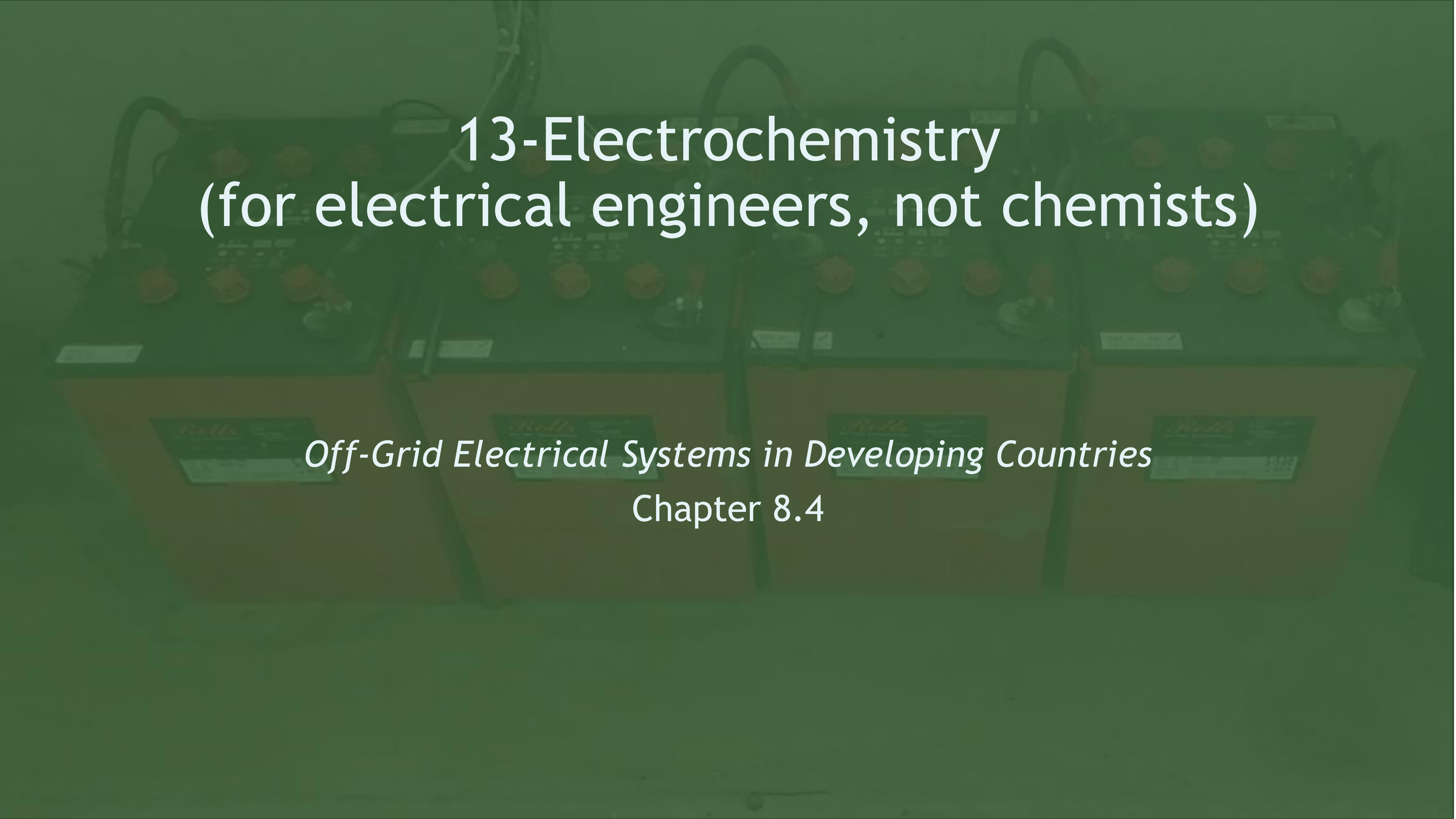


13-Electrochemistry
(for electrical engineers, not chemists)

Off-Grid Electrical Systems in Developing Countries

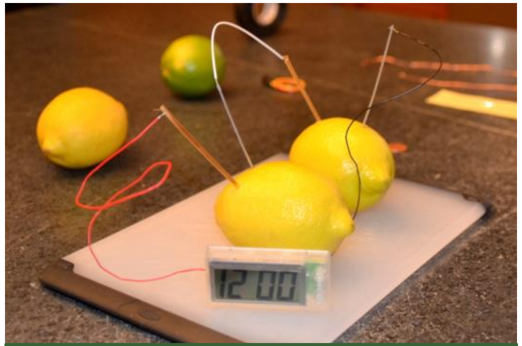
Chapter 8.4

Learning Outcomes

At the end of this lecture, you will be able to:

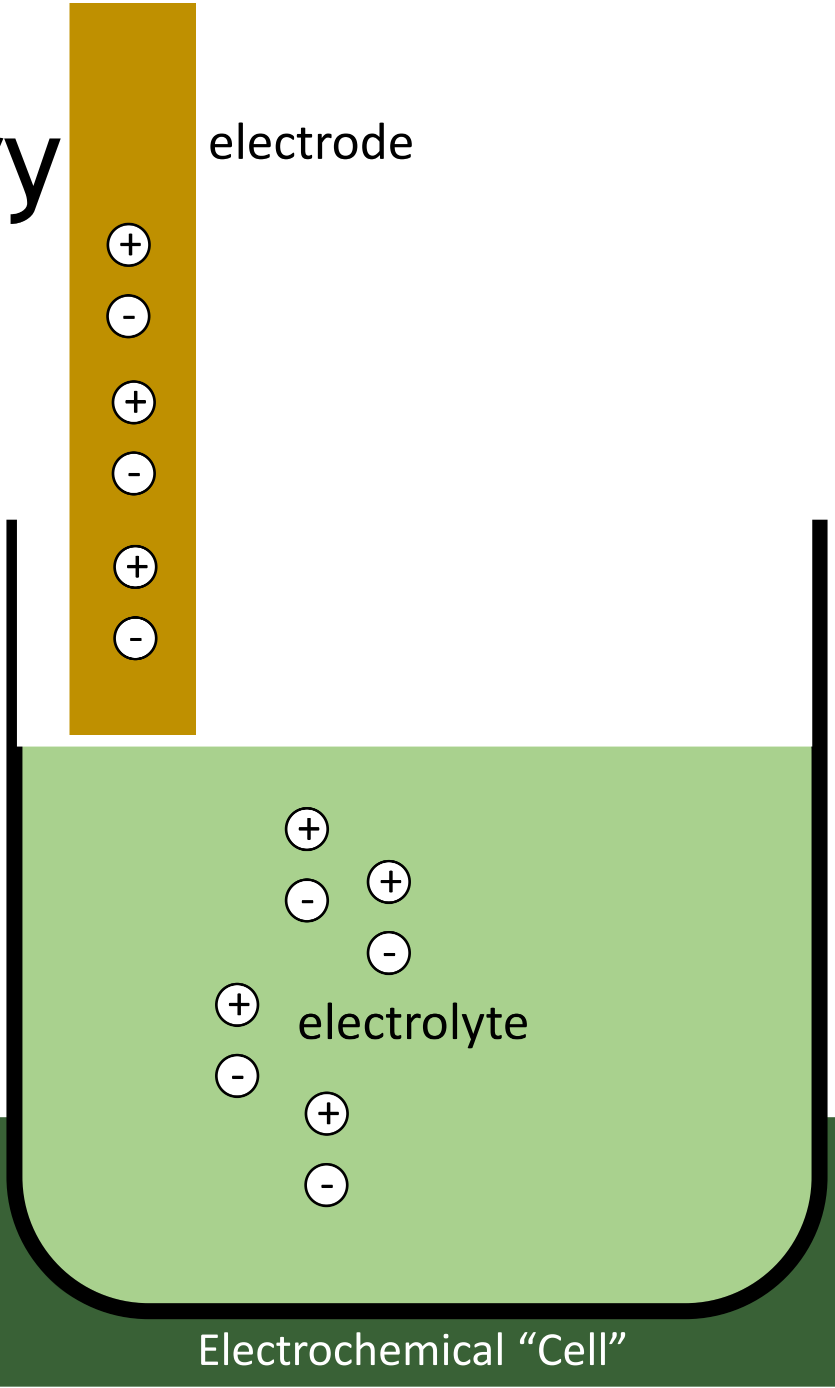
- ✓describe the basic principles of electrochemistry that produce voltage in a battery
- ✓understand what "standard cell potential" is and how to adjust it for non-standard conditions using the Nernst Equation

