



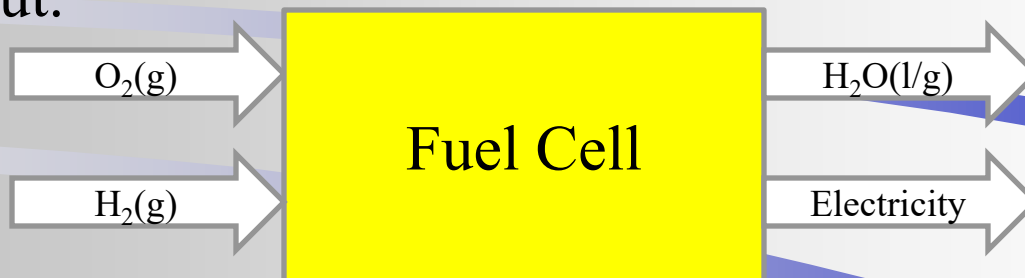
# Electrochemistry

CHEM 5390

# Fuel Cells

An electro-chemical energy conversion device

A “factory” that takes fuel as input and produces electricity as output.



Converts chemical energy  $\rightarrow$  electricity without intermediate heat step.

# Fuel Cells

## Basic Fuel Cell Model

The real voltage output of a fuel cell can be written by starting with the thermodynamic predicted voltage and subtracting the overvoltages:

$$V = E_{\text{thermo}} - \eta_{\text{act}} - \eta_{\text{ohmic}} - \eta_{\text{conc}}$$

where

$V$  - the operating voltage of fuel cell

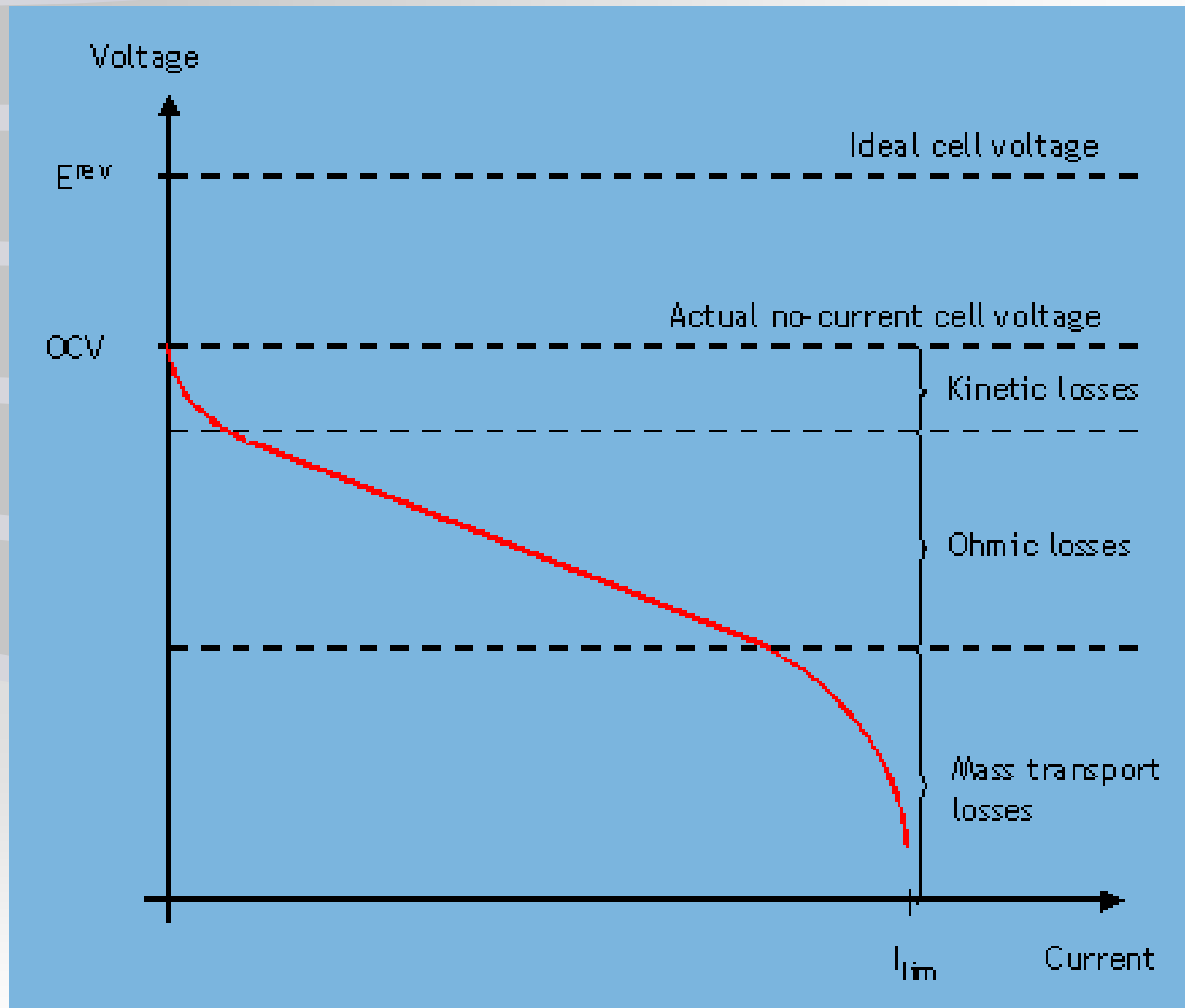
$E_{\text{thermo}}$  - thermodynamically predicted voltage

$\eta_{\text{act}}$  - activation loss due to reaction kinetics

$\eta_{\text{ohmic}}$  - ohmic loss from ionic and electronic resistance

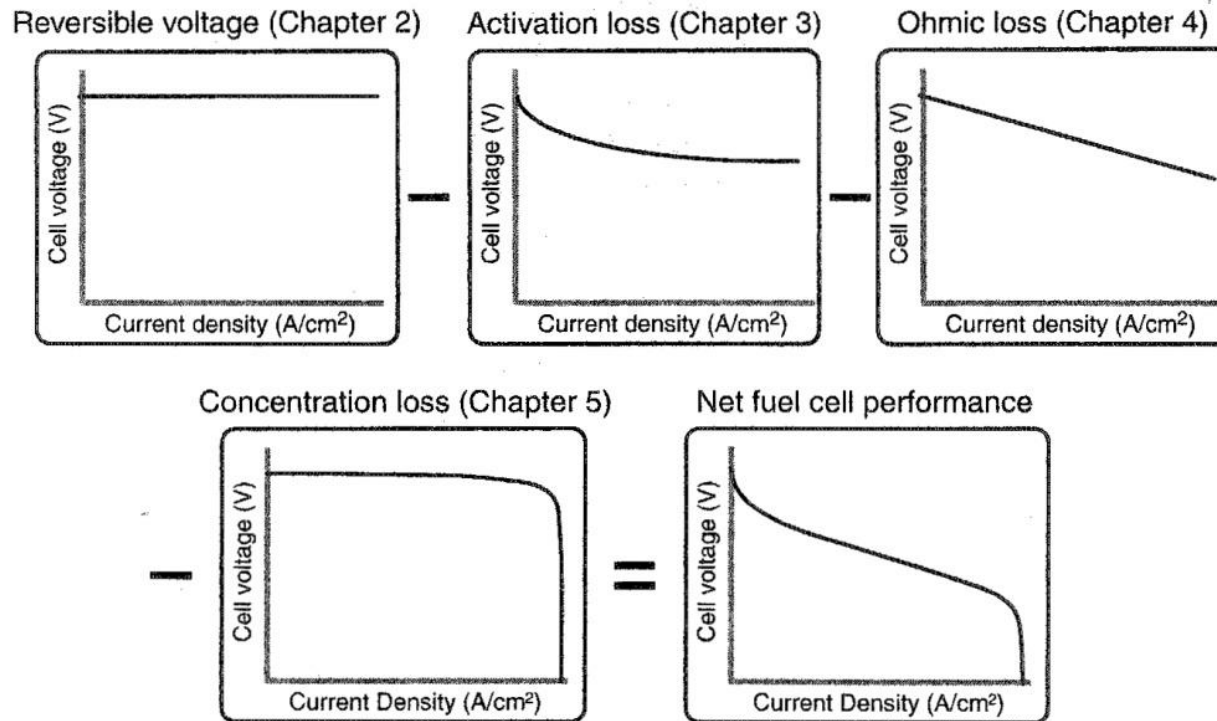
$\eta_{\text{conc}}$  - concentration losses due to mass transport

