

**Enhancing a Hydrogen PEM Fuel Cell Stack with  
Gold-Dodecanethiolate Core-Shell Nanoparticles**

Sean B. Ballinger

## Abstract

Hydrogen fuel cells are currently unsuitable for commercialization due to the high cost of the platinum (Pt) used in the electrocatalyst material, as well as the cost of hydrogen fuel. Gold nanoparticles (Au-NPs) have demonstrated a significant enhancement in single fuel cells, but their behavior in stacks has not been investigated. Au-NPs synthesized according to the Brust-Schiffrin method were deposited on a proton exchange membrane of Nafion 117. Electrocatalyst material was created with a  $0.5 \text{ mg/cm}^2$  Pt loading, and used to create membrane electrode assemblies (MEAs). The MEAs with Au-NPs demonstrated a mean improvement of 38% in a single fuel cell, 17% in a 5-cell stack with 2 cells operational, and 30% in the stack with 3 cells operational. Transmission electron microscopy of the Au-NPs revealed that they were of a diameter at which they would exhibit quantum size effects, and cyclic voltammetry indicated that the Au-NPs provided their enhancement by catalyzing the oxygen reduction reaction and the carbon monoxide oxidation reaction. The Au-NPs' enhancement in the more realistic environment of the fuel cell stack proved that the technology would be extremely beneficial to current commercial applications of hydrogen fuel cell power.

# **Enhancing a Hydrogen PEM Fuel Cell Stack with Gold-Dodecanethiolate Core-Shell Nanoparticles**

## **1. Introduction**

Platinum nanoparticles are currently used as the most effective way to increase the efficiency of a hydrogen fuel cell. The drawback, however, is that the material is extremely expensive, and thus presents a barrier to the widespread adoption of hydrogen fuel cells. It has been shown that gold nanoparticles (Au-NPs) can be added to a fuel cell's Nafion membrane to increase its power output by nearly 80%. But the following questions then arose:

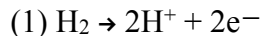
- (a) A small experimental plastic unit rated for less than 0.1 W power output was used for the original experiments. Would the same improvement apply to commonly used 100 kW stacks that have extremely different characteristics?
- (b) The experimental unit had a single operating cell: would a stack containing multiple cell units display the same increase, or would there be an additive effect?
- (c) If this new material were able to overcome carbon monoxide poisoning, which is problematic for conventional fuel cells, would this fuel cell be able to handle a less pure stream of reformat hydrogen? Purifying hydrogen is a major factor in its end price.

Hydrogen can currently be derived from natural gas and coal at \$18.9-23.3/MWh, and from water through electrolysis at \$64.8-75.1/MWh. By comparison, the price of oil rose from 30.7 to 81.9 \$/MWh between 2000 and 2009, and will only continue to increase [1]. The U.S. Department of Energy's Office of Fossil Energy expects that the cost of hydrogen will be less than 13.6

\$/MWh by the year 2020 thanks to the gasification, sequestration, pyrolysis, and steam reforming processes being currently developed [2], which will secure hydrogen an important place in our future.

In addition to lowering the price of hydrogen, current research shows a great interest in improving the efficiency of fuel cells and reducing their high immediate cost of the precious materials they employ, such as Platinum. This precious metal is necessary in a fuel cell to catalyze the oxidation-reduction reaction that is used to create electricity. This reaction is composed of two half-reactions that occur at different sides of the cell, called the anode and cathode, which are separated by a proton exchange membrane (PEM).

The first part of the mechanism by which hydrogen and oxygen are used to create electricity, heat, and water is the hydrogen oxidation reaction (1), which occurs at the anode.



This involves the dissociation of hydrogen gas into hydrogen ions (protons) and electrons. The protons pass through the PEM between the anode and cathode, but the electrons are unable to follow and are diverted into an electric circuit.

The other half-reaction is the oxygen reduction reaction (2), which takes place at the cathode. (2)  $\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$  The oxygen-reduction reaction creates water from protons, electrons, and oxygen gas. This is the exothermic half-reaction responsible for giving off heat. The sum of reactions (1) and (2) is the overall reaction (3) that takes place in the fuel cell, in which hydrogen and oxygen form water. (3)  $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$  Both half-reactions in the fuel cell require a catalyst material inside the electrodes in order to function. In a PEM fuel cell, the catalyst is platinum [3]. Gold, along with several alloys of metals, has been investigated as a re-

placement or complement to platinum. They have shown very promising results, but tests involving these new catalysts have only been carried out with single fuel cells.

Single cells are not powerful enough to be used in any industrial applications. Fuel cell stacks, which are composed of many cells connected in series, are instead used as more practical sources of power. One essential difference in stack design is the membrane electrode assembly (MEA), which is used instead of mere pressure holding the electrode components together, as is commonly done in a single cell. MEAs are created by fusing the components of the cell, and increase the contact area between the electrocatalyst material and the PEM. It is possible that the Au-NPs used in single cell tests provide a similar improvement by increasing the surface area of the PEM available for contact. It is therefore necessary to test the fuel cells in MEAs to know whether they are truly acting as catalysts or simply increasing the reaction surface area.

Stacks' behavior is also less predictable than that of single cells: more things can go wrong, such as leaks, blockages, and the “weakest link” problem that arises when a defective cell is in series [4]. Thus, the enhancement provided by Au-NPs in a single cell needs to be tested in the

