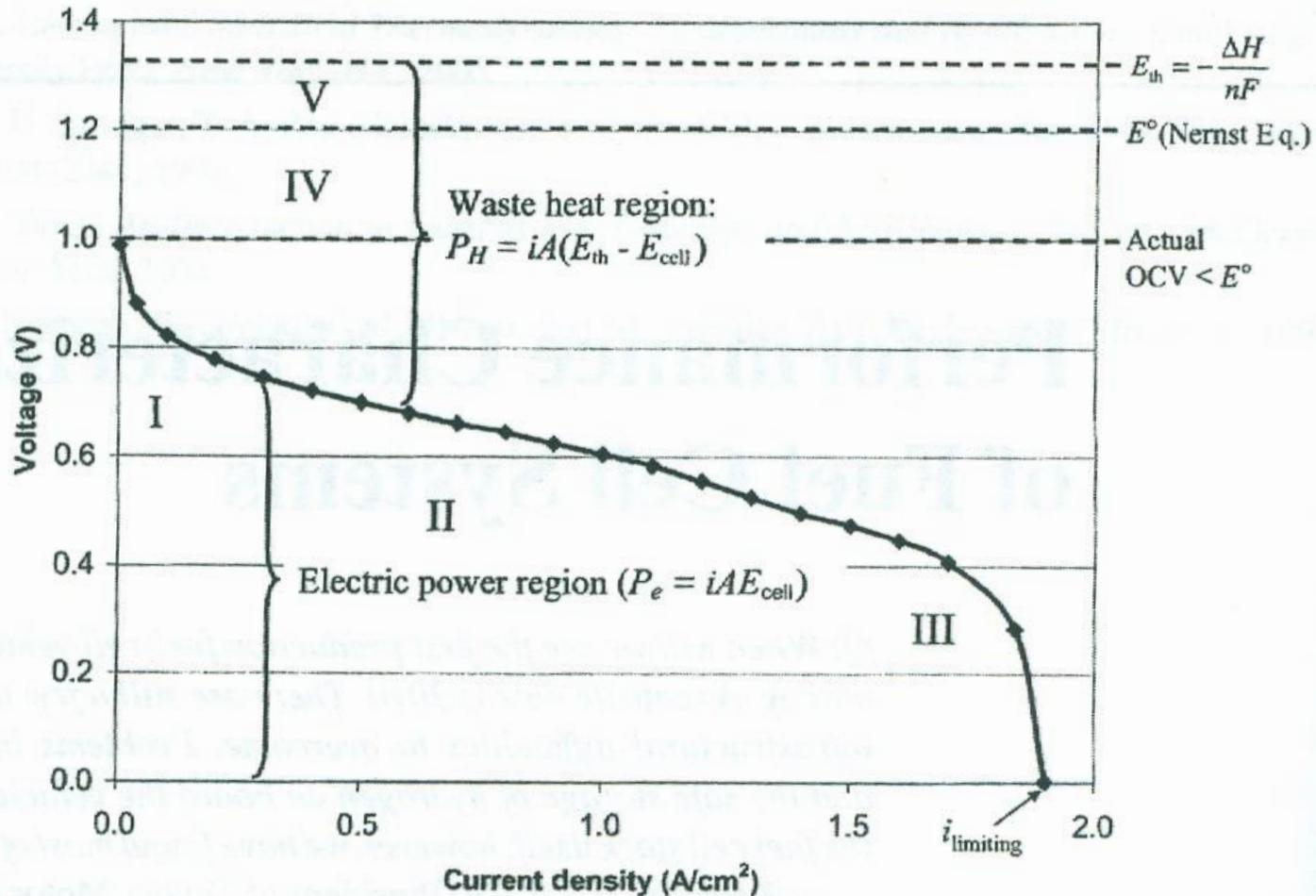


### 3. Performance characterization of fuel cell systems (Mench, ch. 4a)

1. Polarization curve
2. Activation polarization
3. Ohmic polarization
4. Concentration polarization
5. Other polarization losses
6. Polarization curve model

# 1. Polarization curve



**Figure 4.1** Typical polarization curve for fuel cell with significant kinetic, ohmic, concentration, and crossover potential losses.

-negative entropy of reaction such as hydrogen-air FC

-5 regions

- (i) Region I: activation (kinetic) overpotential at the electrodes
- (ii) Region II: ohmic polarization. Electric & ionic conduction loss
- (iii) Region III: concentration polarization. Mass transport limitations
- (iv) Region IV. Departure from Nernst thermodynamic equilibrium potential; undesired species crossover through electrolyte, internal currents from electron leakage, other contamination or impurity
- (v) Region V: the departure from the maximum thermal voltage; a result of entropy change which cannot be engineered

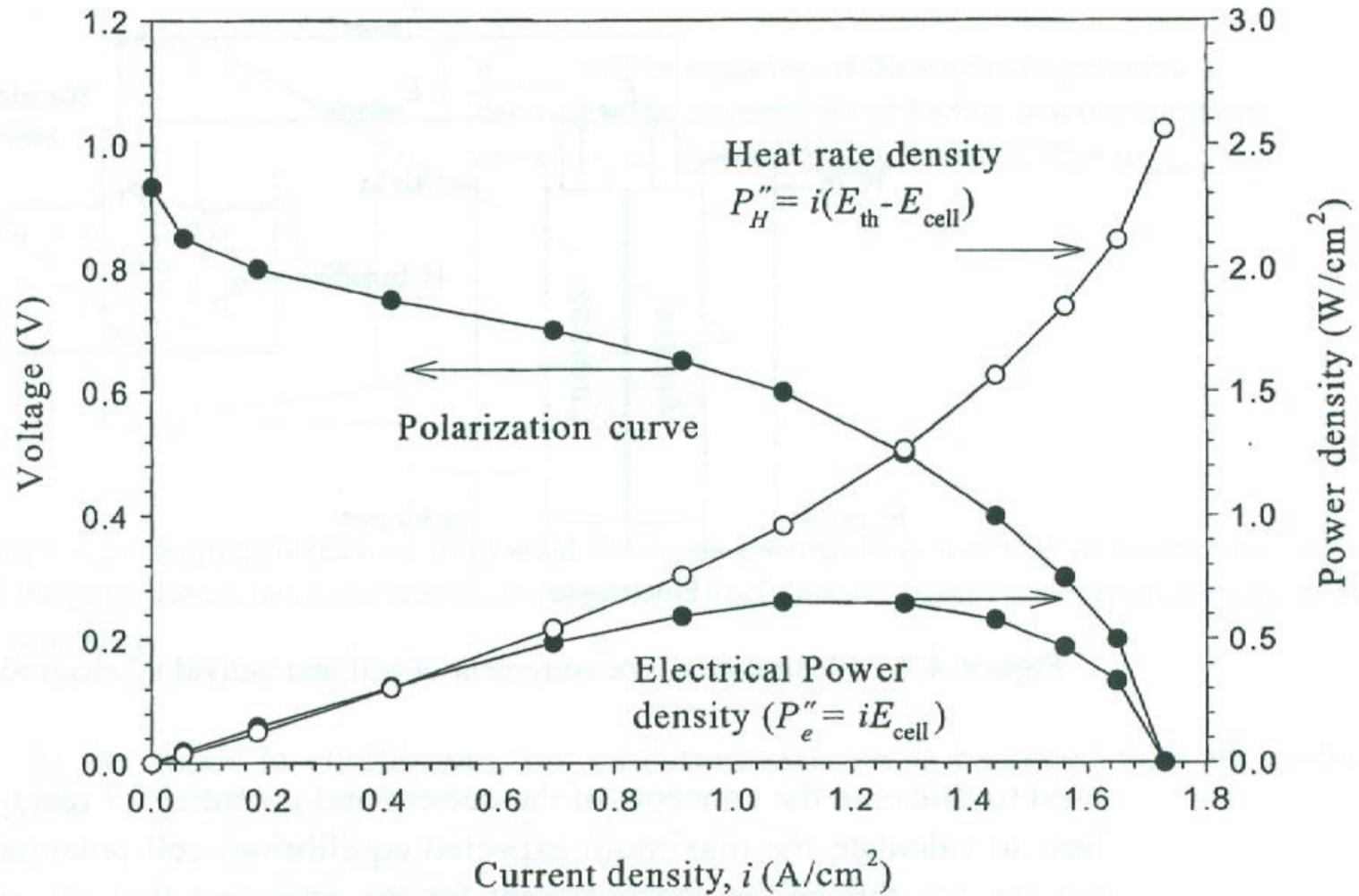
-Regions I, II, III are not discrete → all modes of loss contribute throughout the entire current range

