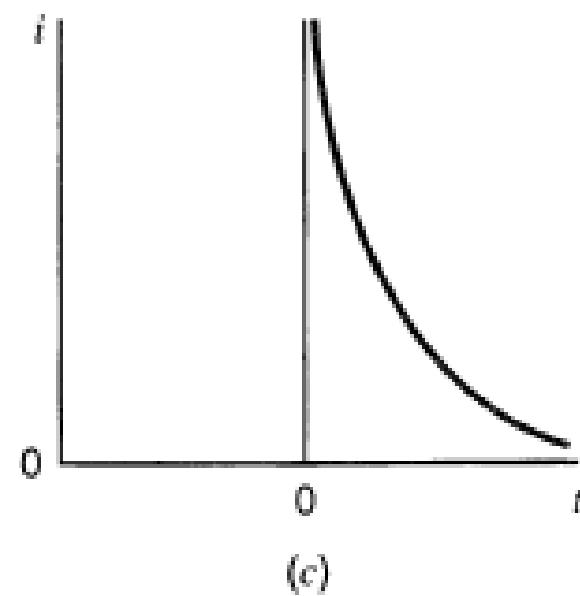
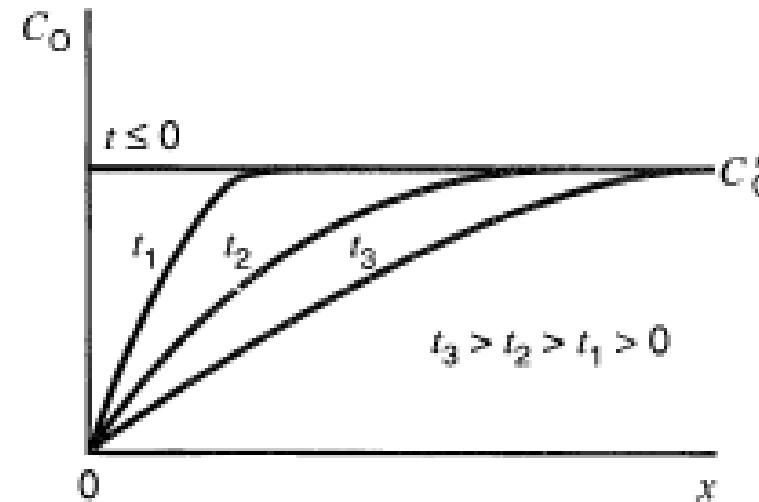
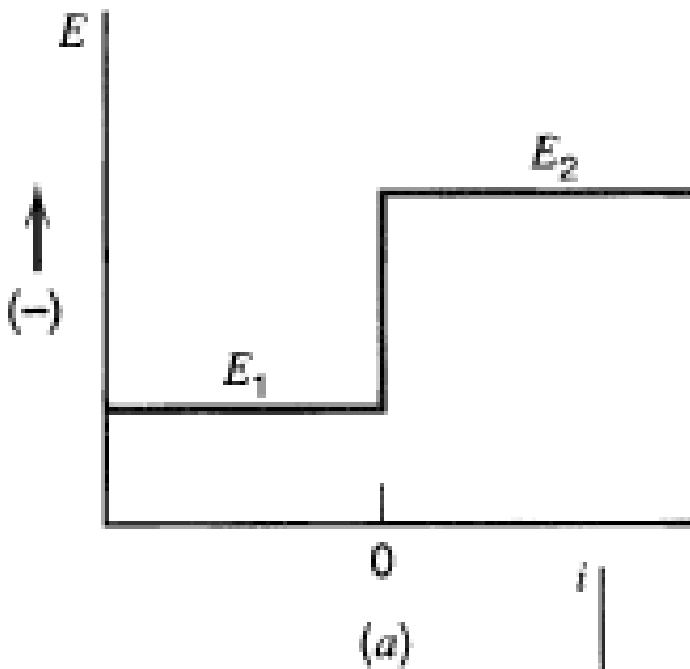


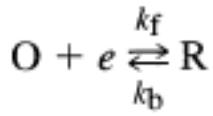
Chronoamperometry

OVERVIEW OF STEP EXPERIMENTS

Types of Techniques



POTENTIAL STEP UNDER DIFFUSION CONTROL



$$i(t) = i_d(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$$

Cottrell equation

i is proportional to t^{-1/2}
it^{1/2} = constant with t

*Linearity is a criterion for a diffusion-controlled reaction
(no convection/migration,
No pre/post kinetics,
E-transfer is rapid)*

Instrumental and Experimental Limitations

Potentiostatic limitations.

