CHAPTER 2 THEORIES

2.1 Fuel cell

2.1.1 Basic elements of fuel cell:

1) The electrode

The electrode material for fuel cell is made from a noble metal such as Pt or bimetal alloy such as PtRu or PtSn. These metals have a function as catalyst on the redox reaction or electrochemical reaction. The catalyst is an importance material which can provide more accelerated reaction at the electrode surface, but the catalyst does not participate in the reactions.

The most common catalyst for a low temperature fuel cell using hydrogen feed is platinum (Pt) [17]. Normally, for fuel cell, platinum particles are impregnated and distributed around surface of carbon support, in order to use the least amount of platinum and to create the greatest surface area. In addition, the alloy catalyst is prepared for improving the fuel cell's performance such as PtRu for a direct methanol fuel cell and PtSn for a direct ethanol fuel cell [18].

The function of electrode is divided into:

- Anode

The anode is the negatively charged electrode. At the anode, electrons are released from the hydrogen molecules and provided to the external electrical circuit. The anode always supports the oxidation reaction. For this anode side, electron (donor e^-) always goes out from anode and an-ion always goes into anode.

- Cathode

The cathode is the positively charged electrode. At the cathode, electrons are conducted from the external electrical circuit and react with oxygen and hydrogen ions that migrate through the membrane, and then this reaction produces water. Cathode always supports the reduction reaction. For this cathode side, electron (accepter e^-) always goes into cathode and cat-ion always goes into cathode.

2) The electrolyte

The electrolyte is a cat-ion or an-ion in solution. The ions can migrate through the membrane with its concentration difference. In cases of a proton exchange membrane (PEM) fuel cell or direct alcohol fuel cell (DAFC), the membrane is made of a plastic which is specially treated to make it conduct positively charged ions (protons, H^+) such as a Nafion® polymer [19]. The possible mechanisms of proton transfer through the Nafion® membrane are a Vehicle mechanism, a Hopping mechanism and a Combination of two mechanisms. Furthermore, the membrane properties should prevent the electrons and protect short circuit problem.

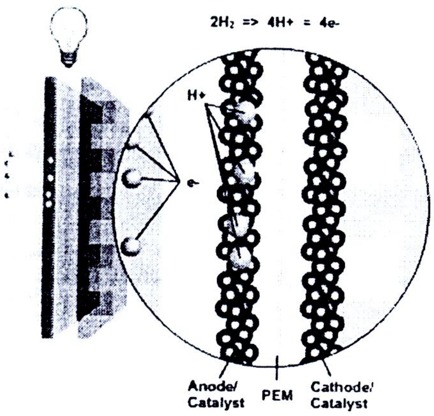
2.1.2 Basic reactions of fuel cell:

Fuel cell reactions are redox reactions. First of all, for the basic fuel cell, the fuel as hydrogen gas (H_2) is fed into flow field at anode side, while the oxidant as oxygen gas (O_2) or air is fed at cathode side. Second, H_2 diffuse through to porous electrode that consist of supporting layer (or backing layer), gas diffusion layer, and active layer, while O_2 also diffuse along the opposite side, too.

Third, the reaction of redox is started. For example, at the anode side on the active layer (or catalyst layer), hydrogen is oxidized to hydrogen protons (H^+) and electrons (e^-) called "oxidation reaction". After that, H^+ migrates through the membrane as solid Nafion® from anode to cathode, while e^- is conducted out through carbon support of metal catalyst, carbon at micro-porous layer, carbon at backing layer, and bipolar plate as graphite, respectively.

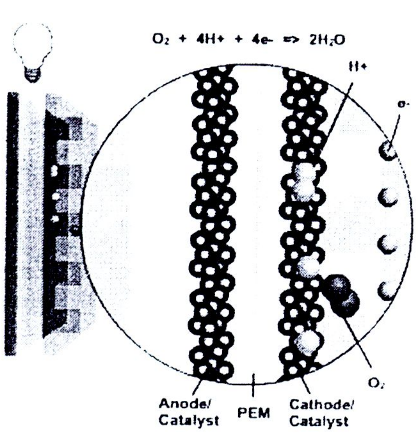
Then, the electrons transfer from anode side to cathode side when the fuel cell connects to the electricity load (or external circuit). This electron transfer is defined as the cell current, and also, the difference amount of electron on both sides of anode and cathode create the potential difference as cell voltage. At cathode side at layer of catalyst, O_2 is reduced with H^+ and e^- called "reduction reaction" which then produces water molecules.

Finally, from the overall reaction, electricity is generated and the heat forms an exothermic reaction. This thermal energy from the fuel cell can be utilized with co-generation system. The reaction occurs on each side of electrode of the fuel cell, as shown in Figure 2.1.



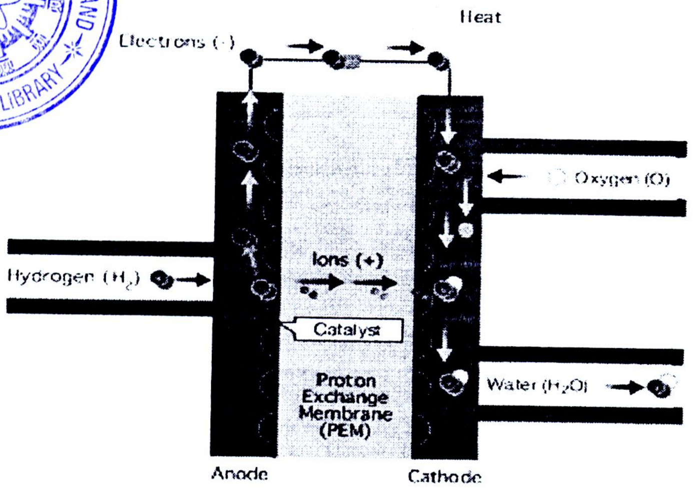
$$H_2 \rightarrow 2\ H^+ + 2\ e^-$$

(a) The anode (oxidation) reaction.



$$\frac{1}{2}O_2 + 2\ H^+ + 2\ e^- \rightarrow H_2O$$

(b) The cathode (reduction) reaction.



