

# **CONTROLLED-CURRENT TECHNIQUES**

## 8.1 INTRODUCTION

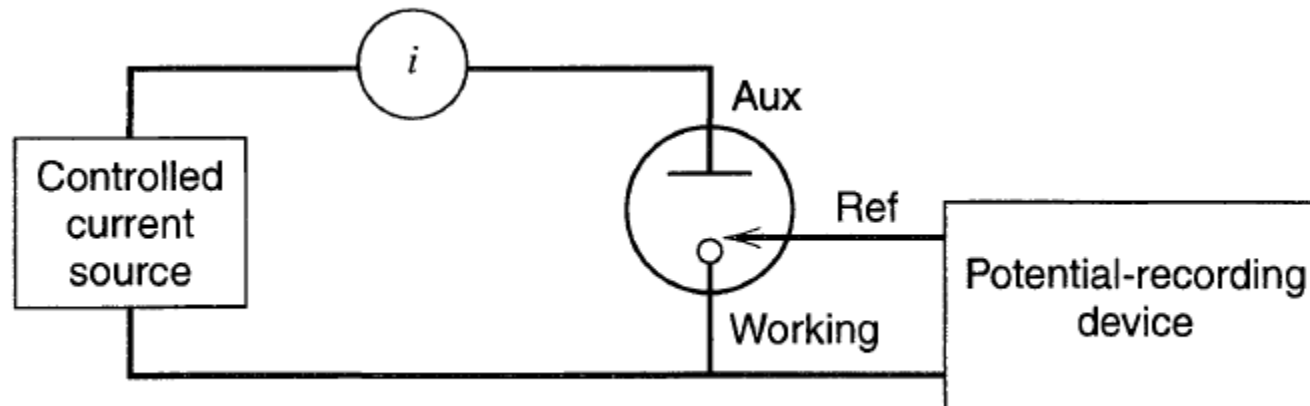
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- Electrochemical methods in Chapters 5-6
  - : the potential (input) of an electrode was controlled as a function of time
    - the **current (output) was determined**.
- In this chapter
  - : the opposite case
  - : the current is controlled (frequently held constant)
    - the **potential is determined** as a function of time.

## 8.1 INTRODUCTION

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- In the experiment
  - : **apply the controlled current** between the working and counter electrodes with a current source (called a galvanostat)
  - **record the potential** between the working and reference electrodes
- : called **chronopotentiometric** techniques,
  - because  $E$  is determined as a function of time
  - **galvanostatic** techniques

