

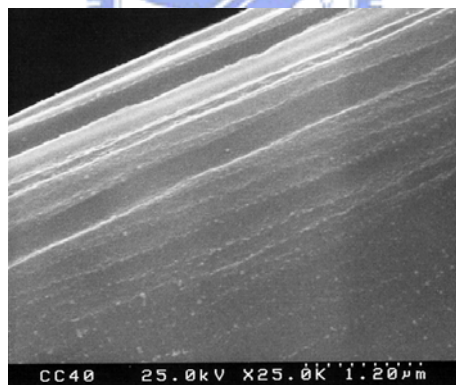
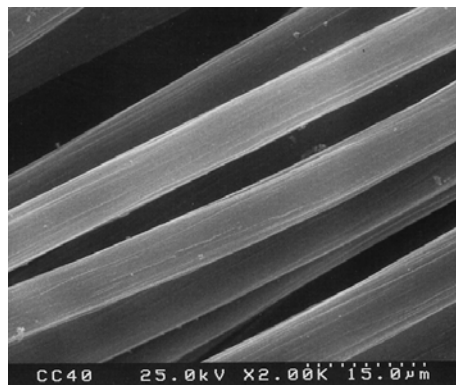
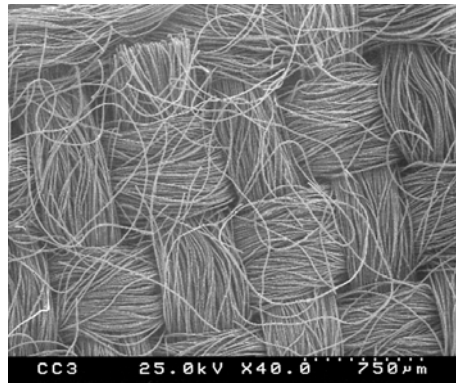
## 4.2. Basic analysis of prepared carbon nanomaterials on carbon cloth.

Fig 4.19 is a piece of carbon cloth with no treatment. It is composed of textured carbon fibers which have a smooth surface. Fig4.20 is the images of CNTs and CNFs deposited on carbon cloth. The left image indicate the porous structure is clear and uniform and between the fibers there're fewer vacancies left.

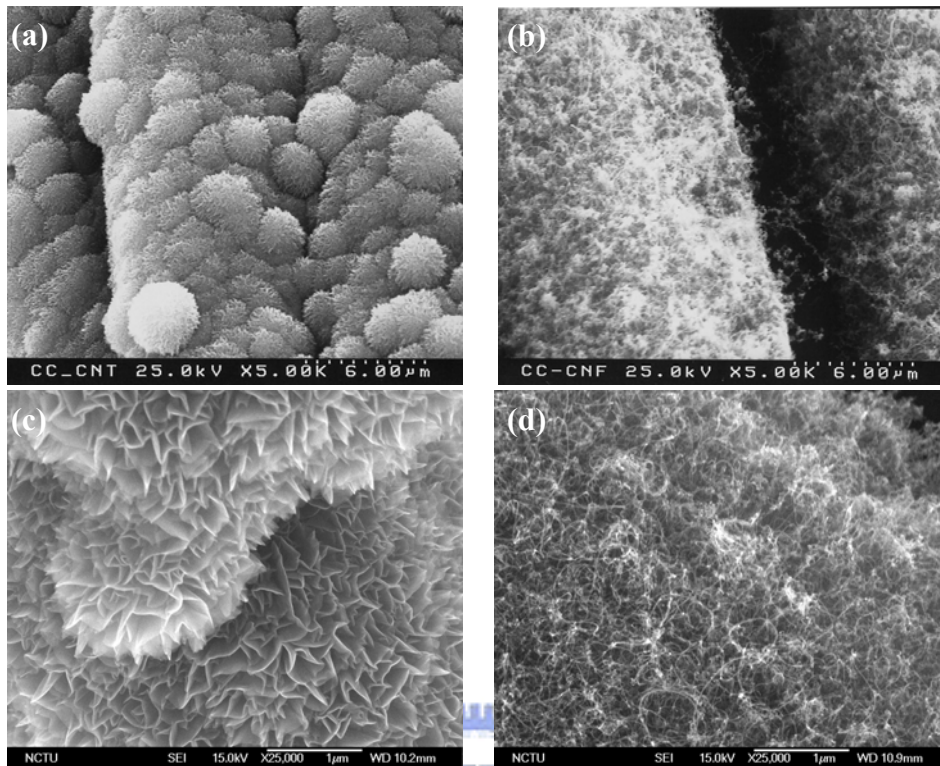
However the carbon nanotubes on carbon cloth (right images) entangle with each other, lay down on the substrate and have random direction due to the round substrate so as the length limited even the negative bias can enhance it. We have another test to get the vertical carbon nanotube s, but if the density of carbon nanotubes isn't be controlled; the spraying of Pt particle may just stop on the top surface. Therefore, even the carbon nanotubes make the smaller pore which still can't be utilized until the density is controlled. In additional, the vacancies between fibers couldn't be stuffed due to carbon nanotubes can't grow across the fiber so the left space wasted.

