# DAT460 ENERGY STORAGE

## BATTERIES AND SUPERCAPACITORS

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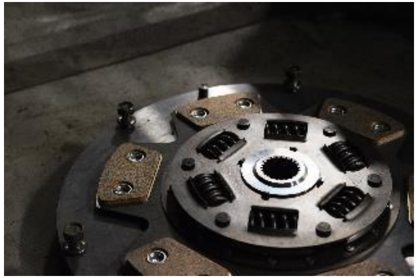
# TEACHING GOALS

- To be able to describe how batteries and supercapacitors work
- To describe what properties limit battery performance
- To identify when the battery performance limits vehicle performance
- To understand the operation of a basic battery model
- To list the most important components of energy storage systems

# ENERGY STORAGE

Dam

Flywheel



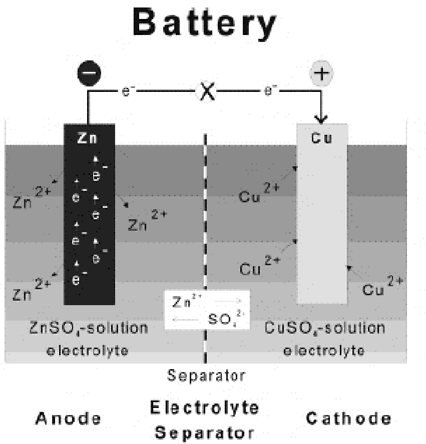
Hydrogen gas

Battery

Capacitor

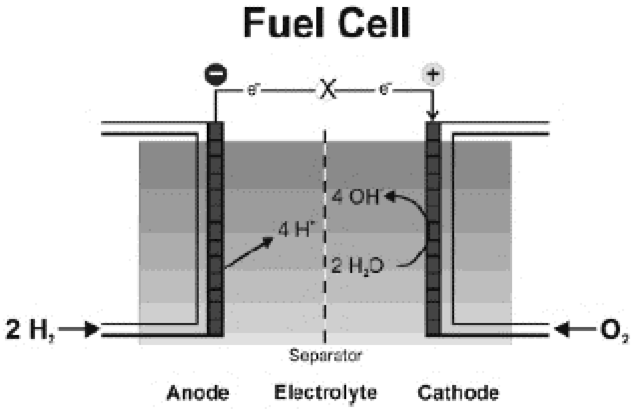
Source: https://www.pexels.com/
https://pixabay.com/

# ELECTROCHEMICAL DEVICES



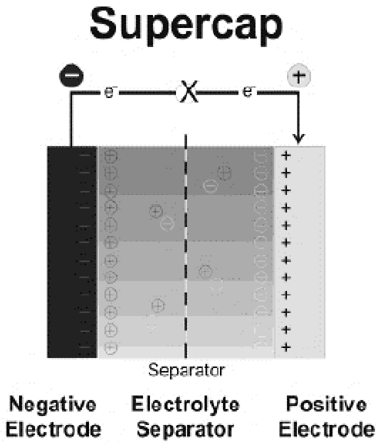

- Redox reactions at the anode and cathode.
- *Closed* system – the materials in the anode and cathode undergo redox processes.

***'Slow'***




- Redox reactions at the anode and cathode.
- *Open* system – the reactants are fed to the electrodes.
- Storage and conversion are separated.

***'Slower'***

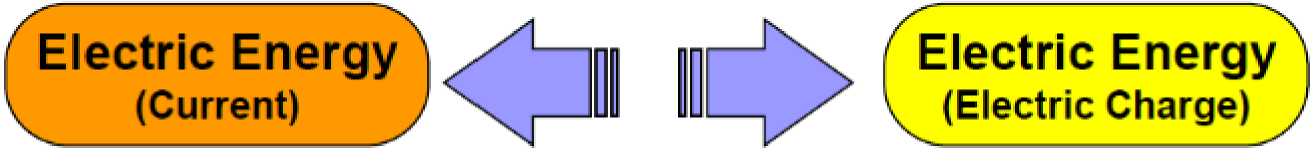



- No redox reactions, ideally.
- *Closed* system – Electrical double layers (EDLs) formed at the electrode/electrolyte interface store energy.
- High surface area needed for the electrodes.