$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

(c) The overall cell (redox) reaction

Figure 2.1 The fuel cell reaction at (a) anode, (b) cathode, and (c) the overall reaction [20].

2.1.3 Membrane Electrode Assembly and its function: [22-32]

The heart of proton exchange membrane fuel cell is the membrane electrode assembly (MEA). The main components of the MEA are an electrode, such as an anode and a cathode, and an electrolyte as (Nafion®) membrane. The electrode components of MEA consist of a supporting layer, a gas diffusion layer, a catalyst layer (or active layer). These components of MEA and their functions on each layer are shown in Table 2.1.

Table 2.1 The component and function of membrane electrode assembly.

Component/Layer	**Substance**	**Function**
Anode substrate	- Carbon cloth/paper - Activated carbon - Teflon® emulsion	- fuel supply and gas distribution (H_2, pure or reformatted) - electron conductivity - heat removal from reaction zone - water as vapor supply into catalyst layer

Component/Layer	**Substance**	**Function**
Anode catalyst layer	- Catalyst (Pt, PtRu, PtSn) on activated carbon - Nafion® solution	- catalyzed anodic reaction (oxidation) - transfer H^+ to membrane - transfer e^- to carbon substrate - provide inlet water transport - provide outlet heat transport
Membrane	- Nafion® membrane	- proton conductivity - water transportation (electro osmosis drag / water diffusion) - electronic insulation
Cathode catalyst layer	- Catalyst (Pt) on activated carbon - Nafion® solution	- catalyzed cathodic reaction (reduction) - oxygen transfer to three phase region - electron conducting (e^- transfer to three phase region) - heat removal (outlet heat transport) - water removal from reaction zone (outlet water transport)
Cathode substrate	- Carbon cloth/paper Activated carbon - Teflon® emulsion	- oxidant supply and distribution (H_2, reformatted) - electron conductivity towards reaction zone - heat removal from reaction zone - water transport (liquid/vapor)

2.1.4 Types of fuel cell: [33-36]

Fuel cells are normally categorized by their ion exchange in electrolyte membrane which is sandwiched between the two electrodes. This electrolyte material's characteristics can determine the optimal operating temperature and the exchange ion as shown in Tables 2.2 and 2.3. Also, the operating use range of each fuel cell type is displayed in Table 2.4.

Common type of fuel cell:

Polymer Electolyte Membrane Fuel Cell (PEMFC)

The PEM fuel cell uses a plastic polymer electrolyte (typically Nafion®) to carry protons from the anode to the cathode. This PEM fuel cell is operated with low temperature, and allows a quick startup. The solid electrolyte in PEM fuel cell can handle and uses a liquid feed as alcohol.

In the past, the platinum has made these devices expensive, but new application technologies have thinner platinum layers so the price is reduced to less than $3000/kW. A thin layer of platinum catalyst activates chemically on both electrodes of anode and cathode as the redox reaction. In addition, PEMs are responsive to varying loads, such as driving conditions or electricity profiles. Also, these fuel cells are increasingly cheap to manufacture and are best suited for 1kW to 100kW applications.

Direct Methanol fuel Cells (DMFC)

Direct methanol fuel cell is a variation of the PEM fuel cell type, and use direct feed of liquid methanol without initial reforming. The efficiency rating is low, but, DMFC has increased benefits, such as easily carried without high pressure, to improve its rating. An active area of PtRu/C is used at the anode side of DMFC to enhance the performance of methanol oxidation. DMFCs are best suited to small applications.

Alkaline Fuel Cell (AFC)

The alkaline fuel cell is a device developed by NASA to power the Gemini missions and subsequent space shuttle operations, also widely used by the space program. AFCs are very efficient and discharge product of only pure water. However, pure hydrogen and oxygen are required for these devices. The electrolyte is alkaline as potassium hydroxide. Since most fuel processing produces some carbon dioxide, which poisons the alkaline catalyst, AFCs will find only few markets.

Phosphoric Acid Fuel Cell (PAFC)

The phosphoric acid fuel cell is known for its high reliability, quiet operation, and high efficiency over 80 percent conversion when it integrates with a co-generation device. This fuel cell is operated by running at a medium temperature range of 220 °C and impure hydrogen can be used for this fuel cell type. These PAFCs have been commercially available since 1992 and best suited for small stationary power-generation systems.

Molten Carbonate Fuel Cell (MCFC)

The molten carbonate fuel cell uses a carbonate-salt-impregnated ceramic matrix as an electrolyte. This fuel cell can provide 85 percent efficiency with a co-generation system. MCFCs are operated at high temperature of 650 °C. MCFCs are best suited for large stationary applications, especially useful in hospitals, hotels, or other industrial applications that consume electricity and require heating (or cooling) around the clock.

Solid Oxide Fuel Cell (SOFC)

The solid oxide fuel cell uses a solid electrolyte of prefabricated ceramic sandwich between electrodes as same as MCFC. This fuel cell type is operated at higher temperature of nearly 1,000 °C and it can be integrated excellently with co-generation devices for industrial applications where high temperature steam is needed. SOFCs are best suited for large-scale stationary power generators that could provide electricity for factories or towns. SOFCs had been commercially started in 2005.

Another type of fuel cell:

Regenerative Fuel Cells

The regenerative fuel cell is a closed-loop form of power generation. By using a solar-powered electrolyzer, water is separated into hydrogen and oxygen and then they are fed into the fuel cell at anode and cathode, respectively. This process generates the product of electricity, heat and water. The product of water is then re-circulated back to the solar-powered electrolyzer and the process begins again.

