



Wrocław University of Technology

Basics of Electrochemistry





Schedule

1. Standard electrode potential
2. Electrolysis
3. Laws and equations
4. Cells
5. Literature



Standard electrode potential

In an electrochemical cell, an electric potential is created between two dissimilar metals. This potential is a measure of the energy per unit charge which is available from the oxidation/reduction reactions to drive the reaction. It is customary to visualize the cell reaction in terms of two half-reactions, an oxidation half-reaction and a reduction half-reaction.



Electrode Potential

1. The electrode potential cannot be determined in isolation, but in a reaction with some other electrode.
2. The electrode potential depends upon the concentrations of the substances, the temperature, and the pressure in the case of a gas electrode.



Thermodynamic conditions

1. Measured against standard hydrogen electrode.
2. Concentration 1 Molar
3. Pressure 1 atmosphere
4. Temperature 25° C



Table of some standard potentials

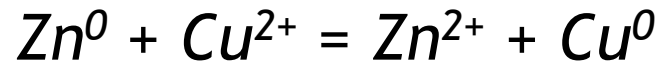
Electrode	Potential E^0 , V	Electrode	Potential E^0 , V	Electrode	Potential E^0 , V
Mg/Mg ²⁺	- 2,37	Cr/Cr ³⁺	-0,740	Cu/Cu ²⁺	+0,337
Be/Be ²⁺	-1,85	Fe/Fe ²⁺	-0,440	Co/Co ³⁺	+0,418
Al/Al ³⁺	-1,65	Cd/Cd ²⁺	-0,402	Cu/Cu ⁺	+0,521
Ti/Ti ²⁺	-1,63	Mn/Mn ³⁺	-0,283	Pb/Pb ⁴⁺	+0,784
Zr/Zr ³⁺	-1,53	Co/Co ²⁺	-0,277	2Hg/Hg ₂ ²⁺	+0,784
Ti/Ti ³⁺	-1,21	Ni/Ni ²⁺	-0,255	Ag/Ag ⁺	+0,799
V/V ²⁺	-1,18	Mo/Mo ³⁺	-0,200	Hg/Hg ²⁺	+0,544
Mn/Mn ²⁺	-1,18	Sn/Sn ²⁺	-0,136	Pd/Pd ²⁺	+0,987
Nb/Nb ³⁺	- 1,10	Pb/Pb ²⁺	-0,126	Ir/Ir ³⁺	+ 1,000
Cr/Cr ²⁺	-0,913	Fe/Fe ³⁺	-0,036	Pt/Pt ²⁺	+1,190
V/V ³⁺	-0,876	½ H ₂ /H ⁺	0,000	Au/Au ³⁺	+1,500
Zn/Zn ²⁺	-0,762	Sn/Sn ⁴⁺	+ 0,007	Au/Au ³⁺	+ 1,680

Tab. 1 Standard Potentials

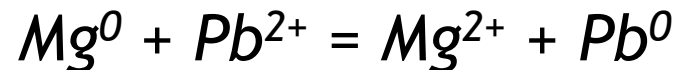


Redox reactions (reduction & oxidation)

- Zn ($E^0 = -0,76$ V), Cu ($E^0 = +0,35$ V)



- Mg ($E^0 = -2,34$ V), Pb ($E^0 = -0,13$ V)





Redox reactions (reduction & oxidation)

Reduction



Oxidation



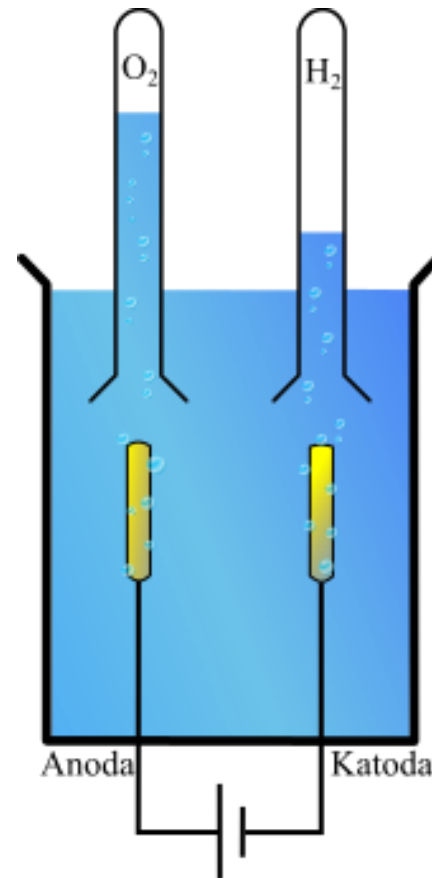


Electrolysis

In chemistry and manufacturing, electrolysis is a method of using a direct electric current (DC) to drive an otherwise non-spontaneous chemical reaction. Electrolysis is commercially highly important as a stage in the separation of elements from naturally occurring sources such as ores using an electrolytic cell.