From the surface areas test by BET, the adsorption area of carbon cloth obviously increased with the surface improvement by CNT and CNF. As prediction of porous structure make it more efficient, the CNF do attribute to more surface areas than CNT on carbon cloth.

The resistance test also revealed the appreciative property of being an electrode of PEM fuel cell and with the graphite component increasing the electric conductivity enhanced. Each data was collected by 10 times of test and get an average.



**Fig4.19 SEM images of plain carbon cloth textured by carbon fiber with different magnitude.**



**Fig4.20 SEM images of plain carbon cloth deposited with CNFs and CNTs:**  
**(a)CNFs (b) CNTs (c)-(d) enlarged image of (a)-(b) separately.**

**Table 4.1 Surface areas and resistance comparison**

	Surface area (m <sup>2</sup> /g)	Resistance (Ω/cm <sup>2</sup> )
Carbon cloth	15.02	0.487
CNTs on carbon cloth	90.31	0.399
CNFs on carbon cloth	130.96	0.328

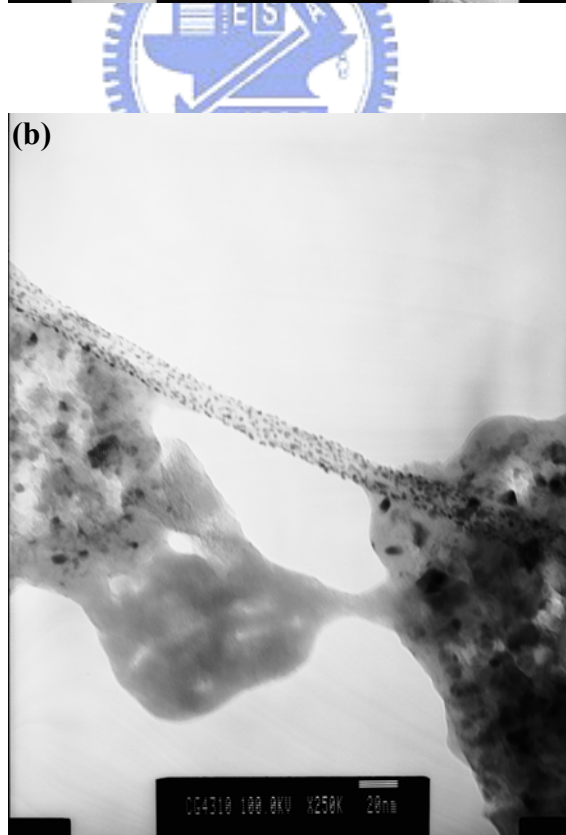
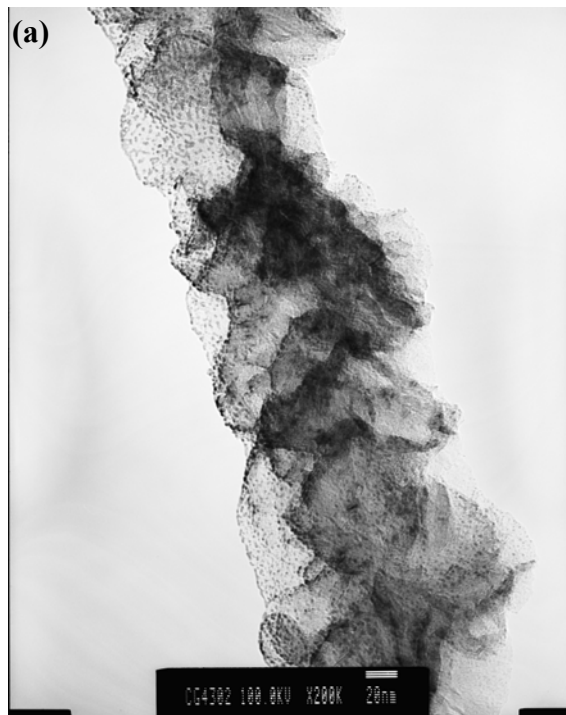
### 4.3 Two methods of dispersing Pt