# Fuel Cells



# Fuel Cells

## Net fuel cell $j$ - $V$ graphical representation



**Figure 6.1.** Pictorial summary of major factors that contribute to fuel cell performance. The overall fuel cell  $j$ - $V$  performance can be determined by starting from the ideal thermodynamic fuel cell voltage and subtracting out the losses from activation, conduction, and concentration.

# Fuel Cells

## Net fuel cell j-V equation

$$V = E_{thermo} - (a_A + b_A \ln j) - (a_C + b_C \ln j) - (j ASR_{ohmic}) - \left( c \ln \frac{j_L}{j_L - j} \right)$$

where

$\eta_{act} = (a_A + b_A \ln j) + (a_C + b_C \ln j)$  activation losses from both anode (A) and the cathode (C) based on natural logarithm form of the Tafel equation.

$\eta_{ohmic} = (j ASR_{ohmic})$  ohmic resistance loss based on current density and ASR.

$\eta_{conc} = \left( c \ln \frac{j_L}{j_L - j} \right)$  combined fuel cell concentration loss.

# Fuel Cells

## Net fuel cell j-V equation

$$V = E_{thermo} - (a_A + b_A \ln j) - (a_C + b_C \ln j) - (j ASR_{ohmic}) - \left( c \ln \frac{j_L}{j_L - j} \right)$$

Since the Tafel plot is used in the approximation for the fuel cell kinetics, this model is only valid when  $j \gg j_0$ .

This model has seven “fitting constants”  $a_A$ ,  $a_C$ ,  $b_A$ ,  $b_C$ ,  $c$ ,  $ASR_{ohmic}$ , and  $j_L$ .

For  $H_2$ - $O_2$  fuel cells, the anode kinetic losses are small compared to the cathode kinetic losses (eliminating  $a_A$  and  $b_A$ ).

Since  $a$ ,  $b$ , and  $c$  are related to  $\alpha$  and  $j_0$ , in many cases only four parameters need to be considered,  $\alpha_C$ ,  $j_{0C}$ ,  $ARS_{ohmic}$ , and  $j_L$ .

# Fuel Cells

## Net fuel cell j-V equation

Typically one other parameter is needed,  $j_{leak}$ , the parasitic loss from current leakage, gas crossover, and side reactions, where extra current has to be produced to compensate for the loss.

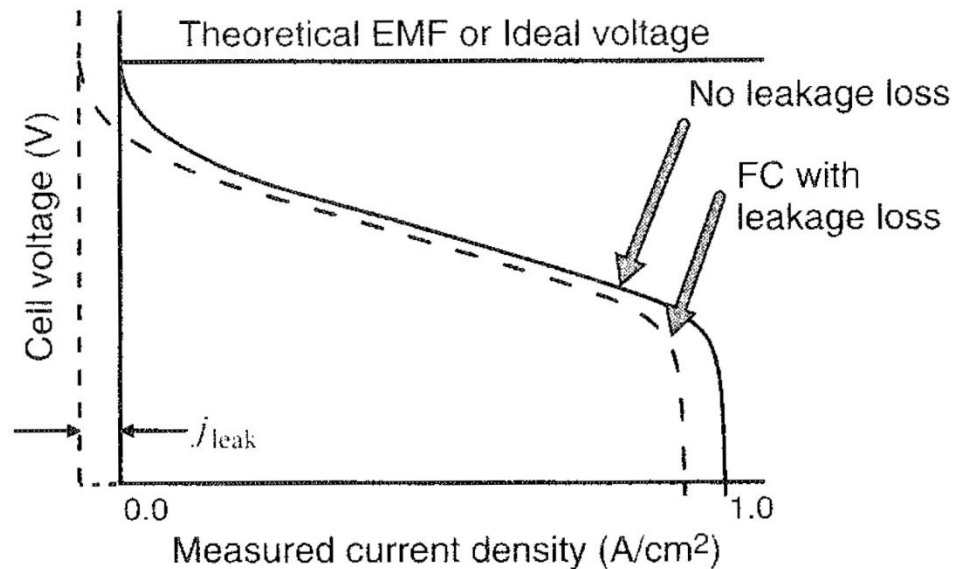
$$j_{gross} = j + j_{leak}$$

where  $j_{gross}$  is the gross current produced at the electrodes,  $j_{leak}$  is the parasitic current that is wasted, and  $j$  is the actual fuel cell operating current that can be used.

$$V = E_{thermo} - [a_A + b_A \ln(j + j_{leak})] - [a_C + b_C \ln(j + j_{leak})] - (j \text{ ASR}_{ohmic}) - \left( c \ln \frac{j_L}{j_L - (j + j_{leak})} \right)$$

# Fuel Cells

## Net fuel cell $j$ - $V$ equation



**Figure 6.2.** Pictorial illustration of the effect of a leakage current loss on overall fuel cell performance. A leakage current effectively “offsets” a fuel cell’s  $j$ - $V$  curve, as shown by the dotted curve in the figure. This has a significant effect on the open circuit voltage of the fuel cell (y-axis intercept), which is reduced below its thermodynamically predicted value.

# Fuel Cells

## Net fuel cell j-V equation

The simple fuel cell model can be used to contrast the j-V behavior of a low temperature fuel cell (PEMFC) versus a typical high temperature fuel cell (SOFC).

In a H<sub>2</sub>-O<sub>2</sub> PEMFC, activation losses are significant but ohmic losses are small.

For a H<sub>2</sub>-O<sub>2</sub> SOFC, ohmic losses tend to dominate but activation losses are minor.