-Heat: current x (thermal voltage – FC voltage)

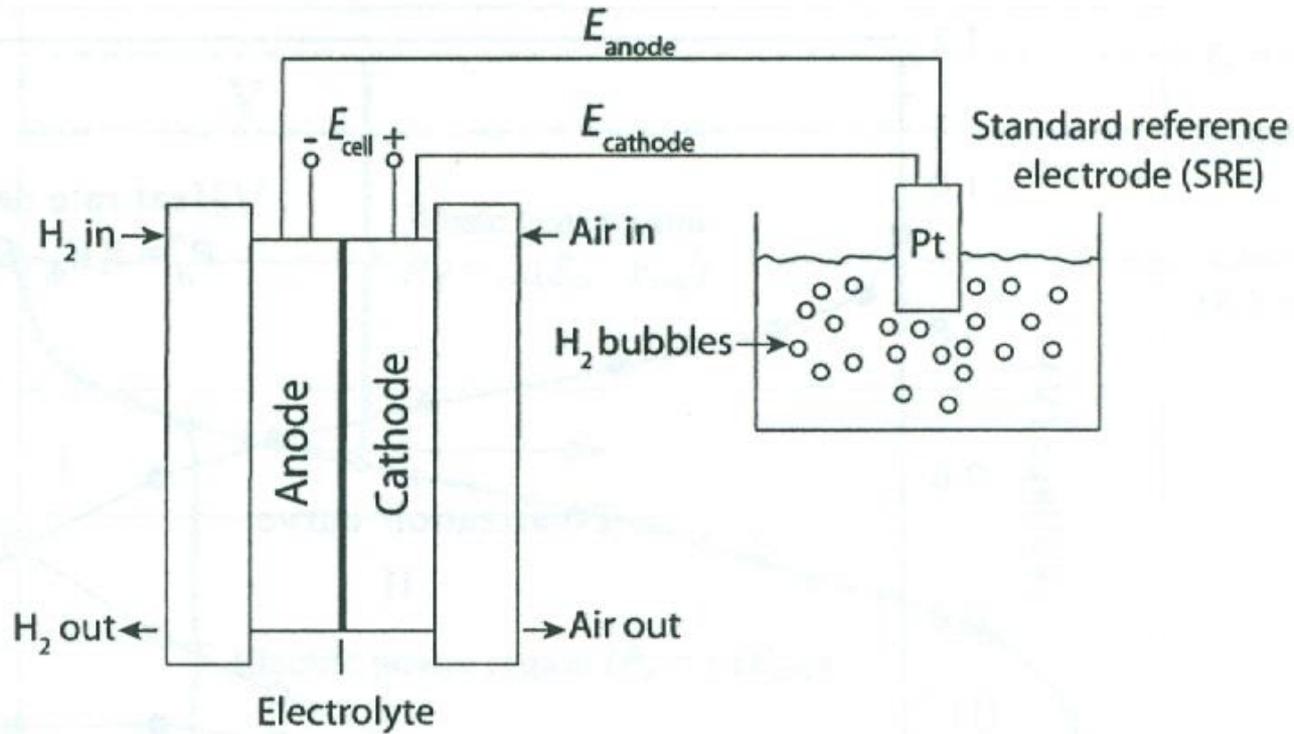
& electrical generation: cell current x FC voltage

-FC voltage:

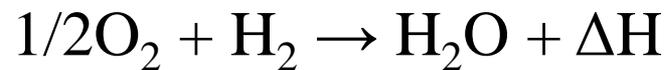
$$E_{\text{cell}} = E^{\circ}(T, P) - \eta_{a,a} - |\eta_{a,c}| - \eta_r - \eta_{m,a} - |\eta_{m,c}| - \eta_x \quad (4.1)$$



**Figure 4.2** Illustration of polarization curve, waste heat generation, and useful electrical power generation rate density.

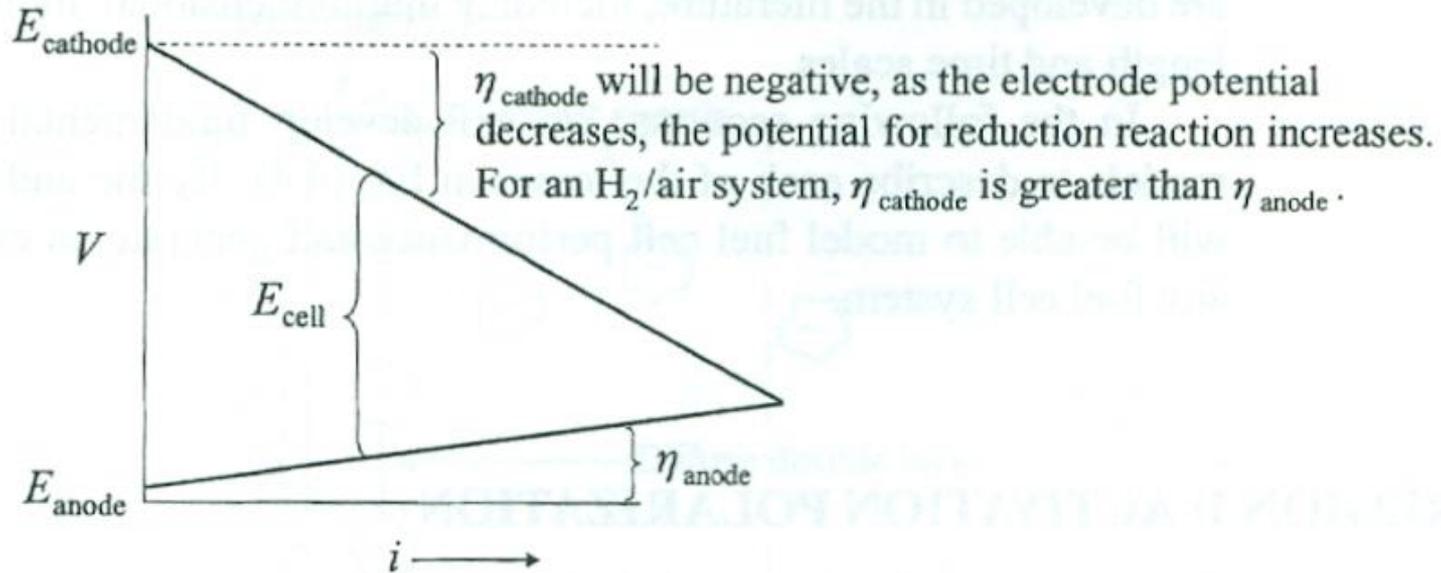


**Figure 4.4** Illustration of measurement of cell and individual electrode voltage in a fuel cell.



Thermal voltage,  $E_{\text{th}} = -\Delta H/nF$

Theoretical OCV from Nernst equation:  $E_{\text{cell}}^{\circ}$



**Figure 4.5** Representation of individual electrode potentials as function of current density. Note that the polarization behavior at each electrode will likely not be linear with current density, as shown for simplicity.