In this part, we will discuss the results of Pt dispersing methods affect the uniformity and procedure's convenience.

By sputtering Pt method, the working time just spend 20~60secs to get the Pt particles size range from 2~5nm. Fig 4.24 shows the TEM images of sputtering Pt on CNT and CNF. Although the outcome on CNT seems to be good, it isn't spray on every CNT. However the Pt on CNF could be seen anywhere especially every petal on it. The reason can be traced to forward preparing carbon cloth experiment, the entangled morphology of CNTs leads to the property decay by sputtering Pt. Comparatively, the random extended CNFs could collect Pt very well as long as they have the top-open structures.

About the chemical solution method, the preparing Pt/Ru mixing solution may need 1~2 hr, and this lead to different ratio of Pt/Ru. The solution were prepared by mixing PVP, Pt/Ru ions and ethylene glycol then put in hot chamber for reacting 1hr. We assume the ratio of Pt/Ru is 1:1. When we get the solution and immerse CNTs or CNFs in it, it should be mixed with acetone to separate the Pt/Ru from other polymer and the dilute ration could affect the later alloy particle size. The separating procedure should be by centrifuge to make sure the pure Pt/Ru, but still has the impurity. After this, ever immersed sample must dry in vacuum oven up to 200°C and this may cost 2 hr. From a succession of procedure, each part may affect the property of Pt/Ru on CNTs or CNFs and hard to exam.

From Fig4.22 we can determine the uniformity between sputtering and solution methods. The particles deposited by sputtering are separated well and the size is also well-controlled, besides each Pt has a single crystal structure by diffraction pattern identification. Otherwise the Pt/Ru on CNFs by poyol isn't generally sprayed but has a twin specific line. Fig 4.24 is EDX sheet shows the particle is Pt on prepared cloth.

