

## **Catalysis of Oxygen Reduction Reaction with modified PtNi Nanostructures in Alkaline Medium**

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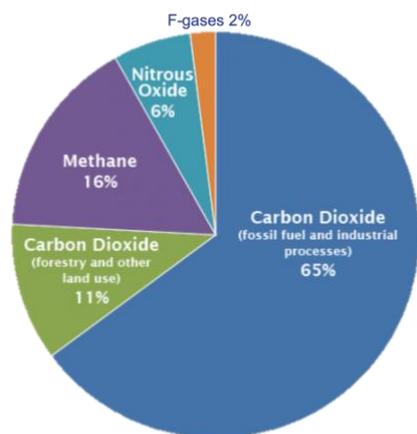
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### **Abstract**

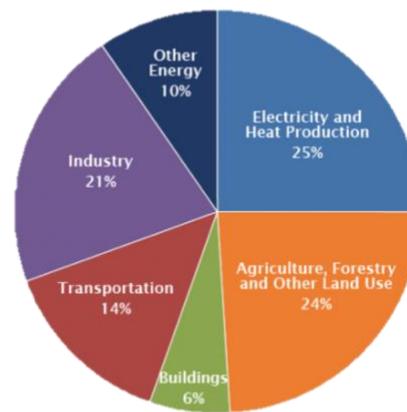
The burning of fossil fuels is one of the main causes of climate change and the consistent rise in the temperature of the global surface. Therefore, big car companies have started to invest in fuel cell technologies in order to replace their combustion engines, as fuel cells can yield the same efficiency in performance and energy output while reduction the gas emissions. The Anion Exchange Membrane Fuel Cells (AEMFCs) where the first type of fuel cell widely used as an energy source but was shortly replaced by acid-based fuel cells. These acid-based fuel cells are inefficient in ORR compared to traditional AEMFCs. Therefore, making the AEMFCs preferable as a new energy source because of the capability to use non-metals and non-precious metals as catalysts. Common catalysts used for ORR are mainly Pt/C based, however, the application of a novel bimetallic catalyst like PtNi-Nanowires (NWs), are promising alternatives. Ni-Nanoparticles (NPs) were hydrothermally synthesized and then characterized using Cyclic-Voltammograms, XRD, and TEM imaging to identify the structure of the Ni-Nanoparticles as well as identify the presence of Nickel. Then the Ni-Nanoparticles were modified with a Pt precursor to form the PtNi-NWs using the principle of spontaneous galvanic displacement, but the synthesis resulted in the making of PtNi Core Shells. A Rotating Disk Electrode (RDE) of Glassy Carbon (GC) was then modified with Ni-NPs, and PtNi Core Shells then tested individually as a catalyst for ORR. The Polarization Curves of ORR generated were used to determine and compare the current generated by the reduction of oxygen catalyzed by the different modified RDEs compared to commercial Pt/C 20% catalysts. The ORR catalyzed by synthesized PtNi Core Shells showed an  $E_{1/2}$  of 0.71 V compared to the  $E_{1/2}$  of Pt/C 20% which was 0.92 V. Since the  $E_{1/2}$  of the PtNi Core Shells was less of the Pt/C 20%, it can be concluded that the ORR reaction went through a 2e<sup>-</sup> pathway. These difference in  $E_{1/2}$  can be caused because the catalyst may have different Platinum loading. Therefore, the synthesized PtNi Core Shells did not wild comparable result to a commercially available catalyst for ORR.

## Introduction

A big problem that we are being affected by right now is Global Warming. Global warming is caused by the emissions of Green House Gases from different economy sectors. The burning of fossil fuels for heat and energy production is one of the main sectors responsible for these emissions of Green House Gases. According to EPA, greenhouse gases like CO<sub>2</sub>, Methane, and NO<sub>2</sub> in the atmosphere are the main contributor to these emissions.