Protonic Ceramic Fuel Cell (PCFC)

The protonic ceramic fuel cell is a new type of fuel cell based on a ceramic electrolyte material that exhibits high protonic conductivity. This fuel cell is operated at high temperature of 750 °C [37]. The high operating temperature is necessary to achieve very high electrical fuel efficiency with directly hydrocarbon fuel feed into anode. Gaseous molecules of the hydrocarbon fuel are absorbed on the surface of the anode which has water vapor. Then, the hydrogen atoms are efficiently stripped off to be absorbed into the electrolyte and the carbon dioxide as the primary reaction product is produce at this anode side. Moreover, at a solid electrolyte membrane of PCFCs, the inside liquid of electrolyte cannot leak out so it can provide a good conduct of proton from anode to cathode to enhance the cell performance.

Table 2.2 The categories of fuel cells by operating properties.

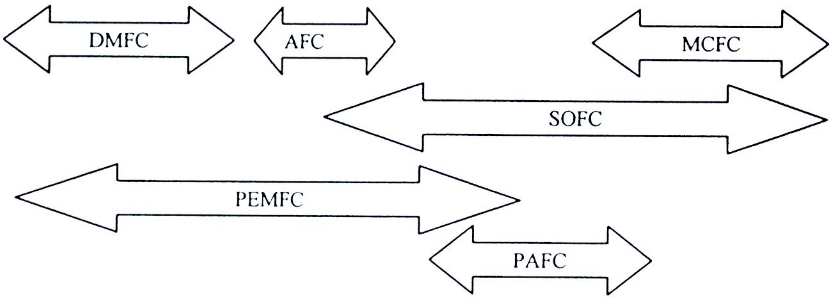
Type	**Electrolyte**		**Feed**		**Area of use**	**Efficiency**
	Material	**Ion**	**Anode**	**Cathode**		
PEMFC	Solid polymer membrane	H^+	H_2	O_2 / air	Space travel, transportation, small CHP, mobile equipment	35 - 60%
DAFC	solid polymer membrane	H^+	MeOH / EtOH	O_2 / air	Transport, mobile equipment	35 - 40%
PAFC	Phosphorous	H^+	H_2	O_2	CHP, power plants	35 - 50%
AFC	potassium hydroxide	OH^-	H_2	O_2	Space travel, transportation	50 - 70%
MCFC	Alkali-Carbonates	CO_3^{2-}	H_2	O_2 / air	CHP, power plants	40 - 55%
SOFC	Ceramic Oxide	O^{2-}	H_2	O_2 / air	CHP, power plants	45 - 60%

*CPH = combine heat power

Table 2.3 The categories of fuel cell by chemical reaction.

Type	Chemical Reaction			Range of Operating Temperature
	Anode Reaction	**Ion**	**Cathode Reaction**	
DMFC & DEFC	$CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2$	H^+	$O_2 + 9H^+ + 9e^- \rightarrow 3H_2O$	20 - 90°C
	$C_2H_5OH \rightarrow CH_3CHO + 2H^+ + 2e^-$		$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	
PEMFC	$H_2 \rightarrow 2H^+ + 2e^-$	H^+	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	30 - 100°C
AFC	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	OH^-	$O_2 + 2H_2O + 2e^- \rightarrow 4OH^-$	50 - 200°C
PAFC	$H_2 \rightarrow 2H^+ + 2e^-$	H^+	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	220°C
MCFC	$H_2 + CO_3^{2-} \rightarrow 2H_2O + CO_2 + 2e^-$	CO_3^{2-}	$O_2 + 2CO_2 + 4e^- \rightarrow CO_3^{2-}$	650°C
SOFC	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$	O^{2-}	$O_2 + 4e^- \rightarrow O^{2-}$	500 - 1,000°C

Table 2.4 The categories of fuel cells by typical applications [38-39].

Typical Applications	Portable electronic equipment	Cars, boats and domestic CHP	Distribution power generation, CHP, also big vehicle
Power (W)	1 10 100	1k 10k 100k	1M 10M
Main Advantages	Higher energy density than batteries Faster recharge	Potential for zero emission Higher efficiency	Higher efficiency Less pollution Quiet
Range of application of the different type of fuel cell			

2.2 Direct methanol fuel cell (DMFC)

2.2.1 Advantages of DMFC: [3, 40-43]

- *Challenge*

Direct Methanol Fuel Cells (DMFCs) can be a viable power source in many applications with their improvements of power density, energy conversion efficiency, and fuel utilization while the cost of DMFCs is also reduced. However, there are two critical challenges have to be resolved: (1) lowering the required amount of platinum catalyst loading while achieving a high level of current and power density, and (2) eliminating the crossover of methanol through the membrane that decreases the performance of cathode and wastes of fuel.

- *Technology Description*

Similar to polymer electrolyte membrane (PEM) fuel cells, DMFCs are powered directly by liquid methanol, instead of hydrogen or reformate (hydrogen produced by reforming liquid fuels). In DMFCs, methanol is the fuel oxidized directly at the anode and also air from the surrounding, instead of oxygen, is the oxidant reduced at the cathode. Therefore, a DMFC system does not need a hydrogen storage tank or reformer and could be an attractive alternative to direct hydrogen or reformate systems.

- *Benefits*

A Direct Methanol Fuel Cell offers a number of advantages, including:

(1) Using a liquid fuel for power generation.
(2) Lightweight packaging by a simpler system design with the potential for low-volume.
(3) Eliminating the requirement for fuel reforming and/or onboard hydrogen storage.
(4) Classification as a zero-emission power system.

- *Commercialization*

Nowadays, a number of companies that project on DMFC research and application are increased. For example, Motorola and Los Alamos National Laboratory (LANL) collaborated in establishing a DMFC Research Center at LANL to develop DMFCs for portable power applications, such as cellular phones and laptop computers. Mechanical

Technology, Inc. has licensed the LANL DMFC technology and spun off a company to commercialize DMFC for portable power applications.