Electrochemistry



https://teachbesideme.com/dirt-battery-experiment/

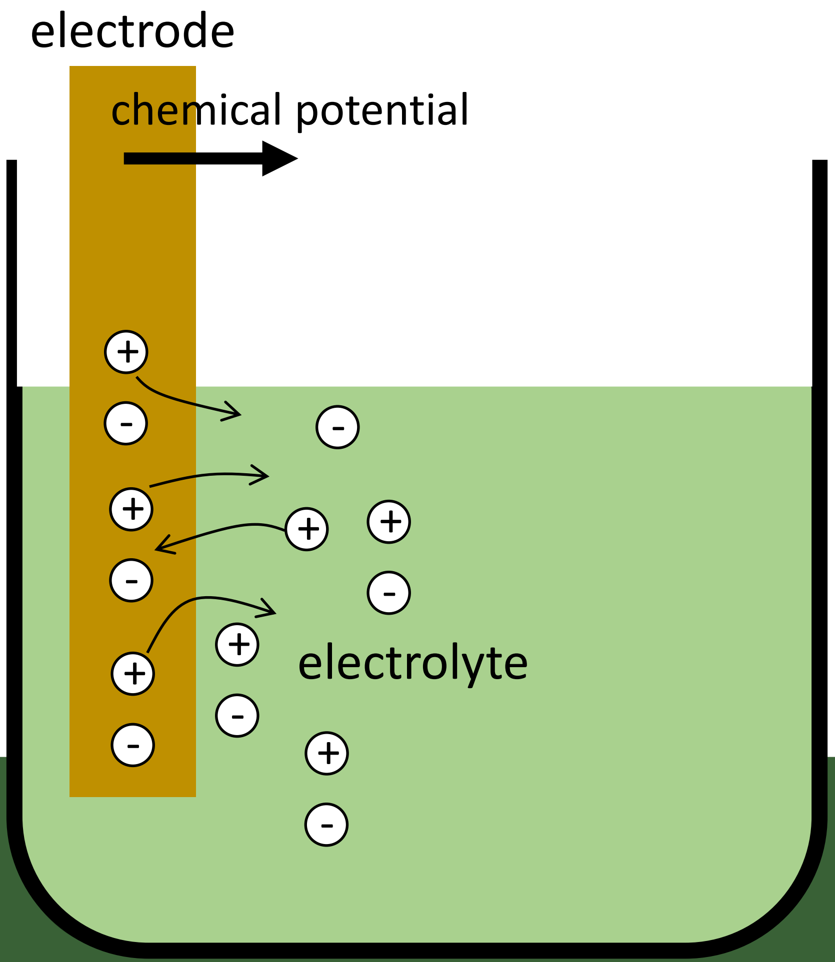
Electrochemistry



Electrode, electrolyte are both <u>electrically neutral</u> (number of electrons = number of protons)

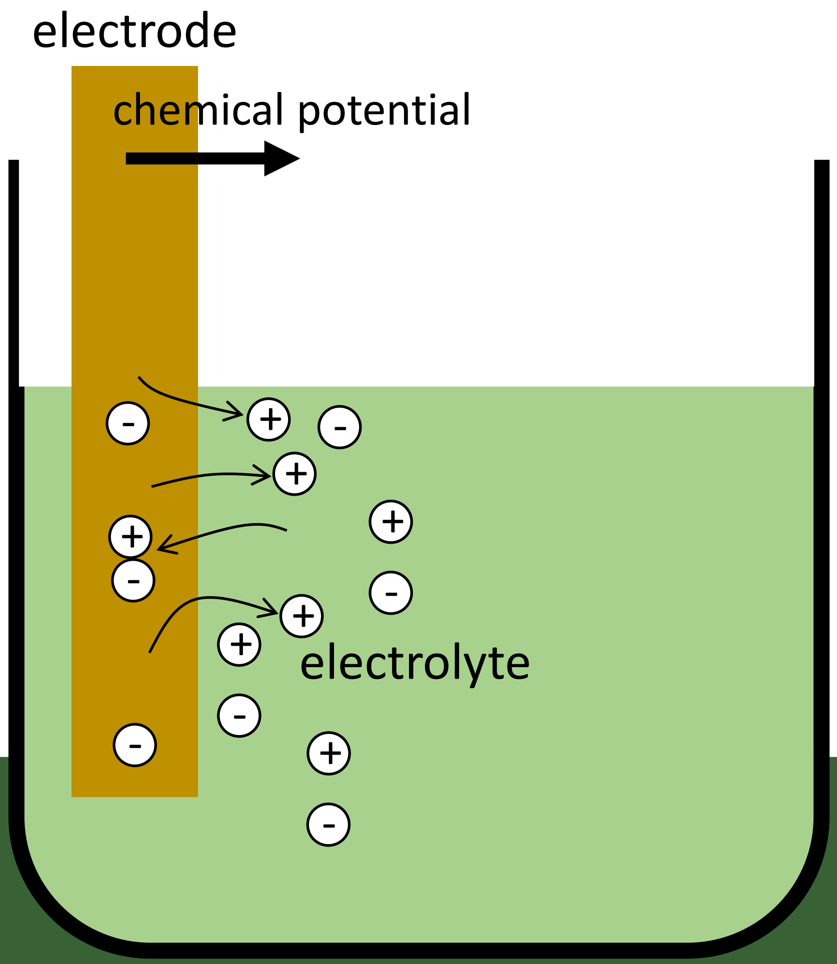
Chemical Potential

When dissimilar conductive substances come in contact, charges are exchanged. (see “*Fermi Level*” for details)



