Chapter 22

Bulk Electrolysis:
Electrogravimetry and Coulometry

Definition

- **Bulk Electrolysis deals with methods that involve electrolysis producing a quantitative change in oxidation state**
- **Example: In a mixture solution of Zn^{2+} and Cu^{2+}, convert all Cu^{2+} to Cu metal and leave Zn^{2+} in the solution.**

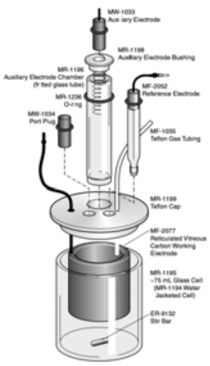
  → Hold the working electrode (e.g. Cu) potential at a certain value (positive than that for Zn reduction)

  $$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$$

Features of Bulk Electrolysis Cells

- **Big working and counter electrodes—~100 times larger than normal electrodes (e.g., in CV)**
- **Large cell currents (mA vs μA-nA)**
- **Stirring Solution (mainly convection)**
- **working and counter electrode placed in two separated cell compartments (avoiding by-products produced at the counter electrode)**

An example of bulk electrolysis cell produced by Bioanalytical System, Inc.



Classification

- Three Types
  - Electrogravimetric analysis

    $M^{2+} + ne \rightarrow M(s)$

    Metal is electrolytically deposited onto a inert electrode (e.g., Pt)—the increase in mass of the electrodes gives the concentration or amount of the metal ion in the solution
  - Constant potential coulometry
  - Constant current coulometry

Effect of Current on Cell Potential

$I = E / R$ (Ohm's Law)

I – current (Amperes, A)--flow of positive charge.

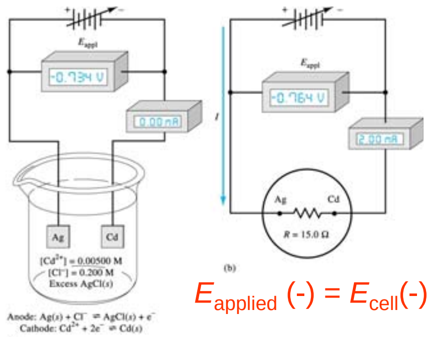
E – potential (Voltage) (Volts,V)

R – resistance (ohms,Ω)

Direct current (dc)--one direction current

Alternating current (ac)--current reverses periodically

Ohmic Potential; *IR* Drop



$E_{applied}$ (-) = E_{cell}(-) – *IR*(+)

(A)Ag|AgCl(s), Cl^- (0.200 M),Cd^{2+} (0.00500 M)|Cd(C)

How to reduce the *IR* drop?

- Always use inert supporting electrolyte (0.1 ~ 1.0 M concentration);
- Reduce the electrochemical cell current (using small electrode);
- Use three-electrode system;
- Compensation

Polarization Effects

- Polarization is the departure of the electrode potential from its theoretical Nernst equation value on the passage of current.
- Factors that influence polarization:

(a) Electrode size, shape, and composition;
(b) Composition of the electrolyte solution;
(c) Temperature of the stirring rate;
(d) Current level; and
(e) Physical state of species involved in the cell reaction.

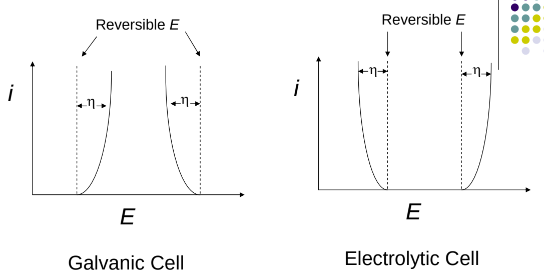
Overpotential (Overvoltage), η

- Overpotential (overvoltage) develops as a result of ***electrode polarization:***

  (1) concentration polarization - mass transport to/from electrode limited

  (2) Kinetic polarization - rate of redox reaction at electrode
- Overpotential means must apply greater potential before redox chemistry occurs

$$\eta = E_{\text{current}} - E_{\text{reverible/equilibrium}}$$



Due to overpotentials, for a galvanic cell, a cell potential is always smaller than that calculated from the reversible potential; for a electrolytic cell, the applied potential is always larger than that calculated from the reversible potential.

Mass transfer to/from electrode

- Mass transfer is the movement of material (ions, molecules etc.) from one location to another (e.g, from bulk to electrode surface).

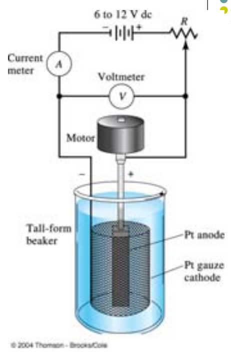
(a) Diffusion—results from concentration gradient;

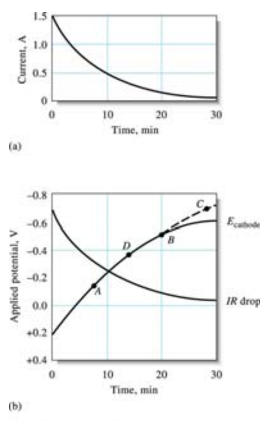
(b) Migration—arises from potential gradient;

(c) Convection—results from stirring, vibration, or temperature gradient.