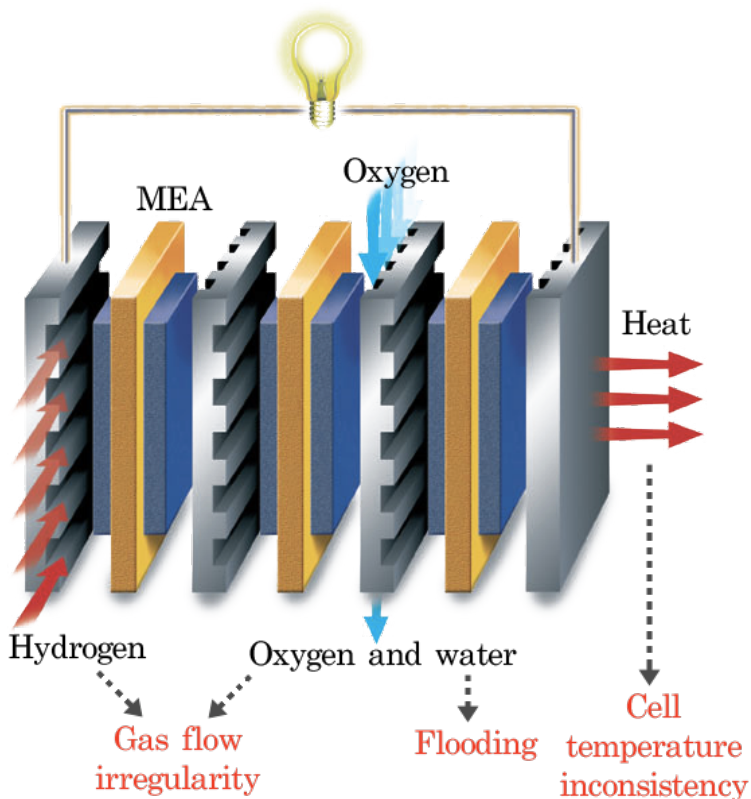


Figure 1. Schematic of a fuel cell stack and its unique issues (image adapted from [http://www.fueleconomy.gov/feg/fcv\\_pem.shtml](http://www.fueleconomy.gov/feg/fcv_pem.shtml))

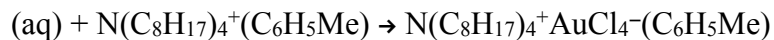
harsher environment of the stack, which will indicate whether the Au-NPs are suitable for real-world use.

The relationship between single cell and stack is therefore not simply analogous: the two have vastly different design parameters and operating conditions. Current research on replacement catalysts for platinum has never involved such realistic testing of these technologies: testing the Au-NPs' effects in a stack will enlighten us as to the precise nature of the enhancement mechanism, as well as the commercial and industrial viability of this innovation.

## **2. Materials and Methods**

### 2.1. Synthesis of Au-NPs

Gold-dodecanethiolate core-shell nanoparticles were synthesized according to the Brust-Schiffrin method, which employs a two-phase system, first devised by Faraday, to attach self-assembled thiol monolayers to growing nuclei during metal nucleation. 0.39 g hydrogen tetrachloroaurate ( $\text{HAuCl}_4$ ) and 2.62 g tetraoctylammonium bromide (TOABr) were weighed. The hydrogen tetrachloroaurate was added to 40 mL deionized water, and the tetraoctylammonium bromide was added to 100 mL toluene. The yellow solution containing hydrogen tetrachloroaurate was added to a round-bottom flask, followed by the solution containing tetraoctylammonium bromide. The mixture separated into two layers, the top one red, and the bottom one yellow. The mixture was stirred magnetically for 20 minutes, and started turning black. At this point it was wrapped in aluminum foil because it was photosensitive. 200 mL dodecanethiol ( $\text{C}_{12}\text{H}_{25}\text{SH}$ ) and 0.45 g sodium borohydride ( $\text{NaBH}_4$ ) were then added to the flask, and the mixture was left to stir for 3 hours. The overall reaction that took place is described by (4) and (5) [5]: (4)  $\text{AuCl}_4^-$



The mixture consisted of an organic phase on top of water, which was drained with a separatory funnel. A rotary evaporator was then used to evaporate the mixture to 5 mL. 200 mL ethanol was added, and the mixture was left overnight at 4°C, forming black precipitate. The mixture was centrifuged at 5000 rpm for 10 minutes, the top solution removed, and 10 mL ethanol added. This process was repeated 3 times. The product was then left to dry in a vacuum desiccator.

## 2.2 Properties of Au-NPs

Although gold is, under most circumstances, a less active catalyst than other transition metals, it has recently been discovered that gold nanoparticles are very active catalysts at the relatively low temperatures at which PEM fuel cells operate [6]. Gold's enhancement lies in catalyzing the reduction of oxygen (ORR) and the oxidation of carbon monoxide (CO oxidation) [7]. The catalysis of the ORR is especially important because its low rate of reaction is one of the greatest barriers to achieving the maximum possible energy conversion efficiency in a fuel cell [8].

Au-NPs have been shown to be highly active catalysts for the two-step oxygen reduction reaction described by (6) and (7) [9]: (6)  $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$  (7)  $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

The Au-NPs change the reduction pathway of oxygen from the single-reaction,  $2e^-$  one shown in reaction (2) into the above two-step,  $4e^-$  process [10]. Au-NPs of the micron scale do not cat-

alyze this reaction [11], so quantum size effects are believed to be responsible for the unusual electronic nature of smaller Au-NPs [7]. Another function that Au-NPs serve is to catalyze the oxidation of CO, which appears in trace amounts in fuel cells among the H<sub>2</sub> and CO<sub>2</sub> products of the steam reforming of a fuel such as methanol [3]. As little as 100 ppm CO can lower the efficiency of a fuel cell considerably [12]. In a fuel cell, the CO oxidation reaction occurs through a process (8) known as the water-gas shift reaction [6]. The Au-NPs have been shown to adsorb both CO and CO<sub>2</sub> in catalyzing this reaction [13]. (8)  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$

Au-NPs are therefore even more useful in real-world scenarios involving steam reforming. They are also effective catalysts of the CO oxidation reaction even at temperatures as low as -70°C, which makes them suitable for a large range of applications [14].