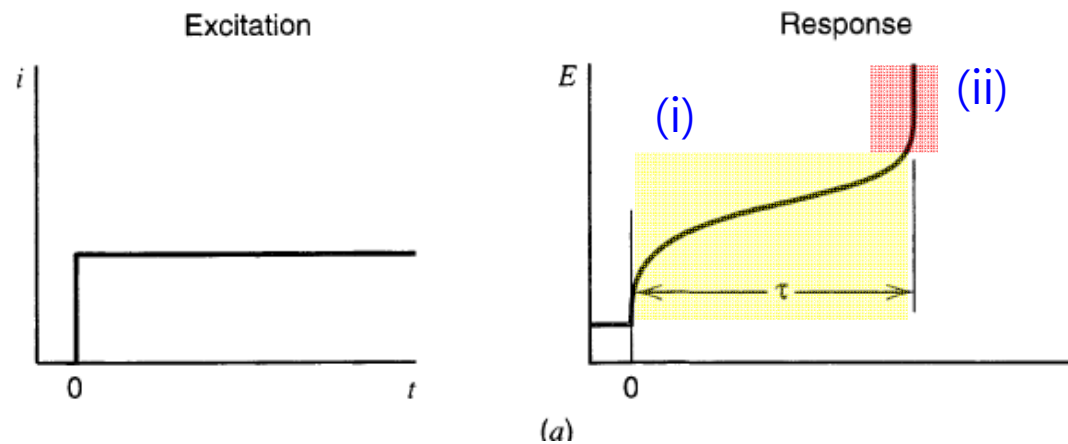


## 8.1 INTRODUCTION

- Various types of controlled-current techniques

### 1) Constant-current chronopotentiometry

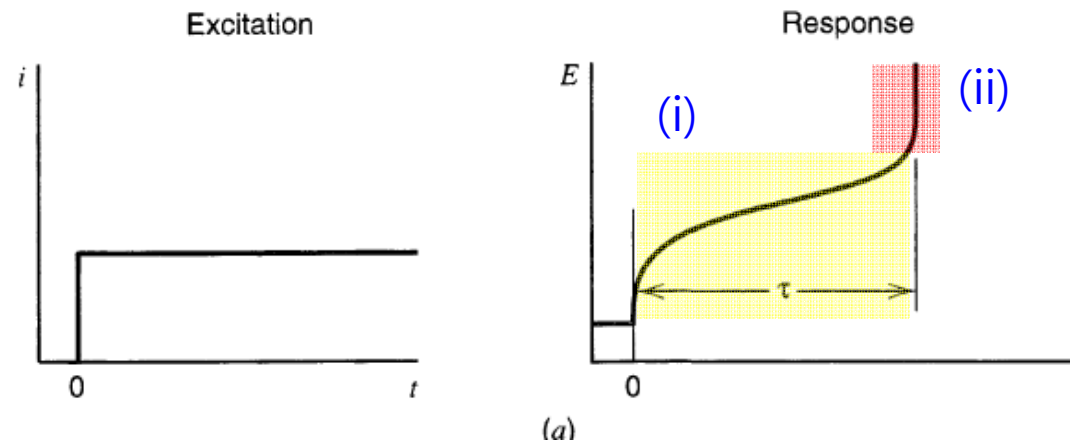
- Consider the anthracene (An) system used as an example in Section 5.1.1.
- The steady current,  $i$ , applied to the electrode
  - the anthracene to be reduced at a constant rate to the anion radical
- As the anthracene/anthracene radical **concentration ratio changes** at the electrode surface
  - (i) the **potential of the electrode varies** with time



## 8.1 INTRODUCTION

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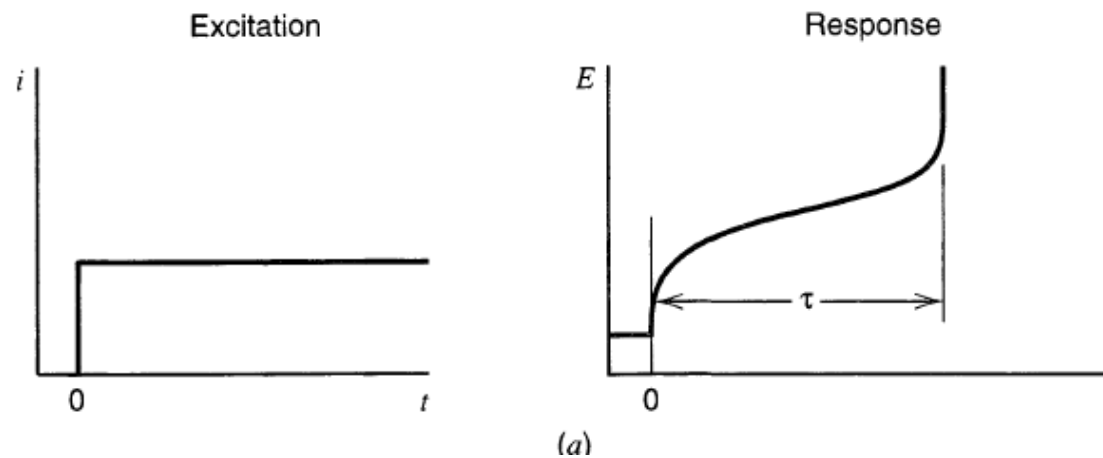
- Eventually, after the concentration of A<sub>n</sub> drops to zero at the electrode surface
  - the flux of O to the electrode surface is not large enough to satisfy the applied current
  - (ii) the potential shifts to a more extreme value where another electrode process can occur



## 8.1 INTRODUCTION

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- The time after application of the constant current when this potential transition occurs
  - called the **transition time**,  $\tau$ .
  - dependent on the concentration and the diffusion coefficient

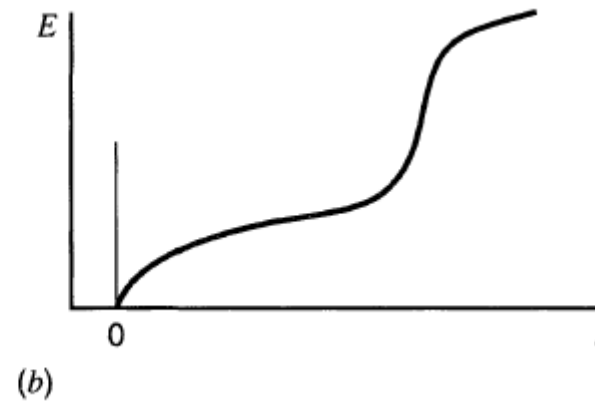


## 8.1 INTRODUCTION

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### 2) Programmed current chronopotentiometry

