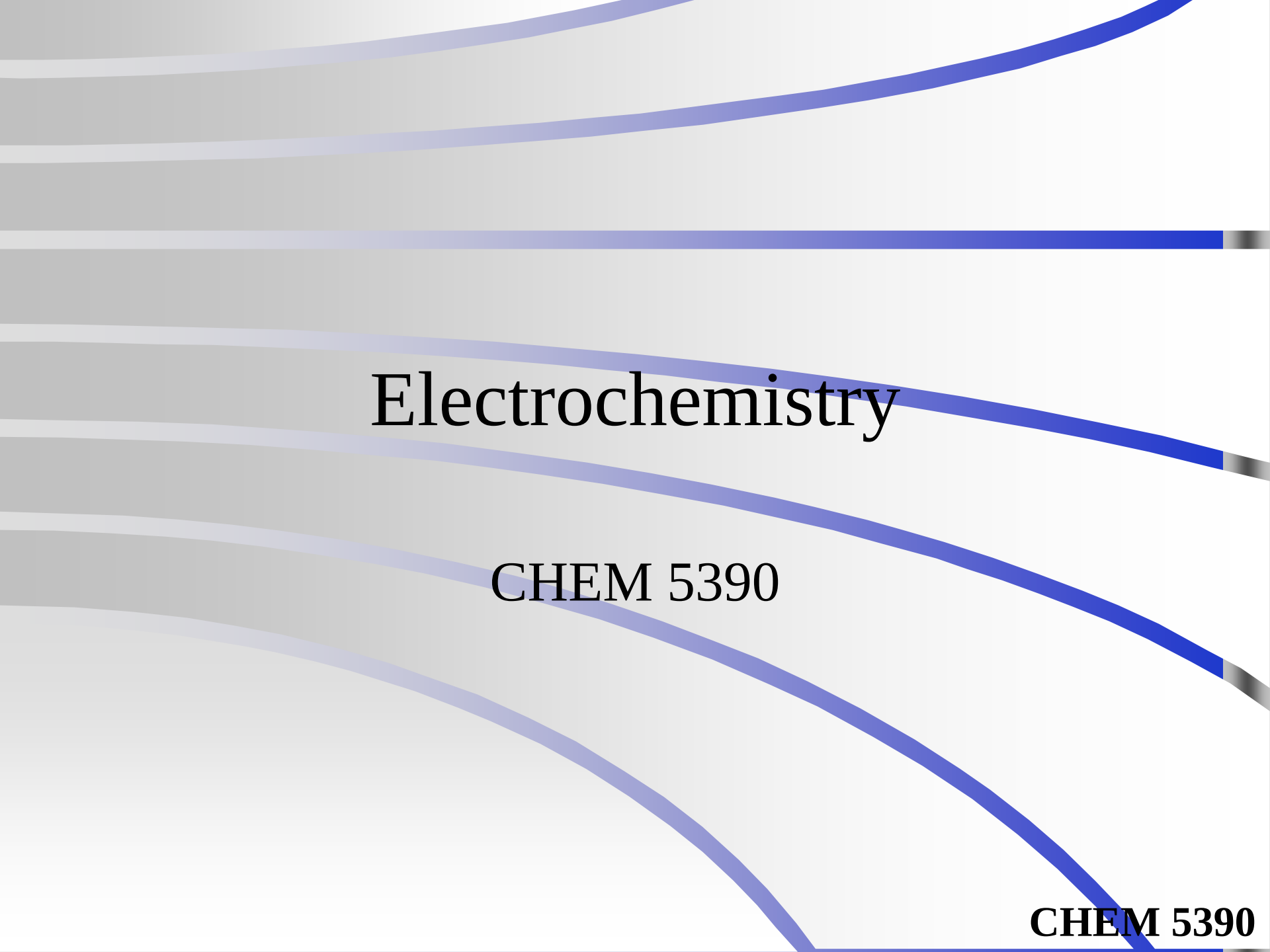




Electrochemistry

CHEM 5390

CHEM 5390

Controlled Current Techniques

Current is controlled and the potential is measured as a function of time.

A current is applied between the WE and CE by a galvanostat and potential is recorded between the WE and RE.

The general technique is called chronopotentiometry, because E is determined as a function of time.

Instrumentation for current-control techniques is simpler than for potential-control techniques.

Potential Step Methods

Chronopotentiometry

Measure the variation of the potential with time.

The potential at a planar electrode is $\sim$ constant until the end of the transition time, τ , which corresponds to the total consumption of the electroactive species at the electrode.

Sand equation describes the transition time:

$$\frac{I\tau^{\frac{1}{2}}}{[O]_{\infty}} = -\frac{nFAD_O^{\frac{1}{2}}\pi^{\frac{1}{2}}}{2}$$

Potential Step Methods

Chronopotentiometry

Sand equation describes the transition time:

$$\frac{I\tau^{\frac{1}{2}}}{[O]_{\infty}} = -\frac{nFAD_O^{\frac{1}{2}}\pi^{\frac{1}{2}}}{2}$$

By setting all the boundary conditions and combining the Sand equation with the Nernst equation:

$$E = E_{\frac{\tau}{4}} + \frac{RT}{nF} \ln \frac{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}}{t^{\frac{1}{2}}}$$

Potential Step Methods

Chronopotentiometry

For a reversible system:

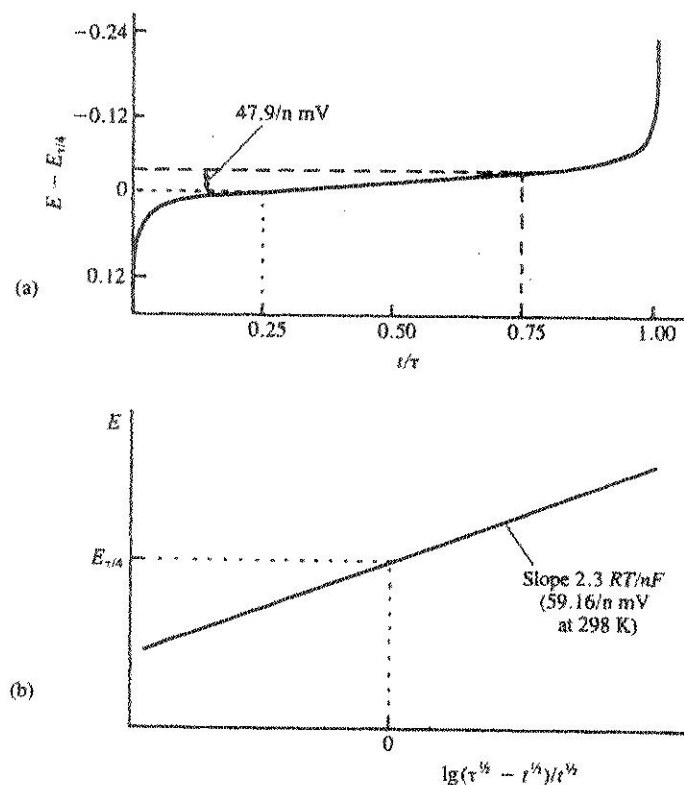


Fig. 10.5. Chronopotentiometry in a reversible system for $O + ne^- \rightarrow R$ (only O present in bulk solution). (a) Chronopotentiogram; (b) Plot of E vs. $\lg[(\tau^{1/2} - t^{1/2})/t^{1/2}]$.

Potential Step Methods

Chronopotentiometry

For irreversible system:

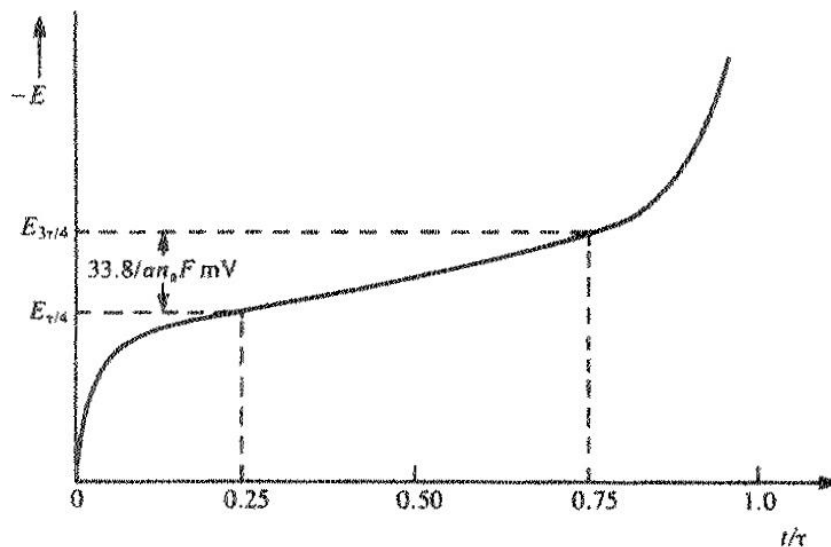


Fig. 10.6. Chronopotentiogram for an irreversible system: $O + ne^- \rightarrow R$.

Controlled Current Techniques

Constant-current chronopotentiometry

Steady-state current reduces, O , at a constant rate.

Potential varies with time as the concentration ratio, O/R , changes at the electrode surface.

Eventually the flux of O cannot keep up with the excess electrons supplied to the electrode, this drives the potential toward more negative potentials.

Time it takes to drive the potential up is called the transition time, τ , and is related to the concentration and diffusion coefficient.

