Chemistry course
ACME Faculty, EHVE course
B.Sc. Studies, I year, I semester
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Electrochemistry, part 2 Electrodes, cells and corrosion

Electromotive force

- It is calculated as a difference between half-cell (electrode) potentials, *i.e.* one subtracts the lower value from the higher value:
EMF = E_2-E_1 (EMF is always positive)
- Apart from **standard electrode potentials** (E^0), half-cell potentials are affected by: temperature, reagents concentration, number of electrons exchanged in electrode reaction and pressure
(only if there is a gaseous reagent – substrate or product).

2

Electrode potential

$E = E^0 + R·T/(z·F) · \ln(c_{ox}{}^n/c_{red}{}^m)$ [Nernst equation]

T – temperature / K;

z – number of electrons exchanged in electrode reaction;

F – Faraday constant; R – gas constant;

n and m – stoichiometric coefficients of a given reagent in a half-reaction;

$C_{ox/red}$ – oxidized/reduced form concentration; if form is in solid form (*e.g.* metal) then c=1, if reagent is in gaseous form, then we take pressure/p_{atm} ratio instead of concentration;

ln – natural logarithm, so in order to use common logarithm (more natural for human) one needs to add coefficient 2.303 ($\ln(x)$ = 2.303·$\log(x)$);
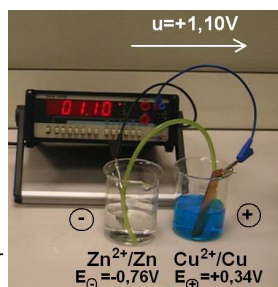
E^0 – standard electrode potential.

3

Electrode potential

- $E = E^0 + R·T/(z·F) · \ln(c_{ox} / c_{red})$ simplifies at standard conditions (T = 25°C, p = 1atm) to
$E = E^0 + 0.0592/z · \log(c_{ox} /c_{red})$
- So for the 1M Li^+ solution in lithium cell (z = 1, c = 1, E^0 = -3.04 V) this formula takes form of:
E = -3.04 + 0.0592 · $\log$(1) = -3.04 [V]
- But for the 0.01M Li^+ solution it will result as:
E = -3.04 + 0.0592 · $\log$(0.01) =
= -3.04 + 0.0592 · (-2) = -3.1582 [V]

4

Electrode potential

Concentration difference of electrolyte in a cell can cause reaction course reversal.
In half-cell direction of reaction (oxidation or reduction) is defined by its surroundings – what is relative potential of the second half-cell in a system. In half-cell of lower potential oxidation takes place and in that of higher potential reduction takes place.

u=+1,10V

Zn^{2+}/Zn Cu^{2+}/Cu
$E_⊖$ =-0,76V $E_⊕$=+0,34V

5

Electrode potential

Example – cell consisting of silver and iron half-cells:

$E^0_{Fe3+/Fe2+}$ = 0.771 V

$E^0_{Ag+/Ag}$ = 0.799 V

Concentration is 1M for all solutions (Fe^{2+}, Fe^{3+} and Ag^+):

EMF = 0.799 - 0.771 = 0.028 [V] (28 mV)

Silver will reduce and iron oxidize.

BUT for the 0.01 Ag^+, 1M Fe^{2+} and 1M Fe^{3+} solutions:

EMF = 0.771 - (0.799 + (-2)·0.0592) ≈ 0.090[V] (90 mV)

Now iron reduce and silver oxidize!

6

Overpotential

- Unfortunately reality is a little more complex than presented theory. Each process (both chemical and physical) needs energy, so all side processes need it as well. That means higher requirements. In case of cells it means higher EMF needed for process initiation or lower effective (yielded) EMF in comparison with one theoretically predicted.
- As an example: lower potential can be obtained due to concentration change of electrolyte, which is caused by its consumption at electrodes.

Overpotential

Another important example is gas bubbles formation at the electrode (gas forms due to electrode reaction). That overpotential is quite high – the best proof is no such observed reaction in lead-acid battery. In water hydrogen should form under 0 V and Pb/Pb^{2+} is -0.126 V vs SHE. However, overpotential of bubbles formation (nucleation) on lead plate is ca. 0.4 V (so in order for bubbles to form, potential must be lower than -0.4 V vs SHE).

