Chapter 1 Introduction

1.1 Preface

Since Grove discovered the reaction between hydrogen and oxygen in 1841, development of the fuel cell has not had much progress because of the low efficiency. However, classical studies in the electrochemical system predict that a direct conversion of chemical energy into electricity using the fuel cell would be far more efficient at low temperature than the combustion processes. In the beginning of the Twentieth century, the internal combustion engine was a vital source of power generation. The fuel cell did not attract much attention until 1960s. Owing to the increased efficiency and the invention of new materials for the fuel cell, applications and many new types of fuel cell have been gradually developed. Fig1.shows present fuel cell stack application on several electronic productions

In recent years, the proton exchange membrane fuel cell (PEMFC) used for space mission, terrestrial vehicle transportation, and local power generation has received increasing attention. Due to its high electrochemical performance efficiency, simple stack design, pollution-free, noise-free, and low temperature operation, PEMFC has become a promising candidate for portable power source. Besides, PEMFC with the promises such as the elimination of electrolyte leakage and lower corrosion has applications in the areas of military, aerospace and transportation. Emission product from PEMFC is free of environment-undesired gases, such as nitrogen oxide, carbon monoxide, carbon dioxide, and hydrocarbon, which are usually produced from internal combustion engines. Especially, carbon dioxide is absent in the reaction when the hydrogen is used as fuel [1].

PEMFC has incorporated various electrodes containing Pt / C. Due to cut the catalyst costs, many researchers have been studying the membrane and electrode assembly (MEA) manufacturing process that can reduce the content of Pt in the electrocatalyst layer while maintaining the performance. In this work, we applied carbon nanomaterials as the substitution for commercial carbon black to support Pt which dispersed by two methods becoming an assembled electrode.

Fig 1.1 Fuel cell stack application on several electronic productions.
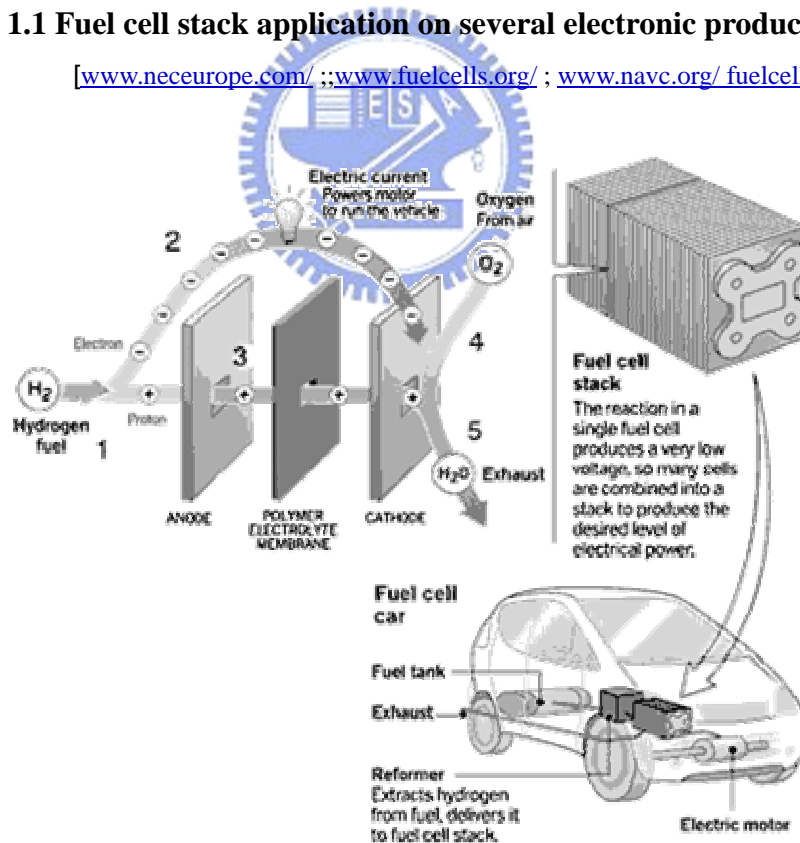
Fig 1.2 The schematic images of fuel cell stack.

