Electrochemical Cell – Basics

Most information from Chapter 2 in the course book
The electrochemical cell

(a) 

Load

M

E

M

(b) 

Load

M

E

M

Anode  Cathode  

Anode  Cathode
Notations

• Electrolytic cell: electric energy is converted to chemical energy, i.e., charging of a battery

• Galvanic cell: chemical energy is converted to electric energy, i.e., discharging of a battery, fuel cell in general
Notations-Conventions

• Negative electrode to the left
• Positive electrode to the right
• In between, the electrolyte

• Discharge: electrons flow from left to right via an external circuit and ions flow in the same direction internally in the electrolyte.
• Charge: reversed compared to discharge
Chemical reactions

- Electrochemical oxidation and reduction reactions “redox” at the electrodes
- Oxidation at the negative electrode, the anode
- Reduction at the positive electrode, cathode

- The negative electrode is an electron donor while the positive is an acceptor.
Cell Voltage

- $E_{\text{cell}} = E(\text{right}) - E(\text{left}) = E(+) - E(-) = E_{\text{positive}} - E_{\text{negative}}$
Fundamental design of an electrochemical cell

- Electrode
- Separator
- Electrolyte
- Current collector
- Casing
Components

• Active ones: electrodes

• Non-active ones: electrolyte, separator, current collectors, casing
Electrodes
Electrodes

- An electrode is an electrically and ionically conducting material.
- Metal electrodes allow the electrochemical reactions to occur only at the outermost layers; called *blocking electrodes*.
- In insertion or *non-blocking electrodes* the redox reactions occur at the surface and in the bulk of the electrodes; used for rechargeable cells.
Electrolyte

- Often a solution of one or several salts dissolved in one or several solvents
- Main task is to conduct ions
- Prohibit short circuit
Separators

• Improve the mechanical strength of the electrolyte
• Help to avoid internal short circuit
• Porous membrane
• High ion conductivity
• Good electronic insulation
Current Collectors

- Used for efficient transfer of electrons
- Thin foils of copper or aluminum
- Remove heat from the electrodes
Casing

• Provides mechanical stability
• Prevents outside influence
• Protects a liquid electrolyte from evaporating
• Plastic or metallic material
Example Daniell Cell, example EC3

Zinc electrode in zinc sulfate solution

Zn

2e⁻

Zn²⁺

SO₄²⁻

Copper electrode in copper sulfate solution

Cu

2e⁻

Cu²⁺

SO₄²⁻

Salt bridge allows ions to move between half cells
Electrochemical processes

Let us now consider the so-called Daniel cell as shown in the previous slide. The two half-cell reactions are given by the eqs. below, i.e.,

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- (\text{oxidation}) \]

\[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} (\text{reduction}) \]

and the net reaction is

\[ \text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu} \]
The task is to find the cell voltage
The Cell Voltage

\[ E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{positive}} - E_{\text{negative}} \]
Use Tables for half cell reactions to find electrode potentials

From one of the tables in the provided Chapter 12, Appendices, one finds that oxidation reaction \((\text{Zn}/\text{Zn}^{2+})\) gives \(E_{\text{ox}} = -0.764 \text{ V}\) and reduction reaction \((\text{Cu}^{2+}/\text{Cu})\) gives \(E_{\text{red}} = 0.337 \text{ V}\). (note that the values in the table are written for reduction reactions). For \(E_{\text{cell}}^0\) one then has

