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**14. ABSTRACT**  
This project focused on developing cathode catalyst for oxygen reduction reaction (ORR). Our approach combined the advantages of platinum catalyst and non-precious catalysts to decrease the cost and to maintain or enhance catalytic activity compared to that of platinum catalysts. The results from our experiments showed that the proposed composite catalysts increased the cost-effectiveness and utilization of platinum, and exhibited enhanced durability.

**15. SUBJECT TERMS**  
oxygen reduction reaction, core-shell catalyst, PEMFC

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### Project Summary To-Date

Project Reference:	N62909-16-1-2235
Title of Project:	NICOP - Novel carbon-supported PtCo core-shell catalysts for high performance PEM fuel cells
Approved Budget and Period:	US\$ 90,000.00 (with overheads) over 1 year

#### 1.1 Principal Investigator & Collaborators

Name	Role	Institution
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#### 1.2 Expenditure Level – Utilisation Rate of Fund

Vote	Total Grant Awarded [A]	Total Actual Expenditure To-Date [B]	Utilisation rate [B/A x 100%]
EOM	S\$ 75,411.00	S\$ 75,411.00	100.00%
Equipment	S\$ 13,266.75	S\$ 10,542.76	79.47%
OOE	S\$ 16,059.75	S\$ 14,473.31	90.12%
Overhead	S\$ 20,947.50	S\$ 20,947.50	100.00%
<b>Total</b>	<b>S\$ 125,685.00</b>	<b>S\$ 121,374.57</b>	<b>96.57%</b>

#### 1.3 Milestones

Tasks	Completed (Y/N)
Procurement of equipment and materials	Y
Development of core-shell PtCo catalyst supported on novel non-porous carbon materials	Y
Characterization and benchmark of developed core-shell PtCo catalysts against commercial Pt/C	Y

Reports detailing the development and the characterization results	Y
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## Summary

Among the various fuel cells, proton exchange membrane fuel cells (PEMFCs) are the most promising because of the high power density, high energy conversion efficiency, quick start and response, and nearly-zero emission. However, the commercialization of PEMFCs is seriously hindered by the high cost, in which electro-catalyst accounts for almost 40% of total cost of the PEMFC stack. Platinum or platinum-based alloys are the most widely employed electro-catalysts in PEMFCs, and around 75% of platinum is used for oxygen reduction reaction (ORR). The non-precious carbon materials, usually doped by nitrogen, have not demonstrated obvious advantages over the precious platinum-based catalysts in terms of activity and long-term stability towards ORR, except in costs. This project focused on developing cathode catalyst for ORR. Our approach combined the advantages of platinum catalyst and non-precious catalysts to decrease the cost and to maintain or enhance catalytic activity compared to that of platinum catalysts. The results from our experiments showed that the proposed composite catalysts increased the cost-effectiveness and utilization of platinum, and exhibited enhanced durability. The single cells employing core-shell samples showed markedly improved performance compared to the ones with Pt/r-GO sample. The single cell that has Pt@Co/N-(CNT-graphene) as the cathode catalyst has the best and most stable performance among the various samples. We attributed the enhancement to the following possible factors: the interaction between the metallic particles and the composite materials; the favorable mass transfer properties; and electronic conductivity improved by the 3D structure of composite materials. It is also possible that the surface of composite material has additional active sites caused by the doped nitrogen. We strongly recommend that the future work should include 1) Optimization of the graphene/CNT ratio to obtain desirable morphology and pore structures, 2) Increase poisoning tolerance to carbon monoxide, sulfur and chloride, and 3) production techniques to scale-up the synthesis of core-shell nano-structure catalysts.

## Introduction

As global energy demand continues to soar to new highs in recent decades, fossil fuel resources are being consumed at unprecedented rates leading to more serious greenhouse emissions and global warming. It is clear that, as a society, we need affordable, sustainable and clean technologies that can revolutionize the way we produce, transport and energy use.

Electrochemical devices, such as, fuel cells have demonstrated the ability to satisfy the requirements, operating with only environmentally benign emissions and boasting excellent operational efficiencies. The potential market for fuel cells includes unmanned aerial vehicles (UAV) and portable power systems, backup power for telecoms and mission critical applications, auxiliary power units (APUs), electric vehicles (car, bus, forklift and truck), ships and military (submarines, individual power supply systems).

The global fuel cell market size is expected to reach USD 25.5 billion by 2024, according to a new research report by Global Market Insights. Global fuel cell market includes PEMFC, SOFC, and DMFC as key product segments. PEMFC dominated with 60% of global revenue and generated revenue over USD 2 billion in 2015. Direct methanol fuel cells (DMFC) is a sub segment of PEMFC which uses methanol. They find application in portable energy source where power density and energy is more important than efficiency. Increasing demand for portable energy source is likely to drive global fuel cell market from 2016 to 2024. Portable application is projected to expand at over 22% CAGR during the forecast period of 2016 to 2024. Increasing demand for portable charging source in consumer electronic goods such as laptops, tablets, camera and cell phones is likely to drive portable fuel cell market trends.

On the basis of region, the market has been segmented into Asia-Pacific, North America, Europe, and Rest of the World. Asia Pacific is presently the leading regional market, accounting for a share of 38% of the global market, trailed by North America, which commands a share of over 35% of the market.

The growth of fuel cell market is, however, hampered by the durability, reliability and cost. In low temperature fuel cell, such as, proton exchange membrane fuel cells (PEMFC), the electro-catalyst plays the key role in increasing the durability and reducing the cost.

The electro-catalytic processes in the low temperature fuel cells can be controlled and promoted by using appropriate electro-catalysts. To ensure that a fuel cell delivers maximum efficiency, both electrode reactions need to take place close to their thermodynamic potential as possible. The ORR is the primary electrochemical reaction occurring at the cathode of low temperature fuel cells, and is a key contributor to efficiency loss. The slow kinetics of the ORR, both in acidic (proton-exchange membrane) and alkaline (OH<sup>-</sup> anion-exchange membrane) environments, are attributed to the losses. Similar losses have also been reported for electrolyzers and metal-air batteries.

In the present hydrogen-fed PEMFCs, the catalyst is the major cost contributor, around 40%, in which around 75% precious metal loading is used as the cathode catalyst to promote the oxygen reduction reaction. The high catalytic nature and chemical stability of platinum made it the ideal catalyst to be used in the oxidation and reduction conditions found in fuel cell. The relatively high cost counteracts the advantages and competitiveness of PEMFCs, and is one of the major obstacles restraining the commercialization of PEMFC. Hence, it is imperative to reduce or eliminate the use of platinum in the cathode, which would lead to a more affordable fuel cell system as a whole and made it economically feasible for adoption.