# Fuel Cells

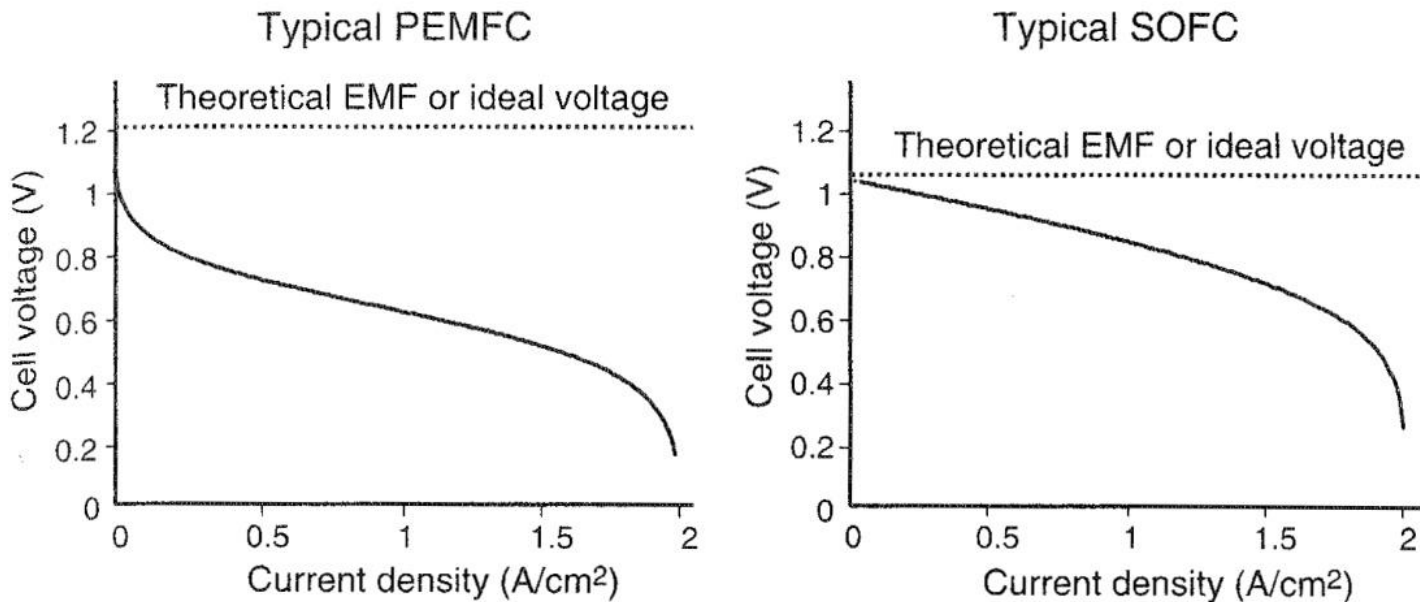
## Net fuel cell j-V equation

TABLE 6.1. Summary of Typical Parameters for Low-Temperature PEMFC versus High-Temperature SOFC

Parameter	Typical Value for PEMFC	Typical Value for SOFC
Temperature	350 K	1000 K
$E_{\text{thermo}}$	1.22 V	1.06 V
$j_0(\text{H}_2)$	$0.10 \text{ A/cm}^2$	$10 \text{ A/cm}^2$
$j_0(\text{O}_2)$	$10^{-4} \text{ A/cm}^2$	$0.10 \text{ A/cm}^2$
$\alpha(\text{O}_2)$	0.50	0.50
$\alpha(\text{H}_2)$	0.30	0.30
$ASR_{\text{ohmic}}$	$0.01 \Omega \cdot \text{cm}^2$	$0.04 \Omega \cdot \text{cm}^2$
$j_{\text{leak}}$	$10^{-2} \text{ A/cm}^2$	$10^{-2} \text{ A/cm}^2$
$j_L$	$2 \text{ A/cm}^2$	$2 \text{ A/cm}^2$
$C$	0.10 V	0.10 V

# Fuel Cells

## Net fuel cell j-V equation



**Figure 6.3.** Comparison of our simple model results for a typical PEMFC versus a typical SOFC. As shown by the shape of the curves, the PEMFC benefits from a higher thermodynamic voltage but suffers from larger kinetic losses. SOFC performance is dominated by ohmic and concentration losses. The input parameters used to generate these model results are summarized in Table 6.1.

# Fuel Cells

## A 1D Fuel Cell Model

Model based on the flux balance (movement of species) through a fuel cell.

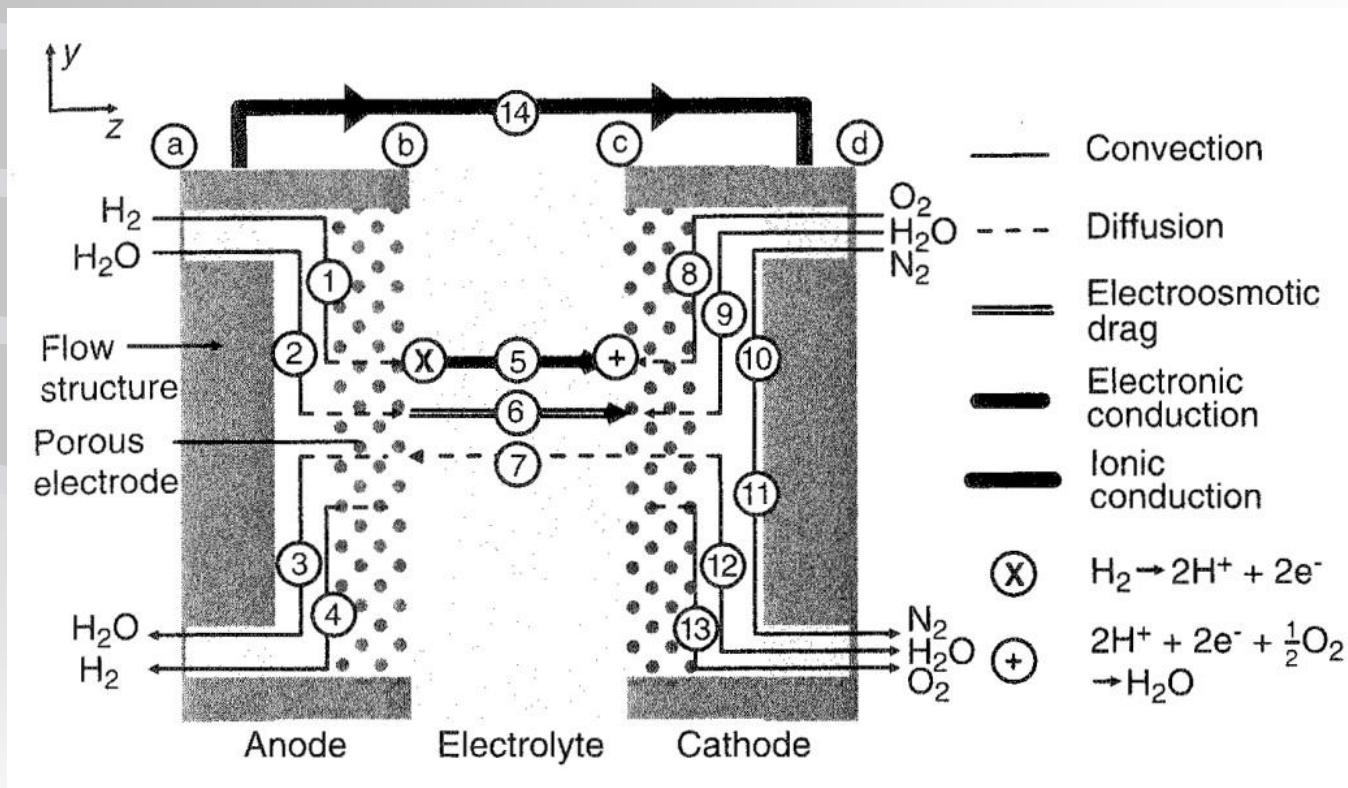
Flux balance keeps track of all the species that flow in, out and through a fuel cell.

Flux balance models are popular in fuel cell literature. Flux balance models are really just careful bookkeeping models.

