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Investigation of Binary Nanocomposites Towards High performance Fuel Cells and Supercapacitor Applications

Frank Beissel
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Student Name: Frank Beissel

Student Email: fu0996ke@winona.edu

Student Major: ACS Chemistry Education

Faculty Sponsor: Tamanna McFarland

Faculty Sponsor Email: tshanta@winona.edu

Title of Project: Investigation of Binary Nanocomposites towards High-Performance Fuel Cells and Supercapacitative Applications

Project Abstract:

Energy demands continue to grow with a rapidly increasing demand for portable energy sources that exceed the current standards that are in circulation with every new electronic device on the market in an ever-growing global economy. A method commonly investigated are materials with supercapacitance capabilities towards energy storage. Supercapacitors surpass normal fuel cells with a significantly higher number of charge and discharge cycles, the ability to reach a high charge density rapidly, and more readily transferring stored energy. To the end of investigating potential supercapacitor materials, two binary metal nanocomposites were constructed with varying ratios of nickel (10% and 15%) and a fixed amount of palladium (20%) dispersed in multiwalled carbon nanotubes (MWCNTs) support material in a one-pot synthesis before being reduced with a large excess sodium borohydride. 20% palladium nanomaterials on the MWCNTs were also synthesized for comparing the effect of adding the earth abundant and cost-effective nickel with the palladium. Scanning electron microscopy (SEM) was utilized to observe the resulting surface texture of the nanocomposites that demonstrates the uniform dispersion of the nanomaterials on the MWCNTs. The capacitance of the materials was tested using a modified glassy carbon working electrode (GCE). A cyclic voltammogram (CV) analysis elucidated the super-capacitative activity and stability of the synthesized PdNi/MWCNT nanocomposites in a 0.10 M potassium nitrate (KNO3) electrolyte solution with a constant material load of 0.025 mg/cm2 GCE. The nanocomposites were compared to the commercially available 20% Pd/C Pearlman catalyst. Cyclic voltammograms have shown promising super-capacitative behavior of the PdNi/MWCNT nanocomposites v. Pd/MWCNT.

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Investigation of Binary Nanocomposites towards Supercapacitor Applications

Frank Beissel, Dr. Tamanna McFarland

Winona State University, Chemistry Department

Abstract

Energy demands continue to grow with a rapidly increasing demand for portable energy sources that exceed the current standards that are in circulation with every new electronic device on the market in an ever-growing global economy. A method commonly investigated are materials with supercapacitance capabilities towards energy storage. Supercapacitors surpass normal fuel cells with a significantly higher number of charge and discharge cycles, the ability to reach a high charge density rapidly, and more readily transferring stored energy. To the end of investigating potential supercapacitor materials, two binary metal nanocomposites were constructed with varying ratios of nickel (10%, and 15%) and a fixed amount of palladium (20%) dispersed in multiwalled carbon nanotubes (MWCNTs) support material in a one-pot synthesis before being reduced with a large excess sodium borohydride. 20% palladium nanomaterials on the MWCNTs were also synthesized for comparing the effect of adding the earth abundant and cost-effective nickel with the palladium. Scanning electron microscopy (SEM) was utilized to observe the resulting surface texture of the nanocomposites that demonstrates the uniform dispersion of the nanomaterials on the MWCNTs. The capacitance of the materials was tested using a modified glassy carbon working electrode (GCE). A cyclic voltammogram (CV) analysis elucidated the super-capacitative activity and stability of the synthesized PdNi/MWCNT nanocomposites in a 0.10 M potassium nitrate (KNO_3) electrolyte solution with a constant material load of 0.025 mg/cm^2 GCE. The nanocomposites were compared to the commercially available 20% Pd/C Pearlman catalyst. Cyclic voltammograms have shown promising super-capacitative behavior of the PdNi/MWCNT nanocomposites v. Pd/MWCNT.

