Electrochemical Properties of Materials for Electrical Energy Storage Applications

Lecture Note 3
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Nernst Equation

**Nernst equation** for an electrode reaction of \( \text{O} + ne = \text{R} \) as:

\[
\Delta G = \Delta G^0 + RT \ln \left( \frac{a_{(\text{Reductant})}}{a_{(\text{Oxidant})}} \right)
\]

\[-\Delta G = zF \Delta E, \quad -\Delta G^0 = zF \Delta E^0\]

\[E = E^0 - \frac{RT}{nF} \ln \left( \frac{a_{(\text{Reductant})}}{a_{(\text{Oxidant})}} \right)\]

Other thermodynamic quantities can be derived from electrochemical measurement.

\[\Delta G = \Delta H - T \Delta S, \quad dG = VdP - SdT\]

\[\Delta S = -\left( \frac{\delta \Delta G}{\delta T} \right)_p\]

\[\Delta S = nF \left( \frac{\delta E_{\text{cell}}}{\delta T} \right)_p\]

\[\Delta H = \Delta G + T \Delta S = nF \left[ T \left( \frac{\delta E_{\text{cell}}}{\delta T} \right)_p - E_{\text{cell}} \right]\]

\[RT \ln K_{\text{rxn}} = -\Delta G^0 = zF \Delta E^0\]
Reversibility

Thermodynamics: system at equilibrium: reversibility

Chemical reversibility:
Pt/H₂/H⁺, Cl⁻/AgCl/Ag

Overall \( H₂ + 2AgCl \rightarrow 2Ag + 2H^+ + 2Cl^- \)

One can overcome the cell voltage by opposing it with the external dc source, then the current flow through the cell will reverse. The new cell reaction is

\( 2Ag + 2H^+ + 2Cl^- \rightarrow H₂ + 2AgCl \)

Thermodynamic reversibility

A process is thermodynamic reversible when an infinitesimal reversal in the driving force causes it to reverse direction. Obviously, this cannot happen unless the system feels only an infinitesimal driving force at any time. Hence, the system essentially be always at equilibrium.
Reversibility

Thermodynamics: system at equilibrium: reversibility

**Practical reversibility:**

Reversible process: infinitely slow process

Since all actual processes occur at finite rates, they cannot proceed with strictly thermodynamic reversibility. However, a process may be in practice be carried out in such a manner that thermodynamic equations apply to a desired accuracy.

Example: Removal of a large weight from a spring balance

Reversible removal of a weight requires continuous equilibrium of \( Kx = mg \).

The spring is never prone to contract more than an infinitesimal distance because the weight is removed progressively in infinitesimal portions.
Reversibility

**Practical reversibility** (continued)

\[ \text{O} + \text{ne} = \text{R} \]

\[ E = E^o - \frac{RT}{nF} \left( \frac{a_r}{a_o} \right) \]

If the system follows the Nernst equation, the electrode reaction is often said to be thermodynamically or electrochemically reversible (or nernstian).

Reversibility of a process; one’s ability to detect the signs of disequilibrium

Rate of change of force driving the observed process vs. speed with which the system can reestablish equilibrium

If the perturbation applied to the system is small enough, or if the system can attain equilibrium rapidly enough compared to the measuring time, thermodynamic relation will apply.
Differing reactivities of metals of Mg and Cu:

When metals react, they give away electrons and form positive ions. This particular topic sets about comparing the ease with which a metal does this to form hydrated ions in solution - for example, Mg$^{2+}_{(aq)}$ or Cu$^{2+}_{(aq)}$. 

$$\text{Mg}_{(s)} \rightarrow \text{Mg}^{2+}_{(aq)} + 2e^-$$

$$\text{Cu}_{(s)} \rightarrow \text{Cu}^{2+}_{(aq)} + 2e^-$$
Electrode/Solution Interface