### 2.3 Transmission Electron Microscopy Imaging

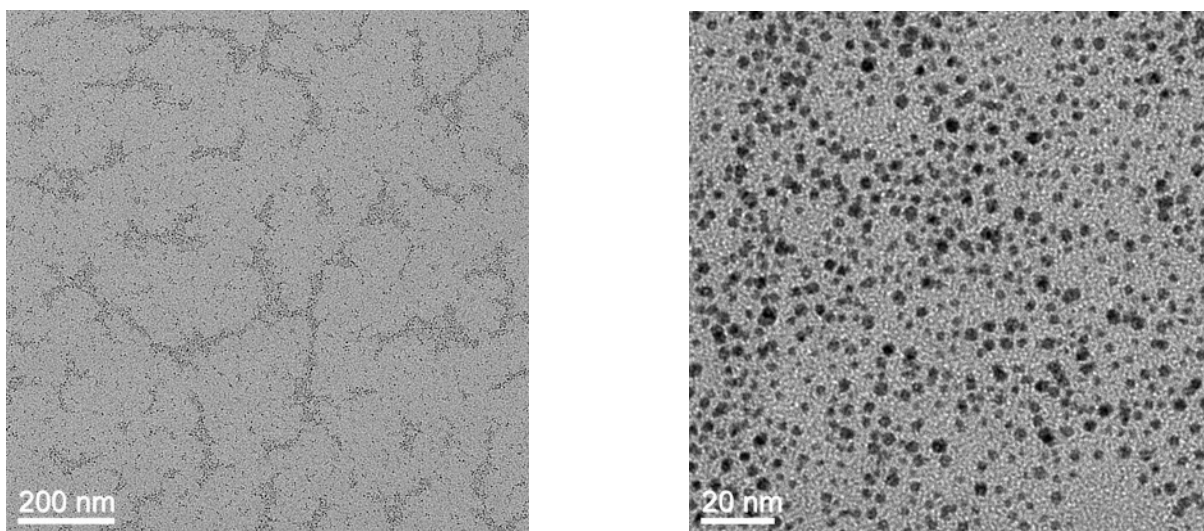


Figure 2. Transmission electron microscopy (TEM) images of the Au-NPs at different magnifications.

Au-NPs were deposited on the surface of a TEM copper mesh, and a graduate student used the Phillips CM12 STEM at 80 KeV to produce the TEM images. These were analyzed using



ImageJ, and a distribution chart of the Au-NPs' diameters was created.

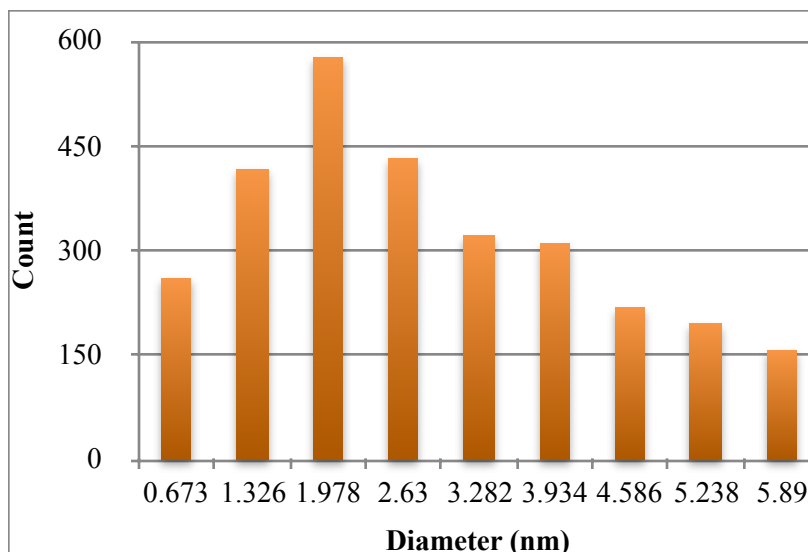


Figure 2. Diameter distribution of the Au-NPs in the TEM images.

Au-NPs only behave as catalysts when they form clusters of diameter around 3.5 nm, because at that point quantum size effects imbue the nanoparticles with electrical properties that are otherwise uncommon in metals [15].

The TEM images confirmed that the nanoparticles were in the size

range at which quantum size effects occur.

#### 2.4. Coating a Nafion Membrane with Au-NPs

The Langmuir-Blodgett trough is an instrument used to deposit a monolayer of particles on a film. The film is submerged in water with an aqueous subphase at the surface, which barriers compress until the surface pressure is high enough for a single molecule thick monolayer to form. The film, when withdrawn, is coated with the monolayer [16]. Before each use, the Langmuir-Blodgett trough was cleaned with ethanol, and the water was suctioned and replaced with distilled water three times. The

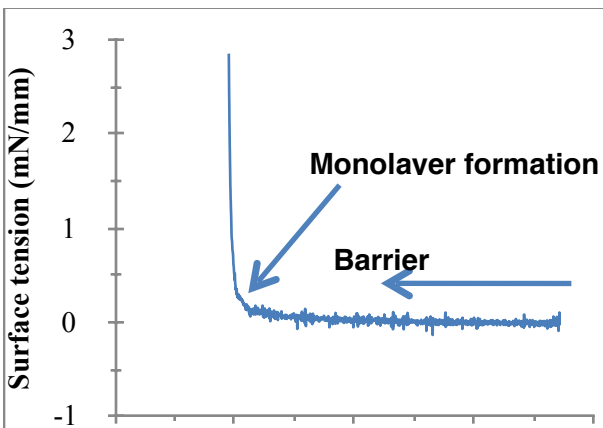


Figure 4.  $\pi$ -A isotherm graph showing the point at which the monolayer of Au-NPs begins to form.

trough was verified to be free of impurities using an isotherm curve. The Nafion membrane was suspended and submerged. A microsyringe cleaned with toluene was used to deposit 400  $\mu\text{L}$  1 mg/mL Au-NP/toluene mixture on the surface of the water in the trough. The barriers were made to compress at a rate of 5 mm/min, and stopped when the surface tension of the water reached 3 mN/m. The Nafion membrane was withdrawn slowly as the barriers maintained a constant surface pressure, to ensure the creation of a uniform monolayer.