There are two ways to reduce the electrode catalyst cost, which would lead to reduce the cost of PEMFC stack. One way is to decrease the Pt-based catalyst loading and increase the cost-effectiveness and the other way is to employ non-precious metal catalysts or non-metallic catalysts.

Various methods have been reported to prepare supported Pt or Pt-based catalysts with high metallic loading. Procedures reported and published (US Patent 7713902, 4,044,193 & 3992331, 5641723, J. Electroanal. Chem. 229, 1987, 395–406, H. Bönemann et al. Angew. Chem. Int. Ed. Engl. 30(1991)1312) can produce very small nanosized platinum-based catalyst particles from 1.0 to 5.0 nm, and obtain high activity and high platinum utility. However, the complicated and costly procedure counteracts their advantages, and restricts the adoption of these methods. The carrier properties also affect or even determine the supported particle deposition, size distribution and active element properties.

While two patented methods, hydrogen content in carbon materials (US Patent 6689505) and alkali treatment (US Patent Appl. 2012/0149545), where the surface area and pore structures of carbon materials, and surface oxygen-containing radicals can promote the platinum-based metallic particle distribution and activity, there remains a need for novel preparation methods for advanced platinum and platinum-based catalysts to improve the platinum mass activity and durability, and to decrease



the catalyst cost and production time. The synthesis procedure should be feasible, cost-effective and scalable for mass production of catalysts.

In parallel, to overcome the high cost of platinum-based catalysts, tremendous amount of work have been devoted to exploring non-precious metal catalysts with lower costs, improved activities, superior durability, and better selectivity towards ORR.

Despite the efforts to improve the quality of the catalysts, the use of non-precious metal catalysts is still limited by the poor activity in the acidic environment of solid polymer proton conducting electrolyte. Due to this reason, non-platinum catalysts have little opportunity to compete with platinum-based catalysts in the foreseeable future.

Our approach is to develop a composite catalyst that combine the positive features of precious and non-precious metal catalysts that are low-cost and comparable/better catalytic activity with long term stability.

## Methodology

### Approach

The approach for development of composite catalyst is as follow:

1. Synthesize and compare graphene supported platinum, and platinum-cobalt with different structures catalysts towards ORR
2. Using the above synthesized catalysts, optimize the supporting material to further enhance the activity

### Methods

Graphene supported Platinum and platinum-cobalt alloy catalysts

The platinum and alloyed platinum-cobalt catalysts are synthesized according to the following process. The platinum content in alloyed samples are consciously reduced to decrease the cost and partly due to the fact that the addition of cobalt can enhance the activity.

The supported platinum catalyst synthesis included (i) mixing and dispersion of supporting materials, graphene oxide herein, surfactant citrate acid and ethylene glycol to form uniform ink; (ii) adding metallic precursors ethylene glycol solution into the carrier ink and the modification of pH value higher than 10; (iii) heating with microwave the mixture to reduce and deposit the metallic nanoparticles onto the

carrier surface. The metallic nanoparticles supported on carrier are centrifugalized from the liquid, washed copiously with ethanol and DI water, and freeze-dried to get the final product. In a typical procedure of graphene supported platinum (Pt/graphene), graphene (0.26 g) is dispersed into ethylene glycol (150 mL) to get uniform ink. Chloroplatinic acid hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , 1.05g) is added into the carbon ink after which the solution pH is increased to 10 by the addition of sodium hydroxide. The mixture is heated in a spiral glass tube reactor to 150 °C by microwave for 10 minutes. Following this, the mixture is centrifugalized and the solid is washed copiously by DI water and ethanol. The product Pt/graphene (60%wt) is collected after freeze dried for 3 days.

Graphene supported PtCo alloy catalyst is also synthesized according the above procedure where mixed solution containing cobalt (II) nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and chloroplatinic acid are prepared ahead in ethylene glycol. The Pt mass content in this catalyst is 10%wt, and the molar ratio of Pt to Co is 1: 6.

#### Core-shell Co@Pt/graphene catalyst

Core-shell PtCo catalyst synthesis is conducted in aqueous solution. The mixed aqueous solution of cobalt (II) nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and PVP (Polyvinylpyrrolidone,  $(\text{C}_6\text{H}_9\text{NO})_n$ , average mole wt 10,000) is prepared with the molar ratio 1:2. The graphene oxide is dispersed into deionized water in ultrasonic bath for 1 hour, after which the graphene ink is added into the metallic precursor solution and stirred for another 1 hour with nitrogen bubbling. The fresh sodium borohydride solution is added dropwise into the above mixture solution and stirred overnight with nitrogen bubbling. The diluted potassium tetrachloroplatinate ( $\text{K}_2\text{PtCl}_4$ ) solution is added into dropwise and stirred for further 6 hours. After centrifuged, washed and freeze-dried, the final product is collected and characterized. The mass percentage of platinum, cobalt and graphene in this sample is 5%, 10%, and 83% respectively. Based on the EDX analysis, the content of platinum and cobalt in the final product is 6% and. The molar ratio of Pt to Co in this catalyst is 1: 5.8. The molar ratio of sodium borohydride to cobalt nitrate is five.

All catalysts are tested in three-electrode electrochemical cell with 0.1 molar/liter KOH solution as supporting electrolyte, platinum sheet as counter electrode and Ag|AgCl as reference electrode. Samples are also characterized by XRD and TEM to check the structures and nanoparticle images.

#### Optimization of supporting material for core-shell PtCo

In order to increase the chemical stability of supporting materials of electrocatalysts, we selected multi-wall carbon-nanotube (MW-CNT, 280  $\text{m}^2/\text{g}$  BET), graphene, and



nitrogen-doped carbon-nanotube-graphene composite materials. Core-shell Pt@Co nanoparticles are synthesized and deposited according to the same procedure described above. All the samples have the same platinum content. Special attention is given to the nitrogen-doped carbon-nanotube-graphene composite as it has shown superior performance.

*Nitrogen-doped carbon-nanotube-graphene composite*

The nitrogen-doped carbon-nanotube-graphene composite (N-CNT-graphene) material was produced according to the following procedure: A certain amount of CNTs (100 mg) and 1.2 mg of polyvinylpyrrolidone (PVP) were added to 30 mL of ethanol and the resulting mixture was sonicated for 5 h to form a uniform dispersion. 300mg GO was dispersed in 50 ml ethanol to get well-dispersed GO ink in ultrasonic bath for 2 hours. Then both solid/ethanol mixture were mixed together and continued to stir for 1 hour to form a uniform GO–CNT dispersion. 300  $\mu$ L of EDA was added into the mixture after which the dispersion was transferred into a Teflon-lined stainless steel autoclave and heated at 150 °C for 12 h to prepare a graphene–CNT hybrid hydrogel. The resulting hydrogel was washed several times with ethanol and DI water, and finally freeze-dried at –80 °C for 4 days to obtain N-doped CNT-graphene aerosol (N-CNT-graphene).

