

Electrochemistry

CHEM 5390

Electrical Double Layer

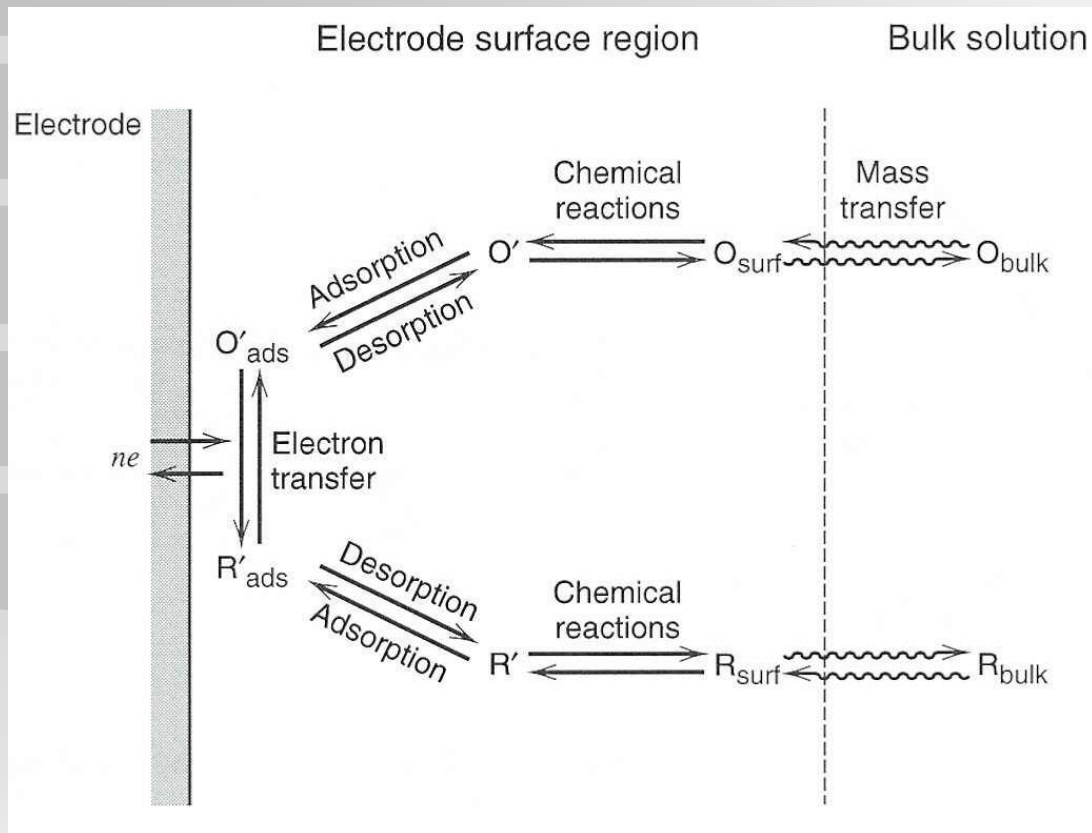


Figure 1.3.6 Pathway of a general electrode reaction.

Mass Transfer

Nernst-Planck Equation

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

$J_i(x)$ – flux of species i (mol/s cm²) at distance x from surface.

D_i – diffusion coefficient (cm²/s)

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

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

z_i and C_i – charge (dimensionless) and concentration (mol/cm³) of species i

$v(x)$ – velocity (cm/s)

Mass Transfer

Diffusion

Boundary Conditions

For an electrochemical problem, a diffusion equation is written for each dissolved species. The equation for C_O , $C_R, \dots$ as a function of x and t requires an initial condition (concentration profile at $t = 0$) and two boundary conditions (functions at certain values of x).

Mass Transfer

Diffusion

Boundary Conditions

Initial Conditions

Example:

If O is uniform through the solution at start of experiment:

$$C_O(x,0) = C_O^* \quad (\text{for all } x)$$

If R is initially absent in the solution:

$$C_R(x,0) = 0 \quad (\text{for all } x)$$

Mass Transfer

Diffusion

Boundary Conditions

Semi-Infinite Boundary Conditions

Cell is large compared to the length of diffusion, at large distances from the electrode ($x \rightarrow \infty$), the concentration reaches a constant value.

$$\lim_{x \rightarrow \infty} C_O(x,t) = C_O^* \quad (\text{at all } t)$$

$$\lim_{x \rightarrow \infty} C_R(x,t) = 0 \quad (\text{at all } t)$$

Mass Transfer

Diffusion

Boundary Conditions

Electrode-Surface Boundary Conditions

At electrode surface, under potential control possible to have:

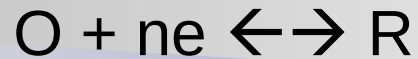
$$C_O(0,t) = f(E) \quad \text{or}$$

$$C_O(0,t)/C_R(0,t) = f(E)$$

$f(E)$ – function of the electrode potential

Mass Transfer

Steady State Mass Transfer



When electrolysis starts, $[O]$ at electrode surface, $C_o(x = 0)$ becomes smaller than value in the bulk, C_o^* .