***'Fast'***

Adapted from M. Winter and R.J. Brodd, *Chem. Rev.* 104 (2004) 4245

# SUPERCAPACITOR – ELECTROCHEMICAL CAPACITORS




- No energy conversion
- High efficiency
- Fast charge / discharge possible
- Low specific energy

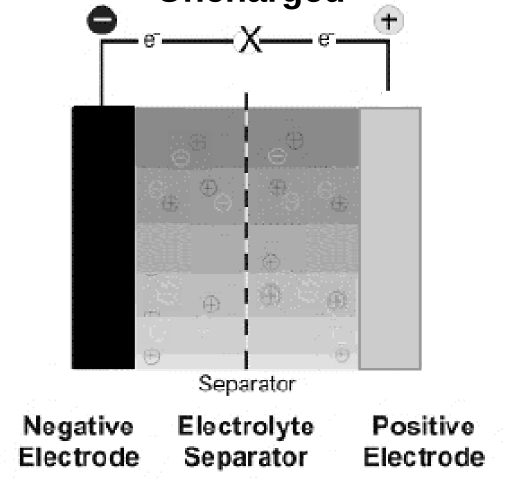
# SUPERCAPACITOR – ELECTROCHEMICAL CAPACITORS

Ions as charge carriers.

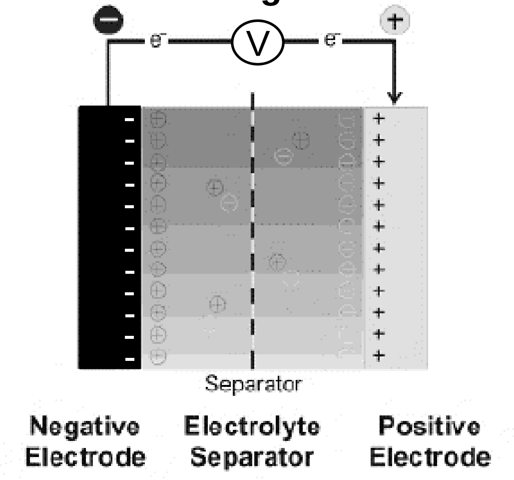
Ion - an atom or molecule with an electric charge due to the gain or loss of one or more electrons.

By applying an external voltage electric double layers are formed by orientation of electrolyte ions at the electrolyte/electrode interface.

**Uncharged**




**Charged**



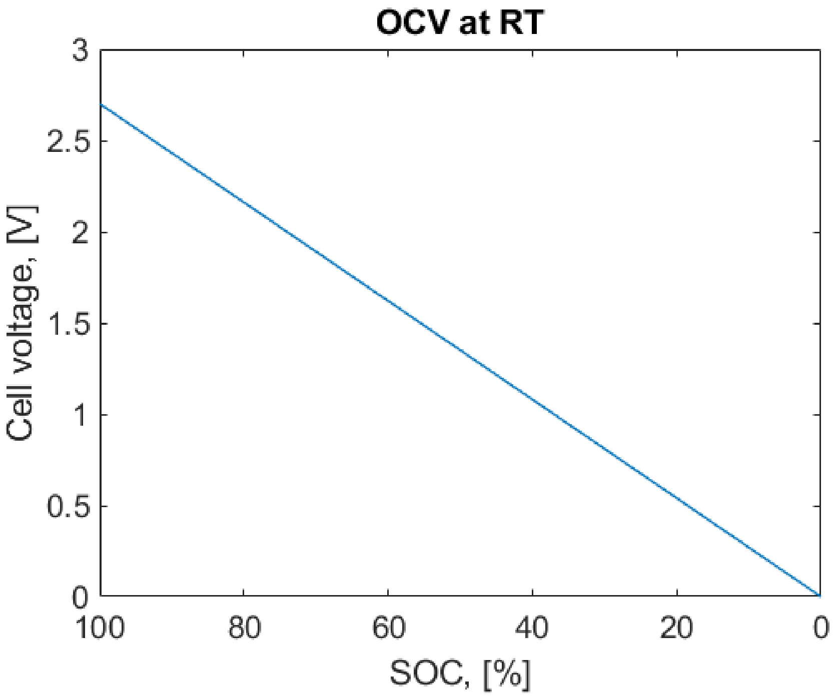
# SUPERCAPACITOR – ELECTROCHEMICAL CAPACITORS