Controlled Current Techniques

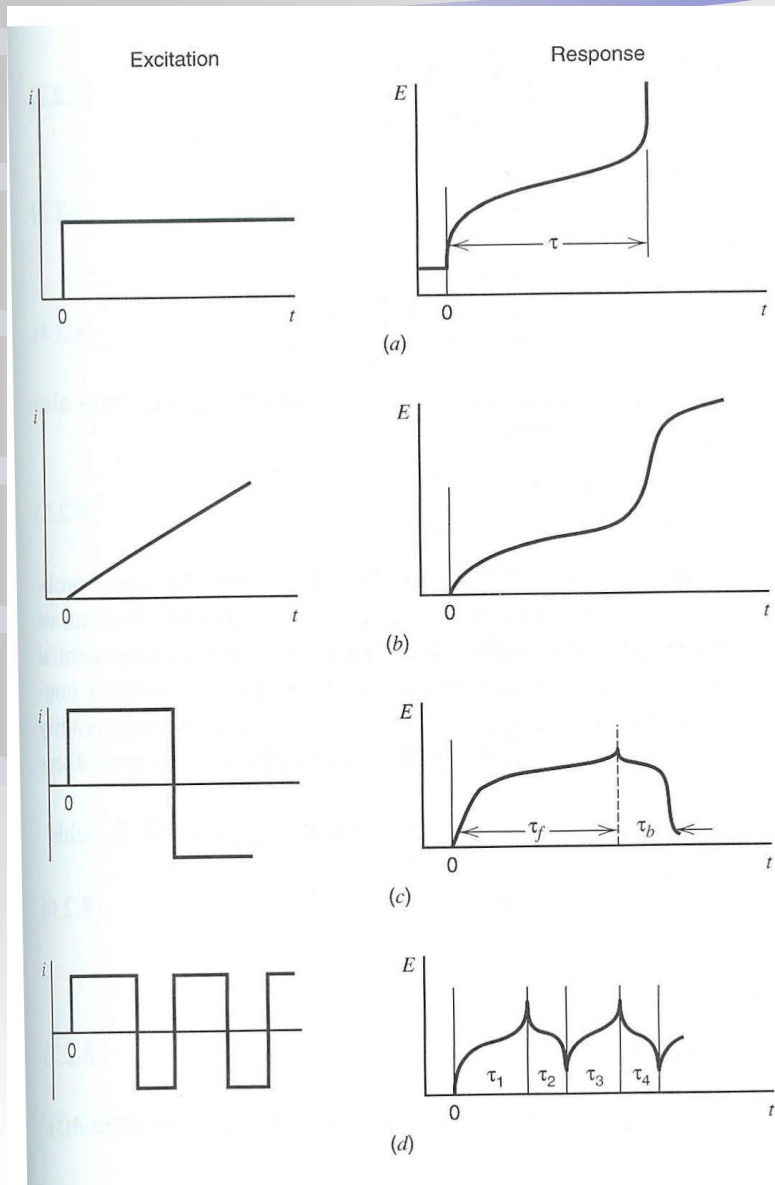


Figure 8.1.2 Different types of controlled-current techniques.
 (a) Constant-current chronopotentiometry.
 (b) Chronopotentiometry with linearly increasing current.
 (c) Current reversal chronopotentiometry.
 (d) Cyclic chronopotentiometry.

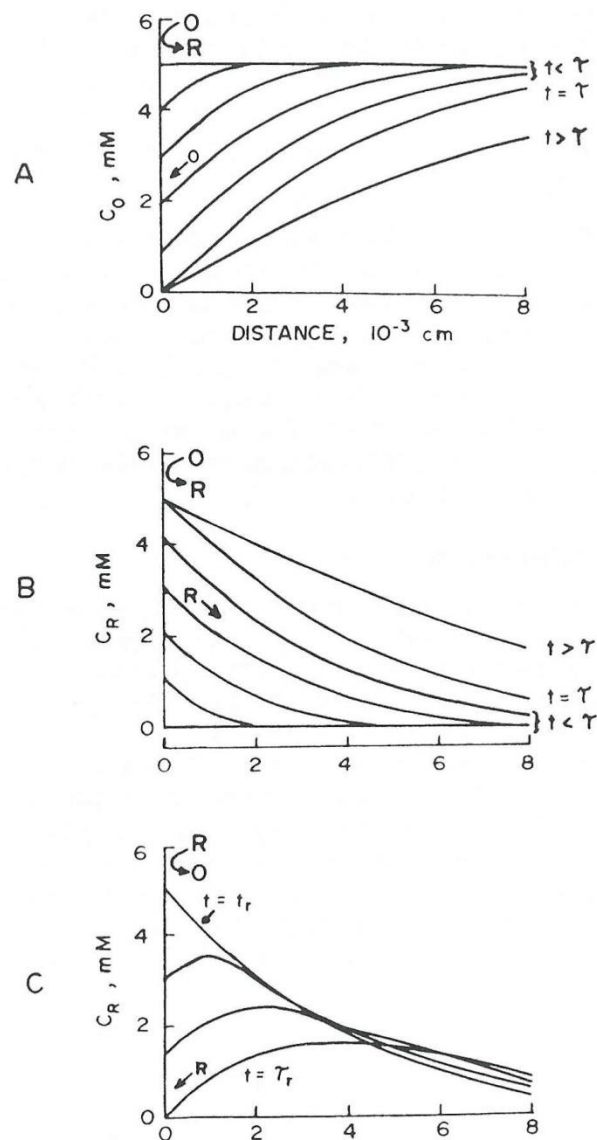


Figure 4.2 Concentration-distance profiles during reduction of O to R at a planar electrode by current-step excitation. Quiescent solution. $D_O = D_R = 10^{-5} \text{ cm}^2/\text{s}$, $C_O^0 = 5 \text{ mM}$, $C_R^0 = 0 \text{ mM}$, $i = 10^{-2} \text{ A/cm}^2$. (A) C-x profiles for O. Curves for 0, 0.07, 0.3, 0.7, 1.2, and 1.8 s. (B) C-x profiles for R. Curves for 0, 0.07, 0.3, 0.7, 1.2, and 1.8 s. (C) C-x profiles for R after current reversed at $t = \tau$. Curves for 0, 0.007, 0.3, and 0.6 s after current reversal. [Adapted from Ref. 1.]

Controlled Current Techniques

Nernstian Systems

$$(i \tau^{1/2})/C_O^* = (nFA D_O^{1/2} \pi^{1/2})/2 \quad \text{Sand equation}$$

$i \tau^{1/2}$ can be used to determine n , A , C_O^* , or D_O

Controlled Current Techniques

Nernstian Systems

$$E = E_{\tau/4} + RT/nF \ln (\tau^{1/2} - t^{1/2})/t^{1/2}$$

$E_{\tau/4}$ – quarter-wave potential, corresponds to the potential where the surface concentration of the redox species are equal ($C_O = C_R$)

$$E_{\tau/4} = E^{\circ'} - RT/2nF \ln D_O/D_R$$

If the reaction is reversible, a plot of E versus $\log[(\tau^{1/2}-t^{1/2})/t^{1/2}]$ will be linear with a slope of $59/n$ mV.

Controlled Current Techniques

Irreversible Reactions



$$E = E^{o'} + RT/\alpha F \ln[2k^o/(\pi D_O)^{1/2}] + RT/\alpha F \ln[\tau^{1/2} - t^{1/2}]$$

For irreversible reduction, the whole E-t curve shifts to more negative potentials with increasing current.

Ru between the RE and WE will also cause a E-t shift with increasing i.

Controlled Current Techniques

Quasireversible Reactions



Kinetics for the reactions by constant-current techniques usually involves small current changes and looking at potential change from equilibrium position.

$$-\eta = RT/F \ln \left[\frac{(2t^{1/2})}{(FA\pi^{1/2})} \left(\frac{1}{C_O} D_O^{1/2} + \frac{1}{C_R} D_R^{1/2} \right) + \frac{1}{i_o} \right]$$

Plot of η versus $t^{1/2}$ will be linear and i_o is obtained at the intercept.

Controlled Current Techniques

Double Layer Capacity

Since the potential constantly changes during the current step, a nonfaradaic current is always present due to changing of the double-layer capacitance.

$$i_c = -ACd(d\eta/dt) = -ACd(dE/dt)$$

So only a fraction of the total applied current, i , goes into the faradaic reaction.

$$i_f = i - i_c$$

Controlled Current Techniques

Double Layer Capacity

Since dE/dt is a function of time, i_c and i_f also vary with time, even as i is constant.

Assume i_c is constant for $0 < t < \tau$, and the approximation gives:

$$(i \tau^{1/2})/C_O^* = (i_f \tau^{1/2})/C_O^* + (i_c \tau)/(C_O^* \tau^{1/2})$$

$$\text{if } (i \tau^{1/2})/C_O^* = (nFA D_O^{1/2} \pi^{1/2})/2$$

Effect of double-layer charging is larger at small τ values.

Controlled Current Techniques

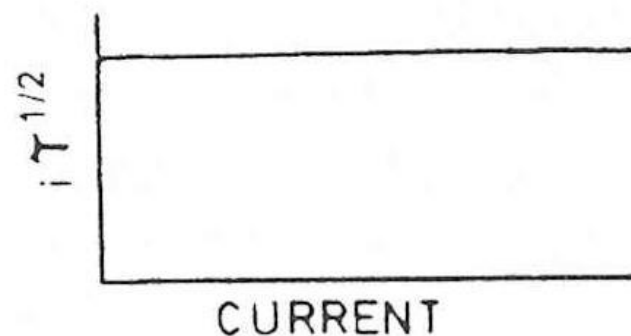
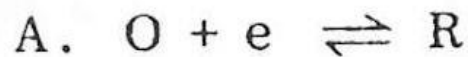
Mechanism Studies

Behavior of $i\tau^{1/2}$ can be used to diagnose certain mechanisms of electrode reactions.