Mass Transfer

Steady State Mass Transfer

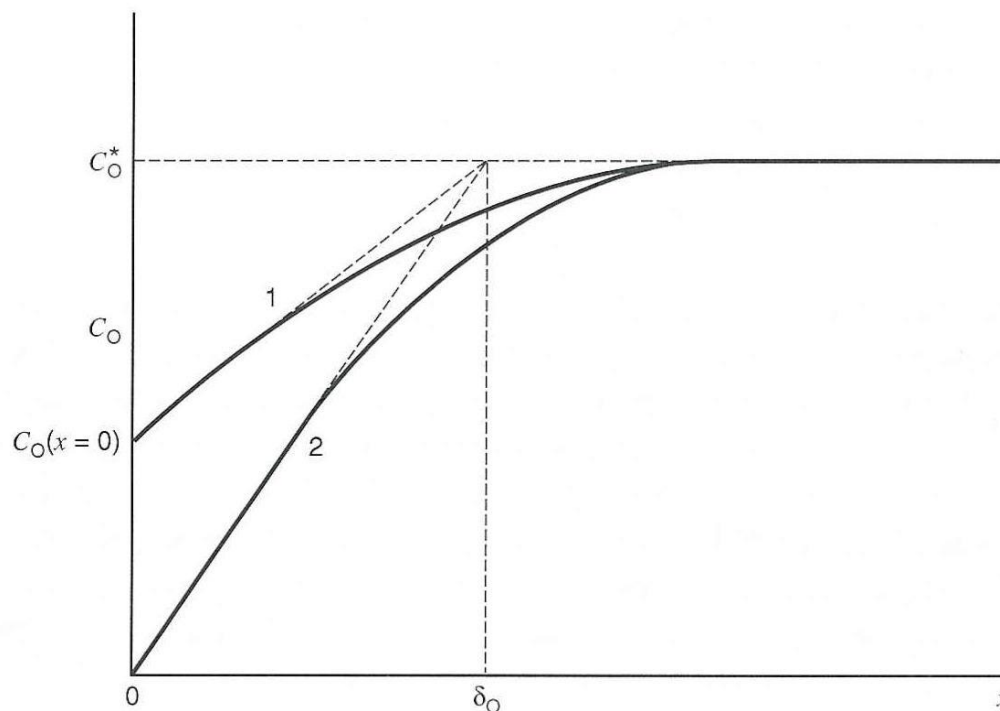


Figure 1.4.1 Concentration profiles (solid lines) and diffusion layer approximation (dashed lines). $x = 0$ corresponds to the electrode surface and δ_O is the diffusion layer thickness. Concentration profiles are shown at two different electrode potentials: (1) where $C_O(x = 0)$ is about $C_O^*/2$, (2) where $C_O(x = 0) \approx 0$ and $i = i_l$.

Mass Transfer

Steady State Mass Transfer

For a positive reduction current:

$$\frac{i}{nFA} = m_O[C_O^* - C_O(x = 0)]$$

m_O – mass transfer coefficient (cm/s) $m_O = D_O/\delta_O$

D_O – diffusion coefficient

δ_O – diffusion layer thickness

$$\frac{i}{nFA} = m_R[C_R(x = 0) - C_R^*]$$

Mass Transfer

Steady State Mass Transfer

If no R in bulk then:

$$\frac{i}{nFA} = m_R C_R(x = 0)$$

At the highest rate of mass transfer:

$$i_l = nFAm_O C_O^*$$

i_l – limiting current

At limiting current, the electrode process is occurring at the maximum rate possible.

Mass Transfer

Steady State Mass Transfer

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{C_O(x=0)}{C_R(x=0)}$$

$E^{0'}$ – formal potential – the adjusted standard potential (E^0) – using activity coefficients.

Above Equation for Nernstian reaction (kinetics of electron transfer rapid)

Mass Transfer

Steady State Mass Transfer

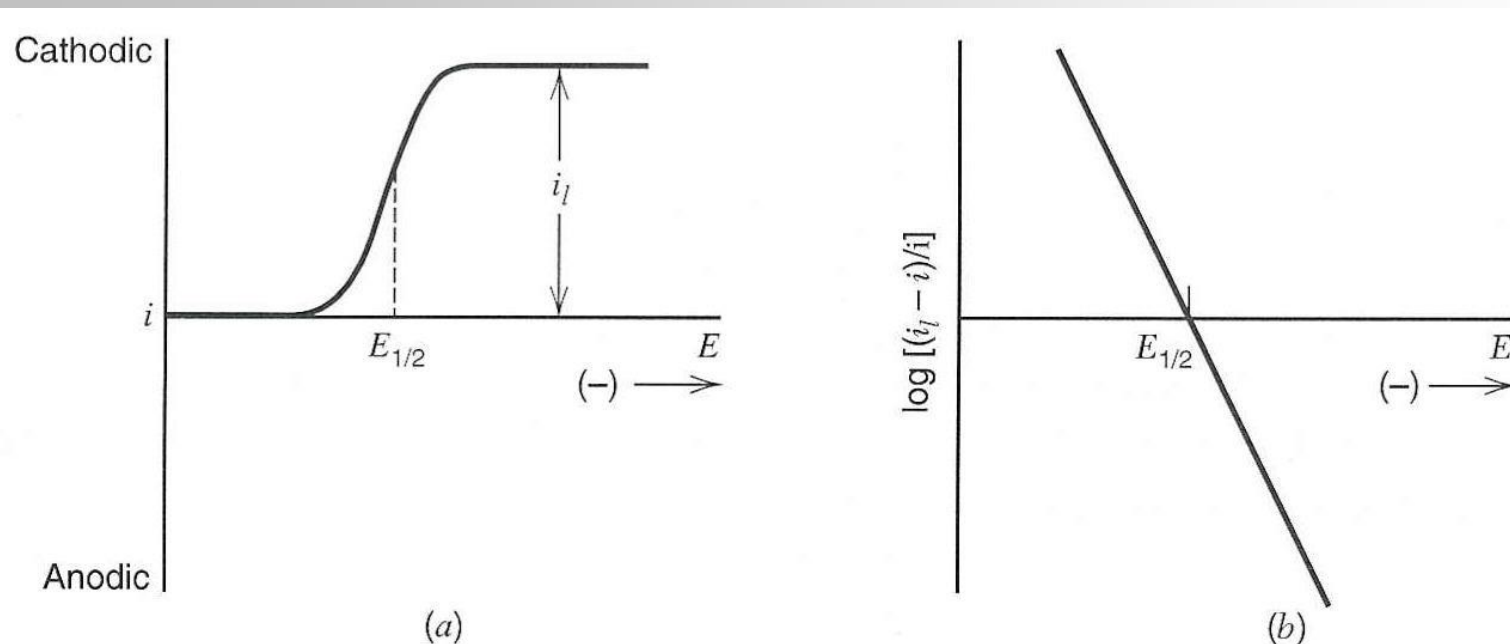


Figure 1.4.2 (a) Current-potential curve for a nernstian reaction involving two soluble species with only oxidant present initially. (b) $\log[(i_l - i)/i]$ vs. E for this system.

Mass Transfer

Steady State Mass Transfer

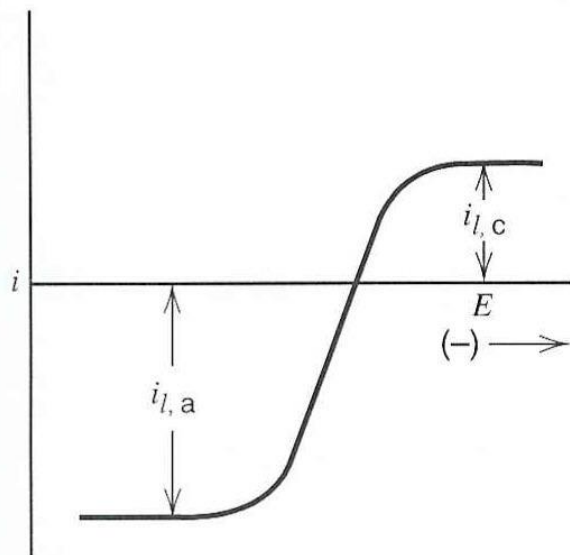


Figure 1.4.3 Current-potential curve for a Nernstian system involving two soluble species with both forms initially present.

