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Synthesis and Electrochemical Analysis of PdCO/MWCNT and PdCo/GO Towards Formic Acid Fuel Cells

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Title of Project: Synthesis and Electrochemical Characterization of PdCo/MWCNT towards Formic Acid Fuel Cells

Project Abstract:

A growing global population, the technological advances being made, and the greater push towards greener energy bring a great need for alternative sources of energy. In order to keep up with ever increasing demands for energy, direct formic acid fuel cells (DFAFCs) show great promise. However, the need for a cost effective, robust and efficient anodic catalyst towards DFAFCs is still imminent. Therefore, this study aims to investigate the efficiency, conductivity, and stability of palladium and cobalt binary nanocomposites on multiwalled carbon nanotubes (MWCNTs) substrate. Three nanocomposites were synthesized with varying amounts of cobalt (0%, 10% and 15%) and a fixed amount of palladium (20%) on MWCNTs using a simple one pot synthesis utilizing sodium borohydride as a reducing agent. This allowed the palladium and cobalt nanoparticles to disperse along the carbon nanotube surface to provide greater catalytic surface area. The morphology was characterized by scanning electron microscopy (SEM) imaging technique showing the binary nanocomposites were dispersed along the carbon nanotube surface. Cyclic voltammetry (CV) was then employed for the electrochemical characterization of formic acid oxidation (FAO) using the nanocomposites in a 0.50 M HCOOH with 0.10 M H2SO4 electrolyte. A glassy carbon working electrode (GCE) was modified with a fixed amount of the nanocomposites (0.025 mg/cm2 GCE) to enable correct comparisons of the catalytic effect of various amounts of cobalt. The nanocomposites have demonstrated the direct formic acid oxidation pathway facilitated by a bifunctional effect. This along with all other electrochemical data was compared to a standard commercially available 20% palladium on carbon Pearlman catalyst.

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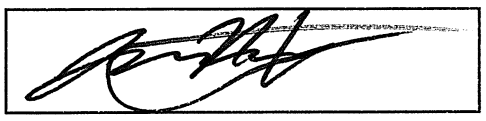
Applicant Signature: 

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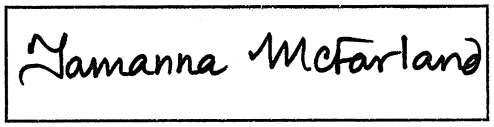
Faculty Sponsor Signature: 

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Synthesis and Electrochemical Characterization of PdCo/MWCNT towards Formic Acid Fuel Cells

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Winona State University, Chemistry Department

Abstract

With more and more technological advances being made, a growing global population, and greater push towards greener energy brings a great need for alternative sources of energy. In order to keep up with ever increasing demands for energy, direct formic acid fuel cells (DFAFCs) show great promise. However, the need for a cost effective, robust and efficient anodic catalyst towards DFAFCs is still imminent. Therefore, this study aims to investigate the efficiency, conductivity, and stability of palladium and cobalt binary nanocomposites on multiwalled carbon nanotubes (MWCNTs). Three nanocomposites were synthesized with varying amounts of cobalt and a fixed amount of palladium on MWCNTs using a simple one pot synthesis utilizing sodium borohydride as a reducing agent. This allowed the palladium and cobalt nanoparticles to disperse along the carbon nanotube surface to provide greater catalytic surface area. The morphology was characterized by scanning electron microscopy (SEM) imaging technique showing the binary nanocomposites were dispersed along the carbon nanotube surface. Cyclic voltammetry (CV) was then employed for the electrochemical characterization of formic acid oxidation (FAO) using the nanocomposites in a 0.50 M formic acid with 0.10 M sulfuric acid electrolyte. A glassy carbon electrode was modified with a fixed amount of the nanocomposites to enable correct comparisons of the effect of various amounts of cobalt. So far, the nanocomposites are demonstrating the direct

formic acid oxidation pathway. This along with all other electrochemical data will be compared to a standard commercially available 20% palladium on carbon Pearlman catalyst.