$i \uparrow \rightarrow$  anode voltage becomes more positive to promote oxidation of the fuel

$i \uparrow \rightarrow$  cathode voltage is reduced to promote the oxidizer reduction  
 $\rightarrow$  overall FC voltage ( $E_{\text{cell}}$ )  $\downarrow$ , finally zero current “limiting current ( $i_{\text{lim}}$ )”

## 2. Region I: activation polarization

-It dominates loss at low current density  $\rightarrow$  voltage overpotential required to overcome the activation energy of the electrochemical reaction on the catalyst surface

$$E_{\text{cell}} = E^{\circ}(T, P) - \eta_{a,a} - |\eta_{a,c}| - \eta_r - \eta_{m,a} - |\eta_{m,c}| - \eta_x \quad (4.1)$$

### (a) Electrical double layer

- Inner Helmholtz plane (IHP): specifically adsorbed ions
- Outer HP(OHP): solvated (hydrated) ions
- diffusion double layer: long range electrostatic interaction
- potential difference across interface: source of the activation overpotential

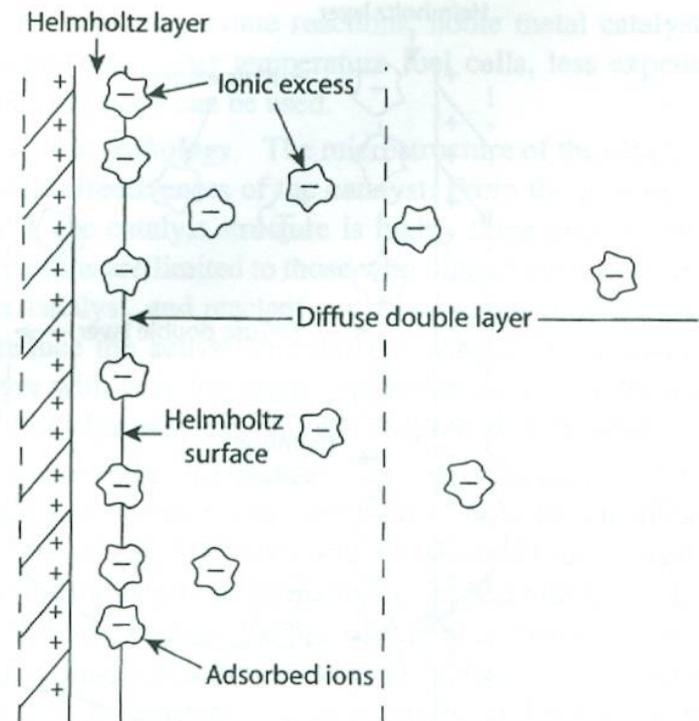


Figure 4.6 Schematic of electrical double layer. (Reproduced from [1].)

-typical oxidation activation overvoltage of  $\sim 0.2$  V at an electrode over double layer distance of 10 nm  $\rightarrow$  electric field strength  $2 \times 10^8$  V/cm  $\rightarrow$  behaves like a capacitor  $\rightarrow$  typical capacitance  $\sim$  order of  $5\sim 20$  mF/cm<sup>2</sup>

-FC be modeled as a resistance capacitance RC circuit (R: ohmic drop and charge transfer resistance in the circuit)

### (b) Activation polarization

-highly nonlinear loss with current: sharp initial drop in cell voltage from OCV followed by diminishing additional losses as  $i$  is increased

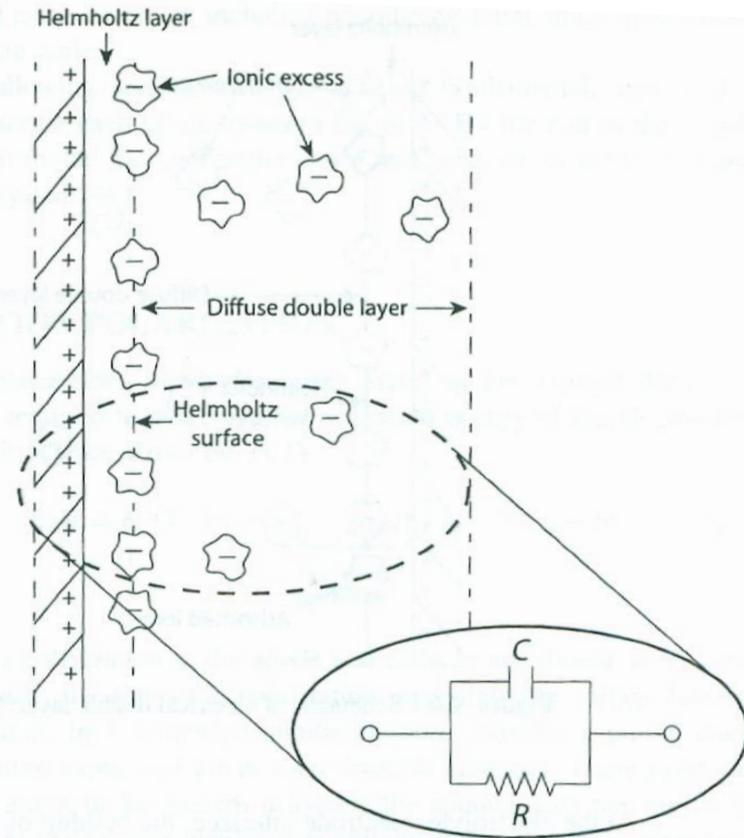


Figure 4.7 Schematic of electrical double layer with electrical circuit analogy. (Adapted from [1].)

-  $i_{\text{cell}} = i_a = i_c$

-polarization losses required to achieve this level of current on each electrode are independent

-activation polarization losses are influenced by:

- (i) Reaction mechanism: the more complex a rxn mechanism, the greater the overpotential required to break the chemical bonds and generate current
- (ii) Catalyst type: poor catalyst requires a greater polarization
- (iii) Catalyst layer morphology: maximization of catalyst triple phase boundary (ionic, electronic conductors, reactant gas)
- (iv) Operating parameters: T, P... e.g.  $T \uparrow \rightarrow$  electrochemical rxn  $\uparrow$
- (v) Impurities and poisons: e.g., CO, SO<sub>2</sub>  $\rightarrow$  performance  $\downarrow$
- (vi) Species concentrations
- (vii) Age: operating lifetime
- (viii) Service history: load cycle, voltage history  $\rightarrow$  degradation

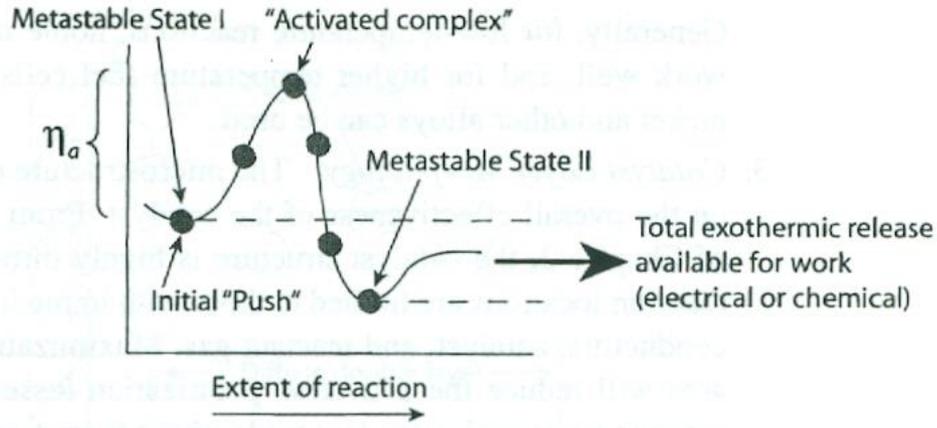


Figure 4.8 Schematic of reaction coordinate pathway for given reaction.

-consider an individual electrode

e.g. HOR,



-At equilibrium (open circuit)  $\rightarrow$  rxn proceeds in both directions across the anode double layer  $\rightarrow$  no net rxn in either direction  $\rightarrow$  "exchange current density ( $i_0$ )"

-moving electrode out of equilibrium into net hydrogen oxidation and current generation  $\rightarrow$  net flow of  $\text{e}^-$

- $i \uparrow \rightarrow$  overpotential  $\uparrow$

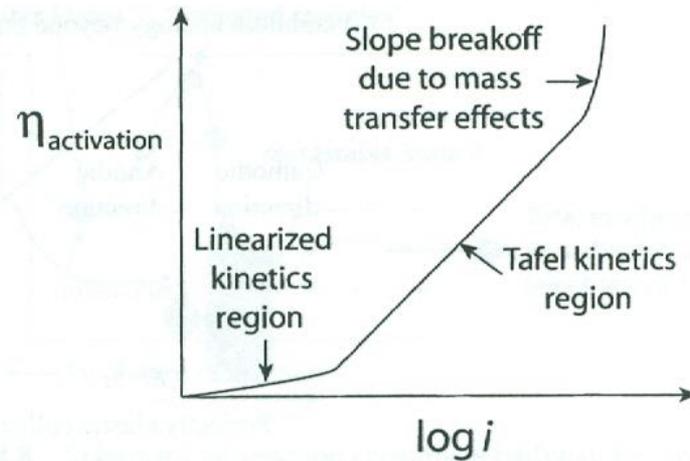


Figure 4.12 Schematic of activation overpotential with respect to current.