Potential Step Methods

Quantitative Information

Alternatives

- Large amplitude step***

Potential is stepped to mass controlled region (diffusion control), so concentration at electrode is near zero, i controlled by mass transfer.

- Small-amplitude potential changes

Close to equilibrium, $i = -iof\eta$

- Reversible electrode process

$$E = E_o' + \frac{RT}{nF} \ln C_O(0,t)/C_R(0,t)$$

- Totally reversible process

k^0 is small – in tafel regions

- Quasireversible system

Much more complicated (Ch. 12)

Potential Step Methods

Potential Step Methods – have mass transport of electroactive species only by diffusion and have an electrode area, A , small compared to solution volume, so the bulk is not altered.

Potential Step Methods

Considered a large amplitude controlled potential technique.

(small amplitude techniques fall into the linear region and are useful for kinetic studies – electron transfer)

Operate in the non-linear region in which current is exponentially related to overpotential.

Useful for certain analytical problems and studies of coupled chemical reactions.

Mass Transfer

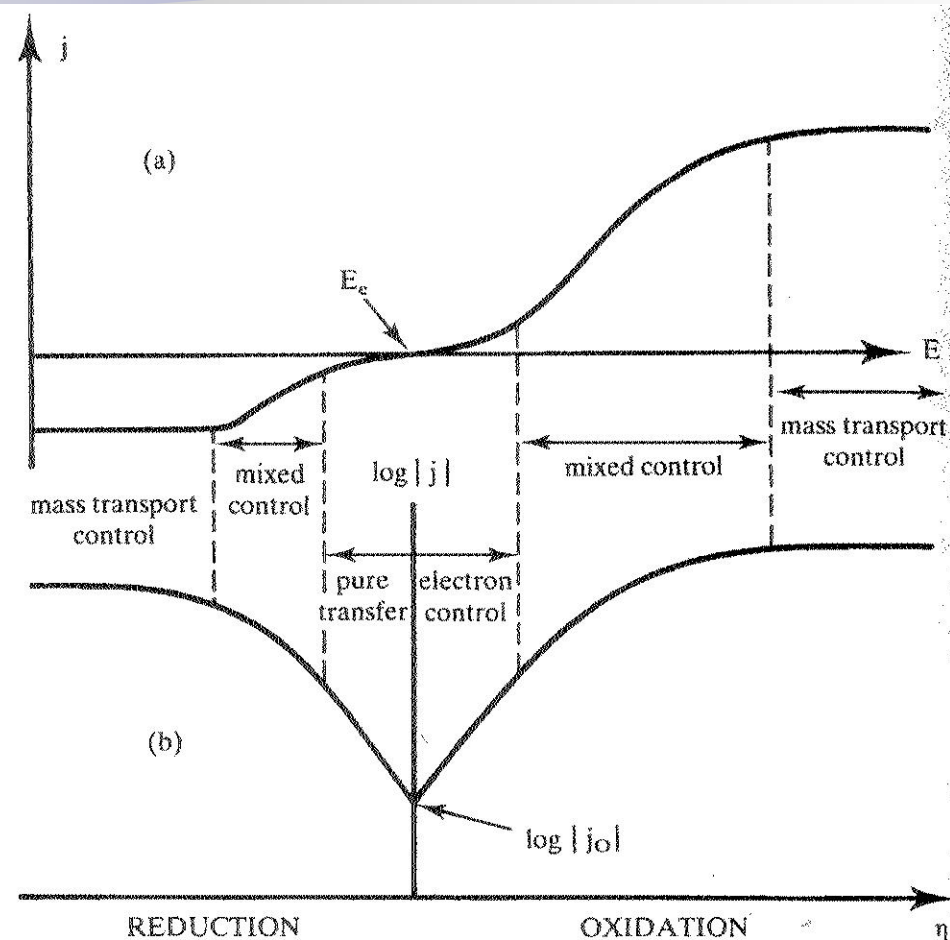


Figure 1.14 $j - E$ response and the corresponding $\log j - \eta$ curve for an irreversible electrode reaction $O + e^- \rightleftharpoons R$. $c_R = 10c_O$.

Potential Step Methods

Voltage or Potential Step

For a potential step, the current decays exponentially with time.

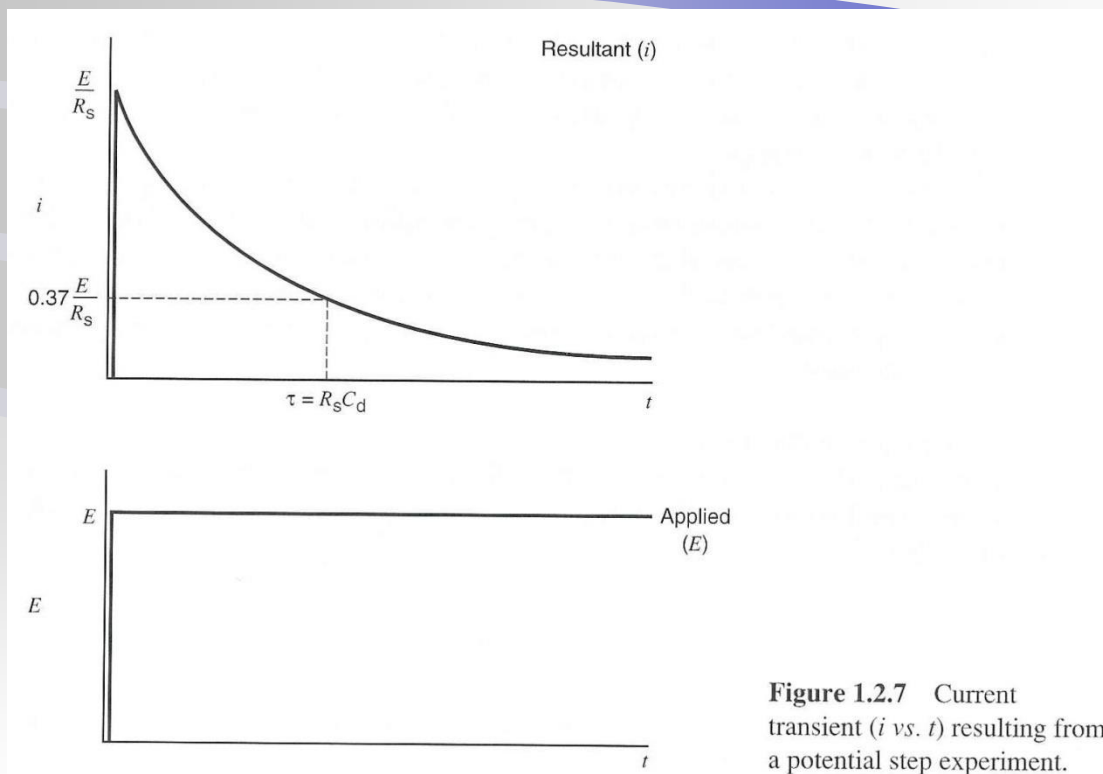


Figure 1.2.7 Current transient (i vs. t) resulting from a potential step experiment.