Introduction

Currently in the world technology has become a huge aspect of day to day life. Batteries are constantly increasing in use as a need for people to carry out daily tasks. Whether it's a high-tech gadget or a cell phone, the world is taking a dive into technology. The world is in constant need of energy for communication, work, and food. While the world's needs grow the technological world must try to keep up. Currently there are shortages of energy worldwide.[1] In order to help the growing need for energy, we must devise new and more efficient ways to preserve and use batteries. The main goal of the project is to synthesize an energy storage composite. More specifically, creating a high efficiency storage composite which is more resistant to degradation over time as well as cost efficient. As power storage items are charged and used, they degrade over time. Other considerations include the availability and cost of components. Cost efficient components are important as to ensure accessibility of the power cell. Currently, lithium batteries are the most common type of battery. Lithium ion batteries have a high energy density of greater or equal to 180 Wh/kg.[2] This along with a long lifecycle of over 100 recharges, makes lithium batteries favorable. However, these batteries can also at times become a safety concern. A main problem with these batteries is that they contain lithium metal and other solvents which are flammable.[3] These batteries have various safety mechanism in place although fires and overheating of the batteries remain a common occurrence.[3] The solvents used are also flammable under pressure which then become dangerous if the battery were to rupture.[3]

The method being explored in this project is using multiwalled carbon nanotubes (MWCNT) and graphite oxide (GO) as the backbones for transition metals. This method takes

advantage of the large surface area provided by the carbon support as well as its high conductivity and uses it to store energy in the metal on the surface of the nanotube.[4] The use of the support is important as it can use the metal very efficiently with less of the metal needed. This would also mean a lower production cost which is also important in making the power cell more accessible. Carbon nanotubes can also exhibit semiconducting behavior which make it very efficient as a base for the transition metal. Carbon nanotubes also have high thermal conductivity (6000W/Mk) and are stable up to 2800 C.[5] While in partnership with other studies which explore the use of palladium on GO using a simple one-pot microwave synthesis, and nickel (II) chloride hexahydrate using the same methods as in this study. This study focuses on the use of a 1:1 ratio of palladium (II) chloride, and cobalt (II) chloride hexahydrate. This study will focus on varying weight to weight percentages on the carbon nanotubes in order to determine the most effective power cells.

There are currently similar ongoing projects to create supercapacitors using a carbon nanotube base. In one study, the carbon nanotube is also taken advantage of with the use of manganese oxide.[6] Other studies also exist such as also using tin (IV) oxide.[7] While these studies prove to be promising, palladium in combination with copper still show to be a great ideal. This is due to the combination allowing for greater stability and less side reactions when in the formic acid cell.[8] The carbon nanotube also allows for a much greater dispersion for the metal oxide deposit as well as also having conductivity itself.[9,10] The preparation is also simple and energy efficient which also makes this type of fuel cell favorable.[11] This promises a high efficiency and very stable fuel cell which has potential to be applied to various needs.

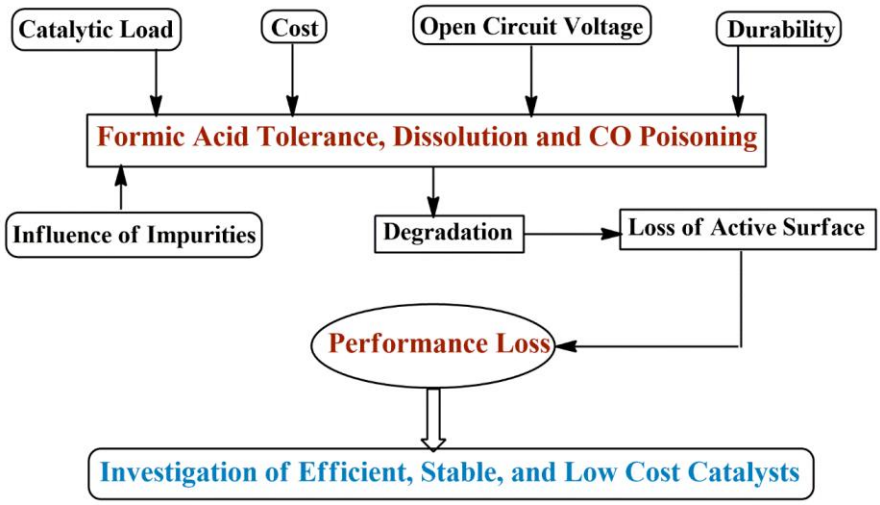

Figure 1. Research problems and justification.

