Chemistry 4631

Instrumental Analysis

Lecture 19

Electroanalytical Chemistry

Sign Convention for Electrode Potentials (IUPAC)

Electrode potential is for half-reactions written as reductions.

Determined by the actual sign obtained when coupled with SHE in a galvanic cell.

Sign Convention for Electrode Potentials (IUPAC)

Sign of the electrode potential, E^0 ,

- is positive when the half-cell behaves spontaneously as the cathode.
- is negative when the half-cell behaves as an anode.
- is a measure of driving force for the half-reaction.

Positive sign - Cathodic (red) reaction is spontaneous.

Electroanalytical Chemistry

Relationship between Concentration and Potential

$$aA + bB + ne^- \rightarrow cC + d\,D$$

$$K = (a_C{}^c)(a_D{}^d)/(a_A{}^a)(a_B{}^b)$$

$$\Delta G = -n\,F\,E_{cell}$$

n -- # of moles of electrons in half-reaction

F -- 96,485C

Electroanalytical Chemistry

Relationship between Concentration and Potential

$$aA + bB + ne^- \rightarrow cC + d\,D$$

$$E_{cell} = E^o - RT/nF \ln [C]^c[D]^d/[A]^a[B]^b$$

R -- 8.314 J/Kmol

T -- Kelvin

n -- # of moles of electrons in half-reaction

F -- 96,485C

ln -- 2.303log

Electroanalytical Chemistry

Relationship between Concentration and Potential

At 25°C, Nernst Equation:

$$E = E^0 - \frac{0.0592}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Electroanalytical Chemistry

Relationship between Concentration and Potential

$$aA + bB + ne^- \rightarrow cC + d\,D$$

$$E^o = RT/nF \ln K$$

Notice $E_{cell} = E^o$ when the activities are at unity.

Using molar concentrations instead of activities is valid only in dilute solutions.

Electroanalytical Chemistry

Examples

$Zn^{+2} + 2e^- \rightarrow Zn(s)$

$$E = E^0 - \frac{0.0592}{2}\log\frac{1}{[Zn^{+2}]}$$

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{+2} + 4H_2O$

$$E = E^0 - \frac{0.0592}{5}\log\frac{[Mn^{+2}]}{[MnO_4^-][H^+]^8}$$

Electroanalytical Chemistry

Standard Electrode Potential, E^0

is referenced to Standard Hydrogen Electrode

-- refers to the reduction reaction (equation written as reduction)

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad E^0 = 0.000V$$

-- independent of # of moles of reactant or product

$$Fe^{+3} + e^- \rightarrow Fe^{+2} \qquad E^0 = +0.771V$$

$$5Fe^{+3} + 5e^- \rightarrow 5Fe^{+2} \qquad E^0 = +0.771V$$

-- positive value means reaction is spontaneous with respect to hydrogen electrode.