## 2.5. Creation of Membrane Electrode Assemblies

The essential component of a fuel cell stack is the membrane electrode assembly (MEA). An MEA is created by heat pressing the proton exchange membrane (PEM) between two smaller sheets of electrocatalyst material. Using an MEA has many benefits over simply holding together the components with pressure. MEAs require less platinum loading in the electrocatalyst for the fuel cell to function properly, because they take greater advantage of the surface areas of the platinum nanoparticles. MEAs make thermal and water management more effective in fuel cells without external humidification, and increase their lifetimes in demanding stationary and transportation applications [17]. All these advantages combined make the MEA reduce the cost of the fuel cell while improving its performance. MEAs are therefore used in all industrial scenarios, and in order to optimize the real-world performance of new materials and processes, these must be tested using MEAs. The electrocatalyst material required for the MEAs was created by depositing platinum catalyst on a sheet of carbon paper. The total surface area to be covered was 600  $\text{cm}^2$ , and with a target of 0.5  $\text{mg}/\text{cm}^2$  loading (the same as that used in the smaller single fuel cell tests), 300 mg platinum was needed. 1.5 g platinum/vulcan mixture (20% platinum) was dis-

solved in 4 mL Liquion (15% Nafion by weight) according to proportions used in other experimental setups [18]. The mixture was stirred magnetically and sonicated, then deposited evenly on the carbon paper and allowed to dry. The PEM material used in each MEA was a film of Nafion 117, which was heat-pressed between the sheets of electrocatalyst material at 140°C and 3500 psi.

## 2.6. Testing the Fuel Cells

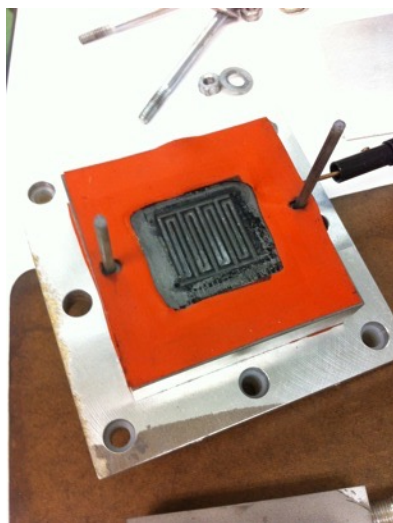


Figure 5. (left) Inside of the 7.8 cm<sup>2</sup> cell with gas flow channels visible.



Figure 6. (right) The assembled 5-cell 50 cm<sup>2</sup> stack.

The fuel cells were tested under identical conditions. Hydrogen and air were both supplied at 1 bar pressure, and the air was let to flow at 10 SCFH; the fuel cell was purged of hydrogen manually. The electrodes were connected to a multi-channel electronic load device that maintained constant resistance, and the fuel cell's voltage was measured as the current was controlled manually. Nafion 117 was always used as the PEM, and stack tests all used the same sheet of electrocatalyst material. First, a small single cell of active area 7.8 cm<sup>2</sup> was tested with a control MEA vs. one with a Nafion membrane coated with Au-NPs, to confirm that the Au-NPs weren't

exclusively increasing contact area between PEM and electrocatalyst; if this were the case, hot pressing would have rendered the Au-NPs' enhancements superfluous. After this was confirmed, larger MEAs with Au-NP Nafion membranes of active area 50 cm<sup>2</sup> were compared against control MEAs running in the stack. The stack tests were carried out with 2, 3, and 5 cells operating.

### 3. Results

The first test carried out was cyclic voltammetry, and was used to determine the optimal surface tension at which to deposit the Au-NPs on the Nafion PEM membrane. Cyclic voltammetry measures the performance of a working electrode against that of a reference electrode. In this case the working electrode was the one with Au-NPs, and its potential vs. the reference hydrogen

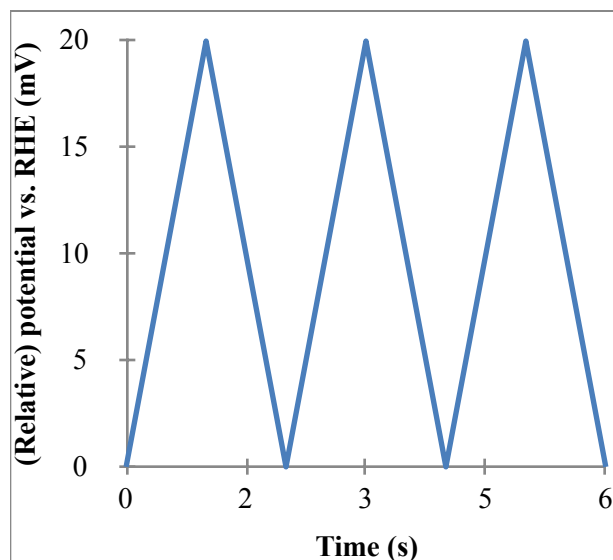


Figure 7. Visualization of the excitation signal used in cyclic voltammetry's potential scanning process.

electrode (RHE) was scanned linearly at a rate of 20 mV/s. The working electrode and the reference hydrogen electrode were operated in 10  $\mu$ L of 1 mg/mL 20wt% platinum/carbon water suspension. A glassy carbon electrode supported the Pt-Au-Nafion mixture (5  $\mu$ L of 1/10 dilution of 10wt % Nafion). The procedure was carried out by a graduate student.

The peaks in figure 4 mark the points at which the voltage was great enough to result in oxidation or reduction at the working electrode. Oxidation occurs when it scans positively (the potential decreases), and reduction occurs when it scans negatively [19].