- Instead of a constant current,  
→ apply a current that varies as a known function of time

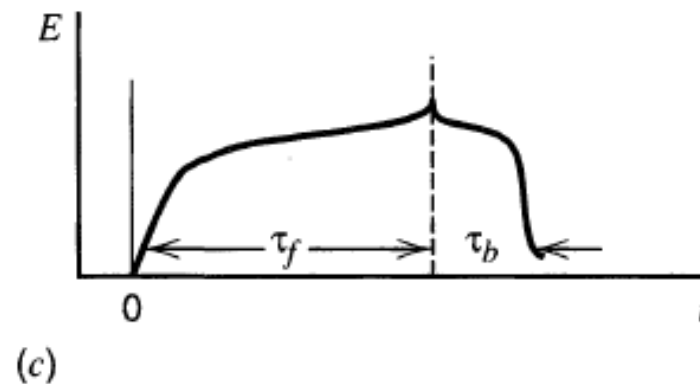
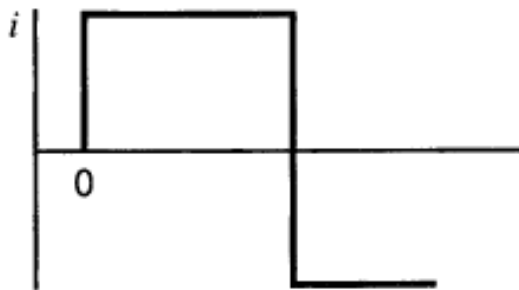


## 8.1 INTRODUCTION

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### 3) Current reversal chronopotentiometry

- The current can be reversed after some time
- For example, in the case of An,
  - if the current is suddenly changed to an anodic current of equal magnitude at, or before, the transition time,
    - : the An radical formed during the forward step will start oxidizing.

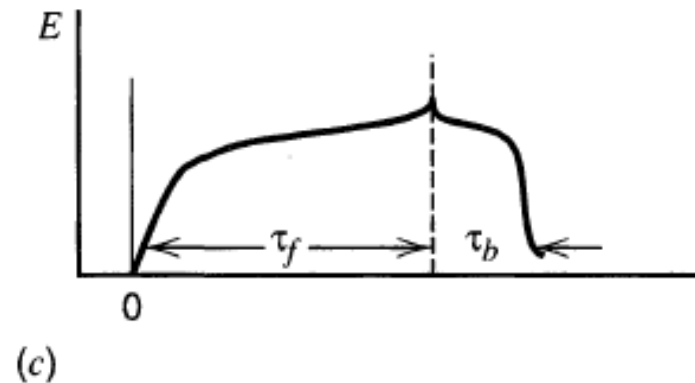
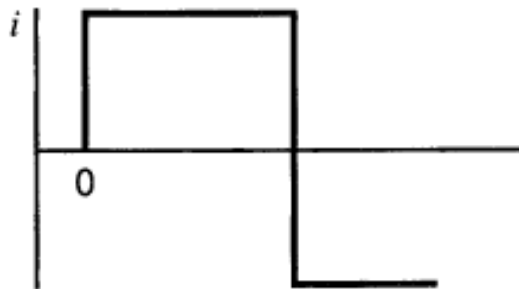




## 8.1 INTRODUCTION

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- As the  $A_n/A_n$  radical concentration ratio increases.
  - the potential will move in a positive direction
- When the  $A_n$  radical concentration falls to zero at the electrode surface
  - a potential increases highly toward positive potentials
  - a reverse transition time can be measured.