Global Greenhouse Gas Emissions  
by Gas



Global Greenhouse Gas Emissions  
by Economy Sector

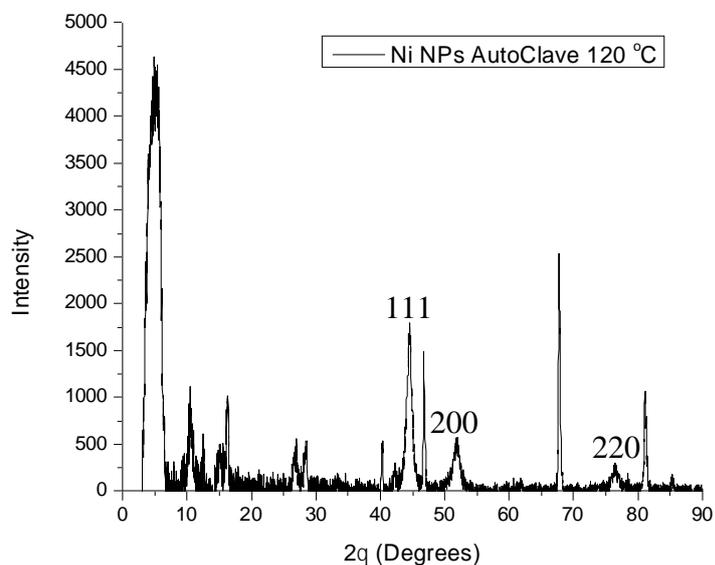
This concern has started a wave of research on alternative energy sources such as solar power, wind power, batteries, fuel cells, among others. Thanks to recent developments on alternative energies proving to have the same to better efficiencies to traditional energy sources like combustion engines, companies have started to invest in these technologies. Moreover, big car companies have started to invest in fuel cell technologies in order to replace their combustion engines, as fuel cells can yield the same energy output as combustion engines cars without creating emissions. Fuel cells are one of these alternative energy sources that harness the chemical power created in a chemical reaction. Fuel cells are made of two main parts where the reactions take place separated by a solution. These parts are the anode, where the oxidation of a reactant takes place, and the cathode, where the reduction takes place. Moreover, they are different types of fuel cells that work with different fuels and uses different solutions. Among all the different types of fuel cells, the Anion Exchange Membrane Fuel Cells (AEMFCs) is one of the most efficient, but least studied.



## Results

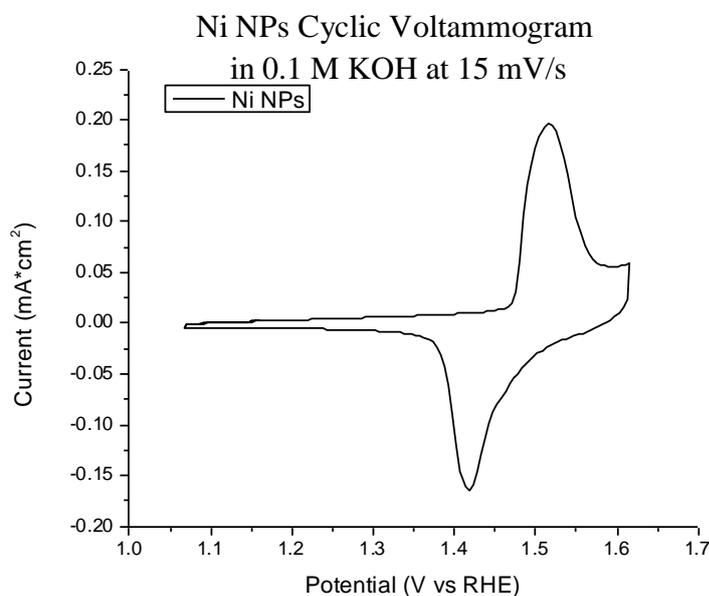
### Nickel Nanostructures

- **Synthesized Nickel Nanoparticles Characterization:**
  - **Powder X-ray Diffraction Pattern**