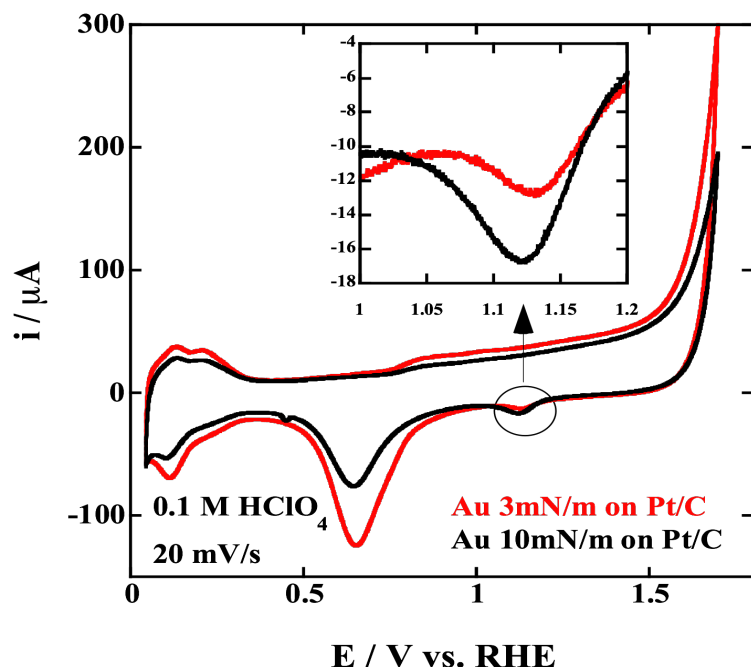


Figure 8. Cyclic voltammogram of 5  $\mu\text{L}$  of 1 mg/mL 20wt% Pt/C suspension in 0.1 M  $\text{HClO}_4$  on a glassy carbon electrode. (Note to Evaluator from SSP - You may request a color copy of this page from SSP Staff.)

The working electrode's current during the potential scanning was measured, and the voltammogram plots the current against the potential vs. the RHE. The graph indicates that the Au-NPs deposited on the Nafion PEM membrane at 3 mN/m surface tension consistently provide a current of higher magni-

tude than those on the Nafion treated at 10 mN/m. These results mean that although the 10 mN/m Au-NPs

are more numerous, because they formed a more dense monolayer with which to coat the Nafion, the 3 mN/m Au-NPs have the advantage of being more dispersed and free to contribute to catalysis.

After it was confirmed that the Au-NPs created with the Brust-Schiffrin method had the potential to act as catalysts, it was necessary to test this ability in the MEA of a real fuel cell. In the next tests, the voltage of the cell or stack was measured as the current was modulated. Voltage was plotted against current density, the average distribution of the total current across the active area of the MEA. The total power output of the cell was calculated as the product of voltage and current, and power density was also plotted against current density. This measurement technique is common in research related to fuel cells, and the resulting graphs are called polar-

ization curves.

The test involving a smaller single fuel cell with an MEA was necessary to determine whether the Au-NPs were significantly catalyzing reactions, or improving the cell in a way that would be irrelevant to stacks (and, thus, all real-world ap-

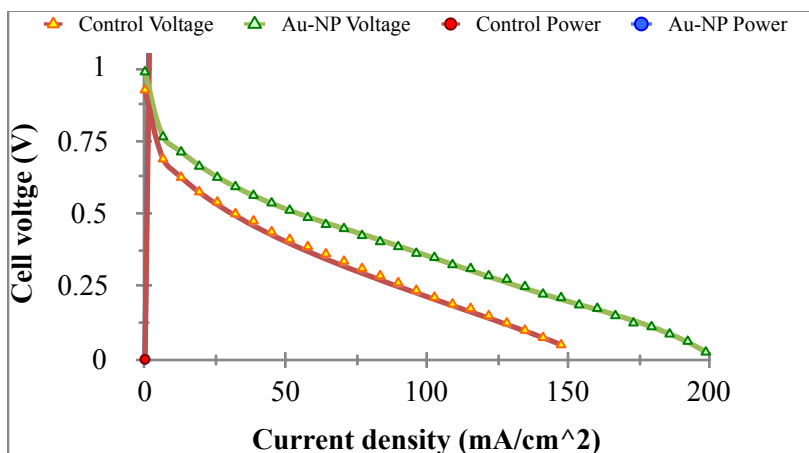
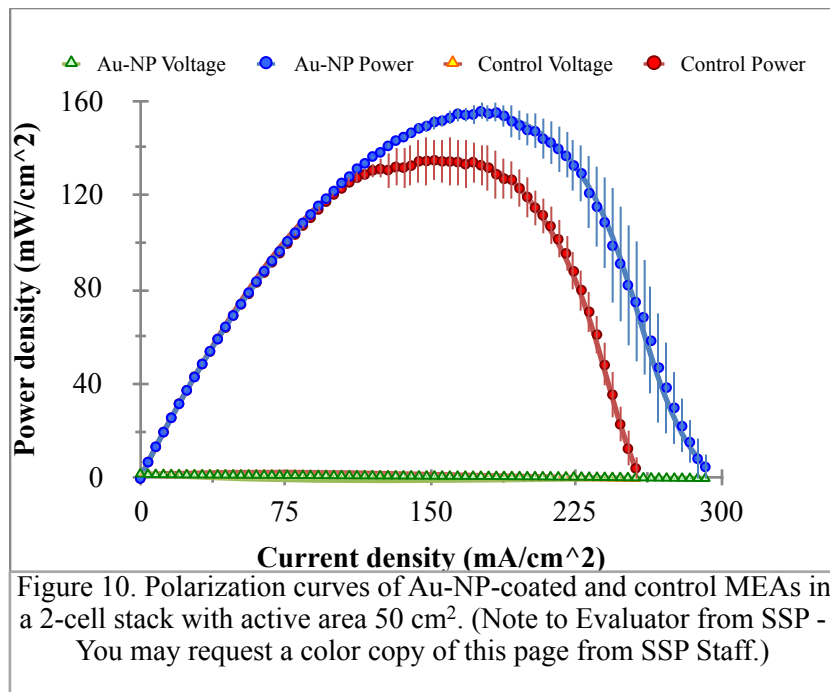


Figure 9. Polarization curves of Au-NP-coated and control MEAs in a single cell with active area 7.8 cm<sup>2</sup>. (Note to Evaluator from SSP - You may request a color copy of this page from SSP Staff.)

plications of the technology). As Au-NPs had been previously tested in single cells in which the components were held together using pressure alone, it was hypothesized that the Au-NPs were merely increasing the contact area between the electrocatalyst material and PEM. The structural nature of the MEA increases the contact surface of these components so greatly that any improvement provided by Au-NPs in this regard would be rendered insignificant. Thus, the hypothesis would be confirmed if the Au-NPs were not beneficial to a fuel cell employing MEAs. On the other hand, if the Au-NPs did indeed provide an advantage, then it could be said with certainty that the Au-NPs catalyze one or more of the reactions taking place inside the cell. The test of the single cell and MEA, whether successful or not, would give a rough of idea of the kind of improvement the Au-NPs would provide in a stack.