Electrogravimetric Methods

- Electrogravimetry without potential control.
- Electrogravimetry is potential-controlled—potentiostatic method.





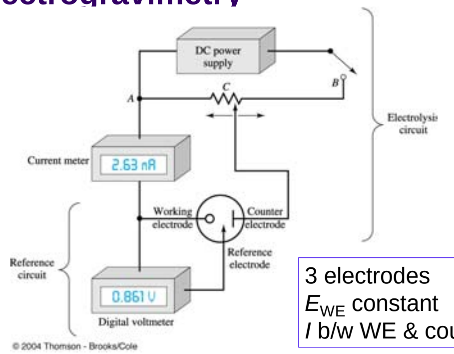
$Cu^{2+} \rightarrow Cu(s)$

$E_{cathode} = E^0 + (0.0592/2)\lg[Cu^{2+}]$

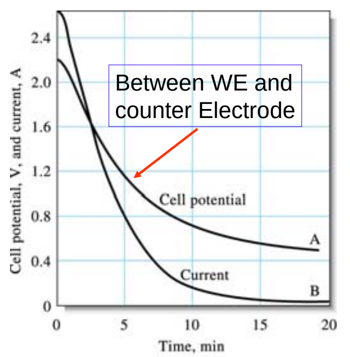
TABLE 22-1
Some Applications of Electrogravimetry without Potential Control

Analyte	Weighed as	Cathode	Anode	Conditions
Ag^+	Ag	Pt	Pt	Alkaline CN^- solution
Br^-	AgBr (on anode)	Pt	Ag	
Cd^{2+}	Cd	Cu on Pt	Pt	Alkaline CN^- solution
Cu^{2+}	Cu	Pt	Pt	H_2SO_4/HNO_3 solution
Mn^{2+}	MnO_2 (on anode)	Pt	Pt dish	HCOOH/HCOONa solution
Ni^{2+}	Ni	Cu on Pt	Pt	Ammoniacal solution
Pb^{2+}	PbO_2 (on anode)	Pt	Pt	HNO_3 solution
Zn^{2+}	Zn	Cu on Pt	Pt	Acidic citrate solution

Controlled-Potential Electrogravimetry



3 electrodes
E_{WE} constant
I b/w WE & counter



$Cu^{2+} \rightarrow Cu(s)$ at constant E

TABLE 22-2
Some Applications of Controlled-Potential Electrolysis*

Metal	Potential vs. SCE	Electrolyte	Other Elements That Can Be Present
Ag	+ 0.10	Acetic acid/acetate buffer	Cu and heavy metals
Cu	− 0.30	Tartrate + hydrazine + Cl^-	Bi, Sb, Pb, Sn, Ni, Cd, Zn
Bi	− 0.40	Tartrate + hydrazine + Cl^-	Pb, Zn, Sb, Cd, Sn
Sb	− 0.35	HCl + hydrazine at 70°C	Pb, Sn
Sn	− 0.60	HCl + hydroxylamine	Cd, Zn, Mn, Fe
Pb	− 0.60	Tartrate + hydrazine	Cd, Sn, Ni, Zn, Mn, Al, Fe
Cd	− 0.80	HCl + hydroxylamine	Zn
Ni	− 1.10	Ammoniacal tartrate + sodium sulfite	Zn, Al, Fe

*From J. J. Lingane, *Electroanalytical Chemistry*, 2nd ed., p. 413. New York: Interscience, 1958. This material is used by permission of John Wiley & Sons, Inc.

Constant Potential Coulometry

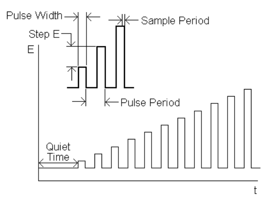
- Control *E* of the anode or cathode relative to some reference electrode in order to control the reaction that takes place on the working electrode.

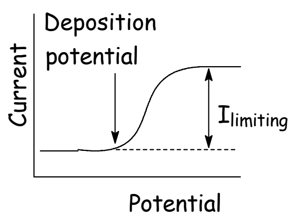
For reaction:

$$M^{n+} + ne \rightleftharpoons M(s)$$

What dose the Potential~Current profile look like?

