



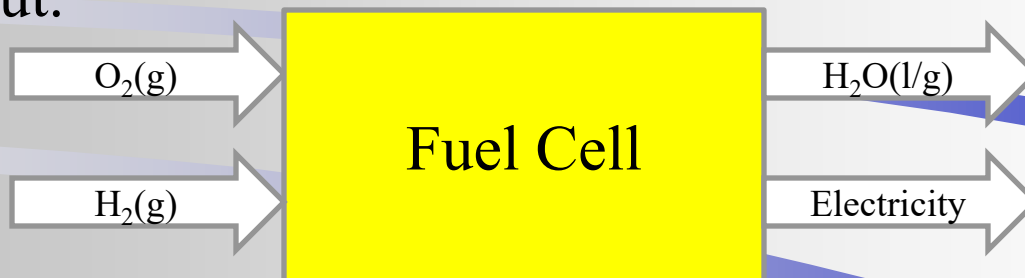
# Electrochemistry

CHEM 5390

# Fuel Cells

An electro-chemical energy conversion device

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

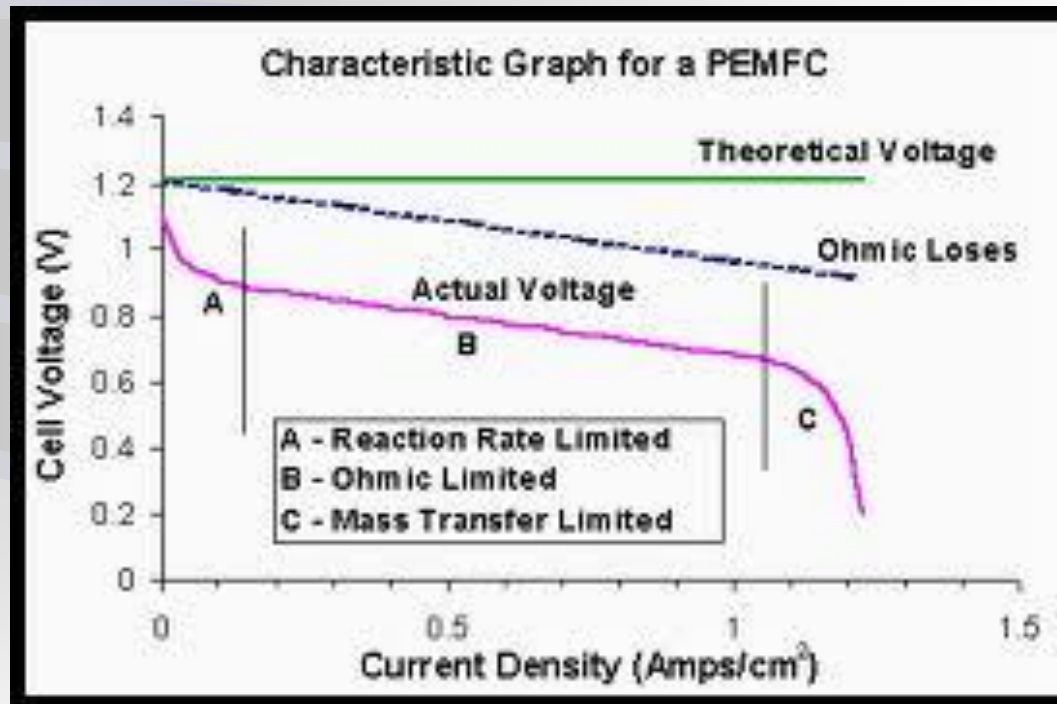


Converts chemical energy → electricity without intermediate heat step.

# 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

## Introduction to Charge Transport

Charge transport completes the circuit in an electrochemical system, moving charges from the electrode where they are produced to the electrode where they are consumed.

Two types of charges species: electrons and ions.

Ion charge transport (ionic conductivity) is more difficult than electron charge transport.

Resistance to charge transport results in a voltage loss for fuel cells. This loss is called ohmic, or IR, loss.

