Chapter 2 Fundamentals of PEMFC and Carbon nanomaterials

2.1 Principle of PEMFC

The schematic of a unit cell of conventional PEMFC is shown in Fig. 2.1.

Typically, the PEMFC is composed of a membrane electrode assembly (MEA) and two graphite flow-field plates, which are pressed against the MEA. These plates have a manifold of grooves to distribute the reactant gas to the electrodes. The space for the hydrogen flow is separated from air or oxygen, and the other side may be for oxygen or exposed to ambient air.

The MEA (Fig.2.2) includes a proton exchange membrane and two catalyst layers, each of which is brush spread on a piece of carbon cloth or carbon paper. Platinum powders are used as catalyst in the PEMFC system.

The proton conductive membrane for PEMFC is commercially available from DuPont Incorporation and has a commercial name, Nafion®. This organic proton-conductive membrane is a sulfonic acid-based perfluorinated polymer or polystryene sulfonate polymer. It is used as electrolyte and the protons (cations) are allowed to permeate through it, but anions are rejected. The Nafion® structure is composed of three different parts, namely, rigid hydrophobic backbone, flexible perfluorocarbon, and hydrated ionic cluster region. The chemical formula and physical structure of the membrane is shown in Fig.2.3.

The proton exchange process occurs through the sulfonic acid root and then cations go through the polymer to the cathode. The cations permeating through the electrolyte are probably in the form of H_3O^+. Thus, water plays an essential role in the PEMFC [6].

The specific conductivity of the membrane is related to the content of the sulfonic acid and the characteristics of various proton conductive membranes are listed in Table 2.1 [3]. The

effective proton conductivity involves electromigration as well as electro-osmosis, and the conductivity is thus highly dependent on the degree of hydration.

The "liquid-like" mechanism makes proton transport as hydrated hydronium ions through water-filled ionic pores and channels. Besides, the membrane has twofold functions. It transfers the ion between the anode and cathode and it serves as gas separator or insulator for the two reactant gases. It should have many desirable properties, including good mechanical strength, good chemical stability, and high ionic conductivity under high humidity conditions at about $1000°C$ [1, 38, 39].
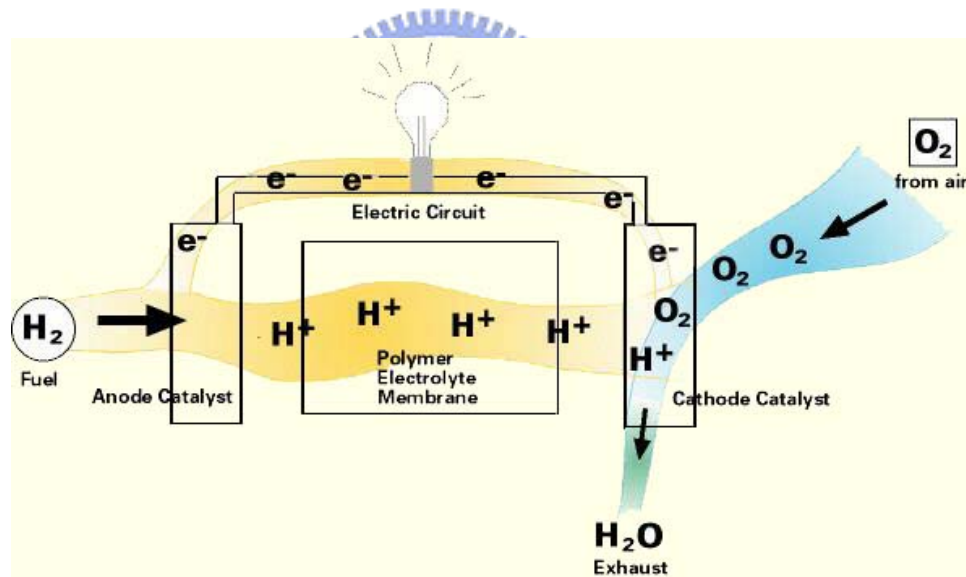