# Fuel Cells

## A 1D Fuel Cell Model

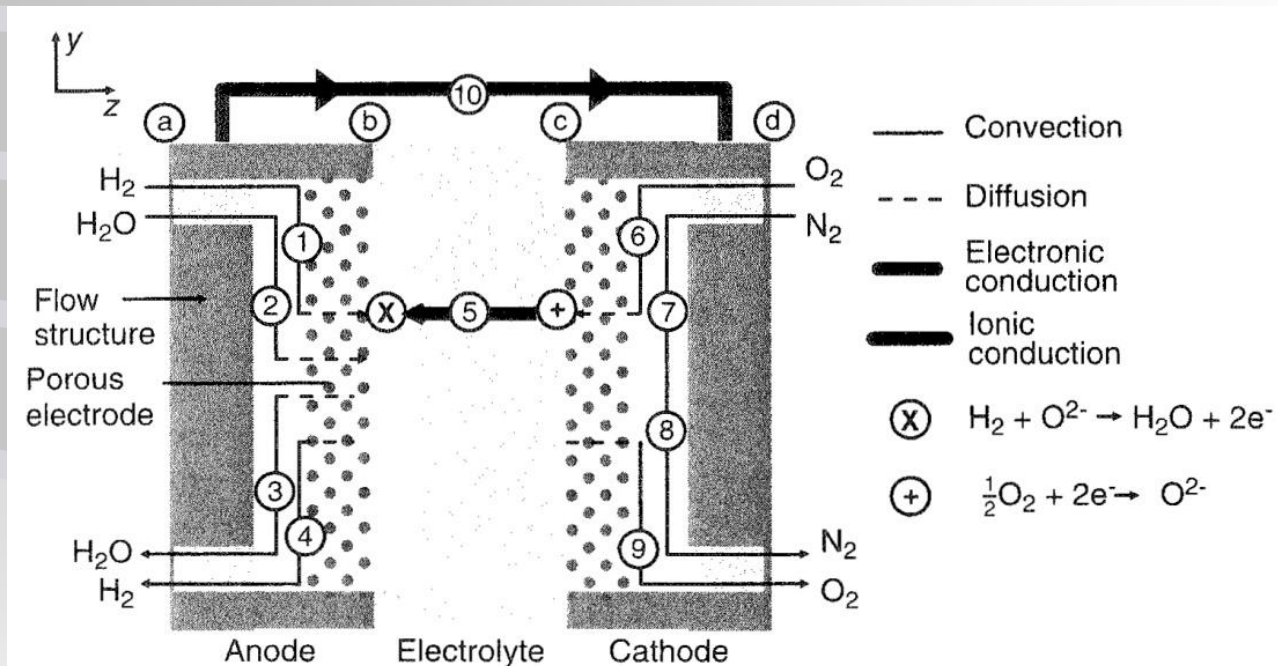
For PEMFC



# Fuel Cells

## A 1D Fuel Cell Model

For SOFC



**Figure 6.4.** Flux details for (a) 1D PEMFC model and (b) 1D SOFC model. (a) In a PEMFC, water ( $\text{H}_2\text{O}$ ) and protons ( $\text{H}^+$ ) transport through the electrolyte. (b) In a SOFC, oxygen ions ( $\text{O}^{2-}$ ) transport through the electrolyte.

# Fuel Cells

## A 1D Fuel Cell Model

Equations can be assigned to each domain of the fuel cell and the  $j$ - $V$  curve constructed. (governing equations)

Electrode layer

Model the diffusion process of species at the electrode.

$$J_i = \frac{-pD_{ij}^{eff}}{RT} \frac{dx_i}{dz}$$

Where  $x_i$  is the mole fraction of species  $i$ ,  $p$  is the total gas pressure (Pa) at the electrode,  $D_{eff}$  is the effective diffusivity – the diffusion of gas through porous structures where  $i$  is the species and  $j$  is the material that  $i$  is diffusing through.

# Fuel Cells

## A 1D Fuel Cell Model

Equations can be assigned to each domain of the fuel cell and the j-V curve constructed.

### Electrolyte

Model the species transport in the electrolyte. For SOFCs only have to know the  $O^{2-}$  flux, and can relate this to the current density:

$$J_{O^{2-}}^M = \frac{j}{2F}$$

Then the ohmic voltage loss is:

$$\eta_{ohmic} = j(ASR_{ohmic}) = j\left(\frac{t^M}{\sigma}\right)$$

# Fuel Cells

## A 1D Fuel Cell Model

Electrolyte (SOFC)

Then the ohmic voltage loss is:

$$\eta_{ohmic} = j(ASR_{ohmic}) = j\left(\frac{t^M}{\sigma}\right)$$

where  $t_M$  is the thickness of the electrolyte and  $\sigma$  is the electrolyte conductivity, which can be calculated:

$$\sigma = \left(\frac{A_{SOFC} e^{-\Delta G_{act} / RT}}{T}\right)$$

# Fuel Cells

## A 1D Fuel Cell Model

Equations can be assigned to each domain of the fuel cell and the j-V curve constructed.

### Electrolyte (PEMFCs)

Model the species transport in the electrolyte. For PEMFCs need to know the proton and water flux.

For as Nafion membrane, two water fluxes exist: back diffusion and electroosmotic drag.

$$J_{H_2O}^M = 2n_{drag} \frac{j}{2F} \frac{\lambda}{22} - \frac{\rho_{dry}}{M_m} D_{\lambda} \frac{d\lambda}{dz}$$

# Fuel Cells

## A 1D Fuel Cell Model

Electrolyte (PEMFCs)

For as Nafion membrane, two water fluxes exist: back diffusion and electroosmotic drag.

$$J_{H_2O}^M = 2n_{drag} \frac{j}{2F} \frac{\lambda}{22} - \frac{\rho_{dry}}{M_m} D_{\lambda} \frac{d\lambda}{dz}$$

where  $n_{drag}$  is the electroosmotic drag (when protons traveling through pores of Nafion drag one or more water molecule with them),  $\lambda$  is the water content (fully hydrated Nafion membrane holds 22% water),  $\rho_{dry}$  is the dry density ( $\text{kg/m}^3$ ),  $M_m$  is the Nafion equivalent weight ( $\text{kg/mol}$ ),  $z$  is the direction through the membrane thickness, and  $D_{\lambda}$  is diffusivity of water in the membrane.

# Fuel Cells

## A 1D Fuel Cell Model

Equations can be assigned to each domain of the fuel cell and the j-V curve constructed.

### Catalyst

Model only the cathode reaction kinetics. Since the oxygen partial pressure at the cathode is the dominate factor in determining the overvoltage, can use a simplified version of the Butler-Volmer equation.

$$\eta_{cathode} = \frac{RT}{4\alpha F} \ln \frac{j}{j_o p^c x_{O_2}}$$

Where 4 is the electron valence number for an oxygen molecule,  $p^c$  is the total pressure at the cathode, and  $x_{O_2}$  is the oxygen mole fraction at the cathode catalyst layer.

# Fuel Cells

## Fuel Cell Characterization

Several techniques can be used to quantitatively compare fuel cell systems.

These techniques also indicate why a fuel cell behaves well or poorly.

The techniques used to analyze fuel cells need to discriminate between the sources of loss in a fuel cell, i.e., fuel crossover, activation, ohmic, and concentration losses.

Also must do the test in situ to mimic realistic operating conditions. (test stations)

# Fuel Cells

## Basic Fuel Cell Test Station

Test Station allows flexible control over the operating pressures, temperatures, humidity levels, and flow rates of the reactant gases.

