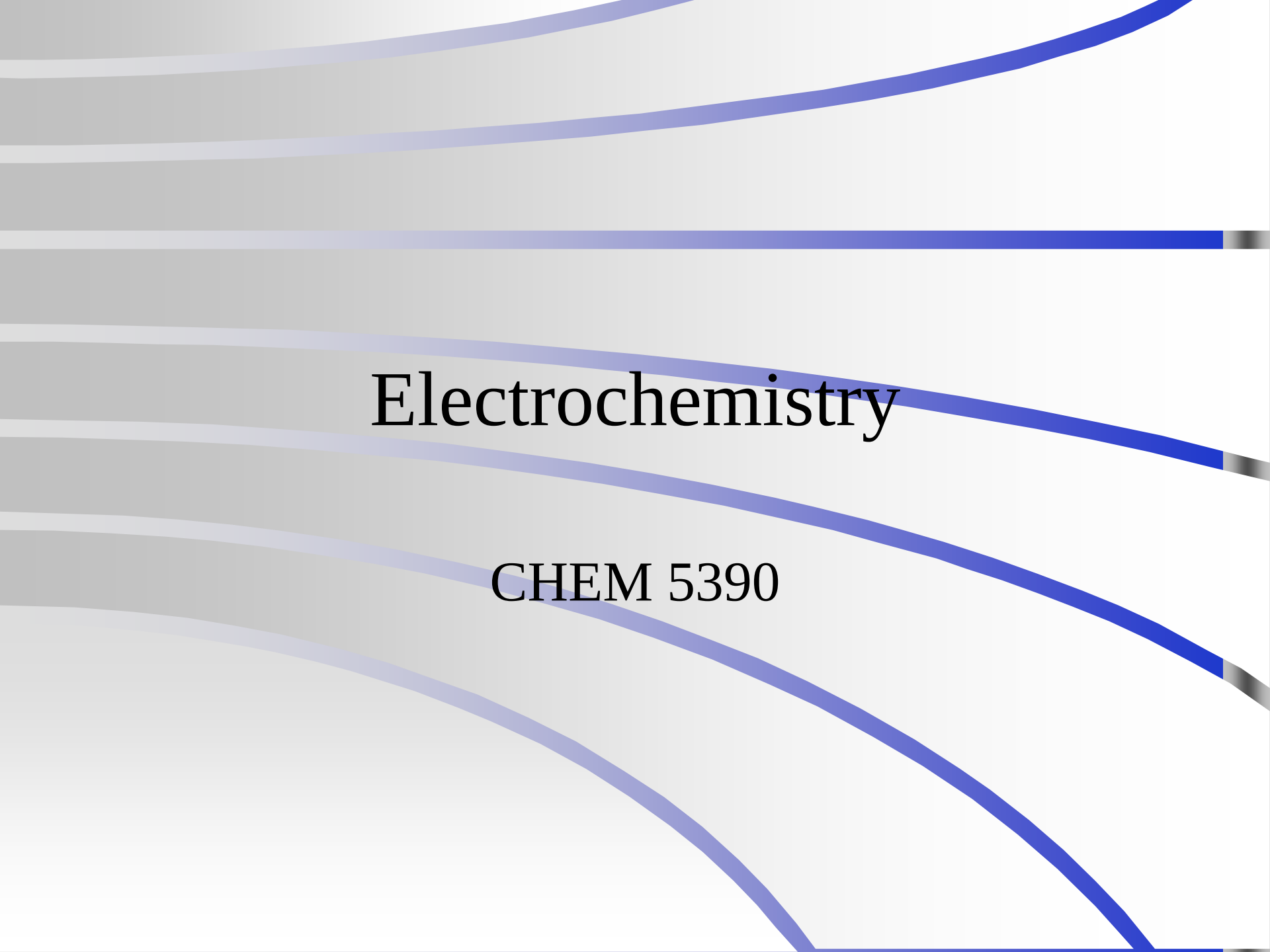




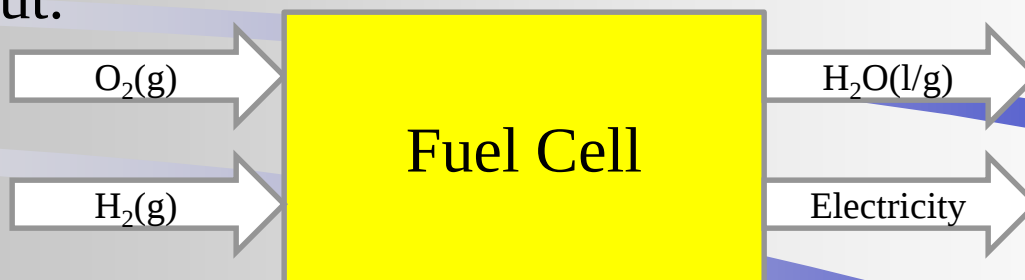
Electrochemistry

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

Fuel Cell kinetics

Kinetics of electrochemical reactions – the mechanism by which electron transfer occurs.

The current produced by a fuel cell (# of electrons per time) depends on the rate of the electrochemical reaction.

To increasing the rate and improve performance need

- Excellent catalyst

- Efficient electrode design

Fuel Cells

Fuel Cell kinetics

The current produced by a fuel cell (# of electrons per time) depends on the rate of the electrochemical reaction.

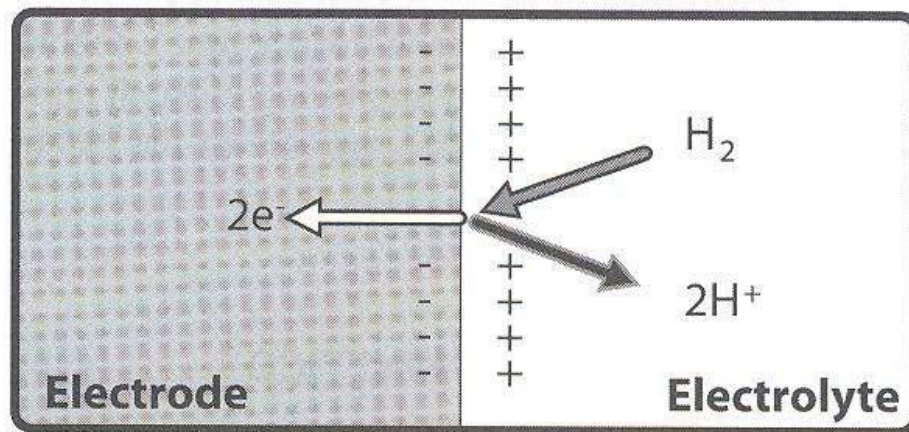
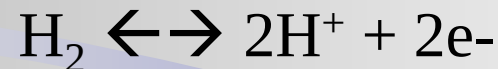
- Electrochemical reactions are heterogeneous
- Current is a rate
- Charge is an amount
- Current density is more fundamental than current
- Potential controls electron energy
- Reaction rates are finite

Fuel Cells

- Electrochemical reactions are heterogeneous

Electrochemical reactions can only take place at the interface between an electrode and electrolyte.

i.e. HOR:



Fuel Cells

➤ Current is a rate

The current in an electrochemical reaction is a direct measure of the rate of the reaction. (Faraday's Law)

$$i = \frac{dQ}{dt} = nFv = nF \frac{dN}{dt}$$

where Q – charge (C), t – time (s), n - # of e-'s transferred, F – Faraday's constant (96,400 C/mol), v – rate of the reaction (mol/s)

Fuel Cells

- Charge is an amount

Integrating Faraday's law,

$$\int_0^i i dt = Q = nFN$$

The total amount of electricity produced is proportional to the number of moles of material processed in the electrochemical reaction.

Fuel Cells

- Current density is more fundamental than current

Since electrochemical reactions occur at interfaces, the current produced is proportional to the area of the interface. To compare different surfaces use current density, j (A/cm²).

$$j = \frac{i}{A}$$

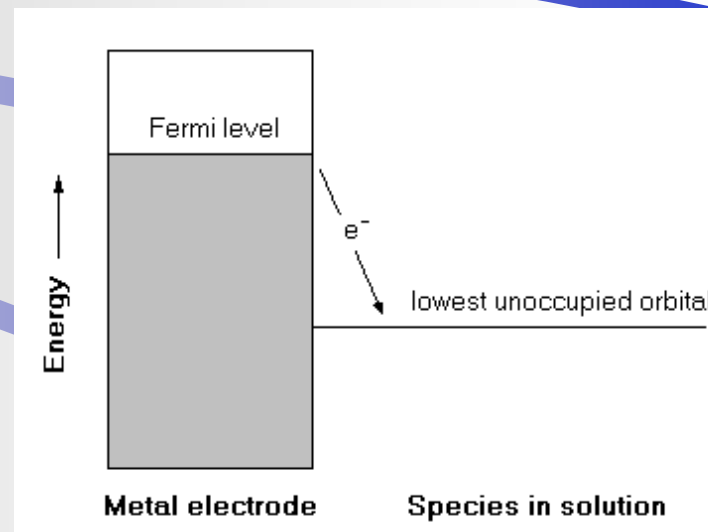
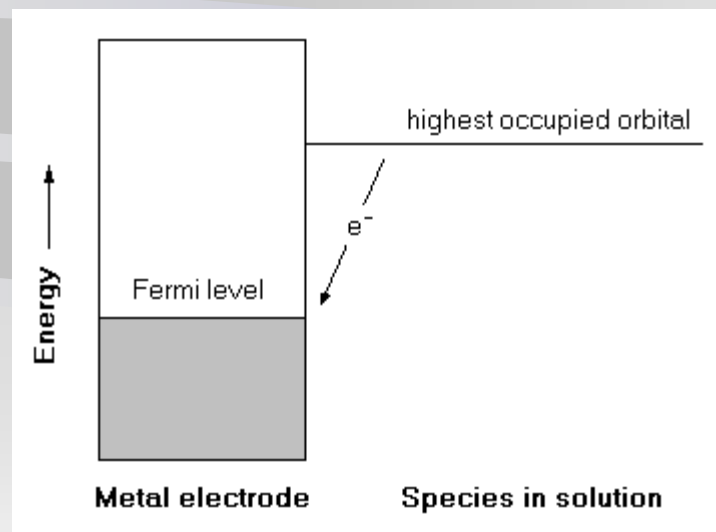
$$v = \frac{i}{nFA} = \frac{j}{nF}$$

v (sometimes represented as J) (rate of electrochemical reaction per unit area) – mol s⁻¹ cm⁻²