Controlled Current Techniques

Mechanism Studies

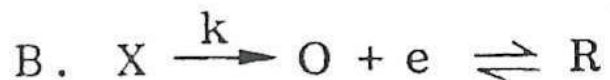
A constant value of $i\tau^{1/2}$ over τ is characteristic of diffusion-controlled reaction with no kinetic or adsorption phenomenon at a planar electrode.



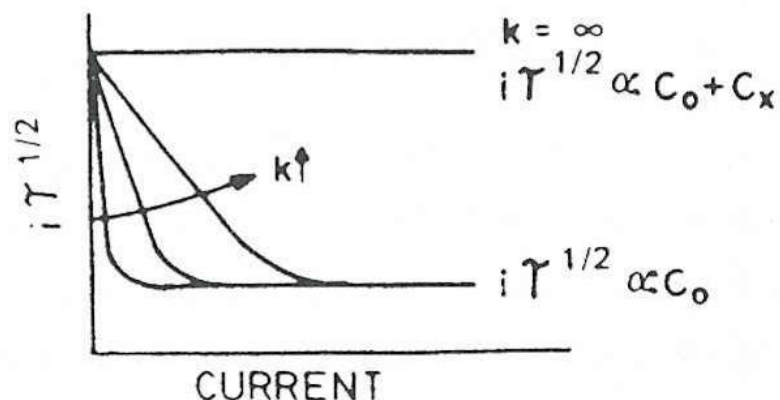
Controlled Current Techniques

Mechanism Studies

An electron transfer reaction coupled to a preceding chemical reaction shows a decrease of $i\tau^{1/2}$ as i increases.



Preceding chemical reaction



Controlled Current Techniques

Mechanism Studies

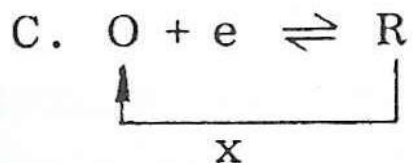
At large i (short τ), $i\tau^{1/2}$ determines $[O]_{eq}$,
since τ is reached before X can generate O
by a chemical reaction.

Magnitude of k for the chemical reaction can
be calculated from the slope.

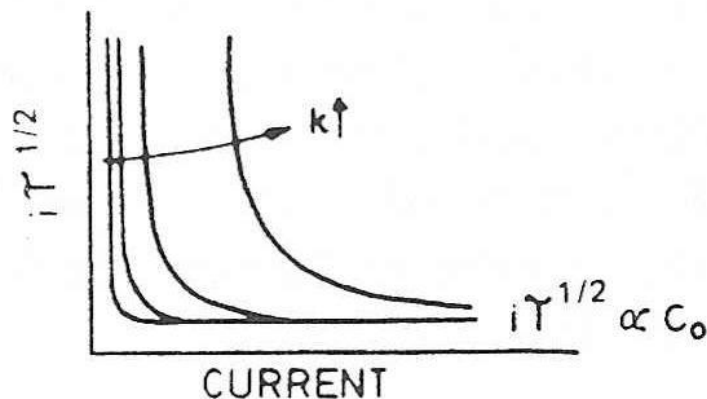
Controlled Current Techniques

Mechanism Studies

For a catalytic chemical reaction, $i\tau^{1/2}$ increases to infinity as i decreases.



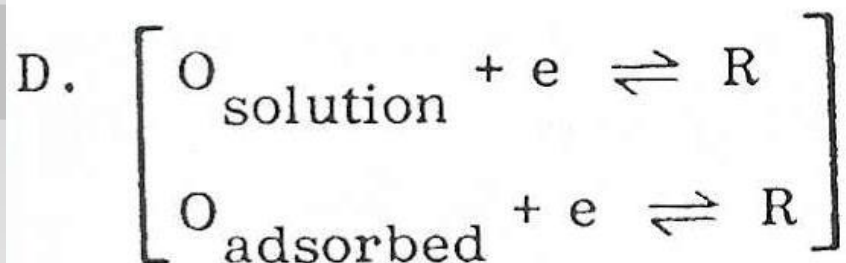
Catalytic reaction



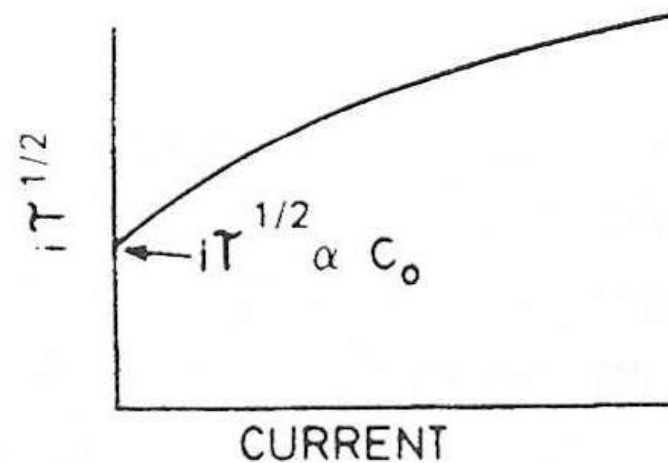
Controlled Current Techniques

Mechanism Studies

When the electroactive species, O, is adsorbed on the electrode, $i\tau^{1/2}$ increases with increasing i .



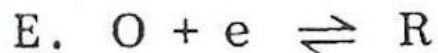
Adsorbed reactant



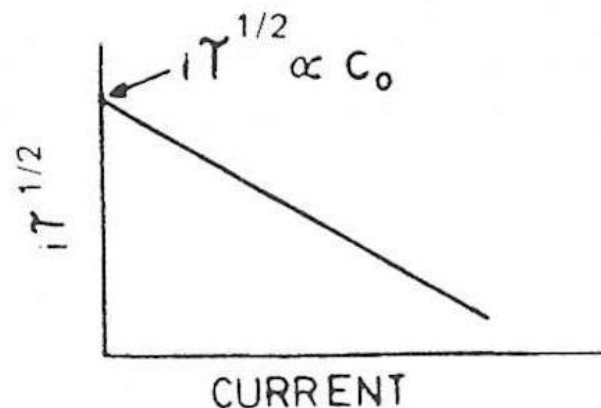
Controlled Current Techniques

Mechanism Studies

Inhibition of electrode reaction caused by material adsorbed on the electrode surface causes $i\tau^{1/2}$ to decrease with increasing i .



Reduction inhibited by
nonelectroactive material
adsorbed on electrode



Controlled Current Techniques

Chronopotentiometry as an experimental technique is difficult since the transition time is hard to pinpoint and the charging current is mixed with the faradaic current.

Controlled Current Techniques

Current-Reversal Chronopotentiometry

Polarity of the applied current is reversed during the regular chronopotentiometry experiment.

R, produced during the initial reaction undergoes oxidation and becomes zero at the electrode surface.

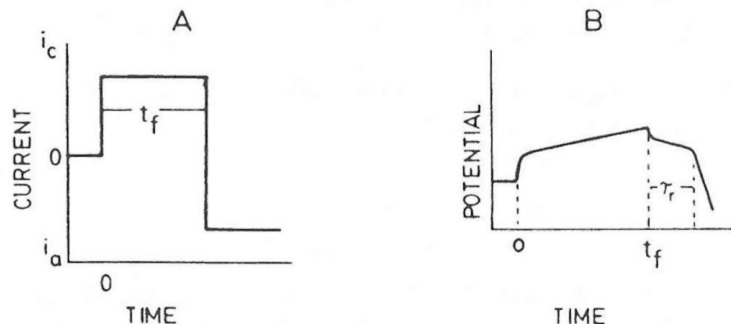


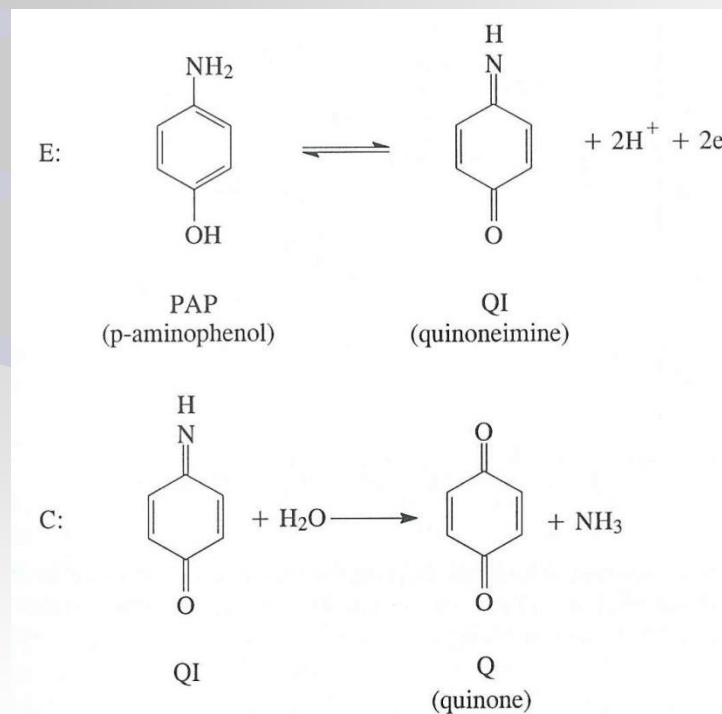
Figure 4.5 Current-reversal chronopotentiometry. (A) Current excitation signal. (B) Potential response.

Controlled Current Techniques

Applications

EC mechanisms are especially amenable to study by this technique.