Electroanalytical Chemistry

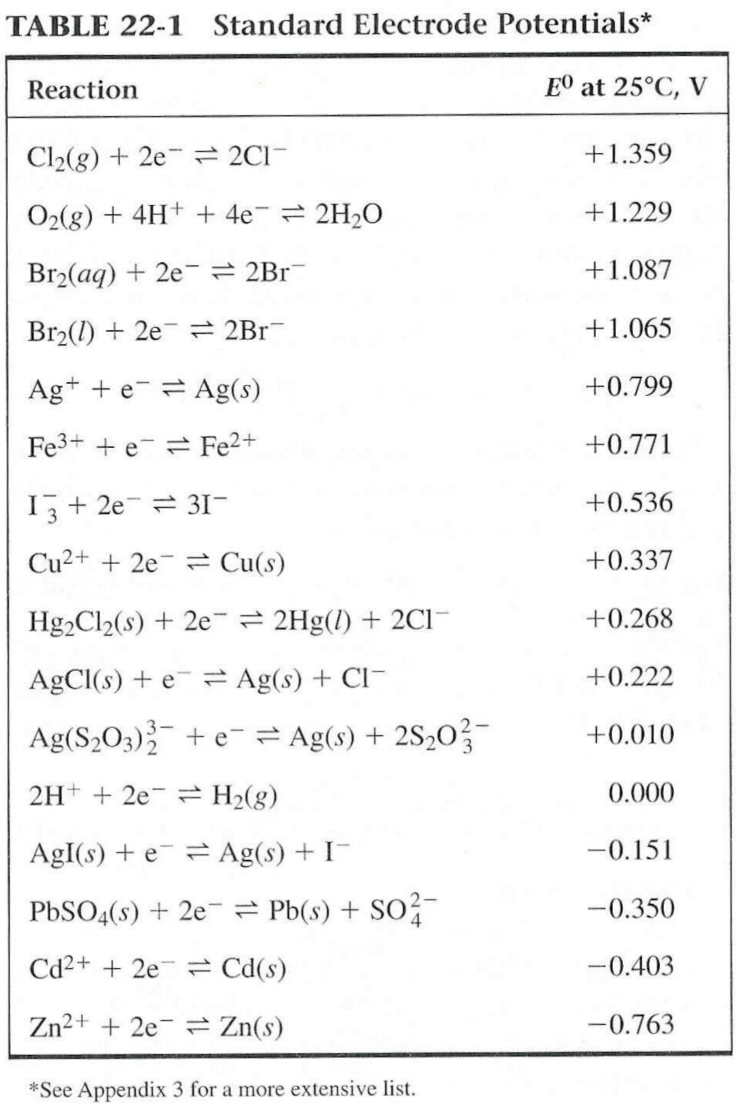


TABLE 22-1 Standard Electrode Potentials*

Reaction	E^0 at 25°C, V
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.359
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-$	+1.087
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	+1.065
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+0.799
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771
$I_3^- + 2e^- \rightleftharpoons 3I^-$	+0.536
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	+0.337
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$	+0.268
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	+0.222
$Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag(s) + 2S_2O_3^{2-}$	+0.010
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0.000
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	−0.151
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	−0.350
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	−0.403
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	−0.763

*See Appendix 3 for a more extensive list.

Electroanalytical Chemistry

Standard Electrode Potential, E^0

Limitations

- Use concentrations not activities (ionic strength not taken into account).
- Is temperature dependent, must specify.
- Other side reactions
- Formal potential, $E^{0'}$ - ratio of reactants and products must be unity and other[ ]'s are exactly known.

Ohmic Potential or IR drop

Cells resist the flow of charge.

Ohm's Law $V = IR$ or $E=IR$

- **I -- current in amper(A),**
- **R -- resistance in ohms(Ω)**

$$E_{cell} = E_{cathode} – E_{anode} - IR$$

Electroanalytical Chemistry

Ohmic Potential or IR drop

What leads to IR drop?

- Electrochemical cells have points of resistance throughout the cell, i.e. interfaces, wires, junctions, solution, etc...

- A higher potential than the thermodynamic potential, must then be applied in order to generate a current in the cell.

Electroanalytical Chemistry

Polarization

Many electrochemical methods are based on current-voltage curves.

Use:

-Ideal polarized electrodes

-Ideal nonpolarized electrodes

Can study an electrode by coupling it with an electrode that does not readily polarize (large area, rapid reaction, reversible).