Potential Step Methods

Overview of Step Experiments

For controlled step experiments can record:

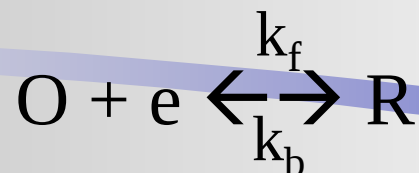
- current as a function of time (chronoamperometry)
- potential as a function of time (chronopotentiometry)
- charge as a function of time (chronocoulometry)
- absorbance as a function of time (chronoabsorptometry)

All based on the same excitation function of one or more potential (or current) steps.

Potential Step Methods

Quantitative Information

For Potential step method where:



can start with

$$i = F A k^0 [C_O(0,t) e^{-\alpha f(E - E_0)} - C_R(0,t) e^{(1 - \alpha) f(E - E_0)}]$$

and Fick's law to give time dependent surface concentrations.

Approach is difficult and may fail to yield close-form solutions.

Potential Step Methods

Potential Step under Diffusion Control

For planar electrode:

Solving the diffusion equation

$$\partial C_O(x,t)/\partial t = D_O \partial^2 C_O(x,t)/\partial x^2$$

The boundary conditions:

$$C_O(x,0) = C_O^* \text{ (initial conditions at } t = 0 \text{)}$$

$$\lim_{x \rightarrow \infty} C_O(x,t) = C_O^* \text{ (semi-infinite condition, region away from the electrode unperturbed)}$$

$$C_O(0,t) = 0 \text{ (for } t > 0, \text{ electrode surface after experiment starts)}$$

Potential Step Methods

Potential Step under Diffusion Control

For planar electrode:

$$i(t) = i(d) = (nFA D_O^{1/2} C_O^*)/(\pi^{1/2} t^{1/2})$$

Cottrell equation

Note $i(t) \propto 1/t^{1/2}$

Potential Step Methods

Cottrell equation

Limitations for the Cottrell equation

- Potentiostat limitations – output of i and V depend on instrument at high currents and at short times
- Limitations of recording device – may need oscilloscope
- Limitations imposed by R_u (uncompensated resistance) and C_d (double layer capacitance) $R_u C_d$ – cell time constant
Cell time constant defines shortest time scale for carrying out a step experiment
- Limitations caused by convection
Density gradients and stray vibrations cause disruptions of diffusion layer

Potential Step Methods

The duration of the potential step (time interval τ) is typically determined by the type of information needed about the system.

Time interval can vary from $10\ \mu\text{s}$ to several seconds.
(determined by potentiostat at short times and vibrations at longer times)

For a reversible system need to step $\sim 200\ \text{mV}$ vs E^0 , for irreversible system even larger.

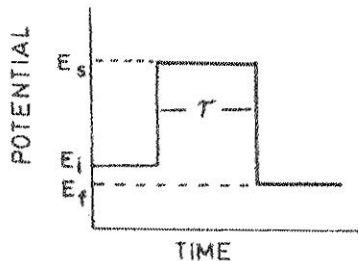


Figure 3.2 Generalized excitation signal for potential-step techniques. Step from initial potential (E_i) to step potential (E_s) to final potential (E_f). τ is the duration of the potential step at E_s .

Potential Step Methods

Concentration Profile

Diffusion layer thickness – the reach of the electrode process into the solution $\sim 6(D_o t)^{1/2}$

Diffusion layer thickness is dependent on time scale of the experiment

Potential Step Methods

Concentration Profile

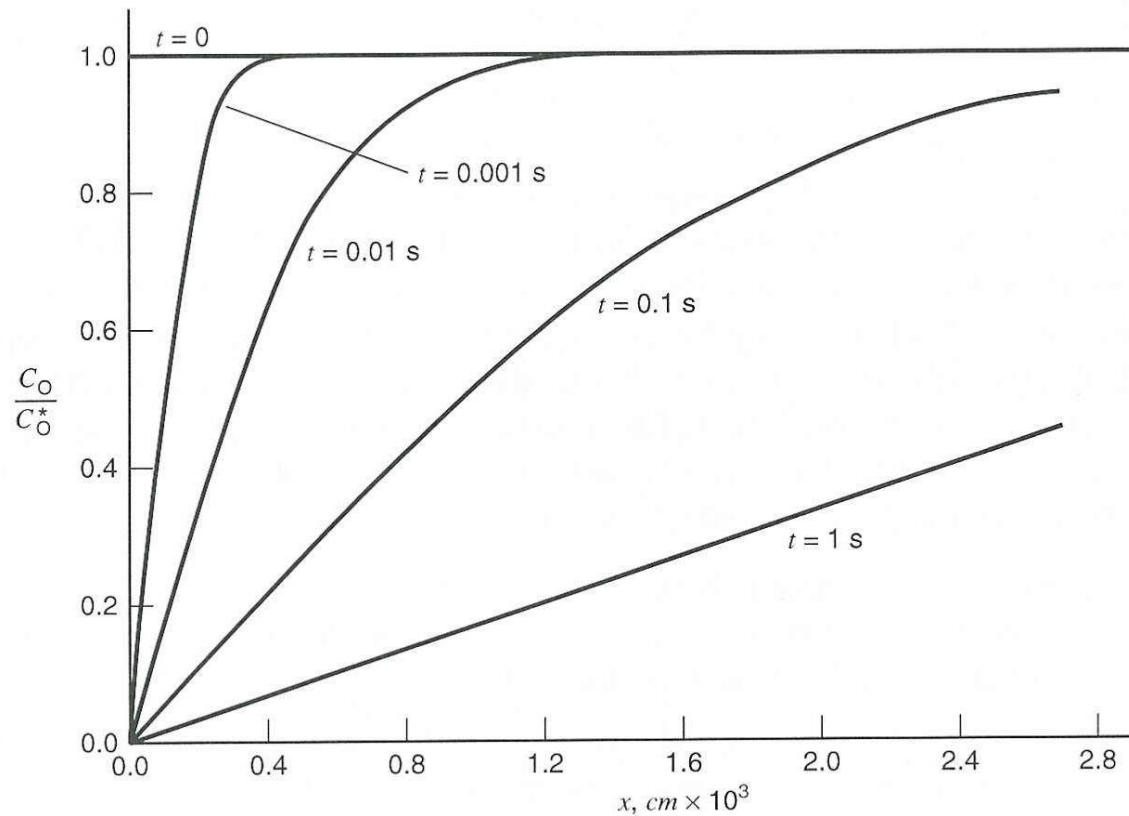


Figure 5.2.1 Concentration profiles for several times after the start of a Cottrell experiment. $D_0 = 1 \times 10^{-5} \text{ cm}^2/\text{s}$.