With the energy crisis and environmental crisis currently in tow, this fuel cell offers a great alternative to current energy storage. A fuel cell is an electrochemical device in which a spontaneous redox reaction takes place in an electrochemical reactor that consumes a fuel (e.g., H_2, CH_3OH, C_2H_5OH, HCOOH, or other organic fuels) and an oxidant (oxygen/air) to generate electricity with efficiencies of up to 60%. Unlike a battery, a fuel cell will continue to produce electricity if the fuel is supplied. Formic acid fuel cells can be applied to solar fuel cells which can provide clean energy and can be stored and recharged over a long life span.[12] Currently battery life spans are still shorter than those of supercapacitors.[13] Formic acid is also FDA approved which makes disposal much easier and cleaner.[14] The success of this supercapacitor can aid into the steps of a cleaner more efficient future. However, the structure, morphology and physicochemical properties of an electrocatalyst could affect the performance of DFAFC and remain to be resolved further as shown in Figure 1.

Experimental Methodology

This project explores utilizing multi-walled carbon nanotubes (MWCNT) as the support for transition metal precursors to create nanocomposites. This method takes advantage of the large surface area provided by nanostructured carbon nanotubes and graphite oxide, as well as the high conductivity.[9] The use of the carbon supports will facilitate lower metal loading. This would also mean a lower production cost which is crucial in making the renewable energy sources more accessible. This study focuses on the use of 20% (w/w) anhydrous palladium (II) chloride ($PdCl_2$) and a variable amount of cobalt (II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$). The quantity of cobalt used will be varied to find an optimized quantity. Two parallel studies will be conducted- firstly, using the same one pot synthesis provided with nickel (II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$). Second project uses a modified one pot synthesis using a household microwave, and varying weight to weight percentages on the fixed amount of MWCNT and GO in order to determine the most effective nanocatalyst. If time permits, the project might also explore 10% (w/w) palladium based ternary nanomaterials.

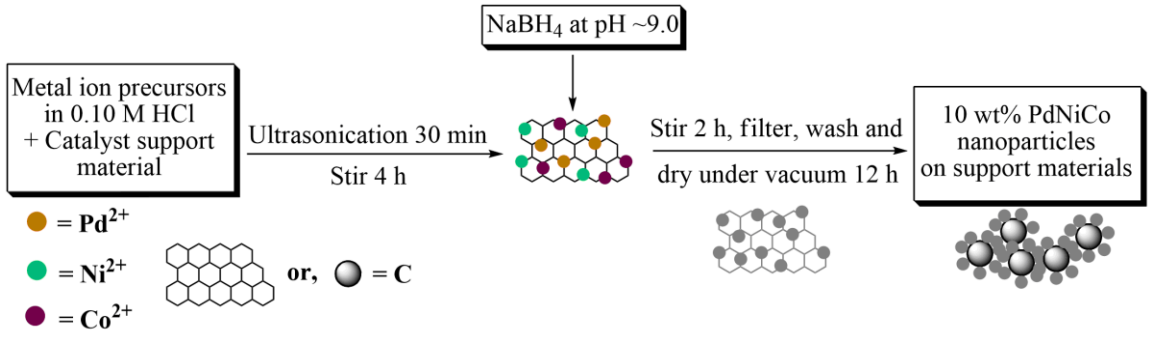

Figure 2. One pot synthesis scheme of carbon-supported nanocomposites.

The modified one pot synthesis (Figure 2) involves dissolving 20 mg of anhydrous palladium chloride with an amount of cobalt (II) chloride hexahydrate in 3.5 mL 0.10 M hydrochloric acid in a round bottom flask. MWCNT or GO (60 mg) is then added followed by 10.0 mL of Millipore

water to the mixture. The round bottom flask is then ultrasonicated for 30 min and stirred for ~4 h to ensure proper and thorough adsorption of the metal ions on the carbon support. After sonication, excess amount of sodium borohydride ($NaBH_4$) solution is added dropwise while stirring for ~2 h to completely reduce the metal ions. The resulting product is then filtered using gravity filtration and set to dry in an oven overnight. The nanocomposite is then transferred into clean and dry labeled vial and stored in a desiccator to be further analyzed as shown in Figure 3 below.