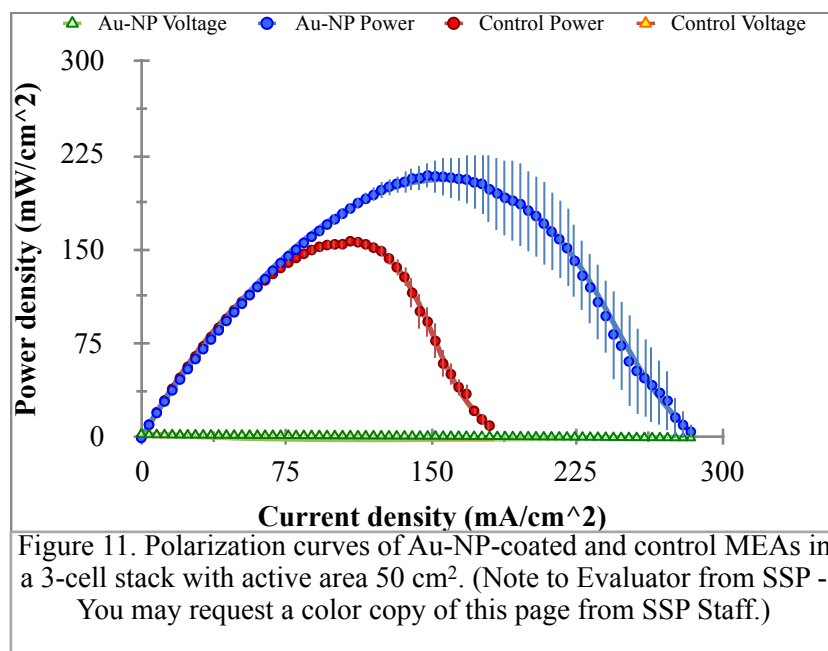
The first test of the stack was carried out using the minimum number of cells: 2. Tests were performed 3 times each using control MEAs and Au-NP-coated MEAs. The graph shows the



mean of each value, and the error bars show the calculated standard error of the mean (the same applies to all subsequent tests). The results obtained would be the first indication of how the Au-NPs' enhancement would compare to the problems that plague stacks. This test would utilize less of the stack's

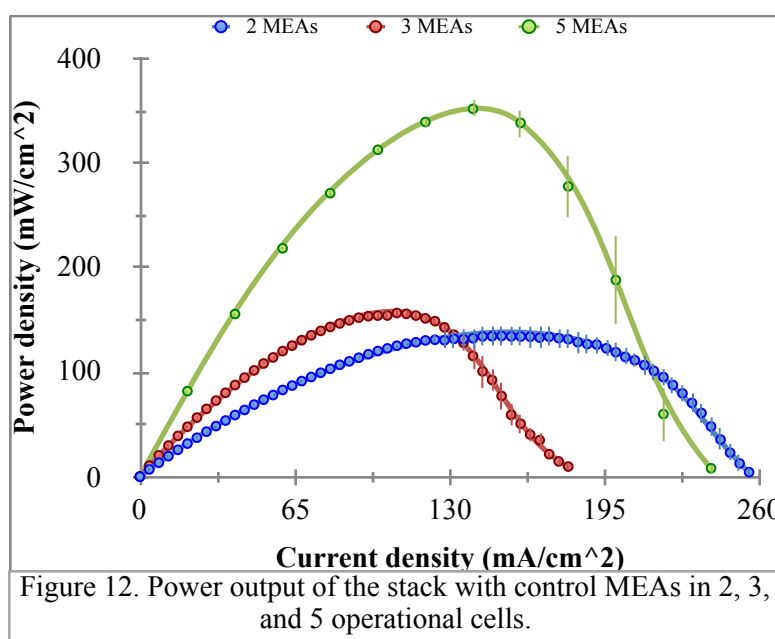
maximum power in order for its defects to become more easily visible. It would be possible to attribute the small enhancing effect of the Au-NPs to the fuel cell's low output struggling against the significant irregularities in gas and water flow.

The next test of the stack with 3 operational cells would provide a more realistic model of the Au-NPs enhancement in larger stacks. Because the stack would provide maximum output at a higher current density, it was anticipated that its problems would be less of a hin-

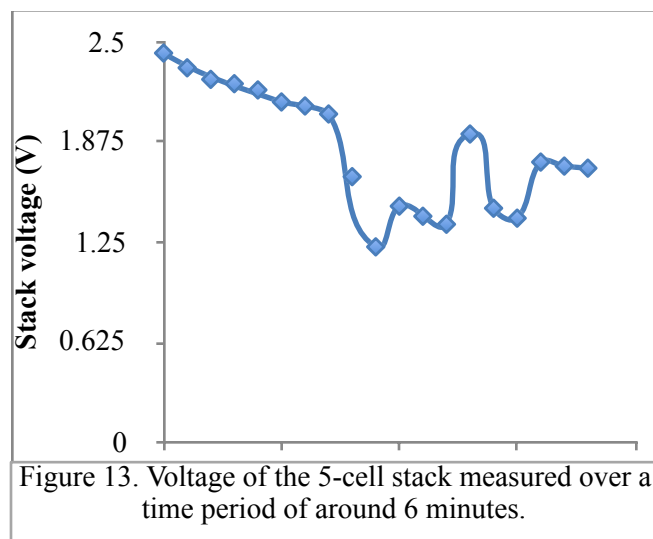


drance to the Au-NPs' catalyst behavior than in the 2-cell test. But the gas and water flow irregularities of the stack would only be further aggravated by the longer pathways, and the issue of cell temperature irregularity would also become more significant as the length of the stack increased. Even if the Au-NPs provided the same percent improvement as in the 2-cell test, their enhancement would outweigh the greater adversities of the 3-cell stack and demonstrate that the Au-NPs are much more beneficial when higher current densities are involved.