Energy: $W = \frac{CV^2}{2}$

Capacitance: $C = \frac{\epsilon A}{d}$

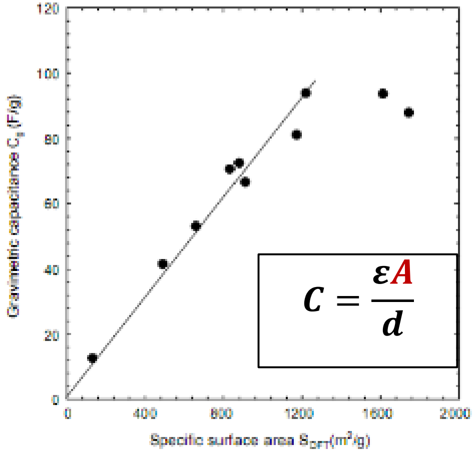
Power: $P = \frac{V^2}{4R}$

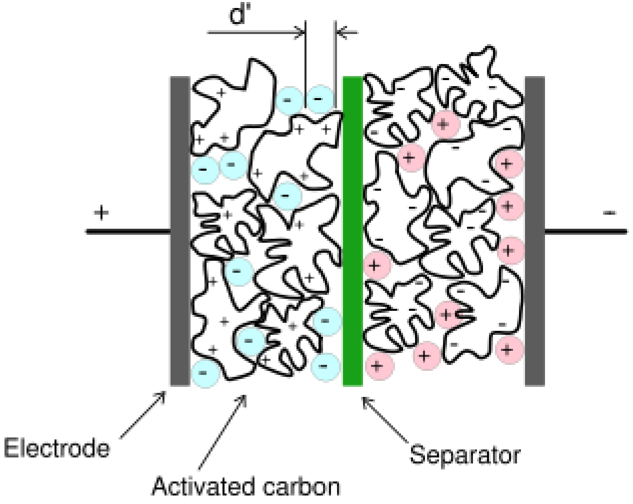
A – electrode area
d – charge separation distance
$\epsilon$ – permittivity (a measure of the polarizability of dielectric materials)
R – load resistance
**OCV** – Open Circuit Voltage, can also be called Open Circuit Potential (OCP). It is the cell voltage at complete rest.
**SOC** – State of charge, the charge level.
**RT** – Room temperature



# SUPERCAPACITOR – ELECTROCHEMICAL CAPACITORS

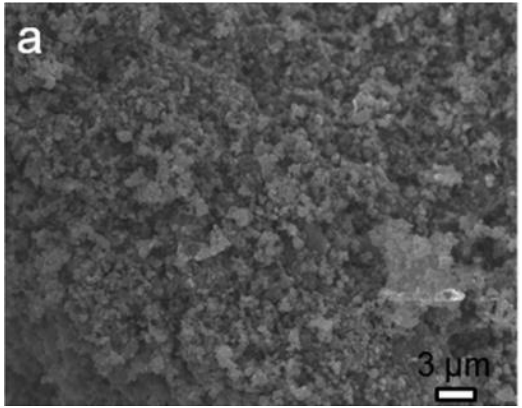
- **Large effective area A:** Electrode materials is most commonly porous carbon materials with high surface area.
- **Small effective distance d:** Molecular interface
- Typical Capacitance: F to kF