Chemical Potential

<u>Rate of charge transfer is not equal</u>, and so the electrode/electrolyte are no longer electrically neutral



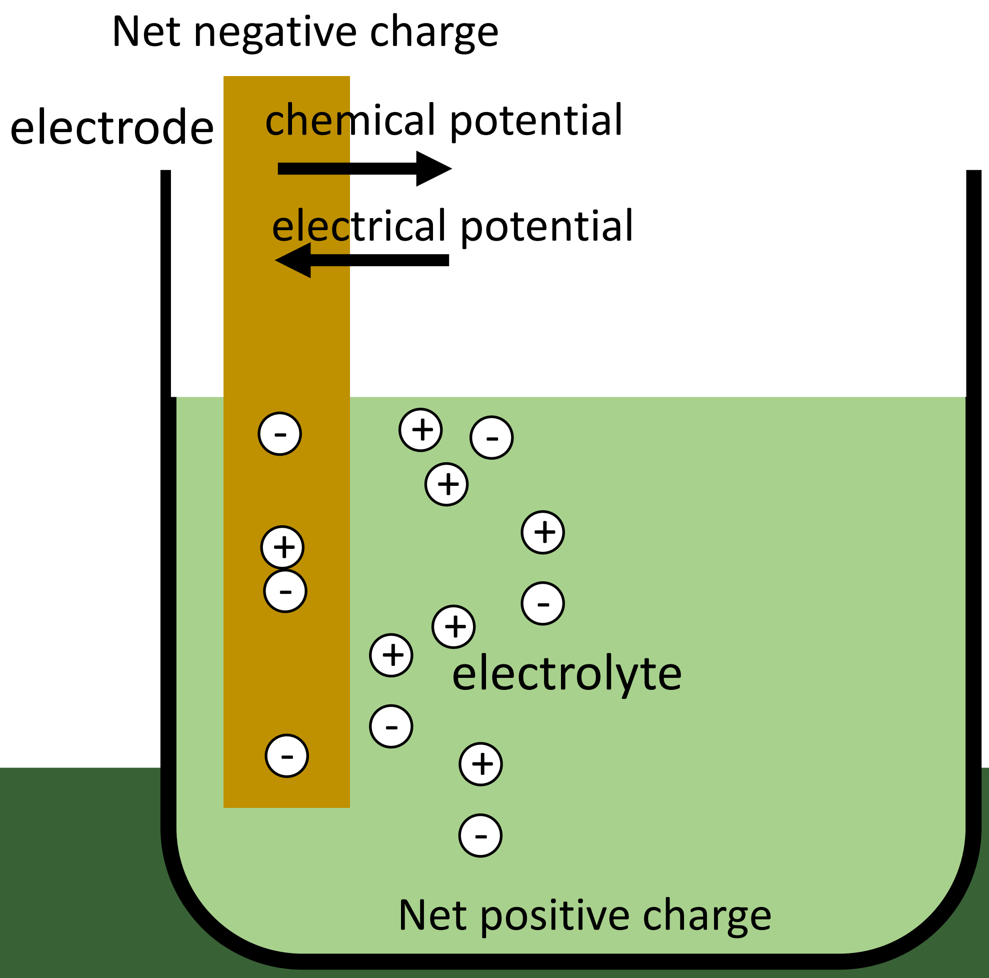
Electrical Potential

Charge imbalance creates an electrostatic field

Electric field makes it “harder” for positive charge to leave electrode

Chemical potential balances the electrical potential

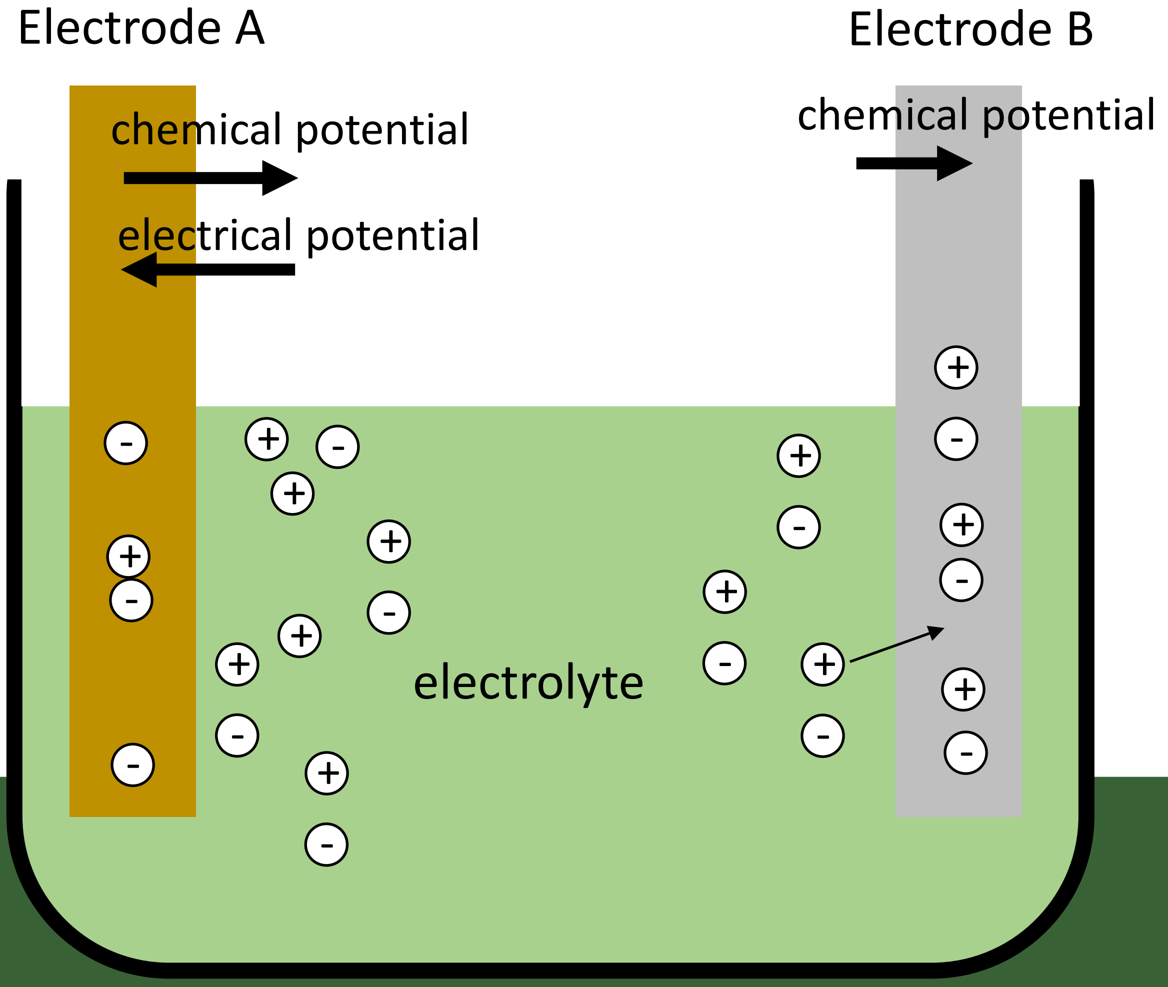
Voltage difference exists between electrode and electrolyte