1.1.1 Classification of Fuel Cells

Fuel cells can be commonly classified into six types according to the electrolyte, operation temperature, and the types of fuel source. The types of fuel include gaseous fuel such as hydrogen and liquid fuel such as methanol. The types of electrolyte also include solid electrolyte and liquid electrolyte. The electrode materials may include noble metals, non-noble metals, carbon, and composite materials. The six types of fuel cell are

(1) proton exchange membrane fuel cell (PEMFC),

(2) alkaline fuel cell (AFC),

(3) phosphoric acid fuel cell (PAFC),

(4) molten carbonate fuel cell (MCFC),

(5) solid oxide fuel cell (SOFC), and

(6) direct methanol fuel cell (DMFC).

The basic characteristics of these six types of fuel cell are listed in Table 1.1 [2]. Among these fuel cells the PEMFC shows great advantages such as low temperature, high power density with respect to weight and volume, and easy start-up.

Comparing with the other low-temperature fuel cells, the PEMFC has high rates of oxidation-reduction. However, it has lower resistance against poisoning by carbon monoxide than AFC. In addition, the solid electrolyte reduces corrosion and management problems [3~6]. The PEMFC can be used in notebook PCs, dispersed power plant, and electrical vehicles. It is expected to be a convenient and efficient portable power generator in the future.

Table 1.1 Several types of Fuel Cell

Typical application	Portable electronics equipment	Cars, boats, and domestic CHP	Distributed power generation, CHP, buses
Power in Watts	1 10 100	1k 10k	100k 1M 10M
Main advantages	Higher energy density ,faster recharging	Potential for zero emissions, high efficiency	Higher efficiency, less pollution, quiet
Range of application	AFC MCFC SOFC PEMFC PAFC		

*CHP: combine heat and power system

[Fuel cell System Explained ,James Larminie]

1.2 Background of the Study

Since carbon is the lightest element in the 4th group elements, which has unique properties comparative with other elements. More then 500,000 compounds of carbon have been synthesized, which are greater than the sum of the other elements. Carbon appears in several kinds in nature. Fig. 1.3 shows various atomic structure of carbon. Zero-dimensional carbon, such as fullerence, was identified by Kroto et al.[8], also lead to the discovery of carbon nanotubes[9]. One-dimensional carbon, such as nanotube discovered by Iijima, exhibit amazing behaviors and attracts a lot of attentions. Two-dimensional carbon, such as graphite, and 3-dimensional carbon, as diamond, bonds in sp^2, bonds in sp^3, respectively, have already been study widely and extensively.

With the development of nano technology, nanostructures-structures that are defined as having at least one dimension between 1 and 100nm-have receive steadily growing interest as a result of their peculiar and fascinating properties, and applications superior to their bulk counterparts. Many applications are predicted to involve with nano technology including optics[10], electronics[11], catalyst[12], ceramics[13], and storage media[14,15], etc. The most pertinent example is microelectronics, which "smaller" means greater performance ever since the invention of integrate circuits: more components per chip, faster operation, lower cost, and less power consumption [16].

One of the most powerful (and yet versatile) means to control the electrical, optical, magnetic and thermoelectric properties of a solid-state functional material.

Ever since the discovery of carbon nanotubes, great efforts were invested in the exploitation of their applications. Carbon related nano materials considered the top priority for nano applications.
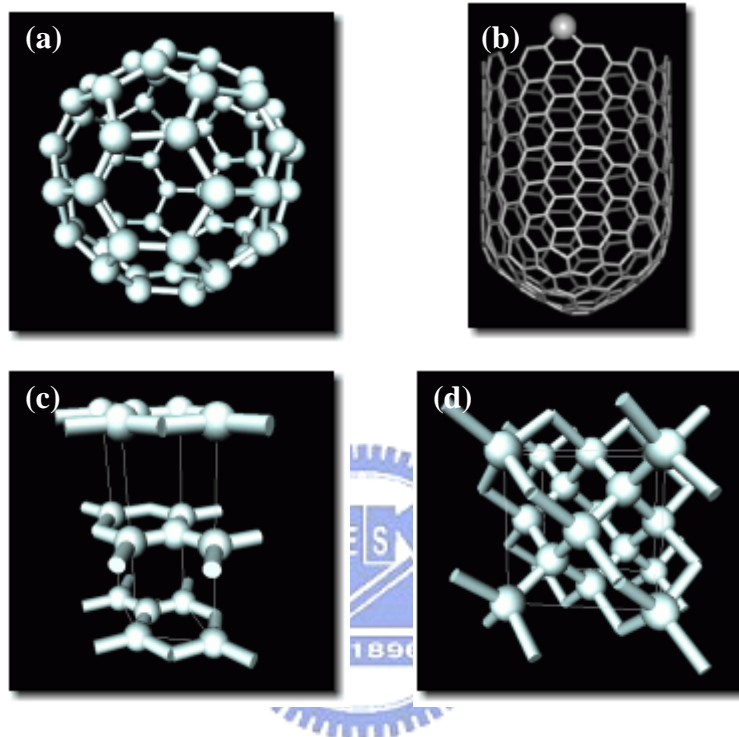
Fig. 1.3 Atomic structure of carbon: (a) fullerence, (b) nanotube, (c) graphite, (d) diamond. [www.ill.fr/ dif/3D-crystals/]