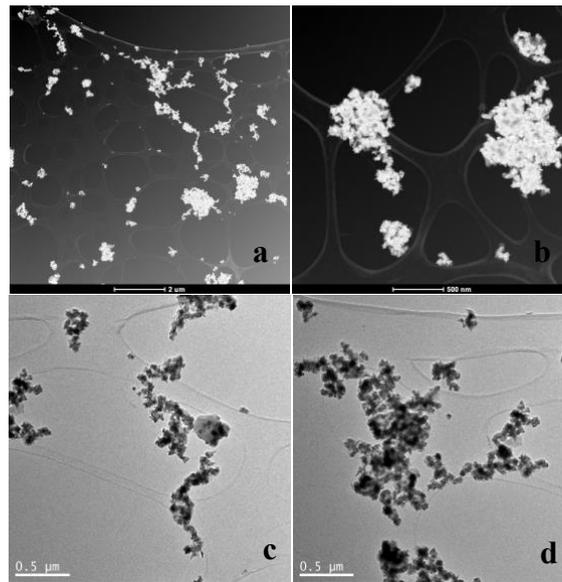
Powder X-ray Diffraction of Nickel Nanoparticles that confirms the crystalline presences of metal Nickel. The Braggs reflection at  $2\theta$  value at approximately  $44^\circ$ ,  $52^\circ$ , and  $76^\circ$  are characteristic for the 111, 200 and 220 facets respectively.

- **Cyclic Voltammetry**



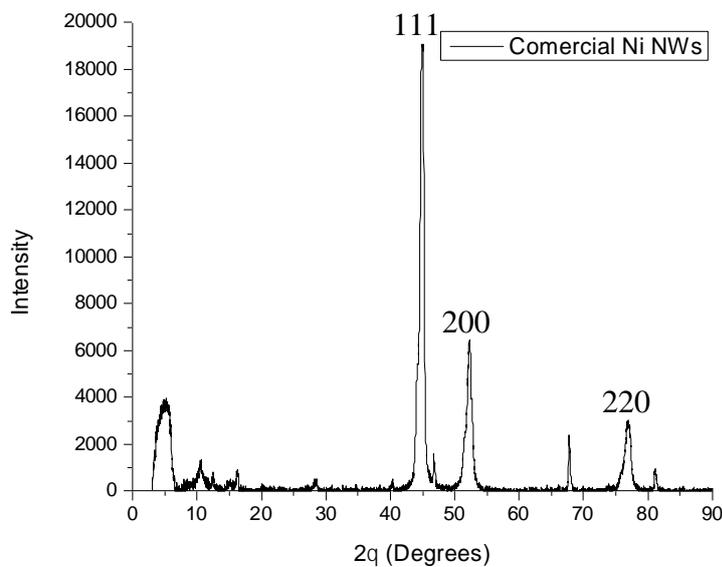
The voltammogram was obtained modifying the surface of a Glassy Carbon RDE with the synthesized Nickel Nanoparticles after purging the solution with Ar for 10 minutes.

- **Transmission Electron Microscopy**



TEM images for synthesized Nickel Nanostructures. **a)**, **b)**, **c)**, and **d)** Shows the presence of Ni NPs with different sizes, confirming that the Ni NWs were not formed.

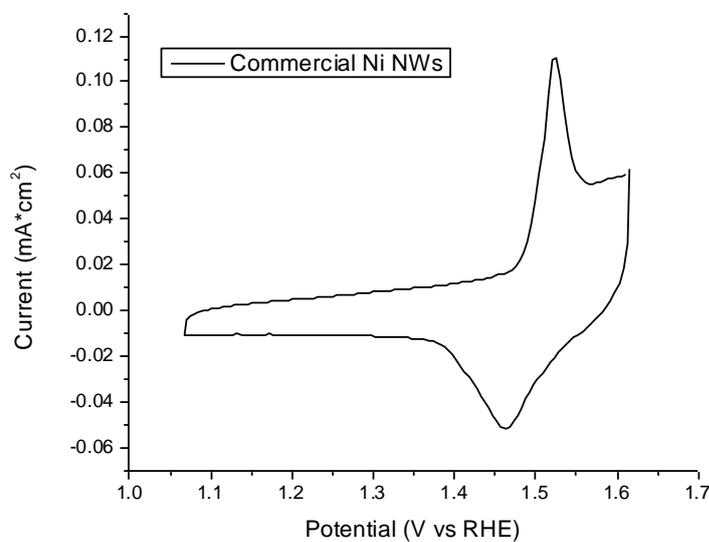
- **Commercials Nickel Nanowires Characterization:**
  - **Powder X-ray Diffraction Pattern**



Powder X-ray Diffraction of Nickel Nanowires that confirms the crystalline presences of metal Nickel. The Braggs reflection at  $2\theta$  value at approximately  $44^\circ$ ,  $52^\circ$ , and  $76^\circ$  are characteristic for the 111, 200 and 220 facets respectively.