Electroanalytical Chemistry

Polarization

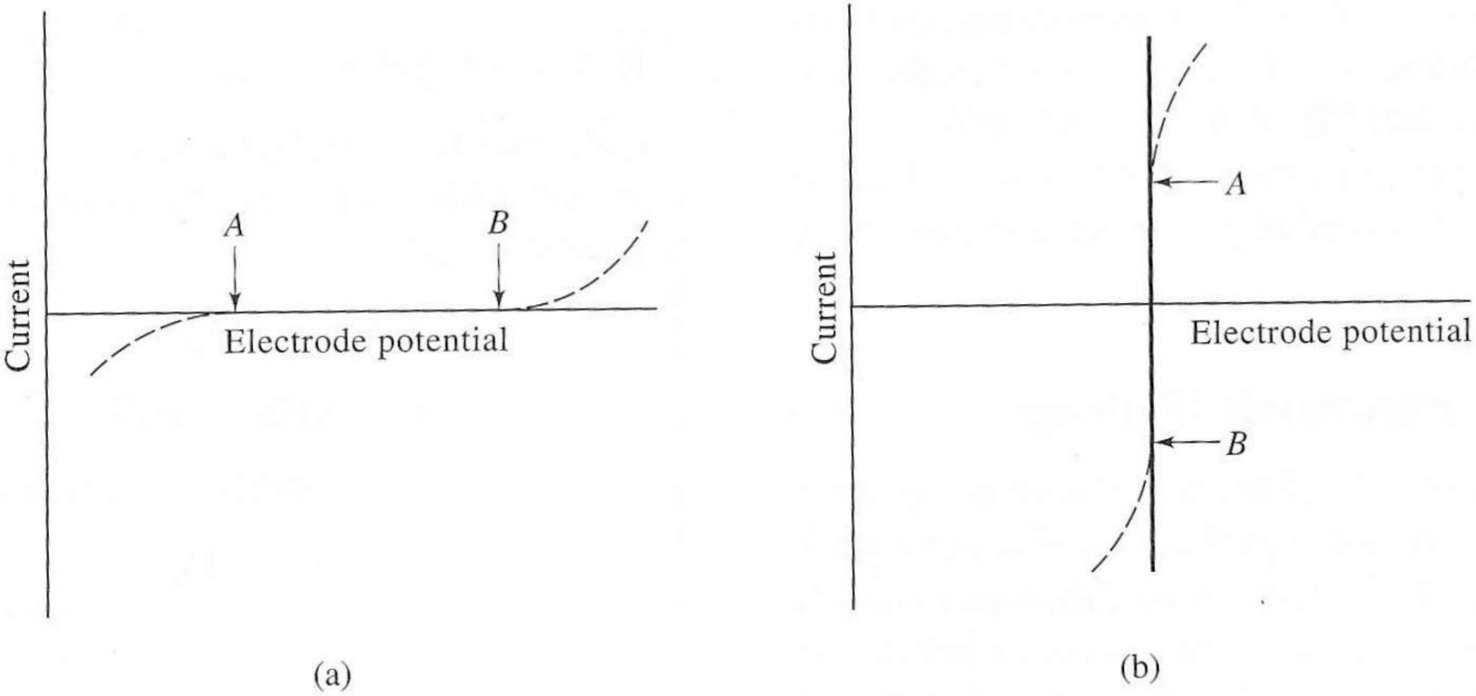


Figure 22-6 Current-voltage curves for an ideal (a) polarized and (b) nonpolarized electrode. Dashed lines show departure from ideal behavior by real electrodes.

Electroanalytical Chemistry

Polarization

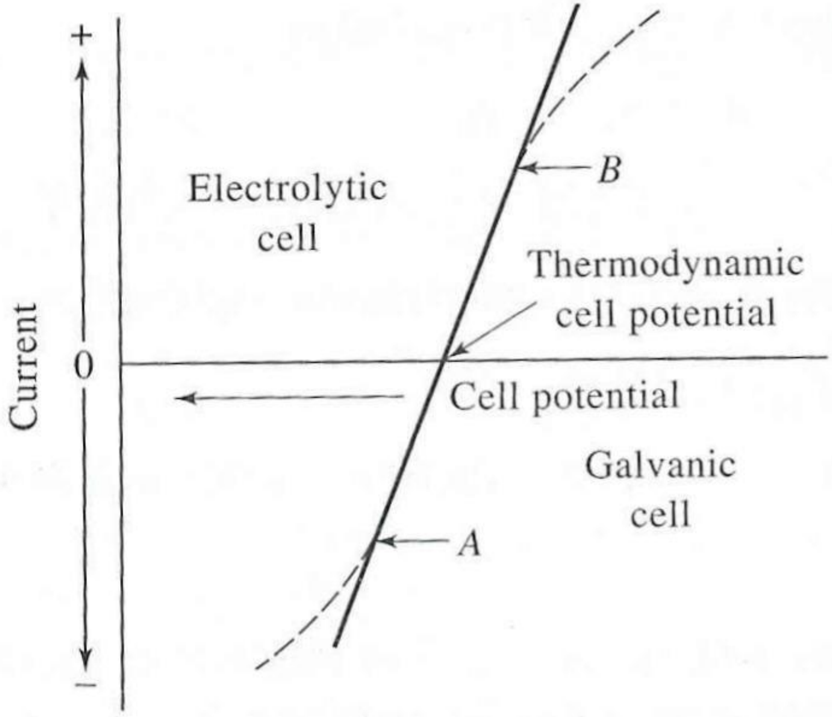


Figure 22-7 Current-voltage curve for a cell showing ideal nonpolarized behavior between *A* and *B* (solid line) and polarized behavior (dashed line).

