Batteries
ACME Faculty, EHVE course
B.Sc. Studies, III year, V semester
Leszek Niedzicki, PhD, DSc, Eng.

Organizational matters

- **30 hours lecture**
- **Two tests - in the eight and the last week**
- **Make-up exam (if necessary) during exam session**
- **Lecturer: Leszek Niedzicki, PhD, DSc, Eng.**

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www: **lniedzicki.ch.pw.edu.pl (lectures/pdf)**
consultations: **MS Teams + office hours on website**

Plan of the lecture

1. Rechargeable cells review. Lead-acid batteries - types, construction, principles of work.
2. Nickel-hydride and nickel-cadmium cells. Construction, materials for components, environmental hazards.
3. High-temperature batteries.
4. Anodes for lithium-ion cells - parameters, materials, manufacturing, modifications. Intercalation phenomenon. Nanometric structures.
5. Cathodes for lithium-ion cells - polymeric, oxide, silicate, phosphate materials - parameters, manufacturing methods, modifications. Fundamentals of ions building into crystal structure.
6. Lithium salts for lithium-ion cells' electrolytes. Chemical, electrochemical and thermal properties, toxicity, recyclability.
7. Liquid electrolytes for lithium-ion cells. Choosing proper solvents or solvent mixtures for the cell application. Economy of manufacturing vs electrolyte parameters. Electrolyte stability and impurities. Separators - their properties and modifications.
8. Polyelectrolytes, gel, polymer, solid and solid polymer electrolytes in lithium-ion cells - manufacturing/synthesis and parameters. Thin-film cells.
9. Ionic liquids in lithium-ion cells. Modifications of ionic liquids, material modification possibilities with ionic liquids.
10. Modifications of electrolytes. Functional additives changing properties or increasing parameters.
11. Materials selection and parameters optimization for lithium-ion cell application. Maximizing parameters for specialized applications.
12. Lithium-ion cell and battery manufacturing in small and industrial scale. Components of the cell that are necessary but not taking part in energy storage. Construction types. Methods of assembly. Casings and protections/safeguards. Design and technological issues in cell manufacturing.
13. Batteries' future. Lithium-air and zinc-air rechargeable batteries. Sodium-ion batteries and beyond.
14. Current-voltage characteristics. Cycling, cell's wear and work regime. Cell diagnostics. Damage and risks of using lithium-ion batteries. Types of protections on chemistry and electronics level.
15. Recycling of batteries. Abundance of materials and other limitations.

Books

The following materials are recommended but NOT compulsory to have. Any books (including these materials) that complement knowledge from lectures, repeat topics, get another point of view on theories are welcome. To pass the final test however, mastery of the lectures content will be both necessary and sufficient.

- G.A. Nazri, G. Pistoia – „*Lithium Batteries*"
- M. Winter, Chem. Rev. 104 (2004) 4245.
- M.S. Whittingham, Chem. Rev. 104 (2004) 4271.
- K. Xu, Chem. Rev. 114 (2014) 11504.
- W. Wieczorek, J. Płocharski (eds.), *Electrolytes for Lithium-Ion and Post-Lithium Batteries*, particularly Ch. 1: L. Niedzicki, M. Kasprzyk, *New strategies in designing salts and solutions for new generation of electrolytes*

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Accumulators review

Measurement units

Voltage	– in V (volts)
Current	– in A (amperes)
Power	– in W (watts)
Energy	– in J (joules), commonly in Wh (= 3600 J)
Energy density	– in Wh/kg or Wh/dm^3
Power density	– in W/kg or W/dm^3
Current density	– in A/cm^2, sometimes by dividing power density by voltage
Life	– in years or number of charge-discharge cycles

Energy storage

Form the biggest to the smallest application scale:

- Pumped storage hydroelectric power station (99%)
- Thermal (molten salts or mineral oils)
- Fuel for fuel cells
- Galvanic cells (rechargeable batteries)
- Supercapacitors (EDLC, hybrid)
- Flow Cells
- Flywheels
- Compressed Air (CAES), or other gases

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Pumped storage hydroelectric power station

- Biggest in Poland:

(only the big ones are making 1.8 GW which covers 5% of country needs):
Żarnowiec 716 MW, Żar 500 MW (+Porąbka 12 MW),
Solina 200 MW (+Myczkowice 8.3 MW), Żydowo 156 MW,
Niedzica 92.7 MW (+3 smaller: 6.6 MW), Dychów 91.3 MW.

- Biggest in the world:

Bath County 3003 MW (USA),
Huìzhōu 2448 MW (China),
Guǎngdōng 2400 MW (China),
Okutataragi 1932 MW (Japan),
Ludington 1872 MW (USA),
Tiānhuāngpíng 1836 MW (China),
Grand'Maison 1800 MW (France)

- Stores 0.1-100 GWh.

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Thermal

Tanks with molten salt (usually mixture of KNO_3 and $NaNO_3$) or with mineral oil (of low volatility) kept at temperatures over 300°C, so it won't solidify upon cooling in heat exchangers (and their viscosity not change drastically). It works as a heat accumulator for heating up the medium with lower boiling point (*e.g.* water) and evaporate it so it would drive a turbine (same type as in regular thermal power station). Typical installations can run the plant at full power for 5-16 hours (to run during cloudy weather and/or night). Such ES are usually built at solar thermal (heliothermic) power plants. Stores 100-1000 MWh.

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Galvanic cells

All chemical energy sources, in which electrons flow through the external circuit occurs due to oxidation-reduction reactions. Contrary to fuel cells and flow cells one cannot "add" capacity during operation and they have closed structure. There are many types of galvanic cells, but the basic division is on rechargeable and non-rechargeable.
Capacity of non-rechargeable ones usually do not exceed few Wh. Sets of rechargeable cells for grid storage purpose have up to 80 MWh.