## Results and discussion

### Graphene supported platinum, platinum-cobalt alloy, and core-shell

The nano-size metallic particles of above samples were checked firstly by TEM. The selected TEM images and corresponding histogram of nanoparticle size statistics. From the Figure 1, it can be seen that the in-house developed synthesis process can effectively synthesize ultrafine nano-size platinum particles supported on graphene as high as 60% Pt content. For the high-loading sample, the average size of platinum nanoparticle is 2.24nm based on more than 300 nanoparticles in randomly selected region. All the nanoparticles are evenly distributed and deposited on the graphene sheet surface. The continuous production procedure can save time and decrease energy consumption, and realize facile production of high-content platinum-based catalysts.

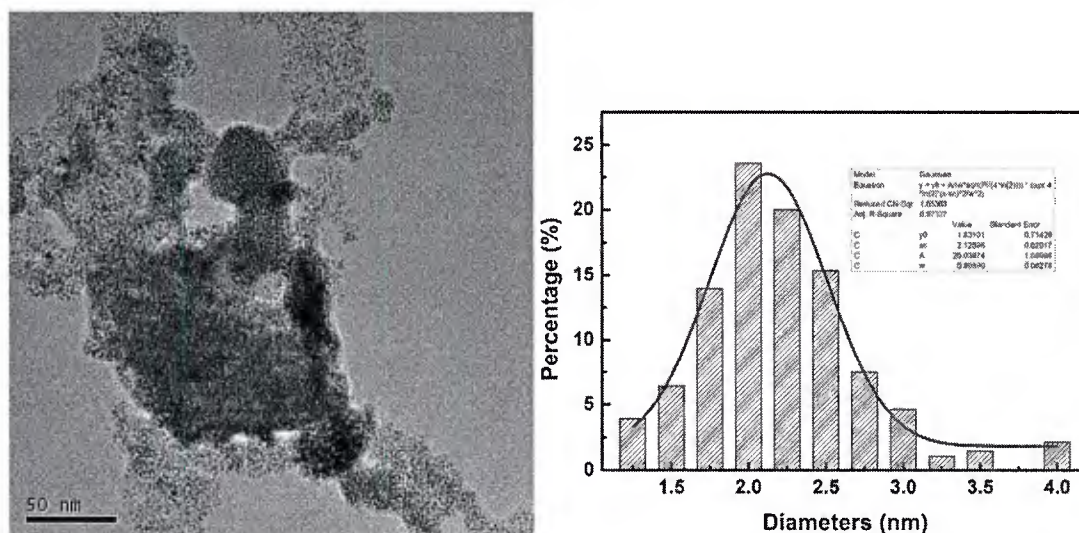


Figure 1. TEM image and histogram of Pt/r-GO (60%) sample.

The synthesis of alloyed PtCo catalyst is slightly different, especially in the case of high cobalt content in which the sample contains 10%wt platinum and 18% cobalt. The molar ratio of platinum to cobalt is 1:6. Cobalt is generally easier to be reduced than platinum, resulting in the bigger particle size if the procedure is not well controlled. After the ratio of metal to citrate is carefully controlled, the prepared sample has the following metallic particle distribution, which can be seen from the selected TEM image of Figure 2. Although the average nanoparticle size is only 2.65 nm (based on more than 200 particles), a number of nanoparticles larger than 5 nm are still found on the graphene sheet surfaces. Compared to the Pt/r-GO sample, the average particle size is increased although both the platinum content and total metal loading are reduced, which is mainly attributed to the presence of high cobalt content. The platinum-cobalt alloyed catalysts used in proton exchange membrane fuel cells typically has low cobalt

content with molar ratio of platinum to cobalt is 3:1. However, in our case, the catalyst has the high cobalt content to reduce the platinum loading. Compared to the sample  $Pt_1Co_6/r-GO$  (Figure 2), the core-shell sample shown in Figure 3 has smaller and more uniform particle sizes. This improvement is mainly attributed to the different synthesis procedure and surfactant used as described below. The presence of PVP is helpful to decrease the average size of firstly reduced cobalt nanoparticles in comparison to citric acid. The cobalt nanoparticle sizes determined the final core-shell particle size because platinum is deposited onto cobalt particle surface. The average particle size of final product is 2.24 nm as shown in Figure 3. This difference also proved that the use of PVP is better than citrate and ethylene glycol to control cobalt nanoparticle sizes.

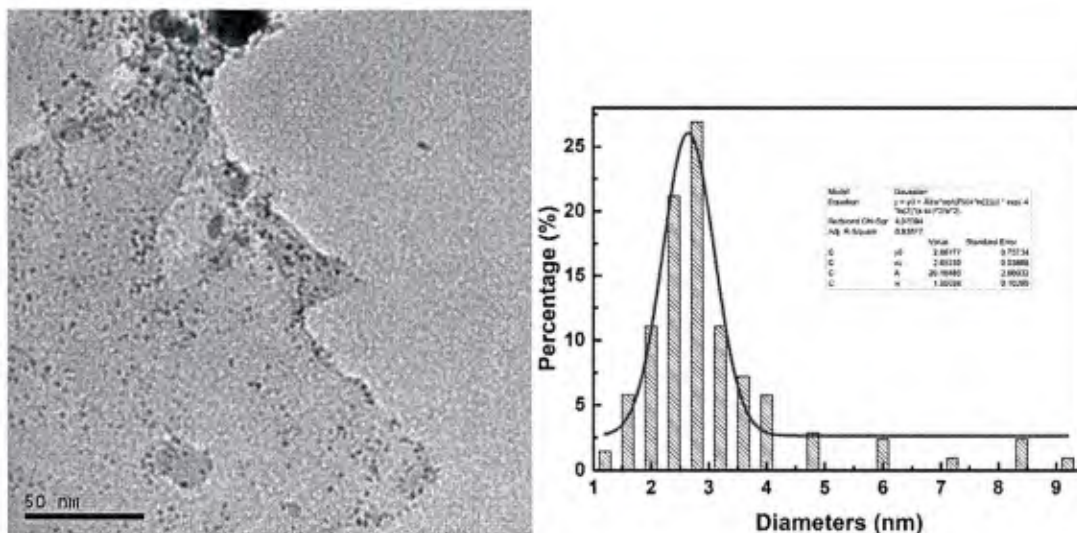


Figure 2. TEM image and metallic nanoparticle histogram of  $Pt_1Co_6/r-GO$  (10% Pt) sample.