Ex. Oxidation of p-aminophenol (PAP)



Controlled Current Techniques

Applications

Ex. Oxidation of p-aminophenol (PAP)

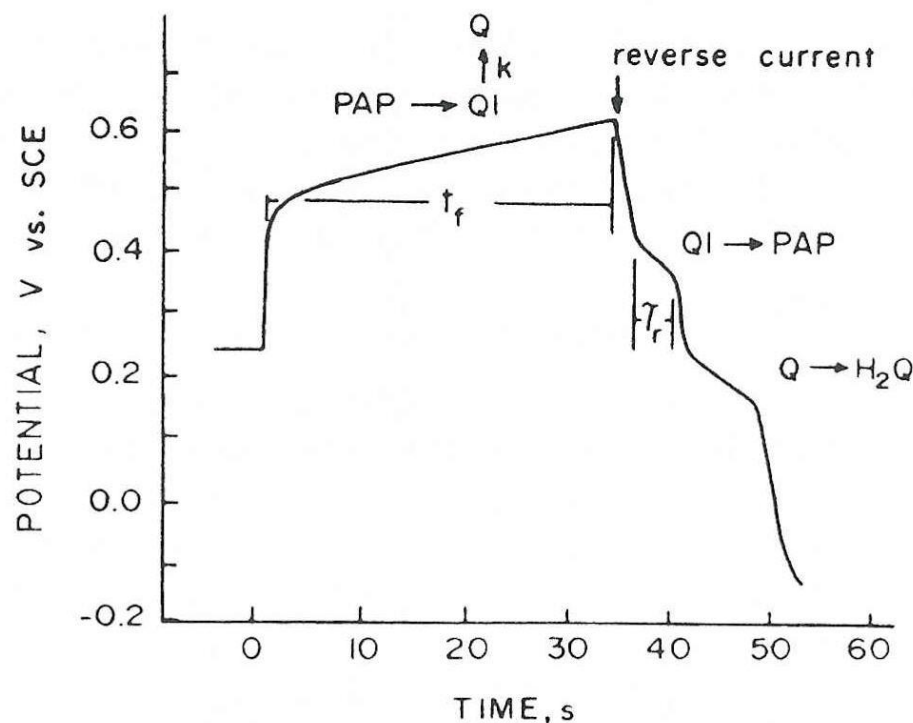


Figure 4.6 Current-reversal chronopotentiogram for the oxidation of 1 mM PAP in 0.1 M H₂SO₄. Pt electrode, $i = 100 \mu\text{A}/\text{cm}^2$. [From Ref. 9, adapted with permission. Copyright 1960 American Chemical Society.]

Controlled Current Techniques

Applications

Ex. Oxidation of p-aminophenol (PAP)

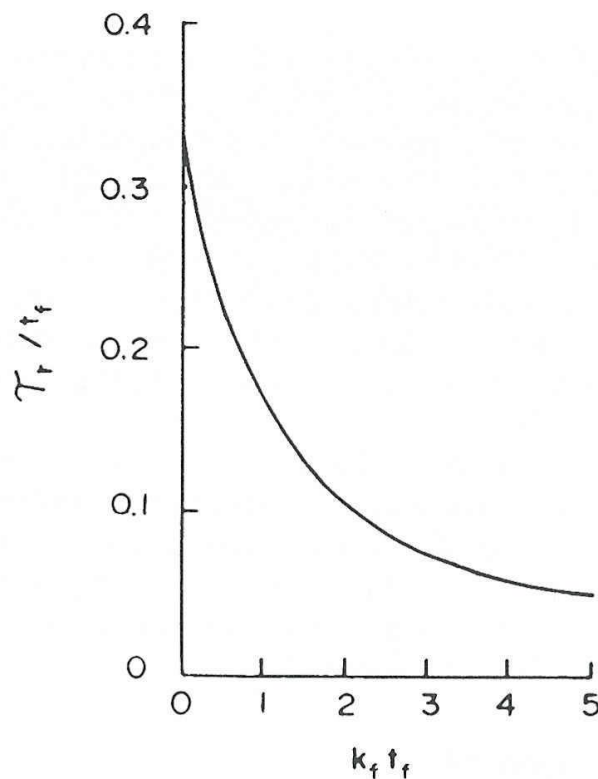


Figure 4.7 Working curve for the calculation of the rate constant k_f for a following chemical reaction from current-reversal chronopotentiometry. [From Ref. 9, adapted with permission. Copyright 1960 American Chemical Society.]

Controlled Current Techniques

Cyclic Chronopotentiometry

Current is continually reversed at potentials corresponding to the forward and reverse transition times.

Not used much.

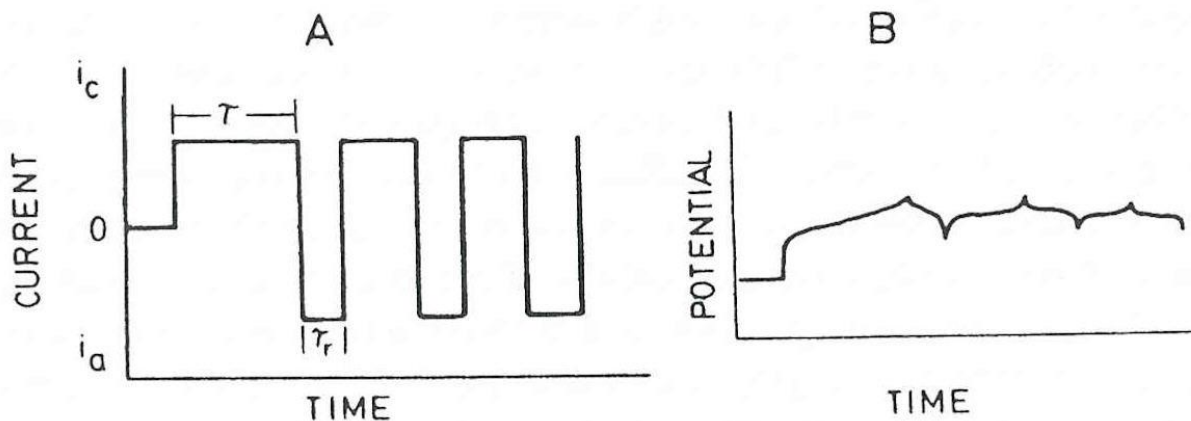


Figure 4.8 Cyclic chronopotentiometry. (A) Current excitation signal. (B) Potential response signal.

Controlled Current Techniques

For most electrochemical techniques can perform measurements for long periods of time without appreciably changing the bulk concentration of analyte (oxidized and or reduced species).

However, there are some bulk electrolysis methods, which alter the solution chemistry.

Controlled Current Techniques

However, there are some bulk electrolysis methods, which alter the solution chemistry.

The typical setup for bulk electrolysis is conducted with large surface area to volume ratios and often convective stirring for enhanced mass transport.

The anticipated outcome is to significantly change bulk solution properties during the course of the electrolysis.

Controlled Current Techniques

Bulk Electrolysis Methods

Alter the composition of the bulk solution by electrolysis, this includes:

- analytical measurements
 - electrogravimetric
 - coulometric
- separation of solution components (electroseparation)
- electrosynthetic methods

Controlled Current Techniques

Bulk Electrolysis Methods

Complete electrolysis techniques have a large area to volume (A/V) and effective mass-transfer (usually stirring).

Typical bulk electrolysis cells are more difficult to design since the experiments have longer times with larger currents.

Controlled Current Techniques

Bulk Electrolysis Methods

Electrodes are usually in separate cells since products of the electrode reaction at the CE may react at the WE.

A cell, consist of either two or three chambers, each separated by a porous material like sintered glass disks (frits) or polymer exchange membranes (*e.g.*, Nafion®).

The working and reference electrodes are often placed into one chamber of a separated cell and the counter electrode in another.

The working electrode chamber should be stirred to provide maximum mass transport to the electrode during electrolysis.

Controlled Current Techniques

Bulk Electrolysis Methods

Electrodes are usually in separate cells since products of the electrode reaction at the CE may react at the WE.

Some electrolysis cells separate each electrode into their own separate chamber.

Both the working and counter electrodes should have a large surface area (typically platinum meshes or high surface area carbon meshes, foam, felts and vitreous carbon materials) to increase current (charge) and reduce time to reach exhaustive electrolysis.