# Fuel Cells

## Movement of charge

The rate at which charge moves through a material is measured in terms of flux,  $J$ .

Flux measures how much of a given quantity flows through a material per unit area per unit time.

# Fuel Cells

## Movement of charge

Charge flux is a measure of the amount of charge that flows through a material per unit area per unit time.

Units for charge flux is  $\text{C}/\text{cm}^2 \cdot \text{s} = \text{A}/\text{cm}^2$

The units for charge transport is the same as for current density.

Charge flux is  $j$  and molar flux is  $J$ .

The quantity  $z_i F$  is required to convert from molar flux,  $J$  to charge flux,  $j$ , where  $z_i$  is the charge number for the carrier (e.g.  $+1$  for  $\text{Na}^+$  and  $-2$  for  $\text{O}^{2-}$ ) and  $F$  is Faraday's constant.

$$j = z_i F J$$

# Fuel Cells

## Movement of charge

A force must act on the charge carriers for charge transport to occur.

In fuel cells there are three major driving forces that give rise to charge transport:

- 1) Electrical driving force (represented by the electrical potential gradient  $dV/dx$ )
- 2) Chemical driving force (represented by a chemical potential gradient  $d\mu/dx$ )
- 3) Mechanical driving force (represented by a pressure gradient  $dP/ds$ )

# Fuel Cells

## Movement of charge

In the electrode, only a voltage gradient drives electron charge transport.

In the electrolyte, both a concentration (chemical potential) gradient and a voltage (electrical potential) gradient drive ion transport.

If electrical transport dominates and drives charge transport, then

$$j = \sigma dV/dx$$

where  $j$  represents the charge flux,  $dV/dx$  is the electrical field driving force, and  $\sigma$  is the conductivity called a coupling coefficient.

# Fuel Cells

## Introduction

$\sigma$  – coupling constant for conductivity

Chemical potential gradient coupling constant is diffusivity

Pressure gradient coupling constant is viscosity

TABLE 4.1. Summary of Transport Processes Relevant to Charge

Transport Process	Driving Force	Coupling C
Conduction	Electrical potential gradient, $\frac{dV}{dx}$	Conductivity
Diffusion	Concentration gradient, $\frac{dc}{dx}$	Diffusivity
Convection	Pressure gradient, $\frac{dp}{dx}$	Viscosity $\mu$

Note: The transport equation for convection in this table is based on Poiseuille constant and  $c$  is the concentration of the transported species. Convection flux is  $vc_i$ , where  $v$  is the transport velocity.

# Fuel Cells

## Charge transport and voltage loss

Charge transport occurs at a cost, a loss in cell voltage.

Fuel cell conductors will have a resistance to charge flow.

$$V = i \left( \frac{L}{A\sigma} \right) = iR$$

where  $L/A\sigma$  is the resistance  $R$  of the conductor, and  $V$  represents the voltage that must be applied to transport charge at a rate given by  $i$ .

This voltage represents a loss (ohmic loss) – it is the voltage expended or sacrificed in order to accomplish charge transport.

# Fuel Cells

## Charge transport and voltage loss

Ohmic loss is represented by  $\eta$ , to distinguish it from overpotential,  $\eta$ , use subscripts.

$$\eta_{\text{ohmic}}$$

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

$$\eta_{\text{ohmic}} = iR_{\text{ohmic}} = i(R_{\text{elec}} + R_{\text{ionic}})$$

Usually  $R_{\text{ionic}}$  is much larger than  $R_{\text{elec}}$  since ionic charge transport is more difficult than electrical charge transport.

# Fuel Cells

## Charge Transport Resistance Characteristics

As fuel cell resistance is decrease, fuel cell performance will improve.

Resistance is geometry dependent.

- Resistance scales with area
- Resistance scales with thickness
- Fuel cell resistances are additive
- Ionic (electrolyte) resistance usually dominates

# Fuel Cells

## Charge Transport Resistance Characteristics

- Resistance scales with area

To normalize for this effect, area-specific resistance are used to compare fuel cells.