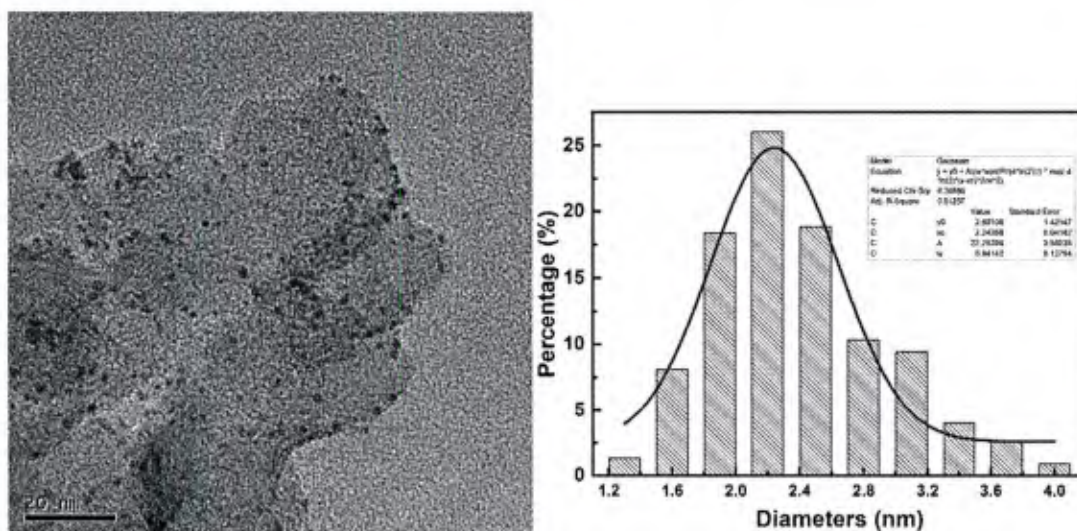


Figure 3. TEM image and metallic nanoparticle histogram of  $Pt@Co/r-GO$  (5% Pt) sample



The graphene supported PtCo sample with Core-shell nanostructure is synthesized in aqueous phase in the presence of PVP, which is used as surfactant to avoid the agglomeration of cobalt nanoparticles during the reduction by sodium borohydride. The surface atoms of cobalt nanoparticles deposited onto graphene sheet is then displaced by platinum through the following reaction after potassium tetrachloroplatinate ( $K_2PtCl_4$ ) solution was added [J. Yang, C. H. Cheng, W. Zhou, *et al.* FUEL CELLS. 10(2010)(6)907-913.]:

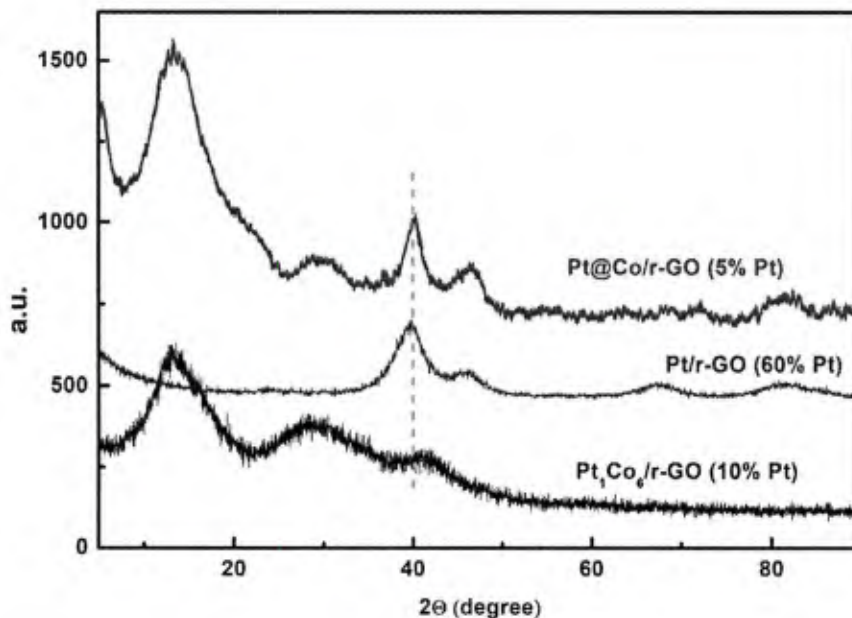


Figure 4. XRD characterization results of r-GO supported Pt, alloyed PtCo and Pt@Co core-shell samples.

The XRD characterization is shown in Figure 4. The peak at  $39.5^\circ$  is attributed to the platinum Pt (1 1 1) face. The PtCo with core-shell structure sample and the platinum sample almost have the similar XRD diffractograms, while the Pt(111) diffraction peak at around  $40^\circ$  shift to higher position indicating that the alloyed nanoparticles is synthesized in the PtCo/graphene sample.

The samples are tested in a three-neck electrochemical cell using 0.1 M KOH as the supporting electrolyte, and the platinum wire and Ag/AgCl as the counter electrode and reference electrode, respectively. 10 gram of sample is dispersed in 1 ml ethanol Nafion solution and 10  $\mu$ L catalyst ink is transferred onto the glassy carbon electrode and treated in oven at  $75^\circ C$  for 15 min before testing. Figure 5 showed the linear scan results of above three catalysts showing their ORR performance. In Figure 5A, the Y axis is current density ( $A.cm^{-2}$ ) and the electrode active area is  $0.19625 cm^2$ . The results showed that the total performance of Pt/r-GO sample is better compared to

other sample because of the high platinum loading of the former. In the activation region where applied potential is higher than 0.0 V, the samples PtCo/r-GO and Pt@Co/r-GO demonstrated similar performance. Notably, at the potential of 0.1 V, the three samples produced almost the same current density.

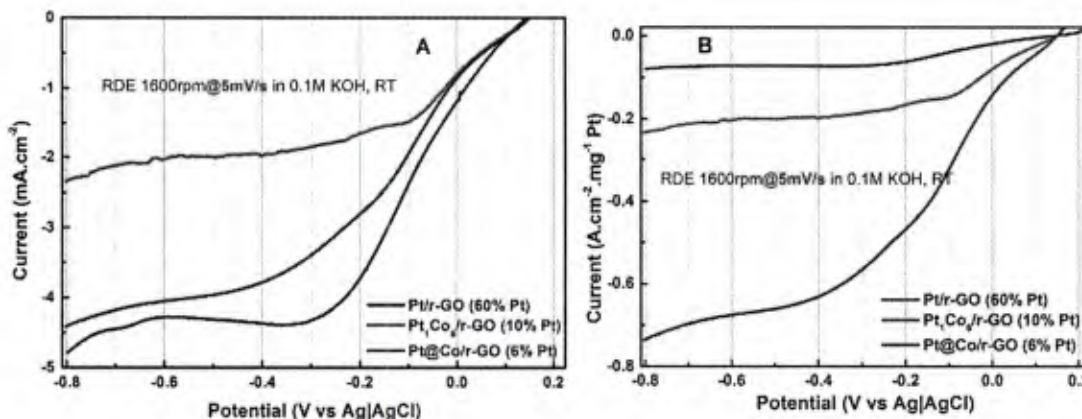


Figure 5. The half-cell test result (RDE) of r-GO supported Pt, alloyed PtCo and Pt@Co core-shell samples at room temperature.

