



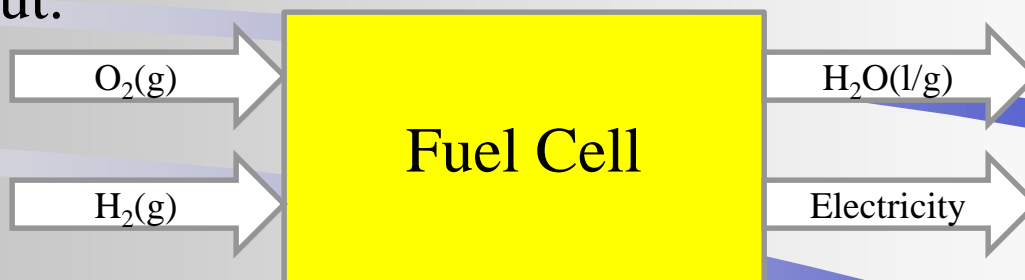
# Electrochemistry

CHEM 5390

# Fuel Cells

An electro-chemical energy conversion device

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

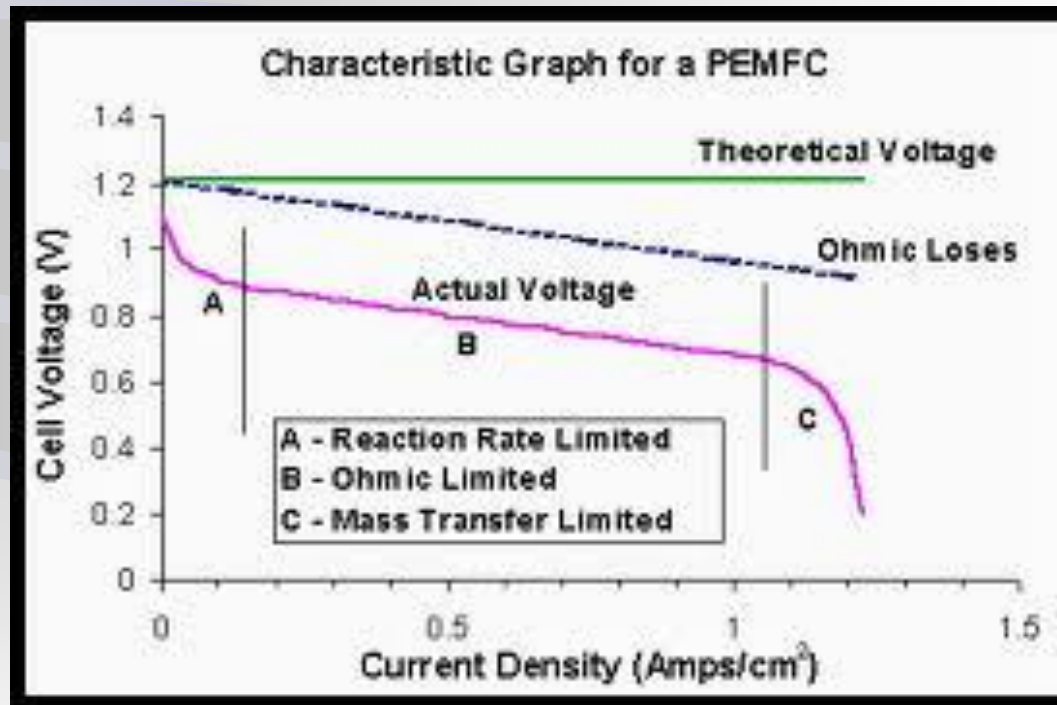


Converts chemical energy → electricity without intermediate heat step.

# Fuel Cells

## Fuel Cell Performance

i-V curve



# Fuel Cells

## Fuel Cell Performance

Three major types of fuel cell losses:

- Activation losses (losses due to the electrochemical reaction)
- Ohmic losses (losses due to ionic and electronic conduction)
- Concentration losses (losses due to mass transport)

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

$V$  – real output voltage of fuel cell

$E_{\text{thermo}}$  – thermodynamic predicted fuel cell voltage

$\eta_{\text{act}}$  – activation losses due to reaction kinetics (affect initial part of the curve)

$\eta_{\text{ohmic}}$  – ohmic losses from ionic and electronic conduction (most apparent in middle)

$\eta_{\text{conc}}$  – concentration losses due to mass transport (most significant at end of i-V curve)

# Fuel Cells

## Fuel Cell Mass Transport

Fuel must be continually supplied with fuel and oxidant while products must be continually removed to avoid “strangling” the cell.

This process is termed fuel cell mass transport. Poor mass transport leads to significant fuel cell performance loss – since performance is determined by reactant and product concentration at the interface (catalyst layer) not the fuel cell inlet (heterogenous reaction).

# Fuel Cells

## Fuel Cell Mass Transport

Ionic charge transport is a subset of mass transport, but in this lecture will focus on transport of uncharged species.

Uncharged species are unaffected by voltage gradients – uses convective and diffusive forces.