Area-normalized resistance, also known as area-specific resistance (ASR) has the units of  $\Omega \text{ cm}^2$ .

By using ASR ohmic losses can be calculated from current density.

$$\eta_{\text{ohmic}} = j (\text{ASR}_{\text{ohmic}})$$

$$\text{ASR}_{\text{ohmic}} = A_{\text{fuel cell}} R_{\text{ohmic}}$$

# Fuel Cells

## Charge Transport Resistance Characteristics

➤ Resistance scales with thickness

Need the shortest path possible for ions between the anode and cathode.

What limits this thickness?

- Mechanical integrity
- Nonuniformities
- Shorting
- Fuel crossover
- Contact resistance
- Dielectric breakdown

# Fuel Cells

## Charge Transport Resistance Characteristics

- Resistance scales with thickness

What limits this thickness?

- Mechanical integrity  
For solid electrolytes, the membrane cannot be so thin that it is easy to break or develops pinholes.
- Nonuniformities  
Thickness cannot vary across the area.
- Shorting  
Extremely thin electrolytes risk shorting if the electrolyte is on the same order of magnitude as the electrode roughness.

# Fuel Cells

## Charge Transport Resistance Characteristics

- Resistance scales with thickness

What limits this thickness?

- Dielectric breakdown  
If the electrolyte is too thin, then the electric field across the membrane can exceed the dielectric breakdown field for the material.

Depending on the electrolyte, the practical thickness limits are about 10-100  $\mu\text{m}$ .

# Fuel Cells

## Charge Transport Resistance Characteristics

➤ Fuel cell resistances are additive

The total ohmic resistance of a fuel cell is a combination of resistances coming from different components of the device.

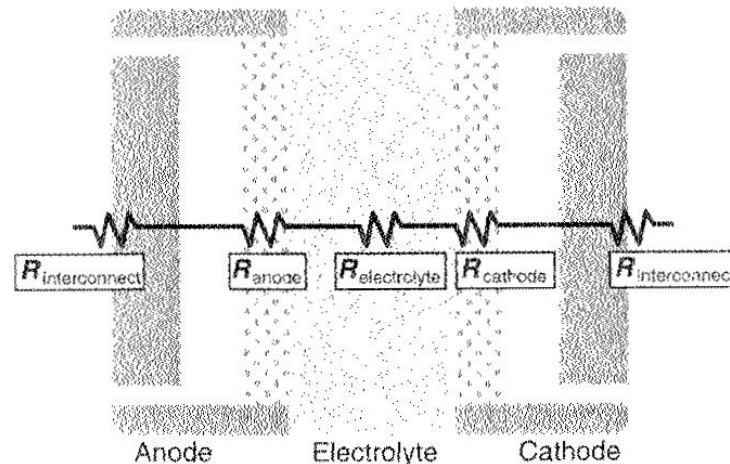
Resistances can come from

- Interconnections
- Anode
- Cathode
- Anode catalyst layer
- Cathode catalyst layer
- Electrolyte

# Fuel Cells

## Charge Transport Resistance Characteristics

- Fuel cell resistances are additive  
The total ohmic resistance of a fuel cell is a combination of resistances coming from different components of the device.



**Figure 4.7.** The total ohmic resistance presented by a fuel cell is actually a combination of resistances, each attributed to different components of the fuel cell. In this diagram, fuel cell resistance is divided into interconnect, anode, electrolyte, and cathode components. Since current flows serially through all components, total fuel cell resistance is given by the series sum of the individual resistance components.

# Fuel Cells

## Charge Transport Resistance Characteristics

- Fuel cell resistances are additive

The total ohmic resistance of a fuel cell is a combination of resistances coming from different components of the device.

Experimentally it is difficult to distinguish between all the different sources of resistance loss.

However typically the electrolyte yields the biggest resistance loss for most fuel cell devices.