Fig.2.1 The schematic of a unit cell of conventional PEMFC
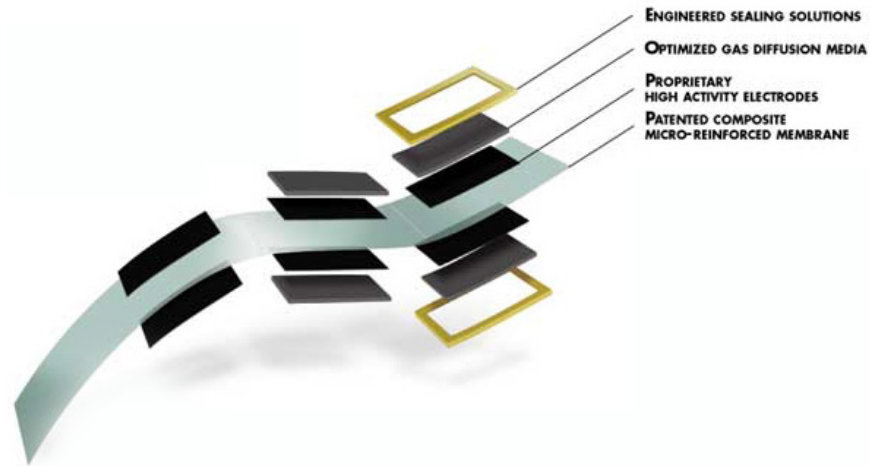[aiche.sdsmt.edu/.../ what_is_a_fuel_cell.htm]

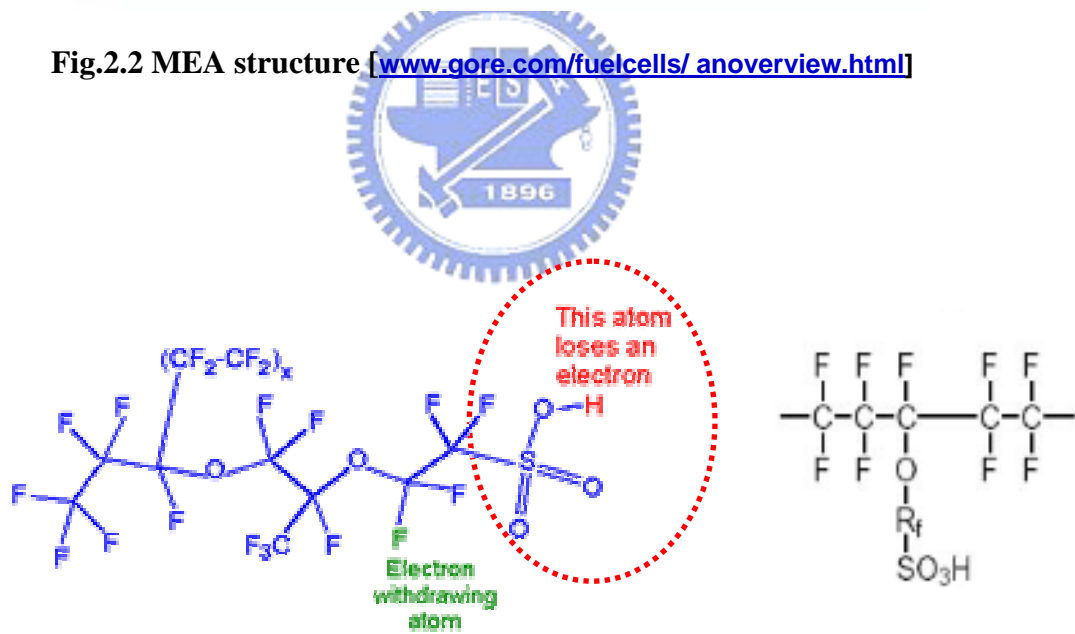**Fig.2.2 MEA structure [www.gore.com/fuelcells/ anoverview.html]**


Fig.2.3 The chemical formula and physical structure of the membrane Nafion®

[Dupont Products information about Nafion]

When hydrogen is charged to the anode, it will be decomposed to protons and electrons by the function of platinum catalyst. The reaction equation is shown as：

$$2H_2 \rightarrow 4H^+ + 4e^- \quad E^0=0V \tag{1}$$

The protons pass through the membrane electrolyte to the cathode and the electrons flow via the outside circuit to the cathode. There they react with oxygen with the help of catalyst to form water according to the reaction：

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E^0=1.229V \tag{2}$$
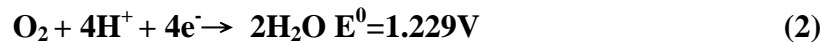
Thus, the total reaction is that hydrogen reacts with oxygen to form water and producing a voltage of 1.229 V. The total equation is as follows：

$$2H_2+O_2 \rightarrow 2H_2O \quad E^0=1.229V \tag{3}$$

In the reaction, suitable proton conducting and water transport properties of the membrane and proper water management are critical for superior fuel cell performance. Dehydration of the membrane reduces proton conductivity, and excess of water will lead to flooding in the electrode.

