# NE 445L/491 Nanomaterials Lab Report

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University of Waterloo
4A Nanotechnology Engineering
Group 7

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# Lab 1 Platinum Catalyst Nanoparticle Synthesis for Fuel Cell Applications

### Introduction and Objective

The purpose of this lab is to deposit platinum (Pt) nanoparticles on multi-walled carbon nanotubes (MWCNT) using ethylene glycol as the reducing agent. Platinum loading will be determined by using thermo gravimetric analysis (TGA) to burn off the MWCNT, while x-ray diffraction (XRD) will be used to determine the size of the platinum nanoparticles.

### Experimental Procedure

In this laboratory, we found that the MWCNT did not completely burn off during the TGA step. Therefore, representative data from another group will be used for analysis. Besides this, no other deviations from the procedure outlined in the NE 454L/491L Nanostructured Materials lab manual 1 part of the Nanotechnology Engineering Program 4A Labs in 2009. The temperature used was 120 °C.

### Results, Discussion, and Analysis

***TGA Analysis***

According to the standard data given to us by the lab instructor, at 3.545 minutes, the temperature reached by the TGA was 100.2009 °C. At this temperature, the weight of the sample was 1.659304 mg. It is assumed that the lowest point of the TGA curve is when the largest majority of the MWCNT has burned off. This occurred at 75.03668 mins at 757.8407 °C with as weight of 0.24461 mg.

The TGA sample weight started to gain weight after this point. Therefore, the loading according to these two readings is as follows:

$$Loading=\frac{W\_{Pt-TGA}}{W\_{Pt-MWNT}}\*100\%=\frac{0.24461}{1.659304}\*100\%=14.4\% (1.7)$$

Assuming the reaction at the cathode is as follows:



then, there is a 1:1 ratio for Pt to PtCl6. In our sample, the amount of PtCl6 used was 3.4 mL, and 7.4 mg/mL is the amount in solution. Thus, the amount of Pt used assuming complete loading is 7.4 mg/mL \* 3.4 mL = 25.16 mg. The calculated weight obtained from the powder was 17.9 mg. By using the loading, we can calculate the amount of platinum in our powder (17.9 mg \* 0.144) which results in 2.575 mg. We can now calculate the experimental conversion percentage:

$$X=\frac{W\_{Pt-TGA}}{W\_{Pt-0}}\*100\%=\frac{2.575}{25.16}\*100\%=10.2\% (1.8)$$

Thus to summarize:

|  |  |
| --- | --- |
| Experimental Conversion X % | 10.2% |
| Loading % | 14.4% |

 ***XRD Analysis***

In the prelab exercise for Lab #3, the following result for the average platinum nanoparticle diameter was calculated:

*D* = **5.03 nm**

The heating profile assigned to our group was Type A, which means the expected particle size is only 2 nm. This means our diameter obtained is off by 2.03 nm. This discrepancy can be due to the fact that the magnetic stir bar was turned on after the reaction started instead of having a steady vortex beforehand which could have led to agglomeration and non-uniformly-sized particles. Other minor factors contributing to the discrepancy are incorrect full-width half max (FWHM) reading from the noisy XRD data, or the Scherrer equation itself being an incorrect estimation of the particle.

The crystal structure of both platinum (Pt) and palladium (Pd) are both face centered cubic (fcc) and both belong to the same group on the periodic table. So we could predict that palladium can be used as a catalyst as well. It is shown in Reference no. 2 in the NE 491 lab manual that Pt can be used as a substrate for Pd to be grown on. Pd-Pt alloy particles are grown as well which shows signs that Pd can be used as a catalyst in addition to Pt. Furthermore, Pd is used in catalytic converters of car exhausts and seen in fuel cells as catalysts. All this provides a strong indication that Pd can be an effective catalyst as well.

