

Electrochemistry course  
 ACME Faculty, EHVE course  
 B.Sc. Studies, II year, IV semester  
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## Galvanic cells. Electrolyzers. Electrorefining. Electroplating.

### Electrochemical series

(standard half-cell potentials vs SHE)

Li <sup>+</sup> /Li	-3.045 V	AgCl/Ag	+0.222 V
Ca <sup>2+</sup> /Ca	-2.864 V	Hg <sub>2</sub> Cl <sub>2</sub> /2Hg	+0.268 V
Na <sup>+</sup> /Na	-2.711 V	Cu <sup>2+</sup> /Cu	+0.338 V
Mg <sup>2+</sup> /Mg	-2.370 V	I <sub>2</sub> /2I <sup>-</sup>	+0.536 V
Al <sup>3+</sup> /Al	-1.700 V	MnO <sub>4</sub> <sup>-</sup> /MnO <sub>4</sub> <sup>2-</sup>	+0.558 V
SO <sub>4</sub> <sup>2-</sup> /SO <sub>3</sub> <sup>2-</sup>	-0.932 V	Fe <sup>3+</sup> /Fe <sup>2+</sup>	+0.771 V
Zn <sup>2+</sup> /Zn	-0.763 V	Ag <sup>+</sup> /Ag	+0.799 V
Cr <sup>3+</sup> /Cr	-0.744 V	Pt <sup>2+</sup> /Pt	+0.963 V
Fe <sup>2+</sup> /Fe	-0.441 V	Cl <sub>2</sub> /Cl <sup>-</sup>	+1.358 V
Ni <sup>2+</sup> /Ni	-0.234 V	Au <sup>3+</sup> /Au	+1.498 V
Pb <sup>2+</sup> /Pb	-0.126 V	MnO <sub>4</sub> <sup>-</sup> /Mn <sup>2+</sup>	+1.531 V
H <sup>+</sup> /H <sub>2</sub>	0.000 V	F <sub>2</sub> /F <sup>-</sup>	+2.866 V

### Galvanic cells

Primary cells and rechargeable cells are galvanic cells which were constructed in such a way that potential differences between their half-cells are maximized. In the same time their electrodes or reaction products can be neither gaseous nor their volume should change considerably.

### Galvanic cells

Electrode materials are chosen in such a way that at least one of them should be solid in the charged form and at least one should be solid in discharged state as well as during operation of the cell. Electrode material should also conduct electrons or easily mix with materials that do. Nowadays it is also important that electrode materials should be size reducible up to micro/nano level.

### Galvanic cells

Design of the galvanic cell requires electrode materials that have high **energy density** and high **current density**.

All types of cells require also low **self-discharge** (capacity fade with time).

### Galvanic cells

Necessary cell components:

- Current collector at the anode
- Anode (or anolyte)
- Electrolyte (or not, if the anolyte/catholyte is used)
- Separator
- Cathode (or catholyte)
- Current collector at the cathode
- Casing/container, tabs, leads...

## Primary cells

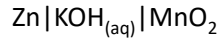
Primary cells have half-cells in such a form, that it is not easy to reverse the electrode processes (cells are not possible to recharge).

It facilitates the design of the process and materials choice, as it is not required to rebuilt the electrode structure due to recharge (contrary to the rechargeable cells). It means bigger freedom during technology design.

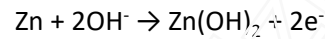
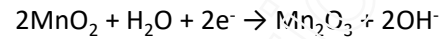
7

## Primary cells

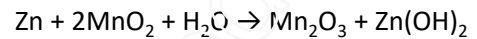
An example of such a cell can be the alkaline cell (commonly known as alkaline battery).



