

Chapter 3 Experimental procedures

3.1 Fabrication of carbon based nanomaterials on silicon

The carbon nanomaterials discussed here were prepared using silicon as substrate to obtain parameters of process. On setting the basis rule of manufacture, the further experiment could help discussing the growth steps of carbon nanomaterials. More, several analyses were using to comprehend what the schema of carbon nanomaterials are. For utilizing carbon nanomaterials into electrode of proton-membrane-exchange fuel cell, the last two steps were introduced to obtain main performance of carbon nanomaterials. Fig. 3.1 shows the three main experimental procedures.

3.1.1 Fabrication of carbon based nano-materials by bias-assisted microwave plasma- enhanced chemical vapor deposition (MPECVD)

The carbon nanotubes(CNT) and carbon nanoflakes(CNF) were fabricated in a MPECVD with bias-assisted. The 100Å of Fe film was deposited on silicon as catalyst for growth of carbon nanotubes by using ion-beam sputter. After that, the prepared substrate was under a series cleaning procedures using acetone, ethanol, and de-ionized water, and then pure nitrogen finally was introduced to dry the prepared substrate.

The chamber was evacuated at pressure of $\sim 10^{-2}$ Torr with a rotary pump. The reactive gases used in deposition were mixture of CO₂ and CH₄, which held ratio of 30/30 sccm to a pressure set at 10 Torr. The microwave power of 300W was applied to light the plasma let the temperature reached up to 700°C, and the reflected power is minimized to <10W with the assistance of a two-stubtuner . In order to make sure the sample is totally immersed into plasma, the position of plasma is adjusted by the sliding short circuit. Biasing system was conducted with upper and lower electrodes made of Mo with a distance of 3cm. Samples were placed on the Mo holder, which is attached to the lower grounded electrode.

DC bias was applied under vapor deposition with a series of parameters to verify how bias

affects the growth of carbon nano-materials to change their morphology.

3.1.2 Bias-assisted microwave plasma chemical vapor deposition system

Fig.3.2 schematically depicts the layout of the MPECVD system. A quartz tube is vertically attached to a rectangular waveguide used as deposition chamber. The microwave from a magnetron source (model IMG 2502-S, IDX Tokyo, Japan) is supplied to the quartz tube through an isolator, and a power meter. Then the microwave power is coupled to the quartz tube through an aluminum waveguide with a hole drilled through from top to bottom face. Aluminum tubes extend out from both holes; the tube extensions are water-cooled as well. A sliding short circuit is then attached at the end of the waveguide. The lower position of the quartz tube is connected to a stainless steel multi-port chamber equipped with a rotary pump.

The substrates are positioned in the middle of the quartz tube waveguide intersection and held vertically by a substrate holder which is 20mm in diameter, made of molybdenum. Under the holder, attached a tantalum wire which is connected to the bias system; it was used as the lower electrode in the bias treatment stage. A quartz protector under the holder to protect the plasma not attracted to the tantalum wire attached to the molybdenum. The upper electrode, a molybdenum plate of 20mm in diameter which is placed 35 mm above the substrate, also attached to a tantalum wire. The controlled amount of the source gases was introduced into the chamber by mass flow controllers (model 647B, MKS instrument, Inc., USA) from the upper end of the quartz tube. A small window was cut in the waveguide at the center of the plasma cavity, allowing direct observation of the plasma.