Recent studies of PEMFC have focused on the improving of conductivity of protons in the proton exchange membrane and the performance of catalyst layer with less loading. Because of the high cost of the major components of MEA, mainly the membrane and catalyst, the progress of commercializing the PEMFC has been delayed. Besides, platinum has low resistivity against the poisoning by carbon monoxide below 1000°C and it is important to find other new materials or to lower the loading of novel metal catalyst.

When the fuel cell is in operation, some factors, including physical processes, polarization, and electrical characteristics of MEA, should be considered [14], as discussed below:

Physical process

Porous carbon fiber is used as a backbone in the electrode for reactant gases to transport into both cathode and anode for reaction. Besides, as the gas approaches to the reaction site, i.e. the catalyst location, capillary action is involved in this process.

Electrochemical reactions

Two half-cell reactions occur in the electrochemical reactions. In the anode, hydrogen oxidizes to form protons and electrons. In the same time, oxygen, proton, and electron in the cathode combine to form water, yielding a voltage, 1.229 V.

Ion transfer

The protons produced at the anode must permeate through the electrolyte membrane to the reaction site at the cathode. The moving process involves the interaction between the protons and water molecules within the membrane. The protons cannot move smoothly through the membrane without water inside, because the sulfonic acid group would bridge the protons strongly for lack of water. Furthermore, accumulation of protons at the anode results in a driving force to move the protons from the anode to the cathode [40].

When the protons move, they proceed with the accompany of water molecules. Hence, there is a close relation between the membrane resistance and water content within the membrane. In other words, the performance of the cell would be improved with a proper water content in the membrane. However, the water molecules may move in either direction, and they would interfere with the transport of the protons from the anode to the cathode. There are two factors affecting the water molecule movement inside the membrane electrolyte. One is electro-osmotic effect and the other is water accumulation at the cathode [41]. Electro-osmotic effect comes from the proton movement in company with the water molecules. With the modulation of operation condition,

the water distribution and the performance of the fuel cell could be improved.

Electron transfer

The oxidation at the anode produces electrons. The electrons would not travel from the anode to the cathode through the membrane electrolyte since it would result in a short circuit. Thus, they go through the outside circuits to the reaction site at the cathode with the help of gas diffusion layer of the anode, bipolar plates, and the current collector in the unit cell setup. The polymer electrolyte membrane is an insulator since the polytetrafluoroethelyene backbone and acid groups make the membrane to have strongly held electrons.

Polarization processes

The theoretical voltage (V) a fuel cell produces in operation can be calculated from the reaction free energy (ΔG^0). Because ΔG^0 is a function of temperature, when the temperature increases, the theoretical voltage would decrease.

In an ideal situation, fuel cell would produce a large current with the theoretical voltage. In practice, however, several types of polarization affect the current density with different various degrees. Each polarization is influenced by many factors and would result in the reduction of cell potential on increasing the current density. When the current density increases, the practical voltage decreases.

Overpotential is defined as the difference between the practical voltage and thermodynamic reversible voltage. With the change of the current density, there exists three kinds of overpotential : (1) activation overpotential, (2) ohmic overpotential, and (3) concentration overpotential.

2.2 Growth of Carbon Related Nano Material

Due to huge amount compounds and various atomic bonding of carbon, plenty of kinds of methods are used for the growth of carbon related nano materials. Each method has its advantages, disadvantages, distinguishing feature, and a range for suitable use. Most of them have been successfully synthesize carbon nanotubes.

The model used for describing the growth of nano materials still is a hot issue because of the difficulty for observation under such extremely small scale. Even though, several mechanisms are brought up to characterize the behavior for the growth. Here we discuss some growth models which are considered to be the major mechanism for nano size material.