(a) Non-Faradaic Process : Double Layer Charge/Discharge
(b) Faradaic Process : Charge Transfer Reaction, Redox reaction

Electrode: Electronic conductor
Charge transported by electron

Solution: Ionic conductor
Charge transported by ion

$C_{dl}$: Electric Double Layer Capacitance
$R_F$: Charge Transfer Resistance
Faradaic and nonfaradaic processes

Faradaic process: charges (e.g., electrons) are transferred across the electrode-electrolyte interface. Electron transfer causes oxidation and reduction to occur: governed by Faraday’s law (the amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed) → “charge transfer electrode”

Nonfaradaic process: no charge transfer reactions occur because of thermodynamically and kinetically unfavorable Adsorption/desorption can occur. The structure of the electrode-solution interface can change with changing potential or solution composition. Transiently external current can flow.

Both faradaic and nonfaradaic processes occur when electrode reactions take place
**Ideal Polarizable Electrode (interface)**

(a) Ideal polarizable electrode

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<th>E</th>
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\( C_{dl} \) : Electric Double Layer Capacitance

\( R_F \) : Charge Transfer Resistance

\( R_F \) : infinite resistance
Ideal Non-Polarizable Electrode (Interface)

$R_F : Zero$

$C_{dl} : Electric\ Double\ Layer\ Capacitance$

$R_F : Charge\ Transfer\ Resistance$

$(b)\ Ideal\ nonpolarizable\ electrode$
The charged surface and the diffuse ion layer of counterions form a double-layer (diffuse) capacitor.
From Coulomb’s Law,

\[ F_c = \frac{q_1 q_2}{4 \pi D \varepsilon_0 r^2} \]

By integration we can estimate the energy to separate a charge \( q_1 \) from \( q_2 \).

In water \( W \sim 1.9 \times 10^{-20} \) J, In Air \( W \sim 1.5 \times 10^{-18} \) J

Clearly it is the high dielectric constant or polar nature of water which causes dissociation. In air or hexane (\( D \sim 2 \)), no dissociation is expected.

This is why NaCl dissolves in water but not in oil.
**Electrical Double Layer**

The model which gave rise to the term 'electrical double layer' was first put forward in the 1850's by Helmholtz.

- No electron transfer reactions occur at the electrode
- Interactions between the ions in solution and the electrode surface are assumed to be electrostatic in nature and resulted from the fact that the electrode holds a charge density \( q_m \) which arises from either an excess or deficiency of electrons at the electrode surface.
- In order for the interface to remain neutral the charge held on the electrode is balanced by the redistribution of ions \( q_s \) close to the electrode surface.

\[
|q_m| = |q_s|
\]
Helmholtz Electrical Double Layer

This theory is a simplest approximation that the surface charge is neutralized by opposite sign counterions placed at an increment of d away from the surface.

The overall result is two layers of charge (the double layer) and a linear potential drop which is confined to only this region (termed the outer Helmholtz Plane, OHP) in solution.

The result is absolutely analogous to an electrical capacitor which has two plates of charge separated by some distance (d) with the potential drop occurring in a linear manner between the two plates.
Electrode possesses a charge density resulted from excess charge at the electrode surface \( (q_m) \), this must be balanced by an excess charge in the electrolyte \( (-q_s) \).
**Helmholtz model**

Two sheets of charge, having opposite polarity, separated by a distance of molecular order → equivalent to a parallel-plate capacitor

Relation of stored charge density, \( q \), and voltage drop \( V \) between the plates

\[
q = (\varepsilon \varepsilon_0 / d) V
\]

\( \varepsilon \): dielectric constant of the medium,  
\( \varepsilon_0 \): permittivity of free space,  
\( d \): spacing

Differential capacitance

\[
\partial q / \partial V = C_d = \varepsilon \varepsilon_0 / d
\]

Weakness of this model: predict \( C_d \) is const
Surface potential

1) Transfer of charged species
2) Specific adsorption of ions
3) Orientation of dipole molecules
Gouy-Chapman layer

