Lecture #7. Fall, 2012
Electrochemical Energy Engineering

Electroactive layers and modified electrodes (Ch. 14)

Types, preparation, & properties of films & modified electrodes
Substrates
Monolayers
Polymers
Inorganic films
Biological related materials
Composite & multilayer assemblies
Electrochemical responses of adsorbed monolayers
Overview of processes at modified electrodes
Blocking layers
Other methods of characterization

Introduction

Chemically modified electrodes: electroactive monolayers & thicker films on conductive substrates

→ fuel cells, batteries, electrochromic devices, active displays, corrosion protection, molecular electronic devices, sensors and so on

Types, preparation, & properties of films & modified electrodes

Substrate

Metal (Pt, Au), carbon, semiconductor (SnO_2 etc),

→ single crystals, films, high surface area small particles

Monolayers

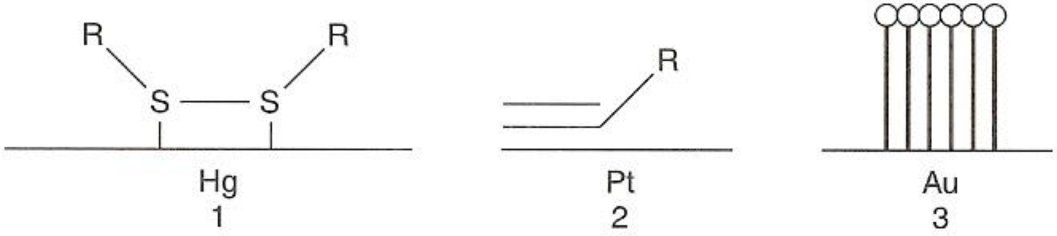
(a) Irreversible adsorption

Substrate environment is energetically more favorable than that in solution

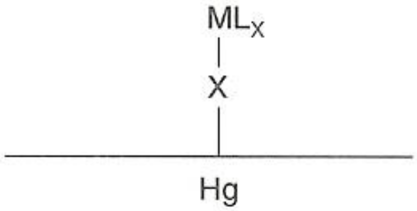
S-containing compds on Hg, Au, other metal surfaces because metal-S interactions

Halides, SCN^-, CN^- & organic compds on metal & carbon surfaces

Functional groups on metal or carbon via oxidation



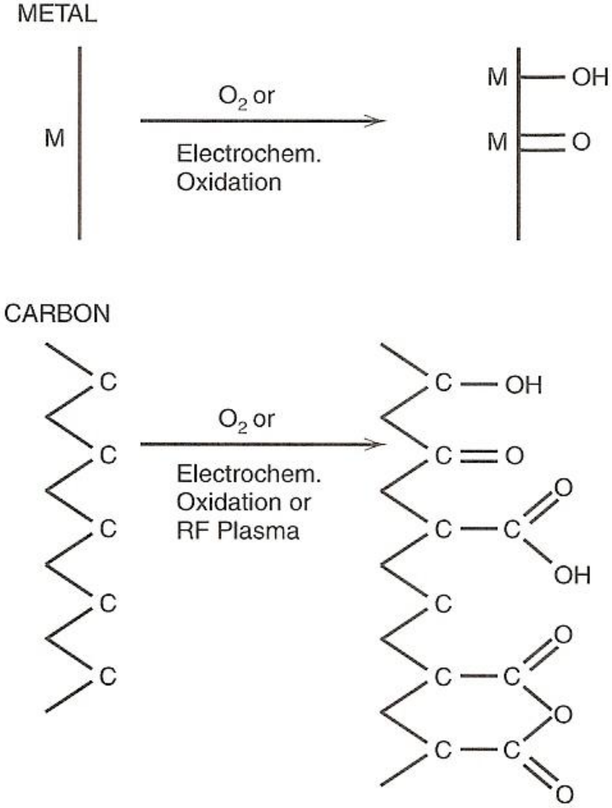
(*a*)



$X = Cl^-, Br^-, I^-, SCN^-$

$M = Cd^{2+}, Zn^{2+}$

(*b*)

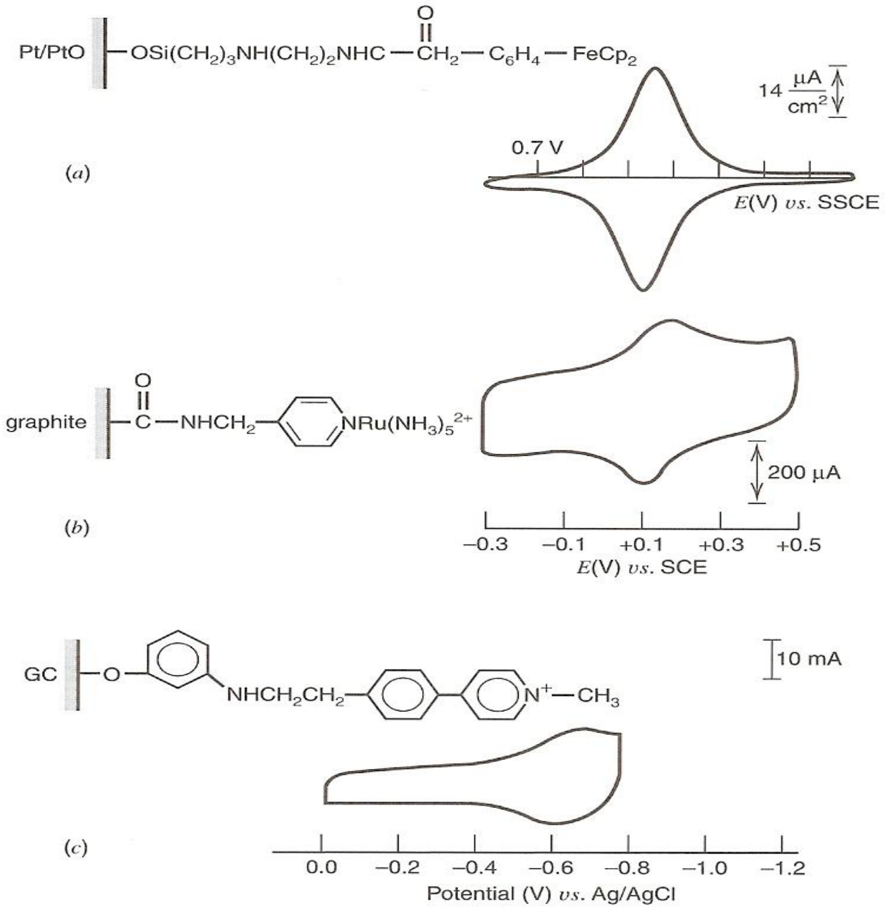


(b) Covalent attachment

Strong attachment to the substrate by covalent linking of the desired component to surface groups