# Fuel Cells

## Fuel Cell Mass Transport

Mass Transport occurs by:

- Diffusion
- Migration
- Convection

Nernst-Planck Equation

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$$

# Fuel Cells

## Fuel Cell Mass Transport

### Nernst-Planck Equation

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$$

(diffusion)

(migration)

(convection)

$J_i(x)$  – flux of species  $i$  (mol/s cm<sup>2</sup>) at distance  $x$  from surface.

$D_i$  – diffusion coefficient (cm<sup>2</sup>/s)

$\partial C_i(x)/\partial x$  – concentration gradient at distance  $x$

$\partial \phi(x)/\partial x$  – potential gradient

$z_i$  and  $C_i$  – charge (dimensionless) and concentration (mol/cm<sup>3</sup>) of species  $i$

$v(x)$  – velocity (cm/s)



# Fuel Cells

## Transport in electrode versus flow structure

Mass transport in fuel cell electrodes distances are in the  $\mu\text{m}$  to nm scales and flow patterns are tortuous. Transport is dominated by diffusion.

Mass transport in fuel cell flow structures distances are in the mm or cm scales and flow patterns are geometric well-defined channel arrays that follow the laws of fluid dynamics. Transport is dominated by convection.

# Fuel Cells

## Transport in electrode versus flow structure

Convection – the transport of a species by bulk motion of a fluid under the action of a mechanical force. In fuel cells – pressure is the driving force to push fuel or oxidant through the flow channels.

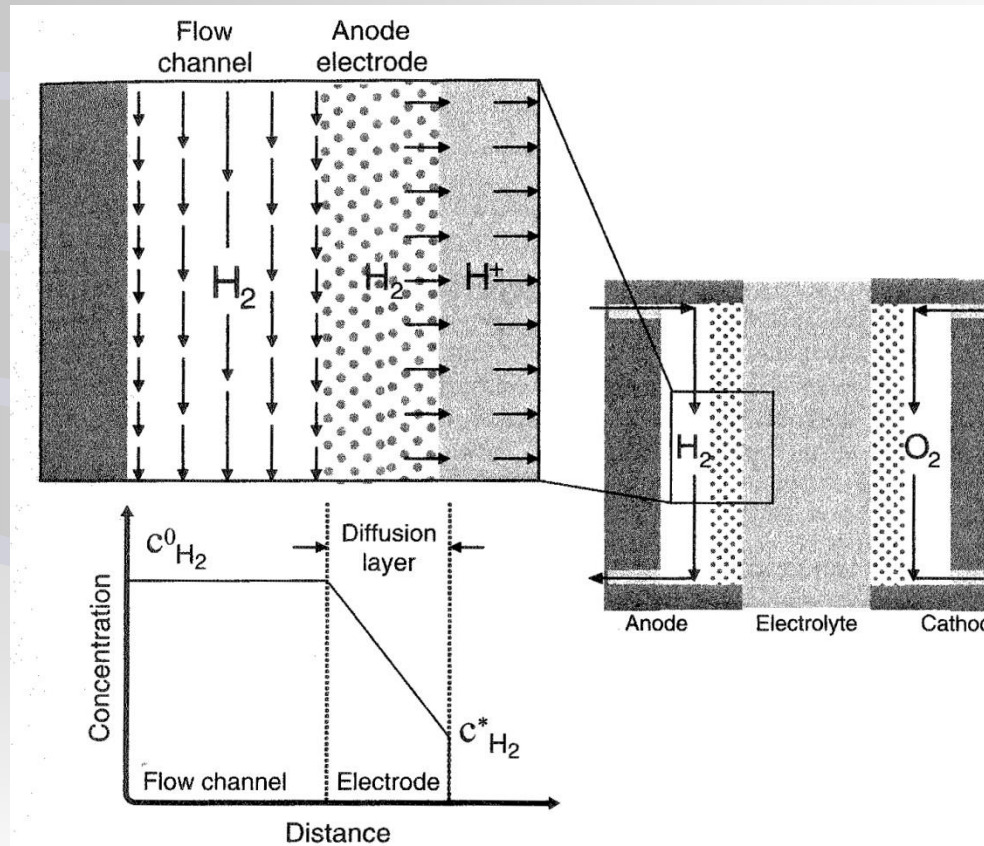
Diffusion – the transport of a species due to a gradient in concentration. Consumption and production of species drives diffusion at the electrode.

Convection is more effective at transporting species than diffusion.

# Fuel Cells

## Transport in electrode versus flow structure

Convection is more effective at transporting species than diffusion



# Fuel Cells

## Transport in electrode versus flow structure

The boundary between convective-dominated flow and diffusion-dominated flow occurs where the fuel cell gas channel and porous electrode meet.

Due to frictional forces, the velocity of the moving gas stream decreases towards zero at the electrode-channel boundary and forms a stagnant gas region (diffusion layer).

Diffusion layer thickness changes depending on

- Flow conditions
- Flow channel geometry
- Electrode structure

# Fuel Cells

## Transport in electrode: Diffusive Transport

Mass transport within the fuel cell electrode is within the diffusion layer.