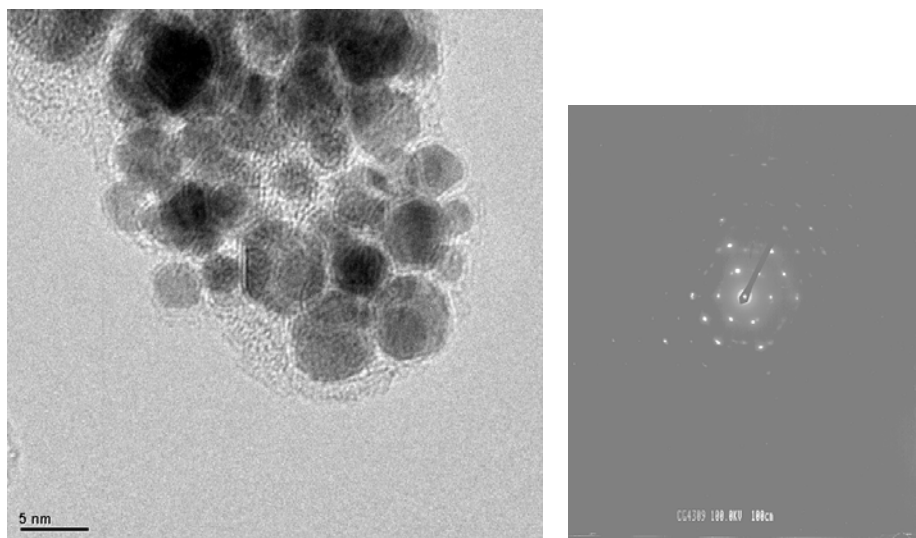


**Fig.4.21 TEM images of Pt on CNF and CNT by sputtering: (a) CNF  
(b) CNT**



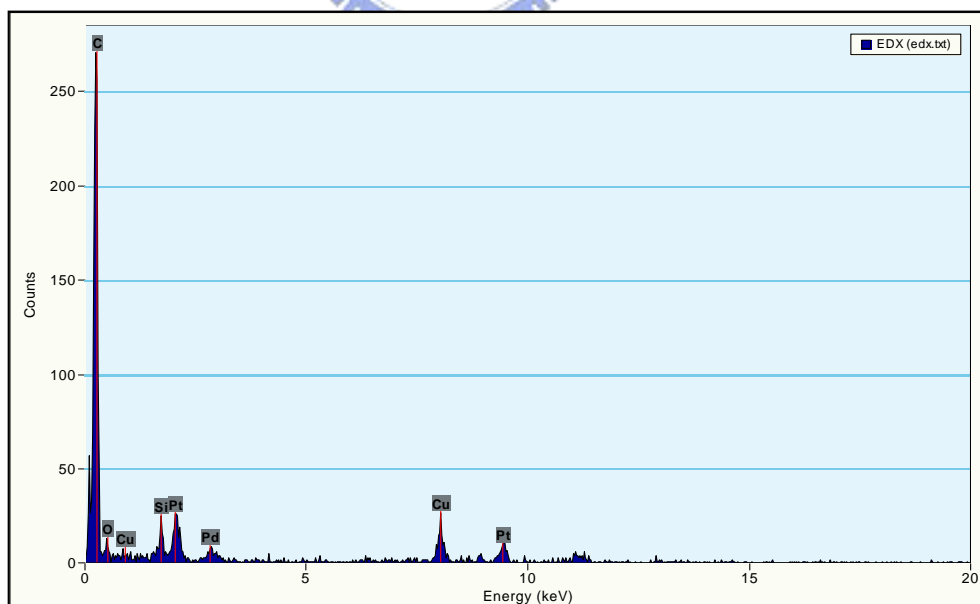
**Fig.4.22 TEM images of Pt on CNF by sputtering and Poyol:**

**(a) Sputtering (b) Poyol .**



**Fig 4.23 HRTEM images of deposited Pt particle: (a) Pt on CNF**

**(b) Diffraction pattern of Pt**

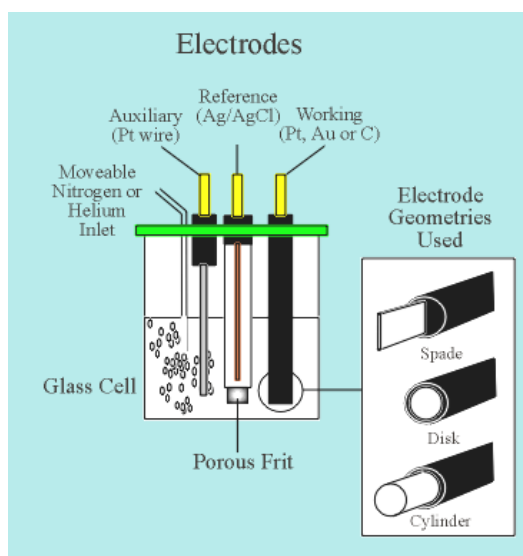


**Fig.4.24 EDX of Pt on CNF**

## 4.4 Cyclic voltammetry experimental results

### 4.4.1 Cyclic voltammetry measurement

An electrochemical cell must consist of at least two electrodes and one electrolyte. An electrode may be considered to be an interface at which the mechanism of charge transfer changes between electronic (movement of electrons) and ionic movement of ions. An electrolyte is a medium through which charge transfer can take place by the movement of ions. In a cell used for electroanalytical measurements there are always three electrodes functions. The first of the three electrodes is the indicating electrode also known as the test or working electrode. This is the electrode at which the electrochemical phenomena being investigated takes place. The second functional electrode is the reference electrode. This is the electrode whose potential is constant enough that it can be taken as the reference standard against which the potentials of the other electrodes present in the cell can be measured. The final functional electrode is the counter or auxiliary electrode which serves as a source or sinks for electrons so that current can be passed from the external circuit through the cell. In general, neither its true potential nor current is ever measured or known.