-typical electrode activation polarization behavior (Fig.4.12)

-At low current density,  $\eta_{\text{act}}$  required to maintain a net rxn rate is small

- $i_0 \uparrow \rightarrow$  additional polarization required for increasing  $i$  is greatly increased  $\rightarrow i_0$  is important ( $i_0 \uparrow \rightarrow \eta_{\text{act}} \downarrow$ )

## 2.1. Butler-Volmer model of kinetics

-general expression to describe activation polarization losses at a given electrode: Butler-Volmer(BV) kinetic  $\rightarrow$  an electrode process limited by the charge transfer of electron

-Fundamental assumption of BV kinetic model is that the rxn is rate limited by a single electron transfer step (which may not actually be true  $\rightarrow$  some rxn may have two or more intermediate charge transfer rxns. Or another step such as reactant adsorption (Tafel rxn) may limit the overall rxn rate)

-In a fuel cell, at each electrode, an equilibrium rxn



$\rightarrow$ : reduction (cathodic),  $\leftarrow$ : oxidation (anodic)

-At open circuit, there is no net current flowing through the electrode

-At out of equilibrium, at the anode, electrode potential becomes higher than its equilibrium potential, resulting in a net oxidation rxn

-At the cathode, electrode potential becomes lower than its equilibrium potential, resulting in a net reduction rxn

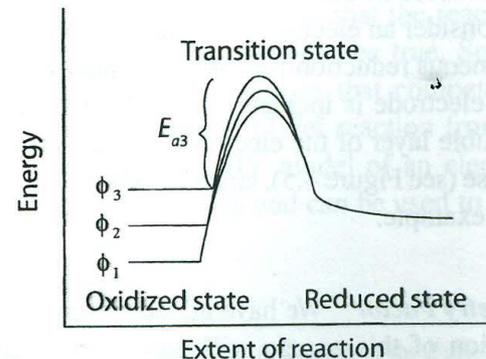
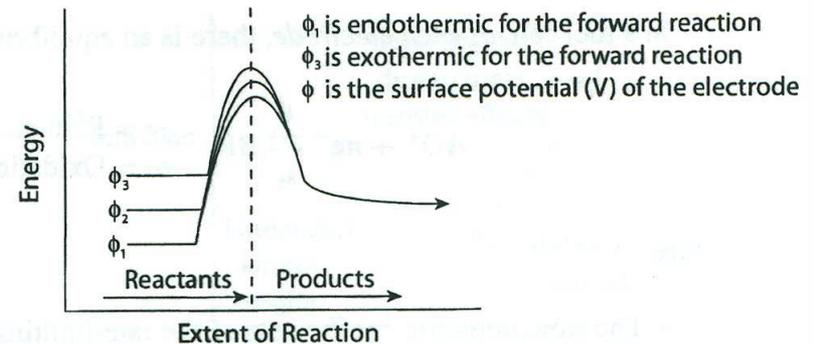
$\phi_1$ : endothermic for forward rxn

$\phi_3$ : exothermic for forward rxn

$\phi_1$ : forward rxn is not favored

$\phi_3$ : forward rxn is favored: final energy state is below the initial energy state

-Spontaneous reduction rxn,  $\phi_1 \rightarrow \phi_2$   
actual overpotential  $\downarrow$



(i) Symmetry factor ( $\beta$ )

$nF(\varphi_2 - \varphi_1)$  added to the system  $\rightarrow$  a fraction of this energy  $\rightarrow$  reducing the activation energy of the cathodic (reduction) rxn at the electrode  $\rightarrow$  promote the reduction rxn  $\rightarrow$  “ $\beta$ ” (symmetry factor)

$$0 < \beta < 1$$

If  $\beta = 1$ : additional overpotential goes completely toward promoting the reduction rxn

If  $\beta = 0$ : all of the additional potential is applied toward promotion of the anodic oxidation rxn

For the oxidation,  $(1 - \beta)$ : anodic symmetry factor

Elementary charge transfer rxn,



Rate equation for electrochemical rxn

$\gamma$ : rxn order of the elementary electron transfer step

$r$ : the rate of consumption/formation of species

$C$ : concentration (mol/cm<sup>2</sup>), for an ideal gas  $C = P/RT$

Taking anodic (oxidation) rxn

(ii) Charge transfer coefficient ( $\alpha$ )

$\alpha_c$ : the fraction of additional energy that goes toward the cathodic reduction rxn at an electrode

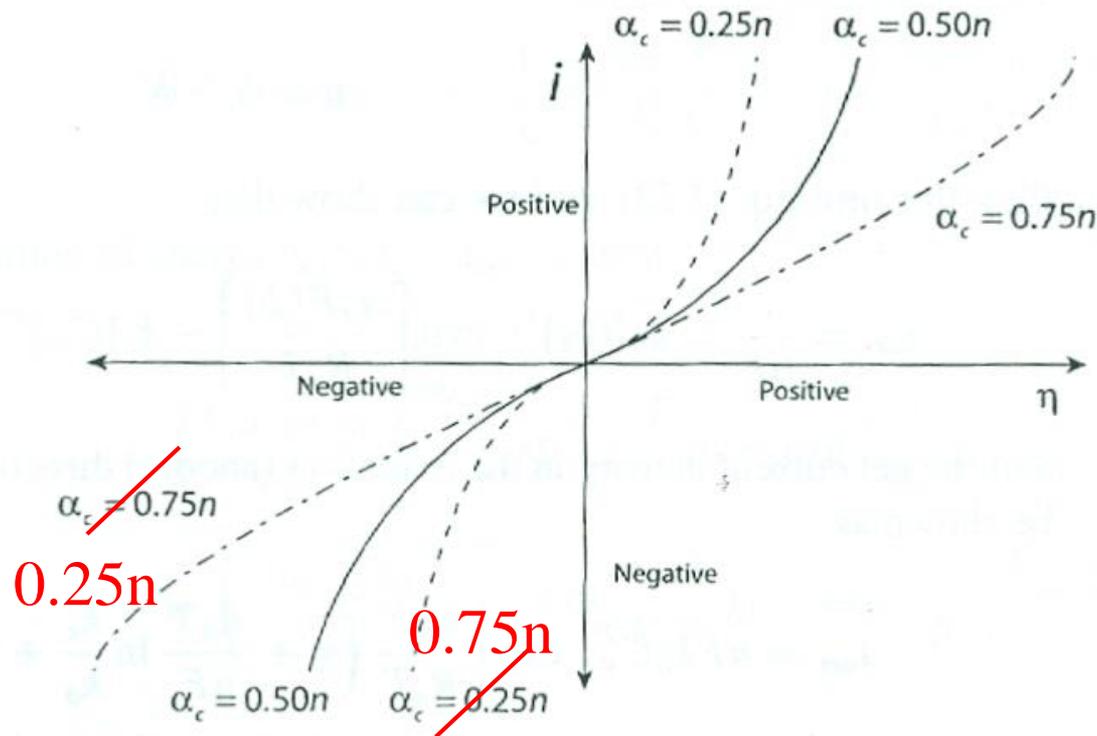


Figure 4.17 Effect of charge transfer coefficient on symmetry of current–overpotential curves. (Reproduced from [1].)

