CC BY-SA Leszek Niedzicki

WELCOME TO

ATHENS WUT21 course

Organizational matters

- **30 hours course (incl. 12h lab and 2-3h seminar)**
- **Project-based learning – 2-3 people groups with ca. 5 minutes seminar at the end of the course**
- **Short test at the end of the course**
- **Coordinator: Leszek Niedzicki, PhD, DSc, Eng.**

Faculty of Chemistry, Old Chemistry Building

(3 Noakowskiego St), room 346 („how to reach 346" description on www)

Contact:

phone: **(+48) 22 234 7421**

email: **leszek.niedzicki@pw.edu.pl**

www: **lniedzicki.ch.pw.edu.pl (lectures/pdf)**

MS Teams: **Leszek Niedzicki**

2

Organizational matters

	Monday (16.11.2026)	Tuesday (17.11.2026)	Wednesday (18.11.2026)	Thursday (19.11.2026)	Friday (20.11.2026)
09:00-09:45	Introduction, 339	Laboratories, 213a/341/351	Laboratories, 213a/341/351	Laboratories, 213a/341/351	Manufacturing methods, 339
09:45-10:30	Electrochemistry, 412 (since 10:00)	Laboratories, 213a/341/351	Laboratories, 213a/341/351	Laboratories, 213a/341/351	Manufacturing methods, 339
10:45-11:30	Electrochemistry, 412	Laboratories, 213a/341/351	Laboratories, 213a/341/351	Laboratories, 213a/341/351	Project seminary, 339
11:30-12:15	Electrochemistry, 412	Laboratories, 213a/341/351	Laboratories, 213a/341/351	Laboratories, 213a/341/351	Project seminary, 339
12:15-13:00	Lunch	Lunch	Lunch	Lunch	Lunch
13:00-13:45	Measuring methods in battery research, 412	Post-Li-ion batteries, 404	Post-Li-ion batteries, 416	Li-ion batteries, 404	Project seminary and Final test, 53
13:45-14:30	Measuring methods in battery research, 412	Post-Li-ion batteries, 404	Post-Li-ion batteries, 416	Li-ion batteries, 404	
14:45-15:30	Measuring methods in battery research, 412				

3

Organizational matters

Topics for the project (describe all components, their form/dimensions, structure, assembly type in ca. 5 minutes):

1. Cell maximized (optimized) for the power density
2. Cell maximized for the longevity (in cycles)
3. Cell maximized for the safety
4. Cell maximized for environmental safety/friendliness
5. Cell maximized for the energy density (Wh/kg)
6. Perfect Li-ion traction cell for large truck/bus
7. Perfect cell for the battery-powered passenger plane
8. Perfect Li-ion cell for small e-scooter/e-motorcycle
9. Perfect cell for the battery-powered passenger car
10. Perfect cell for the battery-powered ferry

4

Safety rules

1. Order and quiet are required, only students participating in the given lab are allowed in the laboratory.
2. Persons in the laboratory are required to wear appropriate clothing (shoes fully covering the feet, long hair tied back), safety glasses, as well as gloves and aprons (where required).
3. Prohibited is: eating, drinking, smoking, work outside the given tasks or time, working alone.
4. Remember: danger may also arise from work of other people!
5. Before work familiarize with hazards of the place - chemicals (all substances may be possibly toxic/harmful), equipment.
6. Please close all containers that are opened, do not allow them to be contaminated, put them back from where you took it.
7. Dispose waste according to the dedicated containers. Clean workplace after the end of classes.
8. All work with toxic substances, especially volatile (gas/vapor) is to be carried out under the fume hood (with ventilation turned on).
9. All malfunctions of equipment, safety equipment should be reported to the instructor immediately.

5

Safety rules

10. Liquids should be heated so that no one is injured in the event of a vessel breaking or spilling liquid. Strictly follow the instructions provided, and in particular, position the vessel outlets so that they are not directed at people (especially the face).
11. All handling of corrosive and hot substances should be performed under a fume hood and with personal protective equipment (safety goggles).
12. When diluting concentrated acid solutions, always pour the acid into the water, not the other way around.
13. In the event of acid or lye burns, rinse the burn area with a large amount of water.
14. Flammable liquids should not be heated using open flame burners.
15. The basic requirement for the proper operation of equipment and devices is to follow their operating instructions.
16. Familiarize yourself with the general instructions and the specific instructions applicable in the laboratory.

6

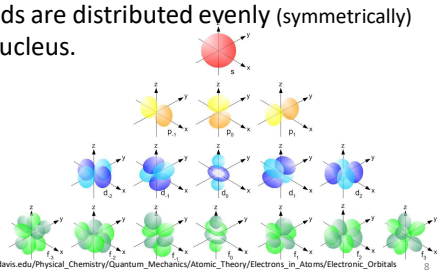
CC BY-SA Leszek Niedzicki

Electrochemistry basics quick course ATHENS WUT21 course

Leszek Niedzicki, PhD, DSc, Eng.

Electron energy

Most of the electrons in the atom are required to stabilize atomic nucleus (that has positive charge) – they take all orbitals and layers from the center (nucleus). Electron clouds are distributed evenly (symmetrically) around the nucleus.



CC BY-SA 3.0 http://chemwiki.ucdavis.edu/Physical_Chemistry/Quantum_Mechanics/Atomic_Theory/Electrons_in_Atoms/Electronic_Orbitals

8

Electron energy

Electrons in the most outward electron shell – the valence shell – are not affecting the stability of the nucleus (especially that, apart from noble gases, they are unevenly distributed around the nucleus). Thus, they can be shared with other atoms. Atom can also accept electrons from other atoms to such shell, given that they would increase the uniformity of charge distribution around the nucleus – increasing its stability.

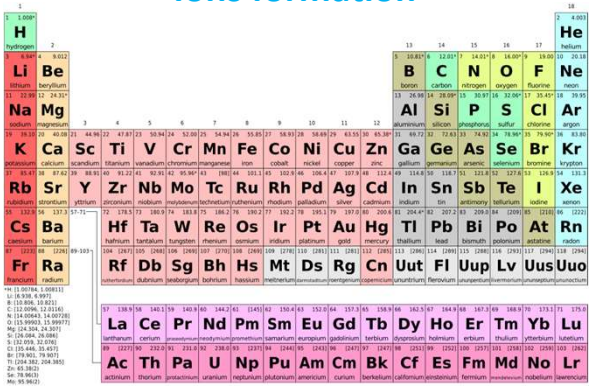
9

Ions formation

- Depending on the highest occupied orbital, atoms have different possibilities to form bonds, *i.e.* to share electrons (accept or give them away) – they tend to have outer electron shell fully occupied.
- Thus, elements from the s-block can form +1 cations (lithium group) or +2 (beryllium group), and p-block elements can have the charge from +1 to +7 range (if they give away electrons) or from -1 to -3 range (if they accept them).

10

Ions formation



11

Chemical bonds

- Bonds between two (or more) atoms can be formed if it is „profitable” for all atoms taking part in bond formation. Atoms tend to obtain fully occupied outer electron subshell. Depending on the initial state – which direction is the closest way to obtain it – they can accept (**acceptor**) electrons from other atoms or “give away” (**donor**) them to other atoms.

12

CC BY-SA Leszek Niedzicki

Chemical bonds

- The profit for atoms is the decrease of energy level – the sum of individual atoms energy is higher than energy of molecules built from them.
- Each atom or group of atoms tends to obtain the lowest possible energy in the given system and conditions (in this case – to share their electrons).

E.g.: two **lithium** atoms (each with 1 valence electron) give away their electrons to **oxygen** atom (which in the ground state have 6 valence electrons - 2s2, 2p4), which, as a result, have 8 electrons in the outer shell (full 2s and 2p subshells). Lithium atoms have also full 1s subshell.