In addition, the commercial interest also exists for DMFCs in remote and auxiliary power applications. The ranging of DMFC starts from low-power instrumentation units in mobile applications to higher power (5 kW) auxiliary units in cars and trucks. Furthermore, the military is also interested in DMFCs as a battery replacement for combat personnel and for battlefield applications. Moreover, in USA, the Defence Advanced Research Projects Agency (DARPA) collaborates with the U.S. Department of Energy (DOE) in sponsoring DMFC research and development.

2.2.2 Methanol oxidation: [44-48]

The different basic material of MEA for the DMFC compared with the PEMFC is the catalyst at anode side. At anode side, PtRu is a famous catalyst for DMFC since the accumulated Ru has a function to prevent the poison from CHO_{ads} and CO_{ads} on Pt catalyst surface. Many chemical mechanisms of methanol oxidation that occur on the catalyst surface are shown in the following equations.

Methanol Oxidation (I)

$CH_3OH \rightarrow CH_2O + 2H^+ + 2e^-$ (reaction 1)

$CH_2O + H_2O \rightarrow HCOOH + 2H^+ + 2e^-$ (reaction 2)

$HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$ (reaction 3)

Methanol Oxidation (II)

$Pt + CH_3OH \rightarrow Pt\text{-}CH_2OH + H^+ + e^-$

$Pt + Pt\text{-}CH_2OH \rightarrow Pt_2\text{-}CHOH + H^+ + e^-$

$Pt + Pt_2\text{-}CHOH \rightarrow Pt_3\text{-}COH + H^+ + e^-$

$Pt_3\text{-}COH \rightarrow Pt\text{-}CO + 2Pt + H^+ + e^-$ (reaction 4)

$Ru + H_2O \rightarrow Ru\text{-}OH + H^+ + e^-$ (reaction 5)

$\text{Pt-COH} + \text{Ru-OH} \rightarrow \text{Pt} + \text{Ru} + CO_2 + 2H^+ + 2e^-$

or

$\text{Pt-CO} + \text{Ru-OH} \rightarrow \text{Pt} + \text{Ru} + CO_2 + H^+ + e^-$ (reaction 6)

In another way, the oxidation mechanism of methanol is explained with the pathway of oxidation. From the hydroxyl group, the directions of oxidation pathways depend on the adsorption energy and the activation energy to the carbonyl group. The pathway of oxidation in the same group of hydroxyl and carbonyl is presented as hydrogen stripping. Another way, the hydroxyl destruction is occurred when the hydroxyl group changes to the carbonyl group. Along the methanol oxidation pathway, the stable species formed are formaldehyde (or metanal), formic acid (or methanoic) and carbon dioxide (CO_2). COH and CO are the poisonous species that form on the surface of the Pt catalyst, as shown in Figure 2.2.

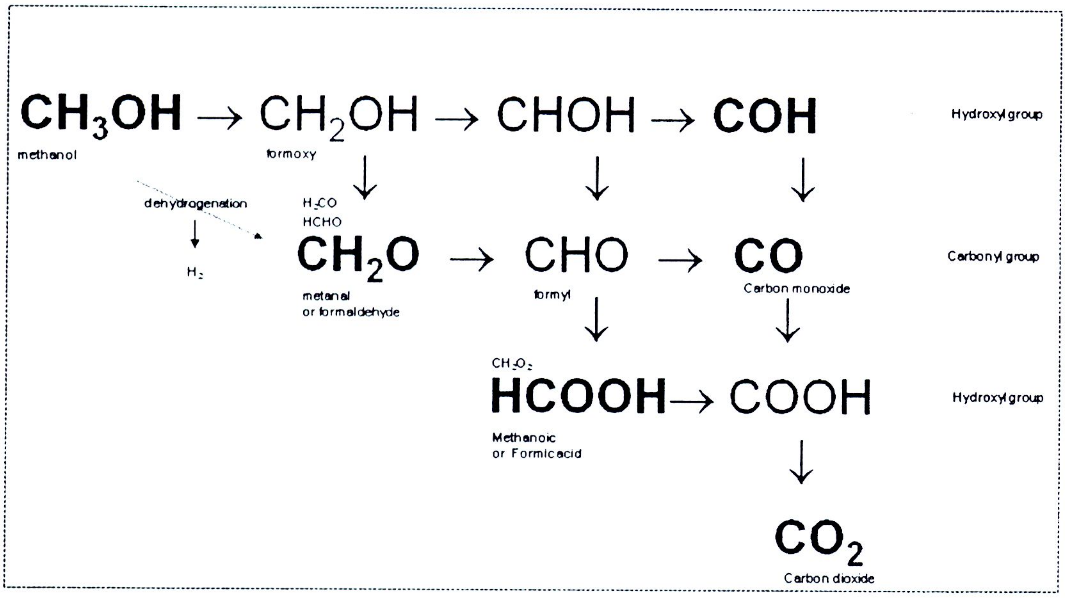


Figure 2.2 The pathway of methanol oxidation.

For the oxygen reduction at the cathode side of DMFC, it is the same reaction for PEMFC. Furthermore, the same product of overall reaction of DMFC and PEMFC is water (H_2O), but for the DMFC, the CO_2 is produced during the methanol oxidation. The comparison of DMFC and PEMFC reactions is summarized in Table 2.5.