Half-cell types

Half-cells can be divided on their structure basis:

- I type – metal immersed in solution of the soluble salt of that metal. *E.g.* $Pb_{(s)}|Pb^{2+}_{(aq)}$. Metal acts both as a reagent and electricity conductor. Reaction that takes place is:

$$Pb^{2+}_{(aq)}+2e^- \rightleftarrows Pb_{(s)}$$
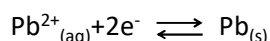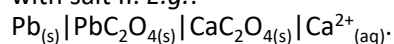
Half-cell types

- II type – metal is covered with insoluble salt of that metal and is immersed in solution of the soluble salt of the anion (from insoluble salt I). *E.g.* $Ag_{(s)}|AgCl_{(s)}|Cl^-_{(aq)}$. Metal acts as an electric conductor and reacts with anion forming/decomposing insoluble salt. Whole electrode is reversible to chloride:

$$AgCl_{(s)}+e^- \rightleftarrows Ag_{(s)}+Cl^-_{(aq)}$$
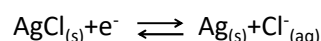
Half-cell types

- III type – metal is covered with inner layer of insoluble salt I of that metal and with outer layer of insoluble salt II of anion common with salt I. Whole electrode is immersed in solution of soluble salt III of cation common with salt II. *E.g.*:
$Pb_{(s)}|PbC_2O_{4(s)}|CaC_2O_{4(s)}|Ca^{2+}_{(aq)}$.
Metal and anion of salt II are reacting with each other forming salt I, but solubilized salt II that way:

$$Pb_{(s)}+CaC_2O_{4(s)} \rightleftarrows PbC_2O_{4(s)}{\downarrow}+Ca^{2+}_{(aq)}+2e^-$$
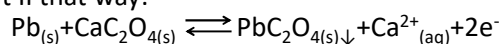
Half-cell types

- Redox half-cells – noble metal which is not taking part in reaction, just conducts electrons, is immersed in solution of reagent. Reagent can change its oxidation state, *e.g.* $Pt_{(s)}|MnO_4^-{}_{(aq)},Mn^{2+}_{(aq)}$
- Subtype of redox half-cell is gas half-cell, which has gas flow around electrode instead of solution. That gas is taking part in electrode reaction, *e.g.* $Pt_{(s)}|H_{2(g)}|H^+_{(aq)}$. Reaction:

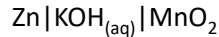$$H_{2(g)} \rightleftarrows 2H^+_{(aq)}+2e^-$$
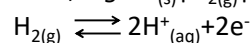
Primary cells and rechargeable cells

- Primary and rechargeable cells are galvanic cells that were designed for potentials difference (between half-cells) maximizing. Also, electrodes and reaction products neither can be gaseous nor they can change volume.
- Primary cells have larger material scope to choose from. Their half-cell do not need to have their electrode process easily reversed in cell conditions (cannot be recharged).
- Rechargeable cells are cells designed in such a way so electrode reaction can be "reversed" (opposite direction of the reaction) by applying external source voltage and force the current flow that way.
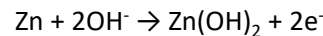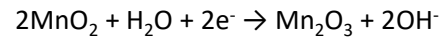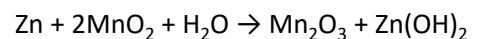
Primary cells

As an example of primary cell can act alkaline cell (commonly known as alkaline battery).

$Zn|KOH_{(aq)}|MnO_2$

Reactions:

$2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$

$Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^-$

After summing up:

$Zn + 2MnO_2 + H_2O \rightarrow Mn_2O_3 + Zn(OH)_2$

Primary cells

- POSITIVE CONNECTION
- CURRENT PICK UP
- ZINC ANODE
- ION CONDUCTING SEPARATOR
- MANGANESE OXIDE CATHODE
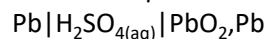- OUTER CASING
- PRESSURE EXPANSION SEAL
- PROTECTIVE CAP
- NEGATIVE TERMINAL
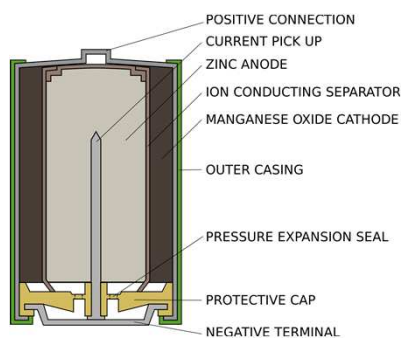
Rechargeable cells