1.3 Literature Review of Carbon based Nanomaterials

1.3.1 Carbon Nanotube

Figure 1.4 shows typical electron microscopy images of carbon nanotubes. Since the first observation of multi-wall carbon nanotubes (MWNTs) by Iijima[9], much attraction has been drawn because of their excellent physical properties and potential applications in various fields. For example, carbon nanotube is probably the best conductor of electricity that can ever be possible [17-19]. Carbon nanotube technology is the other new direction being pursued in the search for high capacity electrode media. Carbon nanotube has comparable thermal conductivity with diamond along the tube axis [20]. With the total area per nanotube bundle for normalizing the applied stress, the calculated Young's modulous for an individual (10, 10) nanotube is ~0.64 TPa[21]. Can be reacted and manipulated with the richness and flexibility of other carbon molecules. Strong van der Waals attraction leads to spontaneous roping of many nanotubes which is important in certain applications.
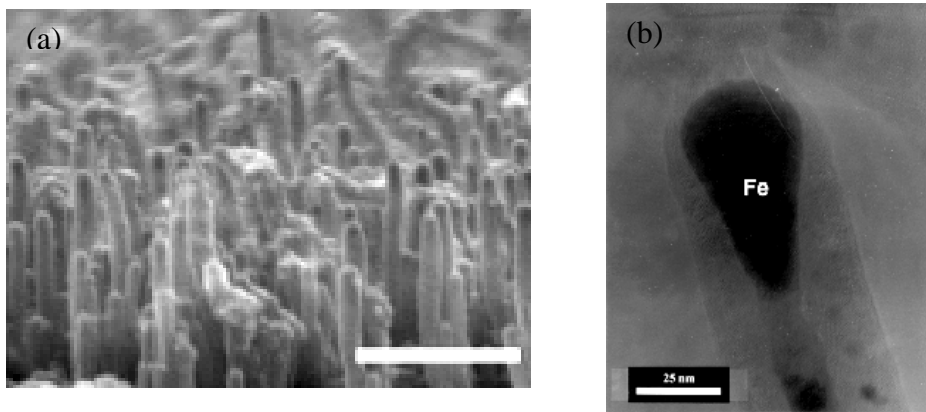

Fig. 1.4 Carbon nanotubes (a) SEM image of as-grown MWNTs

(b)TEM image of an individual MWNT

[Surface and Coatings Technology 169 –170（2003） 348–352]

1.3.2 Carbon Nanofibers

Recently, the particular properties (high accessible surface area, low resistance, etc.) of graphitic carbon nanofibers (GCNFs) have also generated intense concern [22]:GCNFs may be supporting materials, which can support a high dispersion of platinum nanoparticles due to their high surface area [23,24].Additionally, the metal particles supported on the graphitic carbon nanofibers seemed to be less susceptible to CO poisoning than the traditional catalyst systems [23].Currently, two kinds of GCNF electrodes have been developed: binder-free and binder-enriched [25].