2.2.1 Growth Methods

Chemical Vapor Deposition (CVD)

Chemical vapor deposition includes thermal CVD, Hot filament CVD, microwave plasma CVD, etc. Catalysts are normally used for the growth of carbon related material. Typically chemical vapor depositions are used for the production of carbon fibers [42] [43]. It is not until 1993 that Yacaman et. al.[44] successfully use chemical vapor deposition to deposit carbon nanotubes. And till 1997 microwave plasma enhanced chemical vapor deposition is used to deposit carbon nanofibers and carbon nanotubes [45,46]. Hydrocarbon gases are usually mixed with hydrogen (or ammonia) to be the reaction gas [47]. Products may be carbon nanotubes, amorphous carbon, carbon fiber, or even carbon nano tips, which are correlated to growth temperature, flow rate, reaction gas, growth time, bias, and catalyst. Compare with the methods above, CVD has the advantage of low process temperature, relative good uniformity, convenience, large area growth, and easy for in-situ doping [48].
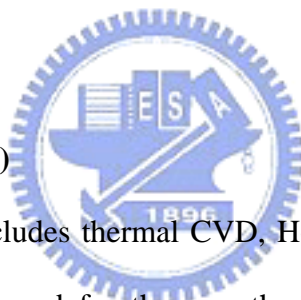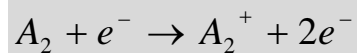
Bias Assisted Microwave Plasma Chemical Vapor Deposition

Microwave plasma chemical vapor deposition is one of the important facilities for thin film deposition, micro manufacturing, and surface treatment [56]. By the advantage of high ion density, high degree of dissociation, high reactivity, and low process temperature, a lot of kinds of substrates are capable of fabrication under low temperature with deposition and etching, which is meaningful for VLSI process, microelectronic device, optoelectronic device, polymer, and thin film sensor.

By applying electric field, the reaction gas breakdown to induce electrons and ions. With electromagnetic field obtained by microwave or RF power, more electrons and ions are generated by colliding with the un-dissociated gas. Stable plasma is reached when the generation rate and consumption rate are equal for all species. Unlike traditional thermal plasma, temperature of electrons, ions, and neutral particles in low temperature plasma induced by discharge are not identical. The temperature of electron is about 1000°K, while the ions and neutral ones are below 500°K. Therefore, low temperature plasma is a non-equilibrium plasma with not only few ions, electrons, but also excite state, transient state, and free radicals. By manipulating these high energy species, reaction which is hard for steady state species are attainable.

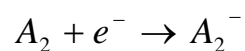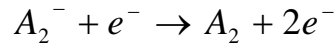Take diatomic plasma for example, the procedure may appear as followed:

(1)Ionization
$$A_2 + e^- \rightarrow A_2^{\,+} + 2e^-$$
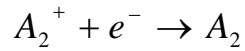(2)Dissociative ionization
$$A_2 + e^- \rightarrow A^+ + A + 2e^-$$
(3)Attachment
$$A_2 + e^- \rightarrow A_2^{\,-}$$

(4)Detachment

$$A_2^- + e^- \rightarrow A_2 + 2e^-$$

(5)Recombination

$$A_2^+ + e^- \rightarrow A_2$$

(6)Atom recombination

$$2A^\bullet \rightarrow A_2$$
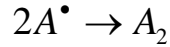
*any polyatomic molecule is substituent for mentioned above.

$\bullet$ Stands for free radical

Basically, microwave plasma chemical vapor deposition does not need any electrode or even heater. But in this thesis, bias plays an important role in the growth of nano materials, and also an essential term. When a DC bias is added on to the substrate, before the ions pass through the plasma sheath area, the movement of the ions do not effect by the collision between the ions, comparatively and statistically. Also means the ions can strike the substrate directly and vertically by the applied field [57].
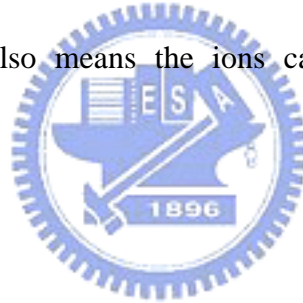
2.2.2 Growth Mechanisms

Growth mechanism of various kind of bottom-up nano size materials are generally considered to be three models: Vapor-Solid (VS) model, Vapor-Liquid-Solid (VLS) model, and recently, Solution-Liquid-Solid (SLS) model. Some modifications [49] have also been published which will not be discussed here.
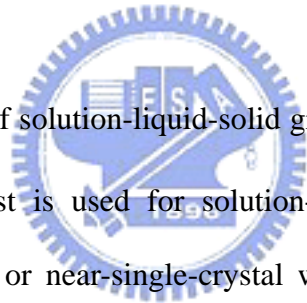
Vapor-Solid (VS) Model

Fig.2.4 shows an approximately growth model of vapor-solid growth mechanism. The diagram takes the growth of GaN for example. Epitaxial growth can be achieved without catalyst or liquid phase. The sum of thermodynamic surface energy and heat of fusion become the driving force for VS growth.