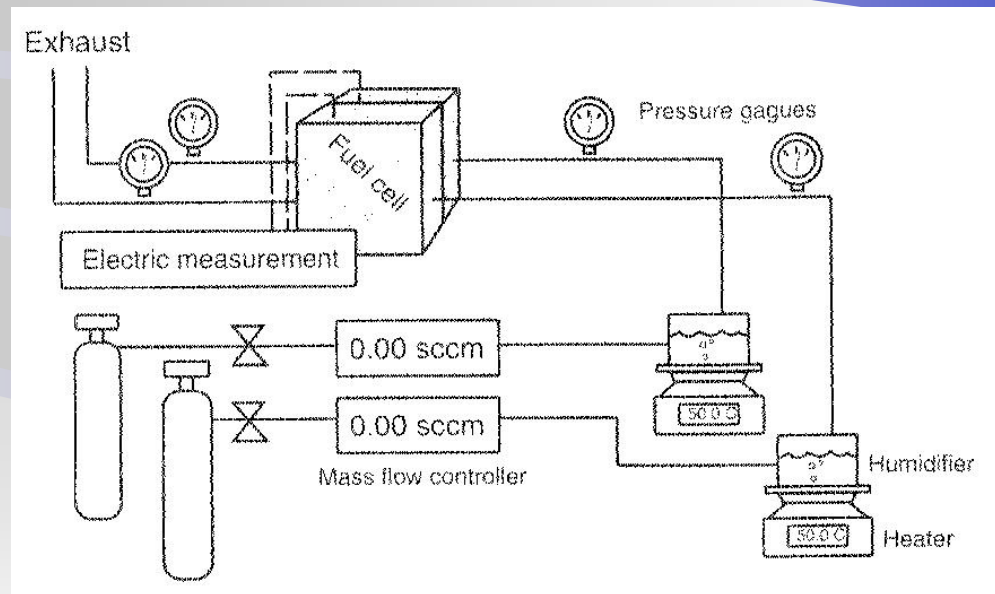
Important to document following test conditions:

- Warm-up
  - Typically a fixed current load for 30-60 min prior to testing.
- Temperature
  - Temperature must be constant during testing. Measure the temperature of the gas inlet, exit temperature, and fuel cell.
- Pressure
  - Monitored at fuel cell inlets and outlets.
- Flow rate
- Compression force

# Fuel Cells

## Basic Fuel Cell Test Station

Test Station allows flexible control over the operating pressures, temperatures, humidity levels, and flow rates of the reactant gases.

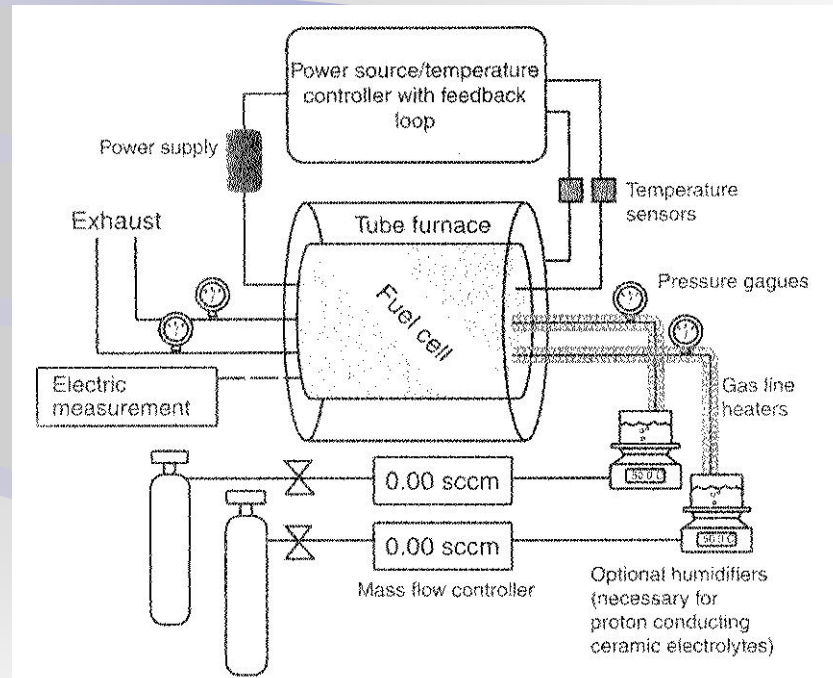


Typical PEM Test Station

# Fuel Cells

## Basic Fuel Cell Test Station

Test Station allows flexible control over the operating pressures, temperatures, humidity levels, and flow rates of the reactant gases.



Typical SOFC Test Station

# Fuel Cells

## Fuel Cell Characterization

Several techniques can be used to quantitatively compare fuel cell systems.

These techniques also indicate why a fuel cell behaves well or poorly.

The techniques used to analyze fuel cells need to discriminate between the sources of loss in a fuel cell, i.e., fuel crossover, activation, ohmic, and concentration losses.

Also must do the test in situ to mimic realistic operating conditions. (test stations)

# Fuel Cells

## What properties are tested?

- Overall performance ( $j$ - $V$  curve, power density)
- Kinetic properties ( $\eta_{act}$ ,  $j_o$ ,  $\alpha$ , active surface area)
- Ohmic properties ( $R_{ohmic}$ ,  $\sigma$ , resistances)
- Mass transport properties ( $j_L$ ,  $D^{eff}$ , pressure losses)
- Parasitic losses ( $j_{leak}$ , side reactions, fuel crossover)
- Electrolyte structure (porosity, tortuosity, conductivity)
- Catalyst structure (thickness, porosity, catalyst loading, particle size, active surface area, TPB, ionic conductivity, electrical conductivity)
- Flow structure (pressure drop, gas distribution, conductivity)
- Heat generation/heat balance
- Lifetime issues (lifetime testing, degradation, cycling, startup/shutdown, failure, corrosion, fatigue)

# Fuel Cells

## Characterization Techniques

Two types:

- Electrochemical Techniques In Situ
  - Use voltage, current and time to characterize performance under operating conditions
- Ex Situ Techniques
  - Characterize the individual components of the fuel cell.

# Fuel Cells

## Characterization Techniques

### Electrochemical Techniques In Situ

- Current-Voltage ( $j$ - $V$ ) Measurement
  - Provides overall quantitative evaluation of fuel cell performance and power density.
- Current Interrupt Measurement
  - Separates the fuel cell performance into ohmic and nonohmic processes.
- Electrochemical Impedance Spectroscopy (EIS)
  - Can distinguish between ohmic, activation, and concentration losses.
- Cyclic Voltammetry (CV)
  - Measures fuel cell reaction kinetics.

# Fuel Cells

## Characterization Techniques

### Ex Situ Techniques

- Porosity Determination
  - Technique to determine electrode and catalyst porosity.
- Brunauer-Emmett-Teller (BET) Surface Area Measurement
  - Allows highly accurate surface area determination
- Gas Permeability
  - Electrodes and catalyst layers need to be highly permeable, while electrolytes should be gas tight
- Structure Determinations
  - Characterization of grain size, crystal structure, orientation, and morphology by various microscopy and diffraction techniques
- Chemical Determinations
  - Characterization of chemical composition of fuel cell materials

# Fuel Cells

## **In situ Electrochemical Characterization Techniques**

Looks at the effect a given variable has on current and voltage.

Current and voltage are the “end indicators” of fuel cell performances.

In an electrochemical experiment, there are three fundamental variables:

- Voltage (V)
- Current (i)
- Time (t)

Can measure and/or control voltage or current of the system as a function of time.

# Fuel Cells

## In situ Electrochemical Characterization Techniques

Two fundamental types of electrochemical characterization techniques:

- Potentiostatic
- Galvanostatic

### Potentiostatic technique

Voltage of a system is controlled by the user and the resulting current response is measured.