In the binder-free electrode, carbon nanofibers are mechanically and electrically loose. When a binder is used, it brings impurities into the electrode and degrades the electrochemical performance. Furthermore, both methods result in high contact resistance between the active material (carbon nanofibers) and current collectors (graphitic or metallic substrate).
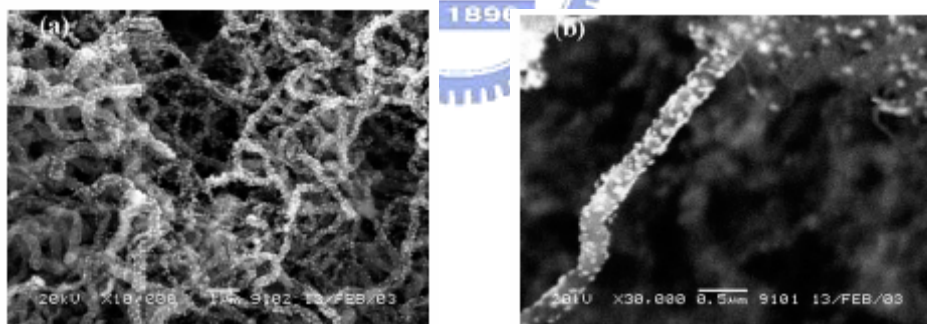

Fig. 1.5 The SEMmicrographs of platinum nanoparticles on GCNFs/graphite electrode and graphite electrode. (a) GCNFs/graphite electrode (low magnification) (b) GCNFs/graphite electrode (high magnification).

1.3.3 Carbon nanocoil

Occasionally, during the preparation of carbon nanotubes or nanofibers by the catalytic pyrolysis of hydrocarbons, the growth of helical-coiled species has been observed.[26-34] . Measured in nanometers, the coil diameters of these nanotubes or nanofibers range from tens to hundreds and the coil pitch from tens to thousands, while the diameter of the tubes or fibers forming the coils is smaller than one hundred. Fig1.6, 1.7.

Due to their characteristic coiling morphology,these carbon microcoils are expected to have many new and important applications, such as electromagnetic wave absorbers, tunable microdevices (microsensors, microactuators, micromachines,etc.), field-electron emitters, etc.
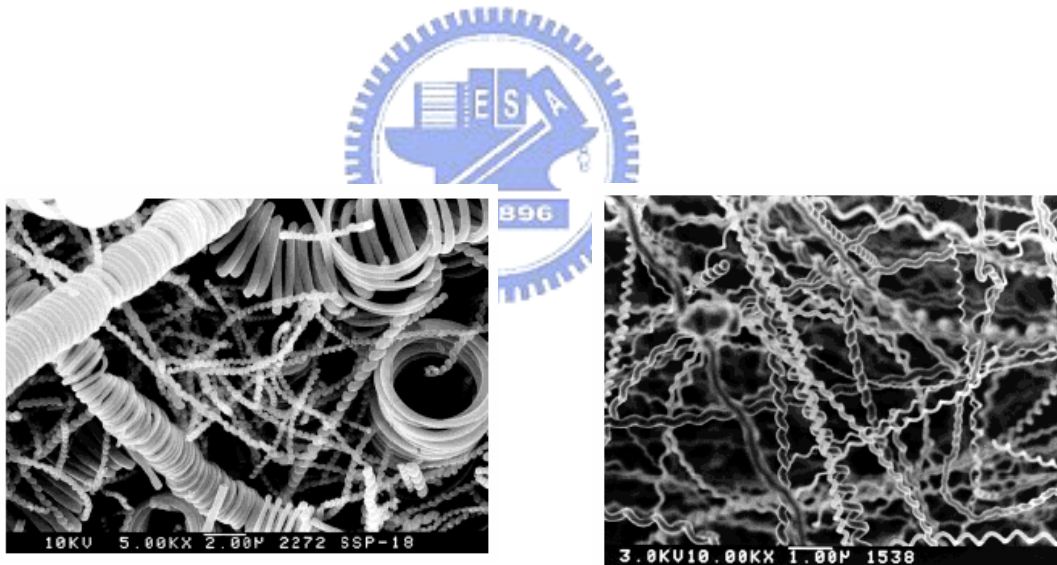

Fig.1.6 (a) Carbon nanocoils grown among the carbon microcoils under an applied

magnetic field in the reaction zone. Catalyst: Ni fine powder

(b) Carbon nanocoils. Catalyst: Au sputtered films [Preparation, Morphology, and

Growth Mechanism of Carbon Nanocoils Chem. Vap. Deposition 2002, 8, No.2]