Figure 5b depicted the ORR performance of the catalyst with Y-axis showing current density per platinum loading. The PtCo sample with core-shell nanostructures demonstrated much better performance and higher platinum utilization. The detailed comparison is summarized in Table 1. It can be clearly seen from this table that depositing platinum thin shell onto cobalt core enhanced the platinum utilization, at least 7 times (from 19.8 to 143.2 mA.cm<sup>-2</sup>.mg<sup>-1</sup> Pt) at 0.0 V and 9 times (from 5.1 to 45.5 mA.cm<sup>-2</sup>.mg<sup>-1</sup> Pt) at 0.1V.

Table 1. Summary of the current density comparison at selected potentials for the above samples.

Catalyst sample	Current density at 0.0 V		Current density at 0.1 V	
	A.cm <sup>-2</sup>	mA.cm <sup>-2</sup> .mg <sup>-1</sup> Pt	A.cm <sup>-2</sup>	mA.cm <sup>-2</sup> .mg <sup>-1</sup> Pt
Pt/r-GO (60% Pt)	1.21	19.8	0.29	5.1
Pt <sub>1</sub> Co <sub>6</sub> /r-GO (10% Pt)	0.78	80.4	0.24	24.8
Pt@Co/r-GO (6% Pt)	0.89	143.2	0.28	49.5

#### Optimization of supporting material for core-shell PtCo

In order to increase the chemical stability of supporting materials of electrocatalysts, we selected multi-wall carbon-nanotube (MW-CNT, 280 m<sup>2</sup>/g BET), graphene, and nitrogen-doped carbon-nanotube-graphene composite materials. Core-shell Pt@Co



nanoparticles are synthesized and deposited according to the same procedure described above. All the samples have the same platinum content.

A typical TEM image of Pt@Co supported on MW-CNT is demonstrated in Figure 6. From this image it can be found some smaller nanoparticles uniformly distributed on the long carbon nanotubes. There are also some bigger particles of size more than 30 nm, which is the carbon sphere attached on the MW-CNT. The presence of such big carbon spheres makes it hard to identify and calculate metallic nanoparticle sizes.

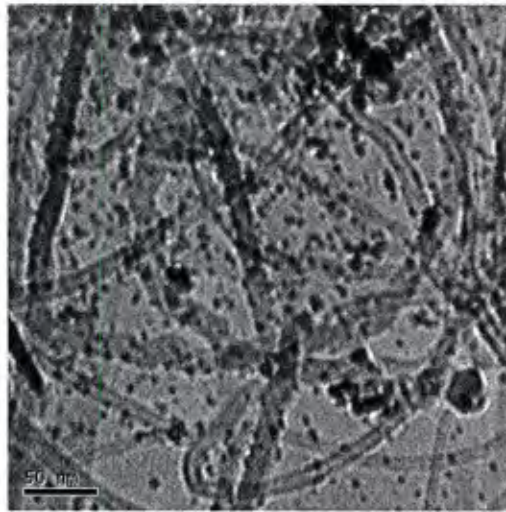


Figure 6. A typical TEM image of Pt@Co supported on MW-CNT.

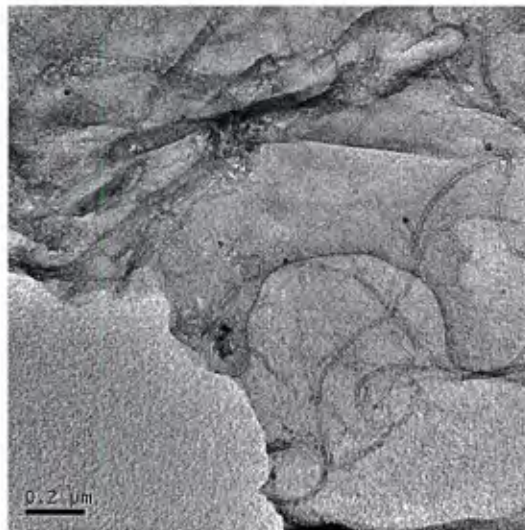


Figure 7. The selected TEM image of produced nitrogen-doped carbon-nanotube-graphene composite (N-CNT-graphene).

The TEM image of the produced nitrogen-doped carbon-nanotube-graphene composite is demonstrated in Figure 7. From this figure, it can be seen that the carbon nanotubes are uniformly distributed along and closely connected to the graphene sheets. This distribution can enhance the graphene strength, the porosity and conductivity. Some carbon spheres are also found attached on the CNT, as described above.

The Pt@Co core-shell nanoparticles are reduced and deposited onto the composite material according to the previous procedure with the same total metal loading and molar ratio (Figure 8). It is hard to identify the metallic spheres and carbon powders but we can see the black spheres are attached on the carbon nanotube and graphene sheets.

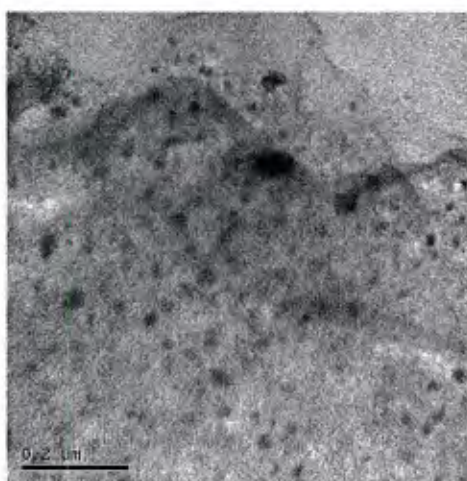


Figure 8. The selected TEM image of the core-shell Pt@Co supported on N-CNT-graphene.