Polarization Effects

- From Ohm's Law if *i* is plotted versus E_{app} the plot should yield a straight line with a Slope = -1/R.
- However, the plot for a cell deviates from a straight line at higher currents. This nonlinear behavior for a cell is called polarization. (Π)
- So a higher than expected potential must be applied to get a certain current.
- Degree of polarization = overpotential

$$\eta = E - E_{eq}$$

(E- actual potential, E_{eq} – thermodynamic potential)

Electroanalytical Chemistry

Polarization Effects

Two types of polarization

- Concentration
- Kinetic

Electroanalytical Chemistry

Polarization Effects

Concentration Polarization

Electron transfer occurs at the interface of an electrode, leaving only a thin film of solution in contact with the electrode.

- Thickness of this solution is only a few nm's and contains a finite number of molecules.
- These molecules must be replaced during the reaction.
- If the transfer of these molecules is slow, then a concentration polarization occurs.
  - How are these molecules replaced?
  - Diffusion, Migration and Convection.

Polarization Effects

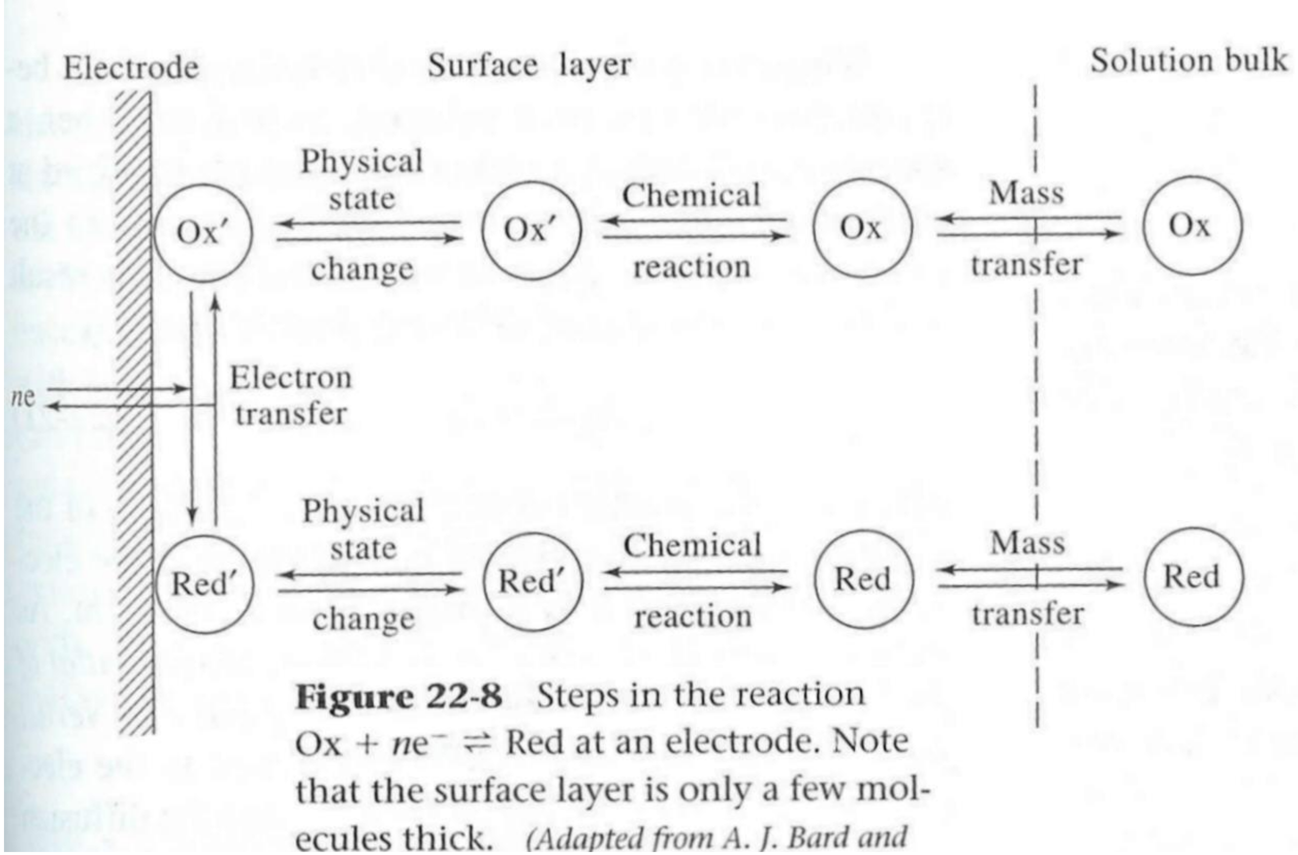


Figure 22-8 Steps in the reaction $Ox + ne^- \rightleftharpoons Red$ at an electrode. Note that the surface layer is only a few molecules thick. *(Adapted from A. J. Bard and*

Electroanalytical Chemistry

Mass Transfer