Charge on the electrode is confined to surface but same is not true for the solution. Due to interplay between electrostatic forces and thermal randomizing force particularly at low concentrations, it may take a finite thickness to accumulate necessary counter charge in solution.
Gouy-Chapman layer

Plane of shear

excess charge $\sigma$

$\sigma_m$

$\sigma_s$

diffuse layer

Distance, $x$, into solution

Diffuse charge density, $q_d$

Total diffuse charge density, $q_d$

$X = 0$

Distance, $x$, into solution

$X = 0$

$\psi_0$

$\psi_x = 0$

$K^{-1}$

$+q_d$

$-q_d$

$+q_m$

$-q_m$
Gouy-Chappman layer

Debye Length

\[ \kappa^{-1} = \left( \frac{2n^* z^2 e^2}{\varepsilon \varepsilon_0 kT} \right)^{\frac{1}{2}} \]

\[ \kappa = \left( \frac{2C_{\text{conc}} N_A z^2 e^2}{\varepsilon \varepsilon_0 kT} \right)^{\frac{1}{2}} \]

\[ \kappa = \left( \frac{2 \left( \frac{\text{moles}}{L} \right) \left( \frac{6.02 \times 10^{23}}{\text{mole}} \right) \left( \frac{1L}{10^3 \text{cm}^3} \right) \left( \frac{100 \text{cm}}{m} \right)^2 \left( \text{charge} \right)^2 \left( \frac{1.60218 \times 10^{-19} C}{\text{charge}} \right)^2}{\left( \frac{78.49}{25^\circ C \text{ unitless}} \right) \left( \frac{8.85419 \times 10^{-12} C^2}{N \cdot \text{m}^2} \right) \left( \frac{m}{100 \text{cm}} \right) \left( \frac{Nm}{J} \right) \left( \frac{1.38065 \times 10^{-23} J}{K} \right)^2} \right)^{\frac{1}{2}} \]

\[ = 1/\text{cm} \]
Gouy-Chapman layer

\[ C_d = \frac{zF(2\varepsilon C^*)^2}{RT} \cosh \frac{zF\phi_0}{2RT} \]

\[ \sinh x = \frac{e^x - e^{-x}}{2} \]

Hyperbolic functions

1) Minimum in capacitance at the potential of zero charge
2) dependence of \( C_d \) on concentration
Stern double layer

Combination of Helmholtz and Guoy-Chapman Models

Now the ions are assumed to be able to move in solution and so the electrostatic interactions are in competition with Brownian motion. The result is still a region close to the electrode surface (100x10^{-10} m) containing an excess of one type of ion but now the potential drop occurs over the region called the diffuse layer.
Stern double layer

Combination of Helmholtz and Guoy-Chapman Models

The potential drop may be broken into two contributions.

\[ \varphi_m - \varphi_s = (\varphi_m - \varphi_2) + (\varphi_2 - \varphi_s) \]
Stern double layer

\[ \phi_m - \phi_s = (\phi_m - \phi_2) + (\phi_2 - \phi_s) \]

Inner layer + diffuse layer

This may be seen as two capacitors in series:

\[ \frac{1}{C_t} = \frac{1}{C_i} + \frac{1}{C_d} \]

\( C^i \): inner layer capacitance

\( C^d \): diffuse layer capacitance—given by Gouy-Chapman
Stern double layer

\[ \frac{1}{C_t} = \frac{1}{C_i} + \frac{1}{C_d} \]

Total capacitance \((C_t)\) dominated by the smaller of the two.