Controlled Current Techniques

Bulk Electrolysis Methods

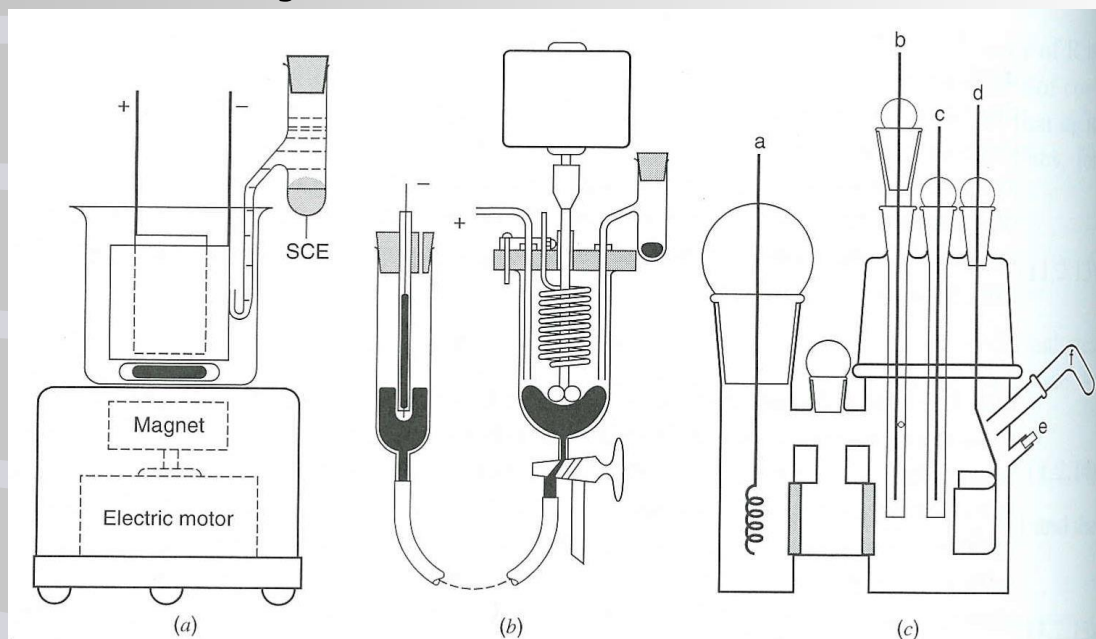
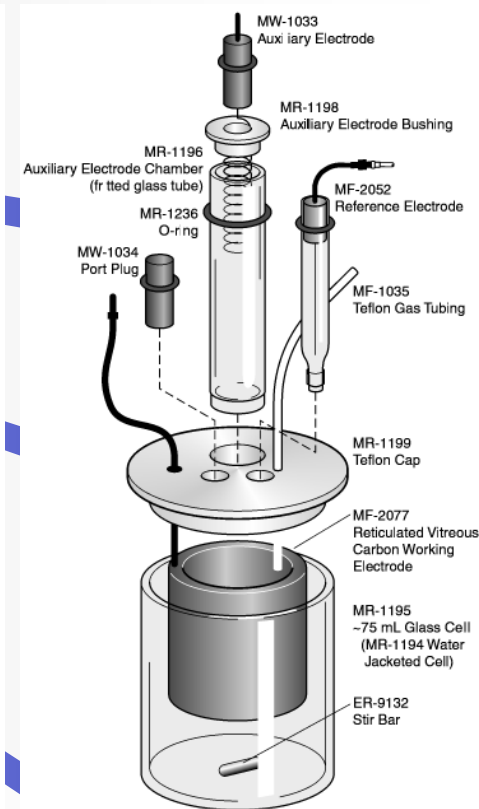


Figure 11.2.2 Typical cells for bulk electrolysis. (a) Undivided cell for controlled-potential separations and electrogravimetric analysis at a solid cathode. [From J. J. Lingane, *Anal. Chim. Acta*, **2**, 584 (1948), with permission.] (b) Undivided cell for coulometric analysis at mercury cathode with a silver anode. [Reprinted with permission from J. J. Lingane, *J. Am. Chem. Soc.*, **67**, 1916 (1945). Copyright 1945, American Chemical Society.] (c) Three-compartment cell, with ground-glass joints, for coulometric and voltammetric studies on a vacuum line. (a) Platinum wire auxiliary electrode; (b) silver wire reference electrode in separate compartment; (c) gold voltammetric working microelectrode; (d) platinum foil coulometric working electrode; (e) silicone rubber septum for sample injection; (f) rotatable side arm for solid sample addition. Arm and joint for attachment of cell to the vacuum line are not shown. [Reprinted with permission from W. H. Smith and A. J. Bard, *J. Am. Chem. Soc.*, **97**, 5203 (1975). Copyright 1975, American Chemical Society.]

Controlled Current Techniques

Bulk Electrolysis Methods

This cell is designed for complete electrosynthesis of a small amount (typically milligram quantities) of a material.



Controlled Current Techniques

Bulk Electrolysis Methods

Electrodes – solid one are usually wire gauzes or foil cylinders, also packed beds of powders, or pools (Hg).

Need large electrode area.

CE or auxillary electrodes placement is critical.

Asymmetrical placement leads to varying areas of solution resistance, producing different iR drops along the current paths.

Proper placement of RE tip is also important.

Should be placed at position of highest current density.

Controlled Current Techniques

Bulk Electrolysis Methods

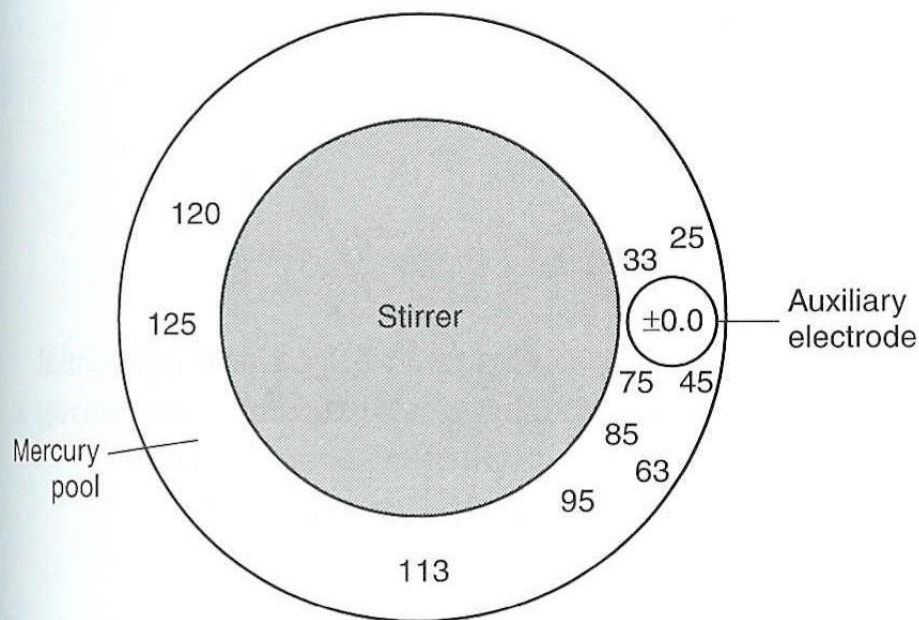


Figure 11.2.3 Potential distribution in mV at surface of ring-shaped mercury pool electrode using an unsymmetrical auxiliary electrode. Solution: 0.5 M H_2SO_4 ; total cell current: 40 mA; pool: 1.5 in. o.d., 1.0 in. i.d. Small circle shows position of the auxiliary electrode's fritted-glass separator, situated 4 mm above the pool surface. [Reprinted with permission from G. L. Booman and W. B. Holbrook, *Anal. Chem.*, **35**, 1793 (1963). Copyright 1963, American Chemical Society.]

Controlled Current Techniques

Controlled – Current Coulometry

An electrochemical method based on the measurement of the quantity of electricity (in coulombs) needed to convert the analyte quantitatively to a different oxidation state.

- a potential is applied from an external source forcing a non-spontaneous chemical reaction to take place: Electrolytic method
- measured quantity and the mass of analyte can be computed from known physical constants, standardization is not usually necessary

Controlled Current Techniques

Controlled – Current Coulometry

An electrochemical method based on the measurement of the quantity of electricity (in coulombs) needed to convert the analyte quantitatively to a different oxidation state.

- as accurate as gravimetric and volumetric procedures
- faster and more convenient than gravimetric measurements

Controlled Current Techniques

Controlled – Current Coulometry

Based on Faraday's law of electrolysis – the amount of electricity passed (coulombs) is directly proportional to the amount of chemical reaction (equivalents) at an electrode. $Q = it$

$$Q = \int_0^t i \, dt = (F)(\text{electrolysis})$$

Q – number of coulombs

i – current in amperes

t – time in seconds

Controlled Current Techniques

Controlled – Current Coulometry

$$Q = it$$

Faraday's law relates the number of moles of the analyte to the charge

$$\text{mols of analyte} = Q/(nF)$$

n = #moles of electrons transferred in the half-cell rxn

F = Faradays constant = 96487 C mol⁻¹

Controlled Current Techniques

Controlled – Current Coulometry

Fundamental requirement is 100% current efficiency

- all e- go to participate in the desired electrochemical process
- If not, then takes more current - over-estimate amount of analyte

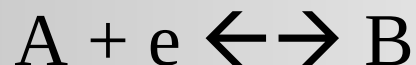
Current efficiency of 100% does not always imply that the analyte must participate directly in the electron-transfer process at the electrode.

The analyte could participate, in part, in a reaction that is secondary to the electrode reaction.

Controlled Current Techniques

Controlled – Current Coulometry

For a reaction



The WE reaction must be limited to the reaction of interest to assure that the charge consumed by electron transfer is equal to the charge applied to the cell.

The current applied to the cell is known directly, but a knowledge of the current-voltage curves for the initial components and supporting electrolyte provides valuable information.

Controlled Current Techniques

Controlled – Current Coulometry

For a reaction



The limiting current, i_l , of the hydrodynamic voltammogram is directly proportional to the concentration of the initial components in the electrolyte.

Controlled Current Techniques

Controlled – Current Coulometry

If a series of solutions were prepared with increasing concentration of the initial component, the limiting current increases.

The series of resulting curves can be normalized and plotted as i/i_1 versus $E - E_{1/2}$.