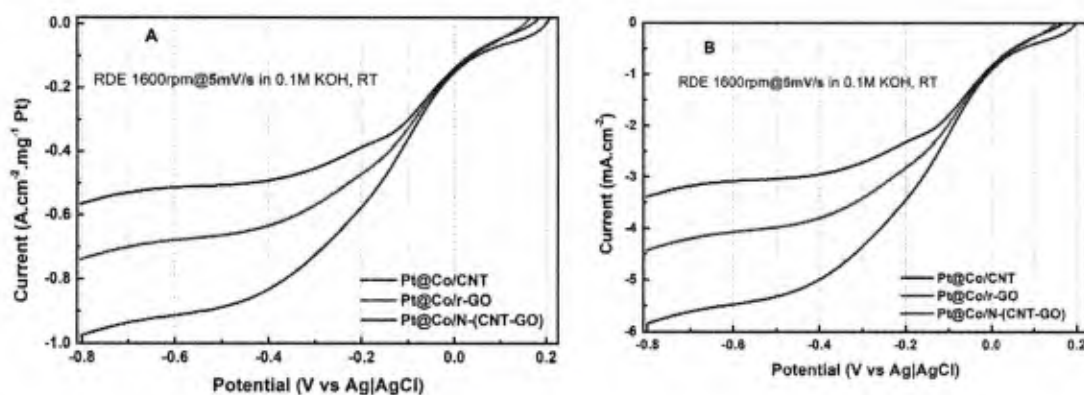
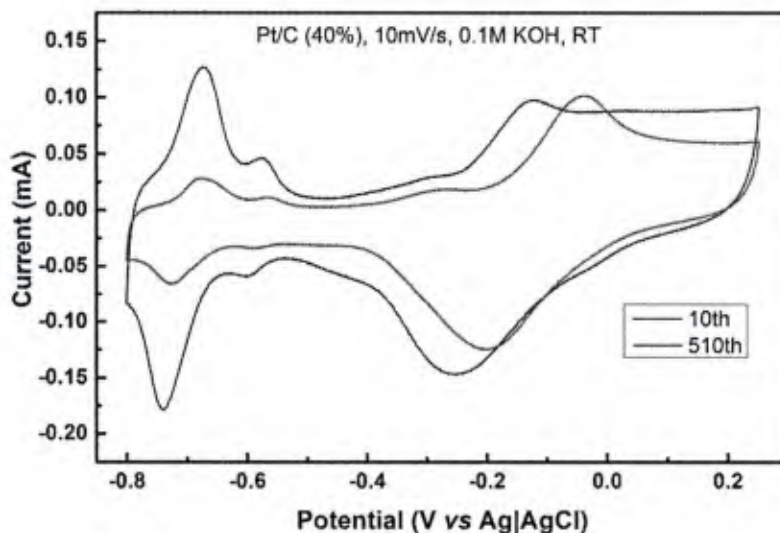


Figure 9. The half-cell electrochemical performance comparison for the Pt@Co samples supported on different supports.

Electrochemical measures of different supports are conducted in half-cell and the results are showed in Figure 9. Figure 9A depicted the results in current density per catalyst loading on the glassy carbon disc. It is obvious that the total performance of Pt@Co supported on the composite material is the best among the different supports used. The results are summarized in Table 2. From this table, it can be clearly seen that the use of composite support can further enhance the catalyst activity.

**Table 2. Current density comparison at selected potentials from different Pt@Co samples.**

Catalyst sample (6% Pt)	Current density at 0.0 V		Current density at 0.1 V	
	A.cm <sup>-2</sup>	mA.cm <sup>-2</sup> .mg <sup>-1</sup> Pt	A.cm <sup>-2</sup>	mA.cm <sup>-2</sup> .mg <sup>-1</sup> Pt
Pt@Co/MWCNT	0.84	138.8	0.27	46.7
Pt@Co/r-GO	0.89	143.2	0.28	49.5
Pt@Co/ graphene	0.94	154.1	0.42	68.5



**Figure 10a. The cyclic voltammetry (CV) results 0.1 M KOH solution at 10mV/s and room temperature of Pt/C (40%) sample at different cycles.**

The long-term performance is also measured by the half-cell testing in 0.1M KOH solution. The long-term cyclic voltammetry (CV) results of platinum supported on carbon powders and graphene are shown in Figure 10a and Figure 10b, respectively. Only the 10<sup>th</sup> cycle and 510<sup>th</sup> cycle are shown and used for comparison. It can be clearly seen that the CV figure changed significantly after 500 cycles for both samples. For the sample supported on carbon powder, the hydrogen region of CV figure is

smoother with less obvious proton desorption peaks. The specific electrochemical surface area (SESA) calculated from the hydrogen region (-0.8V~-0.6V vs Ag|AgCl) changed from 76.2 to 22.0 m<sup>2</sup>/g platinum for Pt/C (decreased by 71.0%), and from 87.5 to 42.6 m<sup>2</sup>/g platinum for Pt/r-GO (decreased by 51.3%). It is observed that the use of graphene prevented the catastrophic recession of platinum catalyst.

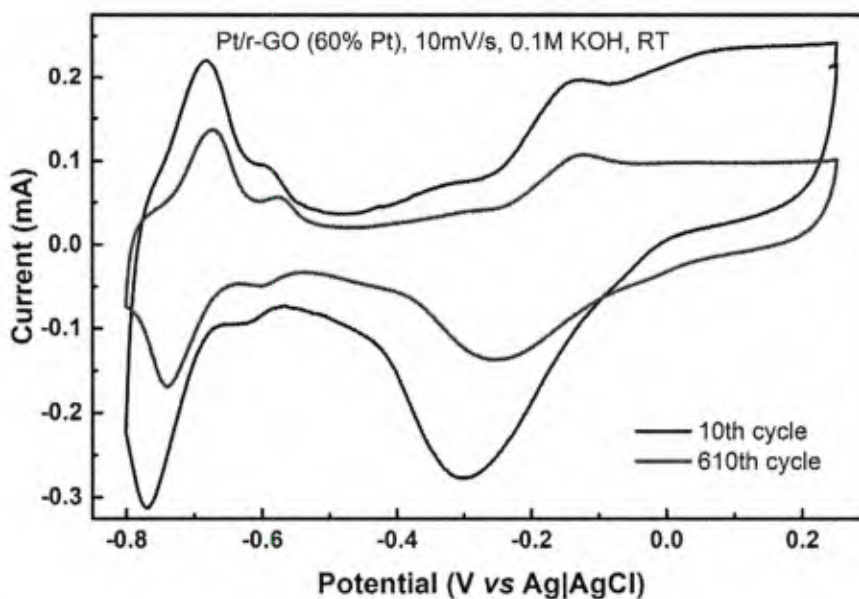


Figure 10b. The cyclic voltammetry (CV) results 0.1 M KOH solution at 10mV/s and room temperature of Pt/r-GO sample at different cycles.