This technique can either be

steady state (voltage is constant with time)

dynamic (voltage varies with time)

# Fuel Cells

## In situ Electrochemical Characterization Techniques

Two fundamental types of electrochemical characterization techniques:

- Potentiostatic
- Galvanostatic

### Galvanostatic technique

Current of a system is controlled by the user and the resulting voltage response is measured.

This technique can either be  
steady state (voltage is constant with time)  
dynamic (voltage varies with time)

# Fuel Cells

## In situ Electrochemical Characterization Techniques

### Steady state Technique

- J-V measurement
  - Hold current or voltage fixed and record the other over time

### Dynamic Technique

- Current Interrupt measurement
  - Current is abruptly imposed at time  $t=0$  and the system voltage is measured over time
- Cyclic Voltammetry
  - Voltage is swept linearly with time back and forth across a voltage window. Current is measured as a function of time but plotted as a function of voltage sweep.
- Electrochemical Impedance Spectroscopy
  - Sinusoidal perturbation (i.e. voltage) is applied to a system and the amplitude and phase shift of the resulting current response are measured. Measurements are done over a wide range of frequencies to give an impedance spectrum.

# Fuel Cells

## In situ Electrochemical Characterization Techniques

### Dynamic Technique

- Current Interrupt measurement

Not as accurate or as detailed as an impedance experiment, but has several advantages compared to impedance:

- It is extremely fast
- Generally requires simpler measurement hardware
- Can be implemented on high-power fuel cell systems
- Can be conducted in parallel with a  $j$ - $V$  curve measurement

# Fuel Cells

## In situ Electrochemical Characterization Techniques

- Current Interrupt measurement

If the current flowing through the cell is abruptly interrupted, the corresponding voltage-time response will immediately rebound followed by an additional time-dependent leveling off.

The immediate rebound is associated with the ohmic resistance of the fuel cell and the time-dependent leveling is associated with the slower mass transport process.

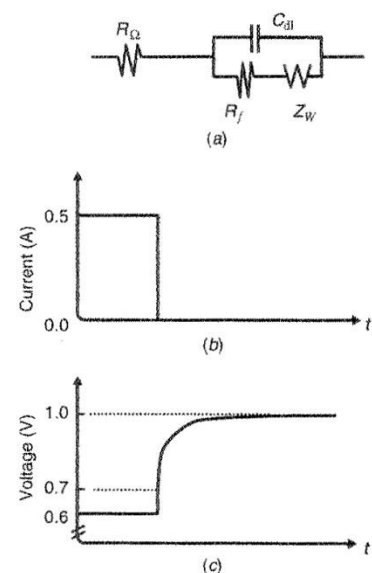


Figure 7.15. (a) Simplified equivalent circuit of a fuel cell system. The  $RC$  components from the anode and cathode have been consolidated into a single branch. (b) Hypothetical current interrupt profile applied to the circuit in (a). In this example, an original steady-state current load of 500 mA is abruptly zeroed. (c) Hypothetical time response of fuel cell voltage when the current interrupt in (b) is applied to the system. The instantaneous rebound in the voltage is associated with the pure ohmic losses in the system. The time-dependent voltage rebound is associated with the activation and mass transport losses in the system.

# Fuel Cells

## In situ Electrochemical Characterization Techniques

### Dynamic Technique

- Current Interrupt measurement

To get accurate results, the current should be interrupted sharply and cleanly (on the order of microseconds to milliseconds) and recorded with a fast oscilloscope.

The measurements are often done in parallel with  $i$ - $V$  curve measurements, to determine the ohmic component of fuel cell loss at each point on the  $i$ - $V$  curve.

# Fuel Cells

## In situ Electrochemical Characterization Techniques

### Dynamic Technique

- Cyclic Voltammetry
  - Typically used to characterize fuel cell catalyst activity in more detail.

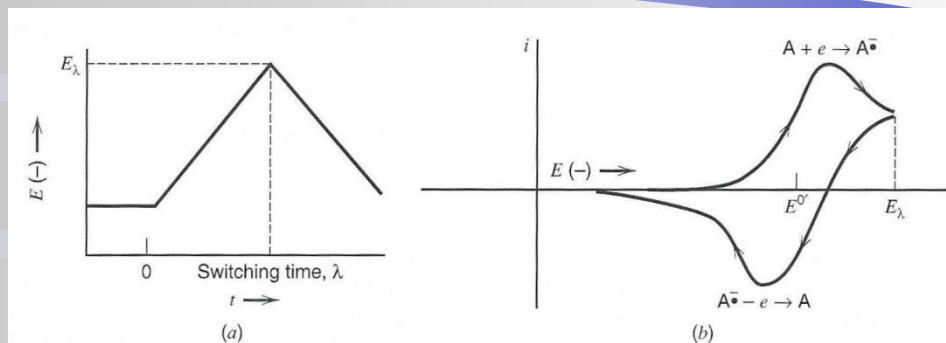


Figure 6.1.3 (a) Cyclic potential sweep. (b) Resulting cyclic voltammogram.

In fuel cells, CV measurements use a “hydrogen-pump-mode” configuration. In this mode, argon gas is passed through the cathode instead of oxygen, while the anode is supplied with hydrogen.

The CV measurement is performed by sweeping the voltage of the system between 0 and 1 V with respect to the anode.

# Fuel Cells

## In situ Electrochemical Characterization Techniques

### Dynamic Technique

- Cyclic Voltammetry
  - For evaluation of catalyst utilization and electrochemical surface area of fuel cell electrocatalysts.

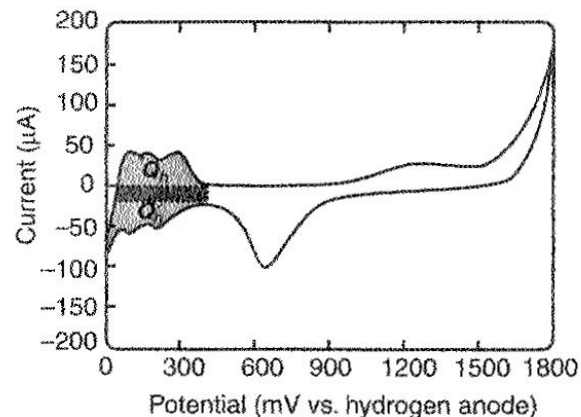


Figure 7.17. Fuel cell CV curve. The peaks marked  $Q_h$  and  $Q'_h$  represent the hydrogen adsorption and desorption peaks on the platinum fuel cell catalyst surface, respectively. The gray rectangular area between the two peaks denotes the approximate contribution from the capacitive charging current. The active catalyst surface area can be calculated from the area under the  $Q_h$  or  $Q'_h$  peak (recognizing that the voltage axis can be converted to a time axis if the scan rate of the experiment is known).

# Fuel Cells

## In situ Electrochemical Characterization Techniques

The procedure involves cycling the electrode of interest over a voltage range where charge transfer reactions are adsorption-limited at the activation sites. The electrode potential is such that the number of reactive surface sites can be obtained by recording the total charge required for monolayer adsorption/desorption.