# Fuel Cells

## Charge Transport Resistance Characteristics

- Ionic (electrolyte) resistance usually dominates

Best electrolytes in fuel cells have ionic conductivities of  $\sim 0.10 \text{ } \Omega^{-1} \text{ cm}^{-1}$ . Even at a thickness of  $50 \text{ } \mu\text{m}$ , this produces an ASR of  $0.05 \text{ } \Omega \text{ cm}^2$ .

Compare this to a  $50 \text{ } \mu\text{m}$  thick porous carbon cloth electrode which has an ASR of less than  $5 \times 10^{-6} \text{ } \Omega \text{ cm}^2$ .

Decreasing ohmic loss depends on finding high- $\sigma$  ionic conductors – which has proven to be quite challenging.

# Fuel Cells

## Conductivity

Conductivity quantifies the ability of a material to permit the flow of charge when driven by an electric field.

A material's conductivity is influenced by two major factors:

- How many carriers are available to transport charge
- The mobility of those carriers within the material

$$\sigma = \left( |z_i| F \right) c_i \mu_i$$

Where  $c_i$  represents the molar concentration of charge carriers,  $\mu_i$  is the mobility of the charge carriers within the material,  $z_i$  is the charge number for the carrier,  $F$  is faraday's constant

# Fuel Cells

## Electron Conductivity in a metal

Carrier concentration in a metal may be calculated from the density of free electrons.

$$\sigma = \frac{|z_e| F c_e q \tau}{m}$$

Where  $\tau$  is the mean free time between scattering events,  
 $m$  is the mass of the electron ( $m=9.11 \times 10^{-31} \text{kg}$ ),  
 $q$  is the elementary electron charge in coulombs  
( $q=1.602 \times 10^{-19} \text{C}$ )

# Fuel Cells

## Electron Conductivity in a metal

Carrier concentration in a metal may be calculated from the density of free electrons.

$$\sigma = \frac{|z_e| F c_e q \tau}{m}$$

Inserting typical numbers into the equation,  $z_e = 1$ ,  
 $\tau = 10^{-12}$ - $10^{-14}$  s in pure metals,  $c_e = 10^4$  mol/m<sup>3</sup>.

Gives  $\sigma$  in the range of  $10^6$ - $10^8$   $\Omega^{-1}\text{cm}^{-1}$

# Fuel Cells

## Ion conductivity in a crystalline solid electrolyte

The overall mobility of ions in the solid electrolyte is given by

$$\sigma = \frac{c(z_i F)^2 D}{RT}$$

Where  $D$  is material's diffusivity.

Carrier concentration in a crystalline electrolyte is controlled by the density of the mobile defect species. Most crystalline electrolytes conduct via a vacancy mechanism. Vacancies are introduced into the lattice by doping. Maximum effective vacancy doping levels are around 8-10% giving carrier concentration of  $10^2$ - $10^3$  mol/m<sup>3</sup>.

# Fuel Cells

## Ion conductivity in a crystalline solid electrolyte

The overall mobility of ions in the solid electrolyte is given by

$$\sigma = \frac{c(z_i F)^2 D}{RT}$$

Typical ion diffusivities are  $10^{-8} \text{ m}^2/\text{s}$  to  $10^{-11} \text{ m}^2/\text{s}$  and ion carrier concentrations are  $10^2$  to  $10^4 \text{ mol/m}^3$ .

Inserting these values into the equation yields ionic conductivity values of  $10^{-6}$  to  $10^0 \text{ } \Omega^{-1} \text{ cm}^{-1}$

# Fuel Cells

## Conductivity

So solid-electrolyte ionic conductivities are well below electronic conductivity values for metals, making much of the focus of fuel cell research placed on looking for better electrolytes.

# Fuel Cells

## Fuel Cell Electrolytes

All fuel cell electrolytes have several requirements:

- High ionic conductivity
- Low electronic conductivity
- High stability
- Low fuel crossover
- Reasonable mechanical strength
- Ease of manufacturability

High conductivity and electrolyte stability requirements are the most difficult to meet.

It is difficult to find an electrolyte that is stable in both a highly reducing and highly oxidizing environment at the anode and cathode.