Electrical Potential

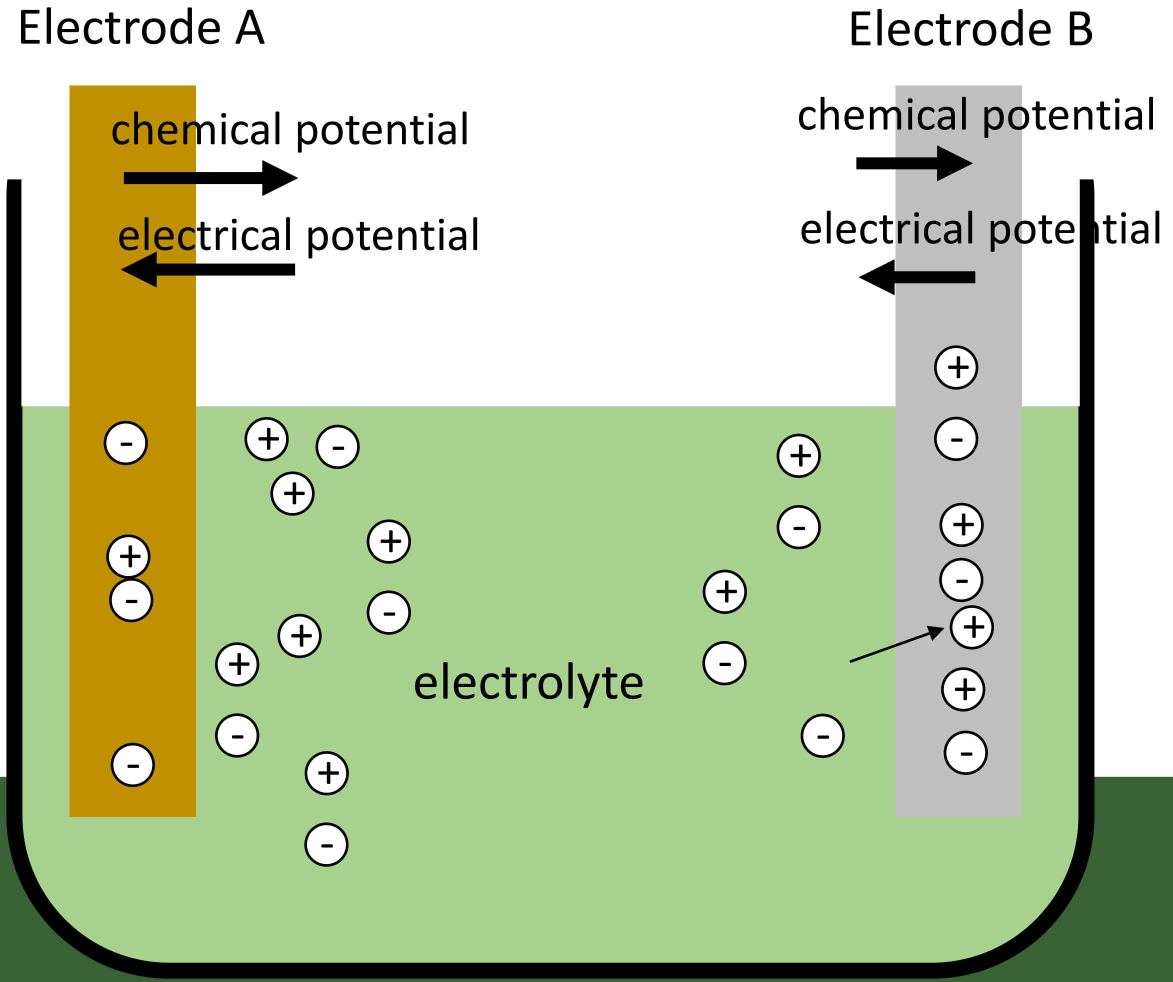
Now add another electrode

Arbitrarily assume chemical potential as shown



Electrical Potential

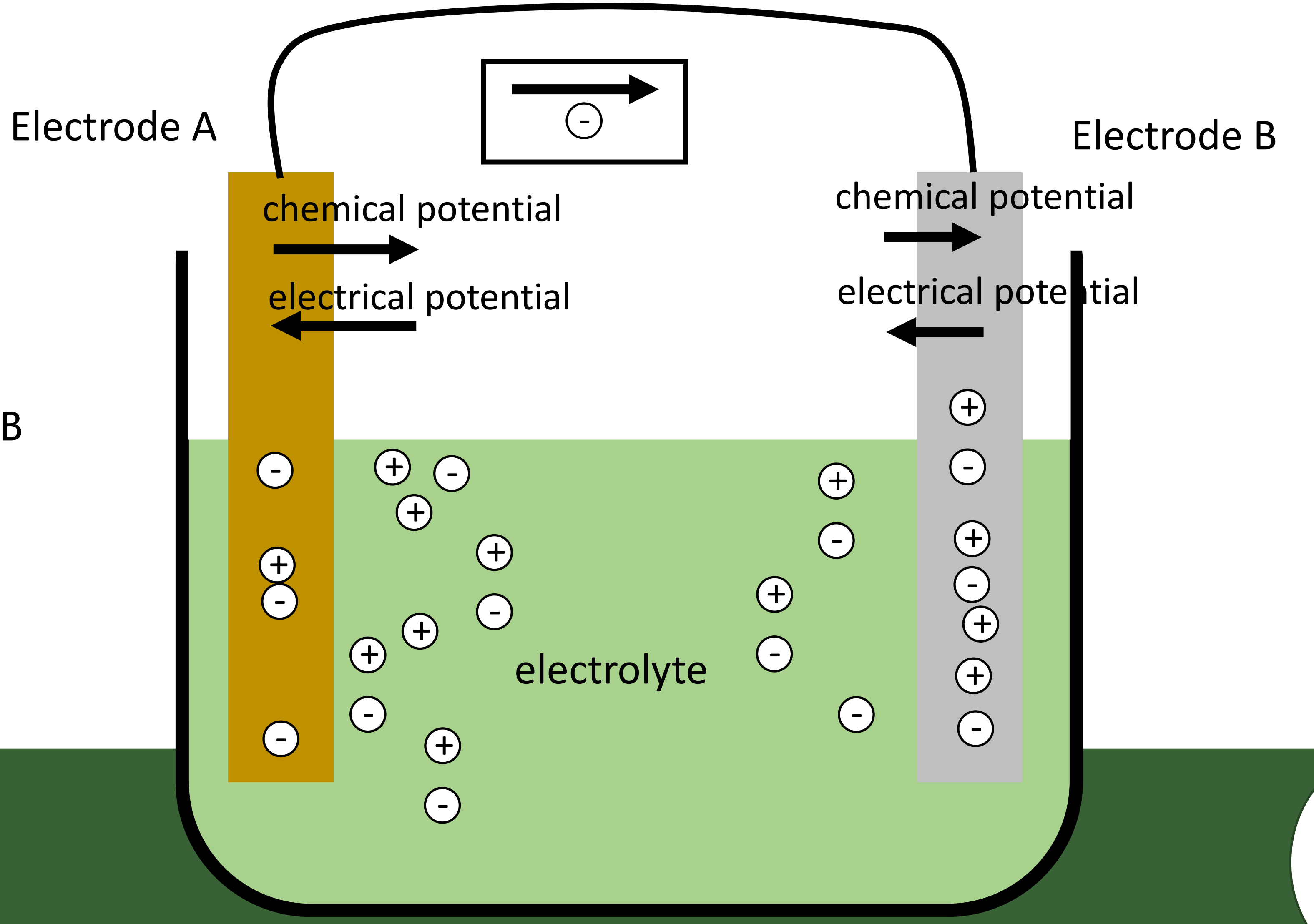
Electrode B electrical potential balances chemical potential