For fuel cells can assume that the electrode thickness equals the diffusion layer thickness.

Concentration gradients occur between the flow channel and electrode.

Electrochemical reaction depletes the reactants and produces products thus driving diffusion.

# Fuel Cells

## Transport in electrode: Diffusive Transport

Electrochemical reaction depletes the reactants and produces products thus driving diffusion.

This affects fuel cell performance in two ways:

- Nernstian losses
- Reaction losses

These losses are called the fuel cell's "concentration" overvoltage,  $\eta_{\text{conc}}$ .

# Fuel Cells

## Transport in electrode: Diffusive Transport

- Nernstian losses
  - The fuel cell voltage will decrease according to the Nernst equation, since the reactant concentration at the catalyst layer is decreased and product is increased relative to the bulk concentration.

$$E = E^0 - \frac{0.0592}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

# Fuel Cells

## Transport in electrode: Diffusive Transport

- Reaction losses
  - The reaction rate (activation) losses will be increased because the reactant concentration at the catalyst layer is decreased relative to the bulk concentration.



# Fuel Cells

## Transport in electrode: Diffusive Transport

To determine the size of these losses, need to know how much the reactant and product concentrations at the catalyst layer differ from the bulk values.

For  $R + ne \rightarrow P$

At time zero (before potential is applied) the reactant and product concentrations are the same throughout the fuel cell,  $c_R^0$  and  $c_P^0$ .

When electrolysis starts at a fixed current density,  $j$ ,  $[R]$  at electrode surface,  $c_R^*$  ( $x = 0$ ) becomes smaller than value in the bulk,  $c_R^0$ .

Eventually a steady-state is reached.

# Fuel Cells

## Transport in electrode: Diffusive Transport

At steady state:

$$j = n F J_{\text{diff}}$$

where  $j$  is the fuel cell's operating current density,  $J_{\text{diff}}$  is the diffusion flux of reactants to the catalyst layer or products away from the catalyst layer.

# Fuel Cells

## Transport in electrode: Diffusive Transport

If we use the part of the diffusion equation:

$$J_{diff} = -D \frac{dc}{dx}$$

at steady state:

$$J_{diff} = -D^{eff} \frac{c_R^* - c_R^0}{\delta}$$

and

$$j = nFD^{eff} \frac{c_R^* - c_R^0}{\delta}$$

$$c_R^* = c_R^0 - \frac{j\delta}{nFD^{eff}}$$

# Fuel Cells

## Transport in electrode: Diffusive Transport

So the reactant concentration in the catalyst layer is less than the bulk concentration by an amount that depends on  $j$ ,  $\delta$ , and  $D^{\text{eff}}$ .

$D^{\text{eff}}$  is the diffusion flux correction to account for the effects of the pores through the catalyst.

$$j = nFD^{\text{eff}} \frac{c_R^* - c_R^0}{\delta}$$

$$c_R^* = c_R^0 - \frac{j\delta}{nFD^{\text{eff}}}$$

# Fuel Cells

## Transport in electrode: Diffusive Transport

$D^{\text{eff}}$  is the diffusion flux correction to account for the effects of the pores through the catalyst. (Effective diffusivity)

$$D^{\text{eff}} = \varepsilon^{1.5} D$$

$\varepsilon$  – porosity represented by the ratio of pore volume to total volume.

Fuel cell electrodes have porosities around 0.4 (40% of total electrode volume is pores)

# Fuel Cells

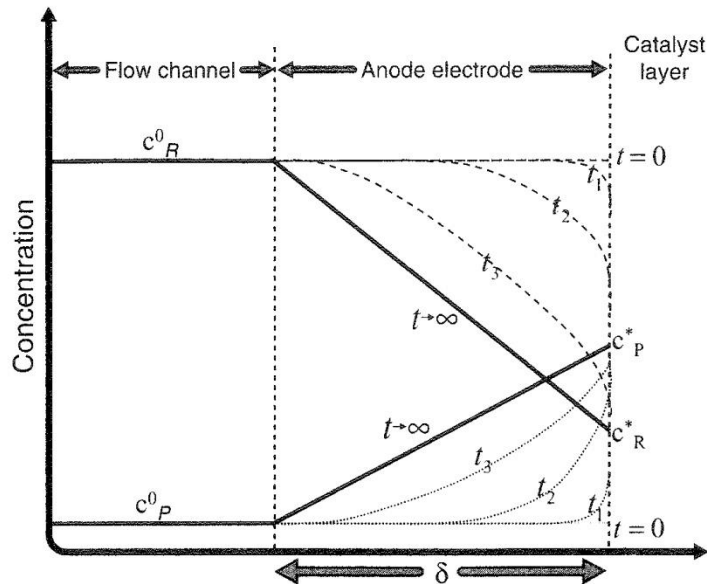
## Transport in electrode: Diffusive Transport

The equation can be modified to include tortuosity,  $\tau$ , the additional impedance to diffusion caused by a convoluted flow path.

$$D^{eff} = D \frac{\epsilon}{\tau}$$

# Fuel Cells

## Transport in electrode: Diffusive Transport



**Figure 5.4.** Time dependence of reactant and product concentration profiles at fuel cell electrode. The fuel cell begins producing current at time  $t = 0$ . Starting from constant initial values ( $c_R^0$  and  $c_P^0$ ), the reactant and product concentration profiles evolve with increasing time, as shown for  $t_1 < t_2 < t_3$ . Eventually the profiles approach a steady-state balance (indicated by the dark solid lines) where concentration varies (approximately) linearly with distance across the diffusion layer. At steady state, the diffusion flux down these linear concentration gradients exactly balances the reaction flux at the catalyst layer.