# Fuel Cells

## Ionic Conduction in aqueous electrolytes/ionic liquids

Aqueous electrolyte – water-based solution containing dissolved ions that can transport charge. (i.e. NaCl in water)

Ionic liquid – material which is liquid and ionic. (i.e. molten NaCl, pure  $\text{H}_3\text{PO}_4$  at  $50^\circ\text{C}$ )

These electrolytes need a matrix, the matrix:

- Provides mechanical strength to the electrolyte
- Minimizes the distance between the electrodes while preventing shorts
- Prevents crossover of reactant gases through the electrolyte

# Fuel Cells

## Ionic Conduction in aqueous electrolytes/ionic liquids

Recall that

$$\sigma = \left( |z_i| F \right) c_i \mu_i$$

The ion mobilities are dependent on ion size, charge and liquid viscosity.

When ionic conductivity is calculated the value is always much higher than the actual value in a fuel cell.

This is because the mobility calculation are only accurate in dilute solutions.

In fuel cells the ions have high concentrations and there are strong electrical interactions between the ions.

Example: pure  $\text{H}_3\text{PO}_4$  conductivity:

calculated =  $18 \Omega^{-1} \text{ cm}^{-1}$

Experimental =  $0.1\text{-}1.0 \Omega^{-1} \text{ cm}^{-1}$

# Fuel Cells

## Ionic Conduction in aqueous electrolytes/ionic liquids

TABLE 4.2. Selected Ionic Mobilities at Infinite Dilution in Aqueous Solutions at 25°C

Cation	Mobility, $u$ (cm <sup>2</sup> /V · s)	Anion	Mobility, $u$ (cm <sup>2</sup> /V · s)
H <sup>+</sup> (H <sub>3</sub> O <sup>+</sup> )	$3.63 \times 10^{-3}$	OH <sup>-</sup>	$2.05 \times 10^{-3}$
K <sup>+</sup>	$7.62 \times 10^{-4}$	Br <sup>-</sup>	$8.13 \times 10^{-4}$
Ag <sup>+</sup>	$6.40 \times 10^{-4}$	Br <sup>-</sup>	$7.96 \times 10^{-4}$
Na <sup>+</sup>	$5.19 \times 10^{-4}$	I <sup>-</sup>	$7.91 \times 10^{-4}$
Li <sup>+</sup>	$4.01 \times 10^{-4}$	HCO <sub>3</sub> <sup>-</sup>	$4.61 \times 10^{-4}$

Source: From Ref. [7].

# Fuel Cells

## Ionic Conduction in polymer electrolytes

In general ionic transport in polymer electrolytes follows an exponential relationship:

$$\sigma T = A_{PEM} e^{-E_a / kT}$$

Where  $A_{PEM}$  is a preexponential factor,  $E_a$  represents the activation energy (eV/atom) ( $E_a = \Delta G_{act}/F$ )

Conductivity increases exponentially with increasing temperature.

For a polymer to be a good conductor:

- It must have fixed charge sites
- It must have free volume (open space)

# Fuel Cells

## Ionic Conduction in polymer electrolytes

For a polymer to be a good conductor:

- It must have fixed charge sites
- It must have free volume (open space)

The fixed charge sites are of opposite charge to the moving ions to ensure net charge balance.

Free volume improves the ability of ions to move through the polymer.

Polymer membranes tend to have relatively high ionic conductivities compared to solid state materials.

# Fuel Cells

## Ionic Conduction in polymer electrolytes

Polymer membranes tend to have relatively high ionic conductivities compared to solid state materials.

Nafion is the most popular electrolyte in PEM fuel cells.