Negative value of overpotential: cathodic

$\alpha_c = 0.5$ : symmetric curve (anodic, cathodic),  $\alpha_c = 0.75$ : polarization required for cathodic reduction rxn for a given current much less than the polarization required for the anodic oxidation ( $\alpha_c > 0.5$  would be preferred for the cathode)

Note that we are still not considering the entire fuel cell yet! We are discussing a single electrode with simultaneously occurring oxidation and reduction reactions. For nonequilibrium operating conditions, we desire a *net* current density. For a net oxidation current density at the anode we consider the net oxidation reaction rate:

$$\begin{aligned}
 r_{\text{net,anodic}} &= r_a - r_c = \frac{i_a}{n_a F} - \frac{i_c}{n_c F} = \frac{i}{n F} \\
 &= k_a [C_R]^{P_a} \exp\left[\frac{\alpha_a F(\phi)}{R_u T}\right] - k_c [C_O]^{P_c} \exp\left[\frac{-\alpha_c F(\phi)}{R_u T}\right]
 \end{aligned}
 \tag{4.23}$$

At open circuit, the fuel cell net current density is zero, but the rates of exchange  $r_a$  and  $r_c$  are *not zero* but equal. We can solve for this resting exchange current density  $i_o$ :

$$\begin{aligned}
 \frac{i_o}{n F} &= r_a = r_c = k_a [C_R]^{P_a} \exp\left[\frac{\alpha_a F \phi^\circ}{R_u T}\right] \\
 &= k_c [C_O]^{P_c} \exp\left[-\frac{\alpha_c F \phi^\circ}{R_u T}\right]
 \end{aligned}
 \tag{4.24}$$

where  $\phi^\circ$  is the equilibrium potential (OCV) at  $i = 0$ . If we rearrange Eq. (4.24) and take the natural log of both sides,

$$\phi^\circ = \frac{RT}{nF} \ln \frac{k_c}{k_a} - \frac{RT}{nF} \ln \left( \frac{C_r^{Pr}}{C_o^{Po}} \right) \quad \text{or} \quad E(\text{OCV}) = E^\circ(T) - \frac{RT}{nF} \ln \left( \frac{C_r^{vr}}{C_o^{vo}} \right)
 \tag{4.25}$$

which is the Nernst equation! This makes sense, since any kinetic theory must reduce to the thermodynamic theory at equilibrium. So at  $i_{\text{net}} = 0$ , we are at equilibrium, and the expected maximum voltage is determined from the Nernst equation, as we have already shown in Chapter 3.

Now, consider the overpotential at an electrode,  $\eta$ , which represents a departure from this equilibrium potential:

$$\eta = \phi - \phi^o \quad (4.26)$$

Plug this into Eq. (4.23), and we can show that

$$r_{\text{net}} = \frac{i}{nF} = k_a [C_R]^{P_a} \exp\left[\frac{\alpha_a F(\phi)}{R_u T}\right] - k_c [C_O]^{P_c} \exp\left[\frac{-\alpha_c F(\phi)}{R_u T}\right] \quad (4.27)$$

and the net current density in the oxidation (anodic) direction,  $i_{\text{net}}$ , at a single electrode can be shown as

$$\begin{aligned} i_{\text{net}} = nF k_a C_R^{P_a} \exp\left[\frac{\alpha_a F}{R_u T} \left(\eta + \frac{R_u T}{nF} \ln \frac{k_c}{k_a} + \frac{R_u T}{nF} \ln \frac{C_o^{P_c}}{C_R^{P_a}}\right)\right] \\ - nF k_c C_O^{P_c} \exp\left[-\frac{\alpha_c F}{R_u T} \left(\eta + \frac{R_u T}{nF} \ln \frac{k_c}{k_a} + \frac{R_u T}{nF} \ln \frac{C_o^{P_c}}{C_R^{P_a}}\right)\right] \end{aligned} \quad (4.28)$$

Simplifying yields

$$i_{\text{net}} = nF k_c^{(1-\beta)} k_a^{(-\beta)} C_O^{(1-\beta)P_c} C_R^{\beta P_a} \left[ \exp \frac{\alpha_a F}{R_u T} \eta - \exp \frac{-\alpha_c F}{R_u T} \eta \right] \quad (4.29)$$

At open-circuit conditions,  $i_{\text{net}} = 0$ , but each component of anode/cathode current must equal the exchange current density  $i_o$ . So the first term in brackets at OCV ( $\eta = 0$ ) is the oxidation branch at the electrode, and the second term is the reduction branch. At  $\eta = 0$ , each branch must be at the exchange current density, so that  $i_o - i_o = i_{\text{net}} = 0$ . So we see that the term outside the brackets in Eq. (4.29) is really the exchange current density.

We can now rewrite our standard BV model of a single electrode as follows:

We can now rewrite our standard BV model of kinetics for an individual electrode:

$$i_{\text{net}} = i_o \left[ \exp \frac{\alpha_a F}{R_u T} \eta - \exp \frac{-\alpha_c F}{R_u T} \eta \right] \quad (4.30)$$

If

$$i_o = i_{o,\text{ref}} \left( \frac{C}{C^*} \right)^\gamma = i_o \left( \frac{C}{C^*} \right)^\gamma \quad (4.31)$$

where  $\alpha_a$  and  $\alpha_c$  refer to the anodic and cathodic charge transfer coefficients at the electrode, respectively. This is to be applied at each electrode. For example, for the anode

$$i_{\text{cell}} = i_{\text{net,anode}} = i_{o,a} \left[ \exp \frac{\alpha_{a,a} F}{R_u T} \eta_a - \exp \frac{-\alpha_{c,a} F}{R_u T} \eta_a \right] \quad (4.32)$$

For the cathode

$$i_{\text{cell}} = i_{\text{net,cathode}} = i_{o,c} \left[ \exp \frac{\alpha_{a,c} F}{R_u T} \eta_c - \exp \frac{-\alpha_{c,c} F}{R_u T} \eta_c \right] \quad (4.33)$$

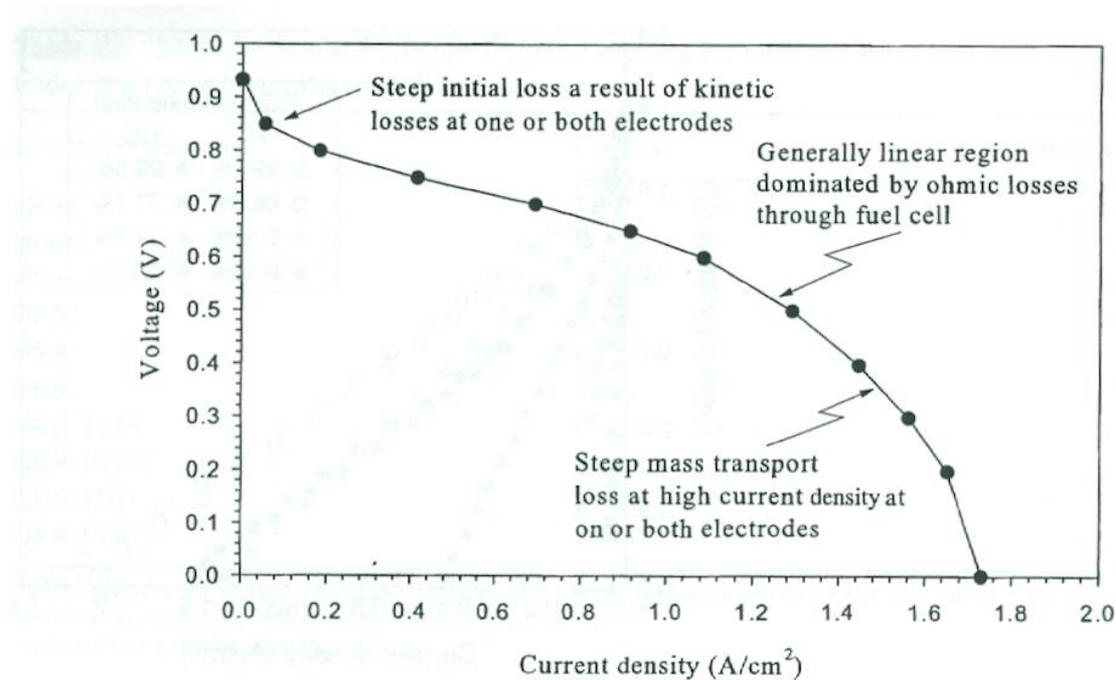
By conservation of charge,  $i_a = i_c = i_{\text{cell}}$ , so that

$$\begin{aligned} & i_{o,a} \left( \frac{C_{\text{H}_2,\text{surface}}}{C_{\text{H}_2}^*} \right)^{\gamma_{\text{H}_2}} \left[ \exp \frac{\alpha_{a,a} F}{R_u T} \eta_a - \exp \frac{-\alpha_{c,a} F}{R_u T} \eta_a \right] \\ & = i_{o,c} \left( \frac{C_{\text{O}_2,\text{surface}}}{C_{\text{O}_2}^*} \right)^{\gamma_{\text{O}_2}} \left[ \exp \frac{\alpha_{a,c} F}{R_u T} \eta_c - \exp \frac{-\alpha_{c,c} F}{R_u T} \eta_c \right] \end{aligned} \quad (4.34)$$