Electrolysis



Pic. 1 Electrolysis of water



Faraday's Laws

1. Faraday's Law

The mass of a substance altered at an electrode during electrolysis is directly proportional to the quantity of electricity transferred at that electrode. Quantity of electricity refers to the quantity of electrical charge, typically measured in coulomb.

$$m = k \cdot I \cdot t = k \cdot Q$$



Faraday's Laws

2. Faraday's Law

For a given quantity of D.C electricity (electric charge), the mass of an elemental material altered at an electrode is directly proportional to the element's equivalent weight.

$$\frac{m_1}{m_2} = \frac{R_1}{R_2}$$



Faraday's Laws

Faraday's laws can be summarized by

$$m = \left(\frac{Q}{F} \right) \left(\frac{M}{z} \right)$$

where:

- m is the mass of the substance liberated at an electrode in grams
- Q is the total electric charge passed through the substance
- $F = 96,485 \text{ C mol}^{-1}$ is the Faraday constant
- M is the molar mass of the substance
- z is the valency number of ions of the substance (electrons transferred per ion)



Nernst Equation

The cell potential can be written:

$$E_{\text{cell}} = \text{oxidation potential} + \text{reduction potential}$$

In general, a real voltaic cell will differ from the standard conditions, so we need to be able to adjust the calculated cell potential to account for the differences. This can be done with the application of the Nernst equation.

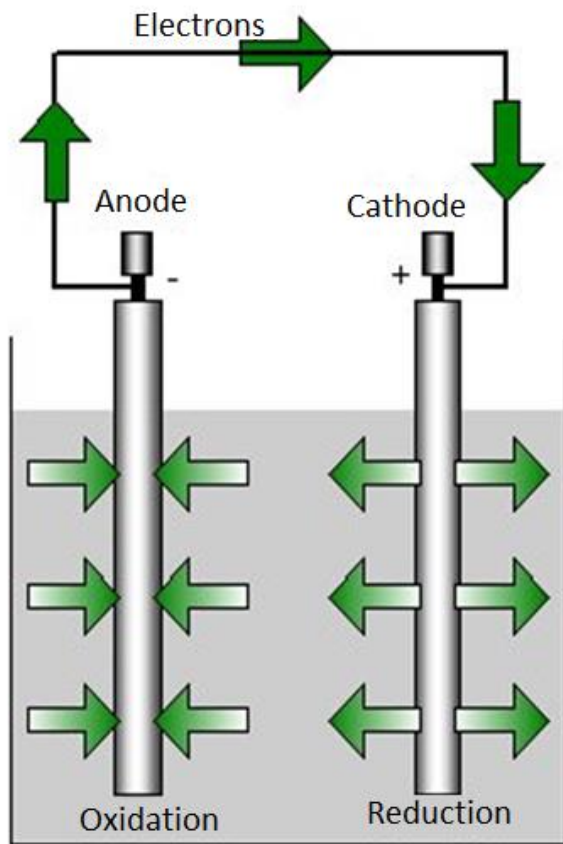
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q$$