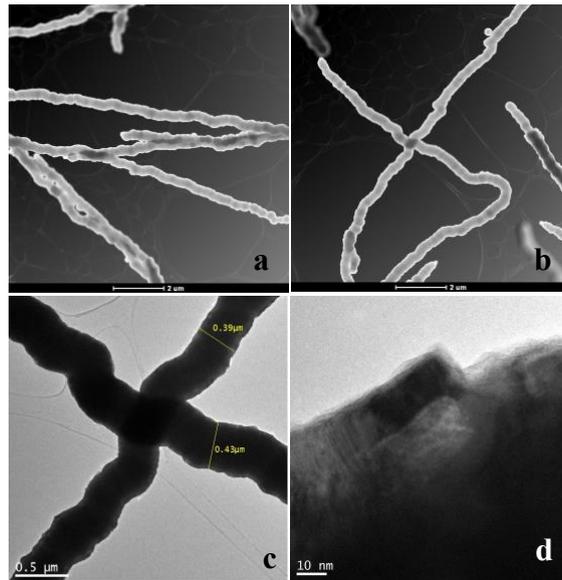
- **Cyclic Voltammetry**

Commercial Ni NWs Cyclic Voltammogram  
in 0.1 M KOH at 15 mV/s



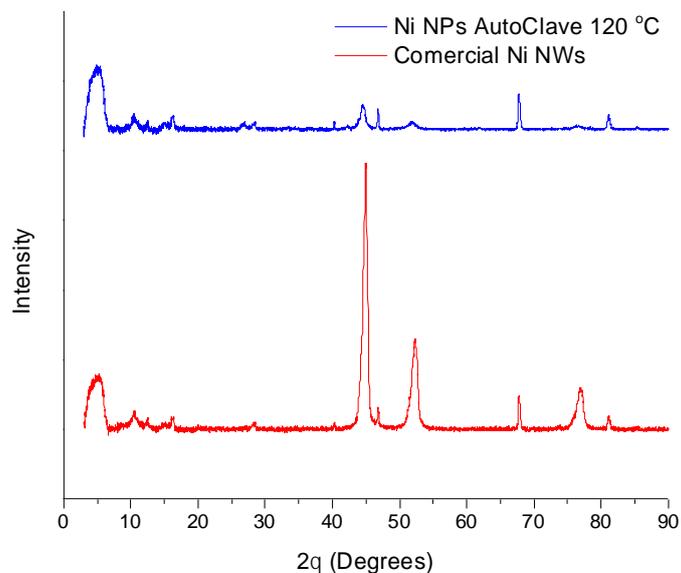
The voltammogram was obtained modifying the surface of a Glassy Carbon RDE with the commercial Nickel Nanowires after purging the solution with Ar for 10 minutes.

- **Transmission Electron Microscopy**



TEM images for commercial Nickel NWs. **a)**, **b)**, **c)**, and **d)** Shows the presence of Ni NWs with diameters between 300 nm and 400 nm. These commercial Ni NWs are too big and thick to make HRTEM.

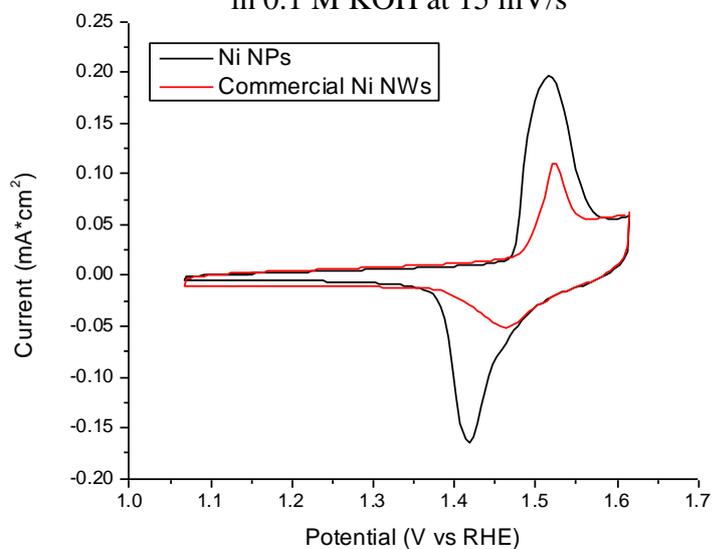
- **Comparison of Nickel Structure**
  - **Powder X-ray Diffraction Pattern**



Powder X-ray Diffraction of Nickel Nanowires compared to the Commercial Nickel Nanoparticles. This confirms the crystalline presences of metal Nickel in both samples since they have similar diffraction patterns.