13

Bond energy

- Chemical bonds have different energies – among the most popular ones, we can distinct the following bonds:
  - **ionic** – electrostatic interactions between two ions formed as a result of electron transfer;
  - **covalent** – bond forms through an equal contribution of electrons from both atoms of the similar electronegativity;

14

Ionic crystal

- Most of phenomena taking place around atoms, ions and molecules can be explained by + and – attraction or repulsion of identical charges.
- Example of such phenomena is existence of ionic compounds in the solid state – crystals built from ions. Ions attract each other evenly and form structures packed as close as it is possible in the given conditions:



15

Solvation

Another example of interaction between + and – is **solvation** of ions in the solution. Ions in a solution are surrounded by solvent molecules, because atoms in solvent molecules also possess charges. Although solvent molecules are neutral as a whole, parts of them are a little more positive or negative. Thus, more negative part of solvent molecule (-) will interact with a cation (+).

16

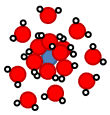
Solvation

Ions are solvated to a greater extent by molecules of **polar** solvents. Those are the solvents with molecules in which charges (from the individual atoms) are unevenly distributed, so they form dipole moment.



The bigger difference between electronegativity of atoms forming solvent molecule, the more polar it is and the better it is for ion solvation. Water is the most common solvent on earth and it is polar. Solvation by water molecules is called **hydration**.

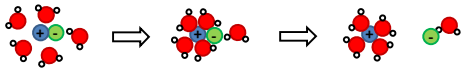




17

Dissociation

Dissociation is a name for a process in which ionic compound (that possess at least one ionic bond) is disrupted into two ions. First, compound is solvated. Consequently, molecules of a solvent interact so strongly with ions that energy of that interaction is higher than that of an ionic bond of the ionic compound. Bond is broken and from that moment off this compound (salt, acid, base) cease to exist and two ions form instead of it – cation and anion (or more of them, if salt, acid or base were multi-ionic).



18

CC BY-SA Leszek Niedzicki

Ions in solution

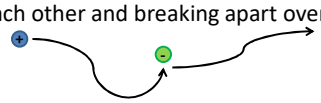
If we put one ion into the basin full of pure solvent, than it would move around without any constraints. Solvation would be the only interaction it would be subject to. Due to lack of any other interactions it would move with maximum velocity available for a given ion in a given solvent. It is the case of infinitesimal dilution (c_∞).



19

Ions in solution

If we add second ion to the solution, then there would be a chance for them to meet eventually. For a moment they would interact with each other. They could to that on distance, by means of electrostatics (indirectly) through molecules of a solvent. Or they can interact with each other directly through a contact and formation of ionic bond. In both cases eventually they would break and move apart, because such an equilibrium is dynamic, although system have stable amount of components (*i.e.* stable number of ion pairs formed). However, it works in a scale of billions of billions ions, so individual ions are all the time interacting with each other and breaking apart over and over again.



20

Ions in solution

The more ions in a solution, the higher chance for them to meet with each other, thus the higher chance to form ionic pairs. With the ions concentration increase, some of them (higher and higher fraction) constantly exist in a form of **ion pairs** (not necessarily direct, thus it is not the same as undissociated salt) or bigger associates.

Picture shows system with solvent molecules excluded; all ions are solvated – all cations (at least with one layer of solvent molecules around them) and anions – at least some of them interact with one solvent molecule.



21

Ions in solution

Those momentary stops of ions due to their interactions with counter-ions in a scale of billions of billions of ions statistically cause decrease of their velocity (**mobility**). As a consequence, the higher concentration, the lower mobility of ions. They are also less prone to interact with other molecules/ions. Lower and lower is their fraction that is in a given moment in a free form (of individual, single ions).

Picture shows system with solvent molecules excluded; all ions are solvated.



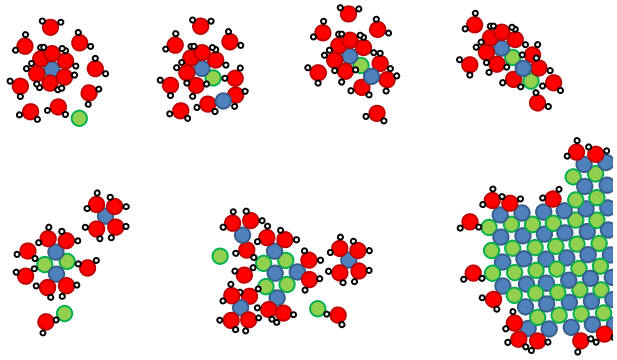
22

Ions in solution

Upon reaching certain concentration it is not possible to add more ions to the solution – it is impossible to dissolve them (dissociation does not occur), or simultaneously to dissolution of one, another is crystallizing. It is due to the fact, that dissociation of one ionic molecule requires a lot of solvent molecules. Each ion has to be surrounded by solvent molecules all the time in order for it to be an ion. If there would be no solvent molecules in a solvation layer, it would connect to any counter-ion on its way and form the initial, undissociated ionic molecule. Thus, solubility of a given compound is defined by the number of solvent molecules in a whole solution and number of them required for effective shielding of ion against the permanent connection with counter-ions.

23

Ions in solution



24

CC BY-SA Leszek Niedzicki

Dissolution of ionic compounds

Crystal of a compound that contains ionic bond (bond between atoms from the opposite sides of the periodic table, *e.g.* Na^+ and Cl^-) is put into the polar solvent (e.g. water). Crystal dissolves, i.e. particles at the edges of a crystal are surrounded by solvent molecules (partial solvation). When strength of interactions between solvent and an ion is higher than that of the ion and its counter-ion (or counter-ions that are still around the ion), ionic bond is broken and ion is torn from the crystal. Counter-ion deprived of bonds with ions, moves into the bulk of a solution as well.

25

Dissociation - again

To what point dissociation goes depends on a structure of a solute and a solvent. The whole solute dissolves (up to a solubility limit), but it stays in a dynamic equilibrium. That equilibrium decides on the level of dissociation of a solute – it is so-called **dissociation degree** (**α**). Its value informs on how many molecules actually undergo dissociation to ions compared to the amount of all molecules dissolved in a solution ($0 < \alpha < 1$).

$$\alpha = c_{ions}/c_{solute}$$

26

Dissociation, cont'd

- Dissociation degree (as well as solubility) of a compound depends, among others, on the solvent used – the more polar it is, the more eager it is to dissolve/dissociate ionic compound. **Polarity** of a solvent is most simply, easily and directly described by **dielectric constant** (relative permittivity) - **ε**.

27

Dissociation, cont'd

- The more ionic is the bond, the easier it is dissociating. Strength of a bond depends on atoms forming it and their electronegativity. Briefly: the higher distance (in a periodic table) of atoms forming the bond, the more ionic is that bond (the weaker it is). HCl, NaCl, LiBr are strongly ionic compounds and thus they are fully dissociating in water. $Al(OH)_3$ is also ionic, but weakly ionic, thus it is hardly dissoluble and hardly dissociates.

28

Electrolyte

- Any matter that conducts ions (that have ions in a mobile state) is an electrolyte.
- Most commonly, electrolyte is understood as a solution of highly dissociated salt, acid or base. In a solutions of ionic compounds ions are mobile and have large degree of freedom, although they exist in a solvated form.

29

Electrolyte

- Melted salt is also the electrolyte. Interactions between ions of salt are so weak compared to temperature-originating vibrations that ionic bonds are broken and ions can freely move around. However, ions in melted salts are mostly forming ionic pairs and associates.
- There are also solid electrolytes. Some of those compounds/alloys/mixtures enable ionic movement in a solid state; solid electrolytes usually conduct poorly.

30

CC BY-SA Leszek Niedzicki

Strong and weak

- Strong electrolyte is the one that is fully or almost fully dissociated (>99% of ions)



$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

- Weak electrolyte is the one that is poorly dissociated (<<99% of ions)



$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$

31

Dissociation consequences

As a result of dissociation solution containing ions differs from the solvent in few important parameters:

- Solution starts to conduct electricity
- Boiling point is increasing
- Melting point is decreasing
- Reaction between ions of different compound are possible if they are dissolved and dissociated in the same solution (also enables reactions with solvent itself).