Introduction

Apple Inc. reported $62.9 billion in the 2018 fourth quarter an increase of 20% in one year.[1] Tesla Inc.'s Model S has only 335 miles maximum driving range.[2] These two statistics have a common factor- they are both about companies built around products that have an integrated lithium ion battery. Due to their increasing use, batteries are constantly being spent and discarded. Much of which does not go through proper channels and ends up in landfills. The United States environmental protection agency (US EPA) reported that 3.1 million tons of consumer electronics, some of which use or contain batteries, were put into landfills in 2015.[3] This is clearly a serious issue, worsened further by that batteries, and their associated devices, are considered hazardous waste by the US EPA.[4] Lithium ion batteries have a cycle life of several hundred charges and a high charge density (≥180 Wh/kg).[5] The batteries are also extremely hazardous if ruptured as they contain pressurized, flammable electrolyte.[6] Large lithium ion batteries, such as those used for electric vehicles, can take up to five hours to fully charge.[7]

While portable energy sources are in demand, so are renewable ones. As said earlier, millions of tons of batteries are put into landfills every year, solar and fuel cells have great potential towards greatly reducing that number. 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. Additionally, solar cells have the potential to create infinite, clean energy and many fuel cells have reversible reactions that can result in an almost zero emission energy source.[8] This is possible through the use of a supercapacitor which have a higher charge density than capacitors, but significantly lower than a fuel cell. Additionally, they have a very long lifespan, up to 1,000,000 charge and discharge cycles.[9]

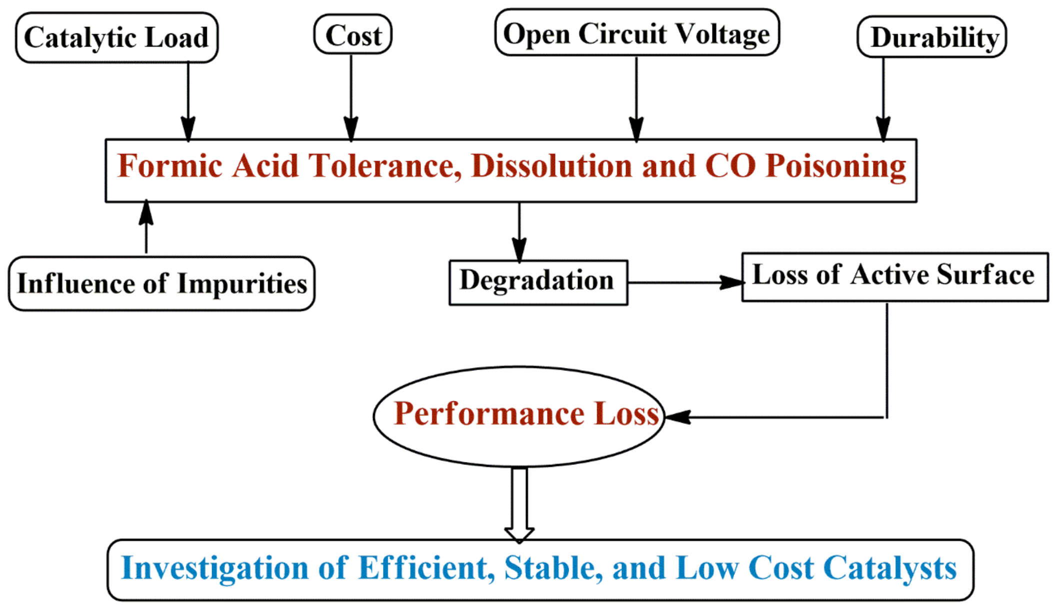

Figure 1. Research problems and rationale.

Combined, these two balances out the failings of the other and accentuate the successes, but the issue remains that the fuel cell still falls behind the solar cell in terms of renewability. A potential solution is what is being investigated in this research: highly efficient palladium and earth abundant transition metal-based binary nanoparticles decorated carbon support structures as the anodic nanocatalysts towards their use as anodic catalyst for direct formic acid fuel cell and as the supercapacitors for potential solar cell application to mitigate the eminent energy crisis of the 21st century.