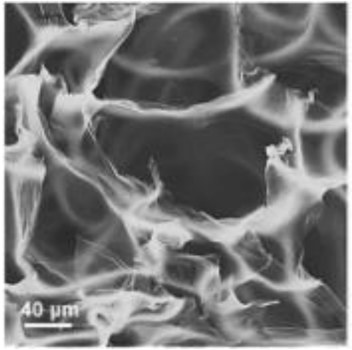
# SUPERCAPACITOR – MATERIALS

Meso-microporous active carbon:
~1000-3000m$^2$/g
~100 F/g



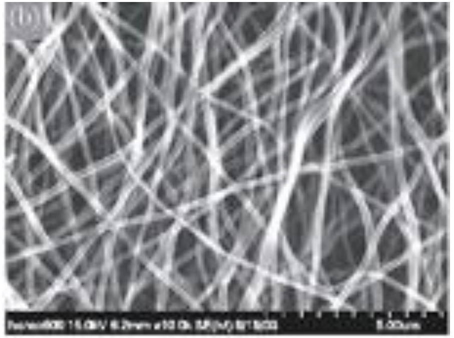

***J. Mater. Chem. A***, 2015,**3**, 15049-15056

Graphene based carbon:
~1000-3600 m$^2$/g
~175 F/g




*Sci Rep* **8,** 1915 (2018) https://doi.org/10.1038/s41598-018-20096-8

Carbon nanofibers:
~1000 m$^2$/g
~100 F/g



C. Kim, K. S. Yang and W. J. Lee, Electrochem. Solid-State Lett. 7 (11), A397 (2004). http://dx.doi.org/10.1149/1.1801631

# SUPERCAPACITOR – PROPERTIES

- Fast charging property, 1-10 s.
- Cycle life: ~1M cycles.
- Operating temperature: -40 to $65^{o}$C.
- Cell voltage: 2.5-2.7 V.
- Self discharge: ~5-60% in a month.
- Capacitance: F to kF

# BATTERIES


# BATTERIES

Store energy in the form of chemical energy.

Primary battery

Chemical energy $\rightarrow$ Electric energy

Secondary battery (rechargeable battery)

Chemical energy $\rightleftharpoons$ Electric energy

Source: https://commons.wikimedia.org/wiki/File:Fruit_battery,_apple,_closeup.jpg

# SPONTANEOUS REACTION

- What happen in the following processes and what are the driving forces?

Source: https://pixabay.com/

# DRIVING FORCE

**Gibbs free energy** - The energy associated with a chemical reaction that can be used to do work.
In a battery, if all the electrochemical energy change is converted into electric energy

$$E_{cell} = -\frac{\Delta G}{nF} = E_{+} - E_{-}$$

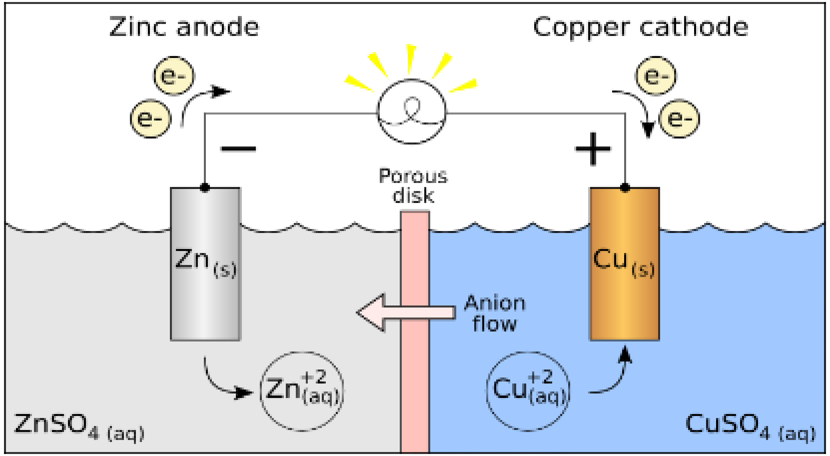
The electrochemical potential difference.