For faradaic current to continue the species must be continuously transferred from the bulk of the solution to the electrode surface.

This occurs by:

- Convection – mechanical motion of the solution.
- Migration – movement of ions by electrostatic attraction.
- Diffusion – motion of species due to a concentration gradient.

Electroanalytical Chemistry

Diffusion

- Molecules or ions move from a more concentrated region to more dilute region to eliminate any concentration gradient.

- Rate of diffusion is proportional to the concentration difference.

$$E_{cathode\_applied} = E^0{}_{X^{+n}} - \frac{0.0592}{n}\log\frac{1}{[X^{+n}]_0}$$

- $[X^{+n}]_0$ -- conc at the electrode

- As $E_{cathode}$ becomes more negative $[X^{+n}]_0$↓ and rate of diffusion↑ and current↑.

Migration

Movement of ions under an electric field.

Negative ions migrate toward positive electrode and positive ions migrate toward negative electrode.

Rate of migration↑ as electrode E↑.

Electroanalytical Chemistry

Convection

Mechanical transport or movement of ions or molecules in solution.

Forced convection; stirring

- **decrease thickness of diffusion layer and ↓ concentration polarization.**

Electroanalytical Chemistry

Polarization Effects

Kinetic Polarization

Measure of the Rate of Electron Transfer

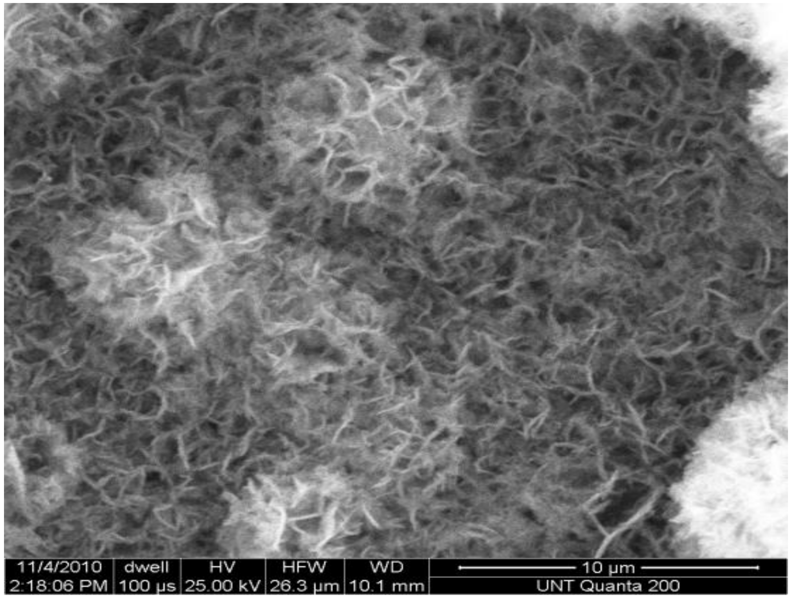
- Magnitude of current is limited by the rate of one or both of the electrode reactions.