32

Solvation once more

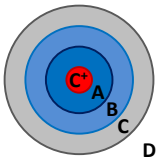
Disturbance of solvent structure by an ion:

A – I solvation layer (directly coordinated by a cation)

B – II and further solvation layers (attracted electrostatically by a cation and can interact with other solvent molecules – *e.g.* through the hydrogen bonds)

C – solvent structure disturbed by the cation presence in the vicinity

D – original solvent structure



33

Dynamic equilibrium

- It is a phenomenon observed when on a large scale (*e.g.* billions of billions of molecules) a statistical equilibrium is observed, *i.e.* mean value of a given parameter is steady, but individual molecules often change their state.
- In practice dynamic equilibrium is defined as an equilibrium of two opposite processes, which occur at the same rate (in a given conditions). In case of solvation solvent molecules are all the time joining and leaving solvation layer (*e.g.* are knocked out of it). However, mean solvent molecules in solvation layer of a given ion stays the same.

34

Dynamic equilibrium

- In dissociation or solvation case dynamic equilibrium forms because solvent molecules and ions are bumping on each other (and at the vessel walls) all the time (due to chaotic moves, vibrations, *etc.*). Thus, constant exchange of molecules in solvation layers is taking place. Due to that, "puncture" of solvation layer by the counter-ion can happen, if it will be not full or/and counter-ion would bump with proper angle and momentum.

35

Solvent

- Solvent in the electrolyte formation process is required to solvate ions (shields them against association or crystal formation) and dissociate compound into ions (strength of interaction with part of the compound tears it from the other part of the compound at the ionic bond).
- The measure of how solvent is eager to interact with ions and how good its molecules are shielding ions against interaction with other ions (counter-ions) is dielectric constant (relative permittivity).

36

CC BY-SA Leszek Niedzicki

Dielectric constant (ε)

ε is dimensionless, because it is ratio of material permittivity to ε_0 – permittivity of free space.
It means, that if certain ions attract each other in vacuum with a certain force, then in a medium (solvent/solution) with a relative permittivity (dielectric constant) ε, they would attract each other ε times more weakly.

Salt as a material with low ε value is decreasing overall dielectric constant of a solution (when considered for next ions/salts addition to that solution).

37

Dielectric constant

Dielectric constant of a material (in that case solvent/solution) can be measured with two methods:

- Capacitance method – requires measurement of a capacitance of a capacitor with vacuum between its plates. Next, material to be measured is placed between those plates and the capacitance measurement is repeated. Dielectric constant is calculated from the capacitance formula:

$$C = \varepsilon \varepsilon_0 A/d$$, where:

ε – dielectric constant of a material between plates;
ε_0 – permittivity of free space;
A – capacitor plates surface (surface of the cross-section of a capacitor);
d – distance between plates.

38

Dielectric constant

- Dielectric spectroscopy (principle of operation is similar to that of impedance spectroscopy, but works at much higher frequencies) – enable dielectric constant measurements with an a.c. signal.
  At the THz frequency order of magnitude relaxation effects of material allows to determine dielectric constant of a material (as a value of extrapolation at 0).
  In practice it is possible to conduct that measurement at the lower frequencies as well.

Dielectric constant is temperature-dependent (for some materials differences are of magnitude order for 50°C temperature change).

39

Dielectric constant

material	**ε (at 20°C)**	material	**ε (at 20°C)**
vacuum	1	glyme	~7
toluene	2	diglyme	~7
ethanol	25	PEO	5
DMF	36		
AN	37	SiO_2	3.9
PC	63	PE	2.3
water	80	PP	2.2
H_2SO_4	~90	glass	~5
EC	100	paper	~4
salts (including ionic liquids)			5-15

40

Solvent-ion interactions

Dielectric constant is not the only way to measure interactions of solution components, as there are secondary parameters such as donor number and acceptor number. Also the temperature dependence of dielectric constant is important – in case of some materials it is not changing much, others show enormous change over only few centigrades.

41

Ionic activity

Increase of ionic concentration above infinitesimal concentration (any non-zero concentration) cause ions to meet and interact with each other as well as change their activity (theoretical) into non-ideal one. It means, that parameters deviate from those calculated by theoretical formulae upon ionic concentration increase. Theoretical equations describe ideal system exclusively (even those taking the concentration into account are taking concentration value as it was group of individual ions not interacting with each other and as the solvent would interact with ions to a maximum extent).

42

CC BY-SA Leszek Niedzicki

Ionic activity

In reality ionic activity depends on concentration, but it is not the same as concentration. Concentration instead of the ionic activity can be used for extremely diluted solutions only, where deviations from theory are negligible. In practice (for useful solutions) ionic activity is used:

$$a_i = c_i \gamma_i$$

where a – ionic activity; c – concentration; γ – activity coefficient;

43

Ionic activity

Activity coefficient γ can be calculated from the empirical formula, where the simplest and basic formula (enriched with additional elements and parameters when complexity increases for use with higher and higher concentrations) is:

$$\log \gamma_i = -A z_i^2 I^{1/2}/(1+I^{1/2})$$

where: A = 0.5091 (water at 25°C); I – ionic strength; z – ionic charge (its electrovalence);

Ionic strength can be calculated from the formula:

$$I = ½ \Sigma (z_i^2 c_i)$$

where: c – concentration. It is the sum of all ions present in the solution. For solutions of one binary salt

I = c.

44

Ionic activity

Example for NaCl (z_{Na}=1, z_{Cl}=1, so I=c).

$\log \gamma_{Na} = -A \cdot z_{Na} \cdot I^{1/2}/(1+I^{1/2})$

$\log \gamma_{Na} = -0.5091 \cdot 1 \cdot c^{1/2}/(1+c^{1/2})$

For **0.0001 mol/kg** concentration:

$\log \gamma_{Na} = -0.5091 \cdot 0.01/(1+0.01) = -0.005091/1.01$

$\boldsymbol{\gamma_{Na}} = 10^{(-0.00504)} = \mathbf{0.988}$

Thus, result is quite close to 1 (1.2% deviation).

45

Ionic activity

For **0.01 mol/kg** concentration:

$\log \gamma_{Na} = -0.5091 \cdot 0.1/(1+0.1) = -0.05091/1.1$

$\boldsymbol{\gamma_{Na}} = 10^{(-0.04628)} = \mathbf{0.899}$

Thus, deviation is higher than 10%.

For **1 mol/kg** concentration (much more complex formulae should be used for such concentration for better results):

$\log \gamma_{Na} = -0.5091 \cdot 1/(1+1) = -0.5091/2$

$\boldsymbol{\gamma_{Na}} = 10^{(-0.2546)} = \mathbf{0.556}$

Thus, deviation is higher than 44%.

46

Ionic activity

In practice ionic activity is used everywhere when theory considers ionic concentration – pH calculation, determining half-cell potential from the Nernst formula and other similar equations, *e.g.*:

$pH = -\log(a_{H_3O^+})$

$E = E^0 + R \cdot T/(z \cdot F) \cdot \ln(a_{ox}/a_{red})$

47

Phenomena in the solution

- Salt/acid/base dissolution
- Dissociation (partial for weak electrolytes)
- Associations formation
- **Acid-base equilibria**
- **Complex formation**

48

CC BY-SA Leszek Niedzicki

Acids and bases dissociation in water

- Acids dissociate into the proton (in H_3O^+ form, as proton immediately combines with water molecule) and the acid radical (anion). If acid has more than one hydrogen atoms that can dissociate as protons, then it happens in stages (protons dissociate one at a stage, with each stage having its own equilibrium).
- Bases dissociate into the hydroxide anion (OH^-) and the cation (usually metal cation).
  (similarly to acids, if base has more than one OH- group, then they dissociate in stages - one group at a time)

49

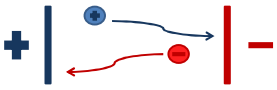
Electrolyte-electrode

- Phases on interface of which electrolyte transfer electrons (by oxidizing/reducing ions/into ions) are called **electrodes** (usually they are solid).
- Conducting electricity is a result of ion movement – electron transfer on the **electrode-electrolyte** interphase, ionic movement in electrolyte to the other electrode and a second electron transfer at the other electrode-electrolyte interphase.