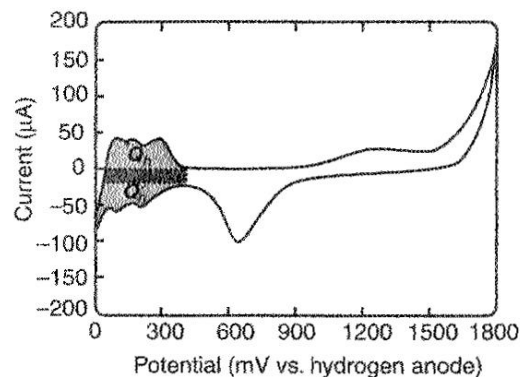


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# Fuel Cells

## In situ Electrochemical Characterization Techniques

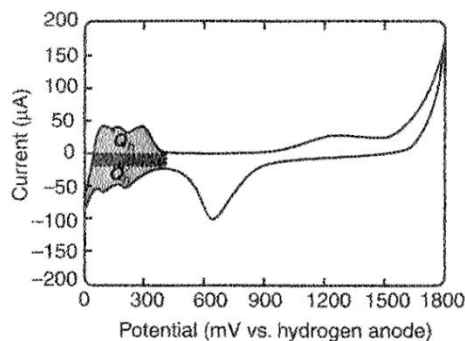


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When the potential increases from 0 V, a current begins to flow which corresponds to a hydrogen adsorption reaction occurring on the electrochemically active cathode catalyst surface.

As the voltage increases the reaction reaches a peak and then falls off as the entire surface becomes fully saturated with hydrogen.

Active catalyst surface area can be obtained by quantifying the total charge ( $Q_h$ ).

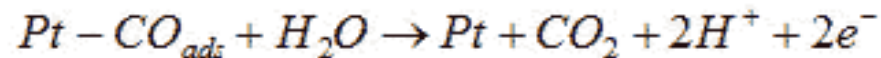
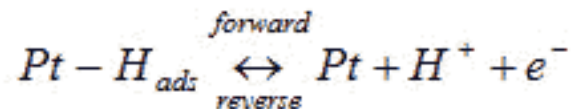
# Fuel Cells

## In situ Electrochemical Characterization Techniques

### Dynamic Technique

- Cyclic Voltammetry

Common reactions used when characterizing PEMFC electrodes are the hydrogen adsorption/desorption (HAD), or the oxidative stripping of adsorbed carbon monoxide.



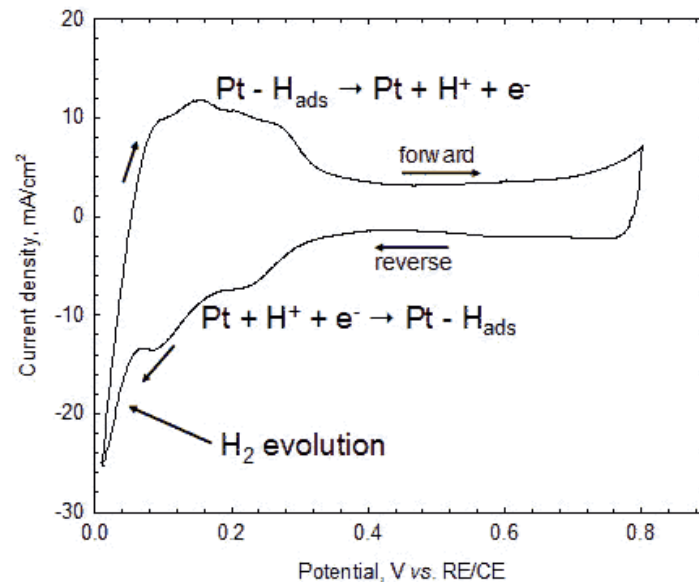
# Fuel Cells

## Dynamic Technique

- Cyclic Voltammetry

The process of interest is the electroreduction of protons and adsorption of hydrogen on the catalyst surface, that is, reaction in the reverse direction.

The hydrogen adsorption charge density ( $q_{\text{Pt}}$  in Coulombs/cm<sup>2</sup>) due to this reaction determined from the CV experiment is used to calculate the ECSA of the fuel cell electrode.



A typical CV voltammogram of the HAD reaction.

# Fuel Cells

## Dynamic Technique

- Cyclic Voltammetry

The electrochemical surface area (ECSA) of the Pt catalyst is calculated from the charge density  $q_{Pt}$  (C/cm<sup>2</sup>electrode) obtained from the CV experiment;

the charge required to reduce a monolayer of protons on Pt,  $\Gamma = 210$   $\mu\text{C}/\text{cm}^2_{Pt}$ ; and the Pt content or loading in the electrode,  $L$  in  $\text{g}_{Pt}/\text{cm}^2_{\text{electrode}}$

$$ECSA \left( \text{cm}^2_{Pt} / \text{g}_{Pt} \right) = \frac{q_{Pt}}{\Gamma \cdot L}$$

# Fuel Cells

## Dynamic Technique

- Cyclic Voltammetry

Not all of the catalyst used to make the fuel cell electrode is accessible to reactants (e.g., protons and oxygen at the cathode) and/or is in electrical contact and thus is not able to participate in the electrochemical reaction.

The fraction of the catalyst that is available to participate in electrode reactions is given by the ratio of ECSA to the specific area of the catalyst obtained by the catalyst manufacturer using chemisorption or other *ex situ* techniques (also in  $\text{cm}^2_{\text{Pt}} / \text{g}_{\text{Pt}}$ ).

This ratio is referred to as utilization. Higher catalyst utilization is better.

# Fuel Cells

## In situ Electrochemical Characterization Techniques

### Dynamic Technique

- Electrochemical Impedance Spectroscopy
  - A technique used to differentiate between all the major sources of loss in a fuel cell.
  - Impedance is a measure of the ability of a system to impede the flow of electrical current.
  - Impedance,  $Z$  is the ratio between a time-dependent voltage and a time dependent current.

$$Z = \frac{V(t)}{i(t)}$$

# Fuel Cells

## In situ Electrochemical Characterization Techniques

### Dynamic Technique

- Electrochemical Impedance Spectroscopy
  - Impedance measurements are made by applying a small sinusoidal voltage perturbation,

$$V(t) = V_o \cos(\omega t)$$

and monitoring the system's resultant current response,

$$i(t) = i_o \cos(\omega t - \phi)$$

$V(t)$  and  $i(t)$  are the potential and current at time  $t$

$V_o$  and  $i_o$  are the amplitudes of the voltage and current signals

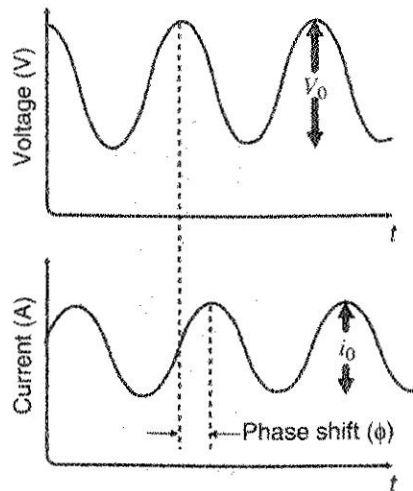
$\omega$  is the radial frequency.

# Fuel Cells

## In situ Electrochemical Characterization Techniques

### Dynamic Technique

- Electrochemical Impedance Spectroscopy
  - In general the current response of a system may be shifted in phase compared to the voltage perturbation. This phase shift effect is described by  $\phi$ .