Cottrell eq. predicts very high currents at short times, but the actual maximum current may depend on the current and voltage output characteristics of the potentiostat.

Limitations in the recording device.

During the initial part of the current transient, the oscilloscope, transient recorder, or other recording device may be overdriven, and some time may be required for recovery, after which accurate readings can be displayed.

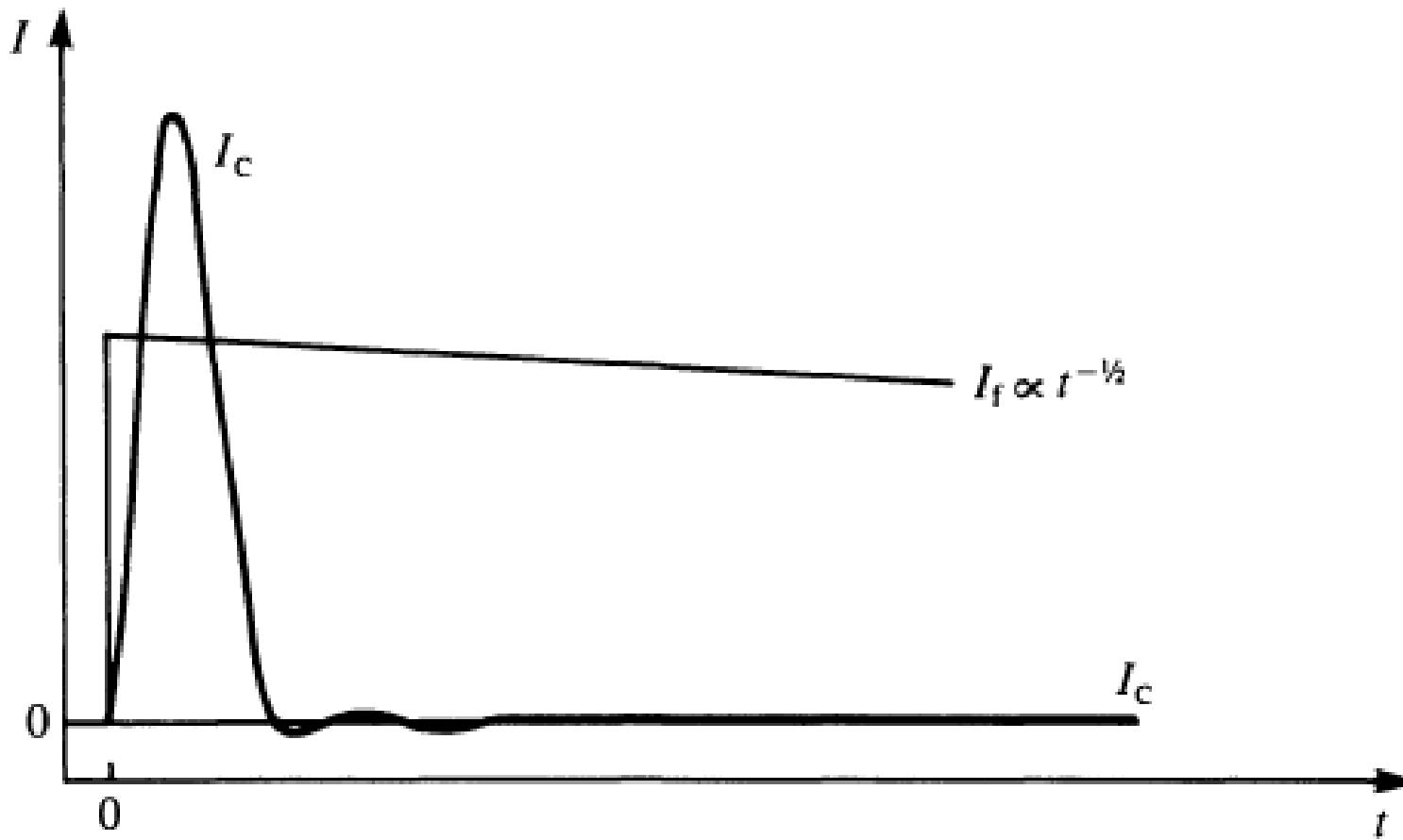
Limitations due to convection.