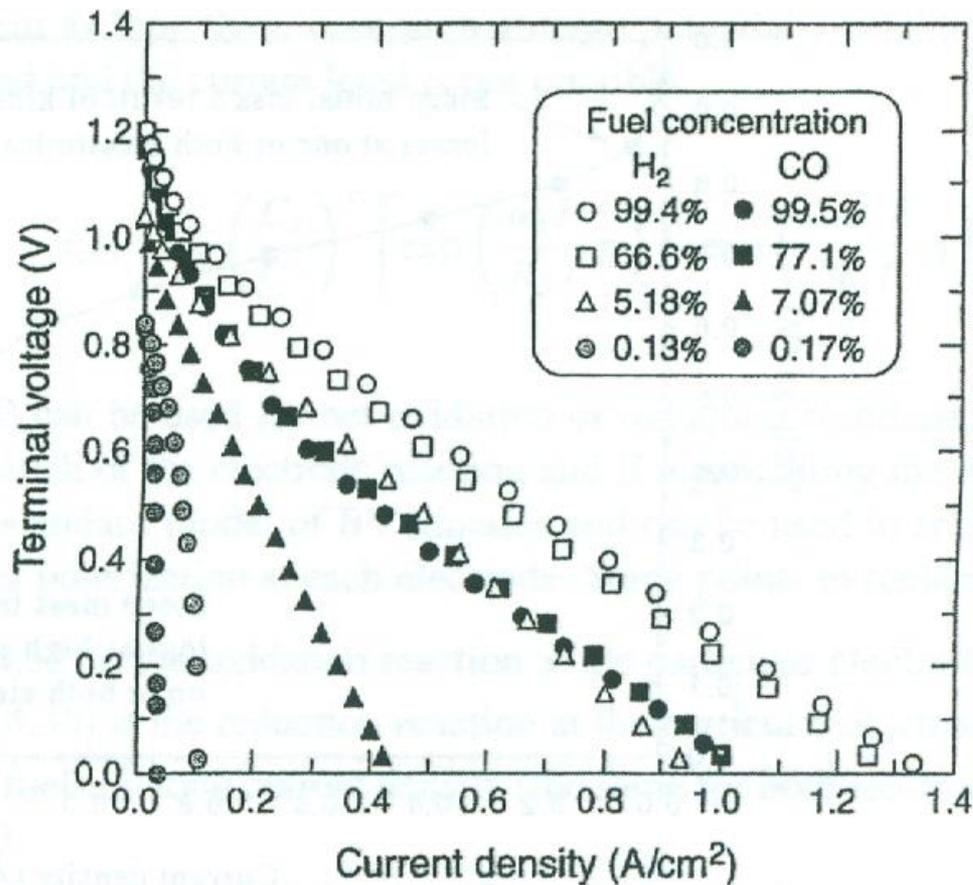


### (iii) Exchange current density

A dominating influence on the kinetic losses



**Figure 4.18** Typical polarization curve for low-temperature PEFC. Despite the use of an expensive platinum catalyst, there is still significant activation polarization. The fuel cell is operating at 65°C, with zero back pressure, 100% RH on anode and cathode, anode stoichiometry of 1.5, and cathode stoichiometry of 2.0.



**Figure 4.19** Typical polarization curves for high-temperature SOFC in different gas environments at 1000°C. The high operating temperature enables the use of low-cost catalyst materials such as nickel (anode) and strontium-doped lanthanum manganite (cathode), with very low kinetic polarization losses. (Reproduced with permission from [5].)

## (iv) Roughness factor (a)

**Table 4.1** Selected Typical Exchange Current Densities for Different Reactions and Smooth Electrodes in an Acid Electrolyte at 300 K, 1 atm.

Electrode Reaction	Catalyst	Value* (A/cm <sup>2</sup> )
HOR	Pt	$1 \times 10^{-3}$
HOR	Pd	$1 \times 10^{-4}$
HOR	Ni	$1 \times 10^{-5}$
ORR	Pt	$1 \times 10^{-9}$
ORR	Pd	$1 \times 10^{-10}$
ORR	Rh	$1 \times 10^{-11}$
ORR-PEFC	Pt-C	$3 \times 10^{-9}$
ORR-PEFC	PtCr-C	$9 \times 10^{-9}$
ORR-PEFC	PtNi-C	$5 \times 10^{-9}$
ORR-PEFC	PtFe-C	$7 \times 10^{-9}$

\*Value given is for smooth electrode surfaces. The roughness factors in fuel cells can range from 600 to 2000, however, increasing the effective exchange current density.  
*Source:* Data adopted from [7].

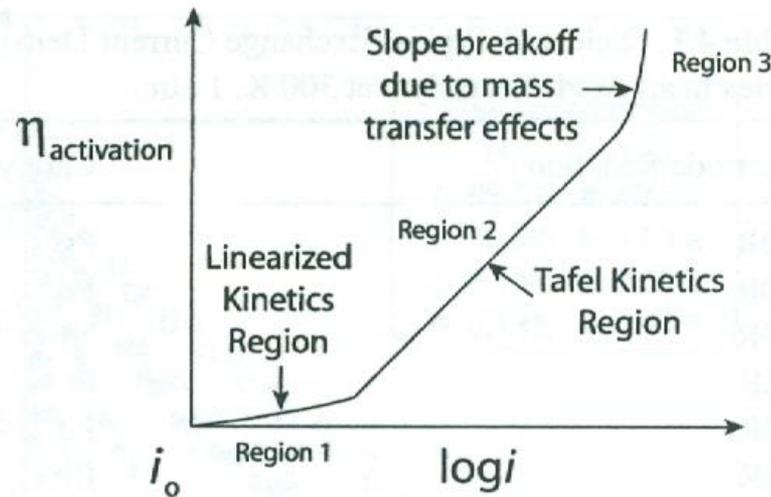
**Table 4.2** Selected Typical Exchange Current Densities for Different Reactions and Smooth Electrodes in an Alkaline Electrolyte at 300 K, 1 atm.

Electrode Reaction	Catalyst	Value* (A/cm <sup>2</sup> )
HOR	Pt	$1 \times 10^{-4}$
HOR	Pd	$1 \times 10^{-4}$
HOR	Ni	$1 \times 10^{-4}$

\*Value given is for smooth electrode surfaces. The roughness factors in fuel cells can range from 600 to 2000, however, increasing the effective exchange current density.  
*Source:* Data adopted from [7].

## 2.2. Butler-Volmer simplifications

1. low-overpotential region where kinetics are facile and relatively low losses occur
2. A higher overpotential region where losses become much more significant
3. A very high current region where mass transport losses dominate



**Figure 4.20** Schematic of activation polarization behavior at an electrode.

## (i) Simplified BV equation 1: facile kinetics-linearized BV model

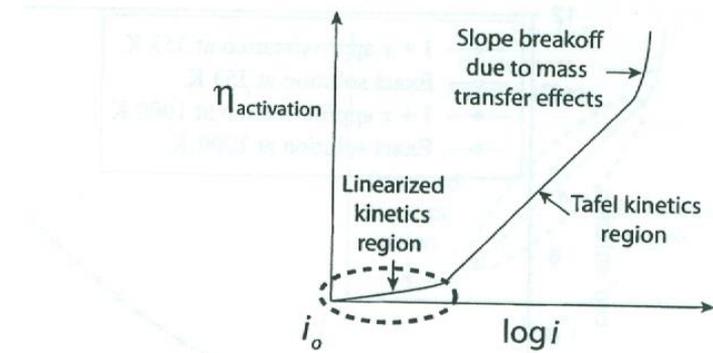


Figure 4.21 Region of applicability for linearized Butler–Volmer model.