### Summary and Conclusions

We see that the results obtained in this laboratory were satisfactory. The discrepancy of 2.03 nm in particle size is large but is not uncommon because there are many factors that contribute to the difference in particle size. In addition to the previously discussed discrepancies resulting from our synthesis, we need to ensure if the synthesis technique and size determination technique to obtain a size of 3 nm is the same. It might prove instructive to examine the accuracy of the Scherrer equation used to determine particle size and also the validity of our XRD data.

We attribute our relatively low loading result to an accidental spill from transferring the solution from the three necked flask to the funnel. In general, there will always be a certain fixed quantity loss of material while transferring solutions between containers.

In conclusion, the results proved in verifying theory and demonstrating the techniques needed to analyze the size of the platinum particles and their loading. The only major concern is that our MWNT did not completely burn off in the TGA and consequently, another group’s data for TGA had to be used. However, this shouldn’t cause too much concern since Pt loading should be fairly similar given both groups followed similar lab procedures.

# NE 491 Lab 2 Electron Tunnelling in Chemiresistive Nanomaterials

### Introduction and Objective

The primary objective of this lab is to experiment with the conductive/insulative properties of encapsulated gold nanoparticles with thiol as a possible candidate for a vapour-based sensor on interdigitated microarray electrodes (IMA). The secondary objective will be to explore the electron hopping between gold nanoparticles determined by the rate constant, and also to examine the changes resulting from different lengths of thiol groups, namely C4, C5, and C6.

### Experimental Procedure

Half-way through the laboratory, we discovered that the IMA assigned to us was broken. This required us to repeat several tests. Apart from this, no deviations were performed from the lab manual found in the NE 454L/491L Nanostructured Materials Laboratory 2 part of the Nanotechnology Engineering Program 4A Labs in 2009.

### Results and Discussion

The IMA that was mainly used in this lab was IMA A since electrodes B and C did not work for us. IMA-A have two readings with spacing of 13.75892 m and 14.09866 m. which results in an average of 13.92879 m. Using the same dimensions as that used in our prelab except for distance, the new cell constant is 145 m-1. The slope is calculated by I-V data given and using the SLOPE() function in Microsoft Excel.

|  |  |
| --- | --- |
| **Values Names for Conductivity** | **Values** |
| Distance Between Digits | 13.92879 m |
| Cell Constant | 145 m-1 |
| C4 MPC Film I-V Curve Slope  | 5.98E-06 Ω-1 |
| C5 MPC Film I-V Curve Slope  | 1.12E-06 Ω-1 |
| C6 MPC Film I-V Curve Slope  | 2.93E-07 Ω-1 |
| C4 MPC Film Conductivity | 8.67E-04 Ω-1 m-1 |
| C5 MPC Film Conductivity | 1.63E-04 Ω-1 m-1 |
| C6 MPC Film Conductivity | 4.25E-05 Ω-1 m-1 |

Using equation 2.4 in the lab manual and prelab values for concentration and core-to-core length (according to the calculation seen in version 1.6 of the lab manual) and the conductivity of the MPCs, we can calculate the rate constant of electron hopping at room temperature.

Table 1: Calculated Ket at Room Temperature

|  |  |
| --- | --- |
| **Values Names for Ket** | **Values** |
| C4 Ket | 3.62E+07 |
| C5 Ket | 5.45E+06 |
| C6 Ket | 1.22E+06 |

As we observe from the above chart, the higher the length in core-to-core distance, the more carbons that will result in our ligand, consequently resulting in a *smaller* rate constant. The relationship between the core-to-core distance and the log of the rate constant seems linear. Thus, the larger number of carbon atoms in the ligand results in slowing the rate of electron hopping between the two electrons. This is probably due to the larger energy barrier created from an increase in the number of carbon atoms.

The equation of this linear line is determined by LOGEST() function in Microsoft Excel. The equation of the line is log(y) = -0.40943\*x - 10.4782 with an R2 value of 0.9955. The results after performing the calculations for C7 and C14 are summarized in Table 2.