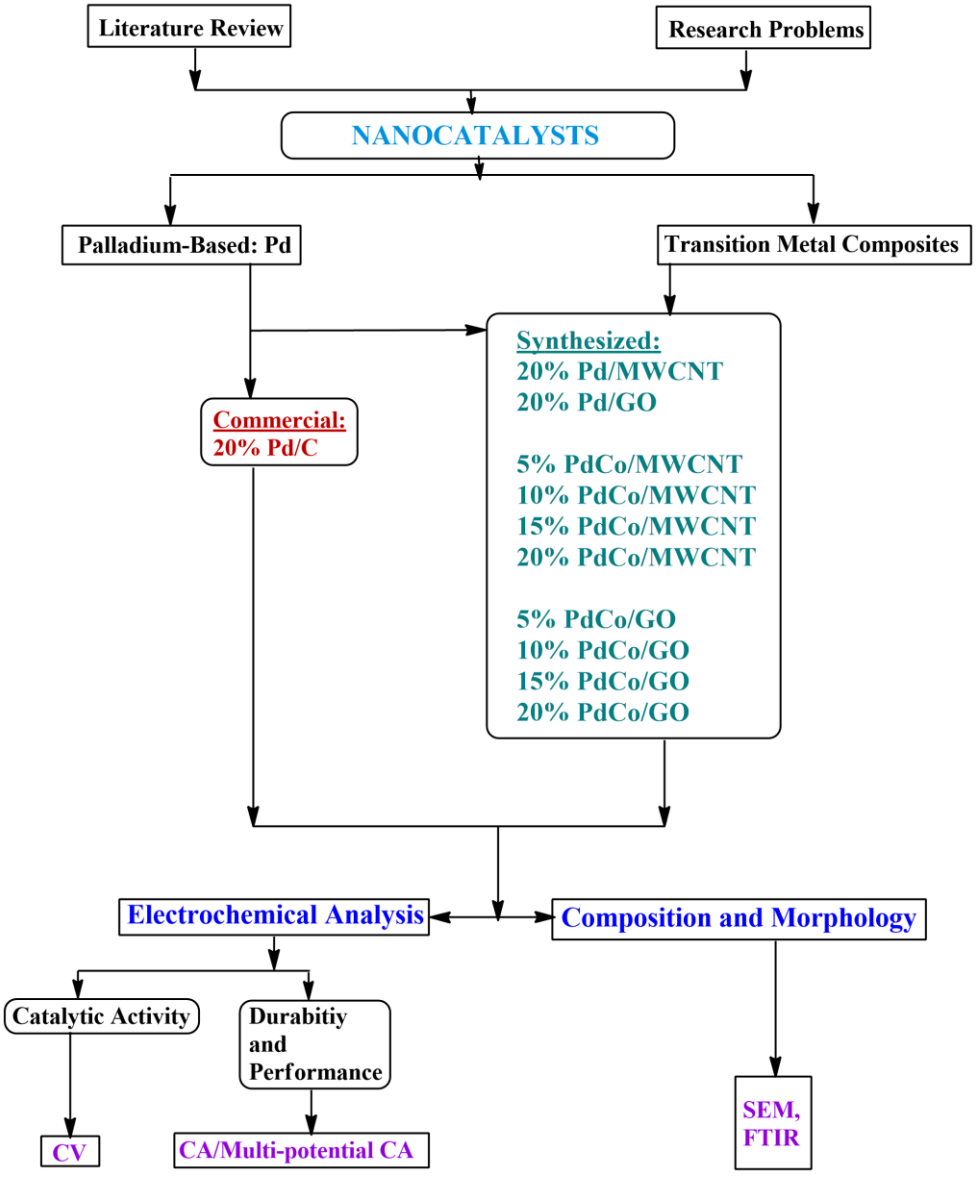

Figure 3. Research methodology.