Research 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, as well as the high conductivity.[10] 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. 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.[11] This study focuses on the use of 20% (w/w) anhydrous palladium (II) chloride ($PdCl_2$) and a variable amount of nickel (II) chloride hexahydrate ($NiCl_2$•6 H_2O). The quantity of nickel used will be varied to find an optimized quantity. Two parallel studies will be conducted- firstly, using the same one pot synthesis provided with cobalt (II) chloride hexahydrate ($CoCl_2$ • H_2O). The second uses a modified one pot synthesis using a household microwave, and varying weight to weight percentages on the fixed amount of MWCNT in order to determine the most effective nanocatalyst.

Supercapacitors similar to the ones being researched in this project are currently under development. Other researchers have used different metal oxide catalysts, like tin (IV) oxide,[13] and yet other research is investigating variations of the carbon support structure.[13,14] While the tin (IV) oxide is a promising oxide for energy cells in general, the combination of palladium and nickel or cobalt might be promising, cost efficient, and effective nanocatalysts. As for carbon supports, both Fan et. al. and Zhu et. al. examine solid carbon supports with a rigid macrostructure; whereas this project investigates MWCNT that is ideal as it allows for more of the metal oxides to be deposited on the support.

With the energy crisis and environmental crisis currently in tow, these nanocomposites would offer a great alternative to the ongoing search for efficient materials for renewable energy sources. 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.[15] Currently battery life spans are still shorter than those of supercapacitors.[16] Moreover formic acid is FDA approved which makes it less toxic, easy to dispose and a greener fuel.[17] The success of this supercapacitor can aid into the steps of a cleaner more efficient future.

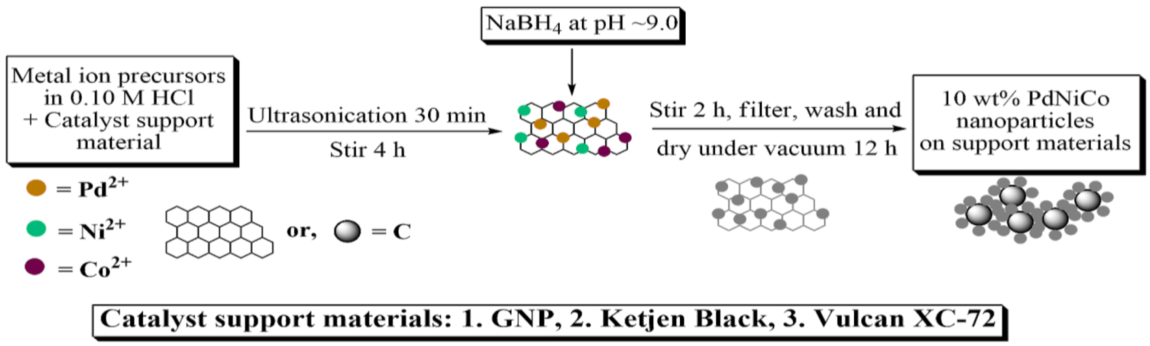

Figure 2. One pot synthesis scheme of carbon-supported nanocomposites.

The one pot synthesis (Figure 2) involves dissolving 20 mg of anhydrous palladium chloride with an amount of cobalt (II) chloride hexahydrate or nickel (II) chloride hexahydrate in 3.5 mL 0.10 M hydrochloric acid in a round bottom flask to create a trinary system. While only a binary system was investigated in this study, the trinary system shown is a potential avenue for future research based on of parallel research done. MWCNT (60.0 mg) is then added followed by 10.0 mL of Millipore water to the mixture. The round bottom flask is then ultrasonicated for 30 minutes and stirred for ~4 hours to ensure proper and thorough adsorption of the metal ions on the carbon support. After sonication, excess sodium borohydride ($NaBH_4$) solution is added dropwise while stirring for ~2 hours 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 in the future.