→ covalent linking procedures employ organosilanes & other linking agents

Ferrocenes, viologens, $M(bpy)_x^{n+}$ (M = Ru, Os, Fe)



(c) Organized assemblies

Monolayers of surface-active compds (*langmuir-Blodgett (LB) films*) can be transferred from liquid/air interface to a substrate surface

Self-assembly as a spontaneous process

e.g., organosulfur (e.g., thiol) compds with long chain alkyl groups on Au

Polymers

(a) Types

Electroactive polymers: oxidizable or reducible groups covalently linked to the polymer backbone. e.g., poly(vinylferrocene), polymerized $Ru(vbpy)_3^{2+}$

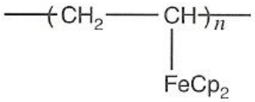
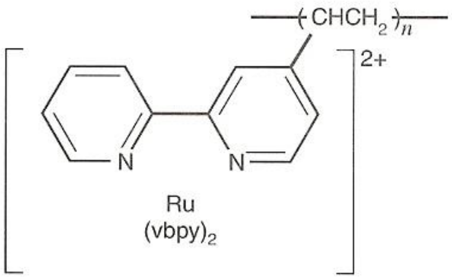
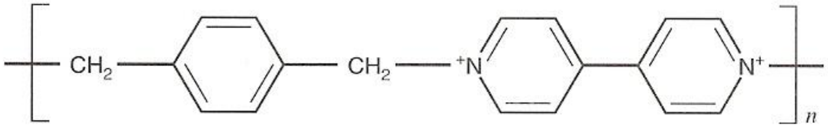
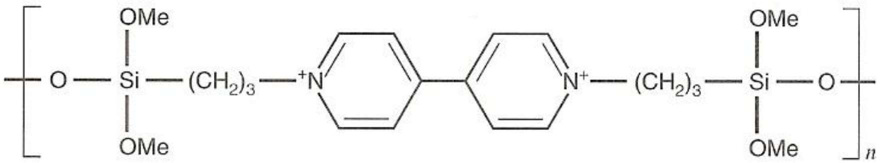
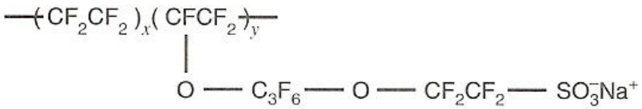
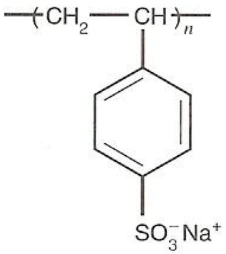
Coordinating (ligand-bearing) polymers: contain groups that can coordinate to species like metal ions. e.g., poly(4-vinylpyridine)

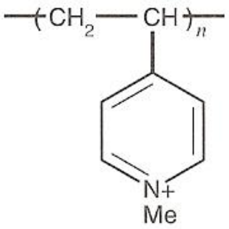
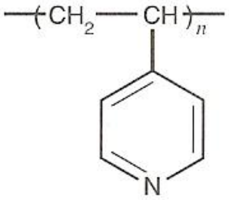
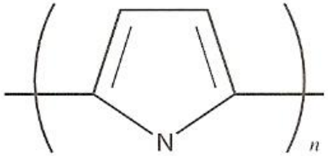
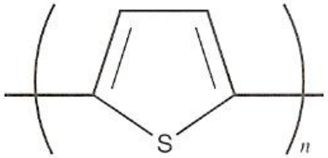
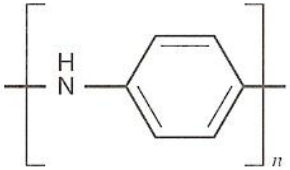
Ion-exchange polymers (polyelectrolytes): contain charged sites that can bind ions from solution via an ion-exchange process. e.g., Nafion, polystyrene sulfonate

Electronically conductive polymers

Biological polymers. e.g., enzymes & other proteins

Blocking polymers: formed from the monolayers, such as by oxidation of phenols, to produce impermeable layers and blocked or passivated surfaces

Name	Structure	Abbreviation
	Electroactive Polymers	
Poly(vinylferrocene)	 $-(\mathrm{CH_2}-\underset{\substack{\vert \\ \mathrm{FeCp_2}}}{\mathrm{CH}})_n-$	PVF
Poly[Ru(vbpy)$_3^{2+}$][b]		
Poly(xylylviologen)		
Polymerized viologen organosilane		PQ^{2+}
	Ion-exchange Polymers (Polyelectrolytes)	
Nafion	 $-(\mathrm{CF_2CF_2})_x(\underset{\substack{\vert \\ \mathrm{O-C_3F_6-O-CF_2CF_2-SO_3^-Na^+}}}{\mathrm{CF}}\mathrm{CF_2})_y-$	NAF
Poly(styrenesulfonate)		PSS

Name	Structure	Abbreviation
	Ion-exchange Polymers (Polyelectrolytes)	
Quaternized poly (4-vinylpyridinium)		QPVP
	Coordinating Polymer	
Poly(4-vinylpyridine)		PVP
	Electronically Conducting Polymers[c]	
Polypyrrole		PP
Polythiophene		PT
Polyaniline		PANI

(b) Preparation

Polymer films on an electrode surface from solution or either the polymer or the monomer

Dissolved polymer: cast or dip coating, spin coating, electrodeposition, covalent attachment via functional groups

From monomer to films by thermal, electrochemical, plasma, or photochemical polymerization

Inorganic films

(a) Metal oxides

By anodization of metal electrodes.