At longer times (20-30 s), vibrations may cause movement of solution → will cause convective disruption of the diffusion layer, and usually result in currents larger than those predicted by the Cottrell equation.

Short-time limitations

***D.L. charging

$$I_C = \frac{\Delta E}{R} \exp(-t/RC)$$



Lasts 0.05 – 10 ms.

Short-time limitations

****Electrode Roughness*

Area determined by Cottrell will be larger than geometrical.

At short time, O species are close to electrode → those in cracks are surrounded by electrode.

At larger times, O near electrode are depleted → species must diffuse longer to reach →

Area from Cottrell will be smaller than that at shorter times

****Any species which is specifically adsorbed will be immediately electrolyzed (if electroactive at the applied E) → will add to measured current.*

→ It $^{1/2}$ will be higher than Cottrell constant behavior at short time

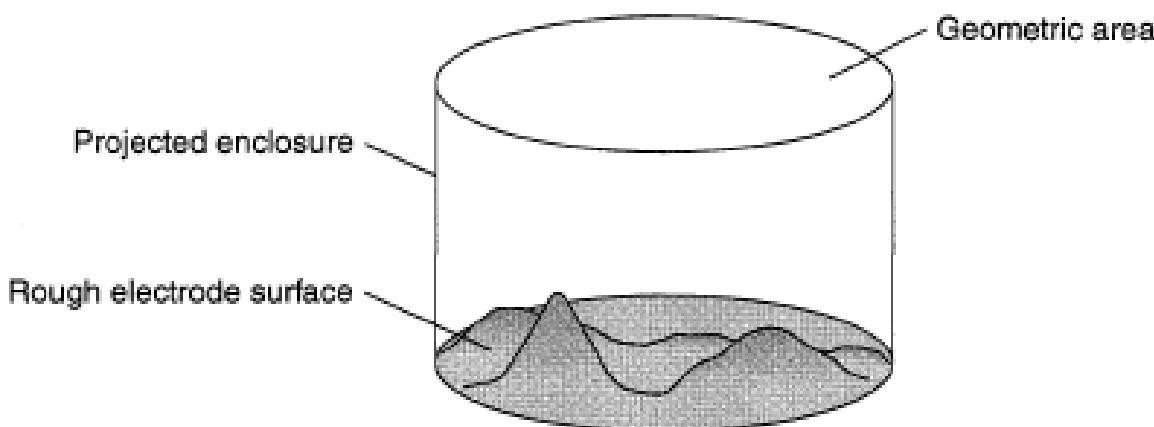
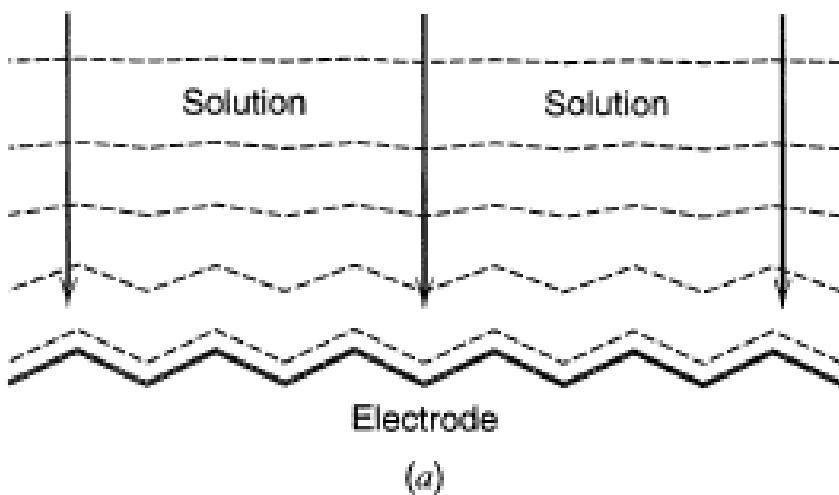