As an example can act lead-acid cell:

$Pb|H_2SO_{4(aq)}|PbO_2,Pb$

Reactions:

$Pb \rightleftharpoons Pb^{2+} + 2e^-$

$PbO_2 + 4H_3O^+ + 2e^- \rightleftharpoons Pb^{2+} + 6H_2O$

After summing it up:

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

Rechargeable cells

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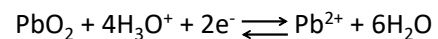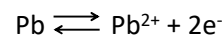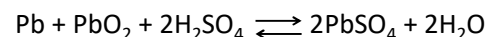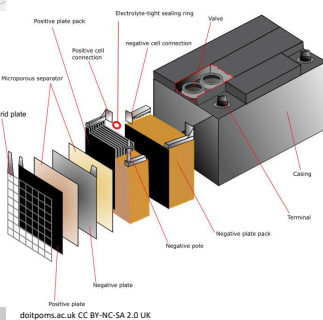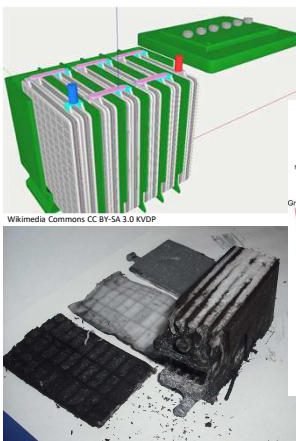
Electrolysis

- **Electrolysis** is a process in which current that is flowing through the electrode|electrolyte|electrode system (in that case called electrolyzer) is a result of external source voltage applied. It is applied in such a way, that process would proceed in an opposite direction to spontaneous one.
- That enables compounds decomposition in such a way that electrolysis product can be easily separated – in a gaseous or solid form (*e.g.* as layers deposited on electrode).

Electrolysis-electrorefining

Electrolysis is a common industrial process
enabling various metal ores refining
and obtaining pure metals (so-called
electrorefining) (aluminum, copper, silver, lead,
etc.) or gases, *e.g.*
hydrogen
or oxygen.

19

Electrolysis-electrorefining

- For instance, water electrolysis yields hydrogen
  at one electrode and oxygen release on another.
  Of course suitable conditions have to be provided
  for electrolysis first (electrode materials, overpotential).
- Electrodes in such process are usually graphite
  or platinum. In electrorefining electrode usually
  consists of very pure metal that will be refined
  (purified).

20

Electrolysis

- Molten salts electrolysis (those are also electrolytes) is
  forming metal at the cathode and nonmetal
  at the anode – which is an industrial method
  for pure aluminum winning (from the mixture
  of molten salt – cryolite - Na_3AlF_6 and aluminum
  oxide - Al_2O_3).
- Similarly, presence of heavier metals
  and/or hydracid anion is causing forming of metal
  or nonmetal, respectively, in pure form (gas
  as well).

21

Electrolysis

- Water electrolysis can take place if only light
  metals are present in solution (that have
  standard electrode potential below
  -1.7 V vs SHE) and only oxy-acid anions are
  present.
- Quantity of yielded materials due to
  electrolysis results from charged that passed
  through electrolyte and number of electrons
  exchanges in a single half-reaction. Charge is
  equal to current multiplied by time.

22

Electrolysis

Mass of a substance
yielded during
an electrolysis:

$$m = M \cdot I \cdot t / (F \cdot z)$$

where:
M – molar mass
of element/substance;
I – current; t – time; F – Faraday constant (96484 A·s);
z – number of electrons exchanged during
half-reaction.

That formula is not containing potential. However,
minimal potential is always needed in order
for the reaction to initiate!

23

Electrolysis

E.g. yielding 1 g of copper with 10 A current will
take:

$m = M \cdot I \cdot t / F \cdot z$

1 g = 64 g/mol · 10 A · t / (96484 A·s · 2/mol)

t ≈ 300 s (ca. 5 minutes)

During industrial metal refining current of tens
of thousands ampere is used.

24

Electrodeposition

- Specific subtype of electrolysis is called **electrodeposition**. It is based on electrolysis using electrode on which yielded substance (usually metal) can deposit (and nucleate at all).
- One of the best and simplest methods of coating one metal with another one (or even nonmetal or metal compounds).
- Quantity of coated substance is calculated as in typical electrolysis.