# Fuel Cells

## Transport in electrode: Diffusive Transport

At a point the current density will be so high that the reactant concentration in the catalyst layer drops to zero.

This is the limit of mass transport and this current density is the *limiting current density*,  $j_L$ , of the fuel cell.

Need to increase the limiting current density by careful design of the fuel cell. (high  $c_R$  and large  $D^{\text{eff}}$  and small  $\delta$ )



# Fuel Cells

## Transport in electrode: Diffusive Transport

Need to increase the limiting current density by careful design of the fuel cell. (high  $c_R$  and large  $D^{\text{eff}}$  and small  $\delta$ )

Typical values for fuel cells are:

$$\delta = 100\text{-}300 \text{ }\mu\text{m}$$

$$D^{\text{eff}} = 10^{-2} \text{ cm}^2/\text{s}$$

$$j_L = 1\text{-}10 \text{ A/cm}^2$$

A fuel cell will never be able to produce a higher current density than its limiting current density.

# Fuel Cells

## Transport in electrode: Diffusive Transport

Concentration affects Nernst voltage

Voltage loss due to the reactant concentration depletion is equal to

$$\eta_{conc} = \frac{RT}{nF} \ln \frac{j_L}{j_L - j}$$

where  $j$  is the operating current density, when  $j \ll j_L$ ,  $\eta_{conc}$  is small, but as  $j \rightarrow j_L$ ,  $\eta_{conc}$  increases sharply.

# Fuel Cells

## Transport in electrode: Diffusive Transport

Concentration affects reaction rate (kinetics)

Remember the Butler-Volmer equation also depends on the reactant and product concentrations at the reaction site.

$$j = j_0^o \left( \frac{C_R^*}{C_R^0} e^{\alpha n F \eta_{act} / (RT)} - \frac{C_P^*}{C_P^0} e^{-(1-\alpha) n F \eta_{act} / (RT)} \right)$$

At high currents when driving the reaction one way,

$$\eta_{conc} = \left( \frac{RT}{nF} \right) \left( 1 + \frac{1}{\alpha} \right) \ln \frac{j_L}{j_L - j}$$