**In a spontaneous process, $\boldsymbol{E_{cell} > 0}$**

$\Delta G$ – Change in Gibbs free energy [J]
$n$ – number of transferred electrons (per mole reactant)
$F$ – Faraday constant, 96485 As/mol

# GALVANIC CELL

A **galvanic cell** is an electrochemical cell that uses spontaneous redox reactions to convert chemical energy to electrical energy.




Anode:
Oxidation – Loss of electrons
$Zn \rightarrow Zn^{2+} + 2e^-$

Cathode:
Reduction – Gain of electrons
$Cu^{2+} + 2e^- \rightarrow Cu$

Cell reaction:
$Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$

Anion - an atom or molecule with a negative electric charge due to the gain of one or more electrons, in this example $SO_4^{2-}$

Source: https://upload.wikimedia.org/wikipedia/commons/2/2f/Galvanic_cell_with_no_cation_flow.png

# REFERENCE ELECTRODE

Half reactions are associated with electrode potentials. The potential can be derived from Gibbs free energy for the reaction (if known).

Electrode potentials, E, are always related to a reference reaction/electrode, which is then 0 V.

| | E [V] | |
|---|---|---|
| **$Li^+ + e^- \rightleftharpoons Li$** | -3.04 | |
| $Na^+ + e^- \rightleftharpoons Na$ | -2.71 | |
| $Mg^{2+} + 2e^- \rightleftharpoons Mg$ | -2.37 | |
| **$Al^{3+} + 3e^- \rightleftharpoons Al$** | -1.66 | |
| **$2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-$** | -0.83 | |
| **$Zn^{2+} + 2e^- \rightleftharpoons Zn$** | -0.76 | |
| $Fe^{2+} + 2e^- \rightleftharpoons Fe$ | -0.45 | |
| $Cd^{2+} + 2e^- \rightleftharpoons Cd$ | -0.40 | |
| $Ni^{2+} + 2e^- \rightleftharpoons Ni$ | -0.26 | |
| **$2H^+ + 2e^- \rightleftharpoons H_2$** | **0.00** | Standard Hydrogen Electrode(SHE) |
| **$Cu^{2+} + 2e^- \rightleftharpoons Cu$** | 0.34 | |
| **$O_2(g) + 2H_2O + 4e^- \rightleftharpoons 4OH^-$** | 0.40 | |
| $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ | 0.77 | |
| $Ag^+ + e^- \rightleftharpoons Ag$ | 0.80 | |
| **$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$** | 1.23 | |
| **$MnO_4^-(aq) + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$** | 1.51 | |

Source: https://en.wikipedia.org/wiki/File:Tallest_buildings_in_the_world.png

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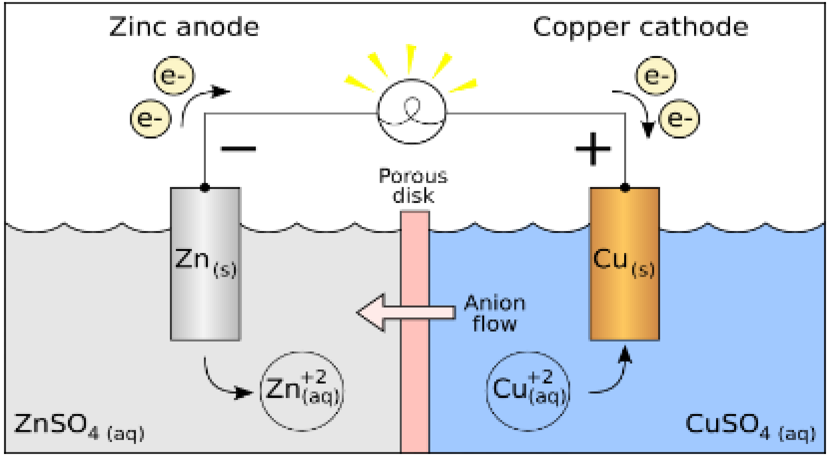