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Fuel for fuel cells

Any substance that can be produced with electricity and then can be used as a fuel for any fuel cell (thus it can be sustainable). Hydrogen is the most common fuel (preferably as an electrolysis product made with fuel cell running backwards powered with renewable energy; usually product of natural gas reforming – then it is not considered an accumulator). In theory, for hydrogen-based fuel cells it can be any substance containing hydrogen like methane, methanol, ethanol, acetaldehyde, ammonia, borates (hydroborates), syngas, *etc.*
There is a big variety of non-hydrogen fuel cells, however most of them are only prototypes or for test purposes. The same substances could be burned for energy in thermal power stations, but fuel cells are much more efficient.

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Flow cells

Emerging for the last few years (still a lot of installations are test or experimental). Galvanic cells using anolyte and catholyte (anodes and cathodes as suspensions in electrolyte) that react through a special ion-selective membrane (traditional galvanic cell separator analog). No limitations to capacity, as it depends on tanks dimensions. Current density depends on membrane's surface. Their disadvantages are number of pneumatic parts (lower reliability) and limited components availability (in case of the most common technology – vanadium). Their advantage is easy upscaling of capacity (not the power, though) non-flammability, long cycle life (over few thousand cycles after solving membranes life and agglomerization of suspensions issues). Scale >1 MWh. Few installations with >10MWh capacity, commercial production up to ~200 kWh.

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Supercapacitors

Capacitors are devices that store energy in a form of electrostatic charge on the plates separated by dielectric. In practice, for industrial scale energy is stored in supercapacitors. They store the charge on very developed and expanded structures (for bigger surface) in which electrode double layers act as both dielectric and capacitor plates (thus, EDLC name). Sometimes, this is extended with ions storage as well (hybrid capacitors).
Store up to 1 kWh (10-20 Wh/kg). Main disadvantages are high cost and low energy density. Big advantage is enormous current density.

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Flywheels

Flywheels are big wheels with big weight that spin quickly, thus gaining very big kinetic energy.
Modern flywheels have magnetic bearings (or air bearings) and the flywheels spin in vacuum (no air friction, low energy loss over time). Small flywheels are used in sport and racing cars, big ones are used as UPS in hospitals, subway stations and data centers. Store 1-100 kWh (up to 5 MW in sets). Low energy density and capacity fade without power supply are their main disadvantages. Their advantages are low requirements for environment, no special or expensive materials used for manufacturing, long life and virtually unlimited charge-discharge cycle life.

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Compressed gases

Compressed gas (mostly air, due to the cost of acquisition) is an experimental technology of energy storage (compression up to the point in which they are liquid).
Apart from small plants based on tanks, big scale applications are planned to use abandoned mines, caverns and depleted natural gas deposits.
In reality, only three big scale CAES installations exist in the world (in Germany and in USA). CAES will have storage range of 1 GWh and power of 10-100 MW. CAES has very low efficiency of charge-discharge cycle or high construction costs (heat exchangers are required for higher efficiency).

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Energy storage

Storing energy with chemical processes:

- Supercapacitors – low energy density
- Non-rechargeable cells – waste of resources
- **Rechargeable cells – high energy density and mature technology**
- Fuel cells – gas supply required, may have application with intermittent energy sources
- Flow cells – still in experimental phase

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Energy storage

Apart from grid storage, testing new energy storage technologies usually is taking place in storage systems. Batteries, fuel cells and supercapacitors are tested in loading units and forklifts. These are non-critical systems and in case of capacity fade they just come back to the charging/filling stations more often.

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Accumulators, batteries, cells; glossary

- **Cell** – galvanic cell (consists of two electrodes, electrolytes, separator and can/casing), can be **rechargeable** or **non-rechargeable**.
- **Battery** – battery of cells – few cells (rechargeable or non-rechargeable) in a stack (serial connection) with voltage equal to the sum of cell potentials and capacity of one cell. Commonly (and incorrectly) single non-rechargeable cells are called like that.
- **Accumulator** – rechargeable cell that can accumulate (store) energy.

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Charge and discharge rate measure

As a standard in the industry (although not exactly scientific way) a measure of charging/discharging rate is C.
C is such a current, with which the given cell (regardless of its capacity) will be fully charged (discharged) in an hour.

Thus, 1C means, that current is matched for the charging to take one hour.

2C – half an hour (twice the current, half the time)

5C – 12 minutes (1/5 of an hour)

C/2 – 2 hours; C/3 – 3 hours; C/20 – 20 hours

1C means that both 1 Ah and 100 Ah batteries/cells will be charged in an hour, however in first case it will mean charging with 1 A current and in the second 100 A current.

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Connecting cells

- Serial – voltage of the resulting battery is a multiplicity of a single cell potential, but the battery capacity is equal to that of a single cell (*e.g.* 4 Li-ion cells with 1200 mAh capacity and 3.6 V voltage connected in series will result in the battery with 1200 mAh capacity and 14.4 V voltage);
- Parallel – capacity of the resulting battery is a multiplicity of a single cell capacity, but the battery voltage is equal to that of single cell (*e.g.* 4 Li-ion cells with 1200 mAh capacity and 3.6 V voltage connected in parallel will result in the battery with 4800 mAh capacity and 3.6 V voltage);
- Obviously one can connect cells both in both ways at the same time, serial and parallel (*e.g.* 2x2 Li-ion cells with 1200 mAh capacity and 3.6 V voltage will result in the battery with 2400 mAh capacity and 7.2 V voltage).

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