# Fuel Cells

## **Transport in flow structures: Convective Transport**

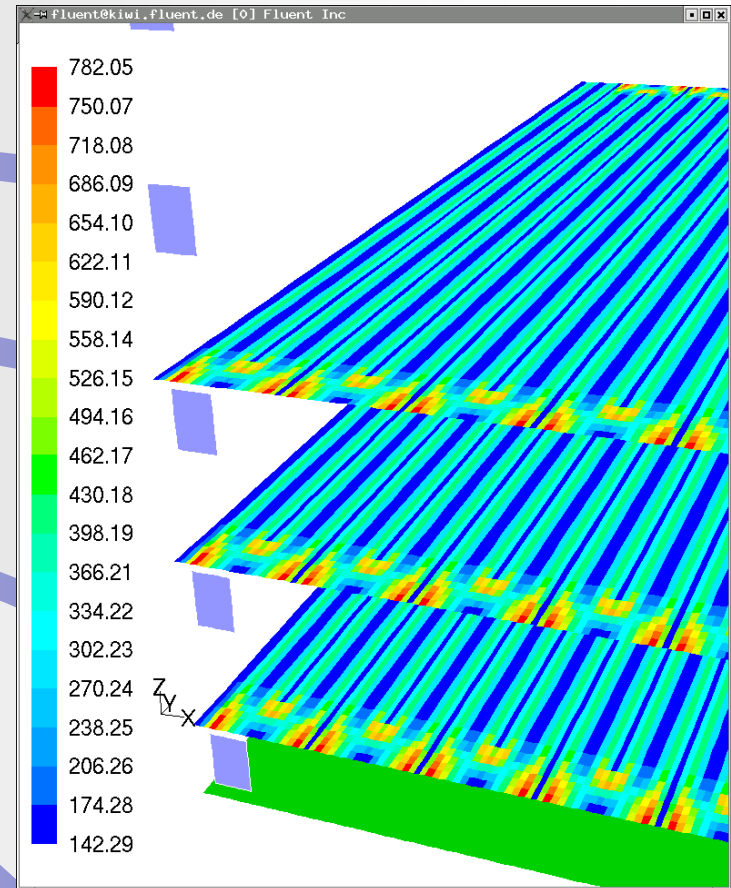
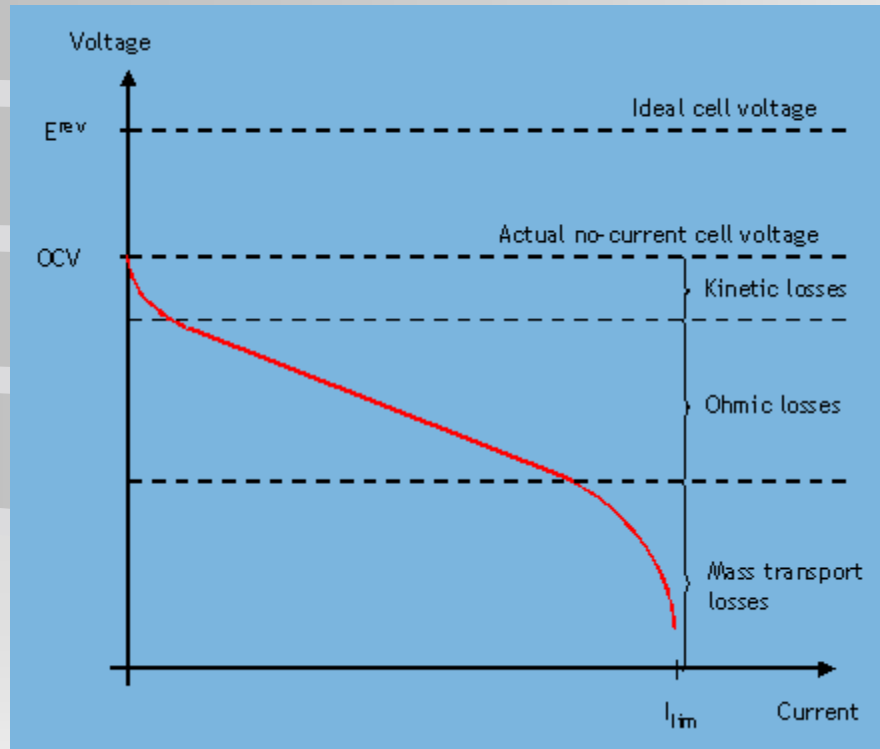
The flow structure provides the best opportunity for mass transport optimization.

The reactants in the bulk decrease with distance along a fuel cell channel as they are being consumed.

Keeping the reactant concentration consistently high across an entire fuel cell device is the best way to minimize concentration losses in a fuel cell.

# Fuel Cells

## Transport in flow structures: Convective Transport



# Fuel Cells

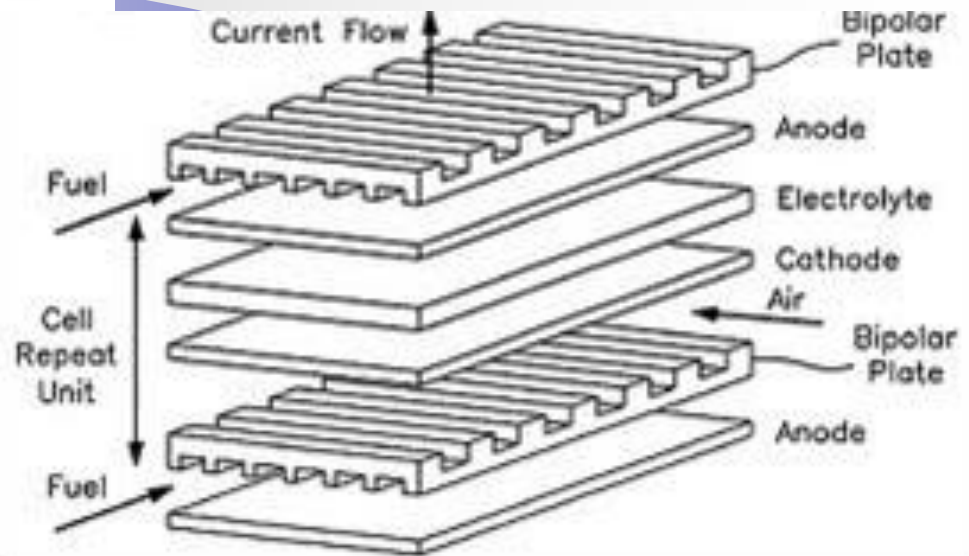
## **Transport in flow structures: Convective Transport**

Fuel cell flow structures are designed to distribute reactants across a fuel cell.

To make a fuel cell structure, the flow channel design is stamped, etched or machined into a flow field plate.

# Fuel Cells

Flow field plates in combination with porous electrode structures help distribute the gas over the surface of the fuel cell.



# Fuel Cells

## Transport in flow structures: Convective Transport

The shape, size, and pattern of the flow channels significantly affect the performance of the fuel cell.

Mass transport, diffusion, and fluid mechanics are important in understanding the flow.

The nature of fluid (gas in the case of a fuel cell) flow in confined channels is characterized by a dimensionless number called the *Reynolds number*,  $Re$ .