Fuel Cells

➤ Potential controls electron energy

Potential (voltage) is a measure of electron energy. The electron energy in a metal is measured by the Fermi level. By controlling the electrode potential, control the direction of a reaction.

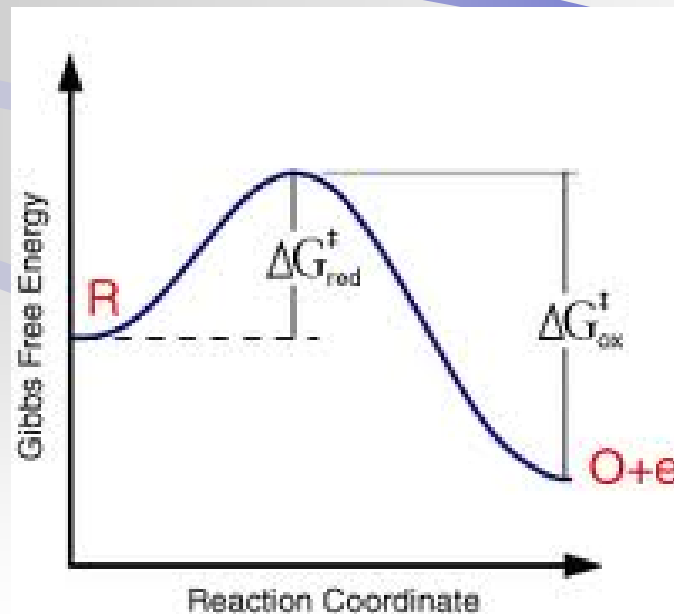


If the electrode potential is made more positive than the equilibrium potential, the reaction will be biased toward the formation of Ox.

Fuel Cells

➤ Reaction rates are finite

The current produced by an electrochemical reaction is limited. Reaction rates are finite because an activation barrier impedes the conversion of reactants into products.

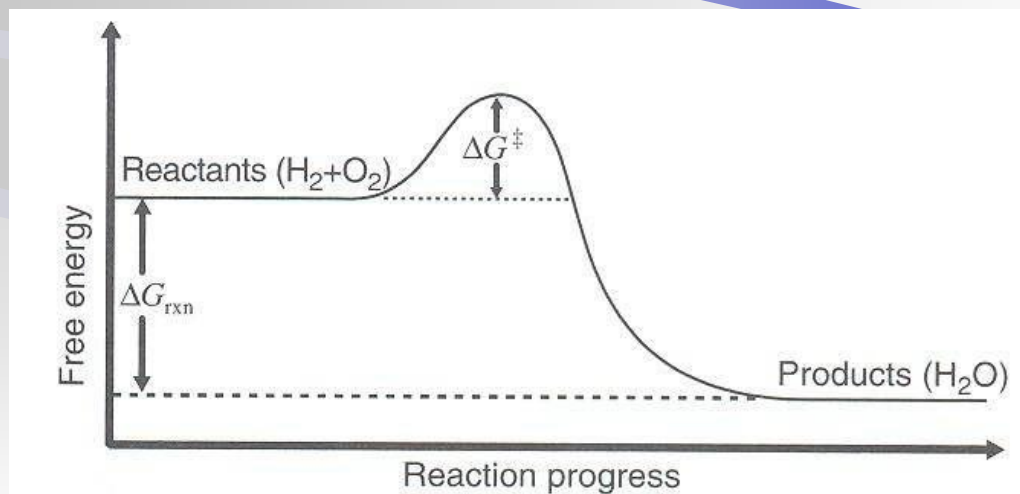


Fuel Cells

➤ Activation Energy

In order for reactants to be converted into products, they must first make it over the activation energy.

The probability that reactant species can make over this barrier determines the rate at which the reaction occurs.



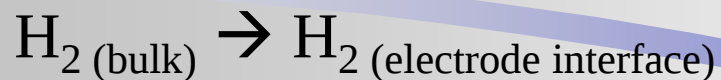
Fuel Cells

Why do charge transfer reactions have an activation energy?

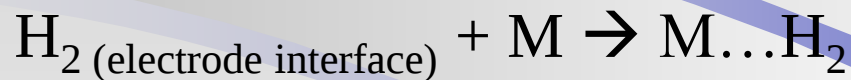
Consider: $\text{H}_2 \leftrightarrow 2\text{H}^+ + 2\text{e}^-$

Overall reaction occurs in a series of steps:

1) Mass transport of H_2 to the electrode



2) Adsorption of H_2 onto the electrode surface



Fuel Cells

Why do charge transfer reactions have an activation energy?

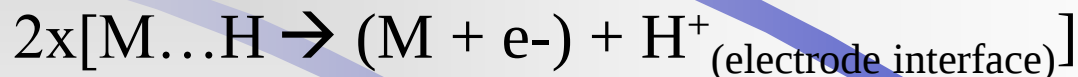
Consider: $\text{H}_2 \leftrightarrow 2\text{H}^+ + 2\text{e}^-$

Overall reaction occurs in a series of steps:

3) Separation of H_2 into chemisorbed hydrogen atoms



4) Transfer of electrons from the chemisorbed species to the electrode



Fuel Cells

Why do charge transfer reactions have an activation energy?

Consider: $\text{H}_2 \leftrightarrow 2\text{H}^+ + 2\text{e}^-$

Overall reaction occurs in a series of steps:

5) Mass transport of ions away from electrode



The overall reaction rate will be limited by the slowest step in the series.

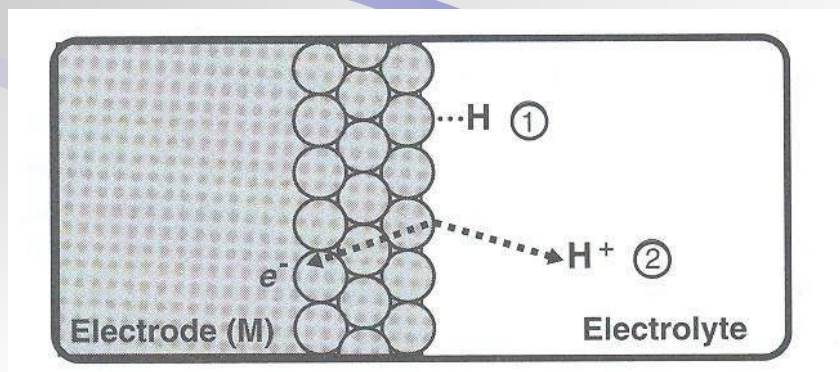
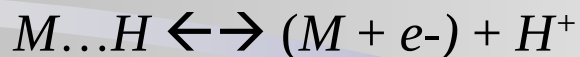
Fuel Cells

Why do charge transfer reactions have an activation energy?

Consider: $\text{H}_2 \leftrightarrow 2\text{H}^+ + 2\text{e}^-$

Suppose that the overall reaction is limited by the electron transfer step between chemisorbed hydrogen and the metal electrode surface.

The slowest step can be represented as:

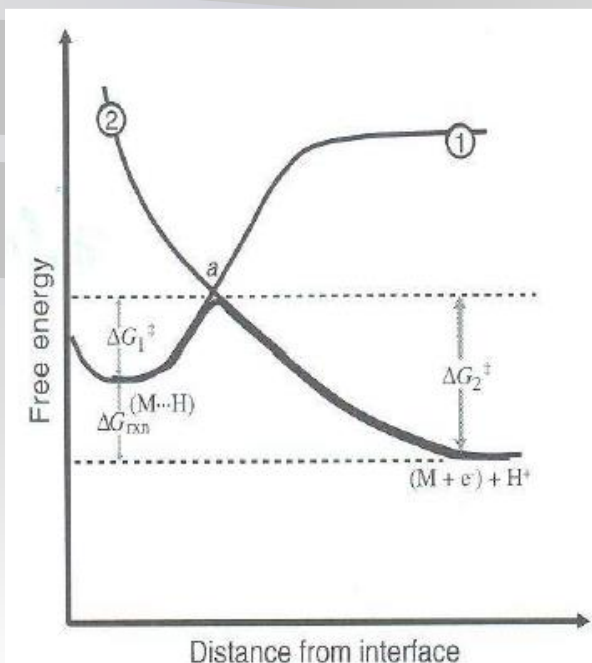
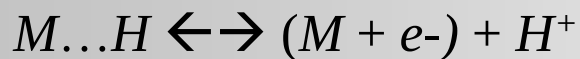


Fuel Cells

Why do charge transfer reactions have an activation energy?