50

Electric field

- Ions in electrolyte can move (if not stirred on purpose and without any current passed through it) due to self-diffusion or convection only.
- In an electric field this movement has an established direction: cations (+) are moving towards negative electrode (-) and anions (-) are moving towards positive electrode (+). This phenomenon is called **migration**.



51

Migration

Movement in the electric field theoretically should be an uniformly accelerated motion, although acceleration is limited at one point due to friction force (it exists at the molecular level as well). It is that force that defines maximum ionic velocity (in the given solvent, at the given electric potential, at the given temperature), that is called **ionic mobility** (**u**), and it is measured in $m^2/(s \cdot V)$ [(m/s)/(V/m)].

52

Ionic mobility

- Mobility of an ion translates into maximum velocity of an ion, that defines maximum current that can flow through the given electrolyte.
- For the electrolyte solution such as NaCl (that fully dissociates, anions to cations ratio is 1:1 and both are singly charged ions) current is defined as:

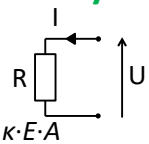
$$I = e \cdot A \cdot E \cdot (N_+ \cdot u_+ + N_- \cdot u_-)$$

$$[A \cdot s \cdot m^2 \cdot V \cdot m^{-1} \cdot m^{-3} \cdot m^2 \cdot s^{-1} \cdot V^{-1} = A \cdot m^{2-1-3+2} = A]$$

current = elementary charge · field cross-section area · · electric field intensity · (number of ions · ionic mobility)
elementary charge is $1.602 \cdot 10^{-19}$ C [C=A·s]

53

Current intensity vs conductivity



- I Ohm's law: $I = U/R$ ($I = E \cdot L/R$)
- II Ohm's law: $R = L/(\kappa \cdot A)$

If R in 1. is substituted with 2. then: $I = \kappa \cdot E \cdot A$
where κ is **electrolyte conductivity**.
If one substitutes I in the previous equation:
$I = e \cdot A \cdot E \cdot (N_+ \cdot u_+ + N_- \cdot u_-)$ with one above, then:
$\kappa = e \cdot (N_+ u_+ + N_- u_-)$ (e – constant – elementary charge)
Conclusion: ionic conductivity depends on mobility and number of ions.

54

CC BY-SA Leszek Niedzicki

Conductivity

- **Specific conductivity** is a parameter of the material (*e.g.* metal, solution), measured in Siemens per centimeter (S/cm). Conductivity is a parameter of a specific sample with a fixed dimensions. Conductivity is the inverse of resistivity.
- In order to convert measured conductivity (or resistance) of a sample to specific conductivity of the material, one have to take into account dimensions of a conductivity cell that are calculated in the form of so-called **cell constant**. Due to the complicated (at least, usually) shape of the conductivity cell, cell constant is calibrated with the solution of a known conductivity, such as KCl solution with 0.01 M concentration.

55

Conductivity

Calculate specific conductivity of the X solution, where resistance is R = 50 Ohm and the cell constant is

k = 0.5 cm^{-1}:

$\kappa = k/R = 0.5 / 50 = 0.01\ S \cdot cm^{-1} = 10\ mS \cdot cm^{-1}$

[Ohm = S^{-1}]

Calculate specific conductivity of the Y solutions, where resistance is R = 20 Ohm and the cell constant is

k = 0.1 cm^{-1}:

$\kappa = k/R = 0.1 / 20 = 0.005\ S \cdot cm^{-1} = 5\ mS \cdot cm^{-1}$

56

Molar conductivity

- Conductivity (and mobility) of an ion per concentration is called **molar conductivity**:

$$\Lambda = \kappa / c$$

$\Lambda = 1000 \cdot \kappa / c$ (1000 is from dm^3 conversion to cm^3)

- It is the highest for the infinitesimal concentration (Λ_0 – **limiting molar conductivity**). When the ion does not have any "obstacles", it is moving the fastest – along with the addition of further ions the mobility relatively drops (and so the molar conductivity, as the concentration is increasing). It is not changing the fact, that the higher concentration, the highest ionic conductivity is (molar conductivity is not decreasing linearly with the concentration).

57

Molar conductivity

- If anions to cations ratio is 1:1 (given that both are singly charged ions) then in the given volume, the number of ions is equal (or number of their charges has to be equal):

$N_+ = N_- = c \cdot N_A$ (concentration · Avogadro number)

number of ions in the dm^3: [dm^{-3} = mol·dm^{-3} · mol^{-1}]

- Faraday constant is equal to a charge in one mole of ions (singly charged):

$F = e \cdot N_A \approx 96500$ C/mol (N_A=6.022·10^{23} mol^{-1} e=1.602·10^{-19}C)

- From the equation $\kappa = e \cdot (N_+ u_+ + N_- u_-)$ one can derive:

$\kappa = e \cdot (c \cdot N_A \cdot u_+ + c \cdot N_A \cdot u_-) = e \cdot c \cdot N_A \cdot (u_+ + u_-)$

$\kappa = F \cdot c \cdot (u_+ + u_-)$

- After substituting above in $\Lambda = \kappa / c$ one gets:

$\Lambda = F \cdot (u_+ + u_-)$

58

Ionic molar conductivity

- As it was shown before, ionic conductivity consists of conductivities of all ions:

$\Lambda = F \cdot u_+ + F \cdot u_-$ $\quad \lambda_i = z_i \cdot F \cdot u_i$ (z – ionic charge)

$\Lambda = \lambda_+ + \lambda_-$

Thanks to that equation one can determine ionic mobility that would not be possible to obtain in any other way. *E.g.* by measuring conductivity of NaCl, KBr and KCl one can determine **molar ionic conductivity** of Cl^-, Br^-, Na^+ and K^+, but also determine without direct measurement the ionic conductivity of NaBr (although only for the given temperature, solvent and concentration; unfortunately, it works properly for the infinitesimal concentrations only).

59

Molar conductivity

Molar conductivity dependence of the concentration for strong electrolytes is linear (for low concentrations) and is described by (empirical) Kohlrausch equation:

$\Lambda = \Lambda_0 - a \cdot c^{1/2}$

where a is an experimental constant determines for the given electrolyte in a given temperature;
c is a concentration;
Λ_0 is a limiting molar conductivity.

Molar conductivity dependence of the concentration for strong electrolytes is non-linear (including electrolytes for new battery generations).

60

CC BY-SA Leszek Niedzicki

Molar conductivity

In reality, the molar conductivity is described by very complicated and multi-parameter equations, usually determined experimentally due to complexity of effects connected to the conductivity phenomenon. They are based on Debye-Hückel theory, that was the first to take ionic solvation layer into consideration. Conductivity calculations also require to take into account that ion in the electric field is moving against the solvent. Solvent molecules that do not solvate ions and surround the solvated ion are not moving in the electric field.

Molar conductivity

Moreover, there are other ions in the vicinity of the ion migrating towards electrode. They are moving in the same or opposite direction. According to Debye-Huckel theory, other ions have share in "slowing down" the ion. That effect can be calculated if other parameters are known, such as the average sphere radius in which the given ion is capable of attracting its counter-ions (so-called ionic atmosphere).

Molar conductivity

Indirect result of existence of such a sphere of interactions is ionic strength and A parameter (for activity coefficient equation). Of course, radius of that sphere is dependent of concentration. Apart from that, equations use also viscosity and solvent dielectric constant.