# Fuel Cells

## Transport in flow structures: Convective Transport

The nature of fluid (gas in the case of a fuel cell) flow in confined channels is characterized by a dimensionless number called the *Reynolds number*, Re.

$$\text{Re} = \frac{\rho V L}{\mu} = \frac{V L}{\nu}$$

where V is the characteristic velocity of the flow (m/s), L is the characteristic length scale of the flow (m),  $\rho$  is the fluid density (kg/m<sup>3</sup>),  $\mu$  is the fluid viscosity (kg/m s or N s/m<sup>2</sup>),  $\nu$  is the kinematic viscosity (m<sup>2</sup>/s) which is a ratio of  $\mu$  over  $\rho$ .

# Fuel Cells

## Transport in flow structures: Convective Transport

The nature of fluid (gas in the case of a fuel cell) flow in confined channels is characterized by a dimensionless number called the *Reynolds number*,  $Re$ .

The Reynolds number physically describes the ratio of inertial forces to viscous forces in dynamic flow.

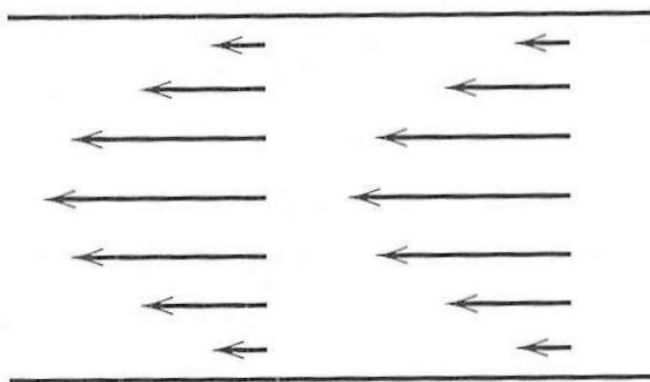
All fluids have a characteristic viscosity – which measures the resistance to fluid flow (how easily molecules slide past one another when driven by shear force).

# Fuel Cells

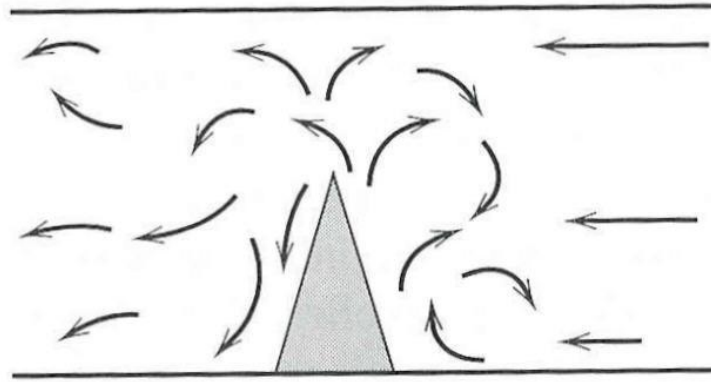
## Transport in flow structures: Convective Transport

### Flow Profiles

Fluid flow in hydrodynamic problems is either laminar (smooth and steady) with a parabolic flow profile or turbulent (unsteady and chaotic) with the net flow in one direction.



Laminar flow



Turbulent flow

**Figure 9.2.1** Types of fluid flow. Arrows represent instantaneous local fluid velocities.

# Fuel Cells

## Transport in flow structures: Convective Transport

Reynolds number is proportional to fluid velocity, so high values imply high flow or electrode reaction rates.

At flow rates below the critical Reynolds number,  $Re_{cr}$  – flow is laminar.

# Fuel Cells

## Transport in flow structures: Convective Transport

If we consider a gas,  $O_2$ , as it is supplied to a fuel cell,  $O_2$  concentration is depleted linearly as the gas moves along the channel.

Channel size,  $H_C$ , diffusion layer thickness,  $H_E$ , and inlet flow velocity,  $u_{in}$  affect the gas concentration.

Increasing  $u_{in}$  (supplying more gas) improves mass transport.

Decreasing  $H_E$  increases gas density at the catalyst layer.

# Fuel Cells

## Transport in flow structures: Convective Transport

Increasing  $u_{in}$  (supplying more gas) improves mass transport.

Decreasing  $H_E$  increases gas density at the catalyst layer.

Effect of  $H_C$  is not always as obvious, but if assume total gas supply to fuel cell is constant, decreasing channel size will increase gas density.

# Fuel Cells

## **Transport in flow structures: Convective Transport**

Flow structure design – materials

Flow structure:

- Supplies the reactant gases and removes the reaction product
- Harvest the electrical current generated by the fuel cell

# Fuel Cells

## Transport in flow structures: Convective Transport

Flow structure design – materials

Materials for flow structures have several selection criteria:

- High electrical conductivity
- High corrosion resistance
- High chemical compatibility
- High thermal conductivity
- High gas tightness
- High mechanical strength
- Low weight and volume
- Ease of manufacturability
- Cost effective



# Fuel Cells

## **Transport in flow structures: Convective Transport**

Flow structure design – materials

Most common material for fuel cell flow plates is graphite.