Anode:
Oxidation – Loss of electrons
$Zn \rightarrow Zn^{2+} + 2e^-$
Redox potential: -0.76 V

Cathode:
Reduction – Gain of electrons
$Cu^{2+} + 2e^- \rightarrow Cu$
Redox potential: 0.34 V

$$E_{cell} = E_+ - E_-$$

Source: https://upload.wikimedia.org/wikipedia/commons/2/2f/Galvanic_cell_with_no_cation_flow.png

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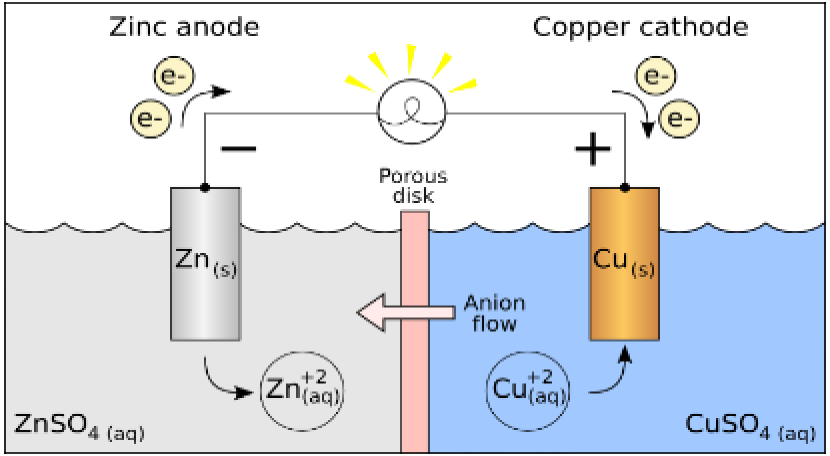



Anode:
Oxidation – Loss of electrons
$Zn \rightarrow Zn^{2+} + 2e^-$
Redox potential: -0.76 V

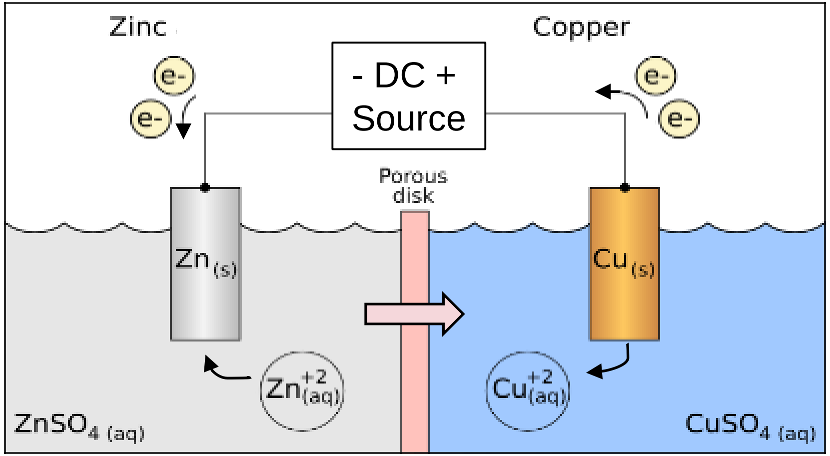
Cathode:
Reduction – Gain of electrons
$Cu^{2+} + 2e^- \rightarrow Cu$
Redox potential: 0.34 V

$E_{cell} = E_+ - E_- = 0.34 - (-0.76) = 1.1$ V

Source: https://upload.wikimedia.org/wikipedia/commons/2/2f/Galvanic_cell_with_no_cation_flow.png

# ELECTROLYTIC CELL

An **electrolytic cell** uses electrical energy to drive a non-spontaneous redox reaction.




Anode:
Oxidation – Loss of electrons
$Cu \rightarrow Cu^{2+} + 2e^-$

Cathode:
Reduction – Gain of electrons
$Zn^{2+} + 2e^- \rightarrow Zn$

Cell reaction:
$Cu + Zn^{2+} \rightarrow Zn + Cu^{2+}$

Source: https://upload.wikimedia.org/wikipedia/commons/2/2f/Galvanic_cell_with_no_cation_flow.png

# GALVANIC CELL / ELECTROLYTIC CELL

- In a galvanic cell, the redox reaction happens spontaneously (battery at discharge).
- In an electrolytic cell, the redox reaction happens nonspontaneous (battery at charge).