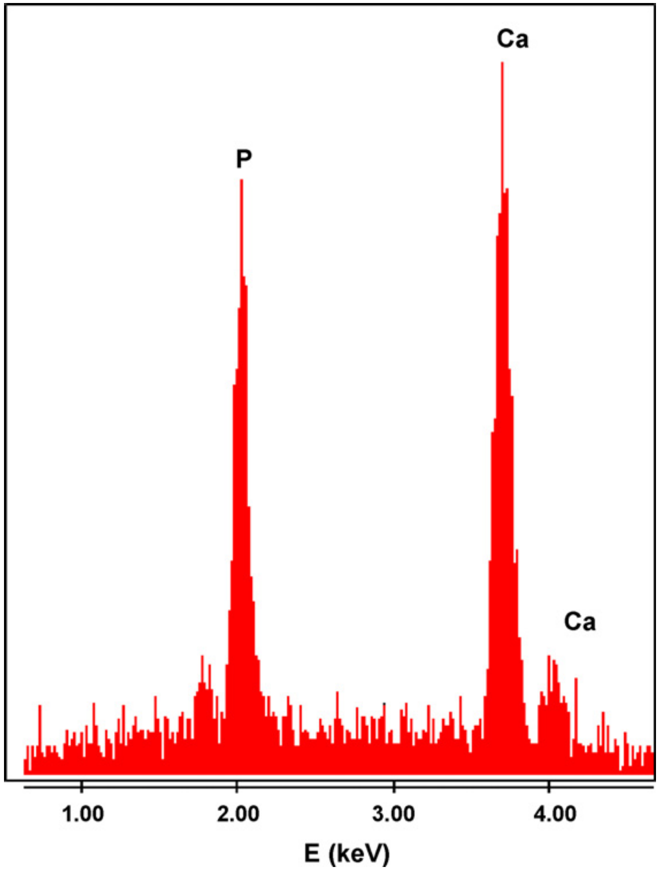
- Decreased by
  - evolved gases
  - polymeric films on the electrode