\[
E_{\text{cell}}^0 = 1.101 \text{ V}
\]
Table A1 Standard electrode potentials in an aqueous electrolyte at 25 C (298 K). Values are written as reduction reactions as this is the convention.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Voltage E in V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$ + e$^-$ → Li</td>
<td>-3.10</td>
</tr>
<tr>
<td>Na$^+$ + e$^-$ → Na</td>
<td>-2.71</td>
</tr>
<tr>
<td>Mg$^{2+}$ + 2e$^-$ → Mg</td>
<td>-2.36</td>
</tr>
<tr>
<td>Mn$^{2+}$ + 2e$^-$ → Mn</td>
<td>-1.18</td>
</tr>
<tr>
<td>Cd(OH)$_2$ + 2e$^-$ → Cd + 2OH$^-$</td>
<td>-0.82</td>
</tr>
<tr>
<td>Zn$^{2+}$ + 2e$^-$ → Zn</td>
<td>-0.76</td>
</tr>
<tr>
<td>Ni(OH)$_2$ +2e$^-$ → Ni + 2OH$^-$</td>
<td>-0.72</td>
</tr>
<tr>
<td>2H$^+$ +2e$^-$ → H$_2$</td>
<td>0.0</td>
</tr>
<tr>
<td>Cu$^{2+}$ + 2e$^-$ → Cu</td>
<td>+0.34</td>
</tr>
<tr>
<td>2NiOOH + 2H$_2$O + 2e$^-$ → 2Ni(OH)$_2$ +2OH$^-$</td>
<td>+0.48</td>
</tr>
<tr>
<td>O$_2$ +4H$^+$ + 4e$^-$ → 2H$_2$O</td>
<td>+1.23</td>
</tr>
<tr>
<td>ZnO +H$_2$O +2e$^-$ → Zn + 2OH$^-$</td>
<td>+1.26</td>
</tr>
<tr>
<td>PbO$_2$ + 4H$^+$ +2e$^-$ → Pb$^{2+}$ + 2H$_2$O</td>
<td>+1.47</td>
</tr>
<tr>
<td>PbO$_2$ + (SO$_4$)$^{2-}$ + 4H$^+$ +2e$^-$ → PbSO$_4$ + 2H$_2$O</td>
<td>+1.70</td>
</tr>
</tbody>
</table>
Battery

• Electrochemical cells are limited in terms of voltage and capacity
• A battery for electric vehicles consists of many cells connected in series and/or in parallel
• Series; Current I the same; Voltage is the sum of individual cells
• Parallel; Voltage the same, Current is the sum of the individual cells
Half cells

- To study the electrodes separately
- Separation of the full electrochemical operating redox cell into half cells
- Study of the oxidation or reduction process
Electrochemistry and Thermodynamics

- Electrochemical conversion of energy is a conversion of chemical energy to electrical energy or vice versa. Associated heat may be generated or drawn from the surroundings.

- According to thermodynamics, the maximum amount of chemical energy of a system that in a given situation can be converted into a high-quality energy form like electricity is given by the free energy $G$, also called the **Gibbs energy**:

  $$G = U - T_{ref}S + p_{ref}V = H - T_{ref}S$$

  where $U$ is the internal energy of the system (e.g., chemical energy), $S$ its entropy, $V$ its volume while $T_{ref}$ is the temperature of the surroundings and $p_{ref}$ the pressure of the surroundings. $H$ enthalpy
Electrochemistry and Thermodynamics

- The first law of thermodynamics states:
  \[ \Delta U = Q + W + M \]

  where M is the net energy of material flowing into the device, W is the net amount of mechanical or electric work performed on the system by the surroundings, and Q is the net amount of heat received from the environment.
Chemical potential

For open systems, i.e., systems in which the number of moles $N$ may vary, and then the quantity chemical potential $\mu$ is introduced. This quantity represents the increase in internal energy as a small amount of material is supplied to the system at constant total values of volume and entropy. One then has

$$\mu = \left( \frac{\partial U}{\partial N} \right)_{V,S} \quad (2.5)$$

The first law of thermodynamics can then be written

$$dU = TdS - pdV + \mu dN \quad (2.6)$$
Electrochemistry and Thermodynamics

- The amount of work performed by the device on its surroundings is \(-W\). Integrated over a time period, it may be expressed as

\[-\Delta W = -\Delta W_{\text{electric}} + \int p \, \text{d}V\]

where the last term is zero if the system is held at a fixed volume. The electric work \(-\Delta W_{\text{electric}}\), which the electrochemical system can deliver to a device (e.g., an electric motor) attached to an external circuit, may be expressed in terms of the electric potential difference between the positive and negative electrodes and the number of electrons travelling, i.e.,