Table 2 Calculated Rate Constants for 7 and 16 Carbon Atoms

|  |  |  |  |
| --- | --- | --- | --- |
| **# of carbons** | **Core to Core (Å)** | **Rate Constant [log(1/s)]** | **Rate Constant (1/s)** |
| 7 | 12.6 | 5.32E+00 | 2.087E+05 |
| 16 | 28.8 | -1.31E+00 | 4.861E-02 |

According to the equation and calculation data, we found that a C7 conductivity of 8.16831E-06 Ω-1m-1 would be too small for the instrument since the conductivity limit of the instrument is 1.56E-05 Ω-1m-1 calculated in the prelab.

The film on the IMA was easily removed with the use of toluene. This shows that the MPCs do not chemically adhere to the surface but adsorb on the surface due to purely physical forces. The cleaning of the IMAs was not a considerable issue since the same IMA was cleaned and used for C4, C5, and C6 without any significant problems.

### Summary and Conclusions

The results seem to fit what is expected from theory. We had smaller rate constants with larger core-to-core ratio and a fairly linear relationship between the log of the rate constant and the length of the thiol molecule. A few of the I-V curves did not have a perfect linear relationship such as C5 which seemed to have a different hysteresis path when increasing the voltage than when decreasing the voltage.

Any discrepancies in our data may have resulted from two main contributing factors: 1) our films do not have a hexagonal close packed crystal structure which the rate constant equation assumes. The MPCs are mostly randomly packed and may not even be close together. 2) the MPC film is covers the entire IMA and not just between the digits. This phenomenon could lead to an anisotropic tunneling or an increased resistance from the MPCs. Both problems can be resolved by performing a layer-by-layer deposition of MPCs and planarizing the IMA afterwards which leads to more isotropic behaviour.

# Lab 3 Eletrochemical Characterization of Carbon Nanotube Supported Platinum Nanoelectrocatalysts

### Introduction and Objective

The primary objective of this lab is to perform an oxygen reduction reaction at the cathode using a rotating disk electrode under a conventional cyclic voltammetry setup. The material being investigated in this laboratory is the Platinum/MWNT catalyst on the cathode. The result of this investigation is to help us determine if this Pt/MWNT support catalyst can be used in a PEM fuel cell.

### Experimental Procedure

No deviations were observed from the experimental procedure outlined in the NE 454L/491L Nanostructured Materials Laboratory 3 part of the Nanotechnology Engineering Program 4A Labs in 2009. Please see this lab manual for a detailed description of the laboratory procedure.

### Results, Discussion, and Analysis

The ESCA can be easily calculated using the integration value from the CV. The equation given is ESCA = QH/m\*c (Equation 3.6 in the lab manual) where QH is equal to the integration of the CV curve divided by the surface area of the electrode. Hence, QH = 1.897 mA\*s / 0.198 cm2 = **9.581E-03 C/cm2**. From lab 1 we determined using TGA that the amount of platinum we have is 2.575 mg. We dispersed the Pt/MWCNT in 3 ml of 0.2 wt% nafion in an ethanol solution. However, we used only 21 μL of the solution. So the amount of platinum used is 2.575 mg / 3 ml \* 21 μL = 1.80E-02 mg. This means that m = 1.80E-02 mg / 0.198 cm2 which is **9.10E-02 mg/cm2** and c = **0.21 mC/cm2**.

Thus the ESCA is = 9.581 mC/cm2 / (0.21 mC/cm2 \* 9.10E-02 mg/cm2) = **5.01E+02 cm2/mg**. The value calculated in the prelab is 5.56\*105 cm2/g or 5.56\*102 cm2/mg. So we find a close match between the two numbers.

Finally, S / ESCA = 5.56E+02 cm2/mg / 5.01E+02 cm2/mg = 1.11 or **111%**. This deviation from the theoretical value could be due to the MWCNT physically interfering with the Pt surface area with reduces the *effective* surface area. Furthermore, it was assumed in the calculation that the sizes of all particles on the MWCNT substrate were the same. However, in reality, the particle size distribution varies as can be seen in the XRD output. This particle size distribution may have a role to play in surface area and reaction mechanics. The equation also assumes perfect conditions but the Pt particles may have defects or may be mixed with other unwanted contaminants.