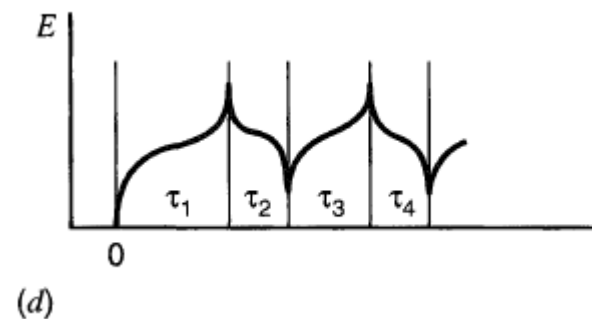
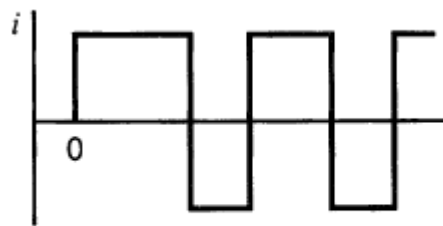


## 8.1 INTRODUCTION

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### 4) Cyclic chronopotentiometry

- In an extension of current reversal chronopotentiometry technique,
  - the current can be **continuously reversed at each transition**
  - **repeat** the current reversal chronopotentiometry
  - conventionally used to measure a capacity in the area of rechargeable batteries such as Li-ion batteries



## 8.2 GENERAL THEORY OF CONTROLLED CURRENT METHODS

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- Consider the [simple electron-transfer reaction](#),  $O + ne \rightarrow R$ .

→ assumptions:

- 1) a planar working electrode and an unstirred solution
- 2) species O initially present at a concentration  $C_O^*$
- 3) semi-infinite linear diffusion

→ the following diffusion equations and general boundary conditions

$$\frac{\partial C_O(x, t)}{\partial t} = D_O \frac{\partial^2 C_O(x, t)}{\partial x^2} \quad \frac{\partial C_R(x, t)}{\partial t} = D_R \frac{\partial^2 C_R(x, t)}{\partial x^2}$$

$$\left. \begin{array}{l} \text{At } t = 0 \text{ (for all } x) \\ \text{and} \\ \text{as } x \rightarrow \infty \text{ (for all } t) \end{array} \right\} \begin{array}{l} C_O(x, t) = C_O^* \\ C_R(x, t) = 0 \end{array}$$

$$D_O \left( \frac{\partial C_O(x, t)}{\partial x} \right)_{x=0} + D_R \left( \frac{\partial C_R(x, t)}{\partial x} \right)_{x=0} = 0$$

## 8.2 GENERAL THEORY OF CONTROLLED CURRENT METHODS

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- Since the applied **current  $i(t)$  is presumed known**,  
→ the flux at the electrode surface is also known at any time

$$D_O \left[ \frac{\partial C_O(x, t)}{\partial x} \right]_{x=0} = \frac{i(t)}{nFA}$$

- For **controlled-potential methods** (Ch. 5-6),  
→ the **concentration-potential boundary condition** was required to solve the governing equations
- For **controlled-current methods**  
→ The above boundary condition involving the concentration gradient

## 8.2 GENERAL THEORY OF CONTROLLED CURRENT METHODS

- For species O, application of the Laplace transform method to

$$\begin{aligned}
 & \frac{\partial C_O(x, t)}{\partial t} = D_O \frac{\partial^2 C_O(x, t)}{\partial x^2} \\
 & \left. \begin{array}{l} \text{At } t = 0 \text{ (for all } x) \\ \text{and} \\ \text{as } x \rightarrow \infty \text{ (for all } t) \end{array} \right\} \begin{array}{l} C_O(x, t) = C_O^* \\ C_R(x, t) = 0 \end{array} \quad \left. \begin{array}{l} \bar{C}_O(x, s) = \frac{C_O^*}{s} + A(s) \exp\left[-\left(\frac{s}{D_O}\right)^{1/2} x\right] \end{array} \right\} \\
 & D_O \left[ \frac{\partial C_O(x, t)}{\partial x} \right]_{x=0} = \frac{i(t)}{nFA} \quad \Rightarrow \quad D_O \left[ \frac{\partial \bar{C}_O(x, s)}{\partial x} \right]_{x=0} = \frac{\bar{i}(s)}{nFA} \\
 & \Rightarrow \quad \bar{C}_O(x, s) = \frac{C_O^*}{s} - \left[ \frac{\bar{i}(s)}{nFAD_O^{1/2}s^{1/2}} \right] \exp\left[-\left(\frac{s}{D_O}\right)^{1/2} x\right]
 \end{aligned}$$

- By substitution of the known function,  $\bar{i}(s)$ , and employing the inverse transform  
 $\rightarrow C_O(x, t)$  can be obtained

## 8.2 GENERAL THEORY OF CONTROLLED CURRENT METHODS

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- Similarly, for species R,

$$\frac{\partial C_R(x, t)}{\partial t} = D_R \frac{\partial^2 C_R(x, t)}{\partial x^2} \quad \Rightarrow \quad \bar{C}_R(x, s) = \left[ \frac{\bar{i}(s)}{nFAD_R^{1/2}s^{1/2}} \right] \exp \left[ - \left( \frac{s}{D_R} \right)^{1/2} x \right]$$