For Pt@Co core-shell catalyst supported on the composite carbon material, there are no obvious proton adsorption/desorption peaks in the low potential region as shown in Figure 11. The CV curve did not change significantly after 600 cycles. For this sample, SESA is not suitable method to determine the robustness of the catalyst. Instead, the integral area of the curve is used to check the catalyst transformation. It is found that the integrated area for this sample changed from 18.5 mQ to 17.1 mQ (decreased by 7.6%). This indicated the chemical stability of the catalyst. The rotating disc electrode test results are also used to compare the activity change before and after the long-term test, which is shown in Figure 12. The current density curves are almost identical in the activation region. The typical current densities are 0.42 and 0.38 mA.cm<sup>-2</sup> at 0.1V (vs Ag|AgCl), respectively. The change is only 9.5%, consistent with the integrated area change and far less than other samples. This indicated that the new composite support and the core-shell nanostructures improved the platinum long-term stability.



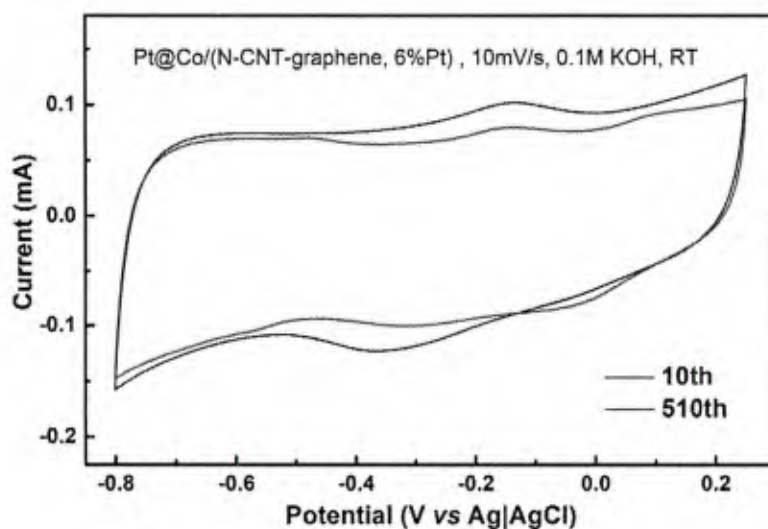


Figure 11. The cyclic voltammetry (CV) results 0.1 M KOH solution at 10mV/s and room temperature of Pt@Co/N-(CNT-G) sample at different cycles

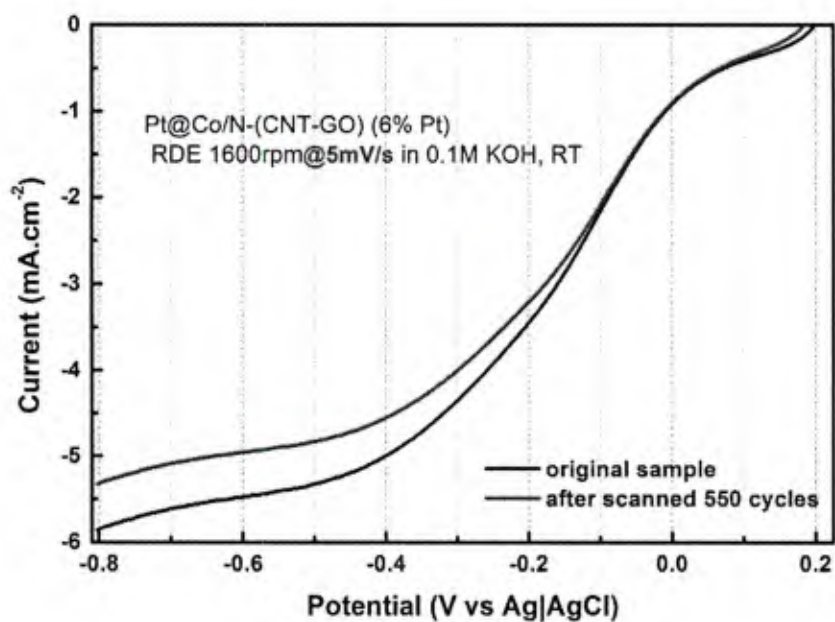


Figure 12. Linear scan results (RDE) of Pt@Co/N-(CNT-G) sample before and after 550 cycles in 0.1 M KOH solution with bubbling oxygen and at room temperature.



### Single cell performance test

The platinum loadings are 0.2 and 0.4 mg/cm<sup>2</sup> platinum on anode and cathode sides, respectively, for all CCMs (catalyst-coated membrane) coated with different catalysts. All CCMs are made by direct spraying process using Sonotek coating machine. On the cathode side, the mass ratio of catalyst to Nafion polymer (solid) is kept at 2:1 for all performance tests. The anode catalyst is carbon supported platinum (Pt/C, 40%wt), and the polymer membrane is 17µm thick. All tests are conducted at room temperature with fixed flow rates of dry oxygen and hydrogen at cathode and anode side, respectively. The active area of CCM is 6.25 cm<sup>2</sup>. The flow rate is 40 sccm and 100 sccm for hydrogen and oxygen, respectively. The measurements are conducted at 60 °C and 85 °C.

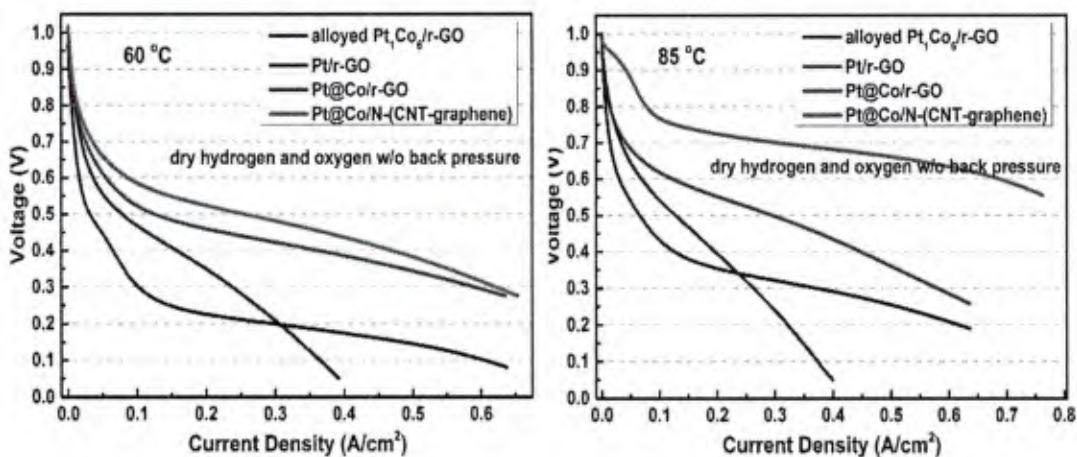


Figure 13. Single-cell measure curves of CCM armed with different cathode catalysts at different temperature.