Supplying Current

Now connect electrodes

Electrons flow from
Electrode A to Electrode B



Supplying Current

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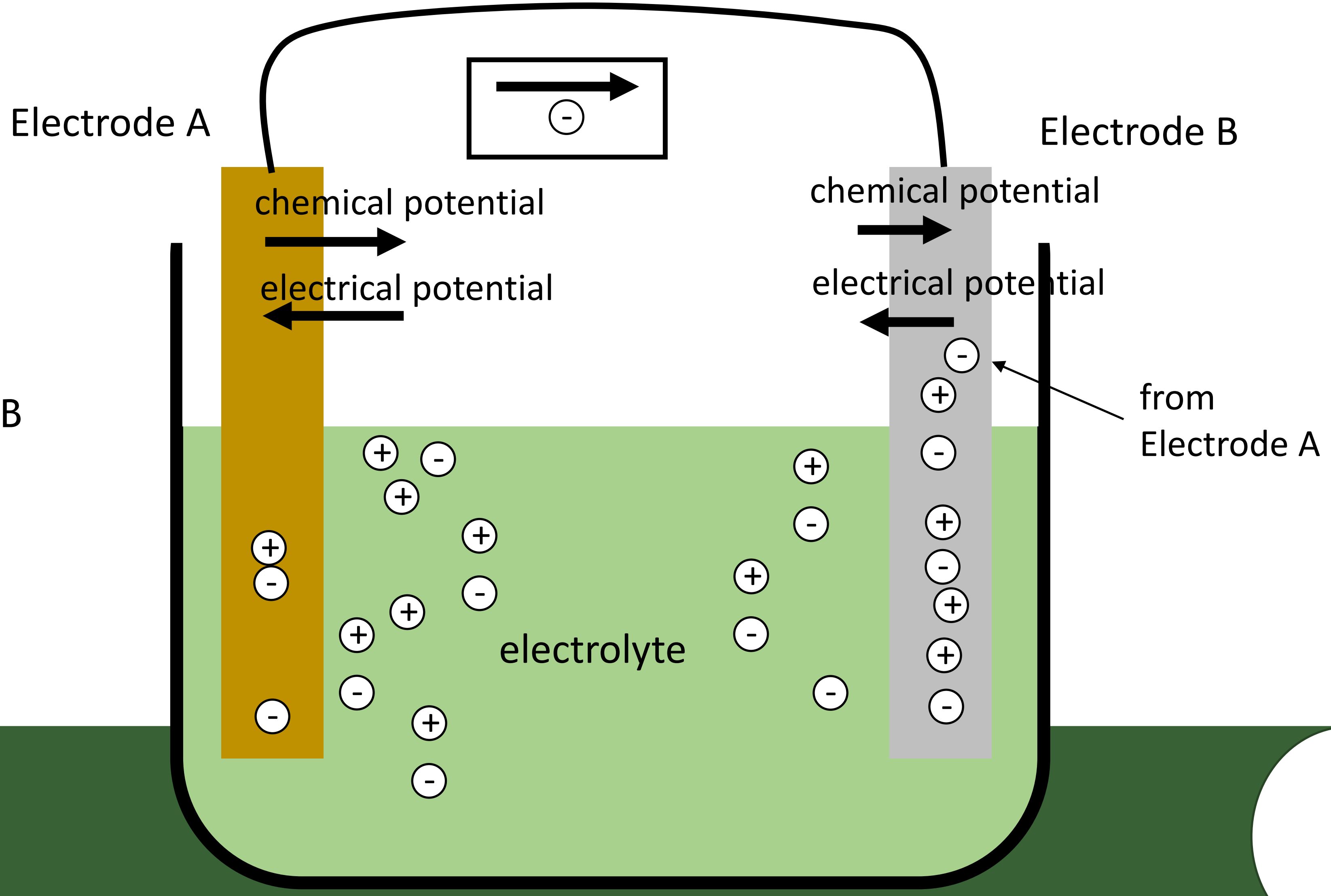
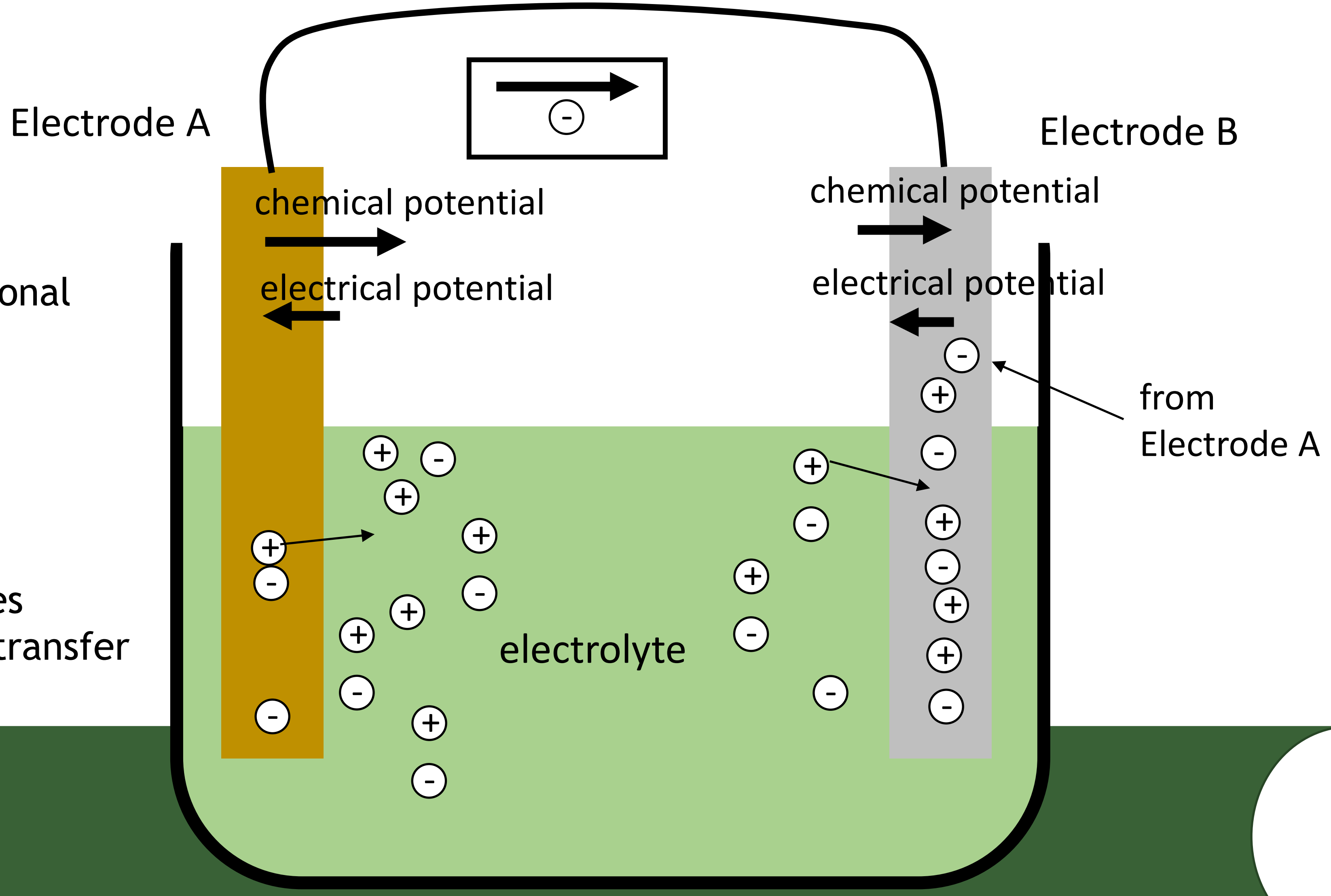