Table 2.5 The comparison of electrochemical reactions between PEMFC and DEMFC

Electrochemical reaction	**PEMFC**	**DMFC**
Anode	$H_2 \rightarrow 2H^+ + 2e^-$	$CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2$
Cathode	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$(3/2)O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$
Cell	$H_2 + (1/2)O_2 \rightarrow H_2O$	$CH_3OH + (3/2)O_2 \rightarrow 2H_2O + CO_2$

2.3 Characterization techniques of electrode and MEA performance

2.3.1 Frequency response analysis:[49-50]

-Basics of electrochemical impedance spectroscopy (EIS)

In EIS, an electrochemical complex impedance of cell electrode sample over a wide range of AC frequencies was measured. Typically, several cell electrode sample elements and characteristics contribute to the EIS spectrum or frequency. Partial lists of possible elements include:

- Electrode Double Layer Capacitance
- Electrode Kinetics
- Diffusion Layer
- Solution Resistance

However, the system's impedance at any given frequency usually depends on cell electrode sample which more than one element. This also complicates the analysis of EIS spectra. The most common method used to analyze EIS spectra is equivalent circuit modelling. The cell electrode sample incorporating the elements mentioned above is simulated. The behaviour of each element can be described in terms of classical electrical components as resistors (R), capacitors (C), inductors (L) plus a few specialized electrochemical elements such as Warbug diffusion element (W) or a capacitive element including diffusion effect (CPE).

- Concept of complex impedance

There are starting with Ohm's law (Eq.1), which is a basic concept to interpret the complex impedance of cell electrode sample, that defines resistance in terms of the ratio between voltage (E) and current (I) as direct current (DC).

$$R \equiv \frac{E}{I} \qquad (1)$$

An ideal resistor (R) has several properties that are (1) it follows Ohm's Law at all current and voltage levels, (2) its resistance value is independent of frequency, and (3) AC current and voltage signals though a resistor are in phase with each other.

In real applications, the circuit element has more complex behaviour and characteristics. As with resistance, impedance is an ability of a circuit to resist the flow of electrical current, and also, unlike resistance, impedance is not limited by the simplifying properties of an ideal resistance.

For the AC current, the signal input can respond to impedance and the signal output can be analyzed as a sum of sinusoidal functions as shown in Figure 2.3. In a linear (or pseudolinear) system, the current response to a sinusoidal potential is a sinusoid at the same frequency but shifted in phase.

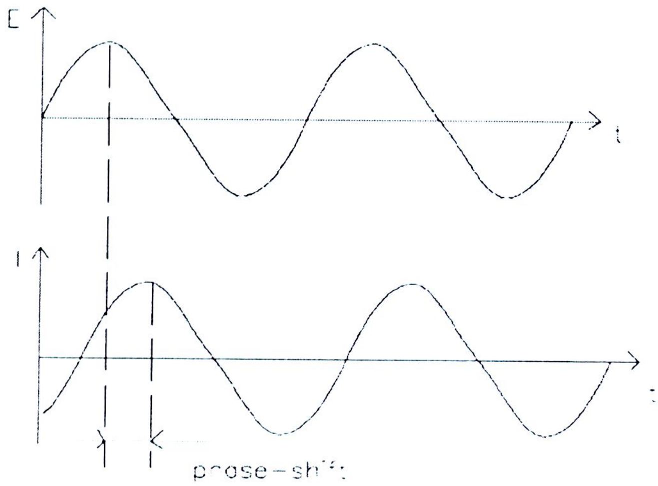


Figure 2.3 Sinusoidal Current Response in a Linear System.

The excitation (input) signal can be expressed as a function of time:

$$E_t = E_0 \sin(\omega t) \tag{2}$$

E_t is the potential at time t, E_0 is the amplitude of the signal, and ω is the radial frequency. In a linear system, the response of signal output is shifted in phase (φ) and has different amplitude of I_0.

$$I_t = I_0 \sin(\omega t + \varphi) \tag{3}$$

An expression analogous to Ohm's Law allows the calculation of the impedance of the system as:

$$Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \varphi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \varphi)} \tag{4}$$

Therefore, the impedance is expressed in terms of a magnitude of Z_0, and a phase shift of φ. Also, the accepted method of impedance measurement can be displayed as a "Lissajous Figure" of modern EIS instrumentation as shown in Figure 2.4.

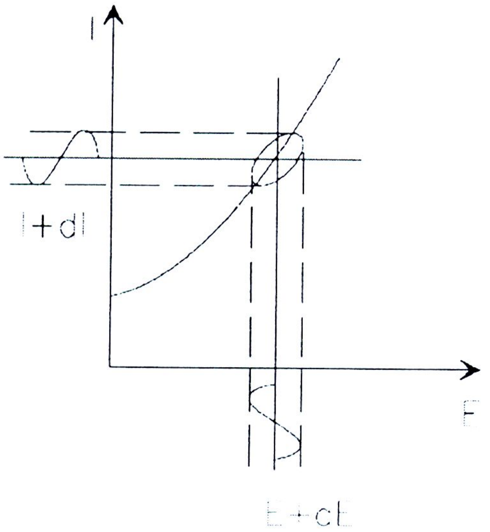


Figure 2.4 Origin of Lissajous Figure.

With the Eulers relationship, $\exp(j\varphi) = \cos\varphi + j\sin\varphi$, it is possible to express the impedance as a complex function.

The potential input is described as:

$$E_t = E_0 \exp(j\omega t) \qquad (5)$$

and the current response as:

$$I_t = I_0 \exp(j\omega t - \varphi) \qquad (6)$$

The impedance is then represented as a complex number:

$$Z(\omega) = \frac{E}{I} = Z_0 \exp(j\varphi) = Z_0(\cos\varphi + j\sin\varphi) \qquad (7)$$

The expression for Z(ω) is composed of a real and an imaginary number which can be plotted as a semicircle, as shown in Figure 2.5.

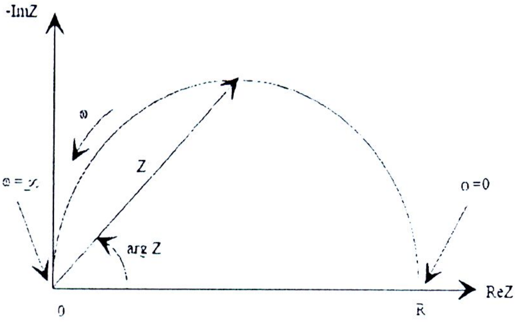


Figure 2.5 Nyquist Plot with Impedance Vector.