Vapor-Liquid-Solid (VLS) Model

The mechanism [50] was first introduced in the 1960s to explain the growth of silicon whiskers or tubular structures [51]. In this model, growth occurs by precipitation from a supersaturated liquid-metal-alloy droplet located at the top of whisker, into which silicon atoms are preferentially absorbed from the vapor phase. The similarity between the growth of carbon nanotubes and the VLS model has also been pointed out by Saito et al [52,53]. on the basis of their experimental findings for multi-walled nanotube growth in a purely carbon environment. Solid carbon sublimates before it melts at ambient pressure, and therefore these investigators suggested that some other disordered carbon form with high fluidity, possibly induced by ion irradiation, should replace the liquid droplet.

Solid-Liquid-Solid (SLS) Model

Figure 2.6[54] shows diagram of solution-liquid-solid growth mechanism which takes Ⅲ-Ⅴ materials for example. No catalyst is used for solution-phase synthesis. The materials are produced as polycrystalline fibers or near-single-crystal whiskers having width of 10 to 150 nanometers and length of up to several micrometers [55]. This mechanism shows that process analogous to vapor-liquid-solid growth operated at low temperatures, while requirement of a catalyst that melts below the solvent boiling point to be its potential limitation.
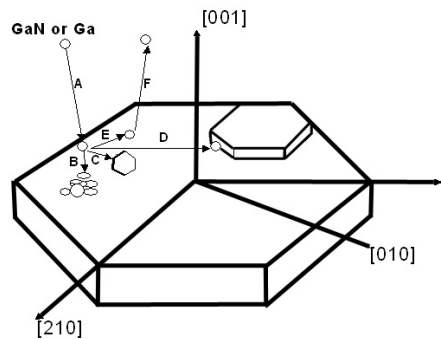
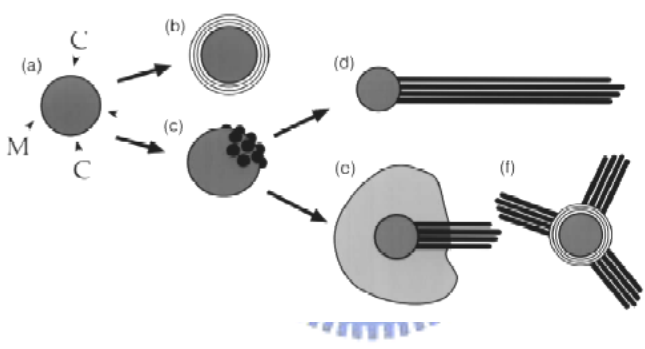**Fig. 2.4 Schematic diagram of vapor-solid (VS) growth model**

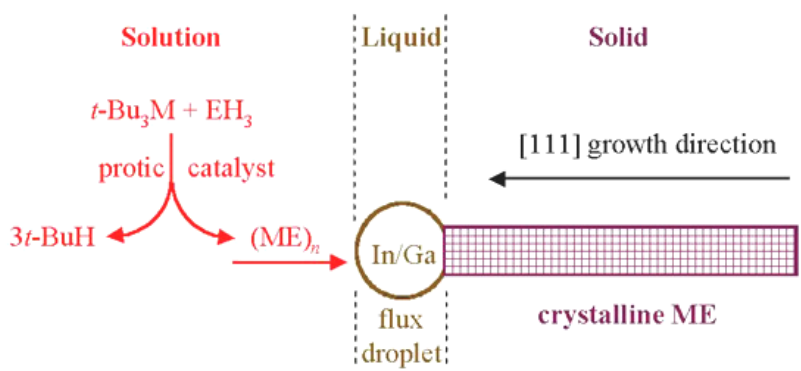**Fig. 2.5 Schematic diagram of VLS growth mechanism for nanotubes**

[Gavillet, et al., 2001]

Fig. 2.6 Schematic of SLS growth mechanism