- Anode is where the oxidation reaction happens (Loss of electrons, current flows in).
- Cathode is where the reduction reaction happens (Gain of electrons, current leaves).

| | **Discharge** | **Charge** |
|---|---|---|
| Negative electrode | Anode | Cathode |
| Positive electrode | Cathode | Anode |

# TURN YOUR KITCHEN INTO A LAB:

Build your own:

- Lemon battery: https://www.youtube.com/watch?v=GhbuhT1GDpI
- Potato battery: https://www.upsbatterycenter.com/blog/make-potato-battery/

# SUMMARY – WORK PRINCIPAL

Supercapacitors:

- No energy conversion.
- No redox reactions.
- Closed system – *Electrical double layers* (EDLs) formed at the electrode/electrolyte interface store energy.
- High surface area needed for the electrodes.

Batteries:

- Chemical energy <-> Electrical energy.
- Redox reactions at the electrodes.
- Closed system – the materials in the anode and cathode undergo redox processes.
- Discharge is spontaneous while the charge is non-spontaneous.

# MAIN BATTERY PROPERTIES

**Cell voltage (E [V]):**

- Depends on the type electrode material. In commercial batteries: ~1-4 V

**Cell capacity (Q [Ah]):**

- Depends on the type & amount of the active materials
- Specific capacity: Gravimetric [Ah/kg], Volumetric [Ah/l]

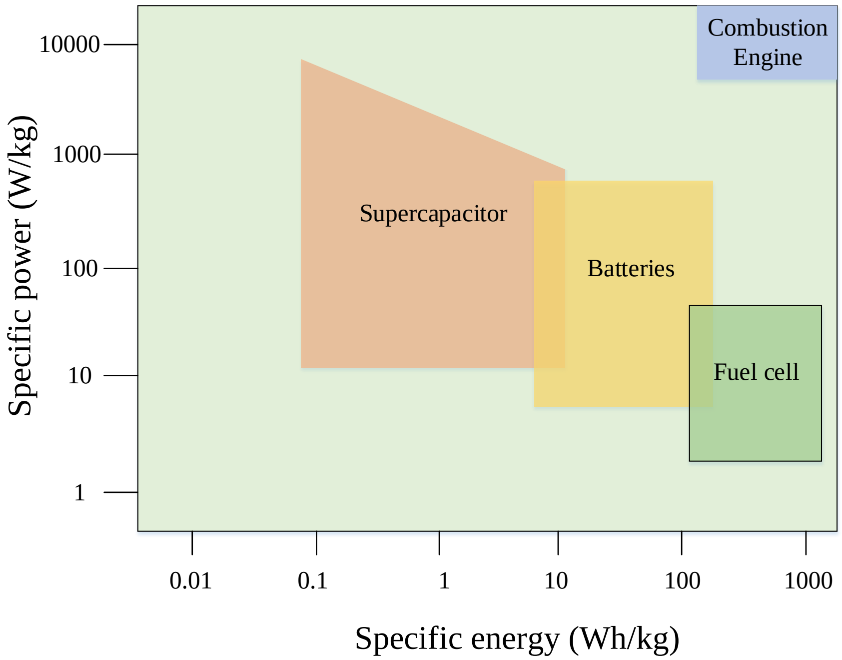
**Power (P [W]):**

- Depends on the type material and design.
- $\mathrm{P} = V(t)I$
- Power density: Gravimetric [W/kg], Volumetric [W/l]