\[-\Delta W_{\text{electric}} = n_e \cdot N_A \cdot e \cdot \Delta \Phi_{\text{ext}} = n_e \cdot F \cdot \Delta \Phi_{\text{ext}}\]

where the electron charge is \(e = 1.6 \cdot 10^{-19} \text{ C}\) (\(e \cdot \Delta \Phi_{\text{ext}}\), the energy difference for a single electron), \(n_e\) is the number of moles of electrons, \(N_A = 6.23 \cdot 10^{23}\) Avogadro’s constant (the number of particles here electrons per mole) and \(F = N_A \cdot e = 96 400 \text{ C/mol}\) is the Faraday’s constant.
Electrochemistry and Thermodynamics

The energy can also be expressed in terms of internal properties of the electrochemical device, namely the chemical potential difference $\Delta \mu$ across the device, eventually built up by more components $\Delta \mu_i$

$$-\Delta W_{\text{electric}} = \sum n_{e,i} \Delta \mu_i$$
Electrochemistry and Thermodynamics

- In case the electrochemical device has a constant volume and the exchange of heat with the environment can be neglected, then the electricity produced must correspond to the loss (conversion) of free energy from the cell, i.e.,

\[-\Delta G = -\Delta W_{\text{electric}}\]
Cell voltage

- The potential difference between the electrodes determines the theoretical cell voltage, $E_{\text{cell}}$, also called the electrochemical force (emf). This is primarily expressed as Gibbs free energy of the charge of the cell, $\Delta G_{\text{cell}}$

As reaction occurs, there is a decrease in the free energy of the cell according to:

$$\Delta G_{\text{cell}} = -nFE_{\text{cell}}$$

where $E_{\text{cell}}$ is related to the sum of the standard potential of each electrode as:

$$E_{\text{cell}} = E_{\text{positive}} - E_{\text{negative}}$$
General Reaction

Consider now a general reaction or generic process in which the two reactants R1 and R2 are giving the products P1 and P2 according to

\[ r_1R_1 + r_2R_2 \rightarrow p_1P_1 + p_2P_2 \]

where \( r_1, r_2, p_1 \) and \( p_2 \) represent the number of moles of the reactants and products, respectively.
Reaction Quotient

The reaction quotient $Q_r$ is the ratio of the concentrations of the reactants and products raised to the power of their coefficients. For the reaction shown on the previous slide, it reads:

$$Q_r = \frac{[P_1]^{p_1}[P_2]^{p_2}}{[R_1]^{r_1}[R_2]^{r_2}}$$
Nernst Equation

\[ E_{cell} = E_{cell}^0 - \frac{RT}{n_e F} \ln Q_r \]

\[ E_{cell} = E_{cell}^0 - \frac{2.303RT}{n_e F} \log Q_r \]
Cell voltage

• The potential difference between the two electrodes, the cell voltage, is measured in volts (V). Some values,

• Pb-acid cell: 2 V
• NiMH cell: 1.2 V
• Li-ion cell: 3 – 4 V
Cell voltage

• The theoretical cell voltage is determined by Nernst equation. At non-load condition, the cell has an “open circuit voltage” OCV, which is close to the theoretical value.

• The cell voltage changes as a function of usage
Discharge profile

- Flat profile
- Multi-step profile
- Sloping profile
Role of temperature

- The performance of an electrochemical cell is highly dependent on temperature.
- All cells should be kept within specific temperature limits, often a narrow range 20-40°C. A cooling or heating system is often required to optimize usage and safety.

- The cell voltage is dependent on temperature according to Nernst equation and the change in Gibbs free energy is proportional to the entropy change during the reaction:

\[ \Delta G = -nF \cdot E_{cell} = \Delta H - T \Delta S = \Delta H - nF \cdot T \cdot \left( \frac{dE_{cell}}{dT} \right) \]
Role of temperature

• The term \((dE_{\text{cell}}/dT)\), i.e., the entropy heat, is positive if heat is generated during charge and the reverse reaction during discharge will consume heat.