Equation that best reflects conductivity dependence of the concentration, that has its base in theory (not empirical one) and is not overly complex is the Fuoss-Onsager equation.

Molar conductivity

Fuoss-Onsager equation:

$$\Lambda = \Lambda_0 - S \cdot c^{1/2} + E \cdot c \cdot \log(c) + J \cdot c$$

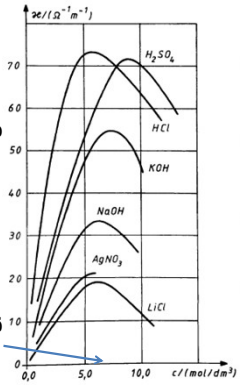
where: Λ – molar conductivity;

Λ_0 – limiting molar conductivity;

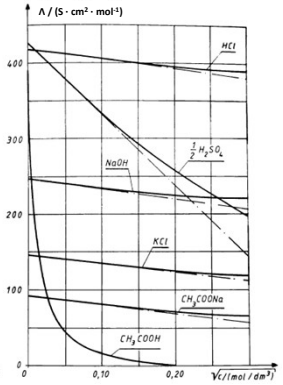
S, E and J – constant derived from dielectric constant, viscosity, temperature, limiting molar conductivity, ionic radii, *etc*.

Conductivity vs ionic conductivity

Very concentrated solutions, of 1 kg/liter order of magnitude!



W. Ufnalski, Elementy elektrochemii, OWPW 1996



W. Ufnalski, Elementy elektrochemii, OWPW 1996

Ionic associations

To explain, why there are drops in conductivity and then (for weak electrolytes) slight increases with the concentration growth, theory of association formation has been formed, so-called Fuoss-Kraus formalism. In modern times, a model have been made, that uses that theory and enables possibility of calculating/estimating fractions of ions, ionic pairs and triplets in the electrolyte (in % of all ionic forms).

CC BY-SA Leszek Niedzicki

Fuoss-Kraus formalism

Normally, dissociation is (C – cation, A – anion):

$CA \leftrightarrow C^+ + A^-$

Formally, in order for triplets to form, they need more electrolyte molecules. Formal notation of such process can look in the following way:

$CA \leftrightarrow 1/3C_2A^+ + 1/3CA_2^-$ (hypothetical electrolyte)

Constants of those equilibria are K_I and K_T, respectively.
(I – "free" ions, P – ionic pairs, T – triplets)

Fuoss-Kraus formalism

$K_I = \frac{1-\alpha_I}{\alpha_I^2 c}$ $\qquad K_T = \frac{\alpha_T}{\alpha_I c(1-\alpha_I-3\alpha_T)}$

After transformation it yields:

$\alpha_I = \frac{-1+\sqrt{1+4K_I c}}{2K_I c}$ $\qquad \alpha_T = \frac{K_T \alpha_I (1-\alpha_I) c}{1+3K_T \alpha_I c}$

$\alpha_P = 1 - \alpha_I - 3\alpha_T$

where α is share of the component in question in the sum of all ionic forms.

Overall molar conductivity is:

$\Lambda = \alpha_I \cdot \Lambda_0^I + \alpha_T \cdot \Lambda_0^T$

And for small enough values of α_I i α_T (infinitesimal dilution) this equation can be substituted with equations for α_I and α_T which gives:

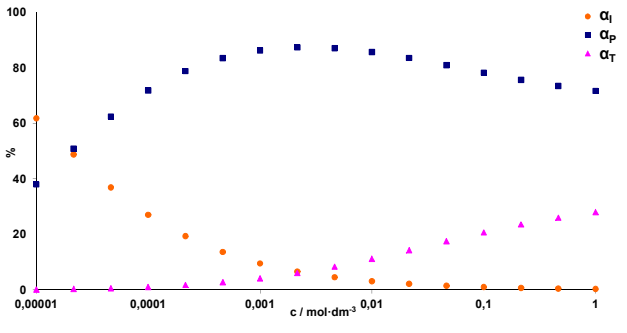
Fuoss-Kraus formalism

$$\Lambda\sqrt{c} = \frac{\Lambda_0^I}{\sqrt{K_I}} + \frac{\Lambda_0^T K_T c}{\sqrt{K_I}}$$

This equation for very low concentrations should give a straight line in $\Lambda c^{1/2} = f(c)$ coordinates (y = ax + b, thus $\Lambda\sqrt{c} = \frac{\Lambda_0^I}{\sqrt{K_I}} + \frac{\Lambda_0^T K_T c}{\sqrt{K_I}}$)

From the linear regression one can obtain a and b coefficients. Limiting molar conductivity can be obtained for instance from Fuoss-Onsager equation. Λ_0^T is 2/3 of the Λ_0^I value. Thus, one can calculate K_I and K_T, from which one can yield fractions of ions, ionic pairs and triplets (α_I, α_P and α_T).

Ionic associations

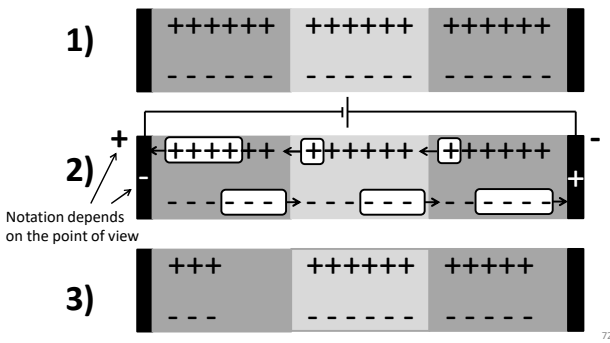


Transference numbers

- In real conductivity measurements (unlike the infinitesimal concentration considerations) it is impossible to determine ions' shares in conductivity (different ions have a different conductivity-concentration relations). In order to determine the (molar) conductivity of ion i, one have to measure the **transference number** (t_i) of that ion.
- If the charge Q was transferred through the electrolyte, then transference number of ion i is: $t_i = Q_i/Q$, so the share of the charge transferred by the given ion in the whole charge transferred is: $t_+ = \lambda_+/\Lambda$

Transference numbers

- If we have only + and - ions, *e.g.* $\boldsymbol{t_+ = 0.25}$ and $\boldsymbol{t_- = 0.75}$



CC BY-SA Leszek Niedzicki

Transference numbers

The above scheme is used to determine transference numbers with Hittorf method. In this method one use cell composed of three glass bulbs with valves between them, that can shut off bulbs from each other and separate them. Upon transferring known charge through the electrolyte bulbs are closed, separated and weighed. Difference in mass can be used to estimate transference number.

Unfortunately, Hittorf method and its modifications are not sufficient to investigate electrolyte for Li-ion cells, because working electrode required for it is lithium that is susceptible to moisture and air.

73

Transference numbers

Bruce-Vincent method bases on transference number definition: $t_i = Q_i/Q$, where $Q = I \cdot T$ (current·time), so in the given moment $t_i = I_i/I$, assuming, that one can measure current for only one ion at the time.

Such situation can take place, if sample is polarized long enough. If electrodes are not accepting and are not producing one of the ions (are blocking against anions), but if they are accepting/producing another ion (reversible against lithium cation), then upon formation of stable concentration gradient the whole current flowing through the cell is the result of lithium cation movement. Transference number can be calculated then from the steady-state current to initial current ratio: $t_+ = I_s/I_0$

74

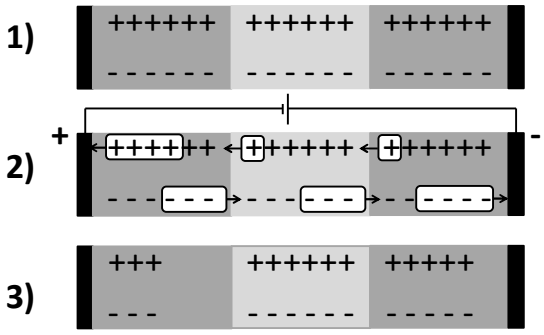
Transference numbers

It was observed, that during the operation of such tested cell electrodes (especially such reactive like metallic lithium) change their properties (particularly resistance at their surface, which changes current). Thus, in order to calculate real transference number, it is necessary to take into account changes in current that result from electrode resistance changes, apart from anion movement fade. Thus, the corrected formula is: $t_+ = \frac{I_s(\Delta V - R_0 I_0)}{I_0(\Delta V - R_S I_S)}$

where: I – current; R – interphase layer resistance; ΔV – polarization voltage; s – steady-state (after polarization); 0 – initial (before polarization).