e.g., Al_2O_3 on Al anode in H_3PO_4 solution, Ti, W, Ta oxides

Film thickness can be controlled by the applied potential & anodization time

By CVD, vacuum evaporation, sputtering, deposition from colloidal solution

e.g., metallic polyanionic species (e.g., of W, Mo, V): electrocatalysis

(b) Clays and zeolites

High stability & low cost, catalytic properties

(c) Transition-metal hexacyanides

Thin films of materials such as Prussian Blue (PB) (a lattice of ferric ferrocyanide)

→ deposited by electrochemical reduction in a solution of $FeCl_3$ & $K_3Fe(CN)_6$

→ blue film, $KFe^{III}Fe^{II}(CN)_6$ can be oxidized in a KCl solution to form $Fe^{III}Fe^{III}(CN)_6$ (Berlin Green) and reduced to form $K_2Fe^{II}Fe^{II}(CN)_6$ (Everitt's salt)

→ PB electrodes show electrocatalytic properties (e.g., for the reduction of oxygen) & color change (for electrochromic applications)

Biological related materials

Immobilization of a biologically sensitive coating (e.g., an enzyme, antibody, DNA) which can interact with ("recognize") a target analyte, and produce an electrochemically detectable signal → biosensors applications

Bacteria and tissue

Immobilization: permeable polymer membrane, entrapment in a gel, encapsulation, adsorption, covalent linkage

Composite and multilayer assemblies

Multiple films of different polymers (e.g., bilayer structures)

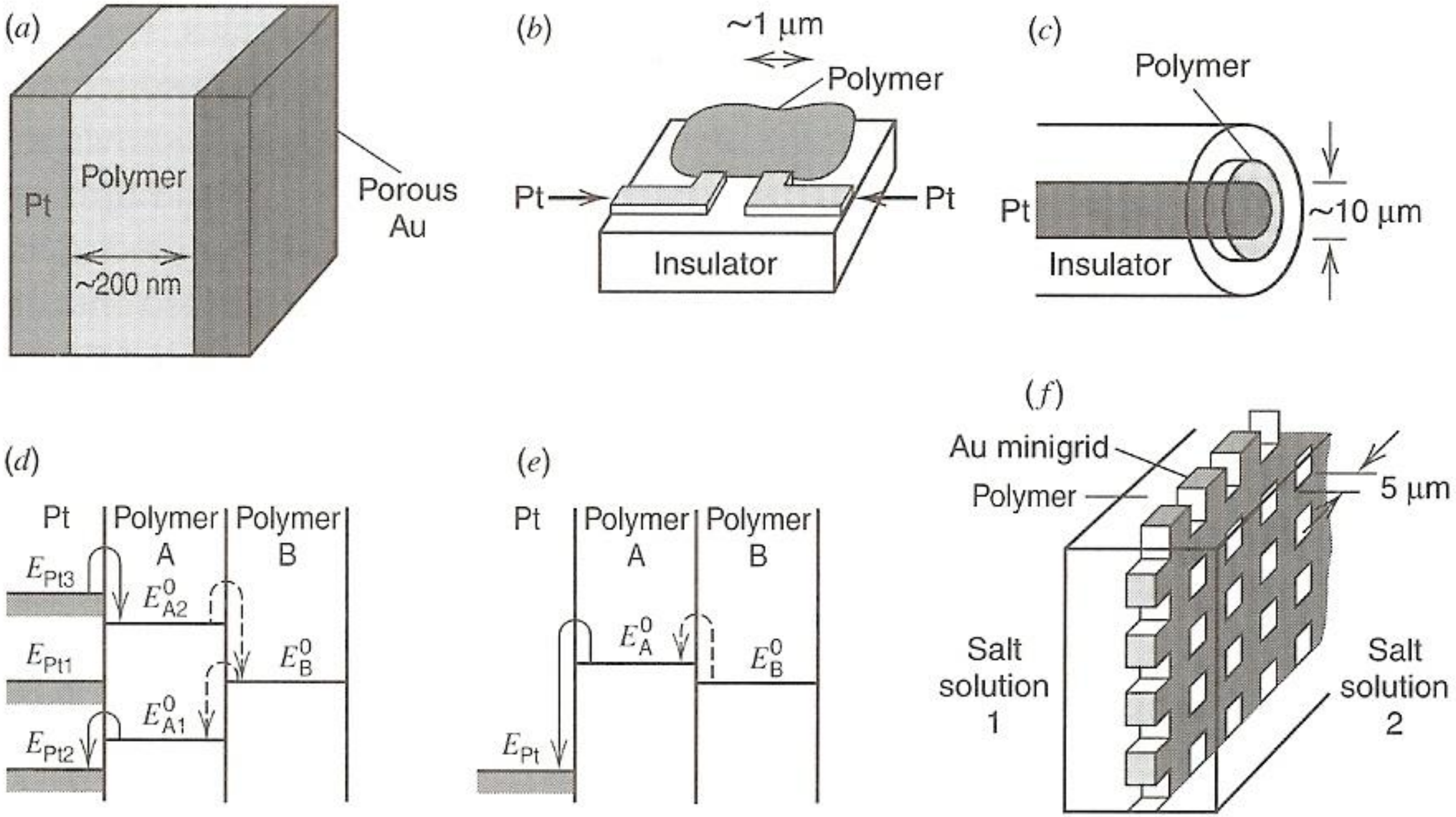
Metal films on a polymer layer (sandwich structures)
Multiple conductive substrates under the polymer film (electrode arrays)
Intermixed films of ionic and electronic conductor (biconductive layers)
Polymer layers with porous metal or minigrid supports (solid polymer electrolyte or ion-gate structures)

Porous metal films (e.g., Au or Pt) can be deposited on free-standing polymer membranes or on polymer films on an electrode surface by chemical reduction or by evaporation in vacuum

e.g., Porous Pt on Nafion from $PtCl_6^{2-}$ & reducing agent (e.g., hydrazine)

→ fuel cell etc

(a) Sandwich electrode, (b) array electrode, (c) microelectrode, (d,e) bilayer electrode, (f) ion-gate electrode



Electrochemical responses of adsorbed monolayers

Principles

Effect of O + ne → R by the adsorption of O or R

Net reaction involves the electrolysis of diffusing O as well as O adsorbed on the electrode, to produce R that diffuse away and R remains adsorbed