Half-reactions:

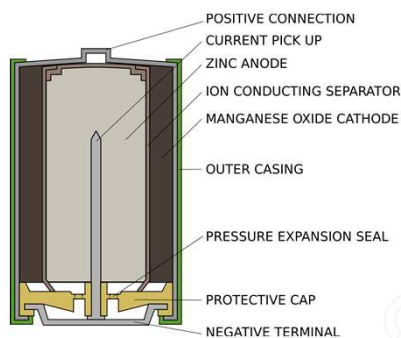


Overall reaction:



8

## Primary cells



9

## Rechargeable cells

Rechargeable cells are designed to “reverse” the reaction (give an opposite direction) by applying external voltage and forcing the current flow from the external source.

Such solution is the more economical due to multiple use of one cell. However, it forms new requirements at the design phase. It is required for electrodes to rebuild their structure during charging process (enforced process reverse to the spontaneous one).

10

## Rechargeable cells

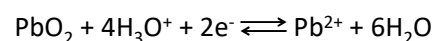
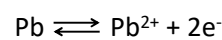
Apart from the requirement of the initial structure rebuilding (in the charged state), electrode materials has to provide fully repeatable crystalline structure in the subsequent cycles (charge-discharge cycle). Macroscopic structure reproduction is also very important (such as size and quantity of grains, etc.).

11

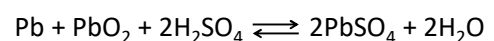
## Rechargeable cells

Commonly known lead-acid battery is an example of the rechargeable cell:  $\text{Pb} | \text{H}_2\text{SO}_{4(\text{aq})} | \text{PbO}_2, \text{Pb}$

Half-reactions:



Overall reaction:



12

## Functional additives/modifications

For smooth operation of the rechargeable cell special additives are added to a cell. Depending on the cell characteristics there can be:

- electrode additives for: enhancing electronic conductivity, enhancing structure rebuilding, improving interfacial layer formation (SEI), binders, enhancing mechanical properties, hindering formation of side-products of the electrode reaction.

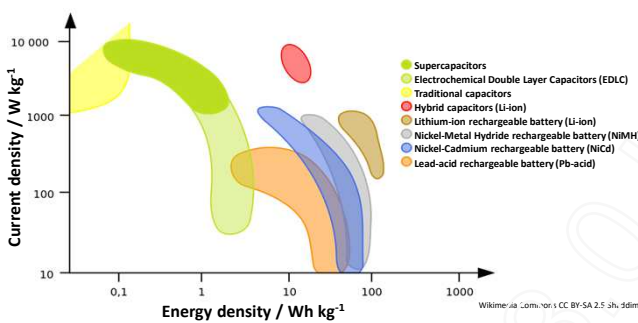
13

## Functional additives/modifications

- electrolyte additives for: increasing ionic conductivity, decreasing viscosity, improving interfacial layer formation (SEI), adsorbing gaseous products of the side-reactions, hindering formation of side-products of the electrode reaction, passivation/preventing corrosion, preventing agglomeration, changing individual parameters (e.g. transference numbers, melting point, etc.).

14

## Galvanic cells and supercapacitors



15

## Cell capacity

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

- Calculate how much of the lead is required in lead-acid cell to obtain capacity of 50 Ah.
- Calculate how much of the lithium is there in the lithium-ion battery with 14.4 V voltage and 103.7 Wh capacity.

16

## Cell capacity

- Calculate how much of the lead oxide is required in cathodic plates of the lead-acid battery, so one can produce a battery with 12 V voltage and 60 Ah capacity.
- Calculate how much lithium iron phosphate is required to manufacture cathode for lithium-ion cell (3.7 V) with 4000 mAh capacity?

17

## Electrolysis

- **Electrolysis** is a process in which current flows through the electrode|electrolyte|electrode system (in this case called an electrolyzer) as a result of the voltage applied from the external source. Voltage is applied in such a way, that the process taking place at the electrodes is running in an opposite way to the spontaneous process.
- It allows for the compounds to break in such a way, that electrolysis product is easy to separate – in a gaseous or solid form (e.g. in the form of layers deposited on the electrode).