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<tr>
<th>At low (c^0)</th>
<th>At high (c^0)</th>
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<td>(C_d) dominant</td>
<td>(C_i) dominant</td>
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<td>(C_d \approx C_t)</td>
<td>(C_i \approx C_t)</td>
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<td>MODEL</td>
<td>RELEVANT EQUATIONS</td>
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| Helmholtz–Perrin Parallel-Plate Model | $q_M = -q_S = -q_{OHP}$
$C = \frac{\varepsilon}{4\pi d}$
$E = \frac{4\pi d}{\varepsilon} q_M$ | ![Potential](Image) | It predicts constant differential capacities. Ions are arranged in a layer (OHP) close to the electrode |
| Gouy–Chapman Diffuse-Charge Model | $q_M = -q_d = -2 \left( \frac{\varepsilon_0 \varepsilon \gamma}{2\pi} \right)^{\frac{1}{2}} \sinh \frac{z\varepsilon_0 \varepsilon \gamma}{2kT}$
$C = \left( \frac{\varepsilon_0^2 \varepsilon_\gamma}{2\pi kT} \right)^{\frac{1}{2}} \cosh \frac{z\varepsilon_0 \varepsilon \gamma}{kT}$
$\psi_x = \psi_0 e^{-z\varepsilon_\gamma}$ | ![Potential](Image) | It predicts that differential capacities have the shape of inverted parabolas. Ions are considered as pointcharges. Ion-ion interactions are not considered. The dielectric constant is taken as a constant. |
| Stern Combination of Parallel-Plate and Diffuse-Charge Models | $q_M = -q_S = -[q_H + q_G]$ 
$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_G}$
$\Delta \phi = \Delta^H \phi + \Delta^G \phi$ | ![Potential](Image) | Ions are under the combined influence of the ordering electrical and the disordering thermal forces. Agrees with the experiment only for ions nonspecifically adsorbed on the electrode (e.g. NaF). |

Fig. 6.67. Helmholtz–Perrin, Gouy–Chapman, and Stern models of the double layer.
Activation Energy - Minimum energy to make the reaction happen
Energy Reaction coordinate

Reactants

Overall energy change

Products
Energy

Reaction coordinate

Reactants

Products
Catalysts

- Hydrogen bonds to surface of metal.
- Break H-H bonds
This reaction takes place in three steps.
First step is fast
Low activation energy
Second step is slow
High activation energy
Third step is fast
Low activation energy
Second step is rate determining
Second step is slow
High activation energy
Because of the many collisions taking place between molecules, there is a spread of molecular energies and velocities. This has been demonstrated by experiment.

It indicated that ... no particles have zero energy/velocity. some have very low and some have very high energies/velocities. most have intermediate velocities.
Increasing the temperature alters the distribution

- get a shift to higher energies/velocities.
- curve gets broader and flatter due to the greater spread of values.
- area under the curve stays constant - it corresponds to the total number of particles.
Decreasing the temperature alters the distribution

- get a shift to lower energies/velocities.
- curve gets narrower and more pointed due to the smaller spread of values.
- area under the curve stays constant - it corresponds to the total number of particles.
No particles have zero energy/velocity.
Some particles have very low and some have very high energies/velocities.
Most have intermediate velocities.
As the temperature increases the curves flatten, broaden and shift to higher energies.
The Activation Energy is the minimum energy required for a reaction to take place. The area under the curve beyond \( E_a \) corresponds to the number of molecules with sufficient energy to overcome the energy barrier and react.

**ACTIVATION ENERGY - \( E_a \)**

The Activation Energy is the minimum energy required for a reaction to take place. The area under the curve beyond \( E_a \) corresponds to the number of molecules with sufficient energy to overcome the energy barrier and react.
Increasing the temperature gives more particles an energy greater than \( E_a \). More reactants are able to overcome the energy barrier and form products. A small rise in temperature can lead to a large increase in rate.
General Chemical Reaction Equation

• \( cC + dD = aA + bB \)

\[
v_A A + v_B B + v_C C + v_D D = \sum v_i S_i = 0 \]

\( v = \) stoichiometric coefficients

\( v_C = -c \)