General flux equation

$$D_O[\partial C_O(x,t)/\partial x]_{x=0} - \partial \Gamma_O(t)/\partial t = -[D_R(\partial C_R(x,t)/\partial x)_{x=0} - \partial \Gamma_R(t)/\partial t] = i/nFA$$

where $\Gamma_O(t)$ & $\Gamma_R(t)$ are the amounts of O & R adsorbed at time t (mol/cm^2)

→ Γ vs. C equation required

Assume Langmuir isotherm ((13.5.9), (13.5.10))

$$\Gamma_O(t) = \beta_O\Gamma_{O,s}C_O(0,t)/[1 + \beta_O C_O(0,t) + \beta_R C_R(0,t)]$$

$$\Gamma_R(t) = \beta_R\Gamma_{R,s}C_R(0,t)/[1 + \beta_O C_O(0,t) + \beta_R C_R(0,t)]$$

Initial conditions

$$(t = 0) \quad \Gamma_O = \Gamma_O^* \qquad \Gamma_R = 0$$

Cyclic voltammetry: only adsorbed O & R electroactive- nernstian reaction

Assume that the contribution to the current from dissolved O is negligible

$$-\partial\Gamma_O(t)/\partial t = -\partial\Gamma_R(t)/\partial t = i/nFA$$

$$\Gamma_O(t) + \Gamma_R(t) = \Gamma_O^*$$

$$\Gamma_O(t)/\Gamma_R(t) = \beta_O\Gamma_{O,s}C_O(0,t)/\beta_R\Gamma_{R,s}C_R(0,t) = b_OC_O(0,t)/b_RC_R(0,t)$$

With $b_O = \beta_O\Gamma_{O,s}$, $b_R = \beta_R\Gamma_{R,s}$

If the rxn is nernstian

$$C_O(0,t)/C_R(0,t) = \exp[(nF/RT)(E - E^{0\prime})]$$

→ $$\Gamma_O(t)/\Gamma_R(t) = (b_O/b_R)\exp[(nF/RT)(E - E^{0\prime})]$$

$$i/nFA = -\partial\Gamma_O(t)/\partial t = [\partial\Gamma_O(t)/\partial E]v$$

$E = E_i - vt$

i-E curve

$i = (n^2F^2/RT)(vA\Gamma_O^*(b_O/b_R)\exp[(nF/RT)(E-E^{0\prime})] /\{1 + (b_O/b_R)\exp[(nF/RT)(E-E^{0\prime}]\}^2)$

cf. similar with thin-layer cell (Ch.11)

The peak current

$$i_p = (n^2F^2/4RT)vA\Gamma_O^*$$

The peak potential

$$E_p = E^{0\prime} - (RT/nF)\ln(b_O/b_R) = E_a^{0\prime}$$

Peak current <u>is proportional to v</u> (in contrast $v^{1/2}$ dependence for diffusing species)

Proportionality betwn i & v = purely capacitive current ((6.2.25))

→ adsorption in terms of "pseudocapacitance"

→ reduction area = charge required for full reduction of the layer: $nFA\Gamma_O^*$

Anodic wave on scan reversal: mirror of the cathodic wave

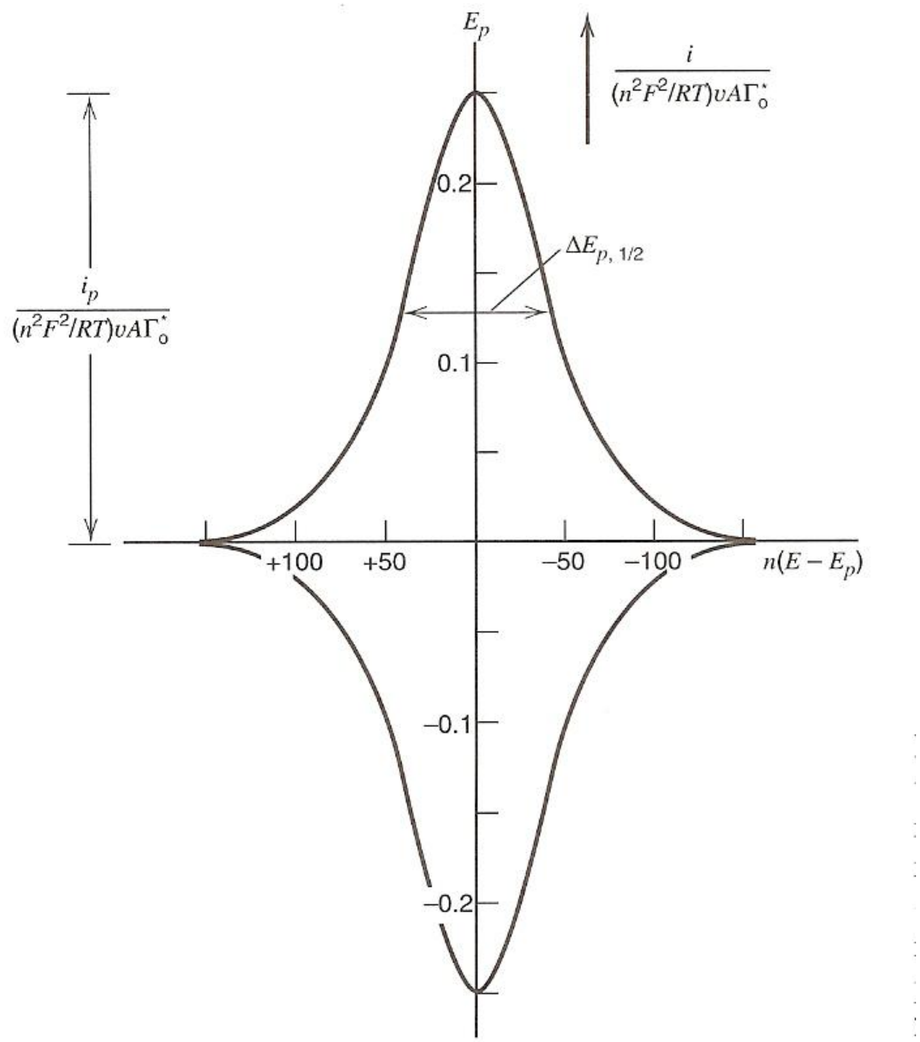
For ideal nernstian rxn under Langmuir isotherm: $E_{pa} = E_{pc}$