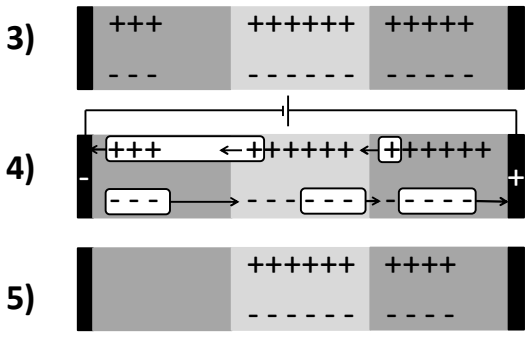
75

Transference numbers



76

Transference numbers



77

Diffusion

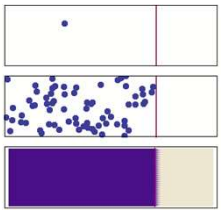
- As shown, in certain moment one side can ran short of ions. Even if ions are appearing on one side (electrode „produces" new ones), then it still can come to that. What happens then?
- Current intensity drops.
- Both types of ion at the electrode are in shortage. On the other side of the cell new ions are still produced. Concentration will be willing to compensate. Thus, concentration gradient will form.
- When voltage increase between electrodes is not causing further current increase, then it means the limiting diffusion current has been achieved. It has a lot of consequences and applications.

78

CC BY-SA Leszek Niedzicki

Diffusion

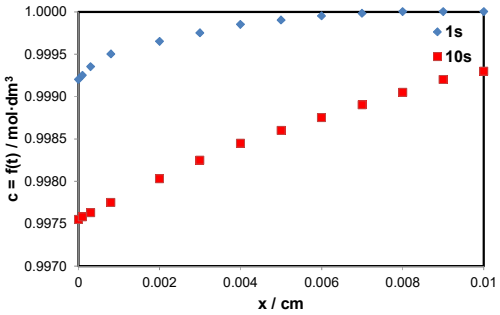
- Diffusion is the phenomenon of particles spreading in the given phase until they achieve uniform distribution (concentration) in the whole available volume of the phase.
- Diffusion is driven by the difference of concentration of the given particle type – the higher difference, the faster diffusion (result of entropy laws).



79

Diffusion

Electrolyte concentration plot change over time due to diffusion near the working electrode interphase:



80

Viscosity

- As mobility is inversely proportional to the viscosity, so is the conductivity (molar as well).
- Viscosity is inversely related to temperature (when temperature increases, viscosity drops). Conductivity is directly proportional to temperature (conductivity increases with temperature).

81

Oxidation state

- Oxidation state is a charge on atom in a compound if assumed, that all bonds made by this atom are ionic.
- It is just a formal description of atom. However, it shows a character of this atom bonds, even if the compound is covalent in character. It also helps with understanding of the nature of the given compound reactions (if they are connected with electron exchange or ligand exchange as well).

82

Oxidation state

In sulfuric acid (H_2SO_4) sulfur is described as possessing +6 „charge". Individually, such cation could not exist. However, theoretically sulfur has such charge, as hydrogen atom has single positive charge (+1; H^+) and oxygen atom has double negative charge (-2; O^{2-}). If one counts charges in the sulfuric acid, it is $2\cdot(+1) + 4\cdot(-2) = -6$. As compound has to be neutral, then sulfur has (by convention) +6 charge.

Oxygen and hydrogen have also conventional charge (oxidation state) as they cannot exist individually. For instance, in water they exist as OH^- and H_3O^+.

83

Oxidation state

- Hydrogen can give away only one electron and it also always does (thus, it has almost always +1 charge).
- Oxygen usually accepts two electrons (-2 charge), so the oxidation state actually corresponds to the reality from the electronic structure point of view.

84

CC BY-SA Leszek Niedzicki

Oxidation state

- Exception to the above rule exist. For instance, if hydrogen meets element more eager to give away its electron, *e.g.* lithium, sodium, magnesium (I and II group in periodic table). Then this other element is giving away the electron and hydrogen is accepting it (and has -1 oxidation state), in compounds such as LiH or MgH_2.
- The only element that has more affinity towards electrons than oxygen is fluorine. In oxygen-fluorine compounds oxygen atoms have oxidation state at +2 or +1 value (*e.g.* OF_2 or O_2F_2).

85

Reaction types

In reality the particle can be the subject to only three types of reactions. All more complex reactions are in fact a series combination of those reactions (together, only 1 and 2 can happen in the same time):

1. Ligand detachment or attachment from/to central atom (of particle);
2. Electron(s) detachment or attachment from/to central atom (of particle);
3. Multi-core particle division into smaller fragments or formation of multi-core particle from the number of single-core particles (in multiple steps).

86

Half-reactions

- Oxidation-reduction process can be treated as a pair of two individual processes – oxidation and reduction (especially when they are mechanically separated).
  Due to that, redox reactions are often noted as two reactions (so-called half-reactions). Then they are balanced for number of exchanged electrons and in that way is stoichiometry of the process can be determined. *E.g.*:

$Na_{(s)} \rightarrow Na^+ + e^-$ /·2 (reductant – sodium – oxidizes itself)

$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-$ /·1 (oxidant – chlorine – reduces itself)

$2Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)}$

87

Redox reactions

- Reactions between metals are typical redox reactions:

  $2Fe^{3+}_{(aq)} + Sn^{2+}_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + Sn^{4+}_{(aq)}$

  $Fe^{3+} + e^- \rightarrow Fe^{2+}$

  $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

- $Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$

Of course, ions are not present by themselves in the vacuum. The real reaction is (taking ions from the example) for instance:

$CuSO_{4(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + ZnSO_{4(aq)}$

88

Red-ac and ox-bas reactions (mixed)

- In reality, a lot of reactions are connected reduction-oxidation and acid-base reactions. They consist in synchronous giving away ligand and accepting electron (ox-bas) or synchronous accepting ligand and giving away electron (red-ac).
- Sodium sulfate synthesis can be an example of such reaction:

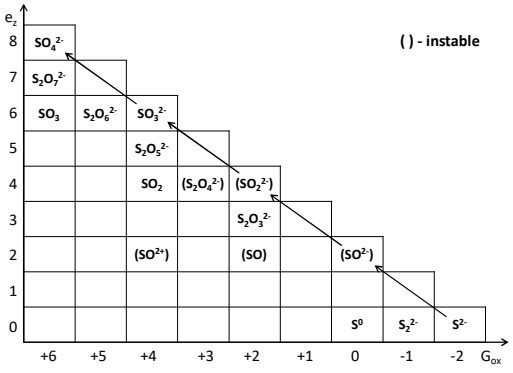
$Na_2S + 2O_2 \xrightarrow{\Delta T} Na_2SO_4$ four stages, including:

I: $S^{2-} \rightarrow S + 2e^- / O_2 + 4e^- \rightarrow 2O^{2-} / S + O^{2-} \rightarrow SO^{2-}$

IV: $SO_3^{2-} \rightarrow SO_3 + 2e^- / O_2 + 4e^- \rightarrow 2O^{2-} / SO_3 + O^{2-} \rightarrow SO_4^{2-}$

89

Red-ac and ox-bas reactions



90

CC BY-SA Leszek Niedzicki

Red-ac and ox-bas reactions

Reactions occurring in lead-acid battery (in this case $H^+_{(aq)}$ notation is equivalent to „H_3O^+", and there is no need to balance water molecules in the chemical equation):

$Pb_{(s)} + H_2SO_{4(aq)} \rightarrow PbSO_{4(s)} + 2H^+_{(aq)} + 2e^-$ ($Pb \rightarrow Pb^{2+} + 2e^-$)

$PbO_{2(s)} + H_2SO_{4(aq)} + 2H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O$

($Pb^{4+} + 2e^- \rightarrow Pb^{2+}$) ($2O^{2-} + 4H^+ \rightarrow 2H_2O$)

Or thermite burning (*e.g.* $Fe_2O_3 + Al \rightarrow Fe + Al_2O_3$)

91

Acids, bases, oxidants, reductant

- Acid can accept the oxide anion (O^{2-}, in water solutions usually in OH^- form) or donate proton (H^+, in water solutions in H_3O^+ form).
- Base can donate oxide anion or accept proton.
- Oxidant oxidates other atoms (it reduces itself). Oxidant accepts electrons (take away from other atoms).
- Reductant reduces other atoms (it oxidizes itself). Reductant donates its electrons to other atoms.