Consider: $\text{H}_2 \leftrightarrow 2\text{H}^+ + 2\text{e}^-$

The slowest step can be represented as:



Curve 1: free energy of the reactant state as a function of the distance separation between the H atom and the metal surface

Curve 2: free energy of the product state as a function of the distance the H^+ ion and the metal surface

Dark line = the minimum energy path for the conversion of $[\text{M}\cdots\text{H}]$ to $[(\text{M} + \text{e}^-) + \text{H}^+]$

a = the activated state

Fuel Cells

$\Delta G^\ddagger$ – standard free energy of activation

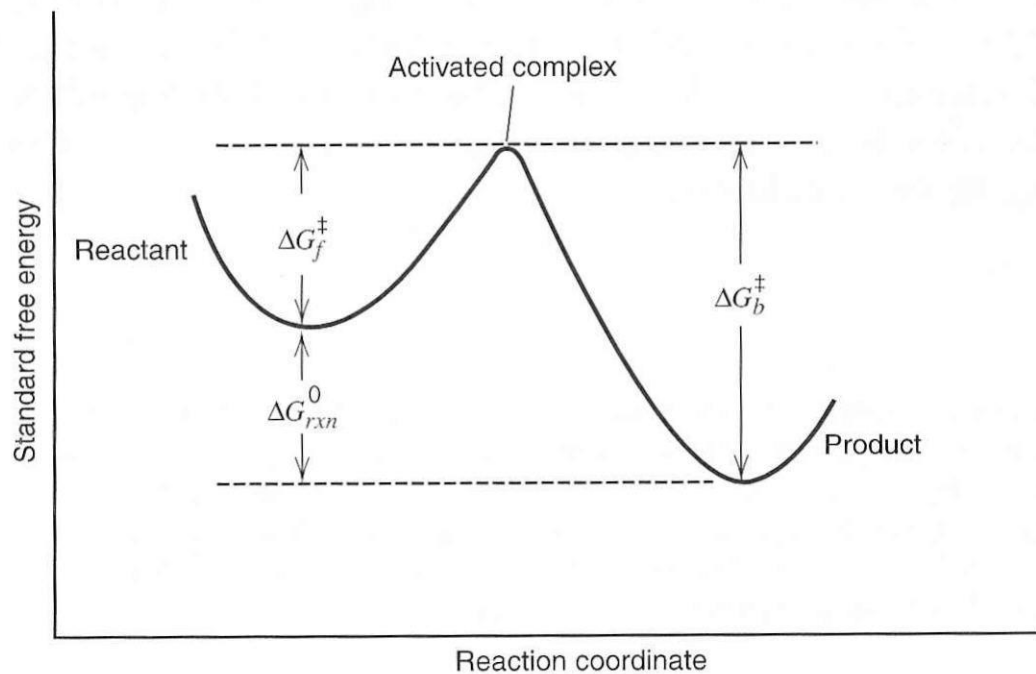


Figure 3.1.2 Free energy changes during a reaction. The activated complex (or transition state) is the configuration of maximum free energy.

Fuel Cells

Activation energy determines reaction rate

Rate of reaction depends on the probability that a reactant species will be in the activated state (conformational changes).

The probability of finding a species in the activated state is exponentially dependent on the size of the activation barrier.

$$P_{act} = e^{-\Delta G_1 / RT}$$

Where P_{act} – probability of finding reactant species in activated state,
 ΔG_1 – size of the energy barrier for reactants, R – gas constant,
 T – temperature.

Fuel Cells

Activation energy determines reaction rate

The reaction rate can then be described as

$$v_1 \text{ or } J_1 = c_R^* \frac{kT}{h} e^{-\Delta G_1 / (RT)}$$

where J_1 – is the reaction rate in the forward direction, c_R^* – the reactant surface concentration (mol/cm²), k – Boltzmann constant, h – Planck's constant.

$$f = kT/h$$

f – decay rate to reactants or products, depending on the direction of the reaction

Fuel Cells

Calculating net rate of a reaction

For the overall rate of reaction – consider the rates for both the forward and reverse directions.

The net rate is given by the difference in rates between the forward and reverse reactions. Net reaction rate is $J = J_1 - J_2$ $\Delta G_{\text{rxn}} = \Delta G_1 - \Delta G_2$

Example chemisorbed hydrogen reaction:

Forward reaction: $\text{M}\dots\text{H} \rightarrow (\text{M} + \text{e}^-) + \text{H}^+$

Reverse reaction $(\text{M} + \text{e}^-) + \text{H}^+ \rightarrow \text{M}\dots\text{H}$

The rates for the forward and reverse reactions are not equal.

$(\Delta G_1 < \Delta G_2)$

$$J = c_R^* f_1 e^{-\Delta G_1 / (RT)} - c_P^* f_2 e^{-\Delta G_2 / (RT)}$$

where J – net reaction rate, c_R^* – reactant surface concentration, c_P^* – product surface concentration, ΔG_1 – activation barrier for forward reaction, ΔG_2 – activation barrier for reverse reaction.

Fuel Cells

Rate of reaction at equilibrium

Exchange Current Density

Since fuel cells produce current from an electrochemical reaction, need reaction rate in terms of current density.

Current density and reaction rate are related $j = nFJ$

At thermodynamic equilibrium, the forward and reverse current densities must balance so there is no net current density.

$$j_1 = nFc_R^* f_1 e^{-\Delta G_1/(RT)}$$

$$j_2 = nFc_P^* f_2 e^{-\Delta G_2/(RT)}$$

$$\text{so, } j_1 = j_2 = j_0$$

j_0 – the exchange current density of the reaction. (Although at equilibrium the net reaction is zero, both forward and reverse reactions are taking place at a rate which is characterized by j_0).

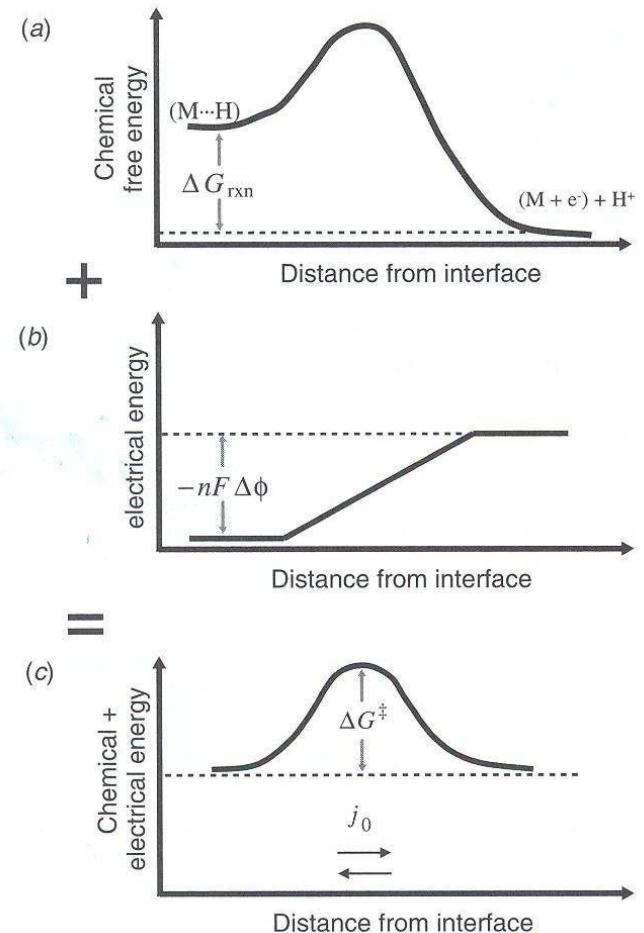
Fuel Cells

Rate of reaction at equilibrium

Potential

Before the build-up of the interfacial potential ($>\Phi$), the forward rate was much faster than the reverse rate.

The build-up of an interfacial potential equalizes the situation by increasing the forward activation barrier from ΔG_1 to ΔG while decreasing the reverse reaction barrier from ΔG_2 to ΔG .



Fuel Cells

Potential and Rate

Butler-Volmer Equation

For electrochemical reactions, **can manipulate the size of the activation barrier by varying the cell potential.**

If the potential across a reaction interface is reduced, the free energy of the forward reaction will be favored over the reverse reaction.

While the chemical energy system is the same as before, changing the electrical potential upsets the balance between the forward and reverse activation barriers.

Reducing the potential by η reduces the forward activation barrier ($\Delta G_1 < \Delta G$) and increases the reverse activation barrier ($\Delta G_2 > \Delta G$).