## 8.2.2 Constant-Current Electrolysis—The Sand Equation

- If  $i(t)$  is constant, then  $\bar{i}(s) = i/s$

$$\bar{C}_O(x, s) = \frac{C_O^*}{s} - \left[ \frac{\bar{i}(s)}{nFAD_O^{1/2}s^{1/2}} \right] \exp \left[ - \left( \frac{s}{D_O} \right)^{1/2} x \right]$$

➡

$$\bar{C}_O(x, s) = \frac{C_O^*}{s} - \left[ \frac{i}{nFAD_O^{1/2}s^{3/2}} \right] \exp \left[ - \left( \frac{s}{D_O} \right)^{1/2} x \right]$$

- The inverse transform of this equation → concentration profiles

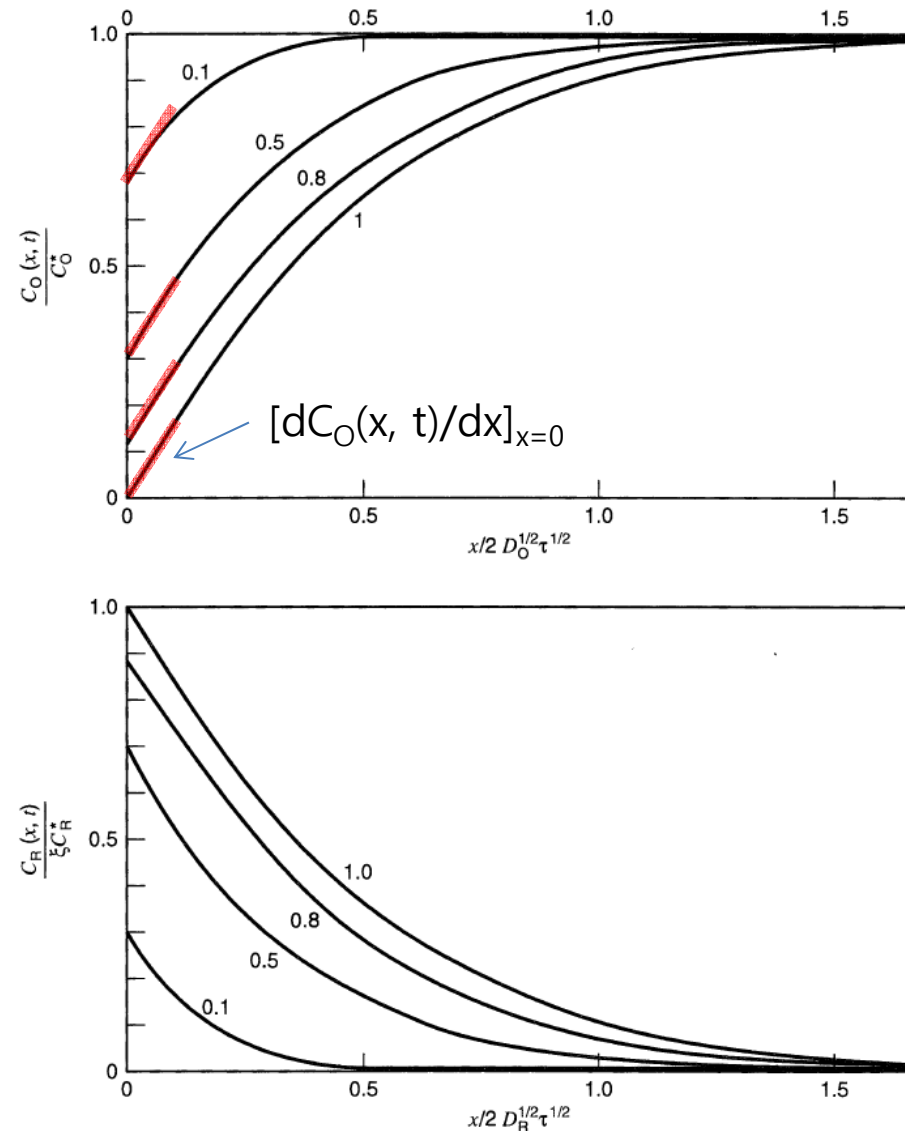
$$C_O(x, t) = C_O^* - \frac{i}{nFAD_O} \left\{ 2 \left( \frac{D_O t}{\pi} \right)^{1/2} \exp \left( - \frac{x^2}{4D_O t} \right) - x \operatorname{erfc} \left[ \frac{x}{2(D_O t)^{1/2}} \right] \right\}$$