Graphite meets many of the criteria except, ease of manufacturability, cost, and high mechanical strength.

Other materials used is stainless steel.

Stainless steel is less expensive to machine and has higher mechanical strength.

One problem is the formation of surface oxides – can use corrosion resistant coatings but stability is not known.

# Fuel Cells

## **Transport in flow structures: Convective Transport**

Flow structure design – materials

Flow plates in SOFCs are made from ceramics (ie. lanthanum chromite,  $\text{LaCrO}_3$ ) or ferritic stainless steel (have chromium as their major alloying element and are typically low in carbon content).

# Fuel Cells

## **Transport in flow structures: Convective Transport**

Flow structure design – patterns

Flow plates contain channel or grooves to distribute the gas flow over the surface of the fuel cell.

Choosing the right flow pattern can be critical (especially for PEMFCs), need to remove water quickly or fuel cell becomes flooded and blocks gas access.

# Fuel Cells

## **Transport in flow structures: Convective Transport**

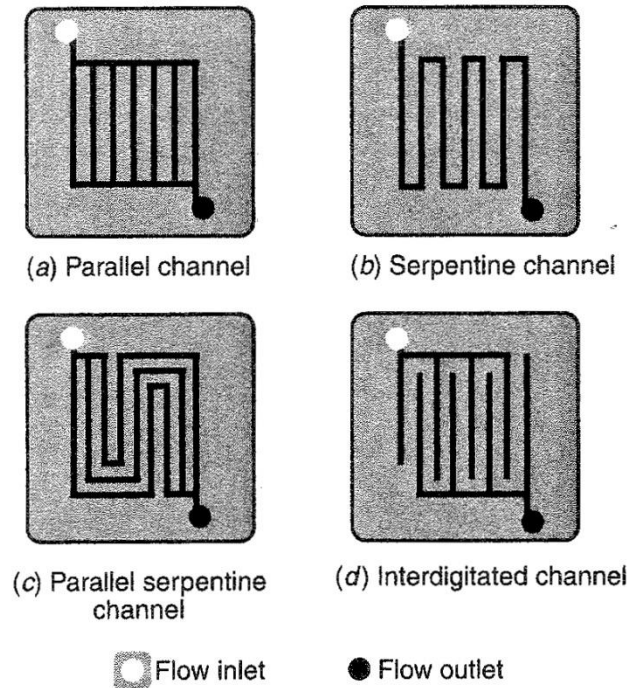
Flow structure design – patterns

Types of flow patterns include:

- Parallel flow
- Serpentine flow
- Interdigitated flow

# Fuel Cells

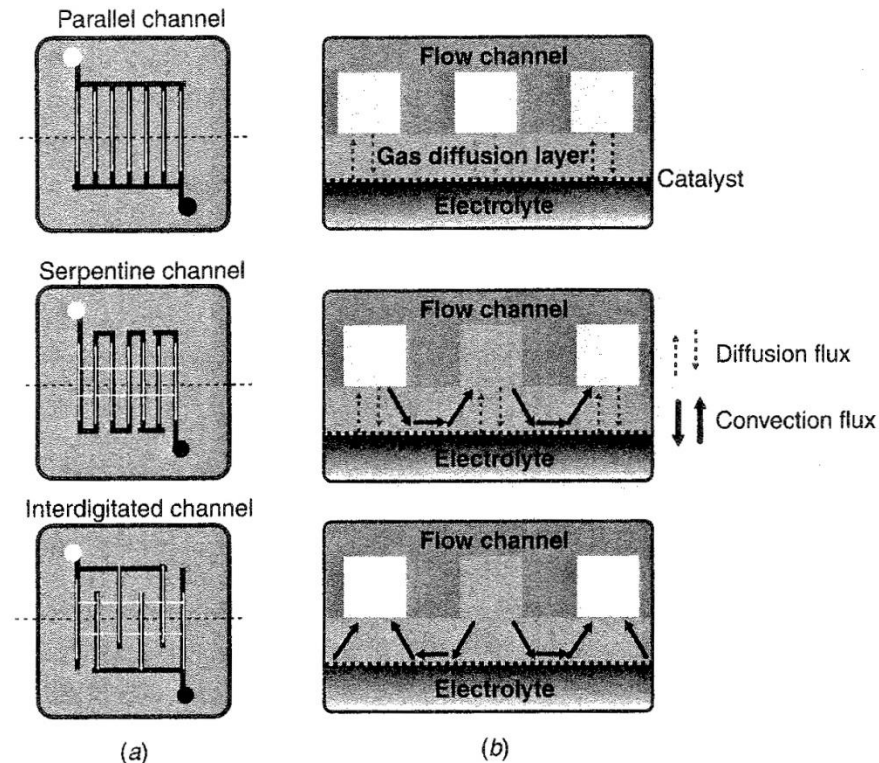
## Transport in flow structures: Convective Transport



**Figure 5.14.** Major flow channel geometries: (a) parallel, (b) serpentine, (c) parallel serpentine, (d) interdigitated. Flow channel geometries seek to provide homogeneous distribution of reactants across an electrode surface while minimizing pressure drop losses and maximizing water removal capability.