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.[16] This will allow us to determine how the cell will respond when it is charged and discharged in presence of the nanocomposites.[17] 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.[18]

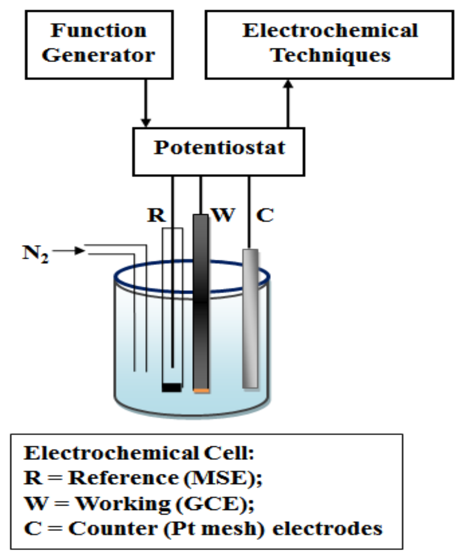

Figure 3. Experimental setup. All potentiostat measurements were conducted in a faraday cage.

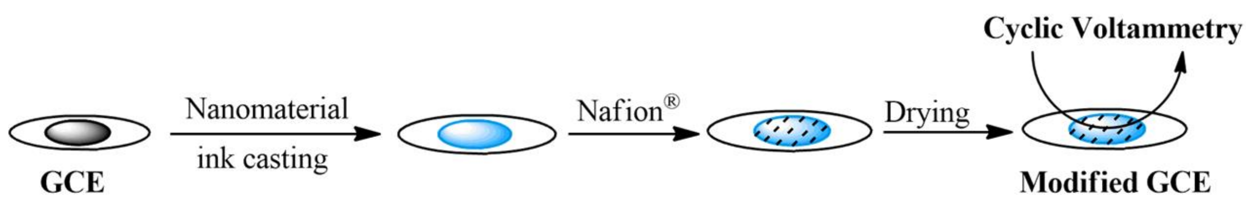

Figure 4. Working electrode modification scheme. Nanomaterial inks were created as to maintain a constant load using a ratio of 2 mg of catalyst dispersed into 5 ml of 100% ethanol.

Figure 3 shows the representative experimental setup and Figure 4 shows the working electrode (WE) modification scheme. Before each electrochemical experiment, the WE is polished with 0.50 µm alumina slurry, rinsed with sufficient amount of Millipore water. Both working and counter electrodes are then sonicated in ethanol and Millipore water for 15 min each, respectively. The WE was dried with a Kimwipes 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 cyclic voltammetry (CV). The SEM and CV will be used in order to determine the morphology and the presence of metal oxides respectively.

Discussion

Upon completion of the synthetic procedures, SEM was used to examine the morphology of the MWCNT. As seen in Figure 5, the nanostructure is highly porous, which is favorable for higher adsorption of the metal oxides onto the walls of the MWCNT, with the tubes being visible.