- **Cyclic Voltammetry**

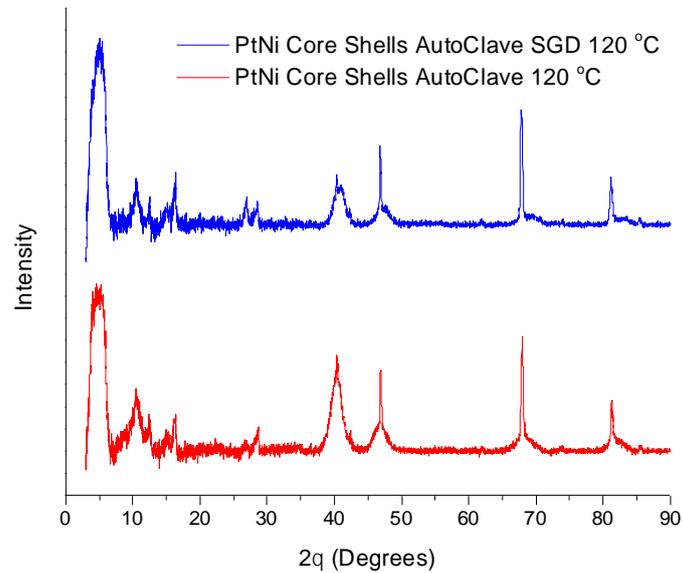
Ni NPs & Commercial Ni NWs Cyclic Voltammogram  
in 0.1 M KOH at 15 mV/s



The voltammogram was obtained modifying the surface of a Glassy Carbon RDE with the synthesized Nickel Nanoparticles and the with the commercial Nickel Nanowires after purging the solution with Ar for 10 minutes.

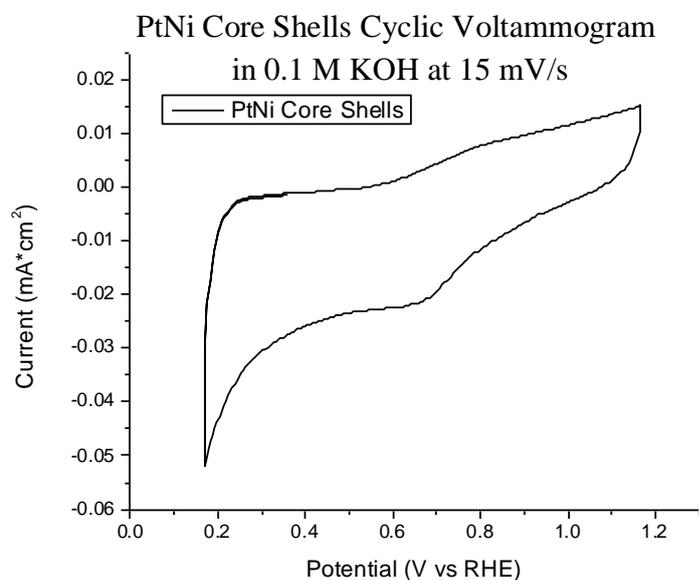
## PtNi Nanostructures

- **PtNi Core Shell with Synthesized Nickel Nanoparticles Characterization:**
  - **Powder X-ray Diffraction Pattern**