18

## Electrolysis-electrorefining

Electrolysis is a common industrial process that allows to refine metal ores and to obtain metals in a very pure form – so-called **electrorefining**. This is the main industrial method to obtain pure aluminum, copper, silver, lead, and so on, as well as very pure gases like hydrogen or oxygen.

19

## Electrolysis-electrorefining

- 1 000 tons of silver is produced annually by electrorefining in Poland (Poland is the biggest refined silver manufacturer in the world).
- 500 000 tons of copper is produced annually by electrorefining in Poland. It is the main way to obtain pure copper for electrical (electronic) purposes.
- 2 million tons of extremely pure hydrogen is produced annually with electrolysis method. (4% of world production of hydrogen).

20

## Electrolysis-electrorefining

- Electrolysis of water is in other words generation of hydrogen at one electrode and oxygen at the other one. Of course, appropriate conditions are to be fulfilled in order for the electrolysis to occur (electrode material, overpotential of 1.5 vs 1.23 V).
- Graphite and platinum are the most common electrode materials for electrolysis. In case of electrorefining electrodes are made of the very pure metal which is to be produced/purified.

21

## Electrorefining

- To produce any metal with electrorefining, an extremely pure electrode made of this metal is required. Process should be carried out slowly in order to allow for reduction on electrode to happen without side-reactions or reduction of other metals (impurities).
- Electrorefining can remove up to 99% of impurities (thus obtaining purity of over 99.96%).

22

## Electrolysis

- Electrolysis of the molten salts (electrolytes as well) deposits metal at the cathode and non-metal at the anode – it is an industrial method by which pure aluminum is made (from the molten salt – cryolite –  $\text{Na}_3\text{AlF}_6$  mixture with an aluminum oxide  $\text{Al}_2\text{O}_3$ ).
- Similarly, heavier metals presence and/or binary acid (one without oxygen) anion causes metal or non-metal (gaseous as well) to be produced at the electrodes.

23

## Electrolysis

- Water electrolysis can occur if solution contains only light metals (those with half-cell standard potential below 1.7 V vs SHE) and anions of the oxy-acids.
- Amount of the material resulting from the electrolysis depends on the amount of charge passed through the electrolyte and of the amount of electrons exchanged in the individual half-reaction. Charge passed through the electrolyte is equal to the product of current and time.

24

## Electrolysis

Mass of the substance resulting from the electrolysis:

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

where:

$M$  – molecular mass of the element/substance;

$I$  – current;  $t$  – time;  $F$  – Faraday constant (96484);

$z$  – number of electrons exchanged in the half-reaction.

Although there is no potential in this formula, a minimum potential is required for the reaction to happen at all!

25

## Electrolysis

Example: To obtain 1 g of copper by using 10 A current (available from the household socket), it will take:

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

$$1 \text{ g} = 64 \text{ g/mol} \cdot 10 \text{ A} \cdot t / (96484 \text{ A} \cdot \text{s} \cdot 2 / \text{mol})$$

$$t \approx 300 \text{ s (ca. 5 minutes)}$$

In the industrial production of gases currents of hundreds or even thousands of amperes per  $\text{cm}^2$  are used and the electrolyzer surfaces of square meters (up to tens of MW applied). In the metal electrorefining industrial processes use hundreds of amperes per  $\text{m}^2$ .

26

## Electrolysis

- How much copper (in grams) one can produce by applying appropriate voltage and 200 A current over 24 hours?
- How much hydrogen (in grams) one can produce in the same conditions (assuming adequate applied voltage and proper electrode)?

27

## Electrolysis

- What hydrogen volume can be obtained with the appropriate voltage (1.5 V) and electrolyzer with the power of 15 MW over 24 hours?
- What chlorine volume can be obtained in the same electrolyzer (assuming change to adequate electrode and adjusted voltage to 3.0 V)? What mass it would be?

28