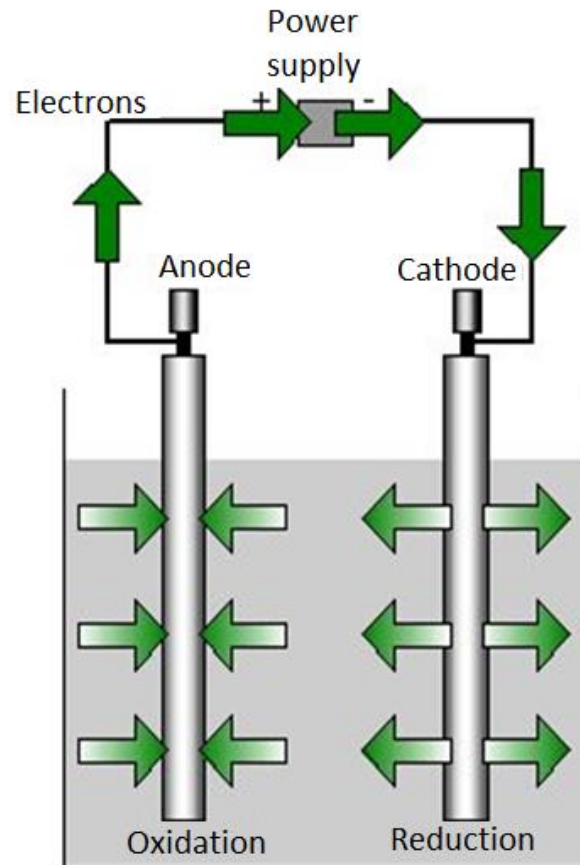
Galvanic cell

A galvanic cell, or voltaic cell, named after Luigi Galvani, or Alessandro Volta respectively, is an electrochemical cell that derives electrical energy from spontaneous redox reaction taking place within the cell. It generally consists of two different metals connected by a salt bridge, or individual half-cells separated by a porous membrane.

Galvanic & electrolytic cell

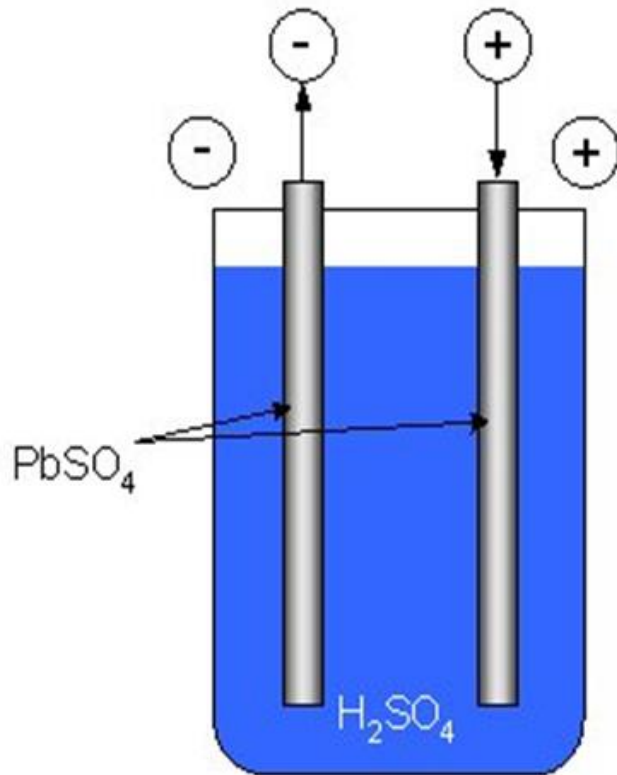


Picture 1a. Galvanic cell

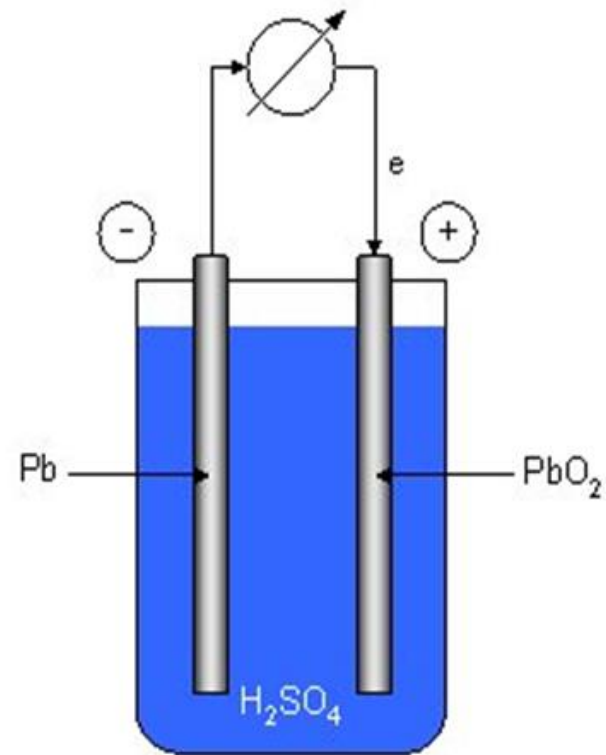


Picture 1b. Electrolytic cell

Lead cell



Discharging a lead cell

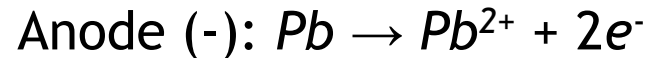
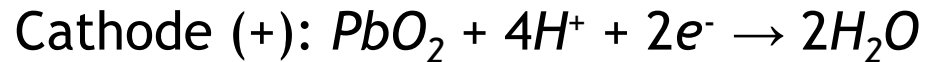