Catalytic performance of the synthesized nanocomposites will be analyzed using cyclic voltammetry (CV) and chronoamperometric (CA) methods utilizing the CH Instruments 700E with Picoamp Booster and Faraday Cage (potentiostat). Cyclic voltammetry is an electrochemical technique which measures currents which develop in the cell where voltage is in excess of the predicted value by the Nernst equation.[15] This will allow us to determine how the cell will respond when it is charged and discharged in presence of the nanocomposites.[16] Chronoamperometric methods will be used in order to determine the amount of charges and discharges until the cell begins to degrade, i.e., the stability of the prepared materials.[17]

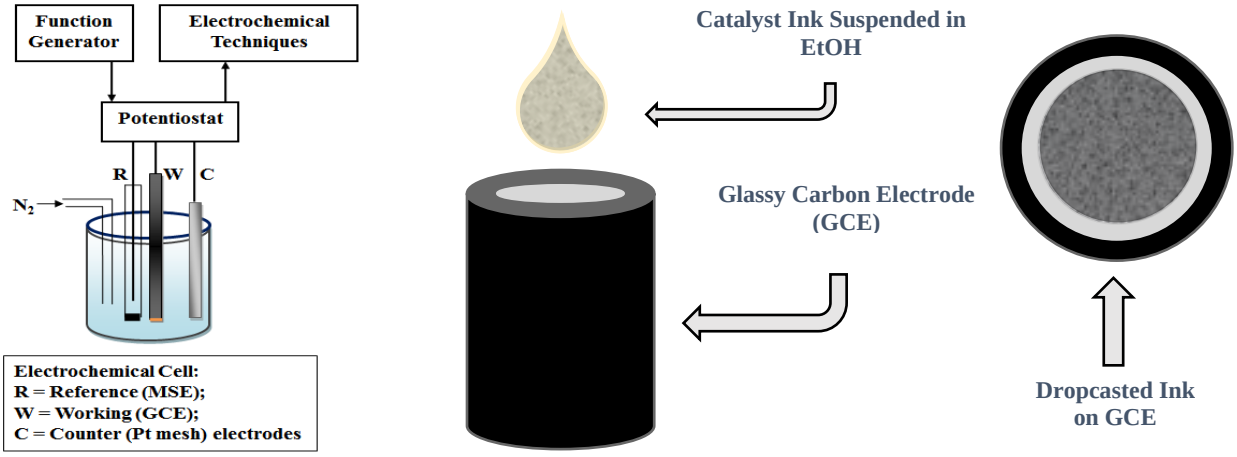

Figure 4. Experimental setup and working electrode modification scheme.

Figure 4 shows the representative experimental setup and working electrode (WE) modification scheme. Before each electrochemical experiment, the glassy carbon WE (GCE) is polished with 0.50 µm alumina slurry, rinsed with sufficient amount of Millipore water. Both working and the platinum counter electrodes are then sonicated in ethanol and Millipore water for 15 min each, respectively. The WE was dried with a Kim wipe tissue and purged with N_2 gas to blow away any dust particles. The catalysts are ultrasonically dispersed in 10 mL ethanol for 30 min to make the catalyst ink. The ink (9 µL) is then pipetted on the clean WE, and dried at room temperature for 20 min, followed by the casting of 3 µL Nafion® to the top of catalyst ink to wrap

the nanomaterials. The electrode is finally dried completely for 30 min prior to use. The prepared materials will be characterized using scanning electron microscopy (SEM) and the PerkinElmer Spectrum Two FTIR with diamond UATR accessory; ThermoScientific Nicolet iS5 FTIR with iD5 AT5 accessory (infrared spectroscopy). The SEM and FTIR will be used in order to determine the morphology and the presence of metal oxides respectively. It might additionally allow for the determination of structure and will aid regulate if the materials are at all damaged.[18]

Discussion

Table 1. Masses of $CoCl_2 \cdot 6H_2O$, $PdCl_2$, MWCNT

	0%	10%	15%
Cobalt (II) Chloride · Hexahydrate	0 mg	24.234 mg	36.351 mg
Palladium (II) Chloride	20 mg	20 mg	20 mg
MWCNT	60 mg	60 mg	60 mg

Table 1 shows the masses of each component used for all samples. The Palladium (II) chloride and MWCNT were held constant. The mass of the cobalt (II) chloride · hexahydrate was determined by weight to weight percentage based off MWCNT as shown in Calculation Set 1 below.