• As the electrochemical reactions are not fully reversible, an irreversible heat \((q)\) is generated during operation according to

\[
q = i \cdot (E_{\text{OCV}} - E_{\text{cell}})
\]

where \(i\) is the applied current.
Electrode kinetics

• The electrode kinetics determine how quickly the chemical energy can be converted to electrical energy, i.e., the power capability of the cell.

• The rate at which chemical energy is converted into electrical energy is expressed as current. At equilibrium the anodic and cathodic currents are equal in magnitude and correspond to the exchange current $i_0$.

• Anodic current positive, cathodic current negative

• During cell operation, non-equilibrium states are reached either in a positive or negative direction and are accompanied by a deviation of the electrode potential from the equilibrium potential. This deviation is called the overpotential $\eta$. 
The relationship between the applied/received current $i$ and the overpotential $\eta$ is given by the so-called Butler-Volmer equation (BVe):

$$i = i_0 \left[ \exp \left( \alpha n F \eta / RT \right) - \exp \left( -(1-\alpha) n F \eta / RT \right) \right]$$

where $n$ is the number of electrons involved in the electrochemical reaction and $\alpha$ is the transfer coefficient (the fraction of the electrode potential involved in the reaction). For small overpotentials, the BVe is approximately linear, i.e.,

$$i = \left( i_0 F / RT \right) \eta$$

or $\eta / i = (RT / i_0 F) = R_{ct}$

where $R_{ct}$ is called the charge-transfer resistance.
Electrochemical Double-Layer

• For any electrode in contact with an electrolyte, an excess of charge is accumulated at the electrode surface and is counterbalanced by an accumulation of ionic species in the electrolyte close to the electrode surface. This interfacial region is called the *electrochemical double layer*. 
Illustration of Electrochemical Double Layer
Mass Transport

- Diffusive mass transfer is the dominant process in the electrolyte. Fick’s law states that the flux of ions, \( m_{\text{ions}} \), follows

\[ m_{\text{ions}} = -D \cdot (\partial C/\partial x) \]

where \( D \) is the diffusion coefficient and \( C \) is the electrolyte concentration.

This flux of ions will limit the current and minimize the polarisation at the double-layer.

This gradient results in a concentration polarisation (\( \eta_C \)) or overpotential. According to Nernst equation, the polarisation across the diffusion layer is expressed as

\[ \eta_C = (RT/nF) \cdot \ln[C_b/C_s] \]

where \( C_b \) and \( C_s \) refer to the concentration of ionic species in the bulk of the electrolyte and at the surface, respectively.
Ion Transport

• The bulk of the electrolyte is more dynamic compared to the almost steady conditions at the electrode surface. Ions have to be transported all across the electrolyte from one electrode to the other requiring retention of a good electrode/electrolyte contact during charge and discharge. This mobility, or ionic conductivity, is another aspect of the cell current.

In the bulk of the electrolyte, the changes in concentration is governed by Fick’s second law, i.e.,

\[ \frac{\partial C}{\partial t} = D \cdot \left( \frac{\partial^2 C}{\partial x^2} \right) \]
Ion Transport

- The total ion transport depends on the processes at both the electrode/electrolyte interfaces and the diffusion in the bulk of the electrolyte (migration). The resulting properties of the ion transport are mainly described in terms of ionic conductivity, ion mobility and transference number. These are related to the current density and the applied electric field.