Fuel Cells

Potential and Rate

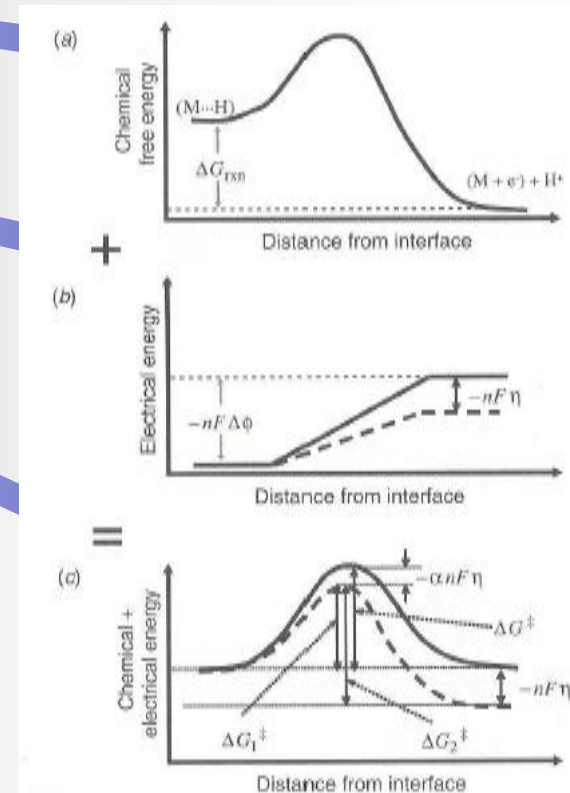
For electrochemical reactions, **can manipulate the size of the activation barrier by varying the cell potential.**

The forward energy changes by $\alpha nF\eta$
and the reverse by $(1 - \alpha)nF\eta$

α – known as the transfer coefficient

α (can be 0 to unity) depends on the symmetry

α of the activation barrier.



Fuel Cells

Potential and Rate

α is potential-dependent, but usually experiments are in the range where it is constant.

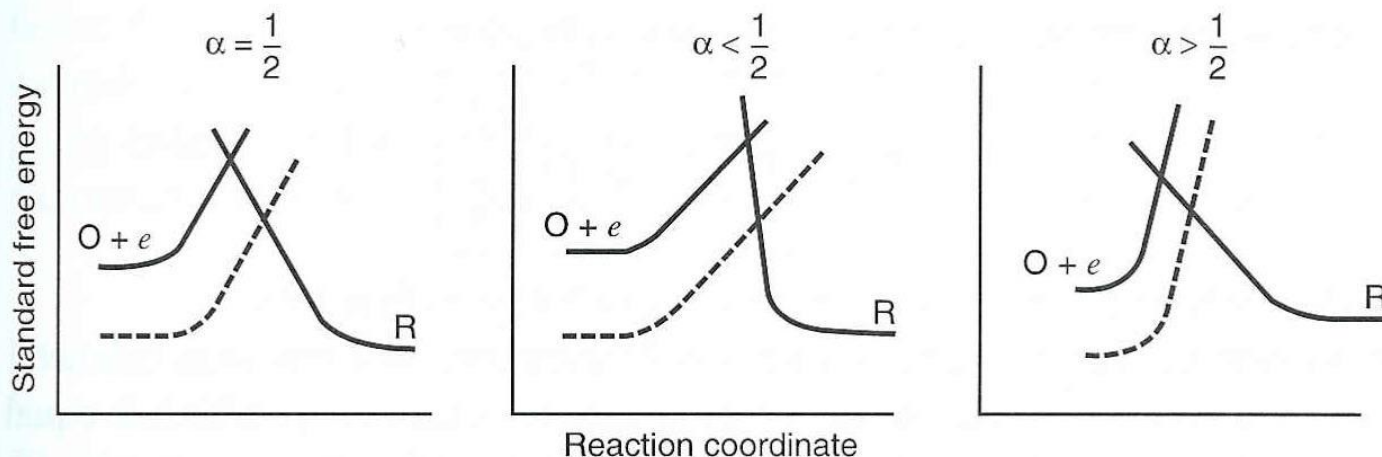


Figure 3.3.4 The transfer coefficient as an indicator of the symmetry of the barrier to reaction. The dashed lines show the shift in the curve for $O + e$ as the potential is made more positive.

Fuel Cells

Potential and Rate

At equilibrium, the current densities for the forward and reverse reactions are given by j_0 .

$$j_1 = j_0 e^{(\alpha n F \eta / RT)}$$

$$j_2 = j_0 e^{-(1-\alpha) n F \eta / RT}$$

Net current ($j_1 - j_2$) is :

$$j = j_0 (e^{(\alpha n F \eta / RT)} - e^{-(1-\alpha) n F \eta / RT}) \quad (\text{Butler-Volmer equation})$$

The current-potential equation is then:

$$i = F A k^0 [C_O(0,t) e^{-\alpha f (E - E^0)} - C_R(0,t) e^{(1-\alpha) f (E - E^0)}]$$

$$k_f = k^0 \exp[-\alpha f (E - E^0)] \quad k_b = k^0 \exp [(1-\alpha) f (E - E^0)]$$

where $f = F/RT$

Fuel Cells

Potential and Rate

Exchange current

i_0 is easier to work with than k^0 since it can be used with potential.

$$i = i_0 \left[\frac{C_O(0, t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0, t)}{C_R^*} e^{(1-\alpha) f \eta} \right] \quad (3.4.10)$$

$$\eta = E - E_{eq}$$

η – overpotential

Fuel Cells

Potential and Rate

Butler–Volmer equation basically states that the current produced by an electrochemical reaction increases exponentially with activation overvoltage, η .

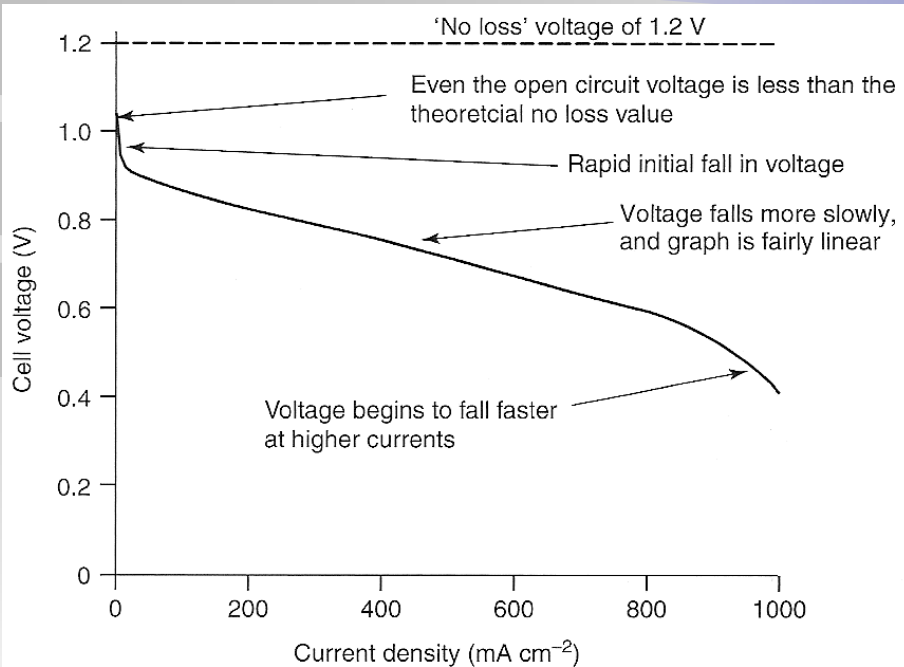
η – represents the voltage which is sacrificed (lost) to overcome the activation barrier associated with the electrochemical reaction.

Butler-Volmer eq: If you want more current from a fuel cell, must pay the price of lost voltage.

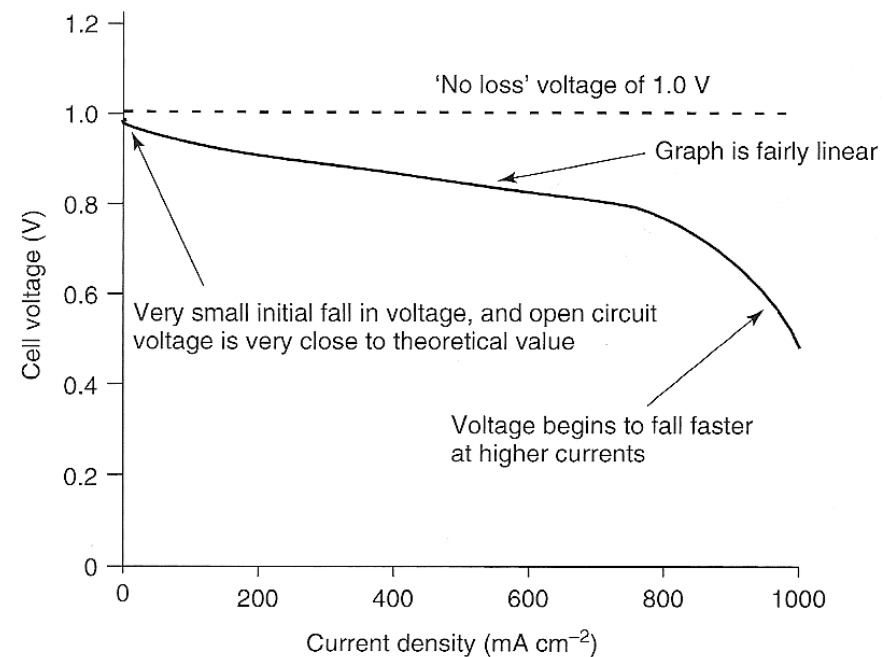
Fuel Cells

Potential and Rate

If you want more current from a fuel cell, must pay the price of lost voltage.