$$60\ mg\ MWCNT * 0.1 = 6\ mg\ cobalt\ for\ 10\%\ w/w$$

$$6\ mg\ cobalt * \frac{1\ mmol\ cobalt}{58.9332 mg cobalt} = 0.10181\ mmol\ of\ cobalt$$

$$0.10181\ mmol\ cobalt * \frac{237.93\ mg\ colbalt\ (II) \cdot hexahydrate}{1\ mmol\ colbalt\ (II)\ \cdot hexahydrate} = 24.234\ mg\ of\ cobalt\ (II) \cdot hexahydrate$$

Calculation Set 1. Calculation of Necessary Cobalt for w/w Percentages of Nanocomposites

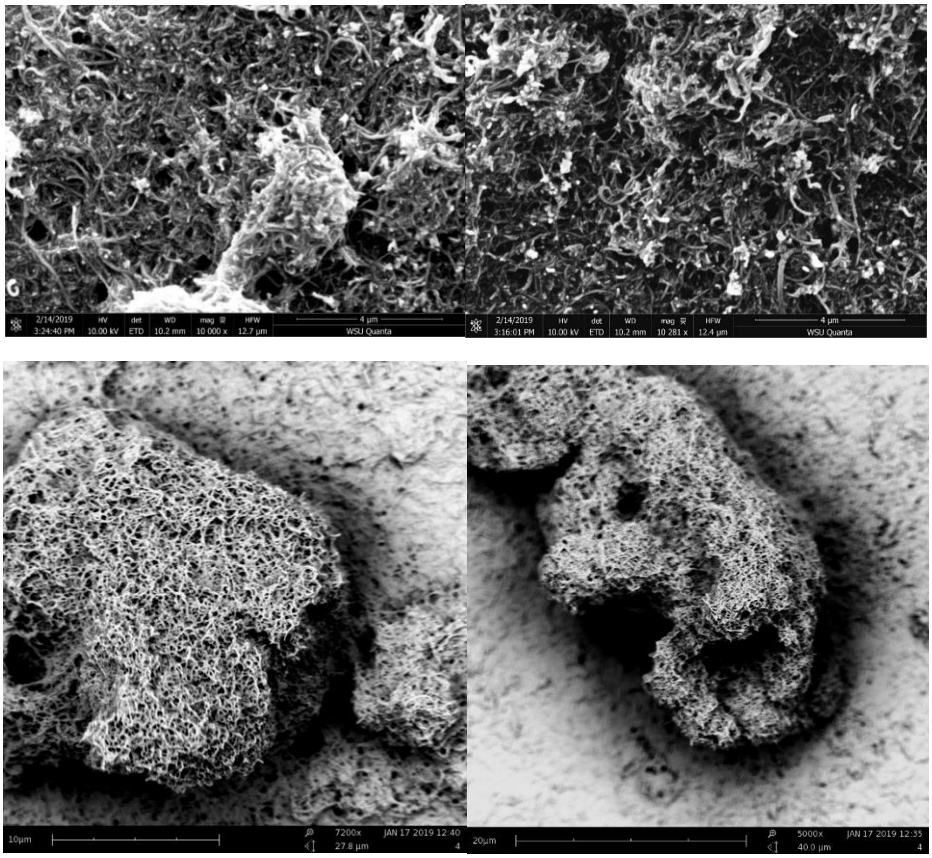

Figure 5. SEM imaging of experimental nanocomposites.

Figure 5 was obtained by using Scanning Electron Microscopy (SEM). These images were used to determine the morphology of the nanocomposites. The use of MWCNT offer a large amount of surface area. It can be assumed that the palladium and cobalt nanoparticles are spread throughout the surface of the MWCNT. Although the size does not allow for full visibility of the nanoparticles, their presence may be supported through electrochemical analysis.