→ total width at half-height of either cathodic or anodic wave

$$\Delta E_{p,1/2} = 3.53(RT/nF) = 90.6/n\text{ mV } (25°\text{C})$$

Location of E_p with respect to $E^{0\prime}$ depend on the relative strength of adsorption of O & R → if $b_O = b_R$, $E_P = E^{0\prime}$

If O is adsorbed more strongly ($b_O > b_R$), the wave displaced toward negative potentials ('postwave")



If R is adsorbed more strongly ($b_O < b_R$), the wave displaced toward positive potentials (‘prewave”)

When lateral interactions exist betwn O & R in the film

→ the shape of i-E curve depends upon the energies of the interactions of O with O, R with R, O with R

If a Frumkin-type isotherm

$$\exp[(nF/RT)(E - E^{0'})] = (\theta_O/\theta_R)\exp[2\nu\theta_O(a_{OR} - a_O) + 2\nu\theta_R(a_R - a_{OR})]$$

where a_{OR}, a_O, and a_R: O-R, O-O, and R-R interaction parameters ($a_i > 0$ for an attractive interaction, $a_i < 0$ for a repulsive one)

ν: # of water molecules displaced from the surface by adsorption of one O or R

A θ_O & θ_R: fractional coverages of O & R

$$i = (n^2F^2A\nu\Gamma_O^*/RT)\{\theta_R(1 - \theta_R)/[1 - 2\nu g\theta_T\theta_R(1 - \theta_R)]\}$$

where $\theta_T = \theta_O + \theta_R$, $g = a_O + a_R - 2a_{OR}$, $\Gamma_O^* = \Gamma_O + \Gamma_R$, $\theta_i = \Gamma_i/\Gamma_O^*$

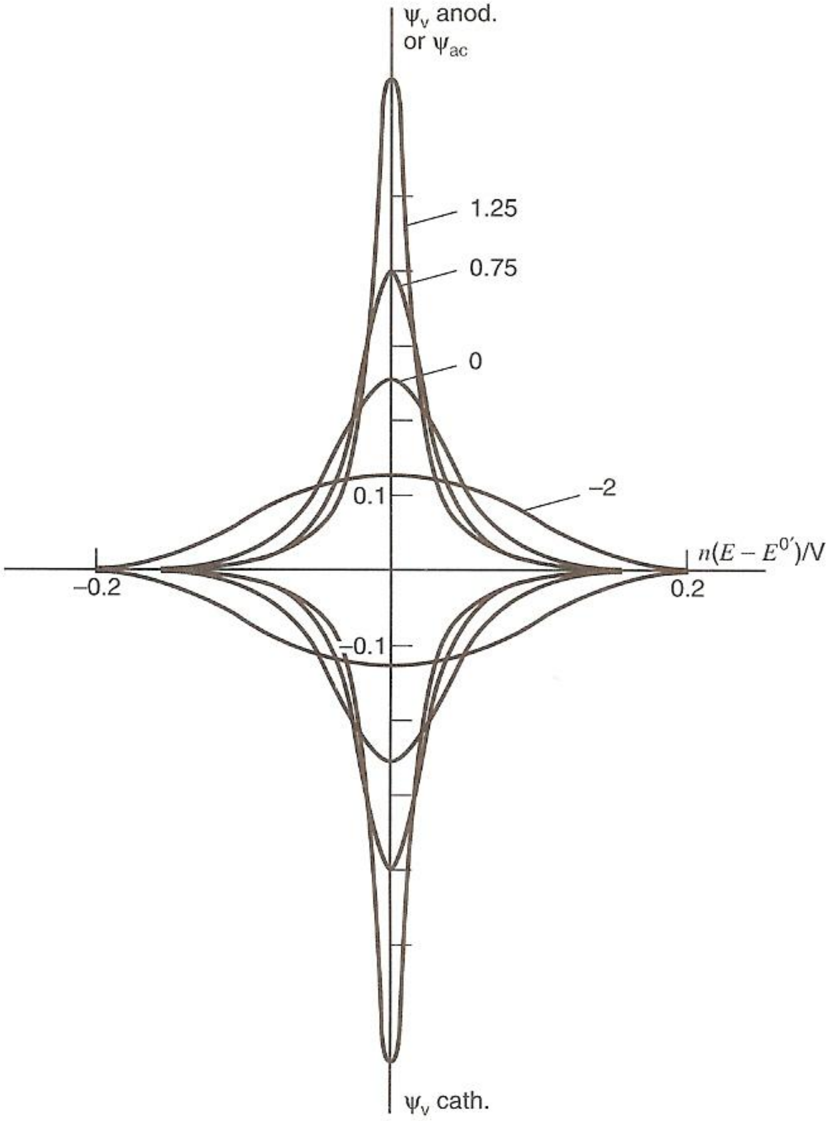
Potential variation arises through the variation of θ_R with E