\( v_D = -d \)

\( v_A = a \)

\( v_B = b \)
Extent of Reaction

\[ \xi = \frac{n_i - n_{i0}}{v_i} \]

\[ n_i = n_{i0} + \xi v_i \]

\( \xi \) = extent of reaction (moles reacting)

\( n_i \) = moles of species i present in the system after the reaction occurs

\( n_{i0} \) = moles of species i present in the system when the reaction starts

\( v_i \) = coefficient for species i in the particular chemical reaction equation

(moles of species i produced or consumed per moles reacting)
Reaction rate

- $2 \text{N}_2\text{O}_5 \rightarrow 4 \text{NO}_2 + \text{O}_2$

If we want to equalize the rates then:

$$\text{Rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$$

- divide by balancing coefficients when we equalize rates.
The problem of having several possibly different rates to describe the same reaction is avoided by defining the unique rate of reaction as the rate of change of the extent of reaction, $\xi$ (small ‘chi’):

\[ \text{Reaction rate} = \frac{d\xi}{dt} \]

Because $n_J = n_{J,0} + v_J \xi$, the change in the extent of reaction is related to the change in the amount of each substance $J$ by $v_J d\xi = dn_J$, so

\[ \text{Reaction rate} = \frac{1}{v_J} \frac{dn_J}{dt} \]
Reaction rate

- In it’s most general representation, we can discuss a reaction rate as a function of the extent of reaction:

\[
\text{Rate} = \frac{d\xi}{Vdt}
\]

where \( \xi \) is the extent of rxn, \( V \) is the volume of the system and \( t \) is time.

Normalized to concentration and stoichiometry:

\[
\text{rate} = \frac{dn_i}{\nu_i Vdt} = \frac{d[C_i]}{\nu dt}
\]

where \( n \) is # moles, \( \nu \) is stoichiometric coefficient, and \( C \) is molar concentration of species \( i \)
Current vs. reaction rate

\[ i \ (A) = \frac{dQ}{dt} \ (C/s) \]
\[ Q/nF = N \ (mol) \]

\( n \): # of electrons in reaction (2 for reduction of \( \text{Cd}^{2+} \))

Rate (mol/s) = \( \frac{dN}{dt} = \frac{i}{nF} \)

Electrode process: heterogeneous reaction

Rate (mols\(^{-1}\)cm\(^{-2}\)) = \( \frac{i}{nFA} = \frac{j}{nF} \)

\( j \): current density (A/cm\(^2\))

Electrode reaction: i-E curves

Polarization: departure of the cell potential from the equilibrium potential

Extent of potential measured by the overpotential: \[ \eta = E - E_{eq} \]

Ideal polarizable electrode: a very large change in potential upon small current

Ideal nonpolarizable electrode: potential does not change upon passage of current (e.g., reference electrode)
Mass transport-controlled reactions

Modes of mass transfer
Electrochemical reaction at electrode/solution interface: molecules in bulk solution must be transported to the electrode surface → “mass transfer”
Mass transfer-controlled reaction
\[ v_{rxn} = v_{mt} = \frac{i}{nF}A \]

Modes for mass transport:
(a) Migration: movement of a charged body under the influence of an electric field (a gradient of electric potential)
(b) Diffusion: movement of species under the influence of gradient of chemical potential (i.e., a concentration gradient)
(c) Convection: stirring or hydrodynamic transport
Non-steady state mass transport: diffusion control
Time-dependent (transient) phenomena

The rate of diffusion depends on the concentration gradients

\[ J = -D(\partial C/\partial x) \]  
Fick’s first law

D: diffusion coefficient (cm\(^2\)/sec)

The variation of concentration with time due to diffusion → Fick’s second law

\[ \frac{\partial C}{\partial t} = -D(\partial^2 C/\partial x^2) \]  
1-D

\[ J = -D(\partial C/\partial x) = \frac{i}{nFA} \]