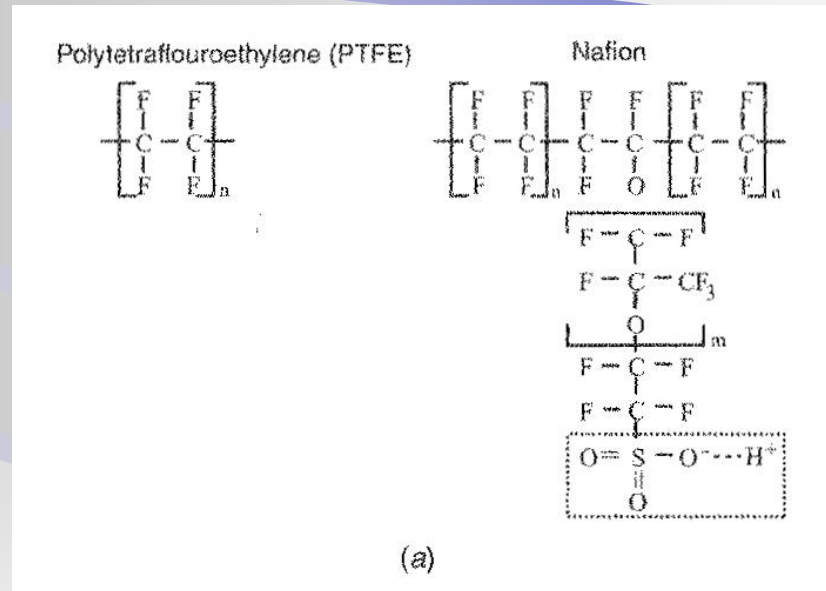
Nafion – persulfonated polytetrafluoroethylene (PTFE)

Has extremely high conductivity due to “vehicle” mechanism (hitches a ride with other ions through the polymer , i.e. water).

# Fuel Cells

## Ionic transport in Nafion

Nafion has a backbone structure similar to Teflon, but Nafion includes sulfonic acid ( $\text{SO}_3\text{H}^+$ ) as a functional group.



The Teflon backbone provides mechanical strength while the sulfonic acid chains provide charge sites for proton transport.

# Fuel Cells

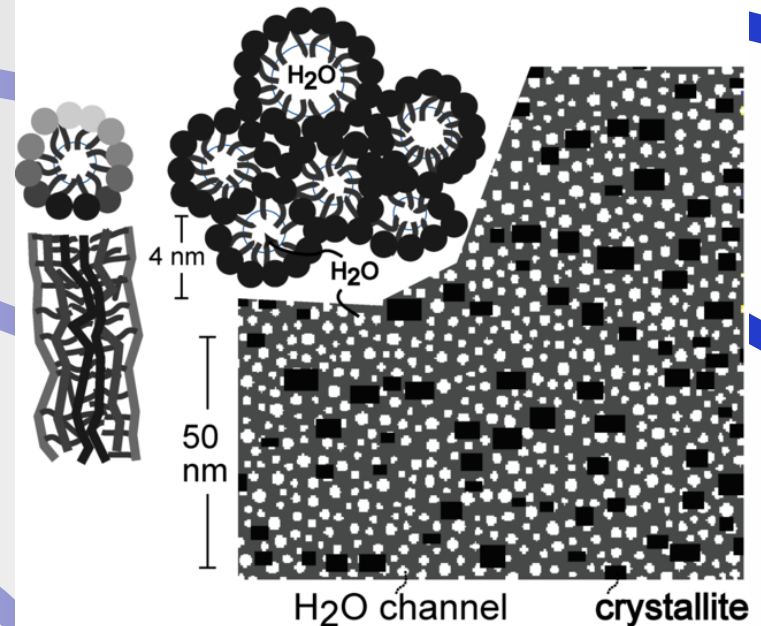
## Ionic transport in Nafion

Recent studies using XRD and NMR suggest that Nafion free volumes aggregate into interconnected pores ( $\sim 2.5$  nm in diameter) which are filled with water and allow small ions (hydronium ions) to transport.

The hydrophobic nature of the backbone accelerates water transport through the membrane.

To achieve high conductivities the Nafion must be fully hydrated with liquid water, by humidifying the fuel and oxidant gases.