Controlled Current Techniques

Controlled – Current Coulometry

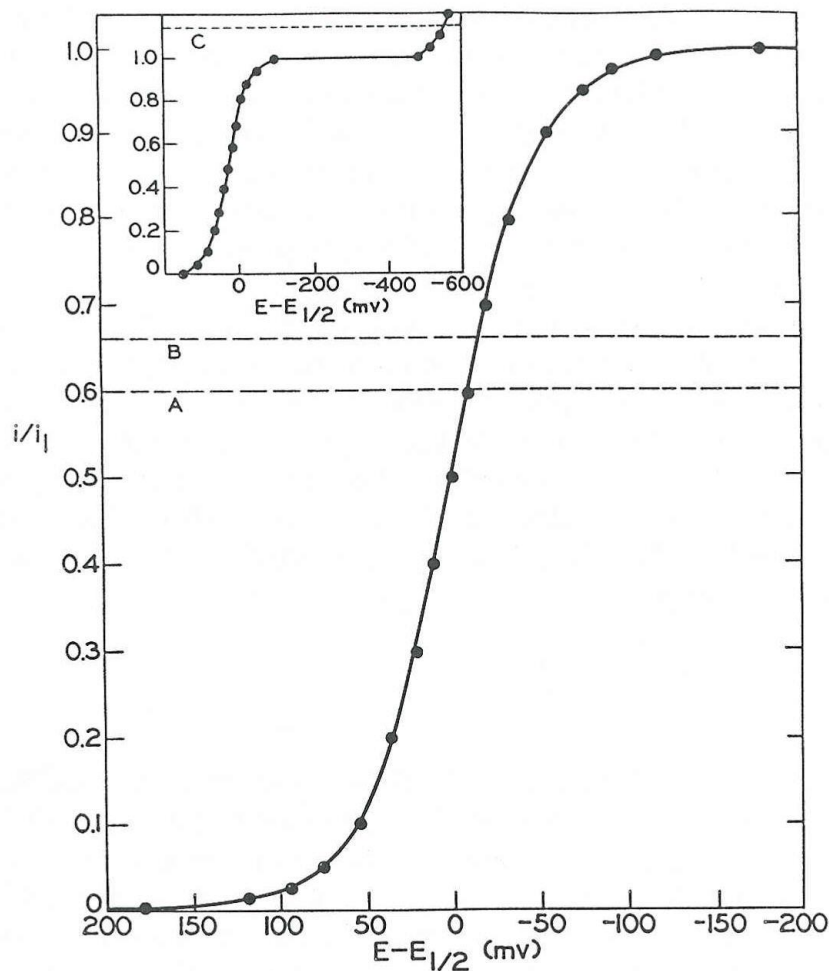


Figure 25.1 Normalized current-voltage curve. Calculated from the equation $E = E_{1/2} + (RT/nF) \ln (i_l - i)/i$, where i_l is the limiting current.

Controlled Current Techniques

Controlled – Current Coulometry

Current efficiency defined as the fraction of the current applied to the cell that goes to the faradaic reaction of the species.

$$\%C.E. = 100(i_{\text{applied}} - i_r)/i_{\text{applied}}$$

i_r – residual or background current from:

- > oxidation or reduction of impurities at WE
- > adsorption process at WE
- > charge or discharging of electrical double layer of WE

Controlled Current Techniques

Controlled – Current Coulometry

Applied current must be 1000 times the residual current to achieve a current efficiency of 99.9%.

Currents in excess of a few hundred mA are not used because the experiment is over too quickly to give accurate measurements, also heating effects are a problem.

Controlled Current Techniques

Controlled – Current Coulometry

For controlled-current conditions – as long as the applied current is less than the limiting current at a given bulk concentration, the electrode reaction proceeds with 100% current efficiency.

As electrolysis proceeds, the bulk concentration of O, $C_O^*(t)$ decreases and i_l decreases linearly with time.

$$C_O^*(t) = i_{app}/nFAm_o$$

Controlled Current Techniques

Controlled – Current Coulometry

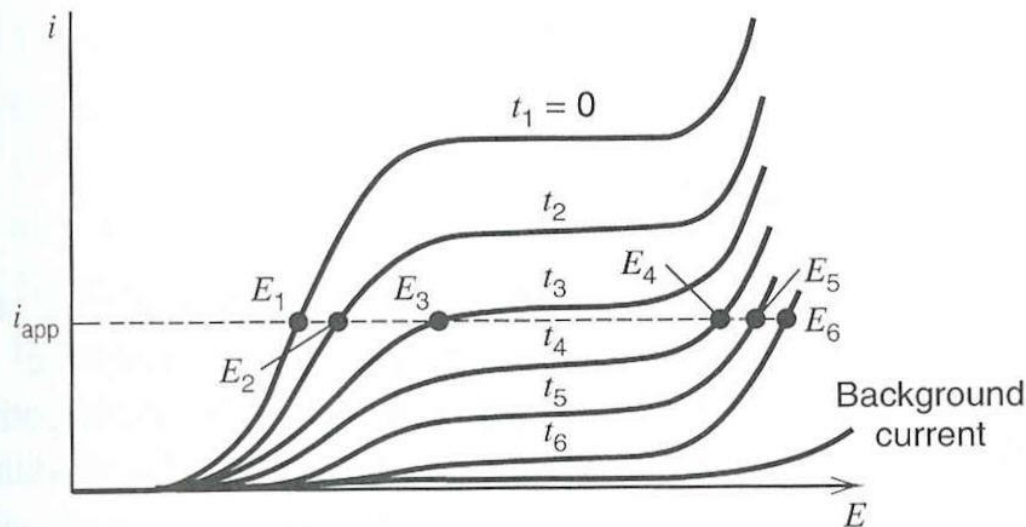


Figure 11.4.1 Current-potential curves at different times (increasing from t_1 to t_6) during bulk electrolysis with an applied constant current, i_{app} . The electrode potential shifts from E_1 to E_6 during the course of the electrolysis, with the largest shift occurring (between curves 3 and 4) when $i_{app} = i_l$.

Controlled Current Techniques

Controlled – Current Coulometry

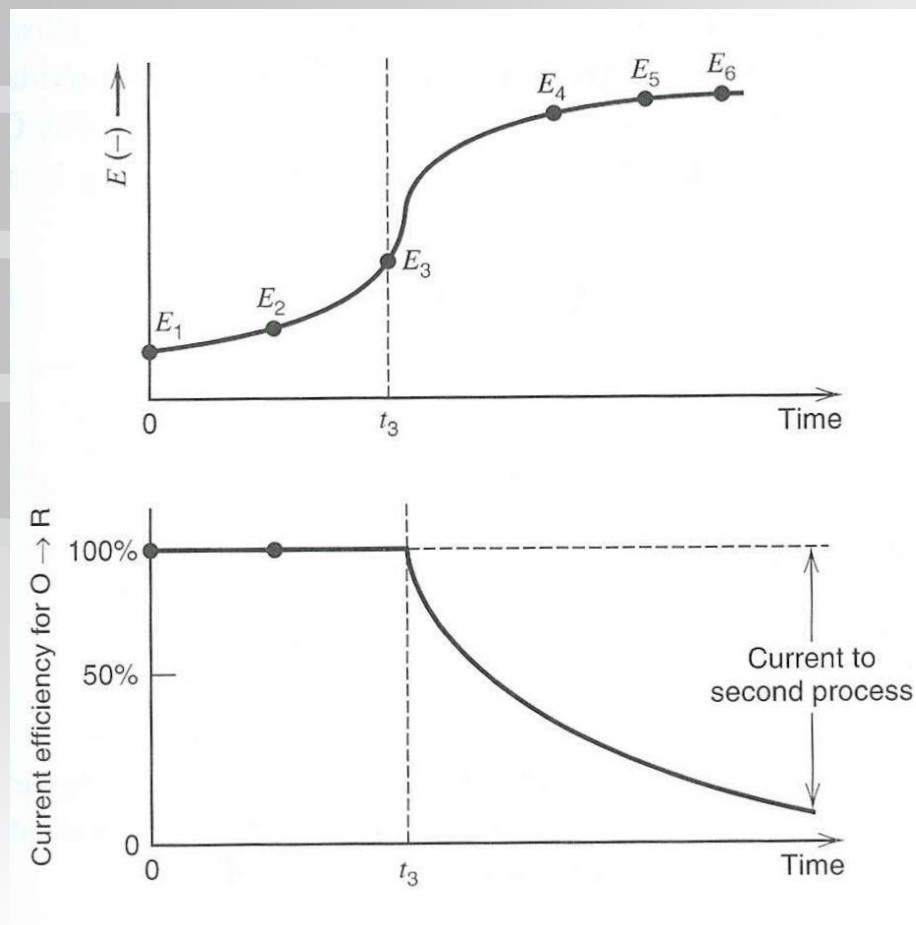


Figure 11.4.2 Potential and current efficiency for the electrolysis illustrated in Figure 11.4.1.

Controlled Current Techniques

Controlled – Current Coulometry

Controlled-current coulometry, has two advantages over controlled-potential coulometry.

- First, using a constant current leads to more rapid analysis since the current does not decrease over time. Thus, a typical analysis time for controlled current coulometry is less than 10 min, as opposed to approximately 30-60 min for controlled-potential coulometry.
- Second, with a constant current the total charge is simply the product of current and time. A method for integrating the current-time curve, therefore, is not necessary.

Controlled Current Techniques

Controlled – Current Coulometry

The selectivity of constant-current separations is poorer than for controlled-potential methods, since the potential must shift during electrolysis for the reaction to continue.

With the commercial availability of suitable potentiostats, controlled-current methods are being replaced with controlled-potential methods in analysis and lab preps.

However in large scale industry applications this is not true.

Controlled Current Techniques

Coulometric Titrations

Internally generate a titrant with current.

Primary process:

Unknown substance reacts directly at an electrode.

Not used as much since the unknown decreases during electrolysis making it difficult to maintain 100% current efficiencies.

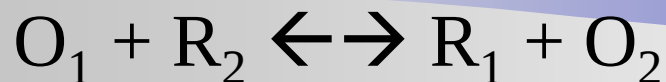
Secondary process:

Electrogenerated reagent reacts with unknown substance in a stoichiometric manner.

Controlled Current Techniques

Coulometric Titrations

Titration Efficiency



O_1 is the titrate and R_2 is the titrant, electrode potential of couple 1 must be more positive than for couple 2.

The titrant, O_1 is more easily reduced than O_2 .

Therefore most of the current is carried by O_1 .

Current efficiency is less than 100% for both couple 1 and 2, but the charge passed is the same whether O_1 is reduced at the electrode or by R_2 .

This gives 100% titration efficiency even though current efficiency is less than 100%.