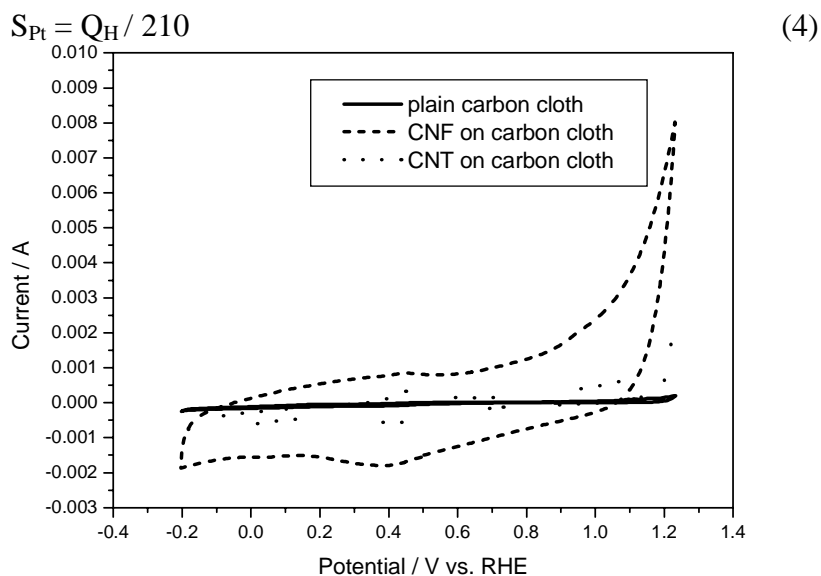


**Fig.4.25 Electroanalytical measurement setup** [<http://www-biol.paisley.ac.uk/marco.htm>]



#### 4.4.2 Effect of carbon nanomaterial on the electrocatalytic properties of Pt nanoparticles

The prepared carbon cloths were immersed in 1M H<sub>2</sub>SO<sub>4</sub>. Scanning range was -0.2~1.3V corresponding by working voltage of typical fuel cell. Scanning rate was constantly at 10mV. There was a significant difference in voltammetry between the non-treated carbon cloth surfaces and the carbon nanomaterials-modified carbon cloth surfaces as shown in Fig.4.26. The Three CVs reproduced well the typical voltammogram taken in sulfuric acid solution <sup>[67]</sup>. The solid curve in Fig.4.26 corresponds to containing only carbon cloth. The dash-line means carbon cloth were covered by carbon nanoflakes so as the current is obviously promoted. The dot-line is carbon cloth covered by carbon nanotubes. It also shows current promoting but the magnitude is smaller. It is well known that the cathodic and anodic peaks appearing between 0.3 and 0.5V versus RHE originate from H-adsorption and H-desorption, respectively. By using the charge passed for H-adsorption, Q<sub>H</sub>, one can estimate surface area of Pt, S<sub>Pt</sub>. <sup>[68]</sup> Suggested equation is (1). The two applied carbon nanomaterials compared here were under the same Pt loading by chemical method of 0.1M Pt/Ru solution.