25

Electrodeposition

- With that industrial method various things are produced: nails (zinc plating on iron), coins (nickel plating, copper plating), roofing-tiles (zinc), computer casings (aluminum), cars and train cars bodies, hulls of ships, *etc.*

- Decorative objects are also coated that way - jewelry, cutlery/tableware, bumpers, rims (chromium), *etc.*

26

Electrodeposition

- Electrodeposition is also used for other reasons:
  - decorative – so the coated object would look better (*e.g.* shiny due to more even surface);
  - Easily wearing metal can be coated with wear resistant layer;
  - Reinforcing surface, smoothing (decreasing surface porosity);
  - Introducing catalytic layer (supporting surface reactions) or chemical resistant layer;
  - Anticorrosive protection;

27

Corrosion

- **Corrosion** is a general name for chemical and/or electrochemical processes that destroy materials (usually metals) due to contact with environment (spontaneously).
- It results from contact with moist air, water (especially salted one), moist soil or certain microorganisms. There is also possible corrosion resulting from contact with gases (especially moist ones) or resulting from high temperatures (notably when it changes often).

28

Corrosion

- Corrosion most commonly happens when metal (*e.g.* iron) upon contact with water forms a half-cell (Fe/Fe^{2+}) and solubilization starts. Water always contains H_3O^+ ions that form in that case H_3O^+/H_2 half-cell.
- All metals with standard electrode potential below o V vs SHE will solubilize in water. The more acidic it is (and/or contains chlorides, fluorides, *etc.*) the faster solubilization goes.
- Corrosion takes place in basic environments as well (reacting with oxygen as O_2/OH^-).

29

Corrosion

Corrosion can also progress in different ways: metal ions that already been form can move away (diffuse away) from surface area. They can also react with available ions, *e.g.* OH^-, forming hydroxides or oxides; sulfides, sulfates, chlorides, *etc.* Rust is an example of such metal behavior.

30

Corrosion

Metals such as aluminum, copper or nickel behave differently. They do also react with water or air, but reaction products (oxides) are covering metal with thin, tight, uniform layer, that is impermeable for air or water. Such metal behavior is called **passivation**. In practice, it causes metal not to corrode at all (apart from forming this thin passive layer at the surface and until no other corrosion factors are present).

31

Corrosion

- Popular example of corrosion resulting from chlorides presence is *aqua regia* that dissolves gold. Hydrochloric acid is chloride donor and nitric acid provided acidic and oxidative environment. Gold chlorides that form are soluble in water and that is why gold dissolves (normally, gold in water forms passive layer with oxides or hydroxides).
- Another example is patina (green rot) – copper is usually is passivating, but in presence of sulfates (acid rain component) it forms complicated salts containing sulfur. These salts covers coppers surface and are permeable for water and further ions.

32

Corrosion types

Corrosion consequences are not limited to solubilization or transformation of metal to salts:

– Weaker structure (salt brittleness);
– Volume changes and resulting stresses in material; That causes cracking and exfoliation of coatings on metal surface.

Especially susceptible to corrosion are untight coatings of metal (coatings usually function as anticorrosive protection) that can cause crevice corrosion.

Another type is pitting corrosion. It is caused by metal/alloy structure and/or processing (*e.g.* surface finishing).

33

Anticorrosive protection

- Standard anticorrosive protection means are coating material with polymer layer (paint, varnish).
- Often due to metal usage and breaking its structure (with riveting, welding, etc.) it is not possible to avoid pitting corrosion. It is also not always possible to coat whole construction with tight varnish layer (untight layer sometimes can be more dangerous than lack of any anticorrosive layer). That is why electrochemical anticorrosive means are used.

34

Anticorrosive protection

Passive protection – protected metal is coated with layer of metal with lower standard electrode potential (*e.g.* iron coated with zinc). That way coating corrodes first, instead of protected construction. Similarly, metal construction can be connected to a big piece of metal with low potential (*e.g.* calcium).

First method is used for protection of small objects/constructions. Big structures, like ship hulls, are often protected with second method (and often with other methods simultaneously).

35

Anticorrosive protection

Active protection (cathodic) can be applied by connecting direct current source to protected structure and to material non-corroding in a given environment (*e.g.* graphite, platinum). Delivering electrons from outside hinders metal from giving its electrons away (so it cannot solubilize – reduction of metal is enforced all the time).

That method is applied to protect pipelines and fuel tanks at gas stations.

36