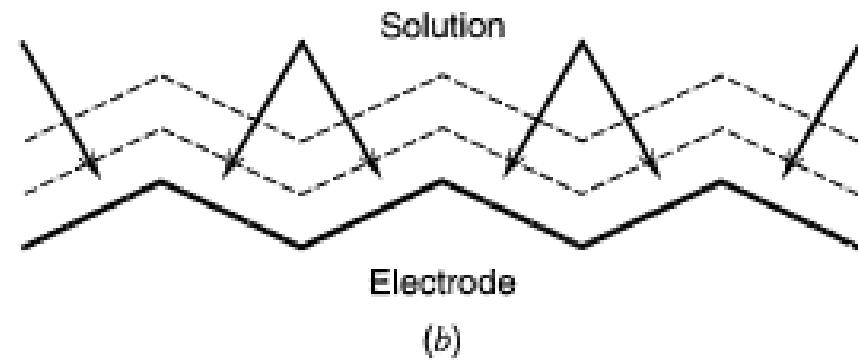
Figure 5.2.2 Electrode surface and the enclosure formed by projecting the boundary outward in parallel with the surface normal. The cross-section of the enclosure is the geometric area of the electrode.

$$\rho = A_m/A_g$$

roughness factor

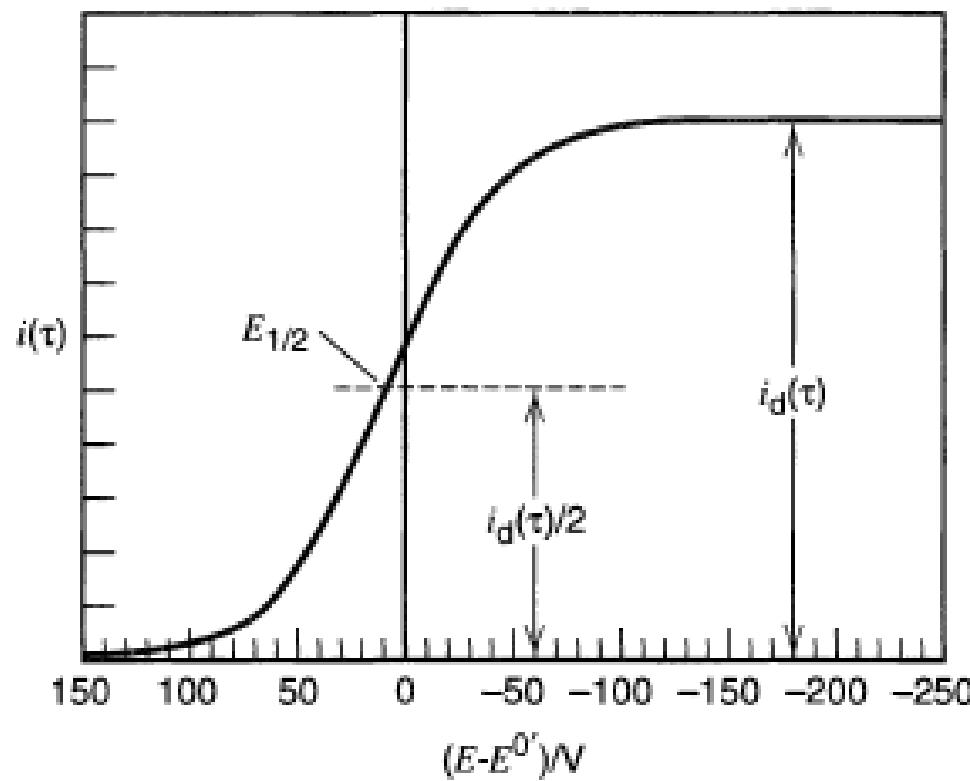


(a)



(b)

Figure 5.2.3 Diffusion fields at (a) long and (b) short times at a rough electrode. Depicted here is an idealized electrode where the roughness is caused by parallel triangular grooves cut on lines perpendicular to the page. Dotted lines show surfaces of equal concentration in the diffusion layer. Vectors show concentration gradients driving the flux toward the electrode surface.



$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{i_d(\tau) - i(\tau)}{i(\tau)}$$

*Applications of Reversible *i-E* Curves*

Information from the Wave Height

Information from the Wave Shape

analyzed in terms of the "wave slope," which is expected to be $0.0592/n$ V at 25°C for a **reversible** system. → a measure for reversibility.

If it's known to be reversible → find n.

Information from the Wave Position

For reversible systems, it is used to calculate $E^{\circ'}$ from $E_{1/2}$