92

Why ions are moving towards electrodes?

The ion movement toward electrodes (and why do electrodes have charges at all) can have two reasons:

- Potential with the outer source applied to electrodes;
- Electrodes can be formed of different materials (of different electrochemical potential). If on every electrode immersed in the electrolyte spontaneous reactions happen, then at every electrode-electrolyte boundary potentials are formed (non-measureable parameter). Their difference is called the **electromotive force** (**EMF**) (it can be measured). EMF is determining current that is possible to obtain from the given electrode set (system).

93

Electromotive force

Electrons between electrodes move through the outer circuit (if they are connected through it). At one electrode oxidation can occur (thus electron can be sent to the outer circuit) and reduction can occur at the other electrode (and electron is received from the outer circuit). All those processes are components of the redox reaction, although its half-reactions are separated (without requirement of contact between reagents, as it was explained during the inorganic chemistry course).

Electrode, at which the oxidation occurs is called the **anode**.

Electrode, at which reduction occurs is called the **cathode**.

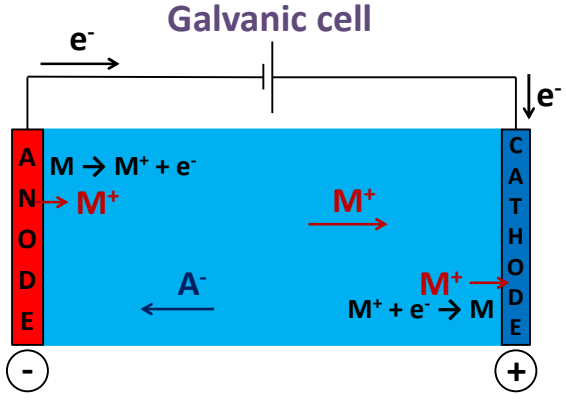
94

Galvanic cell

- Arrangement of anode, electrolyte and cathode is called the **galvanic cell**.
- Current (electrons) flowing through the circuit between electrodes can power the receiver (engine, bulb, *etc.*).
- Arrangement of one electrode and electrolyte surrounding it is called the **half-cell**.
- Half-cells can share one electrolyte or can be connected through the electrolytic bridge (ionic conductor with ion selective membranes that prevent electrolytes of half-cells to mix with each other).

95

Galvanic cell



96

CC BY-SA Leszek Niedzicki

Interphase

- The boundary between phases is very important – it is the contact of electrolyte and electrode where all processes connected to electron transfer occur. Only at the boundary ions can give away or receive electron. Electrode can conduct electrons and electrons only. Electrolyte can conduct ions exclusively.

97

Electrochemical series

- Electrodes (and specific reactions going at them) individually do not possess any potential. It is only after connecting them to any other electrode (redox reaction) one can measure their relative potentials.
- Electrode potentials relative to each other are measured at the standard conditions (25°C, 1013hPa).
- Measured redox reactions are positioned in so-called **electrochemical series**.
- **Standard hydrogen electrode** (SHE) works as a reference point in the electrochemical series ($H_3O^+ + e^- \rightarrow \frac{1}{2}H_2 + H_2O$; half-cell notation: $Pt,H_2|H^+$).
- Above standard potential (of the given half-cell) oxidation occurs (and below it reduction takes place).

98

Electrochemical series

Li^+/Li	-3.045 V	$AgCl/Ag$	+0.222 V
Ca^{2+}/Ca	-2.864 V	$Hg_2Cl_2/2Hg$	+0.268 V
Na^+/Na	-2.711 V	Cu^{2+}/Cu	+0.338 V
Mg^{2+}/Mg	-2.370 V	$I_2/2I^-$	+0.536 V
Al^{3+}/Al	-1.700 V	MnO_4^-/MnO_4^{2-}	+0.558 V
SO_4^{2-}/SO_3^{2-}	-0.932 V	Fe^{3+}/Fe^{2+}	+0.771 V
Zn^{2+}/Zn	-0.763 V	Ag^+/Ag	+0.799 V
Cr^{3+}/Cr	-0.744 V	Pt^{2+}/Pt	+0.963 V
Fe^{2+}/Fe	-0.441 V	Cl_2/Cl^-	+1.358 V
Ni^{2+}/Ni	-0.234 V	Au^{3+}/Au	+1.498 V
Pb^{2+}/Pb	-0.126 V	MnO_4^-/Mn^{2+}	+1.531 V
H_3O^+/H_2	0.000 V	F_2/F^-	+2.866 V

($SO_4^{2-} + H_2O + 2e^- \rightarrow SO_3^{2-} + 2OH^-$) ($2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O$)

99

Half-cell types

Half-cells are divided according to their construction:

- I type – metal immersed into solution of its highly soluble/dissociated salt, *e.g.* $Pb_{(s)}|Pb^{2+}_{(aq)}$. Metal is acting here as both reagent and electrical conductor for electrons. Reaction:

$$Pb^{2+}_{(aq)} + 2e^- \rightleftharpoons Pb_{(s)}$$

100

Half-cell types

- II type – metal covered with its poorly soluble salt I, whole immersed in the solution of highly soluble salt II that shares the common anion with salt I, *e.g.* $Ag_{(s)}|AgCl_{(s)}|Cl^-_{(aq)}$. Metal here is acting as an electrical conductor and reacts with the anion forming/decomposing poorly soluble salt I, but whole electrode is reversible against chlorine. Reaction:

$$AgCl_{(s)} + e^- \rightleftharpoons Ag_{(s)} + Cl^-_{(aq)}$$

101

Half-cell types

- III type – metal covered with its poorly soluble salt I, whole is covered with poorly soluble salt II that share the common anion with salt I, whole electrode is immersed in the solution of highly soluble salt III that shares the common cation with salt II, *e.g.* $Pb_{(s)}|PbC_2O_{4(s)}|CaC_2O_{4(s)}|Ca^{2+}_{(aq)}$. Metal and anion of salt II react forming (decomposing) poorly soluble salt I. Reaction:

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

102

CC BY-SA Leszek Niedzicki

Half-cell types

- Redox half-cells – noble metal not taking part in the reaction, its presence required for electron conductivity only, immersed in reagent solution, that can change its oxidation state, *e.g.* $Pt_{(s)}|MnO_4^-{}_{(aq)},Mn^{2+}{}_{(aq)}$
- Gas half-cell is a subtype of redox half-cells. Instead of solution, electrode is rinsed with gas taking part in electrode reaction, *e.g.* $Pt_{(s)}|H_{2(g)}|H^+{}_{(aq)}$. Reaction:
  $H_{2(g)} \rightleftarrows 2H^+{}_{(aq)}+2e^-$

103

Electromotive force of the cell

- It is calculated as a difference between half-cells potentials. From the higher potential the lower one is subtracted:
  EMF = E_2-E_1 (thus EMF value is always above 0)
- Apart from the **standard half-cell potentials** (E^0) the final half-cell potential is influenced also by: temperature, reagent concentration, number of electrons exchanged in the single reaction and pressure (if any reagent is gaseous).