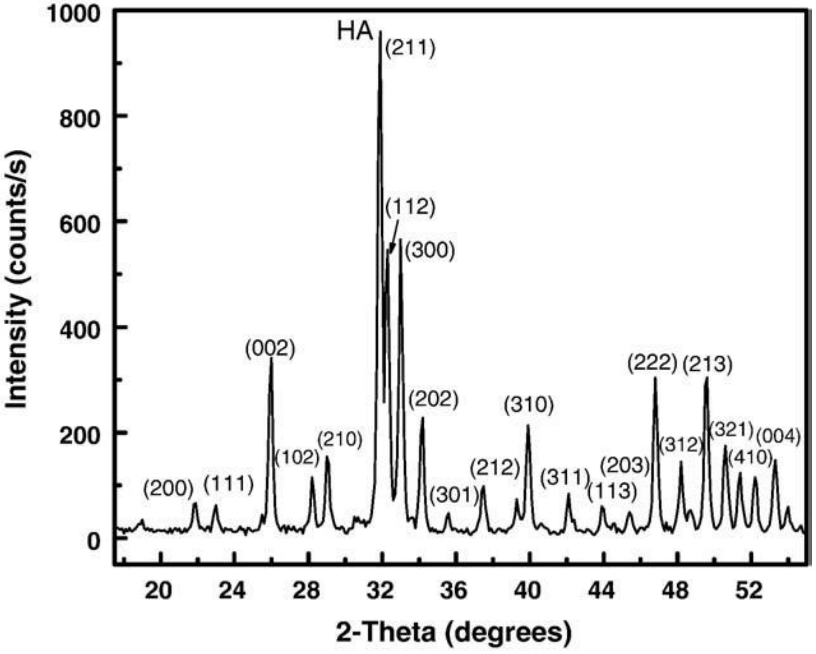
- Increased by
  - catalyst

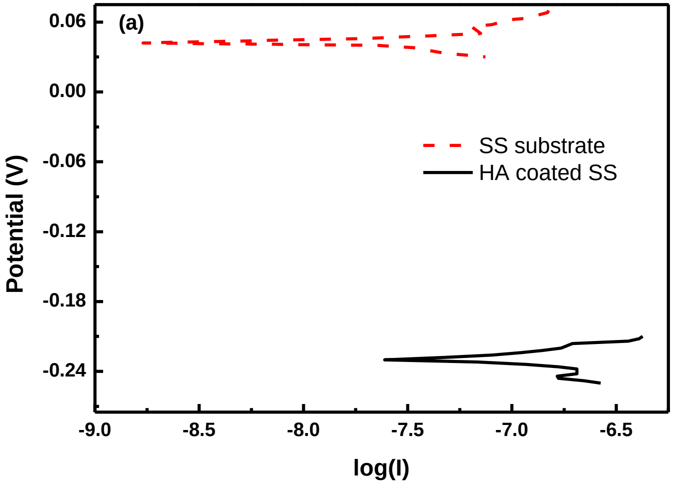
- $2H_2O + 2e^- \leftrightarrows H_2 + 2OH^-$
-
- $2HPO_4^{2-} + 2e^- \leftrightarrows H_2 + 2PO_4^{3-}$
-
- $HPO_4^{2-} + OH^- \leftrightarrows H_2O + PO_4^{3-}$

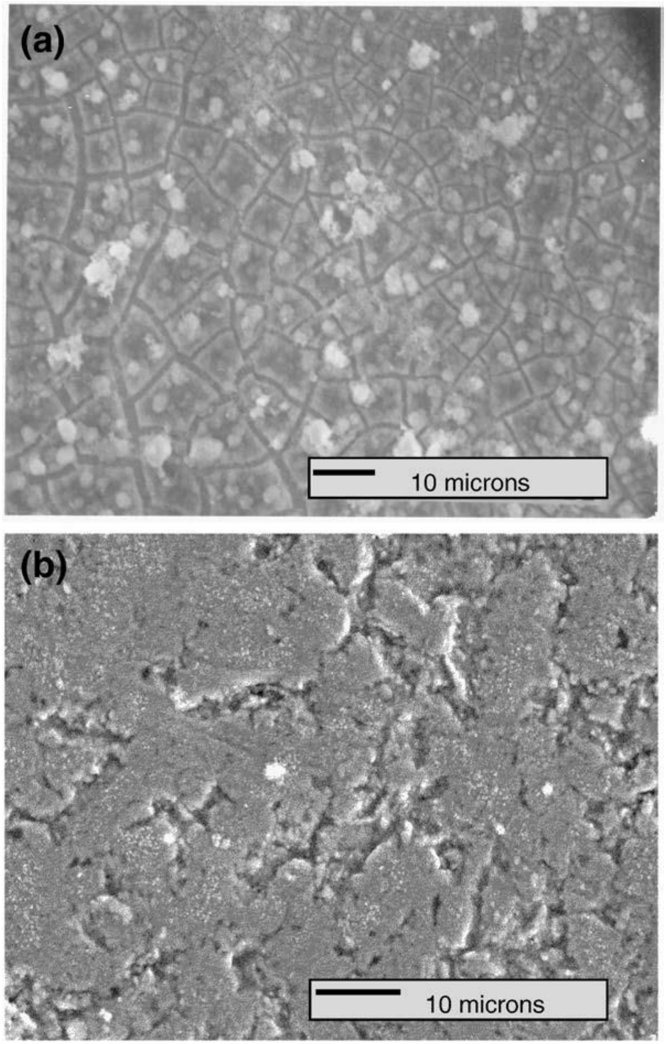
$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \leftrightarrows Ca_{10}(PO_4)_6(OH)_2$, (HA)






HA
(211)
(112)
(300)
(002)
(202)
(210)
(102)
(200)
(111)
(301)
(212)
(310)
(311)
(203)
(113)
(222)
(213)
(312)
(321)
(004)
(410)
Intensity (counts/s)
1000
800
600
400
200
0
20
24
28
32
36
40
44
48
52
2-Theta (degrees)