1.3.4 Carbon Nanoflake

The carbon nanoflake film consists of petal-like graphite flakes with a thickness of less than about 20 nm, is of much interest [35]. Each carbon nanoflake can be considered a quasi-two-dimensional structure with strong anisotropy in physical properties. It is interesting that almost all the carbon nanoflakes are vertical to the substrate. This can lead to a large surface-to-volume ratio for Pt deposition, as in the case of carbon nanotubes and herringbone-like carbon nanofibers[36,37].Fig.1.7 indicates 2-D structure of carbon nanoflke grown on substrate.
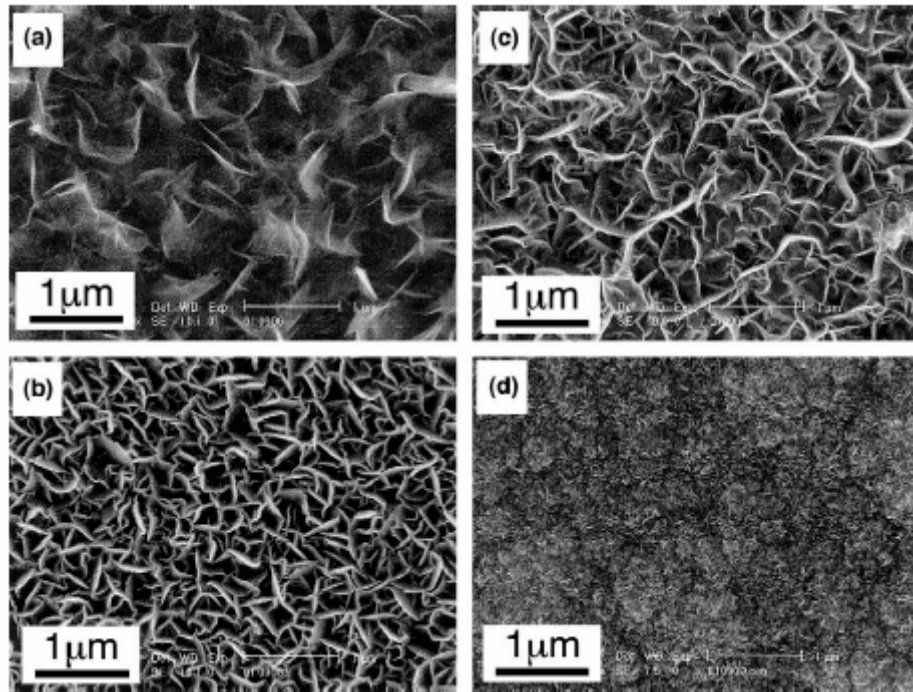

Fig.1.7 SEM images of the carbon nanoflake films deposited at the substrate temperature of (a)400,(b) 500 ,(c) 600 (d) and 700 °C.

[Chemical Physics Letters 358 (2002) 187–191]

1.4 Motivation

Carbon nanomaterials are of significant interest, due to their unique structure, properties and potential applications. If the attention today is mainly focused on the synthesis, purification, functionalization and possible applications of single walled carbon nanotubes (SWCNTs), multiwalled carbon nanotubes (MWCNTs) are certainly closer to commercial applications. For instance, the use of MWCNTs in composite materials, or as electrical field emitters [38], is well established. Our interest in MWCNTs is to use them as electrocatalyst supports in polymer electrolyte membrane (PEM) and in direct methanol fuel cells.

However, carbon nanotubes are hydrophobic materials, rendering difficult the adhesion of metal deposits. It has been reported that carbon nanotubes cannot be wet by liquids with surface tension higher than 100–200 mN/m [39], indicating that most metals would not adhere to them. In order to improve metal deposition onto nano-materials ,we would like to modify the surface morphology of carbon nanotube.

Otherwise, recently a unique CVD procedure is developed to grow carbon nanomaterials on the carbon fibers as a fuel cell backing. In the present work, it is possible to deposit Pt particles on these carbon nanomaterials and, therefore, to obtain a composite electrode for which an electrical path exists between the Pt catalyst and the carbon backing.

The deposition of Pt on carbon nanomaterials has been chosen because Pt and its alloys are currently the most extensively used catalysts in PEM and direct methanol fuel cells.