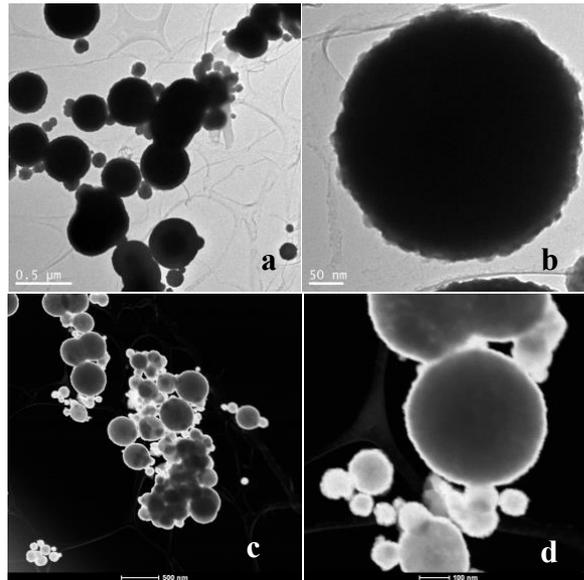
Powder X-ray Diffraction of PtNi Core Shells synthesized using Spontaneous Galvanic Displacement (SGD) and Hydrothermal in an AutoClave at 120 °C. This confirms the crystalline presences of metal PtNi Core Shells in both samples since they have similar diffraction patterns.

- **Cyclic Voltammetry**



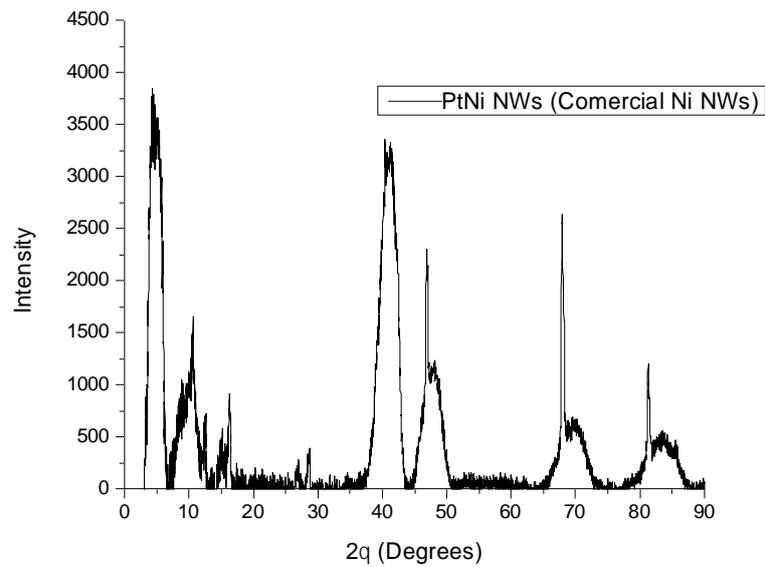
The voltammogram was obtained modifying the surface of a Glassy Carbon RDE with the synthesized PtNi Core Shells after purging the solution with Ar for 10 minutes.

- **Transmission Electron Microscopy**



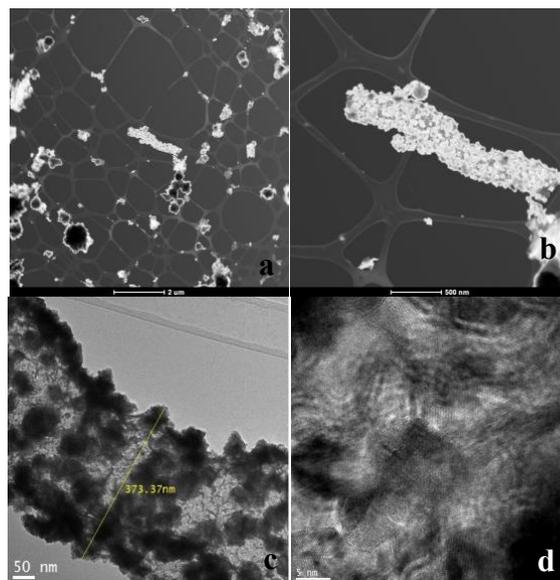
TEM images for synthesized PtNi Nanostructures. **a)**, **b)**, **c)**, and **d)** Shows the presence of spheres of PtNi Core Shells with sizes between 100 nm and 500 nm. The core of the spheres looks to be solid, and possibly be Nickel. Therefore, confirming the formation of Core Shells.

- **PtNi Nanowires with Commercial Nickel Nanowires Characterization:**
  - **Powder X-ray Diffraction Pattern**



Powder X-ray Diffraction of PtNi NWs synthesized. This confirms the crystalline presences of metal PtNi NWs in the samples.