(a)
SS substrate
HA coated SS
Potential (V)
0.06
0.00
-0.06
-0.12
-0.18
-0.24
-9.0
-8.5
-8.0
-7.5
-7.0
-6.5
log(I)


(a)
10 microns
(b)
10 microns

Electroanalytical Chemistry

Types of Electroanalytical Methods

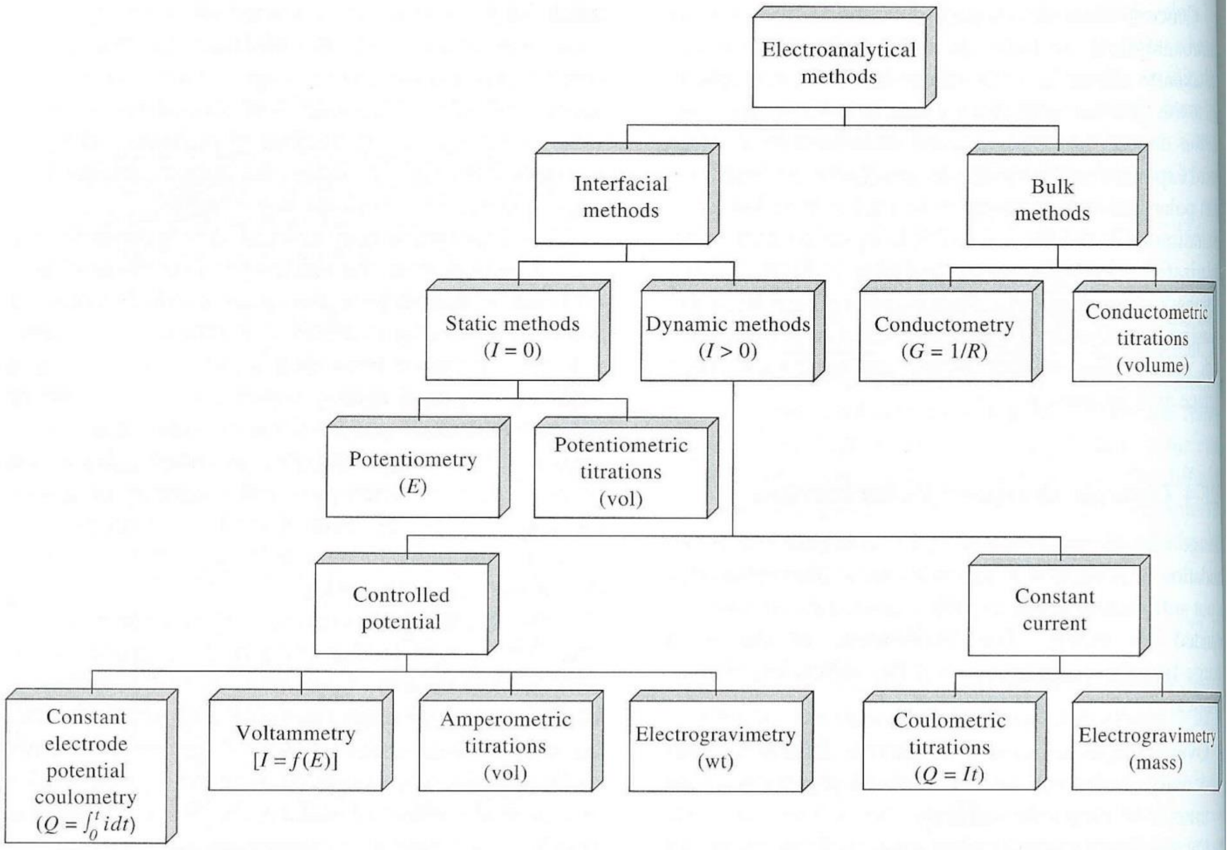


Figure 22-9 Summary of common electroanalytical methods. Quantity measured given in parentheses. (I = current, E = potential, R = resistance, G = conductance, Q = quantity of charge, t = time, vol = volume of a standard solution, wt = weight of an electrodeposited species.)

Assignment

- Read Chapter 22
- HW11 Chapter 22: 1, 5, 7, 9, and 11
- HW11 Due 3/22/24