Supplying Current

Electric potential weakens at each electrode, allowing additional charge transfer to/from the electrolyte
via the chemical potential

Process continues as long as electrode/electrolyte interfaces are intact and electrolyte can transfer ions



Electrochemistry

- The preceding is a rather simplistic description of how charge separation occurs
- Several other mechanisms occur including:
  - Adsorption of charge particles at the interface
  - Orientation of dipoles
  - Formulation of an electrical double layer at the interface

Making a Battery

- Batteries (cells) can be constructed from many different chemicals, although not all combinations are useful or practical
- Examples:
  - Zinc-Carbon: used in inexpensive “dry cell” batteries
    - zinc anode, manganese dioxide (with carbon rod) cathode, ammonium chloride electrolyte
  - Alkaline:
    - zinc powder anode, manganese dioxide mixture cathode, potassium hydroxide electrolyte

By Mcy jerry, CC BY 2.5, https://commons.wikimedia.org/w/index.php?curid=22406581

What Voltage is Produced?

- Electrochemists empirically measure voltage from different cell types and tabulate results
- Each half-reaction is measured in reference to a “standard hydrogen electrode” (SHE)
- Measured voltage is known as the “standard cell potential” E^0_{cell}

Cell Voltage

Voltage is an *intrinsic* property of the cell, which depends on:

- chemical composition
- “activity” (concentration)
- temperature

Tabulated voltages in reference to a hydrogen electrode under certain temperature and pressure conditions

- Temperature of 25 ^{o}C
- Pressure of 1 atm
- Effective concentration of 1 mol/dm^{-3}