i-E curve shape is governed by the interaction parameter, $\nu g\theta_T$

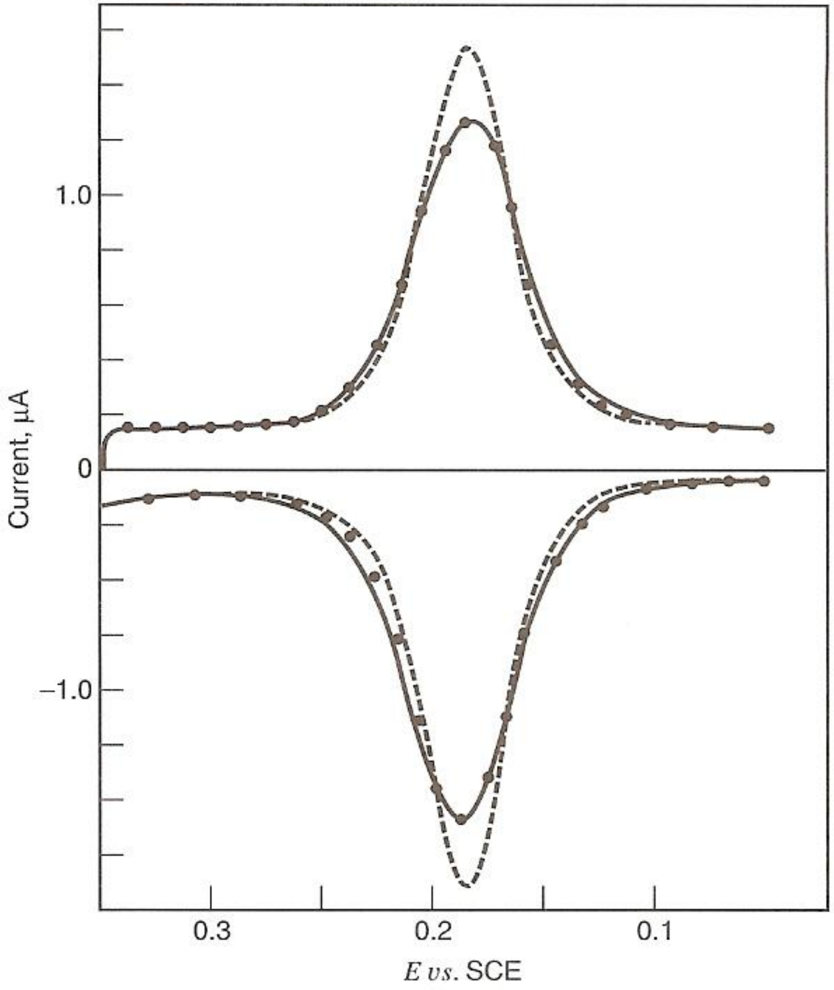
$\nu g\theta_T = 0$ (Langmuir form, Figure in previous page), $\Delta E_{p,1/2} = 90.6/n$ (25°C)

When $\nu g\theta_T > 0$: $\Delta E_{p,1/2} < 90.6/n$, when $\nu g\theta_T < 0$, $\Delta E_{p,1/2} > 90.6/n$

Effect of interactions (Frumkin isotherm assumed):
$\nu g \theta_T$ values (0 → same as the previous figure)



Experimental (solid line) vs. theoretical (dotted line)
Reduction & reoxidation of 9,10-phenanthrenequinone irreversibly adsorbed on carbon electrode ($\Gamma_O = 1.9 \times 10^{-10}$ mol/cm^2)



Cyclic voltammetry: both dissolved & adsorbed species electroactive

Adsorption isotherms + diffusion equation

Consider only <u>nernstian</u> electron-transfer rxn case

(a) Product (R) strongly adsorbed

$\beta_O \rightarrow 0$ & β_R large (i.e., $\beta_R C^* \geq 100$)

Initially $C_O = C_O^*$, $C_R = 0$, $\Gamma_R^* = 0$

Variation of β_R with E

$$\beta_R = \beta_R^0 \exp[(\sigma_R nF/RT)(E - E_{1/2})]$$

where σ_R: parameter for ΔG_i^0 variation with E; $\sigma_R = 0 \rightarrow \beta_R$ is independent of E

→ prewave (or prepeak): same shape (sec (14.3.2)

→ reduction of dissolved O to form adsorbed R

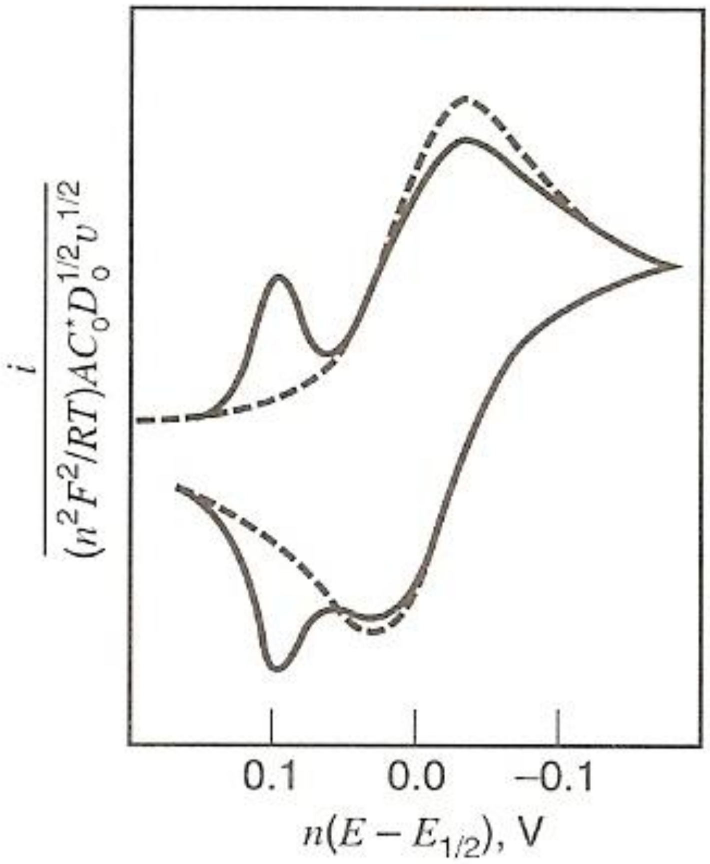
(at E more positive than diffusion-controlled wave

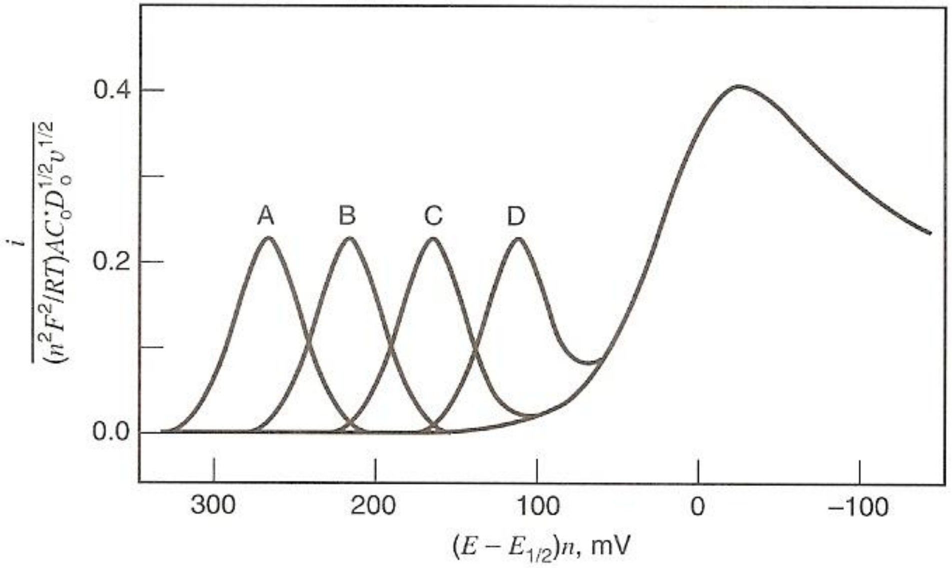
because free E adsorbed R easier than R in soln)