Potential Step Methods

Concentration Profile

For spherical electrode

The solution of the diffusion equation gives:

$$i_d(t) = nFAD_O C_O^* [1/(\pi D_O t)^{1/2} + 1/r_o]$$

r_o – radius of the electrode

Potential Step Methods

Table 10.1. Currents obtained by application of a potential step to the system $O + ne^- \rightarrow R$ with only O initially present in solution

		Current (I)
Reversible	Plane	$-\frac{nFAD[O]_{\infty}}{(1+\theta)(\pi Dt)^{1/2}}$
	Sphere	$-\frac{nFAD[O]_{\infty}}{(1+\theta)} \left[\frac{1}{(\pi Dt)^{1/2}} + \frac{1}{r_0} \right]$
Irreversible	Plane	$-nFAk_c[O]_{\infty} \exp[k_c^2 t/D] \operatorname{erfc}\left(\frac{k_c t^{1/2}}{D^{1/2}}\right)$
	Sphere	$-nFAk_c[O]_{\infty} \left[\left(1 + \frac{D}{k_c r_0}\right) \exp\frac{k_c^2 t}{D} \operatorname{erfc}\left(\frac{k_c t^{1/2}}{D^{1/2}}\right) - \frac{D}{k_c r_0} \right]$
Irreversible (small t)	Plane and sphere	$-nFAk_c[O]_{\infty} \left(1 - \frac{2k_c t^{1/2}}{(\pi D)^{1/2}}\right)$
		$\theta = [O]_{\infty}/[R]_{\infty}$

where $\theta \rightarrow 0$ when at the correct overpotential

Potential Step Methods

Chronoamperometry – record current as a function of time.

Step from E_1 (where no electron-transfer occurs) to E_2 (where reduction or oxidation occurs) while the rate is under diffusion control.

The electroactive species is depleted with time at the electrode surface.

Potential Step Methods

Chronoamperometry

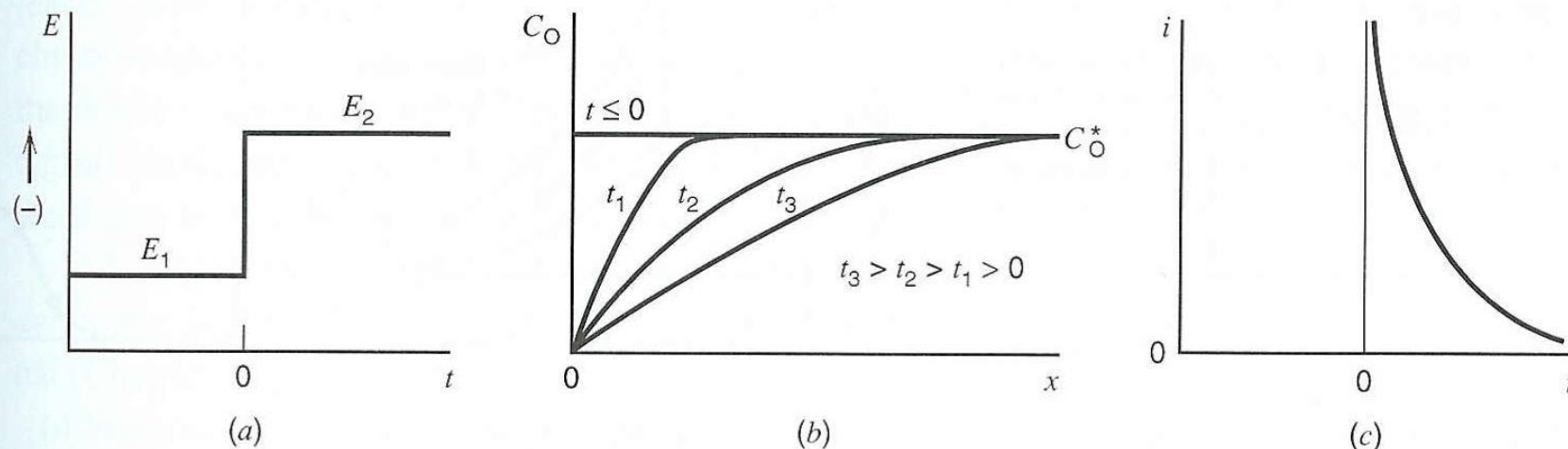


Figure 5.1.2 (a) Waveform for a step experiment in which species O is electroinactive at E_1 , but is reduced at a diffusion-limited rate at E_2 . (b) Concentration profiles for various times into the experiment. (c) Current flow vs. time.

Potential Step Methods

When doing this experiment for a new cell setup
– it is always important to test the system with a known reversible redox system (classical), i.e. ferri/ferrocyanide in 1-3 M KCl at a solid electrode.

Potential Step Methods

Uses for chronoamperometry

- Measure diffusion coefficients of electroactive species. (use Cottrell equation)
- Measure the electrochemical area of an electrode.
- Measure heterogeneous rate constants for sluggish systems
- Study EC or ECE reactions

Potential Step Methods

Study of EC or ECE reactions

The behavior of $i^{1/2}$ as a function of time is influenced by a chemical reaction coupled to an electrode process.



A rate determining step is between two electrochemical reactions.

