their stability and potential to outperform strictly metal catalysts. The second section, researchers discussed techniques such as elemental doping and the layering of metallic nanosheets for increased oxygen evolution reactions. Cobalt and magnesium oxides were found to perform said reactions most effectively. The following nonmetal sub-sections debated the best combination of CNT types and graphene layers, both doped with nitrogen. Lastly, the third section covered dual-use catalysts as well as techniques to transition one to the other. Examples included N-doped carbon overlaying nano-scale cobalt deposits and nickel selenium nanowires, both of which can reduce oxygen or hydrogen depending on solution alkalinity. Researchers stated that to perform hydrogen or oxygen reduction reactions on a mass, usable scale, use of cheap and plentiful materials as catalysts, such as those covered in the review, was indispensable. They encouraged further study of composite catalysts and exploration of new materials to formulate them (Li & Zheng, 2016).

Methodology

Due to COVID-19, no data was generated and this research project remains incomplete

Research Design

Answering the question of a hydrogen-producing reaction's efficiency necessitates a practical approach, meaning data must be procured and analyzed, and conclusions drawn about the performance of the materials involved in order for it to be answered. The practical approach is most suitable for addressing the given hypothesis because the question involves uncertainty about the outcome a physical process. Therefore, a process must be carried out to confirm or disprove the hypothesis. The practical process would have yielded experimental, quantitative data collected in a traditional lab setting.

Procedural and Material Sources

This project's advisor designed the experimental procedure, which is a sequential three-step process. The process would have been carried out by undergraduate students at the lab belonging to the Department of Technology in Material Science and Nanotechnology at Elizabeth City State University. Platinum and CNTs would have been sourced from Sigma-Aldrich, a producer of laboratory-grade materials and chemicals. Nine interdigitated chips would have been used as electrodes. CNTs and platinum would have been added to six of the chips and only platinum will be added to the remaining three, the experimental control group.

Research Process

First, CNTs would have been mixed with a substrate, methanol, and deposited on the six electrodes using filtration to distribute the nanotubes as evenly as possible across the electrodes.

A regular weight to area ratio would have been achieved to ensure comparable samples. The six electrodes would then have been divided into groups two of three, each of which would have comprised a testing set and be separately treated in the next stage. Secondly, platinum will be deposited on the surface of all nine chips. Platinum nanoparticles (at the atomic level) would have been deposited on the chips also containing CNTs through electrochemical pulse deposition. The goal of this technique was to reduce the amount of platinum used, spreading it as thinly as possible without compromising effectiveness. When voltage was applied, platinum would have been deposited on the CNTs and ceased being deposited when the voltage was removed. A cyclical voltage would have run on a predetermined cycle, applied for a certain number of seconds, and removed for a certain number of seconds. Two cycle would have run, with different timing settings, thus depositing different amounts of platinum on the CNTs, decreasing from the first to second cycle. Bulk platinum would have been deposited on the remaining three chips. The third and final step was testing. Each electrode would have been individually used, and its data recorded separately. A round-bottomed glass beaker would have been filled with DI water and placed on a hotplate with a magnetic stirrer. A working electrode (the CNT-Pt electrode) would have been paired with a third reference electrode, along with a counter electrode, for each of the nine tests. The counter electrode would have functioned as an electrode and the working electrode as a hydrogen electrolyzer.

Data Collection

The electrode trios would have been connected to a power source and potentiostat (data-collection device) via wiring and placed in the DI water. Two trials would then have been run for each sample CNT-Pt electrode: chronoamperometry and cyclic voltammetry. In the former trial, a voltage would have been applied to the CNT-Pt, and the current produced recorded as a

function of voltage, which the computer would have logged. In the latter trial, potential of the CNT-Pt electrode would have been increased and decreased, with resulting current recorded as a function of time and logged by the computer.

Data Analysis and Presentation

Data from all nine trials would have been exported into Microsoft Excel, manipulated and charted for clear presentation of results. The statistical function used to present results would have been standard deviation. Based on the deviation of each sample, results would have determined what amount of platinum nanoparticles could be successfully substituted for a purely platinum catalyst or if the substitution could be made at all.

Discussion and Recommendations

Although no results were gathered to be analyzed, several key points emerged from the literature review. First, CNTs are a relatively new development, as is their use for energy production. The author recommends that the general body of knowledge regarding CNTs themselves continue to be expanded. Second, production methods allowing manufacturers to control the size, shape, and chemical characteristics of carbon-based nanostructures, including CNTs but also other structures such as nano-onions, should be explored and developed. Third, as one study highlighted, CNTs have a little-explored potential for hydrogen storage. Finally, a lack of research also exists regarding commercial scale use of CNTs. Experiments employing CNTs on a larger scale must be completed to further this goal and enable companies to utilize that technology. Of course, purely exploratory research is important, but the incredible potential of CNTs to aid in green energy production must be addressed. A substantial body of solid,

scientifically-backed evidence must be built before companies—and the public—are convinced of CNTs' energy production potential and viability.

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