The final test of the stack involved 5 operational cells (control MEAs alone), and its purpose was to find a linear trend in power output vs. number of cells operational (e.g. a 3-cell stack has a 50% higher maximum power output than a 2-cell stack). The ability to create such a model



would make the prediction of the Au-NPs' benefits in much larger stacks a more accurate affair.



The voltage of the stack was also tested at its maximum output (with 140 mW/cm<sup>2</sup> power density), in order to better understand the fluctuations in output due to the problems of flooding and dehydration that only became prevalent when 5 cells were operational.



#### 4. Discussion

The Au-NP MEA used in the single cell showed a 38% improvement in maximum power output over the control MEA. This significant improvement confirms that the Au-NPs are responsible for catalyzing the reactions inside the fuel cell. Although the Au-NPs did likely optimize the contact surface of the components used in previous single cell tests, this improvement was apparently dwarfed by the Au-NPs' contribution to catalysis.

The stack with 2 operational cells showed the smallest mean improvement of 17% higher maximum output for the Au-NP MEA vs. the control. This is most probably due to the low operating current being at odds with the less than ideal conditions inside the stack.

The stack with 3 operational cells showed a very promising amelioration of 30% in maximum power output thanks to the Au-NPs, which appear to provide a greater enhancement at higher current densities. This observation is corroborated by the fact that in all the tests, the Au-NP and control MEAs displayed the same performance at low current densities until they reached around 1/3 of the Au-NP MEA's maximum current density, at which point the Au-NP MEA cells distinguished themselves from the control by providing higher power.

That the Au-NPs' enhancement grows with the stack's current density is an extremely promising result with regards to the commercial applicability of Au-NPs in stacks: most industrial stacks operate at much higher current densities and deliver much more power than the stack used in these experiments. In an attempt to create an accurate scaling model to estimate the enhancement the Au-NPs would provide in a commercial stack, the same stack was tested with 5 operational cells (the highest number it was designed to accommodate). The result of this test, however, showed that this power output of the stack does not follow a linear trend: the 2-cell and

3-cell stacks show nearly identical maximum power output, and the difference lies in the higher current densities at which the 3-cell stack was able to operate. The 5-cell stack has the highest maximum output, but it does not function at current densities any higher than those of the 3-cell stack. During the test, the 5-cell stack also exhibited large fluctuations in power output: while operating at  $140 \text{ mA/cm}^2$  current density, its power density ranged between  $170\text{-}320 \text{ mW/cm}^2$  during 5 minutes of monitoring. This shows that the stack used in these experiments was prone to the same irregularities in gas, water, and heat distribution that are present in larger commercial stacks. These were taken into account in the repeated tests of the stack under the same operating conditions, and the error bars indicate the extent to which these irregularities influence the operation of a typical stack. In so doing, they show that the enhancement provided by the Au-NPs is both statistically and practically significant.

One way Au-NPs could help reduce the cost of a fuel cell stack is by employing fewer cells in the stack but maintaining the same power output. This would be possible thanks to the increase that Au-NPs provide to the voltage of each cell. If the 3-cell stack's 30% increase in maximum output applied to a large commercial stack, it could contribute to an enormous reduction in cost. Let us take for example a 2011 model car with a 100 kW hydrogen fuel cell engine [20]. An 11.5 kW stack used for accurate commercial testing contains 120 cells and provides a precise linear scaling model [4]. If this stack were to provide 100 kW, it would need to be expanded to contain 1044 cells. If each cell were enhanced with Au-NPs, it would only require 731 cells, and the amount saved by dispensing with the platinum and PEM material required for 313 cells would exceed the cost of treating the rest with Au-NPs.

The question of whether Au-NPs would help alleviate the commercial difficulty imposed

on fuel cells by platinum also merits consideration of future trends. If vehicles employing fuel cells take to the streets in significant numbers, it is expected that the demand for platinum would increase at a rate 3 to 6 times faster than between 1960 and 2000 [21]. After such rapid growth, using gold as a cheaper complement to platinum may no longer be just an effective cost-saver but an absolute necessity for the commercial viability of hydrogen energy.

In addition to cost, the fuel cell would benefit in terms of stability: many stacks exhibit erratic behavior when composed of a very large number of cells. Although the performance of a stack agrees with the sum of its individual cells' output, its mass transfer behavior is unpredictable, which makes designing larger stacks less straightforward [22]. Another problem is humidity, which is beneficial to single cells, but proves detrimental to the stack after a certain point due to flooding, and would grow more serious with a larger stack [23]. Finally, heating can also become a barrier to performance when large differences in temperature between cells are present, which additional cells would only further aggravate. For the above reasons, a stack with a larger amount of cells is less stable because of its more numerous opportunities for failure [24]. By reducing the number of required cells in a fuel cell stack, Au-NPs could both lower the cost and improve the stability of stacks.

In addition to reducing the number of cells in a stack, Au-NPs could simply be used to boost the power of a fuel cell that would require a larger initial investment, but have the advantage of being extremely efficient, and thus lower the cost per kW of the energy produced. Efficiency is especially important for transportation, and an unsolved problem in that regard is hydrogen's relatively low energy density per unit volume: although hydrogen has a higher mass energy density at 120 MJ/kg than gasoline at 44.4 MJ/kg, the maximum liquid volumetric energy

density of hydrogen is 10.4 MJ/L, which is much lower than gasoline's 31.1 MJ/L [25]. By lowering the amount of hydrogen fuel required and/or extending the range of fuel cell engines, Au-NPs could help to greatly improve the practicality of hydrogen fuel cells used in transportation.

The data obtained in this research is of immense value because gold's use as a co-catalyst has, to date, only been investigated in laboratory settings that do not accurately reflect the reality in which Au-NPs must be put to the test. The results provide more compelling evidence than other existing literature in indicating that Au-NPs merit serious consideration for real-world use, and demonstrate that the enhancement can greatly improve the price, stability, and efficiency of fuel cell stacks.