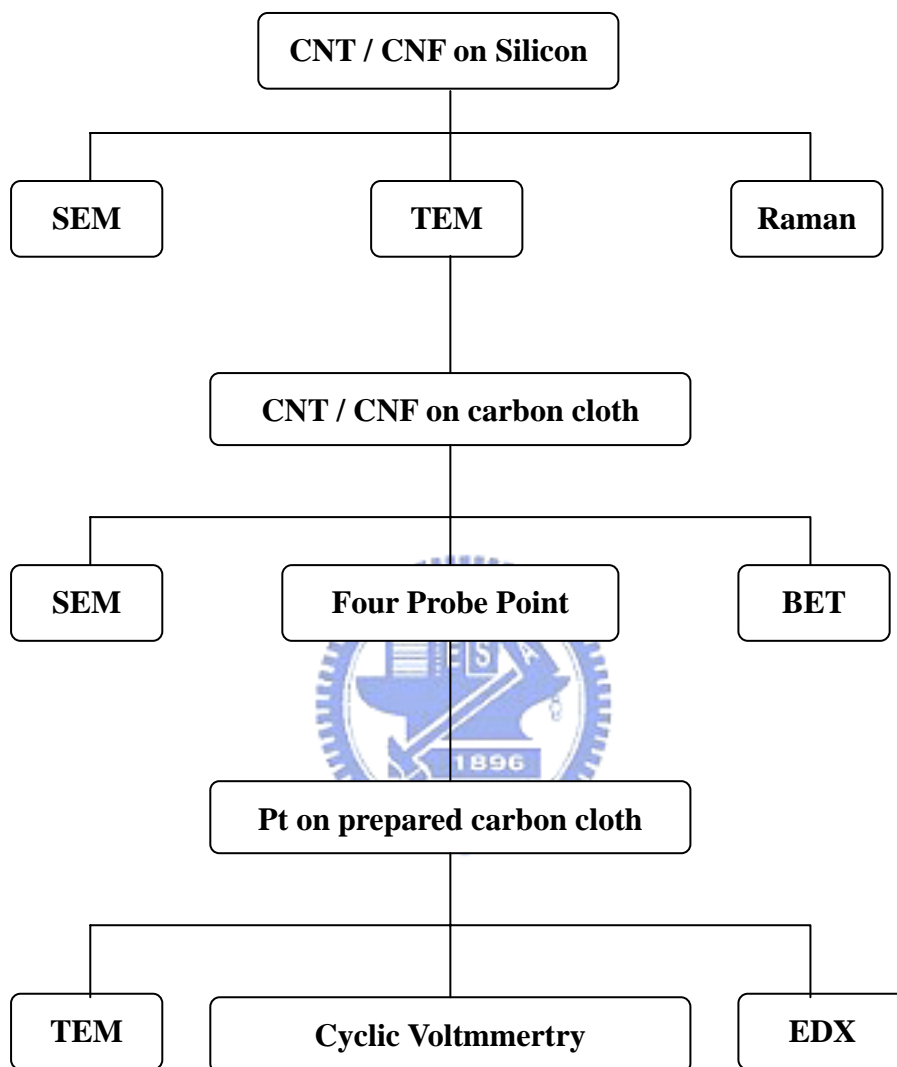


Fig.3.1 Flow chart of experimental procedures.