Controlled Current Techniques

Coulometric Titrations

Endpoint Detection

Table 25.2 Selected Endpoint Detection Methods for Coulometric Titrations

Visual indicators	Potentiometric
Colorimetric	Amperometric
Spectrophotometric	Biamperometric
Pressurometric	Conductometric

Controlled Current Techniques

Coulometric Titrations

Endpoint Detection

The electrometric methods employed for endpoint detection are based on measurements of either the potential difference between the 2 electrodes (potentiometric) or the current passing in that circuit (amperometric).

Controlled Current Techniques

Coulometric Titrations

Applications of Coulometric Titrations:

- Can be used for Acid-Base Titrations
- Can be used for Complexation Titrations (EDTA)
- Can be used for Redox Titrations

Controlled Current Techniques

Coulometric Titrations

Example:

Titration of Fe^{2+} with Ce^{4+}



f = moles Ce^{4+} added / moles Fe^{2+} initially present

Initially $f = 0$, cell contains only Fe^{2+} and only faradaic wave for Fe^{2+} is seen.

When $0 < f < 1$, before equivalent point

When $f > 1$ after equivalent point.

Controlled Current Techniques

Coulometric Titrations

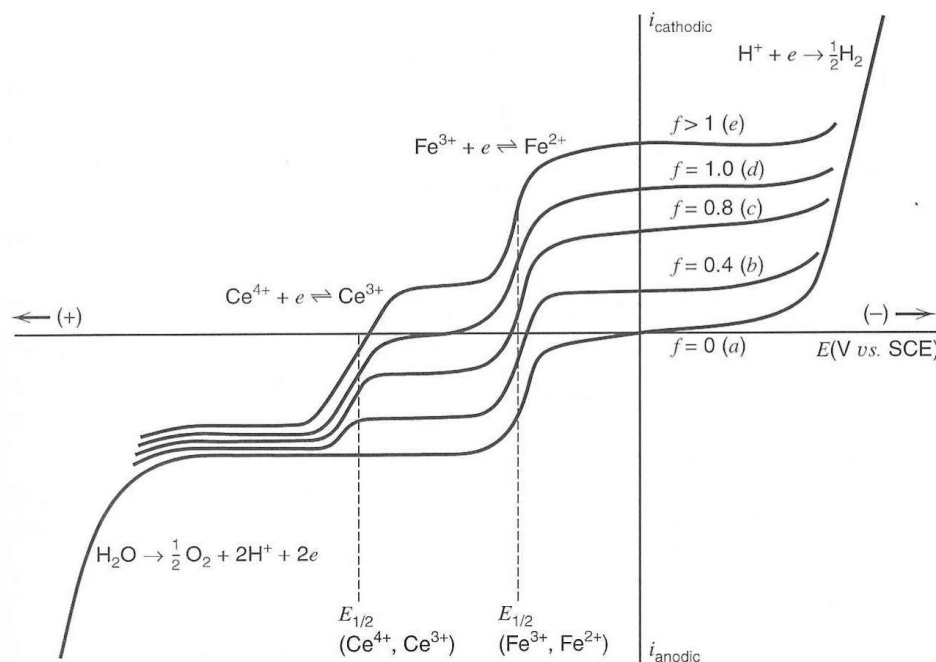


Figure 11.5.1 Idealized current-potential curves at a platinum electrode during titration of Fe^{2+} with Ce^{4+} at different fractions, f , of Fe^{2+} titrated. (a) $f = 0$; only an anodic wave for $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ is observed. (b), (c) $0 < f < 1$; the solution contains Fe^{2+} , Fe^{3+} , and Ce^{3+} . A composite wave for Fe^{3+} , Fe^{2+} couple, as well as an anodic wave for $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+} + e$, are observed. (d) $f = 1$; the solution contains Fe^{3+} and Ce^{3+} . There is a cathodic wave for $\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}$ and an anodic wave for oxidation of cerous. (e) $f > 1$; the solution contains Fe^{3+} , Ce^{3+} , and Ce^{4+} . A composite wave for the Ce^{4+} , Ce^{3+} couple and a cathodic wave for ferric ion are observed. The curves drawn are representative of those obtained for a steady-state voltammetric technique, for example, an RDE or a microelectrode in stirred solution. [Adapted from J. J. Lingane, "Electroanalytical Chemistry," 2nd ed., Wiley-Interscience, New York, 1958.]

Controlled Current Techniques

Coulometric Titrations

Titants

Most titrants are electrogenerated.

In aqueous solution the strongest oxidant is silver(II) ($E^\circ \sim 2\text{V}$) and strongest reductant is uranium (III) ($E^\circ \sim -0.63\text{V}$).

Bromine ($E^\circ = 1.065\text{V}$) is moderately strong oxidizing agent and free of side reactions.

Easily generated with 100% current efficiency at a Pt electrode and used widely in inorganic and organic chemistry.

Controlled Current Techniques

Coulometric Titrations

Titants

Table 25.3 Electrogenerated Titants

A. Oxidants		
Bromine	Cerium(IV)	Thallium(III)
Hypobromite ion	Permanganate ion	Vanadium(IV)
Bromine monochloride	Chromium(VI)	Vanadium(V)
Iodine	Silver(II)	Lead tetraacetate
Chlorine	Manganese(III)	Oxygen
Iron(III)	Mercury(II)	Quinone
Ferricyanide ion	Gold(II)	Silver(I)
B. Reductants		
Iron(II)	Titanium(III)	Vanadium(IV)
Iron(II)-EDTA	Copper(I)	Vanadium(III)
Ferrocyanide ion	Hexacyanomanganese(I)	Uranium(III)
Molybdenum(V)	Tin(II)	Iodide ion
Octacyanomolybdenum(V)	Chromium(II)	Uranium(IV)
C. Precipitants and complexing agents		
Silver(I)	Copper(II)	Iodide ion
Mercury(I)	Lanthanum(III)	Fluoride ion
Lead(II)	Mercury(II)	Sulfide ion
Bismuth(III)	Ferricyanide ion	Thiocyanate ion
Aluminum(III)	Ferrocyanide ion	EDTA
D. Bases		
Aqueous and nonaqueous media		
E. Acids		
Aqueous and nonaqueous media		
F. Miscellaneous		
Tungsten(II) in LiCl-KCL eutectic		
Karl Fischer reagent		

Source: See text.

Controlled Current Techniques

Coulometric Titrations

Titrants

TABLE 11.4.1 Typical Electrogenerated Titrants and Substances Determined by Coulometric Titration

Electrogenerated Titrant	Generating Electrode and Solution	Typical Substances Determined
<i>Oxidants</i>		
Bromine	Pt/NaBr	As(III), U(IV), NH ₃ , olefins, phenols, SO ₂ , H ₂ S, Fe(II)
Iodine	Pt/KI	H ₂ S, SO ₂ , As(III), water (Karl Fischer), Sb(III)
Chlorine	Pt/NaCl	As(III), Fe(II), various organics
Cerium(IV)	Pt/Ce ₂ (SO ₄) ₃	U(IV), Fe(II), Ti(III), I ⁻
Manganese(III)	Pt/MnSO ₄	Fe(II), H ₂ O ₂ , Sb(III)
Silver(II)	Pt/AgNO ₃	Ce(III), V(IV), H ₂ C ₂ O ₄
<i>Reductants</i>		
Iron(II)	Pt/Fe ₂ (SO ₄) ₃	Mn(III), Cr(VI), V(V), Ce(IV), U(VI), Mo(VI)
Titanium(III)	Pt/TiCl ₄	Fe(III), V(V,VI), U(VI), Re(VIII), Ru(IV), Mo(VI)
Tin(II)	Au/SnBr ₄ (NaBr)	I ₂ , Br ₂ , Pt(IV), Se(IV)
Copper(I)	Pt/Cu(II)(HCl)	Fe(III), Ir(IV), Au(III), Cr(VI), IO ₃ ⁻
Uranium(V),(IV)	Pt/UO ₂ SO ₄	Cr(VI), Fe(III)
Chromium(II)	Hg/CrCl ₃ (CaCl ₂)	O ₂ , Cu(II)
<i>Precipitation and Complexation Agents</i>		
Silver(I)	Ag/HClO ₄	Halide ions, S ²⁻ , mercaptans
Mercury(I)	Hg/NaClO ₄	Halide ions, xanthate
EDTA	Hg/HgNH ₃ Y ^{2-a}	Metal ions
Cyanide	Pt/Ag(CN) ₂ ⁻	Ni(II), Au(III,I), Ag(I)
<i>Acids and Bases</i>		
Hydroxide ion	Pt(-)/Na ₂ SO ₄	Acids, CO ₂
Hydrogen ion	Pt(+)/Na ₂ SO ₄	Bases, CO ₃ ²⁻ , NH ₃

^aY⁴⁻ is ethylenediamine-tetra-acetate anion.

Controlled Current Techniques

Flow electrolysis

Another type of bulk electrolysis involving flowing of the solution through a porous WE.

Good method for high efficiencies and rapid conversion with large amounts of solution (industry).

Popular electrodes: packed beds of powders or hollow bundle of rods.