Graph showing the voltage for a typical low temperature, air pressure, fuel cell.



Graph showing the voltage of a typical air pressure fuel cell operating at about 800°C.

Fuel Cells

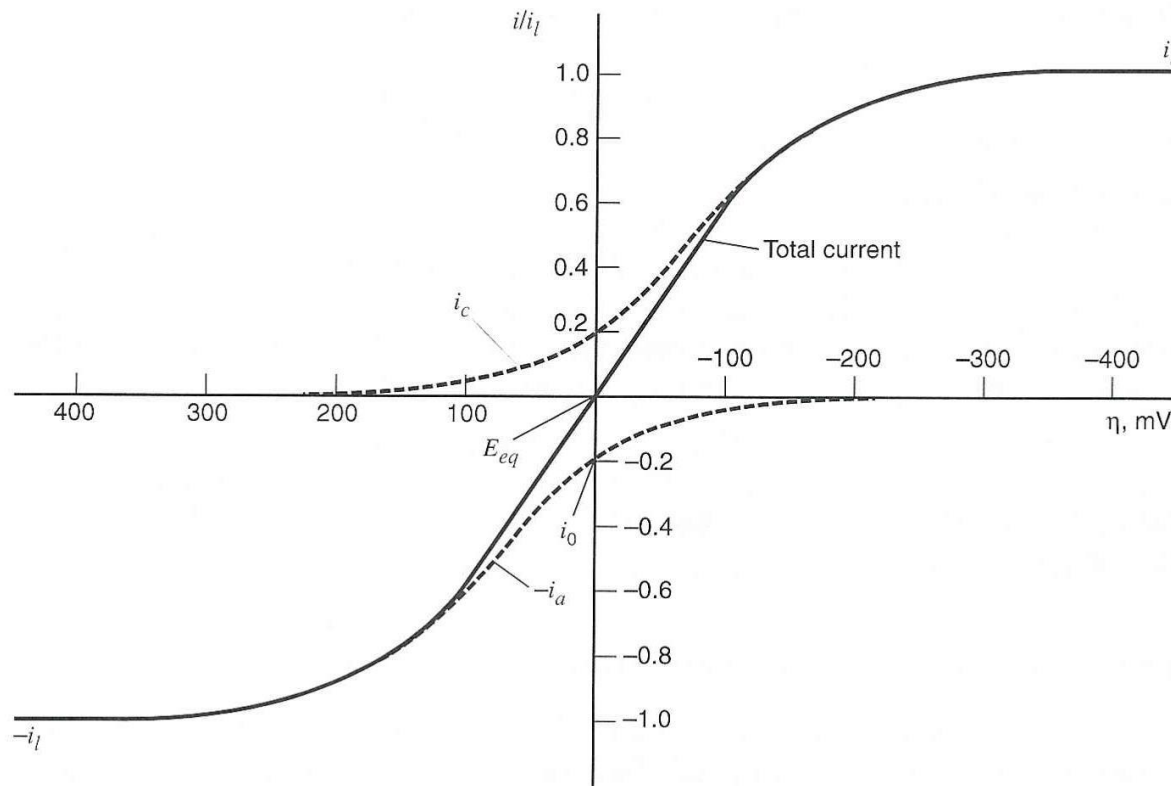


Figure 3.4.1 Current-overpotential curves for the system $O + e \rightleftharpoons R$ with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$ and $i_0/i_l = 0.2$. The dashed lines show the component currents i_c and i_a .

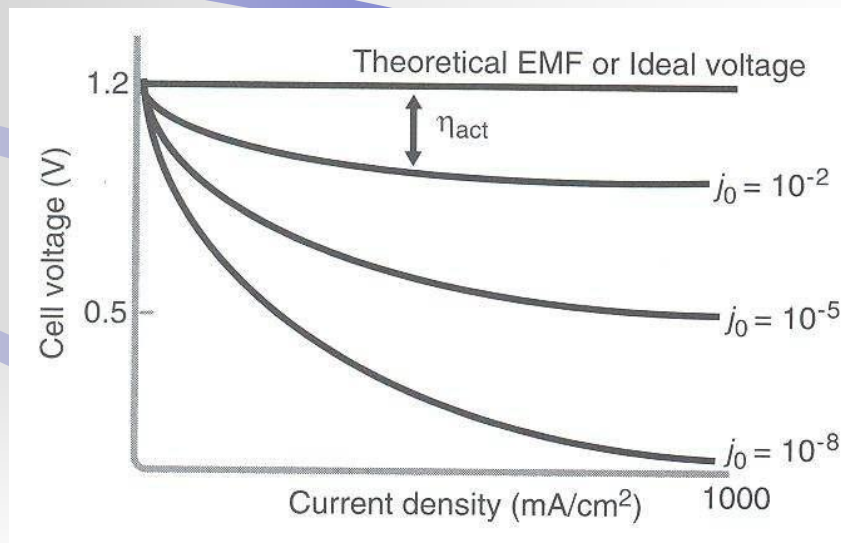
Fuel Cells

Exchange currents and electrocatalysis

To improve kinetic performance need to increase j_0 (rate of exchange). j_0 must be high to get a good fuel cell.

How do we increase j_0 ?

$$j_0 = nFc_R^* f_1 e^{-\Delta G_1/(RT)}$$



Fuel Cells

Exchange currents and electrocatalysis

$$j_0 = nFc_R^* f_1 e^{-\Delta G_1/(RT)}$$

From the Butler-Volmer equation, it is clear cannot change n , F , or R .

So that leaves:

- 1) Increase the reactant concentration, c_R^*
- 2) Decrease the activation barrier, ΔG
- 3) Increase the temperature, T
- 4) Increase the number of possible reaction sites

Fuel Cells

Exchange currents and electrocatalysis

1) Increase the reactant concentration, c_R^*

By operating fuel cells at higher pressure, can increase the concentrations of the reactant gases.

In practice difficult to overcome mass transport limitations.

Fuel Cells

Exchange currents and electrocatalysis

1) Increase the reactant concentration, c_R^*

The thermodynamic benefit is minor, due to the logarithmic form of the Nernst Equation.

In contrast, the kinetic benefit is significant, with a linear impact.

Kinetic reactant concentration effects generally work against us for several reasons:

- most fuel cells use air instead of pure oxygen at the cathode
- reactant concentrations tend to decrease at fuel cell electrodes during high-current-density operation (mass transport) : further kinetic penalties

Fuel Cells

Exchange currents and electrocatalysis

2) Decrease the activation barrier, ΔG

Catalyst significantly lower the activation barrier for the reaction. This is done by changing the free energy surface of the reaction.

Highly catalytic electrode dramatically increases j_0 .

Fuel Cells

Exchange currents and electrocatalysis

2) Decrease the activation barrier, ΔG

A catalytic electrode lowers the activation barrier. The free energy curves depend on the nature of the electrode metal.

Different electrode materials will give different adsorption bond strengths to the species.

Fuel Cells

Exchange currents and electrocatalysis

2) Decrease the activation barrier, ΔG

Different electrode materials will give different adsorption bond strengths to the species.

For the case of the hydrogen charge transfer:

- If the $[M...H]$ bond is too weak, it is difficult for hydrogen to bond to electrode surface and to transfer charge from the hydrogen to the electrode;
- If the $[M...H]$ bond is too strong, the hydrogen bonds too well to the electrode surface and it is difficult to liberate H^+ .

The optimal compromise between bonding and reactivity occurs for intermediate-strength $[M...H]$ bonds: Pt, Pd, Ir and Rh.

Fuel Cells

Exchange currents and electrocatalysis

3) Increase the temperature, T

Increasing the temperature will also increase j_0 , by increasing the thermal energy available in the system.

Changing temperature has an exponential effect on j_0 .

Fuel Cells

Exchange currents and electrocatalysis

4) Increase the number of possible reaction sites

Since j_0 represents current density, or reaction current per unit area, increase in reaction sites per unit area increases j_0 .

Fuel Cells

Tafel Equation

The Butler-Volmer equation can be simplified for very small or very large activation overvoltages, η .

- When $\Delta\eta$ is very small.

For small η (less than 15 mV at RT)

$$j = j_0 \frac{nF\eta}{RT}$$

indicates the current and overvoltage are linearly related for small deviations from equilibrium and are independent of α .

Unfortunately sources of error such as impurity currents, ohmic losses, and mass transport effects make measurements difficult and j_0 is usually extracted from high overvoltage measurements.

Fuel Cells

Tafel Equation

The Butler-Volmer equation can be simplified for very small or very large activation overvoltages, η .

- When $\Delta\eta$ is large.

For large η (50-100 mV at RT)

$$j = j_0 e^{\alpha n F \eta / RT}$$

The forward reaction dominates and becomes irreversible.

Tafel conditions hold when the back reaction contributes less than 1% of the current.

When electrode kinetics are sluggish and η is needed, good Tafel relationship can be seen (irreversible kinetics).