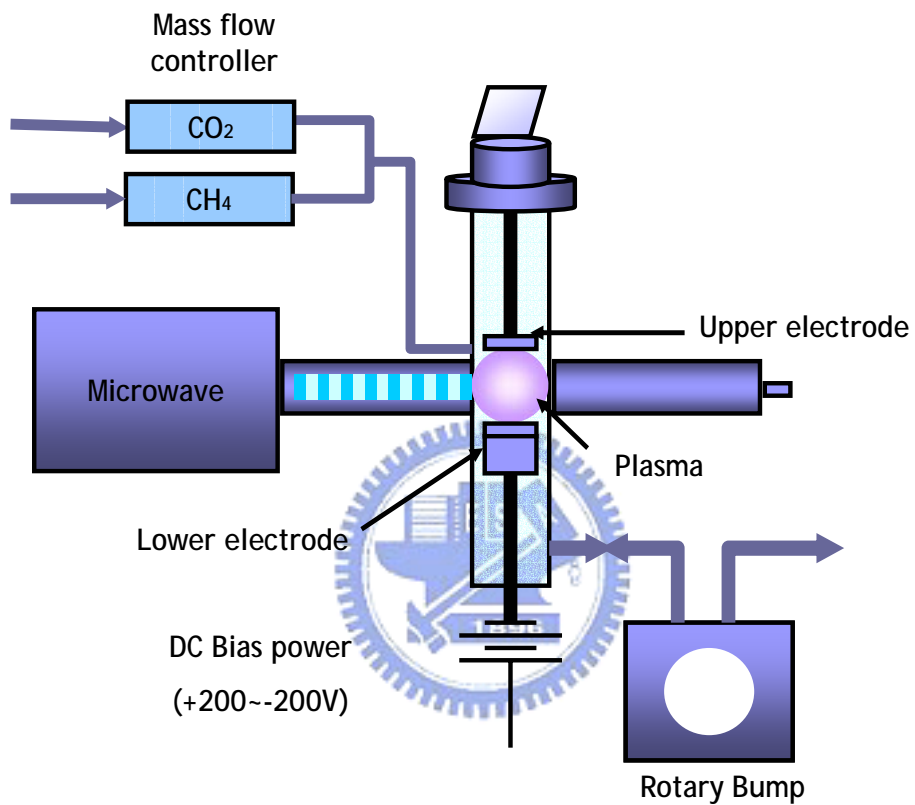


Fig.3.2 Schematic diagram of the bias-assisted microwave plasma chemical vapor deposition system.[Depict by I-Hsuan Lee]

3.2 Fabrication of carbon based nanomaterials on carbon cloth

The better conditions were chosen from the ex-experiment step was applied it on the carbon cloth. Carbon nanotubes and carbon nnoflakes were obtained by heating Fe particles, which deposited by ion-beam sputter on the fibers of the carbon cloth (Electrode Backing , ElectroChem. Inc. Item No. EC-CC1-060) in MPECVD. To ensure their qualities of being catalyst (Pt, for extracting electron from H_2) support, the surface area and resistance were examined.

3.3 Dispersion of Pt on prepared carbon cloth

Two methods of dispersing Pt on carbon cloth were utilized to compare their uniformity and practicability. One was spreading by physical vapor deposition (PVD) of ion-beam sputter , and the other was immersing in a chemical solution containing $H_2PtCl_6 \cdot 6H_2O$, $H_2RuCl_6 \cdot xH_2O$, PVP-40 , and ethylene glycol mixture diluted with acetone. Polymer (PVP) is the protection agent to limit metal particle growth spacing. This method were expected a uniformly homogeneous nucleation and growth mechanism of nanoparticle. The reaction dominates by temperature control and solvent plays as reductant as well. By differing experimental time could obtain various Pt /Ru alloy ratio. Fig 3.3 shows the experimental details of chemical mixed procedure.

In sputtering process, we changed the particle size by controlling depositing time while in chemical method, we diluted the prepared solution of different acetone/ prepared solution ratio to get various particle size.