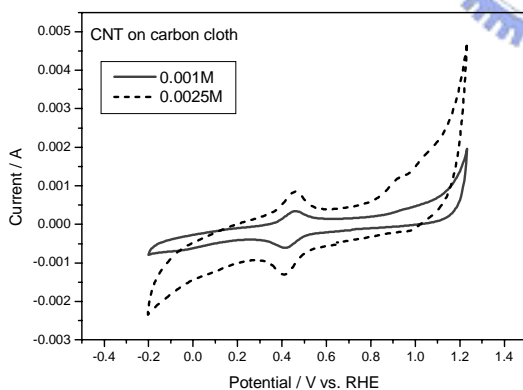


**Fig.4.26 The CVs of carbon cloth, Pt/carbon nanoflakes/carbon cloth, and Pt /carbon nanotubes/carbon cloth**

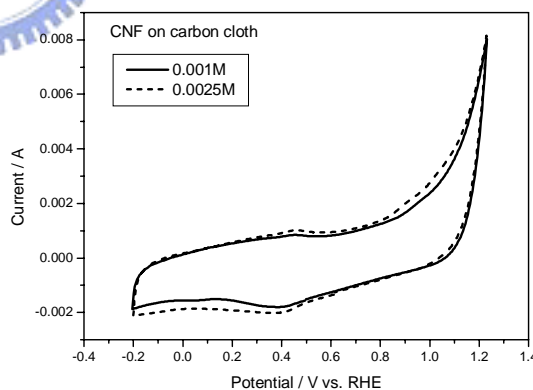
### 4.4.3 Effect of Pt loading by chemical solution

It is obviously indicated in Fig.4.27 that higher concentration of Pt/Ru solution led to large Pt/Ru particle size. The more contacted surface areas of Pt/Ru enhanced the larger current. However, Pt/carbon nanoflakes(Fig.4.28) isn't shown distinguish between different concentration. It is due to utilization of Pt/carbon nanotubes is limited by their tube shape and shown more Pt particle size effect. In another case, Pt/carbon nanoflakes have more available sites for redox reaction occurred so as the small variation by different concentration of chemical solution.

In additional, the current enhanced by two carbon nanomaterials could provide evidence that carbon nanoflakes have more surface advantage than carbon nanotubes to support Pt. But the shape produced by carbon nanoflakes shows rectangular than carbon nanotubes. This could explain of capacitance effect caused by flakes' shape that electron is easily caught in pore.



**Fig.4.27 CVs of Pt/carbon nanotubes/carbon cloth by different concentration of Pt/Ru solution.**



**Fig.4.28 CVs of Pt/carbon nanoflakes/carbon cloth by different concentration of Pt/Ru solution.**

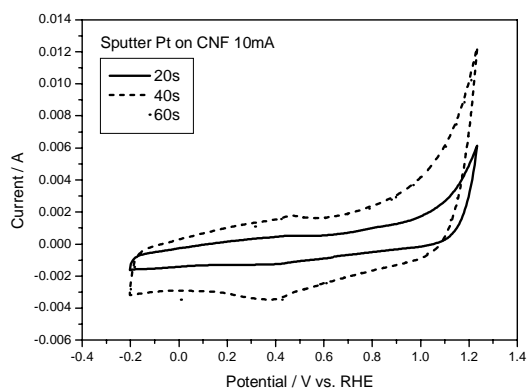
#### 4.4.4 Effect of Pt loading by sputtering

Pt/carbon nanoflakes/carbon cloth was used here to confirm the time or applied current of sputtering effect. From Fig.4.29, current is higher when period of time is 40s~60s. This could also explain that sputtering time extended enlarged Pt particle size. When particle size grown over a limitation, it is well known Pt forms platinum oxide in aqueous solutions. The platinum oxide generated can be reduced reversibly according to the following reaction [69]:

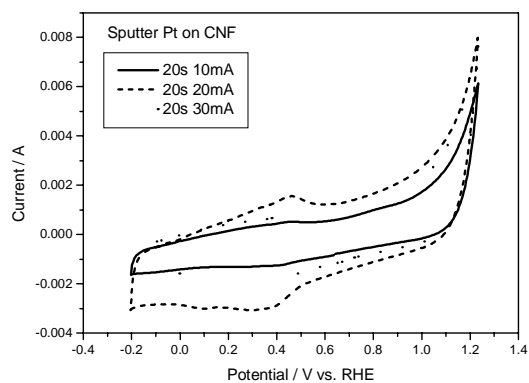


Since this single electron redox reaction involves adsorption process at the Pt surface, the reaction would depend on a surface condition. The Pt particulate size does not influence the H-adsorption /desorption potential, but it affects the oxide formation potential as also reported by some researchers [70~75].

The same results in Fig.4.30 are applied current leading Pt particle size enhancement. The difference is increasing current isn't efficiently promoting the corresponding current occurred in redox reaction.



**Fig.4.29 CVs of Pt/carbon nanotubes/carbon cloth by different time of sputtering.**



**Fig.4.30 CVs of Pt/carbon nanotubes/carbon cloth by different applied current of sputtering.**