### ***Example 4.1 How Applicable Is the Linearized Assumption?***

We should always desire to understand the limitations of our approximations. In this case we would like to examine the applicability of our assumption that, for values of low polarization, we can assume that, mathematically,

$$e^x \approx 1 + x$$

- (a)** Calculate the activation polarization  $\eta$  where the linearized assumption is appropriate for a low-temperature PEFC at 80°C and a high-temperature SOFC at 1000°C.
- (b)** Calculate the value of  $x = \alpha_i F \eta / R_u T$  where the linearization is appropriate.

## (ii) Simplified BV equation 2: high-electrode-loss region of BV model – Tafel kinetics

Very low  $i_0$  or polarization is significant → special BV model to the high-loss region → Tafel kinetics

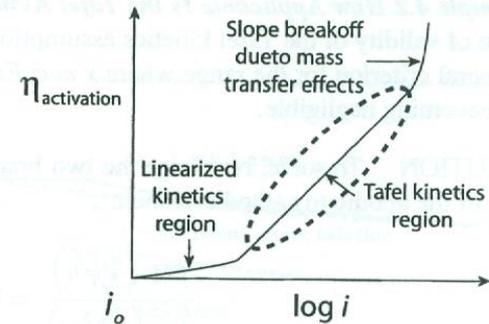


Figure 4.22 Region of applicability for Tafel kinetics model.

For high polarization, one of the branches will dominate → for an anode rxn with positive  $\eta$  → anodic branch will exponentially increase, while cathodic branch will be a diminishing function

For a cathodic rxn with negative  $\eta$  → cathodic branch  $\uparrow$ , anodic  $\downarrow$

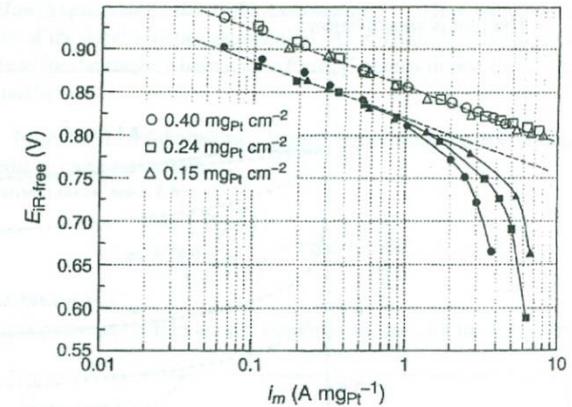
### ***Example 4.2 How Applicable Is the Tafel Assumption?***

Here we wish to evaluate the range of validity of the Tafel kinetics assumption. As in Example 4.1, we wish to evaluate a general criterion for the range where  $x = \alpha_i F \eta / R_u T$  results in one of the branches of the BV becoming negligible.

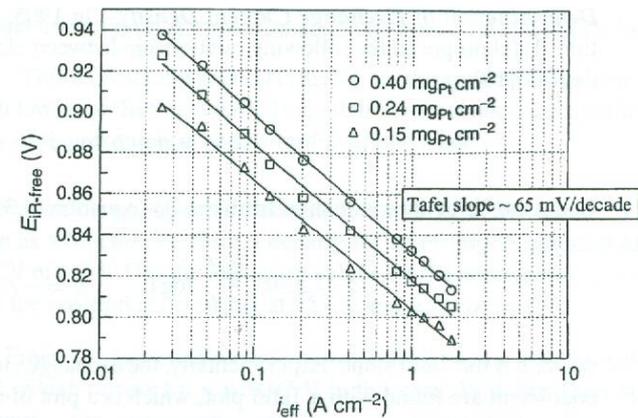
### ***Example 4.3 Calculation of Expected Polarization with Tafel Kinetics***

Plot the activation polarization as a function of current density for an electrode ignoring all other losses for an initial OCV of 1.2 V. Use the following values for the parameters:  $i_o = 0.3 \times 10^{-4} \text{ A/cm}^2$ . Assume the reaction is occurring at 353 K and  $\alpha_a = \alpha_c = 0.5$ .

### (iii) Determination of exchange current density



**Figure 4.23** Experimental Tafel plot of cell voltage versus current, corrected for fuel cell ohmic and other losses, so that only cathode polarization losses are remaining. The results are normalized to platinum loading. Results with open circles are with humidified oxygen, and closed circles are with humidified air. The dashed line represents the Tafel slope behavior. Note that for all loadings the Tafel slope for oxygen reduction on platinum is the same but deviates from this behavior under mass-limiting behavior. Also note that the vertical axis is ohmic corrected fuel cell voltage, not electrode overpotential, so the voltage falls with increasing current density. (Reproduced with permission from [9].)



**Figure 4.24** Tafel plot for ORR current-overpotential curve. Data for a  $H_2$ - $O_2$  PEFC at  $80^\circ C$  with different cathode catalyst loadings. The slope of the line (Tafel slope) for all conditions is approximately  $0.65$  mV/decade. (Reproduced with permission from [9].)

### (iii) Simplified BV equation 3: BV equation with identical charge transfer coefficients – sinh simplification

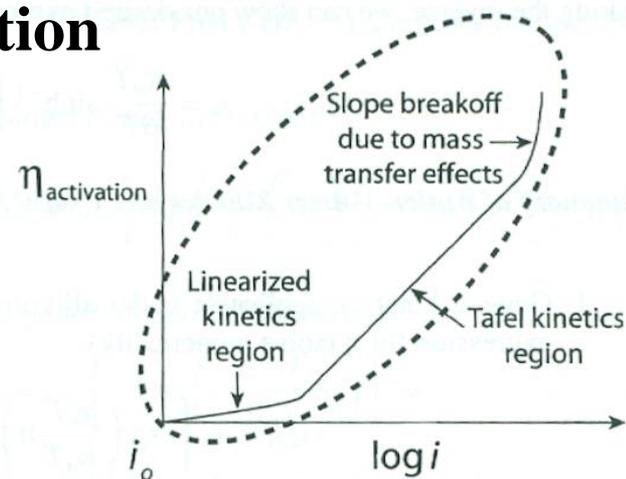


Figure 4.25 Region of applicability for sinh BV simplification.

## Summary of Butler–Volmer Kinetics and Useful Simplifications

1. General kinetics, applicable under all current density conditions; the general BV expression for  $\eta$  (solve numerically):

$$i_{\text{cell}} = i_o \left\{ \exp\left(\frac{\alpha_a F}{R_u T} \eta\right) - \exp\left(\frac{-\alpha_c F}{R_u T} \eta\right) \right\} \quad (4.52)$$

2. Low polarization, facile kinetics, linearized BV approximation (explicit  $\eta$  expression):

$$\eta = \pm \frac{i}{i_o} \frac{R_u T}{(\alpha_a + \alpha_c) F} \quad (4.53)$$

3. High polarization, Tafel approximation (explicit  $\eta$  expression):

$$\eta = \frac{R_u T}{\alpha_j F} \ln\left(\frac{i}{i_o}\right) \quad (4.54)$$

4. Both regions,  $\alpha_a = \alpha_c$  sinh simplification (explicit  $\eta$  expression):

$$\frac{R_u T}{\alpha F} \sinh^{-1}\left(\frac{i_{\text{cell}}}{2i_o}\right) = \eta \quad (4.55)$$

### ***Example 4.4 Selection of Proper Butler–Volmer Kinetic Model***

Solve for the most appropriate symbolic expression for the activation overpotential at each electrode in the given examples.