Tabulated voltage for a lead-acid cell is ~2.04V

Reaction	E°/V
$Ac^{3+} + 3e \rightleftharpoons Ac$	−2.20
$Ag^{+} + e \rightleftharpoons Ag$	0.7996
$Ag^{2+} + e \rightleftharpoons Ag^{+}$	1.980
$Ag(ac) + e \rightleftharpoons Ag + (ac)^{-}$	0.643
$AgBr + e \rightleftharpoons Ag + Br^{-}$	0.07133
$AgBrO_3 + e \rightleftharpoons Ag + BrO_3^{-}$	0.546
$Ag_2C_2O_4 + 2e \rightleftharpoons 2Ag + C_2O_4^{2-}$	0.4647
$AgCl + e \rightleftharpoons Ag + Cl^{-}$	0.22233
$AgCN + e \rightleftharpoons Ag + CN^{-}$	−0.017
$Ag_2CO_3 + 2e \rightleftharpoons 2Ag + CO_3^{2-}$	0.47
$Ag_2CrO_4 + 2e \rightleftharpoons 2Ag + CrO_4^{2-}$	0.4470
$AgF + e \rightleftharpoons Ag + F^{-}$	0.779
$Ag_4[Fe(CN)_6] + 4e \rightleftharpoons 4Ag + [Fe(CN)_6]^{4-}$	0.1478
$AgI + e \rightleftharpoons Ag + I^{-}$	−0.15224
$AgIO_3 + e \rightleftharpoons Ag + IO_3^{-}$	0.354
$Ag_2MoO_4 + 2e \rightleftharpoons 2Ag + MoO_4^{2-}$	0.4573
$AgNO_2 + e \rightleftharpoons Ag + 2NO_2^{-}$	0.564
$Ag_2O + H_2O + 2e \rightleftharpoons 2Ag + 2OH^{-}$	0.342
$Ag_2O_3 + H_2O + 2e \rightleftharpoons 2AgO + 2OH^{-}$	0.739
$Ag^{3+} + 2e \rightleftharpoons Ag^{+}$	1.9
$Ag^{3+} + e \rightleftharpoons Ag^{2+}$	1.8
$Ag_2O_2 + 4H^{+} + e \rightleftharpoons 2Ag + 2H_2O$	1.802
$2AgO + H_2O + 2e \rightleftharpoons Ag_2O + 2OH^{-}$	0.607
$AgOCN + e \rightleftharpoons Ag + OCN^{-}$	0.41
$Ag_2S + 2e \rightleftharpoons 2Ag + S^{2-}$	−0.691
$Ag_2S + 2H^{+} + 2e \rightleftharpoons 2Ag + H_2S$	−0.0366
$AgSCN + e \rightleftharpoons Ag + SCN^{-}$	0.08951
$Ag_2SeO_3 + 2e \rightleftharpoons 2Ag + SeO_4^{2-}$	0.3629
$Ag_2SO_4 + 2e \rightleftharpoons 2Ag + SO_4^{2-}$	0.654
$Ag_2WO_4 + 2e \rightleftharpoons 2Ag + WO_4^{2-}$	0.4660
$Al^{3+} + 3e \rightleftharpoons Al$	−1.662
$Al(OH)_3 + 3e \rightleftharpoons Al + 3OH^{-}$	−2.31
$Al(OH)_4^{-} + 3e \rightleftharpoons Al + 4OH^{-}$	−2.328
$H_2AlO_3^{-} + H_2O + 3e \rightleftharpoons Al + 4OH^{-}$	−2.33
$AlF_6^{3-} + 3e \rightleftharpoons Al + 6F^{-}$	−2.069
$Am^{4+} + e \rightleftharpoons Am^{3+}$	2.60
$As + 3H^{+} + 3e \rightleftharpoons AsH_3$	−0.608
$As_2O_3 + 6H^{+} + 6e \rightleftharpoons 2As + 3H_2O$	0.234
$HAsO_2 + 3H^{+} + 3e \rightleftharpoons As + 2H_2O$	0.248
$AsO_2^{-} + 2H_2O + 3e \rightleftharpoons As + 4OH^{-}$	−0.68
$H_3AsO_4 + 2H^{+} + 2e^{-} \rightleftharpoons HAsO_2 + 2H_2O$	0.560
$AsO_4^{3-} + 2H_2O + 2e \rightleftharpoons AsO_2^{-} + 4OH^{-}$	−0.71
$At_2 + 2e \rightleftharpoons 2At^{-}$	0.3
$Au^{+} + e \rightleftharpoons Au$	1.692
$Au^{3+} + 2e \rightleftharpoons Au^{+}$	1.401
$Au^{3+} + 3e \rightleftharpoons Au$	1.498
$Au^{2+} + e^{-} \rightleftharpoons Au^{+}$	1.8
$AuOH^{2+} + H^{+} + 2e \rightleftharpoons Au^{+} + H_2O$	1.32
$AuBr_2^{-} + e \rightleftharpoons Au + 2Br^{-}$	0.959
$AuBr_4^{-} + 3e \rightleftharpoons Au + 4Br^{-}$	0.854
$AuCl_4^{-} + 3e \rightleftharpoons Au + 4Cl^{-}$	1.002
$Au(OH)_3 + 3H^{+} + 3e \rightleftharpoons Au + 3H_2O$	1.45
$H_2BO_3^{-} + 5H_2O + 8e \rightleftharpoons BH_4^{-} + 8OH^{-}$	−1.24
$H_2BO_3^{-} + H_2O + 3e \rightleftharpoons B + 4OH^{-}$	−1.79
$H_3BO_3 + 3H^{+} + 3e \rightleftharpoons B + 3H_2O$	−0.8698
$B(OH)_3 + 7H^{+} + 8e \rightleftharpoons BH_4^{-} + 3H_2O$	−0.481
$Ba^{2+} + 2e \rightleftharpoons Ba$	−2.912
$Ba^{2+} + 2e \rightleftharpoons Ba(Hg)$	−1.570
$Ba(OH)_2 + 2e \rightleftharpoons Ba + 2OH^{-}$	−2.99
$Be^{2+} + 2e \rightleftharpoons Be$	−1.847
$Be_2O_3^{2-} + 3H_2O + 4e \rightleftharpoons 2Be + 6OH^{-}$	−2.63
p–benzoquinone + $2H^{+} + 2e \rightleftharpoons$ hydroquinone	0.6992
$Bi^{+} + e \rightleftharpoons Bi$	0.5
$Bi^{3+} + 3e \rightleftharpoons Bi$	0.308
$Bi^{3+} + 2e \rightleftharpoons Bi^{+}$	0.2
$Bi + 3H^{+} + 3e \rightleftharpoons BiH_3$	−0.8
$BiCl_4^{-} + 3e \rightleftharpoons Bi + 4Cl^{-}$	0.16
$Bi_2O_3 + 3H_2O + 6e \rightleftharpoons 2Bi + 6OH^{-}$	−0.46
$Bi_2O_4 + 4H^{+} + 2e \rightleftharpoons 2BiO^{+} + 2H_2O$	1.593
$BiO^{+} + 2H^{+} + 3e \rightleftharpoons Bi + H_2O$	0.320
$BiOCl + 2H^{+} + 3e \rightleftharpoons Bi + Cl^{-} + H_2O$	0.1583

Adapted from **ELECTROCHEMICAL SERIES, by Petr Vanýsek**

Cell Voltage

- Just like STC for PV panels, most of the time we expect the battery to be in an a state or environment that is different from which the standard cell potential was measured
- Need to adjust the standard cell potential
  - Temperature
  - Concentration
- Use the *Nernst Equation*

The Nernst equation

- Relates voltage under standard conditions to non-standard conditions (like those encountered outside the laboratory)

$$E_{cell} = E^0_{cell} - \left(\frac{RT}{nF}\right)\ln\left(Q_r\right)$$

E^0_{cell}: tabulated voltage (V)
R: Universal Gas Constant (8.314 J/mol/K)
T: temperature (K)
F: Faraday Constant (96,485 C/mol)
n: moles of electrons transferred in the reaction
Q_r: reaction quotient

- Note:
  - Natural logarithm introduces non-linearity
  - Voltage dependence on reaction and chemicals involved, as well as their “activities” (concentration)
  - Voltage dependence on temperature

Reaction Quotient (Q_r)

- Reaction quotient: measure of the relative amounts of products and reactants in a reaction at a certain point in time
- Reaction quotient is useful in predicting the direction of a chemical reaction as it evolves toward equilibrium---however, we are mostly interested in the reaction quotient it because it is how the concentration of the chemicals is accounted for in the Nernst equation
- Consider the generic reaction:

$$\underbrace{a\mathrm{A} + b\mathrm{B}}_{\text{reactants}} \rightleftarrows \underbrace{c\mathrm{C} + d\mathrm{D}}_{\text{products}}$$

$$\mathrm{Q_r} = \frac{\alpha_{\mathrm{C}}^{c}\alpha_{\mathrm{D}}^{d}}{\alpha_{\mathrm{A}}^{a}\alpha_{\mathrm{B}}^{b}}$$

Calculating the Reaction Quotient

Consider the generic reaction:

$$aA + bB \rightleftarrows cC + dD$$

reactants products

Example

$$N_2(g) + 3H_2(aq) \rightleftarrows 2NH_3$$

a: 1
b: 3
c: 2
there is no d

A: N_2 (nitrogen)
B: H_2 (hydrogen)
C: NH_3 (Ammonia)
there is no D

If there are greater than two products or reactants, just add letters (e.g. *e*E, *f*F).
If there are fewer than two productors or reactants, remove letters

Calculating the Reaction Quotient

The reaction quotient is:

$$Q_r = \frac{\alpha_C^c \alpha_D^d}{\alpha_A^a \alpha_B^b}$$

$$aA + bB \rightleftarrows cC + dD$$

reactants products

The α_i is the activity (effective concentration) of chemical *i*

Effective concentration of solids and pure water is 1.0.