The Nyquist Plot in Figure 2.5 results from the electrical circuit of Figure 2.6. The semicircle is characteristic of a single "time constant". Electrochemical Impedance plots often contain several semicircles. However, it is seen only in a portion of a semicircle.

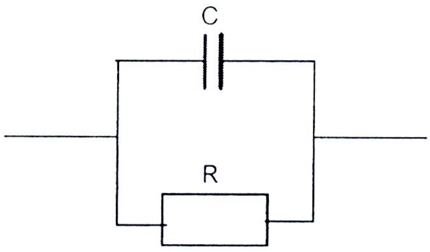
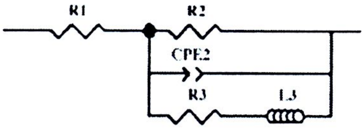
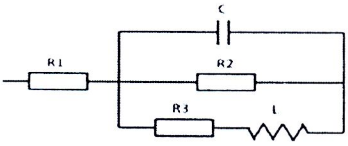


Figure 2.6 Simple Equivalent Circuit with One Time Constant.

Moreover, electrochemical impedance is normally measured using a small excitation signal of voltage or current. The response of cell electrode sample is pseudo-linear of current or voltage depended on the type of excitation signal. In addition, Table 2.6 show the equivalent circuit of model A [51] and model B [14] and the meaning of each component.

Table 2.6 The definitions of impedance analysis elements for DMFC.

Component	**Definition**	
	Model A (Min Ku Jeon et al.[51])  	**Model B** (Junsong Guo et al.[14]) 
R1	an IR resistance (membrane, electrode and interface resistance)	the internal resistance
R2	a methanol electro-oxidation reaction resistance	the charge-transfer resistance at the interface of catalyst
C	a capacitive component including diffusion effect (use in a model in place of a capacitor to compensate for nonhomogeneity in the system) - CPE-T: capacitance - CPE-P: nonhomogeneity constant	the pseudo-capacitance which is related to the morphological properties of the electrode, chemical double layer of the electrode, and to the absorption phenomena. * the capacitance is replaced by a constant phase element due to the porous electrode
R3	an electro-oxidation reaction resistance of CO_{ads}	the phase delay due to the CO_{ads} coverage relaxation process
L	an inductive element which induces phase delay by slow reaction of CO_{ads}	the current signal follows a voltage perturbation with phase delay due to the slowness of reaction of CO_{ads} coverage and not to be parasitic on electrochemical reactions for proton reduction

2.3.2 Cyclic Voltammetry [52-53]

Cyclic voltammetry (CV) and linear sweep voltammogram (LSV) are very similar. In this case, the voltage is swept between two values at a fixed rate as shown in Figure 2.7, however, when the voltage reaches V_2, the scan is reversed and the voltage is swept back to V_1.

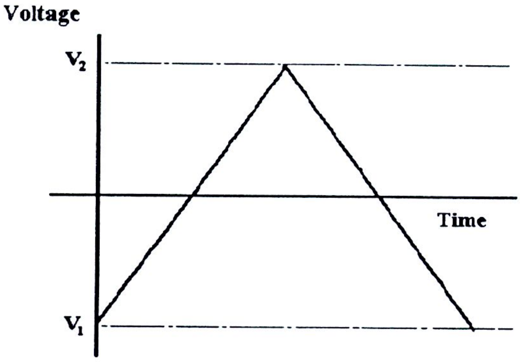


Figure 2.7 Linear potential sweep of cyclic voltammetry.

A typical cyclic voltammogram recorded for a reversible single electrode transfer reaction with the solution contains only a single electrochemical reactant is shown below in Figure 2.8.

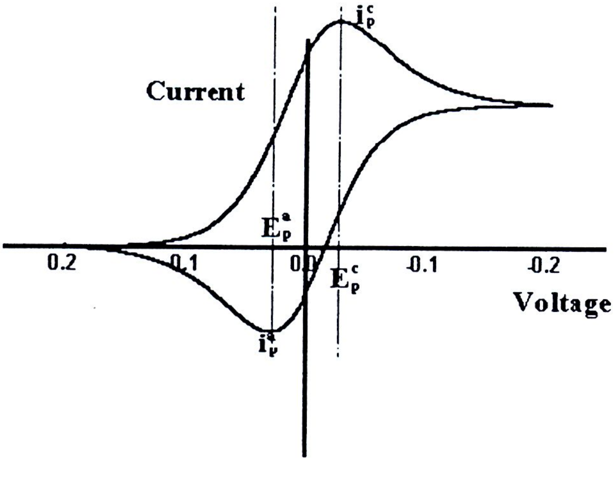


Figure 2.8 Oxidation current with forward and backward sweep.

The forward sweep produces an identical response to the LSV experiment. When the scan is reversed, the curve moves back through the equilibrium positions gradually converting the electrolysis product. The current flow is now from the solution species back to the electrode and then occurs in the opposite sense to the forward sweep. However, the behaviour can be explained in an identical manner.