Fuel Cells

Tafel Equation

- When $\Delta\eta$ is large.

For large η (50-100 mV at RT)

$$\eta = a + b \log j(\text{or } i)$$

Tafel Plots - A plot of η versus $\ln j$ should yield a straight line.

Plot of i vs η – evaluates kinetic parameters

Has an anodic branch with slope = $(1-\alpha) F/2.3RT$

And cathodic branch with slope = $-\alpha F/2.3RT$

The y-intercept = $\log i_0$

Tafel plots used to obtain i_0 and α

Fuel Cells

Tafel Plots.

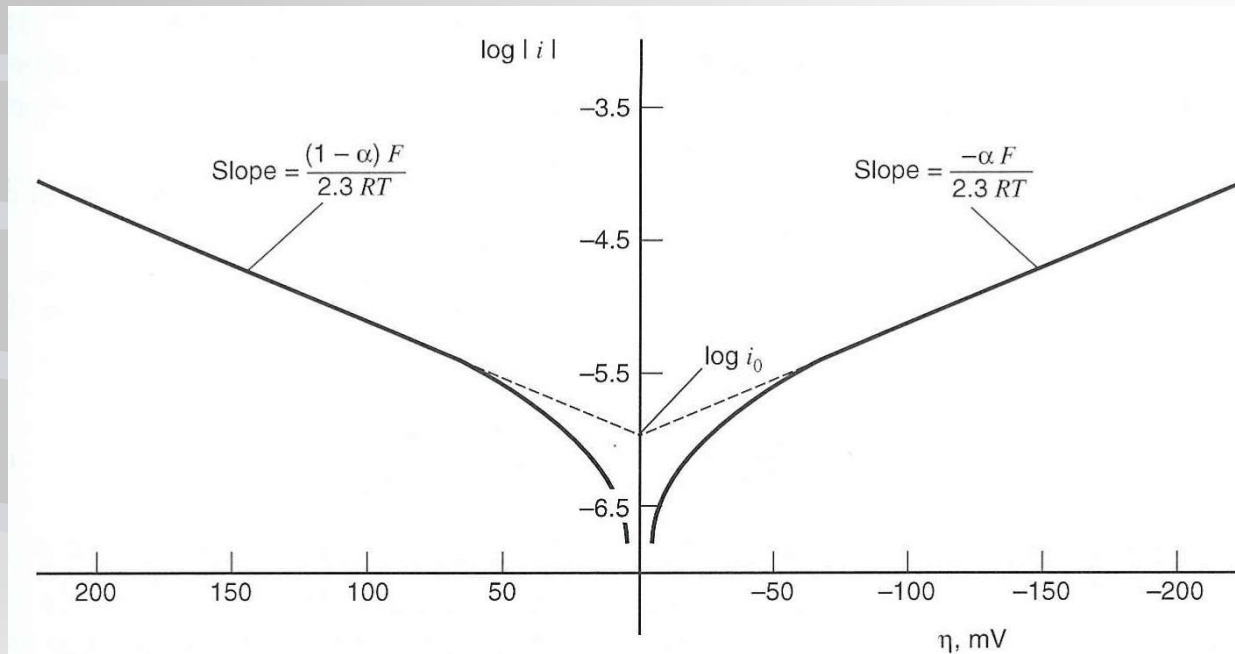


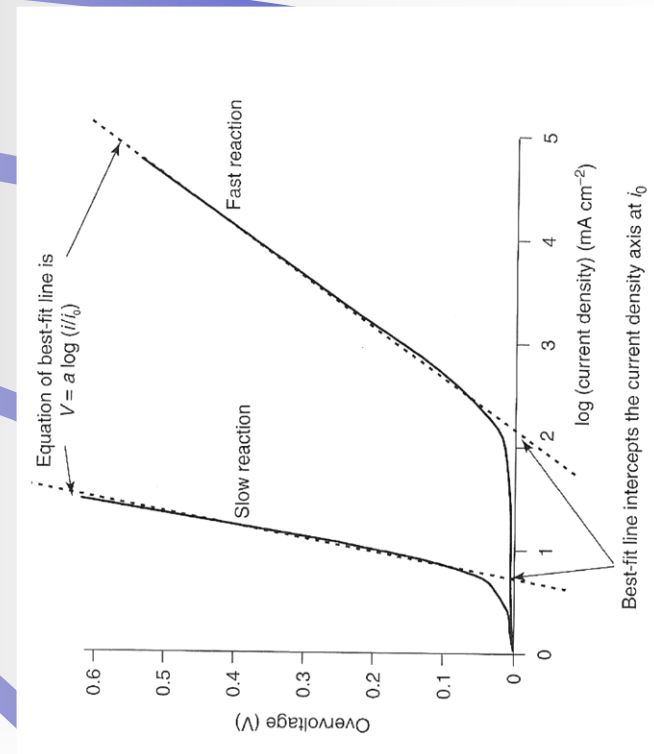
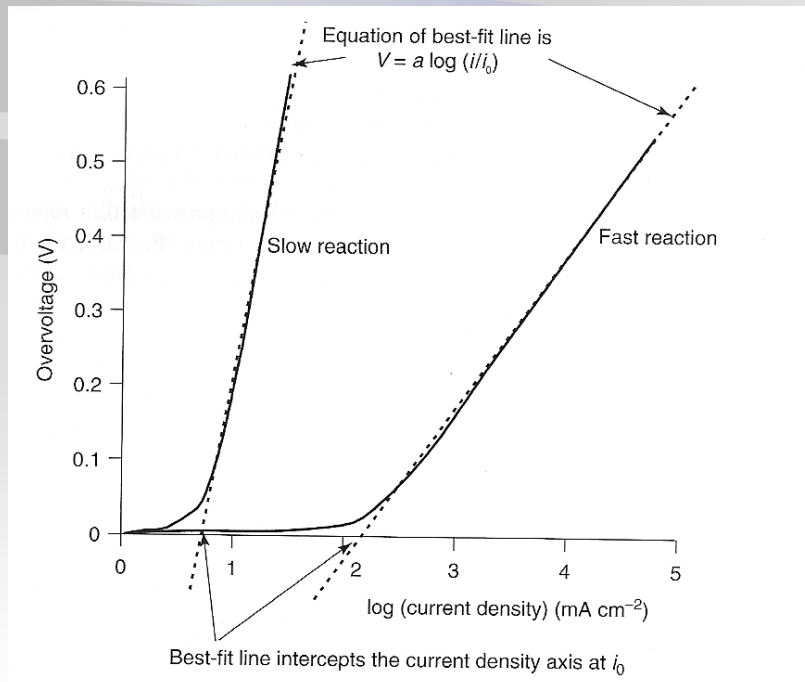
Figure 3.4.4 Tafel plots for anodic and cathodic branches of the current-overpotential curve for $\text{O} + e \rightleftharpoons \text{R}$ with $\alpha = 0.5$, $T = 298 \text{ K}$, and $j_0 = 10^{-6} \text{ A/cm}^2$.

Fuel Cells

Tafel Equation

Deviations at large η is from mass transfer limitations.

Deviations at low η occur because back reactions are no longer negligible.

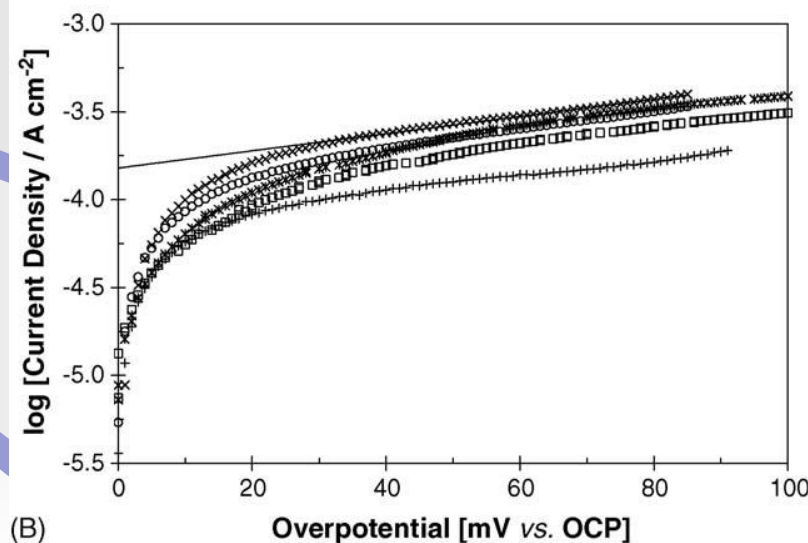
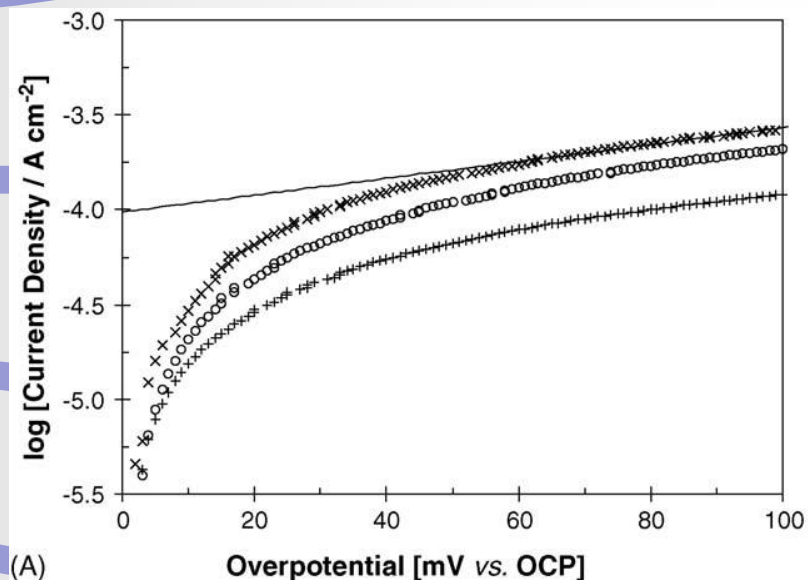


Fuel Cells

Tafel Equation

Fig. 3. Tafel plots: (A) Tafel plots recorded in a fuel cell equipped with two anodes (Fig. 2A), with graphite anodes previously coated with ceramics layers containing (i) $\text{Mn}^{2+} + \text{Ni}^{2+}$ metallic graphite $\times$, (ii) graphite modified with AQDS, relative to a plain graphite anode + (overpotential range: 0–600mV vs. OCP, scan rate: 1mVs⁻¹; reference electrode: Ag/AgCl, sat. KCl, only one linear fir shown).