104

Half-cell potential

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

T – absolute temperature in kelvins;

z – number of electrons exchanged in a single reaction;

F – Faraday constant; R – gas constant;

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

$C_{ox/red}$ – concentration of the oxidized/reduced form if the form is solid (metal) than $c = 1$, if form is gaseous, than the pressure/p_{atm} is used instead.

ln – natural logarithm, to use decimal one, one has to multiply whole term by 2.303 ($\ln(x) = 2.303 \cdot \log(x)$)

E_0 – standard half-reaction potential.

105

Half-cell potential

- $E = E^0 + R \cdot T/(z \cdot F) \cdot \ln(c_{ox}/c_{red})$ simplifies at the standard conditions (T = 25°C, p = 1atm) to $E = E^0 + 0.0592/z \cdot \log(c_{ox})$
- Thus, for 1M Li^+ solution in the lithium cell ($z = 1$, $c = 1$, $E^0 = -3.04$ V) it is
  $E = -3.04 + 0.0592 \cdot \log(1) = -3.04$ [V]
- Although for 0.01M Li^+ solution it will be:
  $E = -3.04 + 0.0592 \cdot \log(0.01) =$
  $= -3.04 + 0.0592 \cdot (-2) = -3.1582$ [V]

106

Concentration and potential

Electrode potential dependence on the concentration stems from the concentration influence on electrode surroundings.

E.g. when ion reduces to metal at the electrode, low concentration of the ion results in low probability of this reaction occurrence and the high concentration results in high probability of it (the more ions, the higher probability of one of them reaching the electrode).

When metal oxidizes to ions, low concentration of ions results in higher rate of oxidation (high chemical potential due to big concentration difference), and high concentration results in lower rate (if it is already high, the concentration gradient/difference is lower).

107

Overpotential

Reality is much more complex than it is presented in theory connected to the Nernst equation. Each process (chemical or physical) requires energy, thus all secondary processes are also requiring it. That means increase of energetic requirements of the main process.

In case of cells it means higher required EMF in order to run process or diminished effective EMF compared to the theoretical calculations (by additional requirements not included in the theory).

108

CC BY-SA Leszek Niedzicki

Overpotential

- Decrease (increase of the required one) of the potential resulting from the electrolyte concentration change at the electrode due to consumption of its part can be an example of overpotential.
- Diffusion overpotential changes EMF due to the local deviations from electroneutrality.
- Process of the ion building into the electrode (or moving out of it) also requires crossing of the certain energetic threshold, thus it requires some energetic sacrifice to move out of the equilibrium state (local minimum). The harder is for an ion to build into the electrode or the stronger crystalline structure keeps this ion, the higher overpotential is required to run this process.

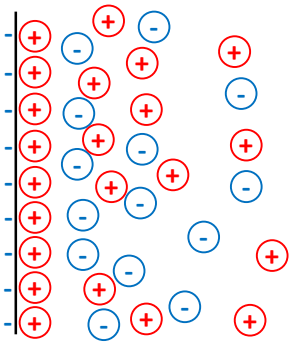
109

Double layer

At the electrode-electrolyte interface (assumed there are no passive layer and electrolyte decomposition products) during the cell operation center of mass of the positive charge and negative charge are separated (starting from the same point during the electroneutrality). It means electrons are on the electrode side and cations from the electrolyte form a layer at the electrode surface. In the same time anions are moving further away, repelled by the negative charge on the electrode. Such formation is called the double layer.

110

Double layer



Double layer or so-called Helmholtz layer is approximated as a planar capacitor in which distance between the plates is equal to that of a distance between atoms – 0.1-nm order.

111

Electrode processes kinetics

Electrode process steps:

- Mass transport toward electrode
- Reaction with an oxidation state change
- Charge transfer
- Phase transitions

Overpotentials:

- Diffusion – transport of ions toward electrode
- Activation – charge transfer
- Reaction – initiation of a chemical process
- of the new phase formation:
  - Crystal – crystalline structure building-in
  - Gas – gas bubbles formation.

112

Electrode processes kinetics

Overpotentials are resistances of each of the process steps and are totalized in an overall overpotential of the whole process.

Polarization curve is an overpotential dependence of a current density.

One can influence this dependence through the minimization of individual overpotentials, like through an intensive stirring (thinner laminar layer, lack of a concentration gradient maintained artificially).

113

Electrochemical series

(standard half-cell potentials vs SHE)

Li^+/Li	-3.045 V	$AgCl/Ag$	+0.222 V
Ca^{2+}/Ca	-2.864 V	$Hg_2Cl_2/2Hg$	+0.268 V
Na^+/Na	-2.711 V	Cu^{2+}/Cu	+0.338 V
Mg^{2+}/Mg	-2.370 V	$I_2/2I^-$	+0.536 V
Al^{3+}/Al	-1.700 V	MnO_4^-/MnO_4^{2-}	+0.558 V
SO_4^{2-}/SO_3^{2-}	-0.932 V	Fe^{3+}/Fe^{2+}	+0.771 V
Zn^{2+}/Zn	-0.763 V	Ag^+/Ag	+0.799 V
Cr^{3+}/Cr	-0.744 V	Pt^{2+}/Pt	+0.963 V
Fe^{2+}/Fe	-0.441 V	Cl_2/Cl^-	+1.358 V
Ni^{2+}/Ni	-0.234 V	Au^{3+}/Au	+1.498 V
Pb^{2+}/Pb	-0.126 V	MnO_4^-/Mn^{2+}	+1.531 V
H^+/H_2	0.000 V	F_2/F^-	+2.866 V

114

CC BY-SA Leszek Niedzicki

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.

115

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.

116

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).

117

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…

118

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.

119

Primary cells

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

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

Half-reactions:

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

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

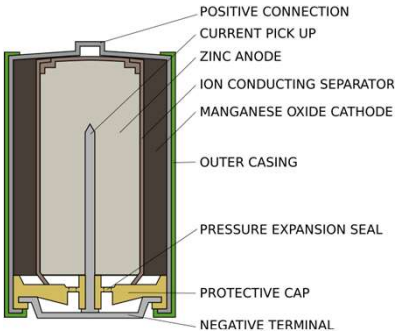
Overall reaction:

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

120

CC BY-SA Leszek Niedzicki

Primary cells



121

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).

122

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.*).

123

Rechargeable cells

Commonly known lead-acid battery is an example of the rechargeable cell: $Pb|H_2SO_{4(aq)}|PbO_2,Pb$

Half-reactions:

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

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

Overall reaction:

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

124

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.

125

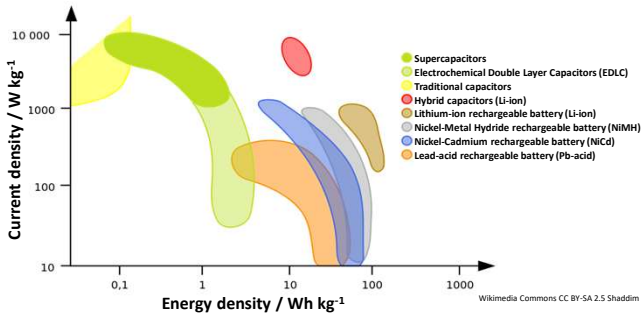
Functional additives/modifications

- 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.*).

126

CC BY-SA Leszek Niedzicki

Galvanic cells and supercapacitors



127

Cell capacity

m = M·I·t/(F·z), where F = 96485 A*s/mol,
m - mass / g, M – molecular mass / g/mol,
I – current / A, t – time / s, z – no. of electrons,

- Calculate how much of the lithium is required in Li-ion 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 129.6 Wh capacity.

128