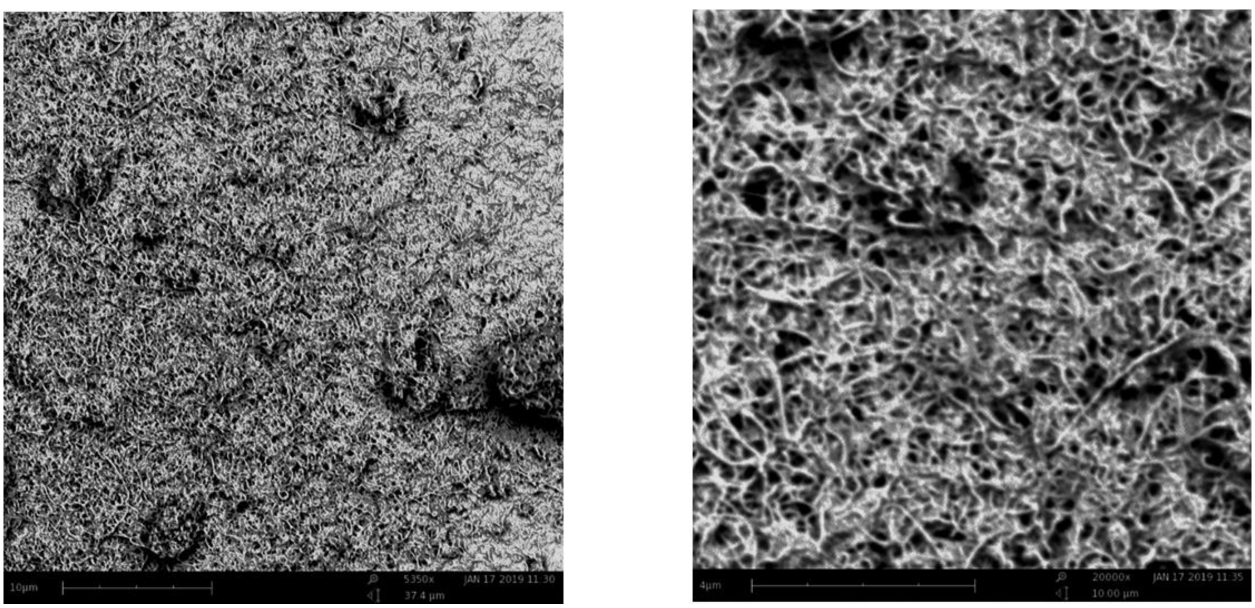

Figure 5. SEM images of synthesized nanocatalysts. Right shows a magnification of 5350x. Left shows a magnification 20,000x.

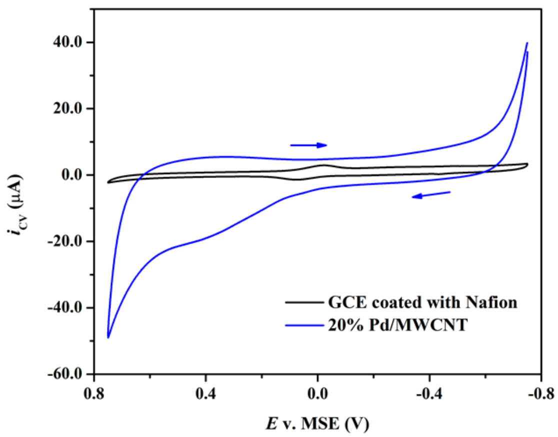

Figure 9. Sample blank v. mono-system.

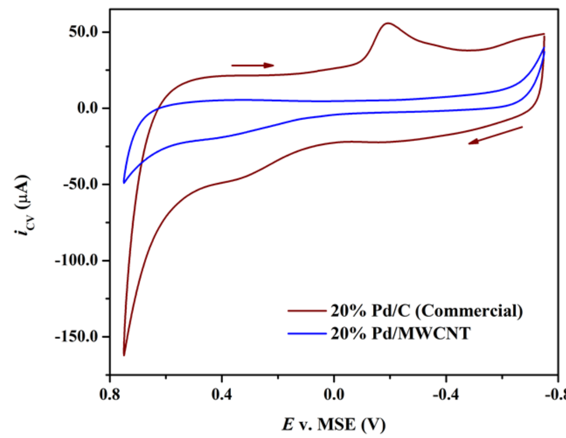

Figure 6. Mono-system v. Pearlman's catalyst.

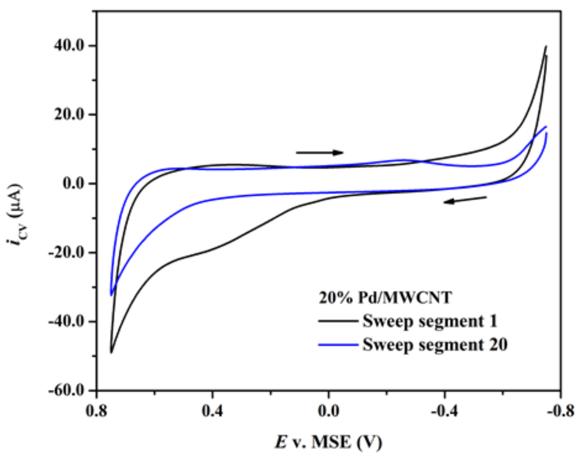

Figure 7. Degradation of the Pd mono-system.