Figure 13 showed the current-output voltage curves of CCMs with different cathode samples. Except cathode samples, all other parameters including anode catalyst are all kept the same, therefore, the differences in the single cell performance are mainly attributed to the cathode catalyst activity. From this figure, it can be seen that the CCM performances varied greatly with different cathode catalysts and operating temperatures. It is quite interesting to see that the alloyed PtCo sample (black line in both inset figures) performed worse than platinum sample (blue line) especially in low to medium current range (< 300 mA/cm<sup>2</sup>) as many work reported that PtCo alloy are superior to pure platinum catalyst. However, this is only true with the high atomic ratio of Pt to cobalt, especially the Pt<sub>3</sub>Co<sub>1</sub>, which is different from the sample tested. The low Pt/Co ratio meant that there are low platinum surface sites available for ORR, especially for the sample without high-temperature treatment that can bring most of platinum to the surface and increase the platinum sites available. From this experiment it can be concluded that the lower platinum content in alloyed PtCo sample does not favor the ORR in practical applications.

The single cells employing core-shell samples showed markedly improved performance compared to the ones with Pt/r-GO sample. This confirmed the above conclusion that the platinum sites on the metallic surface are useful; the more platinum sites available on the surface of cathode catalyst, the better is the single-cell performance. The two core-shell samples have different supporting materials which affect the CCM performance significantly as depicted in Figure 13. The employment of nitrogen-doped composite support, the mixed carbon nanotubes and graphene, brings about enhanced catalytic activity as compared to the sample with single supporting material, Pt@Co/r-GO. It is also noted that the higher operating temperature has positive effect on the CCM performance improvement for core-shell samples.

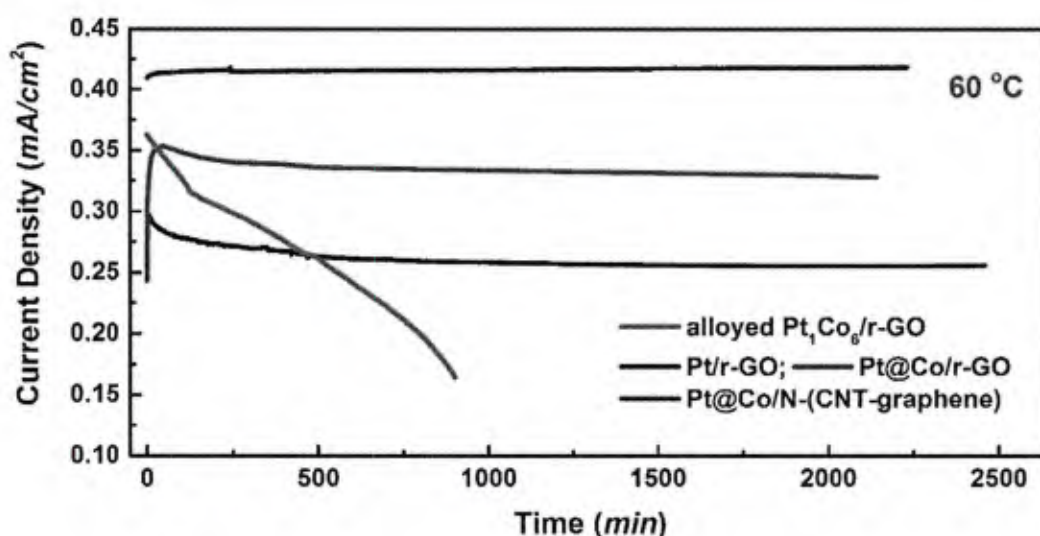


Figure 14. Long-term CCM performance using different catalysts at 60 °C.

The long-term testing for all single cells are conducted at 0.5V by measuring the current with time at 60 °C. The results are shown in Figure 14. As expected, the alloyed PtCo sample with low platinum molar content has the poorest performance although it has higher initial current. The current at fixed voltage decreased very rapidly in less than 20 hours, implying that the PtCo is not a suitable cathode catalyst. The other three samples showed good and relatively constant performance for almost one and half day. Among the samples, Pt@Co/N-(CNT-graphene) showed the best and most stable performance.

Aggregating the results from the half-cell and single cell tests, we believed that the core-shell Pt@Co sample supported on composite supporting materials enhanced the ORR by exposing platinum active sites on the metallic surface as much as possible.

The interaction between the platinum shell and cobalt core, especially the strain effect and the electronic effect as suggested in publications, assisted the O-O bond breaking and the recycling of platinum active sites. The difference between the two core-shell samples, Pt@Co/r-GO and Pt@Co/N-(CNT-graphene), clearly underscored the importance of composite support to significantly improve the CCM performance.

We attributed the enhancement to the following possible factors: the interaction between the metallic particles and the composite materials; the favorable mass transfer properties; and electronic conductivity improved by the 3D structure of composite materials. It is also possible that the surface of composite material has additional active sites caused by the doped nitrogen as reported in recent publications. In summary, the Pt catalyst with core-shell structure and composite support is a favorable cathode catalyst for ORR, and more endeavors are also needed for further optimization.

## Summary and recommendation

The project aimed to develop a composite catalyst that combine the positive features of precious and non-precious metal catalysts that are low-cost and comparable/better catalytic activity with long term stability. Our experiment results confirmed core-shell nanostructure catalyst of its feasibility, high activity and effective usage of costly platinum. With the core-shell structure, the performance of the catalyst with lower platinum loaded on the graphene is on par with the catalyst sample that has 10 times more platinum loading, and has higher specific current density.

We noted that the supporting materials also play an important role in the catalyst performance. The use of nitrogen-doped CNT-graphene composite material to support the Pt@Co core-shell further improved the catalyst activity, and enhanced the long-term chemical stability. The robust properties, high activity and low platinum loading of the novel catalyst would improve the durability of the fuel cell stack and reduce the overall cost.

The results of the single cell tests further supported the above notion. The single cells employing core-shell samples showed markedly improved performance compared to the ones with Pt/r-GO sample. The single cell that has Pt@Co/N-(CNT-graphene) as the cathode catalyst has the best and most stable performance among the various samples.

We attributed the enhancement to the following possible factors: the interaction between the metallic particles and the composite materials; the favorable mass transfer properties; and electronic conductivity improved by the 3D structure of composite materials. It is also possible that the surface of composite material has additional active sites caused by the doped nitrogen.

While the nitrogen-doped carbon composite showed the feasibility and potential in supporting and enhancing the cathode activity in presence of low platinum content, we recommend that the future work should include 1) Optimization of the graphene/CNT ratio to obtain desirable morphology and pore structures, 2) Increase poisoning tolerance to carbon monoxide, sulfur and chloride, and 3) production techniques to scale-up the synthesis of core-shell nano-structure catalysts.