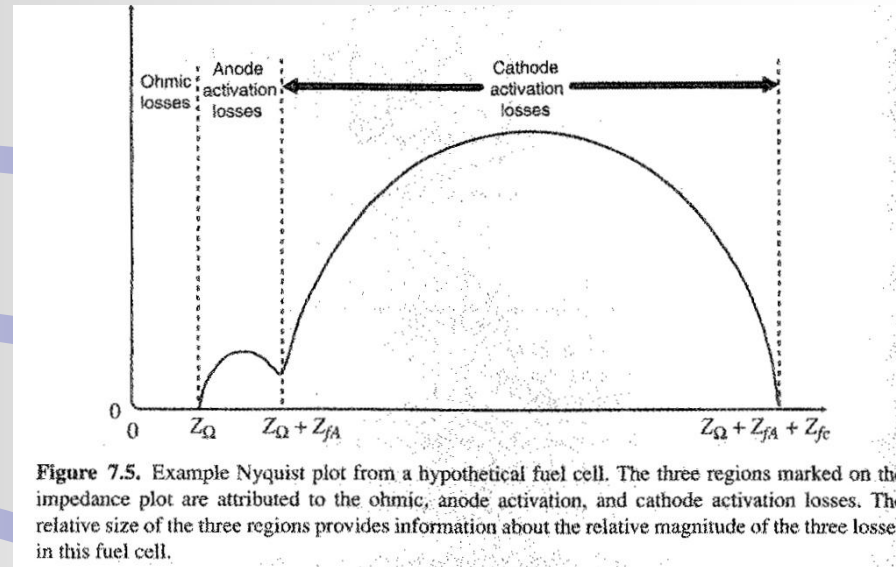
**Figure 7.3.** A sinusoidal voltage perturbation and resulting sinusoidal current response. The current response will possess the same period (frequency) as the voltage perturbation but will generally be phase shifted by an amount  $\phi$ .

# Fuel Cells

## In situ Electrochemical Characterization Techniques

### Dynamic Technique

- Electrochemical Impedance Spectroscopy



The size of the semicircles depict the magnitude of the losses in the typical plot for a fuel cell shown above. The size of the impedance curves correspond to the relative size of  $\eta_{\text{ohmic}}$ ,  $\eta_{\text{act,anode}}$ ,  $\eta_{\text{act,cathode}}$ . The cathode activation loss dominates the fuel cell performance.

# Fuel Cells

## Ex Situ Characterization Techniques

### – Porosity Determination

- Technique to determine electrode and catalyst porosity.

Porosity,  $\phi$  of a material is defined as the ratio of void space to the total volume of the material.

An effective fuel cell and catalyst layers must exhibit substantial porosity and the pore space should be interconnected and open to the surface.

# Fuel Cells

## Ex Situ Characterization Techniques

### – Porosity Determination

- Technique to determine electrode and catalyst porosity.

For fuel cells, the effective porosity counts only the pore space that is interconnected and open to the surface, dead pores are ignored.

To determine effective porosity, the total volume of the sample is determined by immersing the sample in a liquid that does not enter the pores, i.e. at low pressure Hg will not enter pores due to surface tension effects.

Then the sample is inserted into a container of known volume containing an inert gas, the pressure is noted and a second evacuated container is connected to the first and the pressure is noted.

# Fuel Cells

## Ex Situ Characterization Techniques

- Brunauer-Emmett-Teller (BET) Surface Area Measurement
  - Allows highly accurate surface area determination

A dry sample is evacuated of all gas and cooled to 77 K.

A fine layer of inert gas ( $N_2$ , Ar, Kr) is absorbed on the sample surface at the low temperature.

The gas will adhere to the surface, lowering the pressure in the chamber.

From the measured absorption isotherm, the surface area can be calculated.

# Fuel Cells

## Ex Situ Characterization Techniques

### – Gas Permeability

- Electrodes and catalyst layers need to be highly permeable, while electrolytes should be gas tight

Permeability measures the ease with which gases move through a material.

Even highly porous materials can have low permeability if the pores do not connect.

Permeability,  $K$  is measured by the volume of gas ( $\Delta V$ ) that passes through a sample in a given period of time ( $\Delta t$ ) when driven by a pressure drop.

# Fuel Cells

## Ex Situ Characterization Techniques

- Structure Determinations
  - Characterization of grain size, crystal structure, orientation, and morphology by various microscopy and diffraction techniques.

SEM, TEM, AFM, XRD

Provide structure, orientation, chemical info, particle size, grain size, distribution of particles.

# Fuel Cells

## Ex Situ Characterization Techniques

- Chemical Determinations
  - Characterization of chemical composition of fuel cell materials.

TEM, XRD, AES, XPS, SIMS

# Fuel Cells

## Summary

- There are three major fuel cell losses: activation losses ( $\eta_{\text{act}}$ ), ohmic losses ( $\eta_{\text{ohmic}}$ ), and concentration losses ( $\eta_{\text{conc}}$ )
- A simple fuel cell model can be developed by starting with the thermodynamic fuel cell voltage and then deducting the three major loss terms:  $V = E_{\text{thermo}} - \eta_{\text{act}} - \eta_{\text{ohmic}} - \eta_{\text{conc}}$
- To accurately reflect the behavior of most fuel cells, an additional loss term, known as the leakage loss,  $j_{\text{leak}}$ , must be used.
- The leakage loss is associated with the parasitic loss due to current leakage, gas crossover, unwanted side reactions.
- The net effect of the leakage loss is to offset a fuel cell's operating current to the left by an amount given by  $j_{\text{leak}}$ .

# Fuel Cells

## Summary

- The basic fuel cell model requires four parameters. Two parameters ( $\alpha$  and  $j_0$ ) describe the kinetic losses, one parameter ( $ASR_{ohmic}$ ) describes the ohmic losses, and one parameter ( $j_L$ ) describes the concentration losses.
- The governing equations of a fuel cell model are related to one another by flux balance and conservation laws.

# Fuel Cells

## Summary

- In situ electrical characterization techniques make use of the three fundamental electrochemical variables (voltage, current, and time) to probe fuel cell behavior.
- Ex situ characterization techniques focus on correlating the structure (porosity, grain size, morphology, surface area) or the chemistry (composition, phase, spatial distribution) of fuel cell components to fuel cell performance.
- The major in situ electrical characterization techniques are  $j$ - $V$  curve measurements, electrochemical impedance spectroscopy (EIS), current-interrupt, and cyclic voltammetry.
- A  $j$ - $V$  curve yield the steady-state performance of a fuel cell.
- Current interrupt, EIS, and CV measurements utilize the non-steady state (dynamic) behavior of fuel cells.

# Fuel Cells

## Summary

- Current interrupt distinguishes ohmic and nonohmic fuel cell processes.
- EIS measures the ohmic, activation, and mass transport losses in the fuel cell.
- CV determines in situ catalyst activity and detailed kinetic analysis.
- Ex situ characterization techniques include porosity analysis, surface area determination, permeability measurement, microscopy (OM, SEM, TEM, AFM), and chemical analysis (XRD, AES, XPS, SIMS).

# Fuel Cells

## Basic Fuel Cell Model

The real voltage output of a fuel cell can be written by starting with the thermodynamic predicted voltage and subtracting the overvoltages:

$$V = E_{\text{thermo}} - \eta_{\text{act}} - \eta_{\text{ohmic}} - \eta_{\text{conc}}$$

where

$V$  - the operating voltage of fuel cell

$E_{\text{thermo}}$  - thermodynamically predicted voltage

$\eta_{\text{act}}$  - activation loss due to reaction kinetics

$\eta_{\text{ohmic}}$  - ohmic loss from ionic and electronic resistance

$\eta_{\text{conc}}$  - concentration losses due to mass transport.

# Class Assignment

- Research paper – due Dec 2<sup>nd</sup>
- Final – Dec. 9<sup>th</sup> 8 – 10 am