## **5. Conclusion**

The goal of this research was to assess the effectiveness of the Au-NPs in co-catalysis of the reactions inside a hydrogen fuel cell stack. A Langmuir-Blodgett trough was used to coat PEM membranes with Au-NPs synthesized according to the Brust-Schiffrin method, and MEAs were created for use in the stack. TEM imaging and cyclic voltammetry tests showed that the Au-NPs are capable of acting as catalysts of the oxygen reduction reaction and CO oxidation reaction due to quantum size effects. An MEA with Au-NPs was used in a small single cell, and the results from this test encouraged testing in the stack, with 2 and 3 cells operational. The results demonstrated a consistent improvement in stack voltage and maximum power output. The most promising results from the research suggest that an enhancement of at least 30% in maximum power output can be expected in large stacks. It was also found, by testing the stack with 5 control MEAs, that maximizing the output of each cell to use fewer cells in the stack also increases the stack's stability. Au-NPs, which were found to benefit single fuel cells, were far from guaran-

teed to do the same in stacks, because of the great differences in design and operating conditions. Through this research, it has been shown that Au-NPs have the potential to greatly enhance real-world fuel cells.

## References

- [1] "Fossil | Department of Energy," Energy.gov, Department of Energy, <http://energy.gov/fossil> (accessed August 21, 2011).
- [2] U.S. Department of Energy, "Office of Fossil Energy - Hydrogen Program Plan," 2003.
- [3] Thomas, S., Zalbowitz, M., "Fuel Cells: Green Power," 2006.
- [4] Miller, M., Bazylak, A., "A review of polymer electrolyte membrane fuel cell stack testing," *Journal of Power Sources* 2011, 196, 601-613.
- [5] Brust, M., Walker, M., Bethell, D., Schiffrin, D., Whyman, R., "Synthesis of Thiol-derivatised Gold Nanoparticles in a Two-phase Liquid-Liquid System," *Journal of the Chemical Society, Chemical Communications* 1994, 801-802.
- [6] Andreeva, D., Tabakova, T., Idakiev, V., Christov, P., Giovanoli, C., "Au/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> catalyst for water- gas shift reaction prepared by deposition-precipitation," *Applied Catalysis, A: General* 1998, 169, 9-14.
- [7] Daniel, M., Astruc, D., "Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size- Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology," *Chemical Reviews* 2004, 104, 293-346.
- [8] Wang, B., "Recent development of non-platinum catalysts for oxygen reduction reaction," *Journal of Power Sources* 2005, 152, 1-15.
- [9] Maye, M., Lou, Y., Zhong, C., "Core-Shell Gold Nanoparticle Assembly as a Novel Electrocatalyst of CO Oxidation," *Langmuir* 2000, 16, 7520-7523.
- [10] Maye, M., Kariuki, N., Luo, J., Njoki, P., Wang, L., Naslund, Y., Zhong, C., "Electrocatalytic Reduction of Oxygen: Gold and Gold-Platinum Nanoparticle Catalysts Prepared by Two-Phase Protocol," *Gold Bulletin* 2004, 37, 3-4.
- [11] El-Deab, M., Ohsaka, T., "An extraordinary electrocatalytic reduction of oxygen on gold nanoparticles-electrodeposited gold electrodes," *Electrochemistry Communications* 2002, 4, 288-292.
- [12] Steele, B., Heinzel, A., "Materials for fuel cell technologies," *Nature* 2001, 414, 345-352.
- [13] Bond, G., Thompson, D., "Catalysis by Gold," *Catalysis Reviews, Science and Engineering* 1999, 41, 319-388.
- [14] Haruta, M., Kobayashi, T., Sano, H., Yamada, N., "Novel Gold Catalysts for the Oxidation of Carbon Monoxide at a Temperature far Below 0°C," *Chemistry Letters* 1987, 405-408.
- [15] Valden M., Lai, X., Goodman, D., "Onset of Catalytic Activity of Gold Clusters on Titania with the Appearance of Nonmetallic Properties," *Science* 1998, 281, 1647-1650.
- [16] KSV NIMA, "Langmuir and Langmuir-Blodgett Deposition Troughs."
- [17] Costamagna, P., Srinivasan, S., "Quantum jumps in the PEMFC science and technology from the 1960s to the year 2000 Part I. Fundamental scientific aspects," *Journal of Power*

Sources 2001, 102, 242-252.

- [18] Mukerjee, S., Lee, S., Ticianelli, E., McBreen, J., Grgur, B., Markovic, N., Ross, P., Giallombardo, J., De Castro, E. "Investigation of Enhanced CO Tolerance in Proton Exchange Membrane Fuel Cells by Carbon Supported PtMo Alloy Catalyst," *Electrochemical and Solid-State Letters* 1999, 2, 12-15.
- [19] Kissinger, P., Heineman, W., "Cyclic Voltammetry," *Journal of Chemical Education* 1983, 60, 702-706.
- [20] "Compare Fuel Cell Vehicles Side-by-Side," [fueleconomy.gov](http://www.fueleconomy.gov/feg/fcv_sbs.shtml), U.S. Environmental Protection Agency, [http://www.fueleconomy.gov/feg/fcv\\_sbs.shtml](http://www.fueleconomy.gov/feg/fcv_sbs.shtml) (Accessed September 22, 2011).
- [21] U.S. Department of Energy, "Platinum Availability and Economics for PEMFC Commercialization," 2003.
- [22] Chu, D., Jiang, R., "Comparative studies of polymer electrolyte membrane fuel cell stack and single cell," *Journal of Power Sources* 1999, 80, 226-234.
- [23] Bonnet, C., Didierjean, S., Guillet, N., Besse, S., Colinart, C., Carr, P., "Design of an 80 kWe PEM fuel cell system: Scale up effect investigation," *Journal of Power Sources* 2008, 182, 441-448.
- [24] Giddey, S., Ciacchi, F.T., Badwal, S.P.S., "Design, assembly and operation of polymer electrolyte membrane fuel cell stacks to 1 kWe capacity," *Journal of Power Sources* 2004, 125, 155-165.
- [25] Thomas, G., "Overview of Storage Development DOE Hydrogen Program," US DOE Hydrogen Program 2000 Annual Review, May 9-11, 2000, San Ramon, California.