- The ionic conductivity $\sigma$ (often measured as a current) depends on the ion mobility and the number of charged species involved in the electrochemical reactions according to:

$$\sigma = \sum n_i \mu_i z_i e$$

where $n_i$ is the number of charge carriers, $\mu_i$ the ion mobility, $z_i$ the valence of the species, and $e$ the unit charge.
 Ion Transport

- The ion mobility is commonly assumed to follow the Stokes-Einstein equation, i.e.,

\[ \mu_i = \frac{1}{(6\pi \eta r_i)} \]

where \( r_i \) is the solvation radius and \( \eta \) the viscosity of the electrolyte. The unit of \( \mu_i \) is \( \Omega^{-1}\text{cm}^2 \) or \( V^{-1}\text{S}^{-1}\text{cm}^2 \)

Stokes-Einstein equation can also be written in the form

\[ D_i = \frac{(RT/N_A)}{(6\pi \eta r_i)} \]
Ion Transport

• The transference number is defined as the fraction of the total current carried by a specific ion of interest

• \( t_i = \frac{i_+}{\sum i_i} \)
Ion Transport

• For a liquid electrolyte, the dependence of the ion conductivity on temperature is following an Arrhenius type equation as

\[ \sigma = \frac{A}{T} \cdot \exp\left(-\frac{E}{kT}\right) \]

• where \( k \) is the Boltzmann constant, \( A \) a constant and \( E \) the activation energy.
Cell Voltage under Load

- During discharge, the cell transforms chemical energy into electric energy. The voltage then drops below OCV due to losses in the cell. These losses are caused by various types of polarisation or overpotential and occur as a load current $i$ passes through the cell.
  
a) *activation polarisation* originates from the electrochemical reactions at the electrode surface ($\eta_{ct}$)
  
b) *concentration polarisation* arises from concentration differences of charged species between the electrode surface and the bulk electrolyte ($\eta_c$)
  
c) *ohmic losses* due to internal resistance, IR drop (directly proportional to the discharge current
Activation Energy

An activation energy barrier for conversion of reactant to products.
Cell voltage vs Current used

Open circuit voltage

iR loss

Activation polarisation loss

Concentration polarisation loss
Principle sketch of a polarization curve

- Theoretical EMF or Reversible Cell Voltage
- Region of Activation Polarization (Reaction Rate Loss)
- Region of Ohmic Polarization (Resistance Loss)
- Total loss
- Region of Concentration Polarization (Transport Loss)
- Operation Voltage, V. Curve
Cell Voltage under load

• The cell voltage is then given by

\[ E_{\text{cell}} = E_{\text{positive}} - E_{\text{negative}} - [\eta_{\text{ct}} + \eta_{\text{c}}]_{\text{positive}} - [\eta_{\text{ct}} + \eta_{\text{c}}]_{\text{negative}} + iR_{\text{cell}} \]
Activation losses

\[ \eta_{\text{act}} = a \cdot \log \frac{i}{i_0} = A \cdot \ln \frac{i}{i_0} \]  \hspace{1cm} (2.23)

Ohmic losses

\[ \eta_{\text{ohmic}} = R \cdot I \]  \hspace{1cm} (2.26)

Mass Transport Loss or Concentration Loss

\[ \eta_{\text{conc}} = \frac{RT}{n_e F} \ln \left( \frac{i_L}{i_L - i} \right) \]  \hspace{1cm} (2.28)

\( i_L \) is the so-called limiting current density and is related to the electrolyte concentration
The electrolyte is primarily aimed to transport ions but it may also have a small ability to conduct electrons.

In fuel cells a small amount of the fuel may migrate through the electrolyte. However, these effects are not of great significance for the operating efficiency and are omitted in most approaches of analysis.
Voltage hysteresis

• During the charging and discharging processes, the electrochemical and chemical reactions are delayed compared to the external load/discharge reactions. This is observed as a voltage difference.
• Due to the hysteresis, energy or capacity is lost.
Capacity

• The total charge $Q$ is the charge transported by the current during a specific time period and $Q/\text{weight}$ shows the capacity of the cell. (weight is commonly the cell weight).

• The theoretical capacity of an electrode is related to the charge transferred in a specific reaction. It is often given as a specific capacity (Ah/kg) or volumetric capacity (Ah/l) and it is derived from Faraday’s law as

$$Q_{th} = \frac{nF}{M_w}$$

where $(Q_{th})$ is the theoretical specific capacity in Ah/kg, $n$ is the number of transferred electrons, $F$ the Faraday constant and $(M_w)$ the molecular weight of the electrochemical active material (kg/kmol).