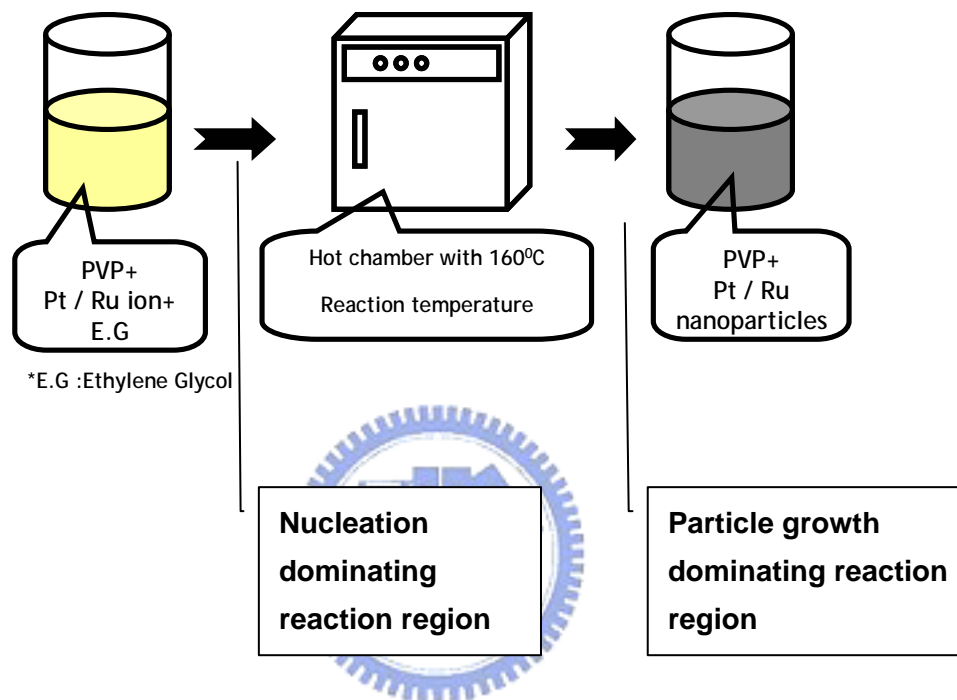


Fig. 3.3 Experimental detail of chemical solution reaction of Pt/ Ru particle

[Depict by I-Hsuan Lee]

3.4 Analysis Instruments

3.4.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is used to observe the surface morphology of wide range kinds of objects ^[58]. It has the advantage of rather easy sample preparation, high image resolution, large depth of field, and high magnification.

A common SEM contains an electron gun to generate electron beams, which will be accelerated under 0.4-40kV voltage. By deflecting the incident beams with the focusing coils, a two dimensional image can be obtained by detect the reflected secondary electrons and the backscatter electrons.

The model we use here is Hitachi S-4000, with field emission electron source and 25kV accelerate voltage.

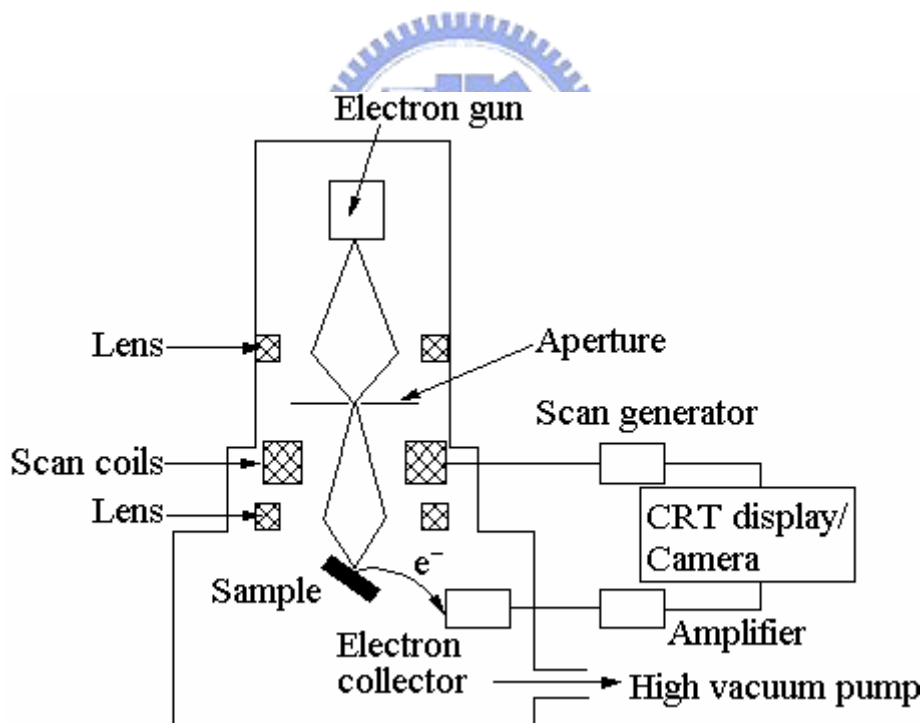


Fig.3.4 Schematic diagram of a Scanning Electron Microscopy

[<http://www.chm.bris.ac.uk/pt/diamond/stuthesis/chapter2.htm>]