***Example 4.5 Activation Polarization Loss Calculation*** Given the table below, solve for the following:

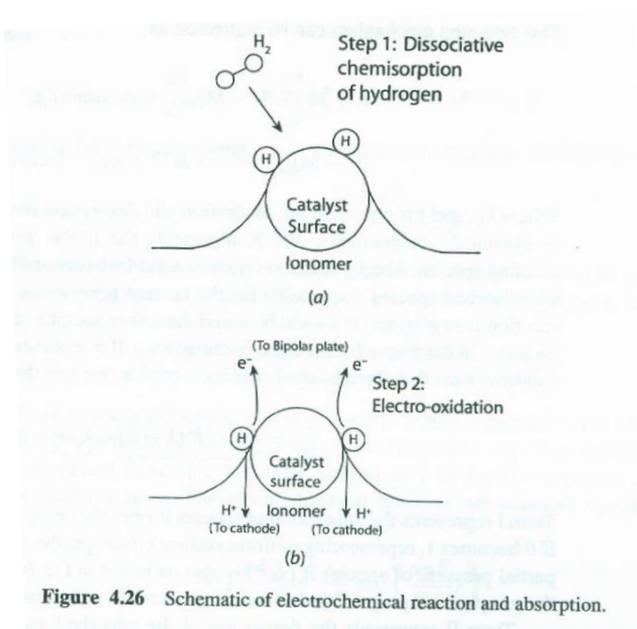
- (a) Using the appropriate kinetics, calculate the anodic activation overpotential ( $\eta_{a,a}$ ) at  $0.5 \text{ A/cm}^2$ .
- (b) Using the appropriate kinetics, calculate the cathodic activation overpotential at  $0.5 \text{ A/cm}^2$ .

Parameter	Value
Temperature	363 K
$n_a$ (elementary charge transfer step)	1
$n_c$ (elementary charge transfer step)	1.2
$\beta_{a,a}$	0.5
$\beta_{a,c}$	0.5
$E^\circ(T, P)$	1.15 V
$i_{o,a}$	$1.5 \text{ A/cm}^2$
$i_{o,c}$	$0.005 \text{ A/cm}^2$

## 2.3. Langmuir and Temkin model of kinetics

For an electrochemical rxn  $\rightarrow$  reacting species must first undergo adsorption or chemisorption onto electrode surface

In BV model: the intermediate charge transfer steps are rate determining, and the adsorption is facile and rapid  $\rightarrow$  this is not always the case. In some situations, rate determining step is surface adsorption/chemisorption



Two common models: Langmuir and Temkin kinetics

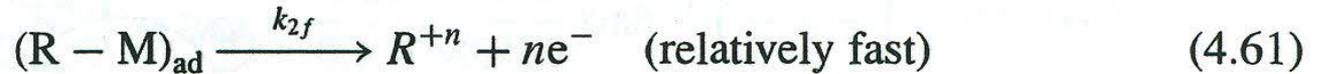
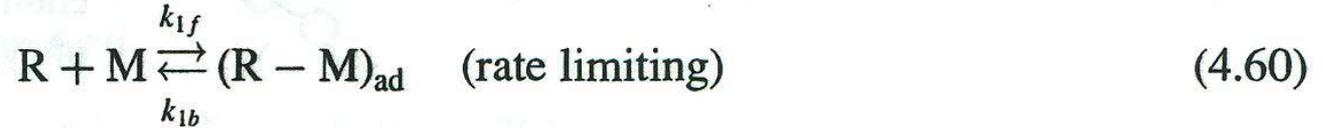
-Langmuir model: surface adsorption rate constant is independent of surface coverage

-Temkin model: adsorption rate constant is modeled as a function of the surface coverage of adsorbed species

-Langmuir & Temkin: two step rxn mechanism

1. A surface adsorption/desorption rxn, one or both of which are rate determining
2. An electrochemical rxn responsible for ion exchange and current generation that is assumed to be much faster than the adsorption/desorption step. In addition, the rxn is assumed to occur so fast that the reverse rxn is assumed to be negligible

This two-step mechanism can be expressed as



Where  $k_{1f}$ , and  $k_{1b}$  represent the adsorption and desorption reactions (which can be physical or chemical), respectively, and  $R$  represents the molar gas-phase concentration of the reacting species. The  $k_{2f}$  reaction represents the fast-forward ion charge transfer reaction of the adsorbed species responsible for the current generation, and it is assumed the reverse reaction is negligible. It should be noted that other species or parallel reactions can also be included in the above formulation methodology. If  $\theta$  represents the fraction of the available catalysis sites that the adsorbed species occupies, we can then write

$$\frac{d\theta}{dt} = \underbrace{k_{1f} y_R P (1 - \theta)}_I - \underbrace{k_{1b} \theta}_II - \underbrace{k_{2f} \theta}_III \quad (4.62)$$

Term I represents the adsorption of species  $R$  onto the remaining noncovered reaction sites. If  $\theta$  becomes 1, representing uniform surface coverage, the adsorption obviously stops. The partial pressure of species  $R$  ( $y_R P$ ) is also included in Eq. (4.62) since the adsorption from the gas phase is proportional to the concentration in the gas phase.

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Term II represents the desorption of the adsorbed species from the reactive surface and decreases the surface coverage. Term III is the forward electrochemical ionization reaction responsible for current flow. From inspection of Eq. (4.62), in the case of an adsorption-limited reaction, the kinetic limiting current density should be the maximum possible adsorption rate where the surface coverage  $\theta$  becomes zero, or

$$i_{\text{lim}} \propto k_{1f} y_R P (1 - \theta) - k_{1b} \theta - k_{2f} \theta \propto k_{1f} y_R P \quad (4.63)$$

The constant of proportionality is the electrons per mole of reactant,  $nF$ , or

$$i_{\text{lim}} = nF k_{1f} y_R P \quad (4.64)$$

so that, for an adsorption-controlled reaction, the limiting current density is linearly proportional to the gas-phase partial pressure, and adsorption rate constant  $k_{1f}$  can be either assumed to be constant (Langmuir model) or a function of the surface coverage (Temkin model). Here, we will show solution for the Langmuir model. The reader is referred to advanced electrochemistry texts for additional details on Temkin kinetics [e.g., 12].

The overall electrochemical reaction rate can be shown as

$$i = nF k_{2f} \theta \quad (4.65)$$

Using this two-step model, which can be expanded to include other intermediate steps as well, a simple formulation for the electrode overpotential current relationship at a given electrode can be developed. If we assume that the reaction rate constants involved are independent of the surface coverage of reactant R, then we can derive the Langmuir kinetics model solution. With constant rate constants in Eq. (4.62), at steady state we can

show that

$$\frac{d\theta}{dt} = 0 = k_{1f}y_R P (1 - \theta) - k_{1b}\theta - k_{2f}\theta \quad (4.66)$$

Then, solving for surface coverage, we can show, from algebraic manipulation, that

$$\theta = \frac{k_{1f}y_R P}{k_{2f} + k_{1b} + k_{1f}y_R P} \quad (4.67)$$

Physically, this shows the surface coverage fraction is simply the ratio of the adsorption reaction to the total sum of parallel reactions. Then the current density  $i$  becomes

$$i = nFk_{2f}\theta = nFk_{2f} \left( \frac{k_{1f}y_R P}{k_{2f} + k_{1b} + k_{1f}y_R P} \right) \quad (4.68)$$

Now we seek to relate this expression to the overpotential required to produce that current density at the electrode of interest, so that we can predict electrode overpotential as a function of current density in a similar fashion as with the BV approach for electron-transfer-limited reactions. The electrochemical reaction rate constant  $k_{2f}$  can be written as

$$k_{2f} \left( \frac{1}{s} \right) = \frac{i_o}{nF} \exp \left( \frac{\alpha nF}{R_u T} \eta \right) \quad (4.69)$$

where  $i_o$  is the exchange current density at  $\theta = 1$ . Using Eq. (4.68), we can achieve our desired result, an explicit expression for electrode overpotential as a function of current density and other measurable parameters for an adsorption-limited electrochemical reaction under the Langmuir model:

$$\eta = \frac{R_u T}{\alpha nF} \ln \left[ \frac{i}{i_o} \frac{nF (k_{1b} + k_{1f}y_R P)}{(nRk_{1f}y_R P - i)} \right] \quad (4.70)$$

The reaction rates required for solution would be determined from existing literature or from direct experimental results.