Potential Step Methods

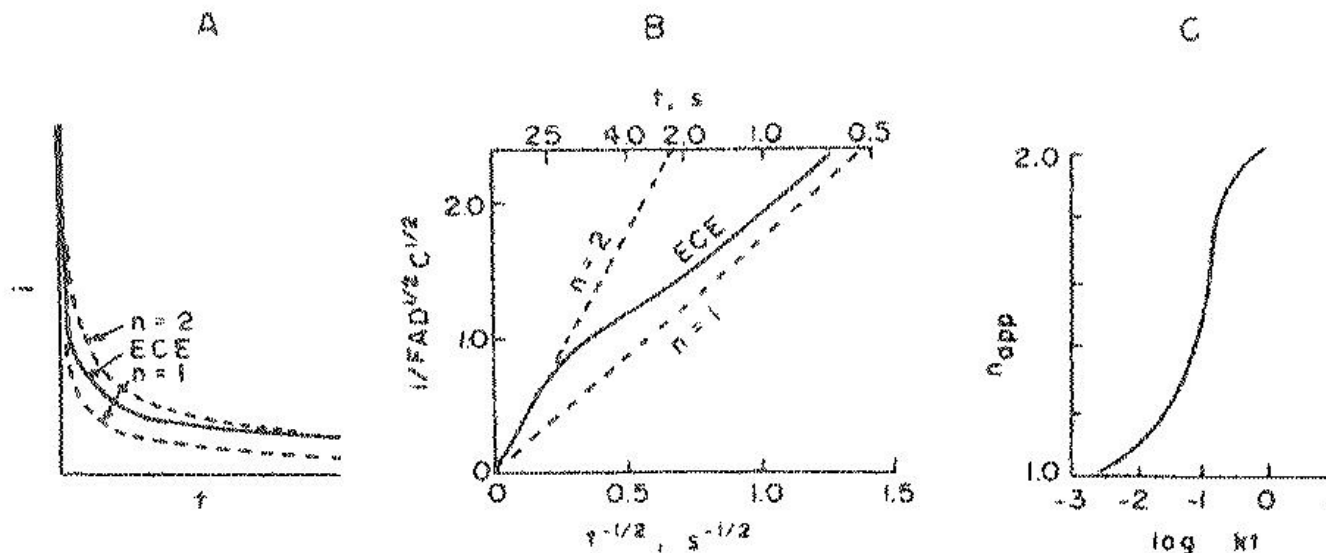


Figure 3.4 Chronoamperometry for ECE mechanism. (A) Current-time response. (B) Data plotted as i versus $t^{-1/2}$. (C) Calculated working curve for obtaining rate constant k from experimental value for n_{app} . [From Ref. 8, adapted with permission.]

Potential Step Methods

Chronoamperometry Reversal Techniques

Apply a series of steps, most common arrangement is the double-step technique –
1st step used to generate a species of interest and
2nd step used to examine the species.

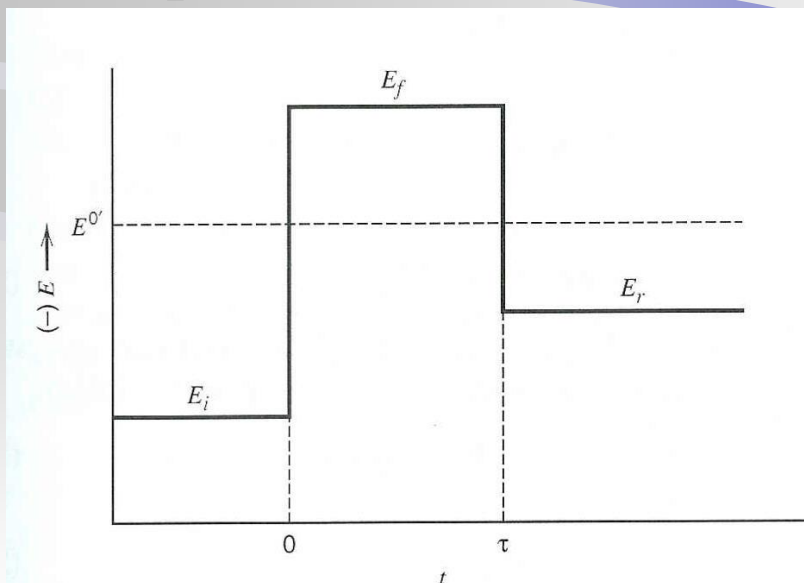


Figure 5.7.1 General waveform for a double potential step experiment.

Potential Step Methods

Chronoamperometry Reversal Techniques

$$i_f = (nFA D_O^{1/2} C_O^*) / [\pi^{1/2} t^{1/2} (1 + \xi \theta')]$$

(for forward step, $\theta' = C_O' / C_R'$)

$$-i_r = (nFA D_O^{1/2} C_O^*) / (\pi^{1/2}) [1/(t-\tau)^{1/2} - 1/t^{1/2}]$$

(for reversal step, $\theta'' = C_O'' / C_R''$)

when $\theta' \sim 0$, $C_O' \sim 0$ and $\theta'' \rightarrow \infty$, $C_R'' \sim 0$

Potential Step Methods

Chronoamperometry Reversal Techniques

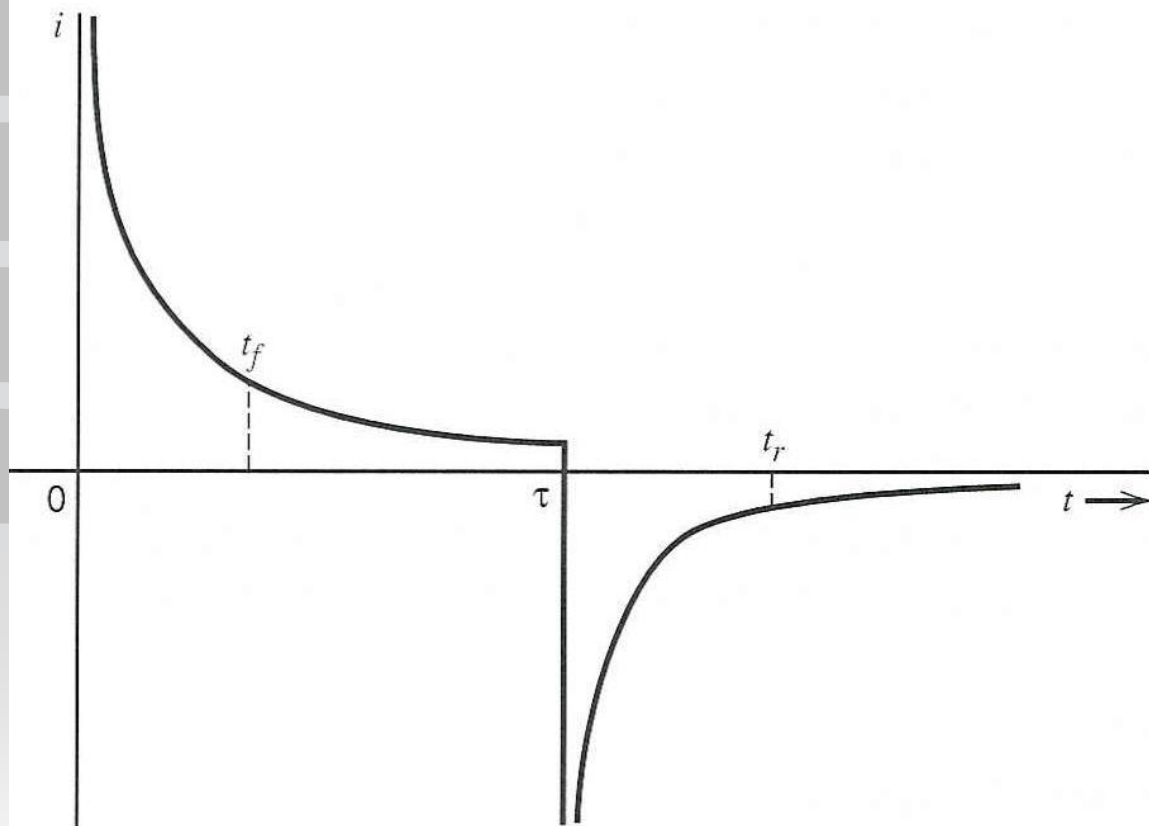


Figure 5.7.3 Current response in double-step chronoamperometry.