3.4.2 Transmission Electron Microscopy (TEM)

In a typical TEM a static beam of electrons at 100-400kV accelerating voltage illuminate a region of an electron transparent specimen which is immersed in the objective lens of the microscope. The transmitted and diffracted electrons are recombined by the objective lens to form a diffraction pattern in the back focal plane of that lens and a magnified image of the sample in its image plane. A number of intermediate lenses are used to project either the image or the diffraction pattern onto a fluorescent screen for observation. The screen is usually lifted and the image formed on photographic film for recording purposes.

3.4.3 Raman Spectroscopy

While photons illuminate a molecule or a crystal, they react with the atoms accompanied with momentum change or energy exchange. By collecting the scattered photons, we can obtain a sequence of spectrum, including Raman scattering (inelastic scattering) and Rayleigh scattering (elastic scattering). The photon of Raman scattering can be classified into two kinds, Stokes side which photons lose energy or the molecules gain energy, and anti-Stokes side, which photons gain energy or molecules lose energy. Generally, Stokes side is used to characterize the material.

As Raman spectrum provides information of crystallinity and bonding, it has become the most direct and convenient way to identify carbon related materials. The Raman spectrum peak of C-C and C=C bond in crystalline graphite are 1380 and 1580 cm^{-1} , respectively, as shown in Fig.3.5.

The instrument we use is Renishaw Raman microscope, Model 2000, equipment settings are shown in Fig.3.6. The source we use is He-Ne laser with wavelength of 632.82nm and power of 200mW. The spectral slit width is 0.4 cm^{-1} .

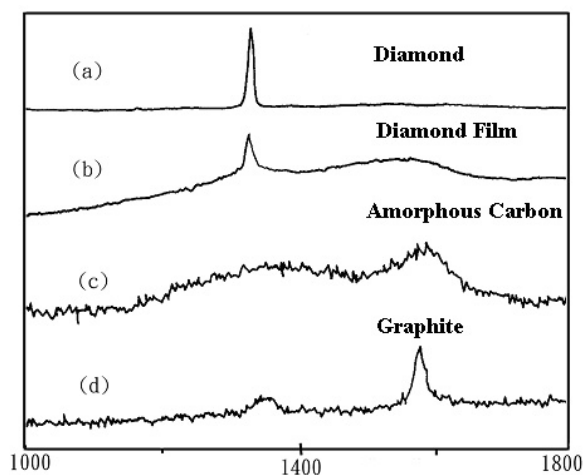


Fig.3.5. Raman shift of (a) diamond, (b) diamond film, (c) amorphous carbon, (d) graphite

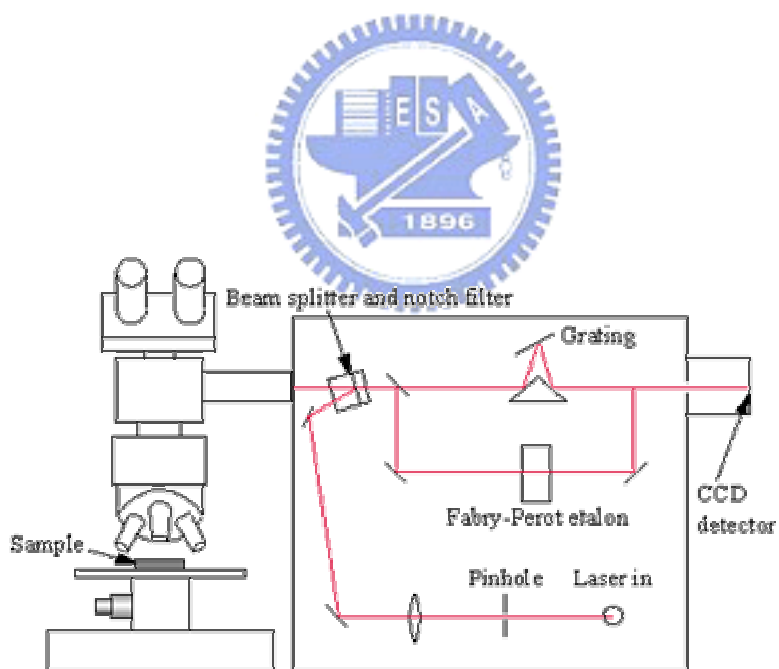


Fig.3.6 Schematic diagram of micro-Raman equipment

[<http://www.chm.bris.ac.uk/pt/diamond/stuthesis/chapter2.htm>]