# Fuel Cells

## Transport in flow structures: Convective Transport



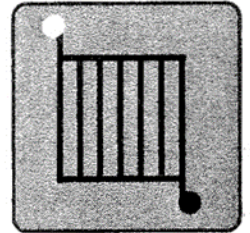
**Figure 5.15.** Gas transport modes in various flow channel geometries. Each channel type induces a different convective transport scheme in the electrode.

# Fuel Cells

## Transport in flow structures: Convective Transport

Flow structure design – patterns

Types of flow patterns include:



(a) Parallel channel

- Parallel flow
  - Flow enters evenly each straight channel and exits through the outlet.
  - Advantage
    - Low overall pressure drop between inlet and outlet
  - Disadvantage
    - Does not work well for larger fuel cells (large flow distributions are not uniform) so used only in portable fuel cells.



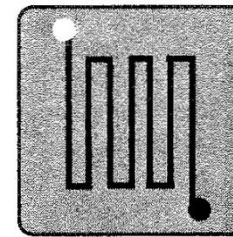
# Fuel Cells

## Transport in flow structures: Convective Transport

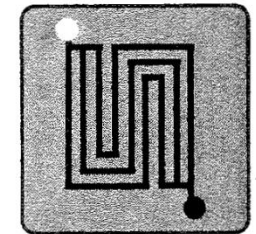
Flow structure design – patterns

Types of flow patterns include:

- Serpentine flow
  - Most common geometry in fuel cells.
  - Advantage
    - Good water removal capability – only one flow path – so water is forced to exit channel.
  - Disadvantage
    - In large area cells have a large pressure drop.
- Parallel-serpentine hybrid design used to overcome some of these problems. (Ballard PEMFC stacks)



(b) Serpentine channel



(c) Parallel serpentine channel

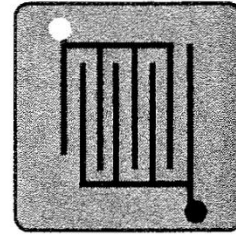


# Fuel Cells

## Transport in flow structures: Convective Transport

Flow structure design – patterns

Types of flow patterns include:



(d) Interdigitated channel

- Interdigitated flow
  - Promotes forced convection of the reactant gases through the diffusion layer.
  - Advantage
    - Improved mass transport
  - Disadvantage
    - Large pressure drops (small rib spacing helps with this)

For all fuel cells – channel pattern, channel shape, and channel size significantly affect performance.

# Fuel Cells

## Summary

- Mass transport governs the supply and removal of reactants and products in a fuel cell.
- Poor mass transport leads to a loss in fuel cell performance due to reactant depletion (or product clogging) effects.
- Mass transport in fuel cell electrodes is typically dominated by diffusion. Mass transport in fuel cell flow structures is typically dominated by convection.
- Convection refers to the transport of a species by the bulk motion of a fluid. Diffusion refers to the transport of a species due to a gradient in concentration.

# Fuel Cells

## Summary

- Diffusive transport limitations in the electrode lead to a limiting current density  $j_L$ . The limiting current density corresponds to the point where the reactant concentration falls to zero in the fuel cell catalyst layer. A fuel cell can never sustain a current density higher than  $j_L$ .
- Reactant depletion affects both the Nernstian cell voltage and the kinetic reaction rate. Depletion leads to a similar loss in both cases. This “concentration loss” can be generalized as  $\eta_{\text{conc}} = c[j_L/(j_L - j)]$ , where  $c$  is a constant that depends on the geometry and mass transport properties of the fuel cell.
- Concentration losses are most effectively minimized by careful consideration of the convective transport situation in the fuel cell flow channels.

# Fuel Cells

## Summary

- Convection in fuel cell flow channels is characterized by the Reynolds number,  $Re$ , a nondimensional parameter that characterizes the viscous behavior of the flow. Usually gas flow in fuel cells is laminar.
- Viscosity,  $\mu$ , characterizes the resistance of a fluid to flow. Viscosity can be thought of as a measure of the “internal” friction in the fluid.
- The viscosity of a gas mixture is dependent on the temperature and composition of the mixture.
- A pressure difference is required to drive gas flow through a channel.

# Fuel Cells

## Summary

- A simple 2D fuel cell mass transport model can be constructed to show how reactant gases are depleted in a flow channel from the inlet to the outlet. In general, increasing the gas flow velocity, decreasing the channel size, or decreasing the diffusion layer thickness will improve the mass transport situation along the length of the flow channel.
- Choice of the flow field pattern significantly affects the size of the mass transport losses. Due to the liquid water formation in the cathode, PEMFCs require flow fields with high water removal capability.
- Serpentine or parallel-serpentine designs are the most commonly used flow field types. They provide a decent compromise between pressure drop and water removal capability.

# 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 December 8<sup>th</sup>