→ then wave for reduction of dissolved O to dissolved R

(perturbed by the depletion of species O during reduction)

The larger β_R → the more the prepeak precedes the diffusion peak



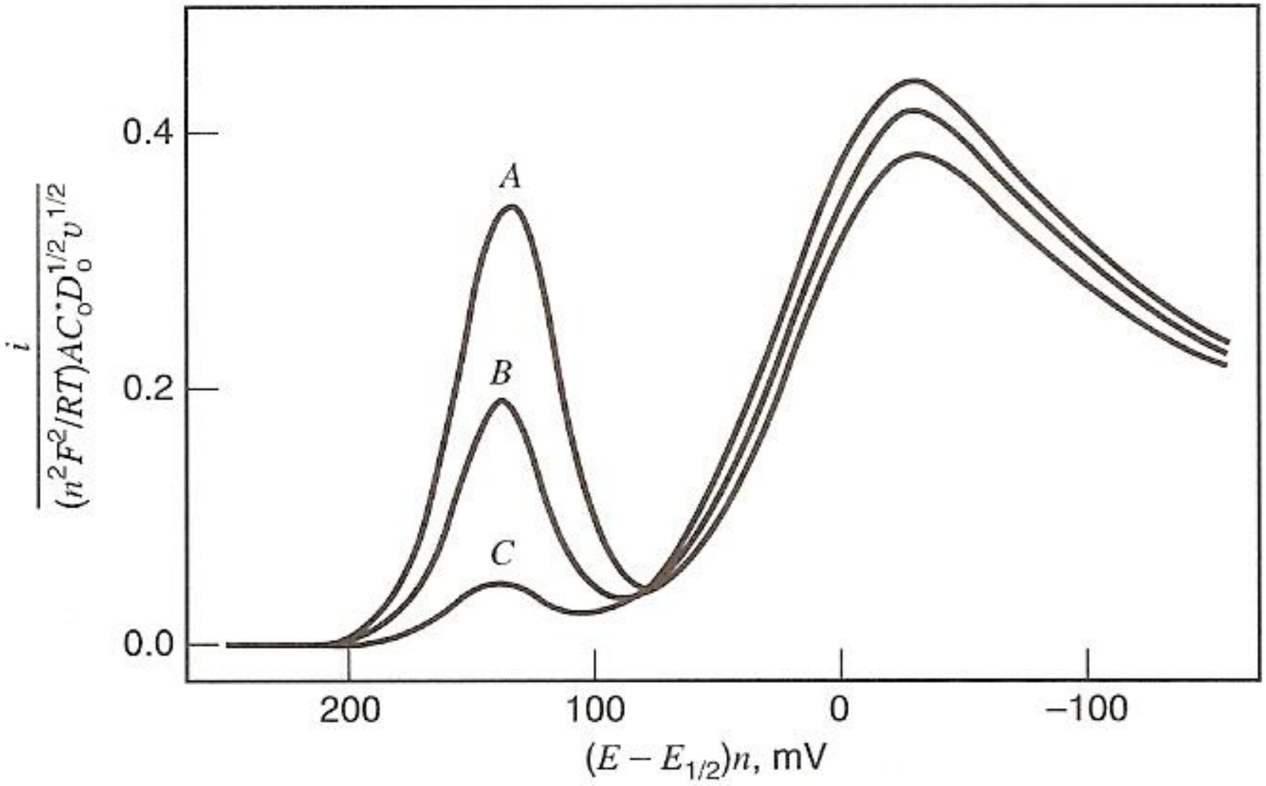


Dashed line:
in the absence of adsorption

β_R : A > B > C > D

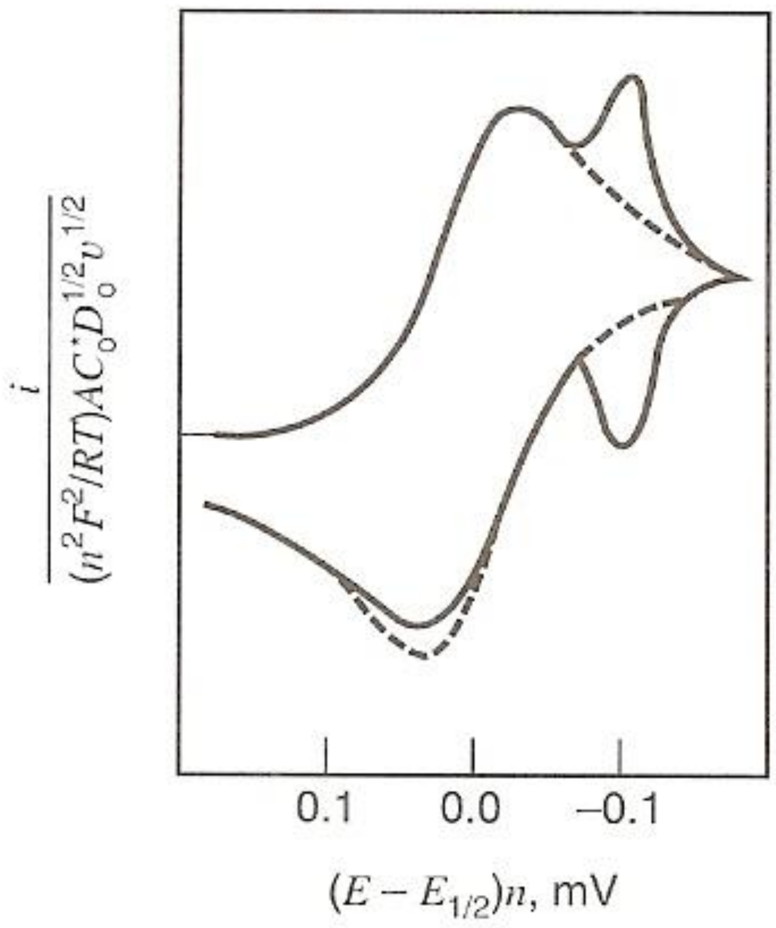
$(i_p)_{ads}$ increases with v & $(i_p)_{diff}$ with $v^{1/2}$ → $(i_p)_{ads}/(i_p)_{diff}$ increases with $v^{1/2}$