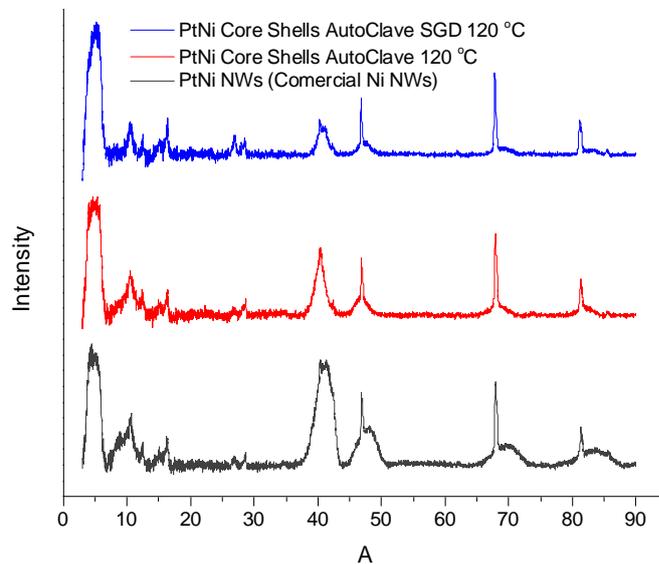
- **Transmission Electron Microscopy**



TEM images for PtNi NWs with Commercial Nickel NWs. **a)** Shows the presence of few PtNi NWs with different diameters around 300 nm and 400 nm, and lengths. **b)**,

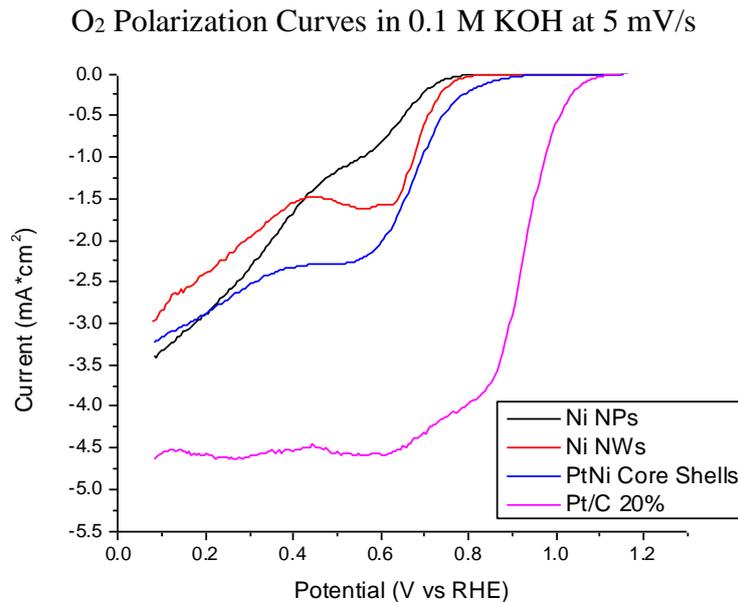
**and c)** A higher magnification image where the bright spots should be Nickel and the darker spots should be Platinum. **d)** Even higher magnification of the PtNi NWs.