(B) Tafel plots recorded in a fuel cell equipped with three square shaped anodes (Fig. 2B): graphite disk modified with (i) magnetite: ($\times$), (ii) Ni-magnetite: ($\circ$), (iii) AQDS: ($*$), (iv) NQ: ($\square$), and (v) plain graphite: ($+$), used alternatively in conjunction with the same plain graphite disk cathode (same conditions as in Fig. 3A).

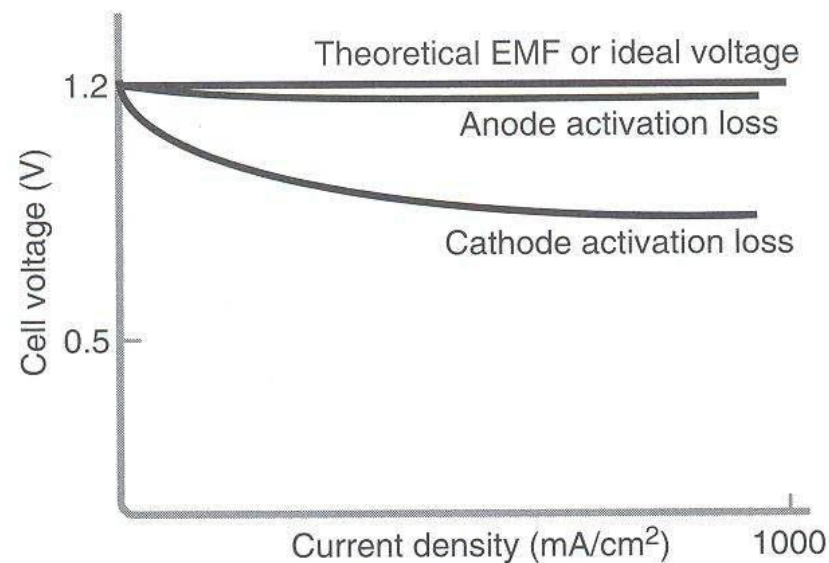
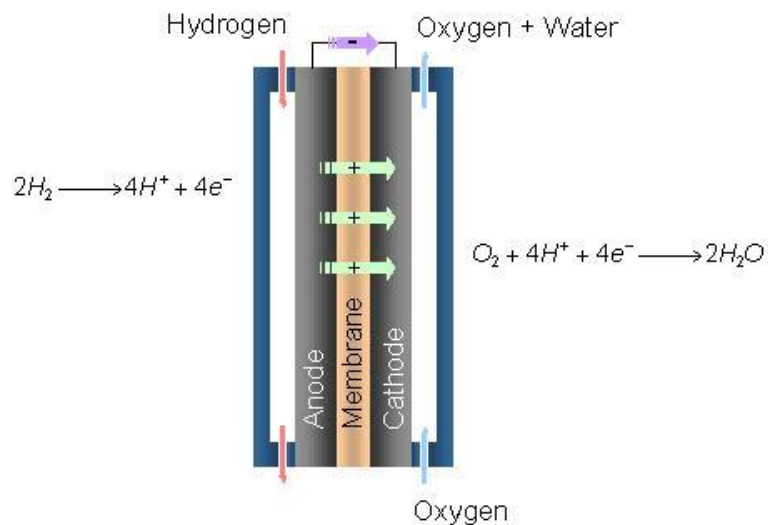


Biosensors and Bioelectronics 21 (2006) 2058–2063 (B)

Fuel Cells

Electrodes have different kinetics

For a basic $\text{H}_2\text{-O}_2$ fuel cell, the HOR kinetics are extremely fast, while the ORR kinetics are extremely slow.



Fuel Cells

Electrodes have different kinetics

The ORR is more complicated and requires more steps.

Completion of the ORR requires many individual steps and significant molecular reorganization.

Also many fuel cells run on air instead of oxygen which causes a significant kinetic penalty.

For HOR, pure hydrogen fuel has a significant kinetic advantage. For complex hydrocarbons as fuel, the kinetics become complicated and sluggish.

Many kinetic problems can be solved at higher temperatures.

Fuel Cells

Electrodes have different kinetics

TABLE 3.1. Standard-State ($T \approx 300$ K, 1 atm) Exchange Current Densities for Hydrogen Oxidation Reaction on Various Metal Surfaces

Surface	Electrolyte	j'_0 (A/cm ²)
Pt	Acid	10^{-3}
Pt	Alkaline	10^{-4}
Pd	Acid	10^{-4}
Rh	Alkaline	10^{-4}
Ir	Acid	10^{-4}
Ni	Alkaline	10^{-4}
Ni	Acid	10^{-5}
Ag	Acid	10^{-5}
W	Acid	10^{-5}
Au	Acid	10^{-6}
Fe	Acid	10^{-6}
Mo	Acid	10^{-7}
Ta	Acid	10^{-7}
Sn	Acid	10^{-8}
Al	Acid	10^{-10}
Cd	Acid	10^{-12}
Hg	Acid	10^{-12}

Note: Rounded to nearest decade. Values are normalized per real unit surface area of metal [4, 5].

TABLE 3.2. Standard-State ($T \approx 300$ K, 1 atm) Exchange Current Densities for Oxygen Reduction Reaction on Various Surfaces

Surface	Electrolyte	j'_0 (A/cm ²)
Metal Surfaces in Acid Electrolyte		
Pt	Acid	10^{-9}
Pd	Acid	10^{-10}
Ir	Acid	10^{-11}
Rh	Acid	10^{-11}
Au	Acid	10^{-11}
Pt Alloys in PEMFC		
Pt-C	Nafion	3×10^{-9}
PtMn-C	Nafion	6×10^{-9}
PtCr-C	Nafion	9×10^{-9}
PtFe-C	Nafion	7×10^{-9}
PtCo-C	Nafion	6×10^{-9}
PtNi-C	Nafion	5×10^{-9}

Note: Values are normalized per real unit surface area of metal. The exchange current density for the ORR is orders of magnitude smaller than for the HOR, although the same group of metals shows the highest activity for both reactions. Pt alloys may show a slight performance enhancement over pure Pt in a PEMFC environment [4, 6].

Fuel Cells

Intermediates affect kinetics

Fuels that involve carbon tend to generate intermediates that “poison” the fuel cell.

For low temperature fuel cells, CO can absorb onto Pt and block reaction sites.

For high temperature fuel cells, sulfur and carbon “coking” can block sites.

Fuel Cells

Type of Electrolyte affects kinetics

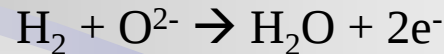
For hydrogen reduction:

In PEM (acidic) fuel cell $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$

In alkaline fuel cell, where OH^- is the charge carrier



In SOFC fuel cell, where O^{2-} is the charge carrier



Fuel Cells

Catalyst-Electrode Design

Fuel cells are designed to maximize the total number of reaction sites.

These reaction sites are called triple phase zones or triple phase boundaries (TPBs).