3.4.4 BET (Brunauer, Emmett and Teller Isotherm)

It is applicable to adsorption of multiple layers onto homogeneous surfaces and a standard method for surface area measurements. The assumptions for the simplest BET isotherm are:

Gas adsorbs on a flat, homogeneous solid surface with a uniform heat of adsorption due to van der Waals forces between the gas and the solid. No lateral interaction between the adsorbed molecules. After the surface is partially covered by adsorbed gas molecules, additional gas can adsorb either on the remaining free surface or on top of the already adsorbed layer. The adsorption of the second and subsequent layers happens with a heat of adsorption equal to the heat of liquefaction of the gas.

Determination of Pore size distribution and surface area by Adsorption isotherm through a gas, usually nitrogen, at its boiling point, is adsorbed on the solid sample. By measuring the volume of gas adsorbed at a particular partial pressure, the specific surface area of the material can be derived by the Brunauer, Emmett and Teller (BET) equation.

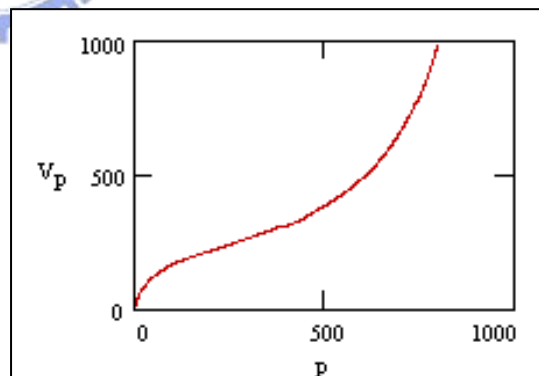


Fig 3.7 Schematic diagram of BET equipment and analysis data

[www3.cems.umn.edu/research/sac/bet.htm]

3.4.5 Four Point Probe

The four point probe is used to measure sheet resistivity of a diffused layer in a silicon substrate, or a deposited conducting film (e.g. Al). The system includes a probe head with four probes in a line separated by a distance of 40 mils, a current source and a digital voltmeter. The current source passes a current, I , through the outer two probes of the probe head, and the voltage drop, V , across the inner two probes is then measured by the DVM.

The sheet resistivity is proportional to the ratio V/I . There is a correction factor which depends on the geometry of the probes and the wafer. The system will automatically apply this correction factor for the reading will be the sheet resistivity. The basic schematic diagram of four point probe is shown below.