**Water Channel Model**



# Fuel Cells

## Ionic Conduction in ceramic electrolytes

SOFC electrolytes are solid, crystalline oxide materials that can conduct ions.

Most popular SOFC materials is yttria stabilized zirconia (YSZ), which contains 8% yttria ( $\text{Y}_2\text{O}_3$ ) mixed with zirconia ( $\text{ZrO}_2$ ).

The yttria stabilizes the zirconium in the cubic phase, which is the most conductive and yttria introduces high concentrations of oxygen vacancies (ionic charge carriers) into the crystal structure.

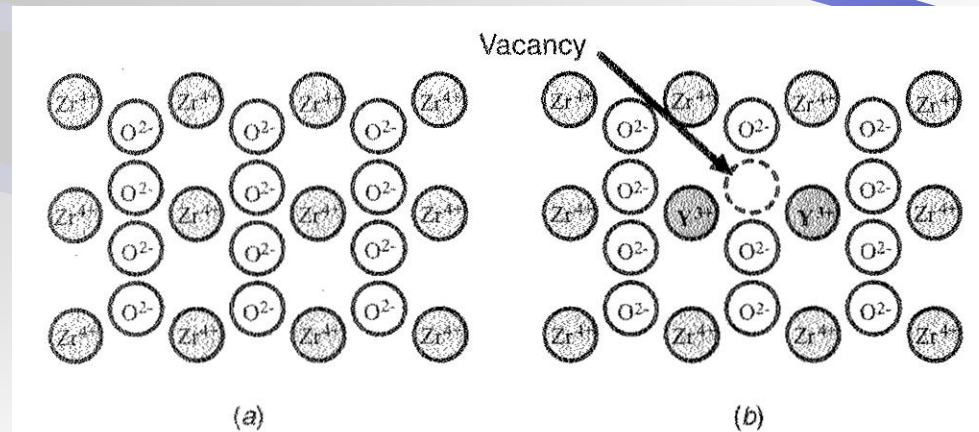


Figure 4.16. View of the (110) plane in (a) pure  $\text{ZrO}_2$ , and (b) YSZ. Charge compensation effects in YSZ lead to creation of oxygen vacancies. One oxygen vacancy is created for every two yttria atoms doped into the lattice.

# Fuel Cells

## Ionic Conduction in ceramic electrolytes

Conductivity expression which combines carrier concentration and carrier mobility is:

$$\sigma = \frac{c(zF)^2 D}{RT}$$

Where  $D$  is carrier mobility, the diffusivity of the carrier in the crystal lattice.  $D$  is the ability of a carrier to move or diffuse from site to site in a crystal lattice.  $D$  is related exponentially to temperature,  $D_0$  is a constant ( $\text{cm}^2/\text{s}$ ).

$$\sigma = \frac{c(zF)^2 D_0 e^{-\Delta G_{act} / RT}}{RT}$$

# Fuel Cells

## **Mixed ionic-electronic conductors**

Materials that can conduct both ions and electrons.

Many doped metal oxides ceramic materials are mixed conductors. This is because doping can introduce both ionic defects (like oxygen vacancies) and electronic defects (like free electrons or holes).

While mixed conductors are unsuitable for fuel cell electrolytes (essentially would short the fuel cell), they are attractive for SOFC electrode structures (can increase electrochemical reactivity).

Since the mixed conductors provide both ionic species and electrons only gas is needed to have a triple phase zone (TPBs – gas, electrode, electrolyte).

# Fuel Cells

## Mixed ionic-electronic conductors

Since the mixed conductors provide both ionic species and electrons only gas is needed to have a triple phase zone (TPBs – gas, electrode, electrolyte).