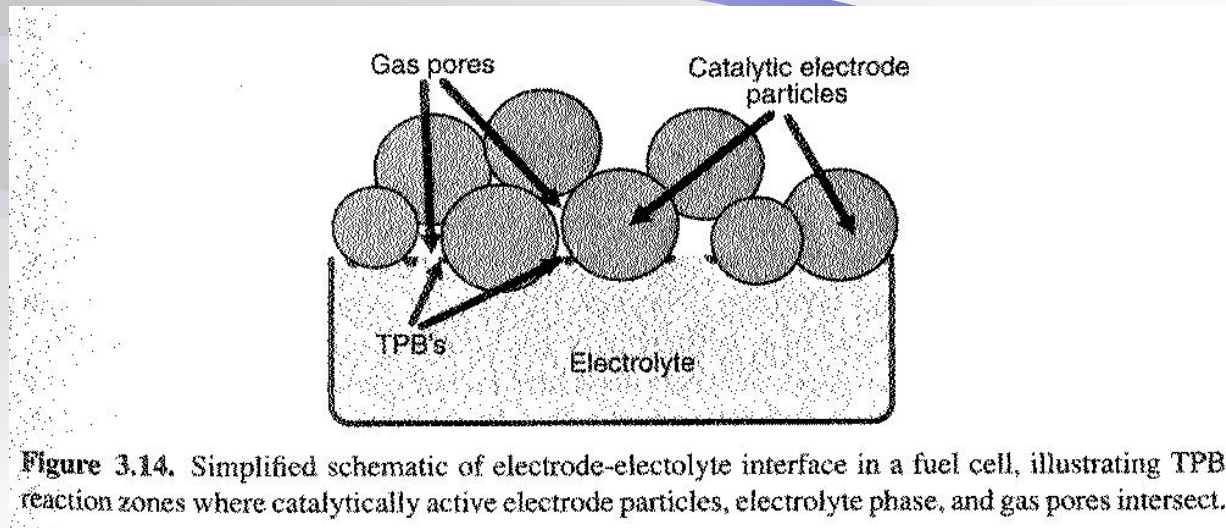
The fuel cell reactions can only occur where the three important phases, electrolyte, gas, and electrically connected catalyst region are in contact.

Fuel Cells

Catalyst-Electrode Design

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Fuel Cells

Catalyst-Electrode Design

Major requirements for an effective catalyst:

- High mechanical strength
- High electrical conductivity
- Low corrosion
- High porosity
- Ease of manufacturability
- High catalytic activity (high j_0)

For PEM fuel cells, Pt is the best catalyst. For SOFCs, Ni or ceramic based catalyst are used.

Designing new catalyst is an area of intense research.

Fuel Cells

Catalyst-Electrode Design

Designing new catalyst is an area of intense research.

Catalyst to date have been discovered by a trial-and-error approach, which is time-consuming and expensive.

Computational tools can be used to help design and search for new catalyst. These tools can also give us insight into how the catalyst works by calculating the electron density and minimum energy of a system.

Fuel Cells

Catalyst-Electrode Design

For example for hydrogen and a platinum catalyst:

- Hydrogen molecule approaches a cluster of Pt atoms
- Hydrogen adsorbs to cluster
- Atomic orbitals begin to overlap
- Complete separation of hydrogen atoms occur upon reaching lowest energy configuration

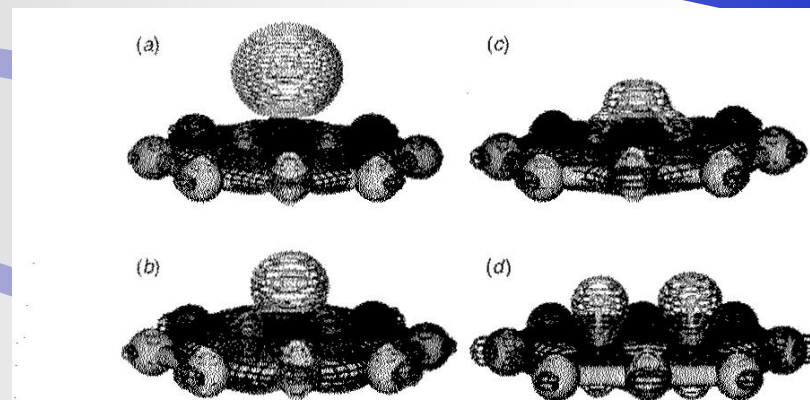


Figure 3.15. Evolution of electron orbitals as a hydrogen molecule approaches a cluster of platinum atoms. (a) Platinum and hydrogen molecule are not yet interacting. (b), (c) Atomic orbitals begin overlapping and forming bonds. (d) Complete separation of hydrogen atoms occurs almost simultaneously with reaching the lowest energy configuration.

Fuel Cells

Catalyst-Electrode Design

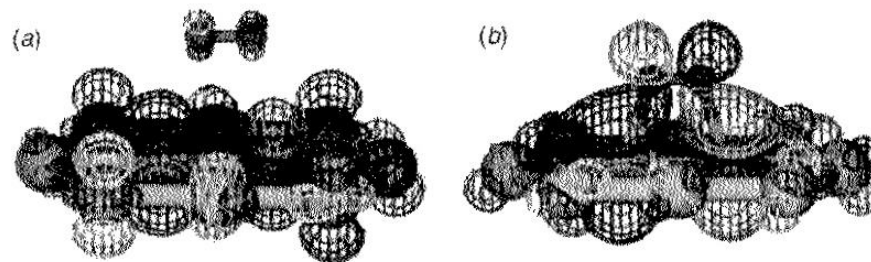


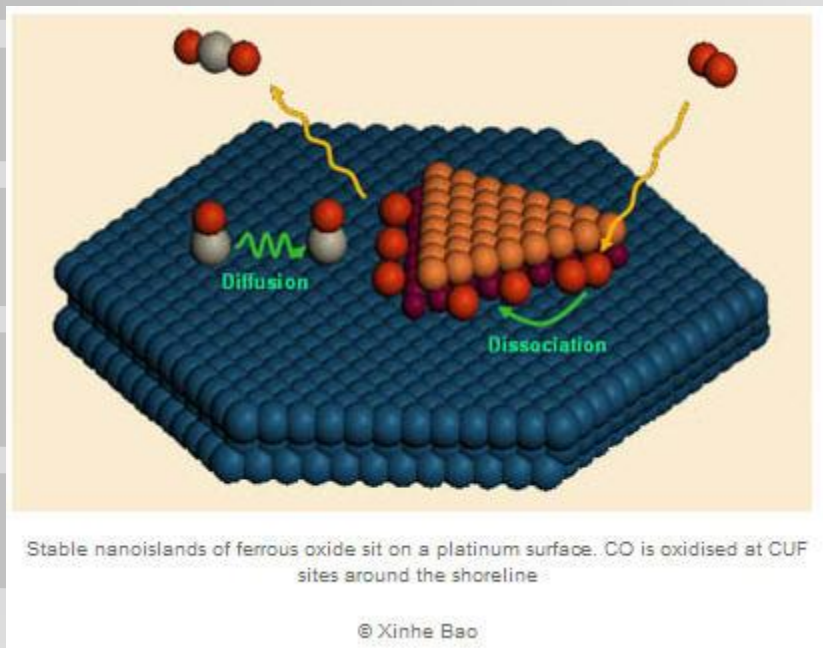
Figure 3.17. (a) Oxygen molecule approaching a platinum catalyst surface. (b) Even after having reached lowest energy configuration via hybrid orbital formation, the oxygen molecule is not completely separated into individual oxygen atoms.

For a fuel cell cathode:

- The p electron of an oxygen molecule approaches the Pt cluster
- Bond formation occurs between oxygen and Pt cluster
- However unlike hydrogen, the O-O bond is not destroyed only weakened, the O-O bond strength on Pt cluster is 2.3 eV, without Pt cluster it is 8.8 eV.
- Therefore excess energy is still needed to complete the reaction.

Fuel Cells

Catalyst-Electrode Design



Royal Society of Chemistry



G. N. Vayssilov, Y. Lykhach, A. Migani, T. Staudt, G. P. Petrova, N. Tsud, T. Skála, A. Bruix, F. Illas, K. C. Prince, V. Matolín, K. M. Neyman, J. Libuda
„Support Nanostructure Boosts Oxygen Transfer to Catalytically Active Platinum Nanoparticles”
Nature Materials, 10, 310-315 (2011) [doi:10.1038/nmat2976](https://doi.org/10.1038/nmat2976).

Fuel Cells

Summary

- Electrochemical reactions are heterogeneous.
- Since these reactions involve electron transfer, the current generated is a measure of the reaction rate.
- Current density is current per unit area and used to normalize the effects of system size.
- An activation barrier impedes the conversion of reactants to products.
- A portion of the fuel cell voltage is sacrificed to lower the activation barrier.
- The sacrificed (lost) voltage is known as activation overvoltage, η .

Fuel Cells

Summary

- The relationship between current density output and the activation overpotential is described by the Butler-Volmer equation.
- The exchange current density, j_0 measures the equilibrium rate at which reactant and product are exchanged in the absence of an overvoltage.
- A high j_0 indicates a facile reaction, a low j_0 indicates a sluggish reaction.
- Activation overpotential losses are minimized by maximizing j_0 . There are four ways to maximize j_0
 - Increase reactant concentration
 - Increase reaction temperature
 - Decrease activation barrier (use a catalyst)
 - Increase number of reaction sites (high surface area, 3D structures)

Fuel Cells

Summary

- Fuel cells are operated at high current densities. At high overpotential, fuel cell kinetics can be simplified to the Tafel equation.
- For $\text{H}_2\text{-O}_2$ fuel cell, the hydrogen (anode) kinetics are faster than the oxygen (cathode) kinetics.
- The fuel cell kinetics are dependent on the fuel, electrolyte, and operating temperature.
- The main requirements for an effective fuel cell catalyst are
 - Activity
 - Conductivity
 - Stability (thermal, mechanical, and chemical)
- To increase j_0 , fuel cell catalyst-electrodes are designed to maximize the # of reaction sites per unit area, which increases the TPBs, where electrolyte, reactant, and catalyst meet.

Class Assignment

- Study notes and handouts at class website.