For our purposes, we will use assume the effective concentration is equal to the concentration (moles per liter), but this assumption introduces some error

Example

Let the standard cell voltage for a lead-acid cell be 2.04 V. The battery is fully charged so the concentration of the sulfuric acid in the electrolyte is 6 moles per liter. Compute the corresponding cell voltage. Assume the temperature of the battery is 25^{o} C.

Example

- First, write out the reaction for lead acid batteries:

$$PbO_2 + Pb + 2H_2SO_4 \rightleftarrows 2PbSO_4 + 2H_2O$$

- Next, assign values to the letters in the reaction quotient:

$$aA + bB + eE \rightleftarrows cC + dD$$

a: 1
b: 1
e: 2
c: 2
d: 2

A: PbO_2
B: Pb
E: $2H_2SO_4$
C: $2PbSO_4$
D: $2H_2O$

Example

Now determine the activities of the chemicals

$$PbO_2 + Pb + 2H_2SO_4 \rightleftarrows 2PbSO_4 + 2H_2O$$

a: 1	A: PbO_2	α_A: 1 (solid)
b: 1	B: Pb	α_B: 1 (solid)
e: 2	E: $2H_2SO_4$	α_E: 6 (per problem statement)
c: 2	C: $2PbSO_4$	α_C: 1 (solid)
d: 2	D: $2H_2O$	α_D: 1 (liquid)

Example

Now compute the reaction quotient

$$Q_r = \frac{\alpha_C^c \alpha_D^d}{\alpha_A^a \alpha_B^b \alpha_E^e} = \frac{1^2 \times 1^2}{1^1 \times 1^1 \times 6^2} = \frac{1}{36}$$

a: 1	A: PbO_2	α_A: 1 (solid)
b: 1	B: Pb	α_B: 1 (solid)
e: 2	E: $2H_2SO_4$	α_E: 6 (per problem statement)
c: 2	C: $2PbSO_4$	α_C: 1 (solid)
d: 2	D: $2H_2O$	α_D: 1 (liquid)

Example

Finally, apply the Nernst equation:

$$E_{cell} = E_{cell}^{0} - \left(\frac{RT}{nF}\right)\ln\left(Q_r\right)$$

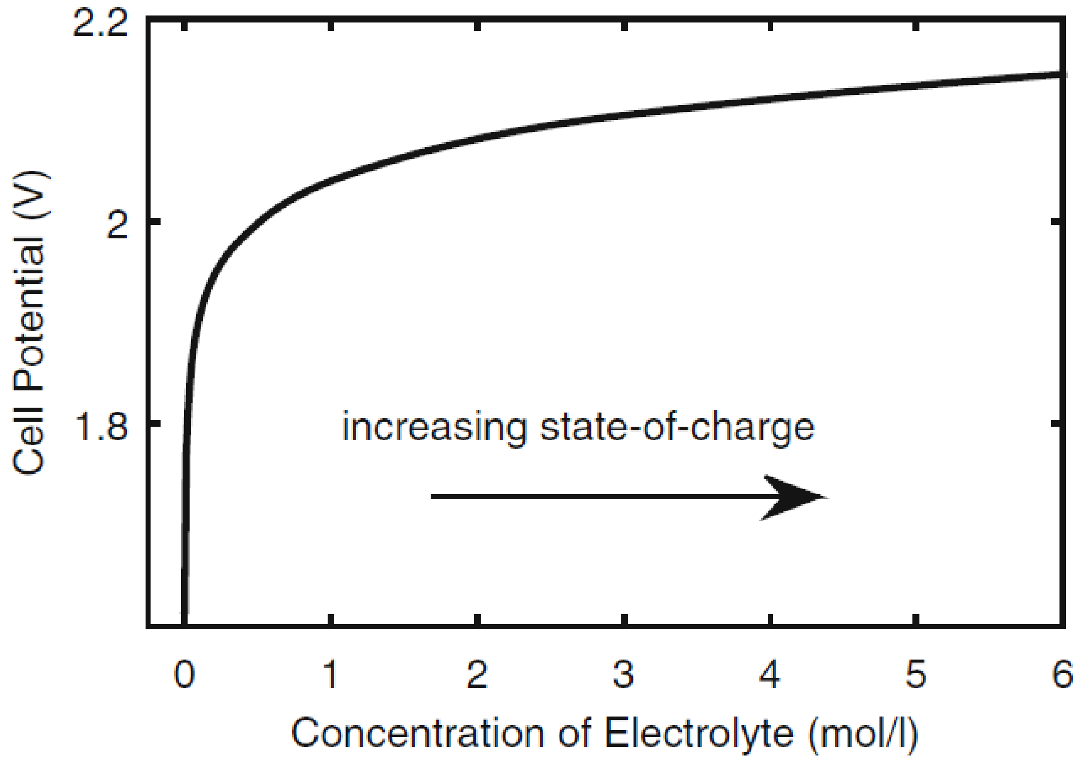
$$E_{cell} = 2.04 - \left(\frac{8.314 \times 298.15}{2 \times 96,485}\right)\ln\left(\frac{1}{36}\right) = 2.086\ \text{V}$$

E_{cell}: tabulated voltage (V)
R: Universal Gas Constant (8.314 J/mol/K)
T: temperature (K)
F: Faraday Constant (96,485 C/mol)
n: moles of electrons transferred in the reaction
Q_r: reaction quotient

If this was a 12V battery, the voltage would be approx. 12.52 V

Cell Potential of Lead-Acid Cells

- Approximated cell potential of a lead-acid cell as a function of electrolyte concentration
- Note:
  - Non-linear
  - Sharp drop at low concentration



Exercise

Consider the battery in the previous example (sulfuric acid concentration of 6 moles per liter). Compute the open-circuit voltage when the battery is at a higher temperature of 35^{o} C

Exercise

Consider the battery in the previous example (sulfuric acid concentration of 6 moles per liter). Compute the open-circuit voltage when the battery is at a higher temperature of 35° C

$$E_{cell} = E_{cell}^{0} - \left(\frac{RT}{nF}\right)\ln\left(Q_r\right)$$

$$E_{cell} = 2.04 - \left(\frac{8.314 \times 308.15}{2 \times 96,485}\right)\ln\left(\frac{1}{36}\right) = 2.088 \text{ V}$$

Exercise

Decreasing the temperature of a lead-acid battery lowers its open-circuit voltage

A. True

B. False

C. It depends…

$$E_{cell} = E^0_{cell} - \left(\frac{RT}{nF}\right)\ln\left(Q_r\right)$$

Exercise

Decreasing the temperature of a lead-acid battery lowers its open-circuit voltage

A. True

B. False

C. It depends…

$$E_{cell} = E^0_{cell} - \left(\frac{RT}{nF}\right)\ln(Q_r)$$

This is true most of the time, however, at very low sulfuric acid concentrations, Q_r can be positive so decreasing the temperature increases the voltage

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