Potential Step Methods

Double – Step Chronoamperometry

Also can be used for mechanism studies to study the fate of an oxidized species being reduced.

However RDE or RRDE could be better for some of these reactions.

Potential Step Methods

Overview of Step Experiments

For controlled step experiments can record:

- current as a function of time (chronoamperometry)
- potential as a function of time (chronopotentiometry)
- charge as a function of time (chronocoulometry)
- absorbance as a function of time (chronoabsorptometry)

All based on the same excitation function of one or more potential (or current) steps.

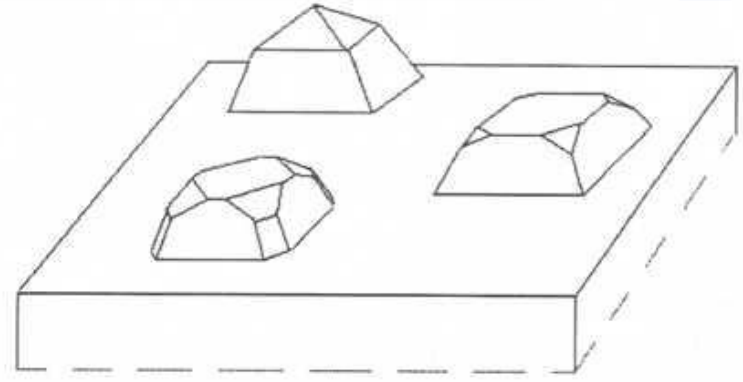
Potential Step Methods

Step Experiment example

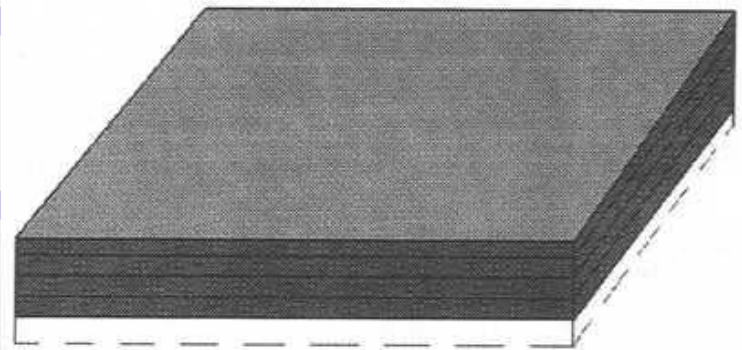
Electrodeposition of Body-Centered Cubic Thallium
(111) Oxide onto Glassy Carbon

Potential Step

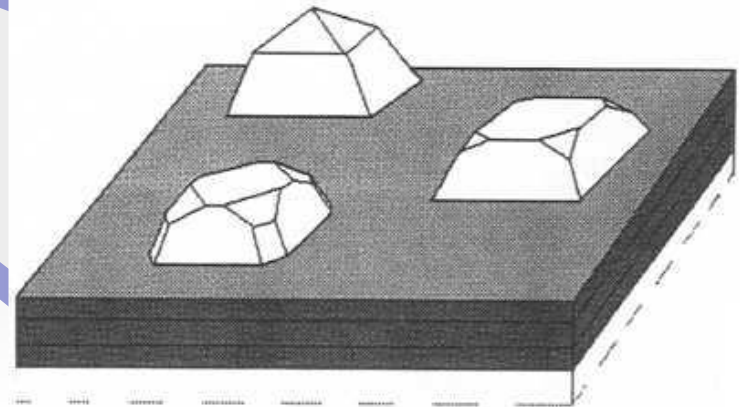
Fig. 1. Growth modes observed during thin film growth. (A) VoJmer-Weber (VW) or 3D, (B) Frank-van der Merwe (FM) or monolayer-by-monolayer, and (C) Sltanski-Krastinov (SK) or 2D growth up to a critical thickness followed by 3D islanding.



A



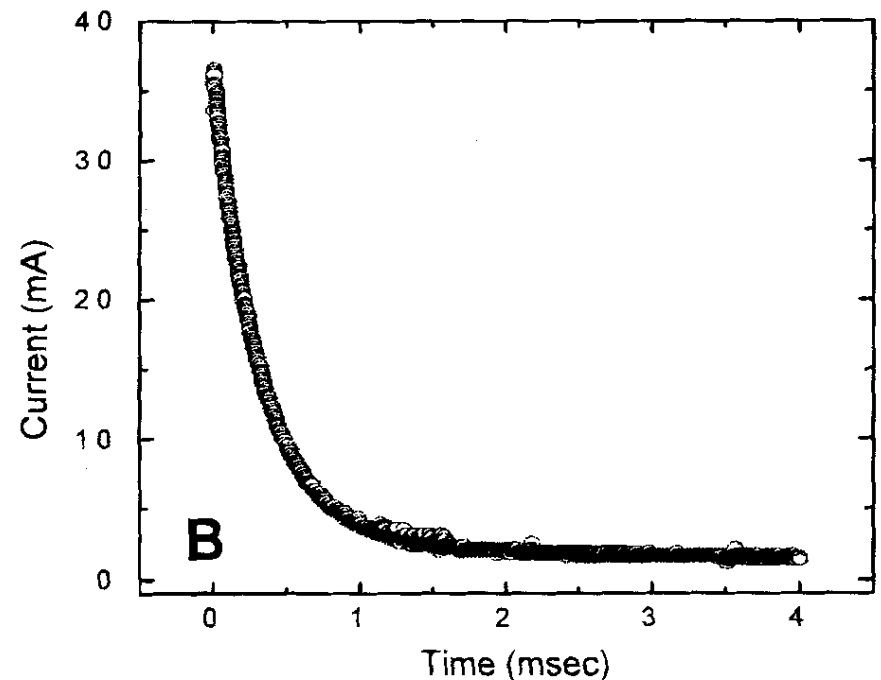
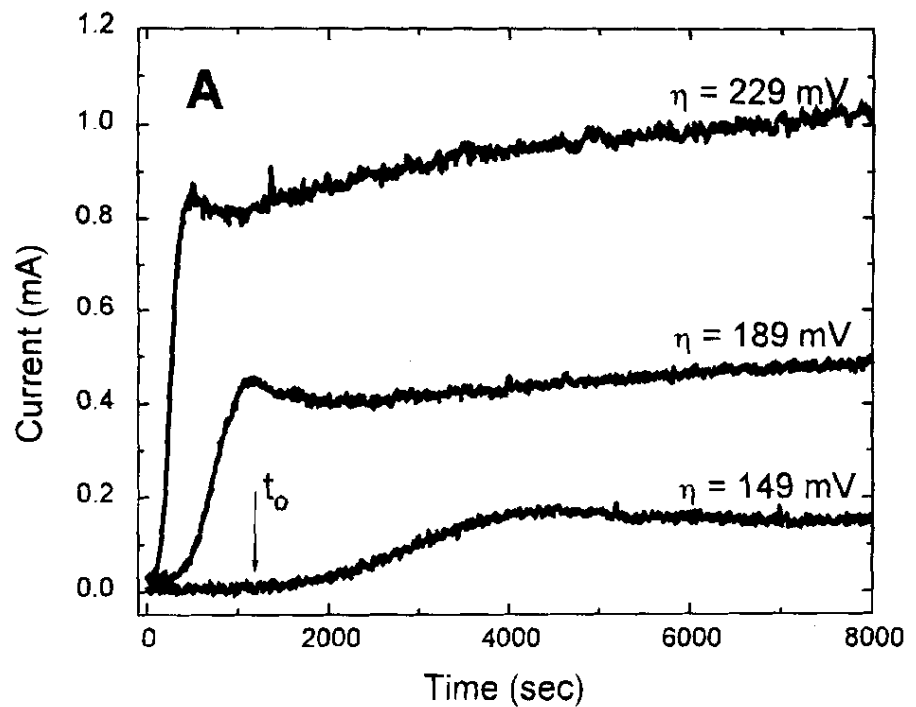
B