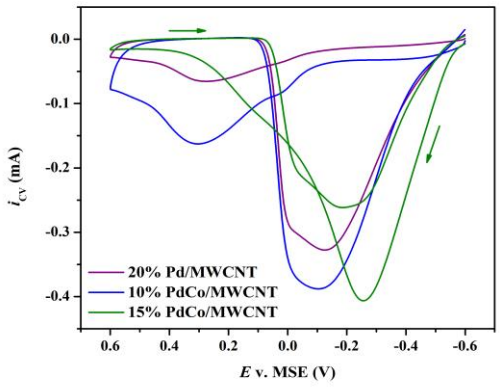

Figure 6. 1st Sweep Cycle of Experimental Nanocatalysts

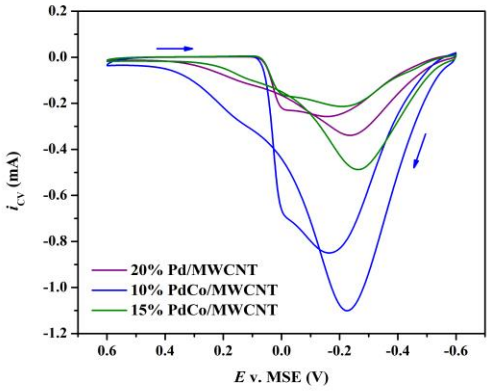

Figure 7. 25th Sweep Cycle of Experimental Nanocatalysts

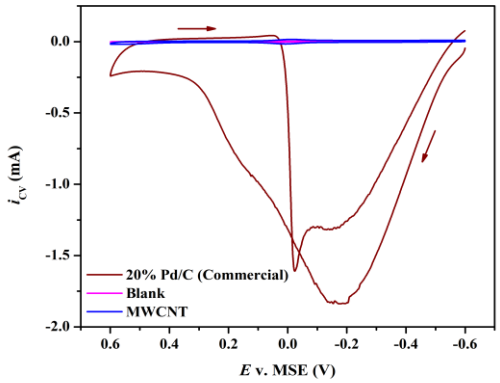

Figure 8. 1st Sweep Cycle of Pearlman Standard and Blanks

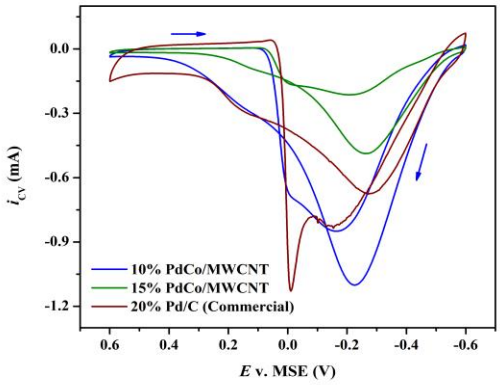

Figure 9. 25th Sweep Cycle of Experimental and Pearlman Nanocatalysts

In Figure 6, the first sweep of the three experimental nanocatalysts shows that all three samples follow the FAO pathway. Among the three, it is clear that the addition of cobalt does allow for a greater peak shift towards the negative voltage direction that explains the enhanced direct FAO. In this segment the 10% and 15% nanocatalysts are in very close range to each other with the 15% falling closer to the direct FAO pathway. Figure 7 shows the 25th sweep segment which shows that in terms of efficiency throughout lifespan, the 10% has more durability even shifting towards the direct FAO pathway over time. In Figure 8, the commercial standard is shown

against a blank run and a run with only the MWCNT showing the importance of the addition of the metals for catabolic activity. Figure 9 is a comparison of the highest performing experimental samples of the 10% and 15% nanocatalyst against the commercial standard at the 25th sweep. The 10% sample keeps up with the commercial standard very well showing very similar results. The 10% also shows exceptional performance in that it may carry more current than the commercial standard after prolonged cycling while still remaining in the direct FAO pathway. All CV's were collected with a constant catalytic load of 0.025 mg/cm^2 of GCE.

Conclusion

Based on results seen on the CV, Pd/MWCNT and PdCo/MWCNT nanocatalysts were successfully synthesized via a simple one pot synthesis. Morphology was characterized by the use SEM microscopy. The CV indicates that Co is a stabilizer for formic acid oxidation in the binary system with improved performance in comparison to the experimental and commercial monosystem. Further studies may include variations in the w/w percentage of PdCo to determine the optimum ratio. The use of other abundant transition metals may also be studied. Different diameters and lengths of MWCNT may also use to vary morphology and surface area available for dispersion.

Acknowledgements

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