Flow electrolysis

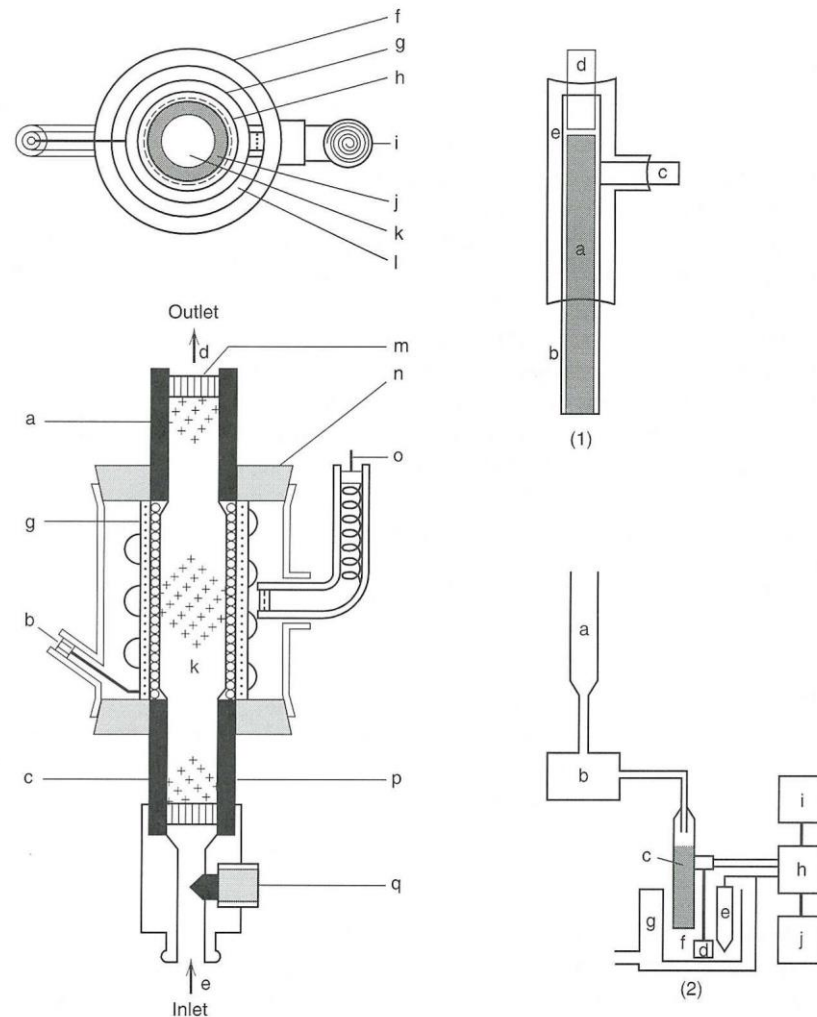


Figure 11.6.1 Flow electrolytic cells. *Left:* Cell utilizing glassy carbon granule working electrode (k), silver auxiliary electrode (g), Ag/AgCl reference electrode (o, i) with porous glass separator (h). Other components are (a, c) lead for working electrode; (b) lead to auxiliary electrode; (d) solution outlet; (e) solution inlet; (f) glass or plastic tube; (j, p) porous carbon tube; (l) saturated KCl solution; (m) silicone rubber. [Reprinted with permission from T. Fujinaga and S. Kihara, *CRC Crit. Rev. Anal. Chem.*, **6**, 223 (1977). Copyright, CRC Press, Inc., Boca Raton, FL.] *Right:* Cell with Reticulated Vitreous Carbon (RVCTM), a conductive foam-type material available in several porosities. (1) (a) RVC cylinder, (b) heat-shrink tubing, (c) graphite rod sidearm, (d) glass tube, (e) glass and epoxy support. (2) Schematic diagram of complete apparatus. (a) Solution reservoir, (b) pump, (c) RVC electrode, (d) platinum electrode, (e) SCE reference electrode, (f) downstream reservoir, (g) runover collector, (h) potentiostat, (i) recorder, (j) digital voltmeter. [Reprinted with permission from A. N. Strohl and D. J. Curran, *Anal. Chem.*, **51**, 353 (1979). Copyright 1979, American Chemical Society.]

Controlled Current Techniques

Flow electrolysis

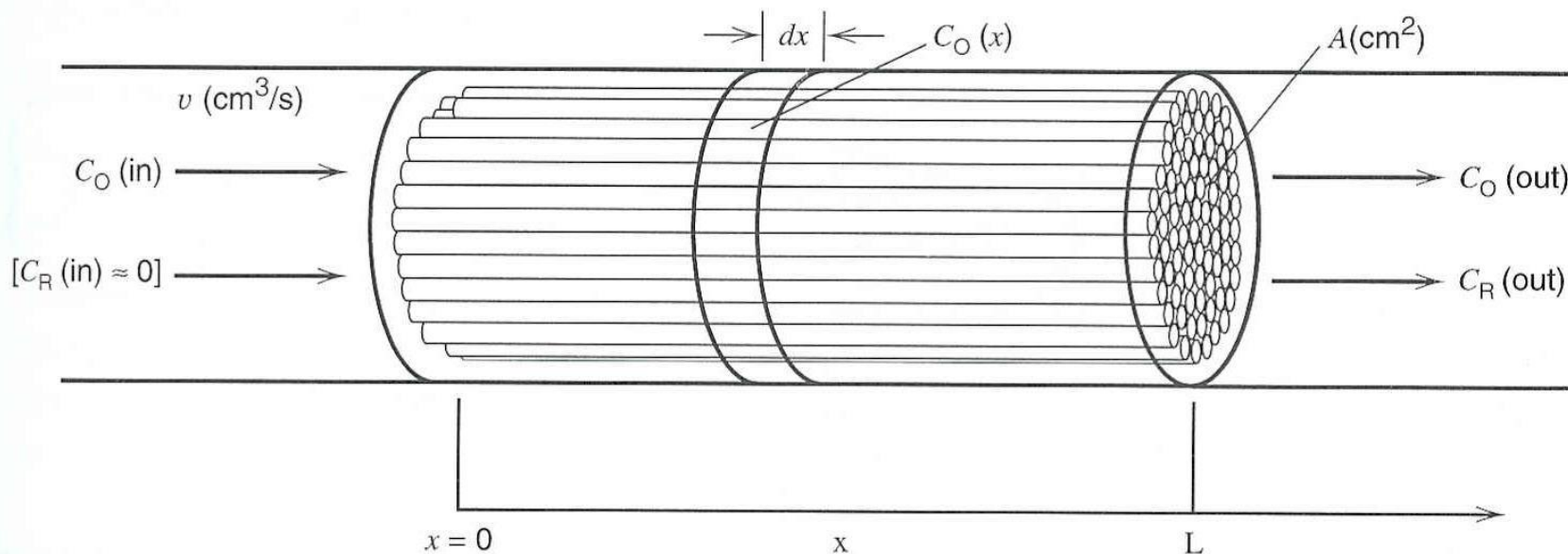


Figure 11.6.2 Schematic diagram of the working electrode of a flow electrolysis cell.

Controlled Current Techniques

Flow electrolysis

By passing a current of electricity through a sodium chloride solution the salt is decomposed into chlorine at the anode and sodium at the cathode.

Sodium reacts with water in the solution, forming caustic soda and setting free hydrogen.

The products of electrolysis are chlorine, caustic soda, and hydrogen.



Controlled Current Techniques

Flow electrolysis

The primary products of electrolysis are chlorine gas, hydrogen gas, and sodium hydroxide solution (commonly called "caustic soda" or simply "caustic").

However, if the electrolyte is maintained at a pH of 6.5 or 10, one can form chlorate or hypochlorite from the electrogenerated chlorine and caustic. This is the basis for the electrolytic production of sodium chlorate or sodium hypochlorite (commonly known as "bleach").

Controlled Current Techniques

Flow electrolysis

Chlorine and sodium hydroxide are among the top ten chemicals produced in the world and are involved in the manufacturing of a wide variety of products used in day-to-day life. These include: pharmaceuticals, detergents, deodorants, disinfectants, herbicides, pesticides, and plastics.

Controlled Current Techniques

Flow electrolysis

Presently, the primary uses of chlorine are in the pulp and paper manufacturing operations for bleaching to produce a high quality whitened material and in water treatment operations as a disinfectant.

Controlled Current Techniques

Flow electrolysis

The other uses of chlorine include the production of organic and inorganic chemicals. The largest volume organic chemical manufactured that involves chlorine is polyvinyl chloride (PVC). PVC is a very versatile thermoplastic, used in a wide variety of daily products. The major use of chlorine in the production of inorganic chemicals is for titanium dioxide (a widely used pigment), manufactured from naturally occurring ores (ilmenite or rutile).

Controlled Current Techniques

Flow electrolysis

The end uses of sodium hydroxide are diverse compared to the uses of chlorine. Its primary applications are in the neutralization reactions and forming anionic species such as aluminates and zincates.

- In the manufacture of organic chemicals, NaOH is used for the neutralization of acids, pH control, off-gas scrubbing, dehydrochlorination, and as a source of sodium during various chemical reactions. For example, it is used in the dehydrochlorination stage of the epoxy resin production and hydrolysis reactions involving epichlorohydrin in the formation of glycerin, used in the pharmaceutical, tobacco and food/beverage industries

Controlled Current Techniques

Flow electrolysis

The end uses of sodium hydroxide are diverse compared to the uses of chlorine. Its primary application are in the neutralization reactions and forming anionic species such as aluminates and zincates.

- The major use of NaOH for making inorganic chemicals is in the production of hypochlorite for household and industrial bleaching purposes. Also, its use in the pulp and paper industry is in the production of sodium sulfide and sodium hydrosulfide for mechanical pulping. It is also used in the food processing applications, which include skin removal of potatoes, tomatoes etc, for further processing.

Controlled Current Techniques

Flow electrolysis

The chlor-alkali (also called "chlorine-caustic") industry is one of the largest electrochemical technologies in the world. It is an energy intensive process and is the second largest consumer of electricity (2400 billion kWh) among electrolytic industries.

In 2006, about 84% of the total world chlorine capacity of about 59 million metric tons was produced electrolytically using diaphragm and membrane cells, while about 13% was made using mercury cells.

Controlled Current Techniques



*Chlor-alkali cell room with BL-2.7 membrane cells
(Courtesy of Uhde GmbH).*

Class Assignment

- Read Chapter 8 – Bard and Faulkner
- Read Chapter 11 – Bard and Faulkner