For a reversible electrochemical reaction, the CV recorded has certain defined characteristics such as:

- The voltage separation between the current peaks is:

$$\Delta E = E_P^a - E_P^c = \frac{59}{n}\,\mathrm{mV}$$

- The positions of peak voltage do not alter as a function of voltage scan rate.
- The ratio of the peak currents is equal to one:

$$\left|\frac{i_P^a}{i_P^c}\right| = 1$$

- The peak currents are proportional to the square root of the scan rate:

$$i_P^a \text{ and } i_P^c \propto \sqrt{V}$$

The influence of the voltage scan rate on the current for a reversible electron transfer can be increased at the same oxidation potential. As with LSV, the influence of the scan rate is explained for a reversible electron transfer reaction in terms of the diffusion layer thickness. In cases of where the electron transfer is not reversible show considerably different behaviour from their reversible counterparts. The oxidation and reduction rate constants of a quasi-reversible reaction are still fast; however, as the rate constants are lowered the curves shift to more reductive potentials. Also, this may be rationalised in terms of the equilibrium at the surface that is no longer establishing so rapidly. In these cases the peak separation is no longer fixed but varies as a function of the scan rate is the same as the peak current that varies as a square root of the scan rate. Moreover, for the variation of peak position as a function of scan rate, it is possible to gain an estimate for the electron transfer rate constants.

- Oxidation on Pt surface

The response curve of CV is first interpreted with the electrochemical reaction of the Pt wire in 0.5M H_2SO_4 by using the following mechanism as shown in Figure 2.11.

At potential scan from 0.35 - 0.05 V, the hydrogen ion is reduced and adsorbed on surface of Pt:

$$Pt + H_3O + e^- \leftrightarrow Pt\text{-}H_{ads} + H_2O$$

$$Pt + H^+ + e^- \rightarrow Pt\text{-}H_{ads}$$

Then, further occupation of adsorbed hydrogen is formed to H_2 evolution.

At potential scan from 0.05-0.35V, the hydrogen adsorbed is oxidized at surface of Pt to hydrogen ion:

$$Pt\text{-}H_{ads} + H_2O \leftrightarrow Pt + H_3O + e^-$$

$$Pt\text{-}H_{ads} \rightarrow Pt + H^+ + e^-$$

After 0.35 V, the double layer region are formed (at 0.35 - 0.8 V) and Pt surface is cleaned and no reaction during this region. Also, the inner surface electrode is filled with e^- , outer surface electrode is full filled with H^+.

At potential scan above 0.8V, the water molecule is oxidized and oxygen is adsorbed on Pt surface or oxide is formed:

$$Pt + H_2O \rightarrow Pt\text{-}O_{ads} + 2H^+ + 2e^-$$

At potential scan above 1.045V, the further occupation of adsorbed oxygen continues to be oxidized and to form an adsorbed oxygen bond:

$$Pt\text{-}O_{ads} + H_2O \rightarrow Pt\text{-}O_{2,ads} + 2H^+ + 2e^-$$

Then, the further occupation of adsorbed oxygen bond forms O_2 evolution.

At reverse potential scan back to 1.045V, further occupation of adsorbed oxygen bond is reduced and formed to adsorbed oxygen on surface of Pt.

$$Pt\text{-}O_{2,ads} + 2H^+ + 2e^- \rightarrow Pt\text{-}O_{ads} + H_2O$$

At reverse potential scan back to 0.8V, the adsorbed oxygen is reduced and forms a water molecule, and after reduction peak of oxygen, the Pt surface is cleaned again.

$$Pt\text{-}O_{ads} + 2H^+ + 2e^- \rightarrow Pt + H_2O$$

For methanol oxidation, the response curve of CV accepts the simplified version of the mechanisms of methanol oxidation, which are:

$$CH_3OH \rightarrow CO_{ads} + 4H^+ + 4e^-$$

$$H_2O \rightarrow OH_{ads} + H^+ + e^-$$

$$CO_{ads} + OH_{ads} \rightarrow CO_2 + H^+ + e^-$$

or

$$CH_3OH \rightarrow CO_{ads} + 4H^+ + 4e^-$$

$$H_2O \rightarrow O_{ads} + 2H^+ + 2e^-$$

$$CO_{ads} + OH_{ads} \rightarrow CO_2$$

The CO is assumed to be the only carbon-containing adsorbed on the surface, the then adsorbed CO is oxidized to CO_2. Since the Pt oxide does not form below 0.75 V, the oxygen source below 0.75 V is assumed to dissociate in water such as OH_{ads}. The adsorbed water or oxide (in activated form) is other species suggested to exist in potential region which below 0.75 V, and the exact identity of the species remains inconclusive. The initial stages of Pt oxide are long through to involve formation of an adsorbed OH species above 0.75 V. The response curve of CV by electrochemical reaction step which depend on potential scan is presented in Figure 2.9.