Charging a lead cell

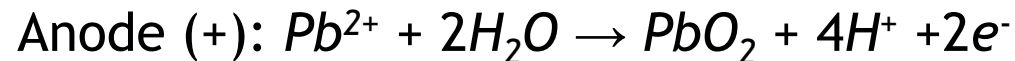


Lead cell reactions

Discharging:



Charging:



Voltage of this cell is near 2V

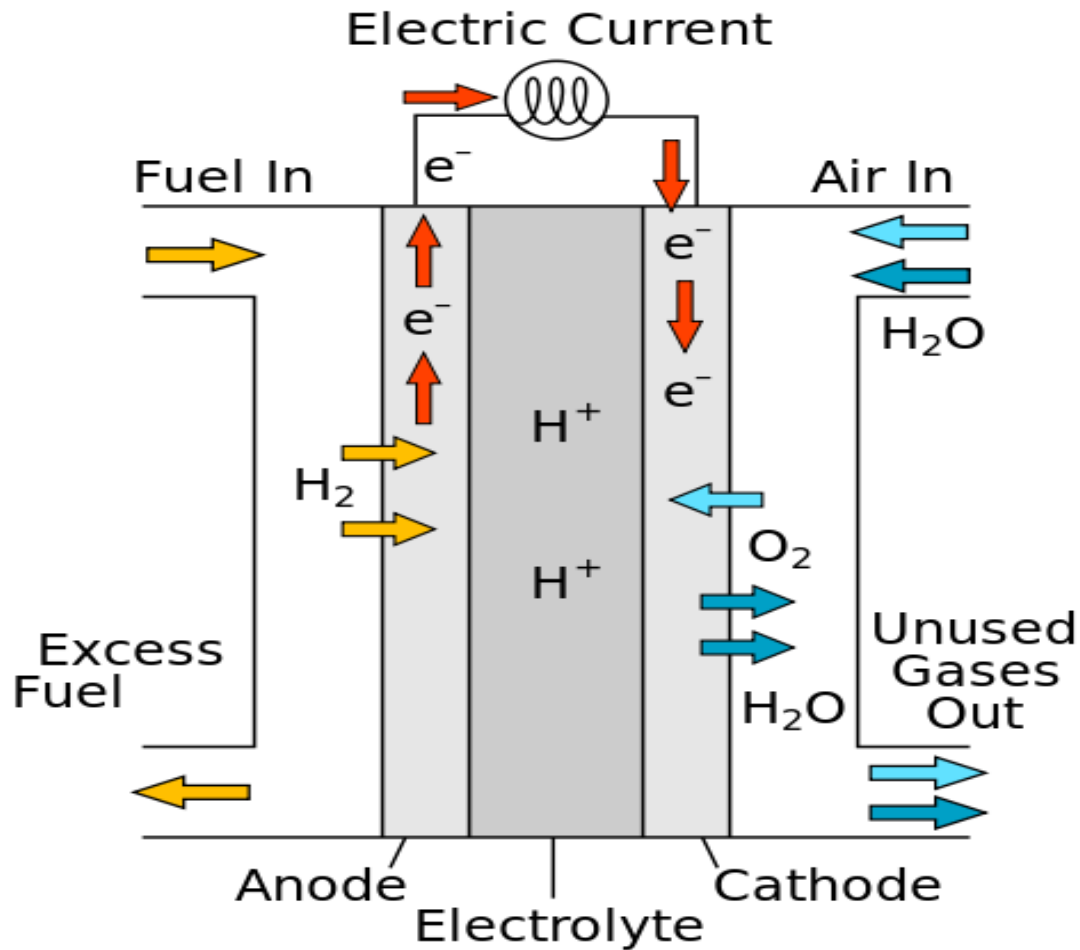


Other Cells

- Daniell Cell
- Leclanché Cell
- Weston Cell

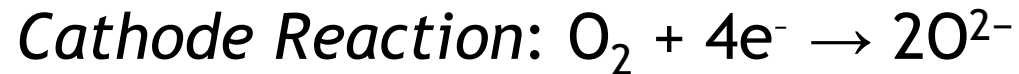
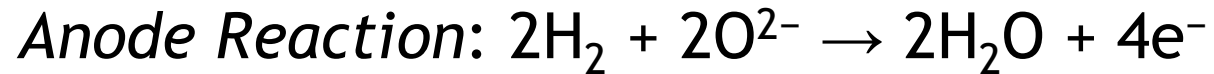


Fuel cell





Reactions





Literatur

- www.wikipedia.org
- <http://hyperphysics.phyastr.gsu.edu/>