**TABLE A.1.1 Laplace Transforms  
of Common Functions (1)**

$F(t)$	$f(s)$
$2 \left( \frac{kt}{\pi} \right)^{1/2} \exp(-x^2/4kt) - x \operatorname{erfc}[x/2(kt)^{1/2}]$	$e^{-\beta x/s\beta}$

## 8.2.2 Constant-Current Electrolysis—The Sand Equation

- Typical concentration profiles at various times during a constant-current electrolysis
  - $C_O(0,t)$  decreases continuously
  - yet,  $[dC_O(x, t)/dx]_{x=0}$  is constant at all times after the onset of electrolysis.



**Figure 8.2.1** Concentration profiles of O and R (in dimensionless form) at various values of  $t/\tau$  indicated on the curves.



## 8.2.2 Constant-Current Electrolysis—The Sand Equation

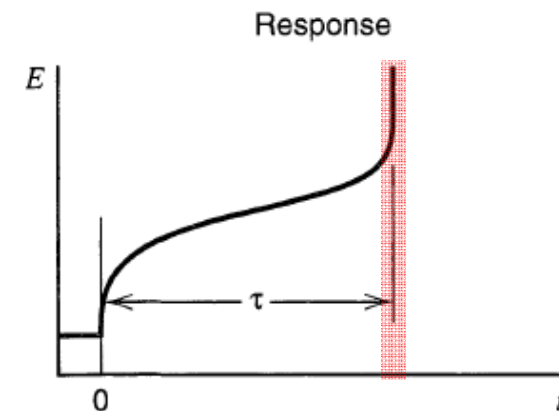
- By setting  $x = 0$ , an expression for  $C_O(0, t)$ :

$$C_O(x, t) = C_O^* - \frac{i}{nFAD_O} \left\{ 2 \left( \frac{D_O t}{\pi} \right)^{1/2} \exp\left(-\frac{x^2}{4D_O t}\right) - x \operatorname{erfc}\left[\frac{x}{2(D_O t)^{1/2}}\right] \right\}$$

$$\Rightarrow C_O(0, t) = C_O^* - \frac{2it^{1/2}}{nFAD_O^{1/2}\pi^{1/2}}$$

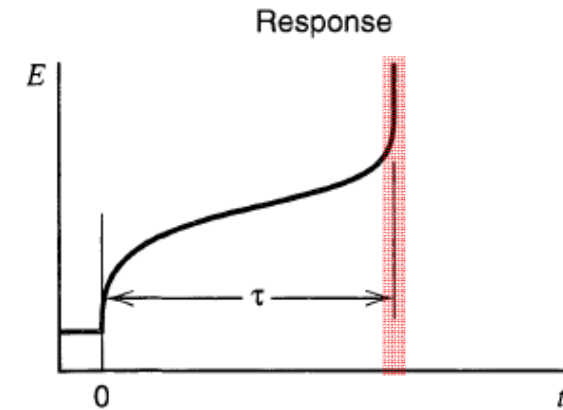
- At the transition time,  $\tau$ ,  
 $\rightarrow C_O(0, t)$  drops to zero

$$C_O(0, t) = C_O^* - \frac{2it^{1/2}}{nFAD_O^{1/2}\pi^{1/2}} = 0 \quad (\text{at } t=\tau)$$



## 8.2.2 Constant-Current Electrolysis—The Sand Equation

$$C_O(0, t) = C_O^* - \frac{2it^{1/2}}{nFAD_O^{1/2}\pi^{1/2}} = 0 \quad (\text{at } t=\tau)$$



➔

$$\frac{i\tau^{1/2}}{C_O^*} = \frac{nFAD_O^{1/2}\pi^{1/2}}{2} = 85.5 nD_O^{1/2} A \frac{\text{mA}\cdot\text{s}^{1/2}}{\text{mM}} \quad (\text{with } A \text{ in cm}^2)$$

: known as the **Sand equation**

- The measured value of  $\tau$  at known  $i$  (or the values of  $i\tau^{1/2}$  obtained at various currents)  
→ used to determine  $n$ ,  $A$ ,  $C_O^*$  or  $D_O$