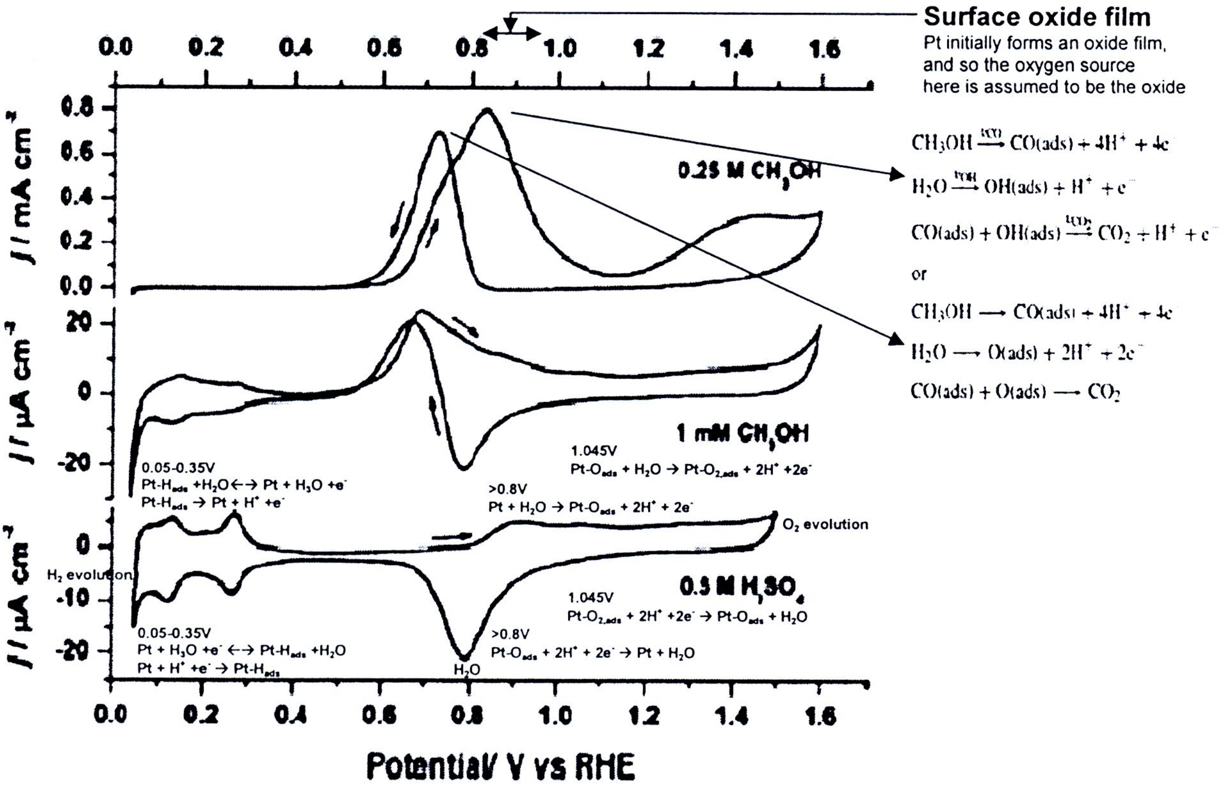


Figure 2.9 The response curve of CV by electrochemical reaction step which depends on potential scan [54].

-Methanol stripping voltammetry [14]

For this work, the method of methanol stripping voltammetry was used to detect the loss of surface catalyst performance for methanol oxidation. By this technique, the anode potential is held at constant low voltage, such as 0.1 V versus DHE, to form adsorbed methanol onto the anode by feeding methanol solution at a low flow rate. After that the anode is washed with de-ionized water to remove un-adsorbed methanol. Then the anode potential was cycled between potential window that cover the range of methanol oxidation such 0.1 to 0.7 V versus DHE at 20 mV s^{-1} for five cycles, and the first and fifth cycles of methanol oxidation were recorded. Moreover, for the result interpretation, the change of peak position and oxidation current were interpreted.

2.3.3 X-ray Diffraction [55-56]

X-ray diffraction (XRD) is a non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials.

- Constructive interference

When a monochromatic X-ray beam with wavelength *lambda* is projected onto a crystalline material at an angle *theta*, diffraction occurs only when the distance traveled by the rays reflected from successive planes differs by a complete number *n* of wavelengths.

- Crystal lattice

A crystal lattice is a regular three-dimensional distribution (cubic, rhombic, etc.) of atoms in space. These are arranged so that they form a series of parallel planes separated from one another by a distance *d*, which varies according to the nature of the material. For any crystal, planes exist in a number of different orientations, each with its own specific *d*-spacing.

- *Bragg's Law*

By varying the angle *theta*, the Bragg's Law conditions are satisfied by different *d*-spacings in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is characteristic of the sample. Where a mixture of different phases is present, the resultant diffractogram is formed by addition of the individual patterns.

Based on the principle of X-ray diffraction, a wealth of structural, physical and chemical information about the material investigated can be obtained. A host of application techniques for various material classes is available, each revealing its own specific details of the sample studied.

2.3.4 Transmission Electron Microscope [57-58]

The transmission electron microscope (TEM) operates on the same basic principles as the light microscope but uses electrons instead of light. TEMs use electrons as a "light source" and their much lower wavelength make it possible to get a resolution that is a thousand times better than with a light microscope.

- *Magnetic Lenses Guide the Electrons*

The light source on top of the microscope emits the electrons that go through a vacuum column of the microscope. The TEM uses electromagnetic lenses to focus the electrons into a very thin beam by glass lenses focusing the light in the microscope. The electron beam then goes through the specimen. Some of the electrons are scattered and disappear from the beam, depending on the density of the material present. At the bottom of the microscope the unscattered electrons hit a fluorescent screen, which gives rise to a shadow image of the specimen with its different parts displayed in varied darkness according to their density. The image of TEM can be studied directly by the operator or photographed with a camera.

2.3.5 Energy Dispersive X-ray [59-60]

EDX Analysis stands for Energy Dispersive X-ray analysis. It is sometimes referred to as EDS or EDAX analysis. This technique use to identify the elemental composition of the specimen or the area of interest. The EDX analysis system works as an integrated feature of a scanning electron microscope (SEM), and cannot operate on its own without the latter.

During EDX Analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atoms' own electrons, knocking some of them off in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an outer shell. However, the transferring outer electron must give up some of its energy by emitting an X-ray.

The amount of energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferring to. Furthermore, the atom of every element releases X-rays with unique amounts of energy during the transferring process. Therefore, the identity of the atom from which the X-ray was emitted can be established by measuring the amounts of energy present in the X-rays being released by a specimen during electron beam bombardment.

The output of an EDX analysis is an EDX spectrum. The EDX spectrum is a plot of how frequently an X-ray is received for each energy level. An EDX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks are unique to an atom, and corresponds to a single element. The higher a peak is in a spectrum, the more concentrated the element is in the specimen.

Moreover, an EDX spectrum plot not only identifies the element corresponding to each of its peaks, but also the type of X-ray to which it corresponds as well. For example, a peak corresponding to the amount of energy possessed by X-rays emitted by an electron in the L-shell going down to the K-shell is identified as a K-Alpha peak. The peak corresponding to X-rays emitted by M-shell electrons going to the K-shell is identified as a K-Beta peak.