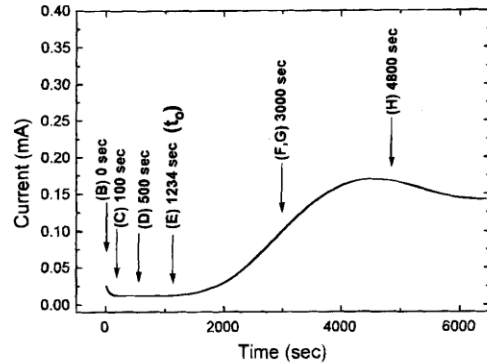


C

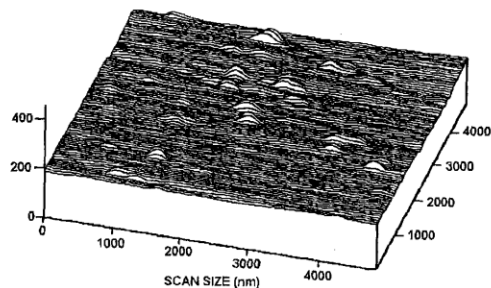
Chronoamperometry

Fig. 2. (A) Potential step transients showing the resulting current time response for three overpotentials. A large increase in the current indicates bulk growth of crystalline TiO_2 . (B) Double-layer charging segment of the transient for an overpotential of 149 mV. A time constant of 40 μs was determined. Deposition was onto the glassy carbon electrode from an unstirred solution of 0.1M TiNO_3 in 5M NaOH .

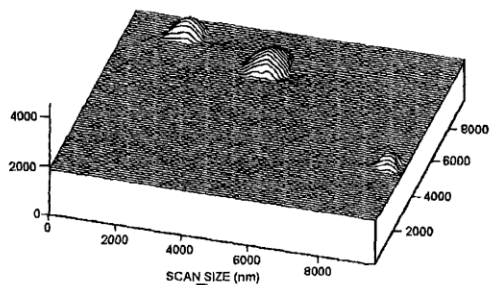




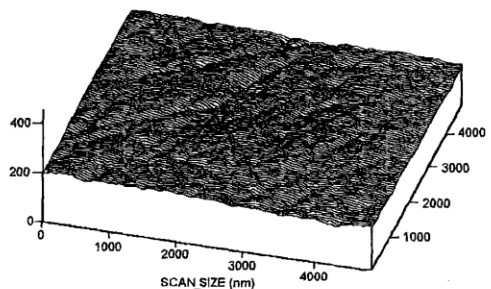
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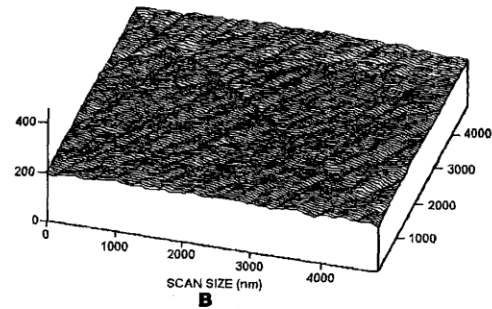
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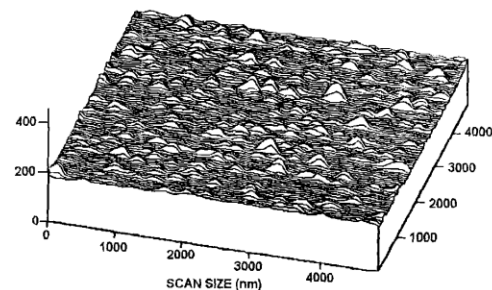
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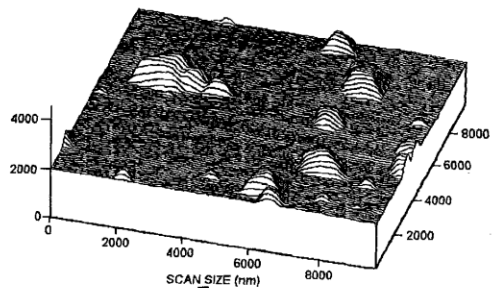
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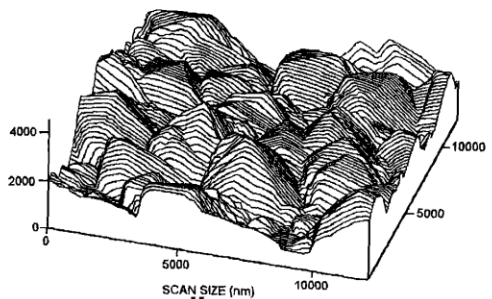
B



D



F



H

Fig. 12. Atomic force microscopy for several deposition times resulting from a potential step to an overpotential of 149 mV. (A) The location along the current-time transient for (B) 0 s, (C) 100 s, (D) 500 s, (E) 1234 s, (F) 3000 s, (G) 3000 s between nuclei over an amorphous surface and (H) 4800 s.

Class Assignment

- Research paper Topic
- Read Chapters 4, 5, 13, and 15
“Electrochemical Methods” Bard