The following are results from calculating the Id values using the initial approach of the CV and assuming Id is reached at 0.2 V. Using the values of the constants provided in the prelab, the values taken in this range after 0.2 V are used to calculate the number of electrons (*n*) using the *Koutecky-Levich* equation. The values for *n* are close to 4 except for 100 RPM (see Table 3). The lower RPMs have a higher number of electrons transferred while the higher speeds have lower number of electrons. It seems that at lower RPMs, the diffusion controlled current may not hold true since the values differ greatly from four. We also calculated 1/ik at 0.4, 0.6, and 0.8 using the intercepts of the plot of 1/id and w-1/2 and thus calculated ik. kf was calculated using Eqn 3.8 supplied in the lab manual and *n* was calculated by using the this relation: slope = (0.62\*nFAD2/3w1/2v-1/6C)-1and thus *n* = (slope\*0.62\*FAD2/3w1/2v-1/6C)-1. We found that *n* is greater than the theoretical value in all three cases. Theoretically, the 0.8 values should yield the correct value of *n* since the graph has reached steady state but this does not seem to be the case. There are a number of factors for this discrepancy. One reason is that the 100 RPM onset is quicker than the other cases in our scenario. Furthermore, a migration of ions may play a role as well.

The value of the current that is not dependent on mass transport is I­k. This is representative to the situation in the beginning of the reaction when the bulk concentration is equal to that found at the electrode. The closest value in our situation to real life would be 0.4 V since this is just right after onset. After 0.4 V, mass transport plays a role which biases our data into larger Ik values since Eqn 3.8 does not account for mass transport, a major component of current at large voltages.

The Tafel slopes shown in Table 4 below were calculated using the return approach since our forward approach data did not show any Tafel behaviour [1]. The slope was taken from data points between 0.55 V to 0.9 V. Our results were less than the expected 15 mV/decade for most results except 1600 rpm. This is not too unexpected since a total absence of mass transfer allows for better Tafel behaviour. The reason for why these data points are non-ideal could be that 1) mass transfer limits current, 2) the electrode kinetics may be fast or 3) the overpotential for activation may be too small. In all these three cases, the Tafel model is not observed.

Table 3: Number of Electrons for Both Calculated and Data Interpolated

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **RPM** | **Id @ 0.20 V** | **n** |  |   | **1/I @ 0.4V** | **1/I @ 0.6V** | **1/I @ 0.8V** |
| 100 rpm | 3.19E-04 | 6.04E+00 |  | **ik** | 6.35E-05 | 2.91E-04 | 1.23E-03 |
| 400 rpm | 5.06E-04 | 4.79E+00 |  | **kf** | 7.55E-04 | 3.46E-03 | 1.47E-02 |
| 900 rpm | 6.52E-04 | 4.12E+00 |  | **n**  | 6.81E+00 | 5.58E+01 | 7.81E+00 |
| 1600 rpm | 7.79E-04 | 3.69E+00 |  |

Table 4: Tafel Slopes

|  |  |
| --- | --- |
| **Rotation Speed (rpm)** | **Tafel Slope** |
| 100 rpm | 13.87929 |
| 400 rpm | 11.35755 |
| 900 rpm | 13.8726 |
| 1600 rpm | 16.94149 |

### Summary and Conclusions

### The quality of the results was not too removed from what was expected from theory. There were several things in this lab that did not make much sense or that were not clearly defined. For example, using the return approach of the IV curve for Tafel slopes yielded better results for the region of Tafel behaviour. Furthermore, the data received was inverted to fit the general trends seen in the lab manual. Regardless, all data still seemed to fit the general trend within the predictive range of theory.

# References

[1] Allen J. Bard & Larry R. Faulkner *Electrochemical Methods*: Fundamentals and Applications, 2nd Ed. Hamilton: John Wiley and Sons Inc. 2001, pp. 100-104.