- **Comparison of PtNi Nanostructures**
  - **Powder X-ray Diffraction Pattern**



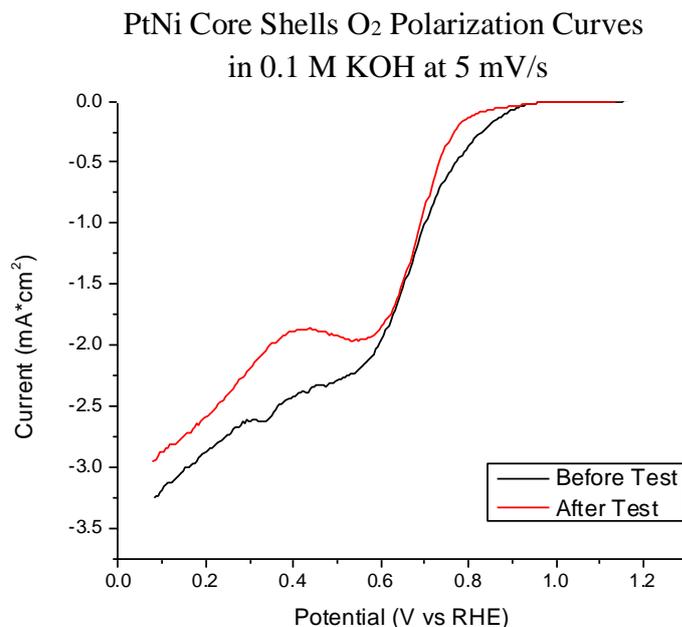
Powder X-ray Diffraction of PtNi Core Shells synthesized using Spontaneous Galvanic Displacement (SGD) and Hydrothermal in an AutoClave at 120 °C compared to the PtNi NWs with commercial Nickel NWs. This confirms the crystalline presences of metal PtNi in all samples since they have similar diffraction patterns even though the different nanostructures.

- **Oxygen Reduction Reaction Experiment:**



The O<sub>2</sub> Polarization Curves was obtained after purging the solution with O<sub>2</sub> for 15 minutes. The Nickel NPs, Commercial Nickel NWs, and PtNi Core Shells were compared to Commercial Pt/C 20% for their catalytic performance.

- **Durability & Stability Experiment:**



The black O<sub>2</sub> Polarization Curves was obtained after purging the solution with O<sub>2</sub> for 15 minutes before running a cyclic voltammetry with 1000 segments at 230 mV/s. The red O<sub>2</sub> Polarization Curves was obtained after purging the solution with O<sub>2</sub> for 15 minutes and after the cyclic voltammetry with 1000 segments at 230 mV/s.

## **Conclusion**

- **Powder X-ray Diffraction Patterns**

X-ray diffraction patterns were analyzed for all the Nickel nanostructures samples as well for the PtNi nanostructures samples. The patterns for the Nickel nanostructures were consistent with the different facets of metallic Nickel. The synthesized Nickel sample also showed the same patterns to the commercial Ni NWs. This confirms that the synthesized Nickel sample was in a metallic reduce state. Moreover, the PtNi nanostructured yield the same patterns between each other, confirming that metallic PtNi was obtained.

- **Transmission Electron Microscopy**

The Nickel nanostructures synthesized were determined to be nanoparticles and not the nanowires that were expected. The commercial Nickel nanowires had the expected wires structure with sizes of around 300 nm and 400 nm but have a very large diameter, therefore, it makes it difficult for the electrons to pass through them. The PtNi Core Shells made using the synthesized Nickel nanoparticles looked like big sphere covered with Pt and not hallow, therefore it can be inferred that Ni can be covered by a layer of Pt making the Core Shells nanostructures. Finally, the PtNi nanowires made using the commercial Nickel nanowires successfully made wire like structures with lengths of around 300 nm and 400 nm much like the commercial Ni nanowires. However, not many nanowires were observed in the sample.

- **Oxygen Reduction Reaction Experiment**

According to the obtained O<sub>2</sub> Polarization Curves, the catalyst of interest, the synthesized PtNi Core Shells, were compared to Commercial Pt/C 20% for their catalytic performance. The ORR catalyzed by synthetized PtNi Core Shells have an E<sub>1/2</sub> of 0.71 V compared to the E<sub>1/2</sub> of Pt/C 20% which was 0.92 V. Since the E<sub>1/2</sub> of the PtNi Core Shells was less of the Pt/C 20%, it can be concluded that the ORR reaction went through a 2e<sup>-</sup> pathway. These difference in E<sub>1/2</sub> can be caused because the catalyst may have different Platinum loading. Therefore, the synthesized PtNi Core Shells did not wild comparable result to a

commercially available catalyst for ORR. Therefore, the synthesized PtNi Core Shells did not yield comparable results to a commercially available catalyst for ORR.

- **Durability & Stability Experiment**

The durability and stability test was made on the synthesized PtNi Core Shells to see its performances on the ORR after a simulated test of use. The O<sub>2</sub> Polarization Curve before the test result was compared to the O<sub>2</sub> Polarization Curve after the test. The O<sub>2</sub> Polarization Curve after the test yields a difference in the reduction potential, which shows a decrease in its performances.

## **References**

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