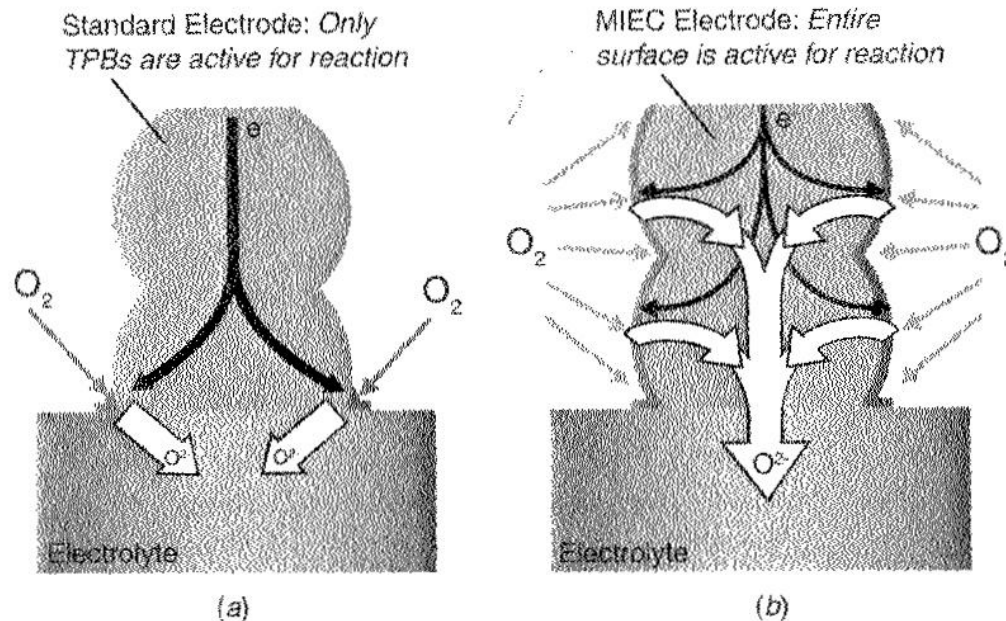


Figure 4.19. A standard SOFC cathode electrode (a) versus a mixed ionic-electronic conducting (MIEC) SOFC cathode electrode (b).

# Fuel Cells

## Summary

- Charge transport in fuel cells is predominately driven by a voltage gradient – conduction.
- The voltage to drive conductive charge transport represents a loss to fuel cell performance, known as ohmic overvoltage.
- Fuel cell ohmic resistance includes
  - Resistance from the electrodes
  - Resistance from the electrolyte
  - Resistance from the interconnects
- Fuel cell ohmic resistance is usually dominated by resistance from the electrolyte

# Fuel Cells

## Summary

- Resistance scales with
  - Conductor area,  $A$
  - Thickness,  $L$
  - Conductivity,  $\sigma$
- Area-specific fuel cell resistivities (ASRs) are used to make comparisons between different size fuel cells ( $ASR = A \times R$ )
- Since resistance scales with thickness, fuel cell electrolytes are made as thin as possible.
- Because resistance scales with conductivity, high-conductivity electrodes and electrolyte materials are needed in fuel cells.
- Conductivity is determined by carrier concentration and carrier mobility

$$\sigma = \left( |z_i| F \right) c_i \mu_i$$

# Fuel Cells

## Summary

- Metals and ion conductors have different structures and conduction mechanisms, giving different conductivities.
- Ion conductivity is 4-8 orders of magnitude lower than electron conductivity in metals.
- Electrolytes must have
  - High ionic conductivity
  - Mechanical stability
  - Stability in highly oxidizing and reducing environments
- Major electrolyte materials in fuel cells are
  - Liquid
  - Polymer
  - Ceramic

# Fuel Cells

## Summary

- Mobility in aqueous electrolytes is determined by the balance between ion acceleration under an electric field and frictional drag due to fluid viscosity. (smaller the ion and higher its charge the greater its mobility)
- Conductivity in Nafion is dominated by water content (high water content leads to high conductivity)
- Conductivity in ceramic electrolytes is controlled by defects in the crystal lattice. Defects are introduced by doping.
- Mixed ionic and electronic conductors conduct both electrons and ions.
- Mixed ionic conductors are useful for SOFC electrodes, since they provide two phase of a triple phase boundary.

# Class Assignment

- Research Paper – Due 12/02/25