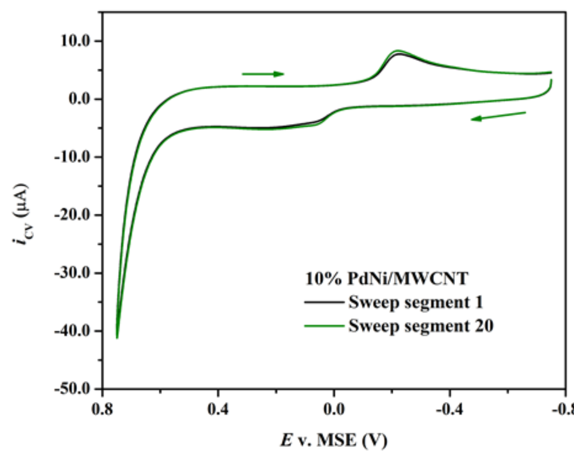

Figure 8. Stability of 10% PdNi/MWCNT.

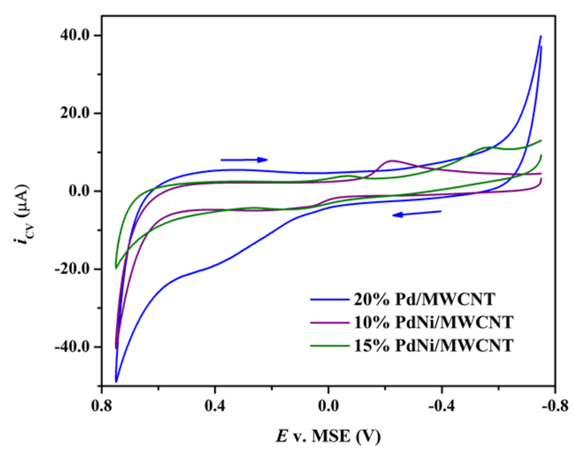

Figure 10. Comparison of synthesized nanocomposites.

As seen in Figure 7, the sample containing Pd/MWCNT has a rectangular shape from approximately 0 to -0.4 V, and as seen in Figure 7, the shape converges to a rectangular shape by the 20th sweep segment of CV. Figures 7 and 8 serve to emphasize the synergetic effect of Ni on the binary system. In Figure 8 it can be seen that the area within the cyclic voltammogram decreasing significantly between the 1st and 20th sweep segment, approximately 30 minutes. Figure 9 indicates that the area change between the 1st and 20th sweep segments in negligible in the binary system. Figure 10 includes all synthesized nanocomposites on the same voltammogram as to compare the three. It can be seen that all three have similar areas within the curves implying that the Pd may be responsible for the amperage range in the mono and binary systems. This in combination with Figures 8 and 9 the effect of Ni can be correlated to the increased stability of the electrochemical cell.

Conclusion

Based on the CV, PdNi/MWCNT and Pd/MWCNT supercapacitors were successfully synthesized via a simple one pot method. SEM imaging was used to characterize the morphology of the catalysts synthesized. CV indicates that the binary systems have a stabilizing effect on the charge and discharge cycles. With Ni being identified as a stabilizer in the electrochemical cell, future research will need to investigate ways increase the current range for the cell. Based on the results of this investigation further research will have to examine the effect of Ni in a DFO cell. Additionally, there could be an emphasis on other transition metals to search for one with a greater synergistic effect. Another option is different carbon support materials as the Pearlman's catalyst greatly outperformed the synthesized equivalent. This research may also include a trinary or ternary metal system to investigate the effects that they have on the PdNi/MWCNT cell.

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