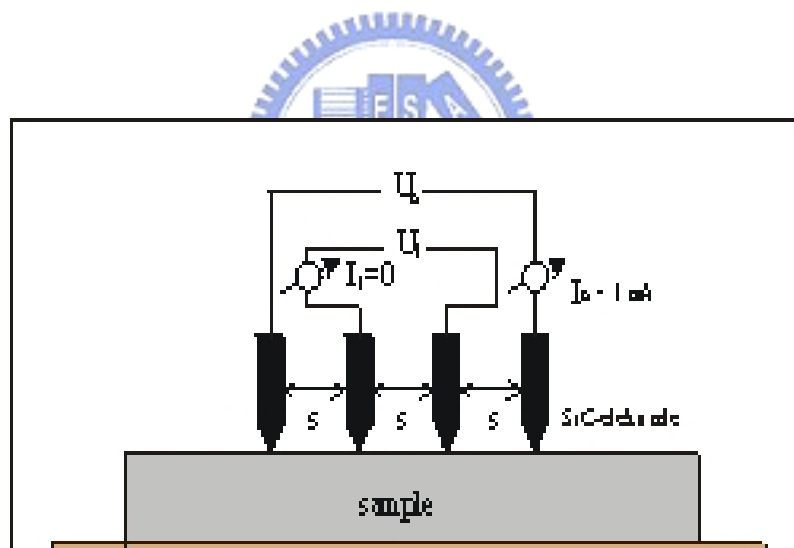


Fig 3.8 Schematic diagram of Four Point Probe working mechanism

[<http://www.mines.edu/academic.htm>]

3.4.6 EDX

EDX is a microanalytical technique that uses the characteristic spectrum of x-rays emitted by the specimen after excitation by high-energy electrons to obtain information about its elemental composition. The ranges of elements detectable by EDX and electron energy loss spectroscopy (EELS) are somewhat complementary; EDX is generally better suited to detecting elements of high atomic number (Z) whereas EELS can readily detect low- Z elements. Unlike EELS, EDX does not provide chemical information (except through quantitative analysis in some cases). Compared to EELS, EDX is a relatively simple technique and provides rapid qualitative microanalysis of the specimen. The spatial resolution is determined by the probe size, beam broadening within the specimen, and the effect of backscattered electrons on the specimen around the point of analysis.

3.4.7 CV (Cyclic Voltammetry)

A simple potential wave form that is often used in electrochemical experiments is the linear wave form i.e., the potential is continuously changed as a linear function of time. The rate of change of potential with time is referred to as the scan rate (ν). A more commonly used variation of the technique is cyclic voltammetry, in which the direction of the potential is reversed at the end of the first scan. Thus, the waveform is usually of the form of an isosceles triangle. This has the advantage that the product of the electron transfer reaction that occurred in the forward scan can be probed again in the reverse scan. In addition, it is a powerful tool for the determination of formal redox potentials, detection of chemical reactions that precede or follow the electrochemical reaction and evaluation of electron transfer kinetics. Fig.3.9 is the basic shape of the current response for a cyclic voltammetry experiment. If a redox system remains in equilibrium throughout the potential scan, the electrochemical reaction is said to be reversible. In other words, equilibrium requires that the surface concentrations of O and R are maintained at the values required by the Nernst Equation.

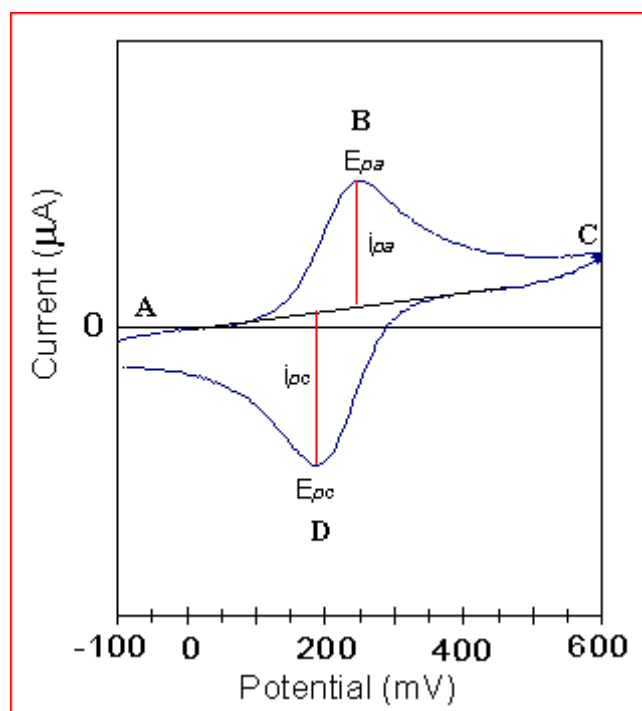


Fig.3.9 The basic shape of the current response for a cyclic voltammetry experiment.

[<http://www-biol.paisley.ac.uk/marco.htm>]