Relative scan rate: A > B > C (64:16:1)



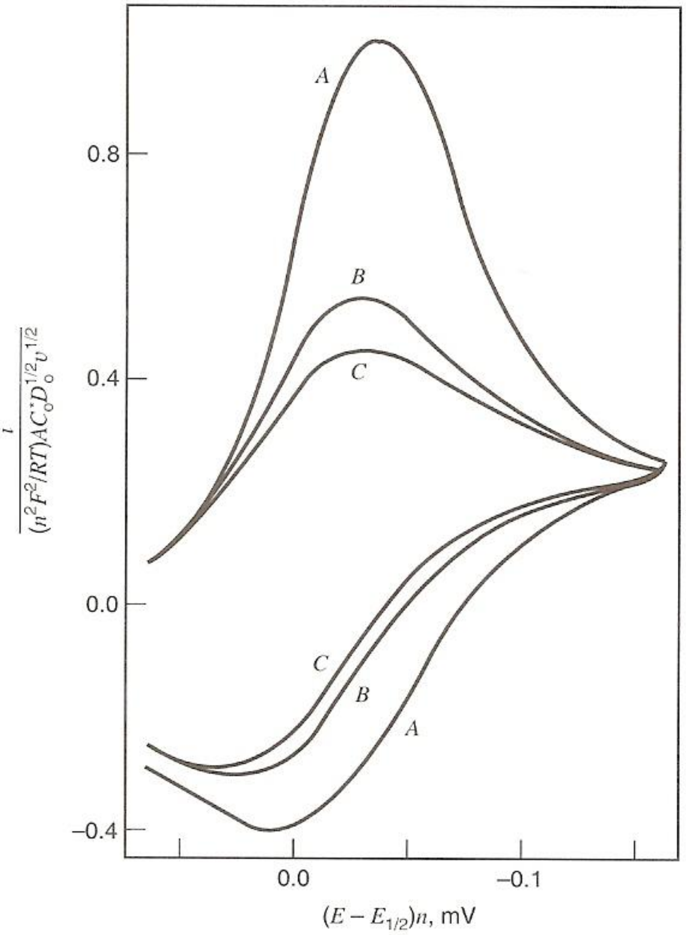
(b) Reactant (O) strongly adsorbed ($\beta_R \rightarrow 0$ & β_O large (i.e., $\beta_O C_O^* \geq 100$)

Postwave (or *postpeak*) for the reduction of adsorbed O, following the peak for the diffusion-controlled reduction of O to R in solution



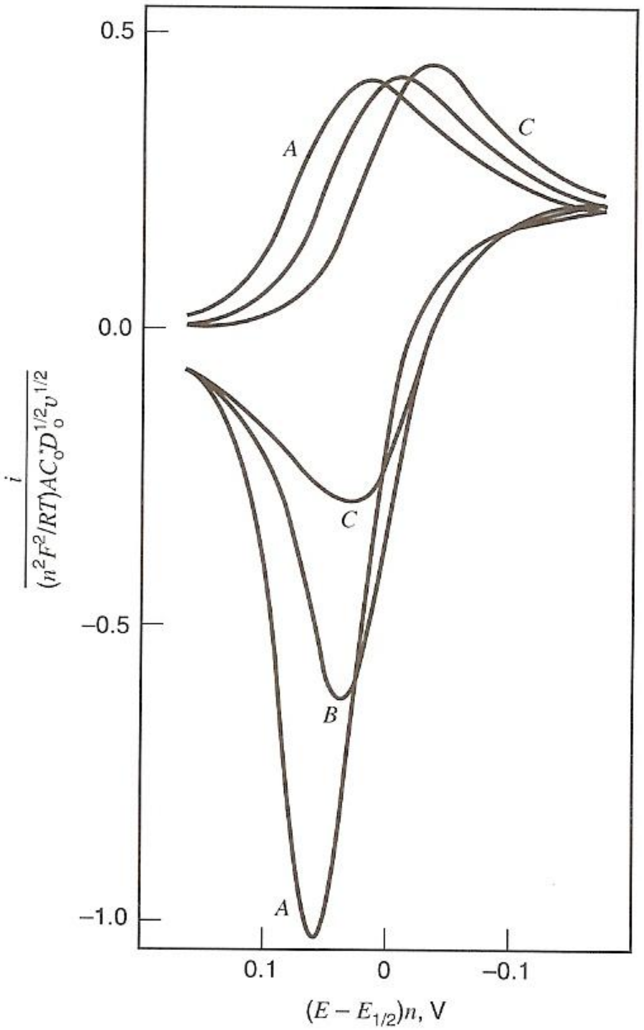
(c) Reactant (O) weakly adsorbed ($\beta_R \rightarrow 0$ & $\beta_O C_O^* \leq 2$)

When adsorption is weak the difference in energies for reduction of adsorbed & dissolved O is small → a separate postwave is not observed → an increase in cathodic peak current because both adsorbed and diffusing O contribute to the current



(d) Product (R) weakly adsorbed ($\beta_O \rightarrow 0$ & $\beta_R C_O^* \leq 2$)

A separate prewave is not observed → an increase in anodic peak current



Overview of processes at modified electrodes

A: a species in solution

P: reducible substance in a film

(1) Heterogeneous e-transfer to P to produce
the reduced form Q

(2) e-transfer from Q to another P in film
(e diffusion or e hopping in film)

(3) e-transfer from Q to A
at film/solutionn interface

(4) Penetration of A into the film

(5) Movement (mass transfer) of Q
within the film

(6) Movement of A through
a pinhole or channel