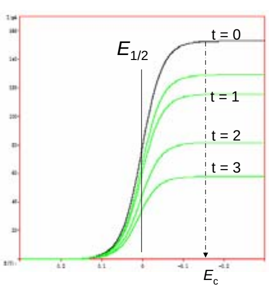
Potential ~ Current Profile





$$M^{n+} + ne \rightleftharpoons M(s)$$

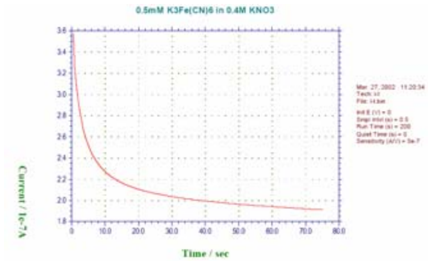
$Current \propto c_{M^{n+}}$



Let $I_{initial} = I_0$, $C_{initial} = C_0$

- When $C_{t2} = 0.5\ C_0$: $I_{t2} = 0.5I_0$
- When $C_{t3} = 0.25\ C_0$: $I_{t3} = 0.25\ I_0$ -- removed 75% of analyte
- When $C_{tx} = 0.01\ C_0$: $I_{tx} = 0.01\ I_0$ -- removed 99% of analyte

Current ~ Time Behavior



Electrochemical cell current decays exponentially as a function of time

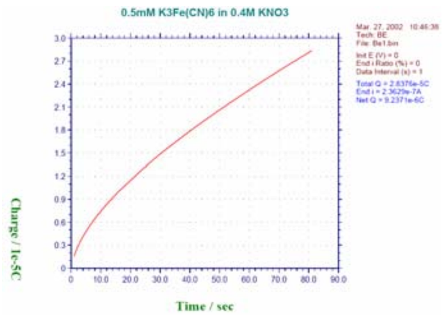
$$I_t = I_0 e^{-kt}$$

- ***k* is related to the conditions of the experiment**
  - *k* increases with increasing electrode area
  - *k* increases with increased rate of stirring
  - *k* decreases with increasing solution volume
  - *k* increases with increasing temperature
- **The current never decays to zero but the value of the current at the end of the experiment determines the *accuracy* of the determination**
- **If I_t/I_0 = 0.01%, then 99.99% of the electroactive species will be converted.**

$$Q = \int_0^t I_t dt = \int_0^t I_0 e^{-kt} dt$$

- **The quantity of electricity is obtained by integrating the current-time function**
- ***k* can be determined by a regression analysis of the I_t-t behavior**
- **Q may be determined by using a Mechanical or electronic coulometer: a current-time integrator**
- **Q may also be determined by using a chemical coulometer**

Integrate the I_t-t curve with softwares—Origin, Kaleidagraph etc



Once Q is determined, Faraday's law can be used to determine the mass of analyte that underwent electrolysis

$Q = nFN = nFW / M.W.$

n = number of electron transfer involved

F = Faraday's constant $(96,487 \frac{coul}{mol\ e^-})$

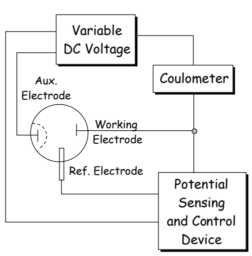
N = number of analyte moles reacted

W = Weight (mass) of analyte (gram)

$M.W.$ = Molecular weight of analyte (grams/mol)

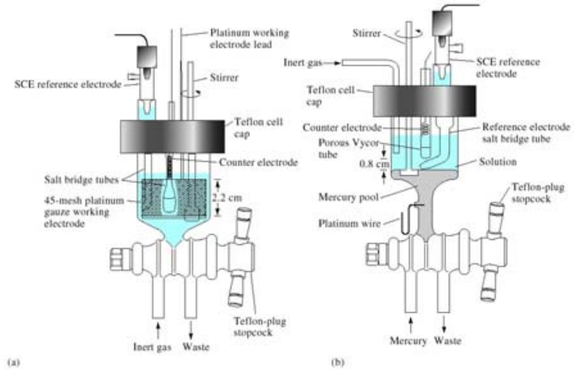
$$W = \frac{Q \bullet M.W.}{nF}$$

Experimental Setup



- **Potentiostat** has feedback circuitry which adjust the potential of the variable DC voltage source to maintain E_w - E_{ref} constant

- **Working electrode** is where the electrolysis takes place
  - E_w is fixed vs the ref. electrode
  - Made from Pt gauze, Hg, Au, C, Ag
- **Auxiliary electrode** is part of the other half-cell
  - Often made from same material as the working electrode
  - Usually separated from the solution in contact with the working electrode to prevent reaction between species produced at Aux. Electrode and species in the bulk of solution
- **Ref. electrode** is often either SCE or Ag/AgCl connected to bulk solution by a salt bridge

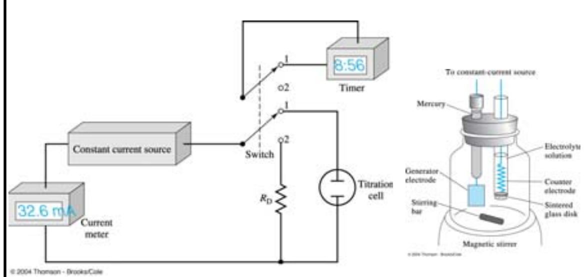


Electrolysis Cells for Potentiostatic Coulometry

Constant current coulometry

sometimes referred to as **coulometric titration** in which the titrant is electrons

- The electrons may let an analyte reduced or oxidized
- The electrons may also produce a species that reacts with the analyte
- The calculation of quantity of electricity involved is straight forward
  - **$Q = I \times t$**



Coulometric titration Apparatus