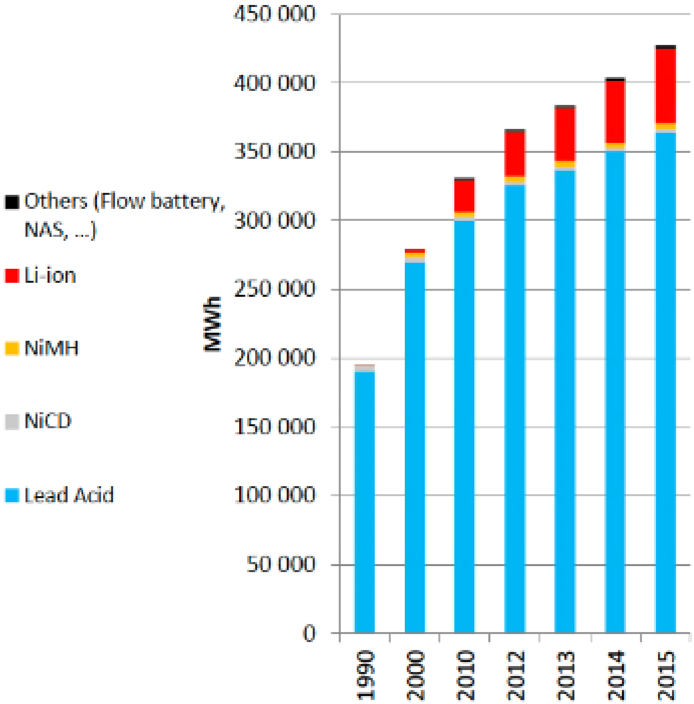
**Energy (W [Wh]):**

- Depends on the capacity and voltage
- $\mathrm{W} = \int_0^t V(t) I dt$
- Energy density: Gravimetric [Wh/kg], Volumetric [Wh/l]

# ENERGY DENSITY / POWER DENSITY

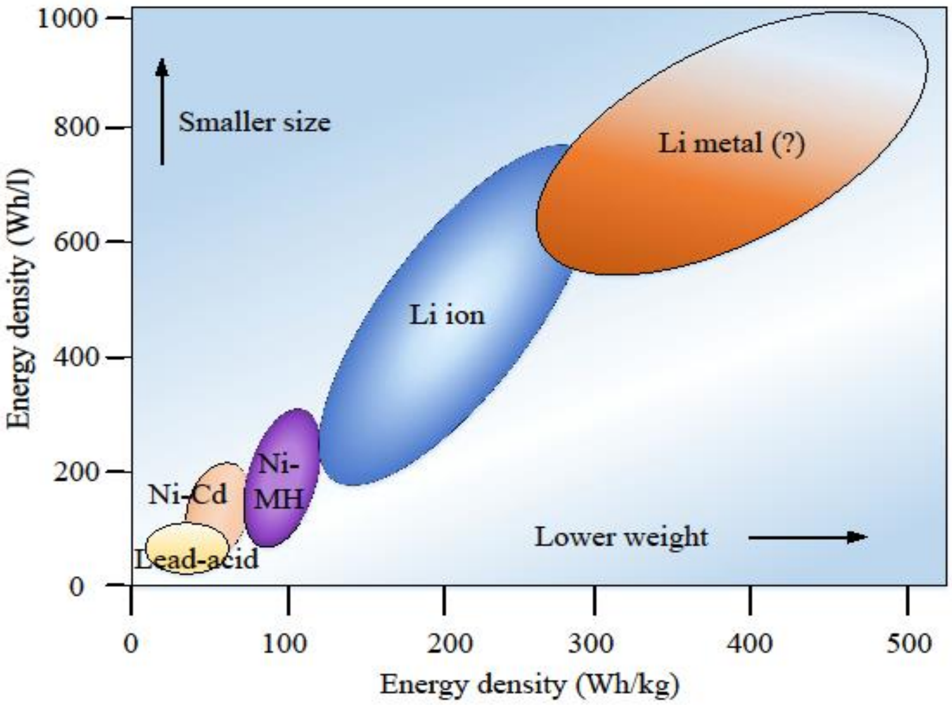


# RECHARGEABLE BATTERIES



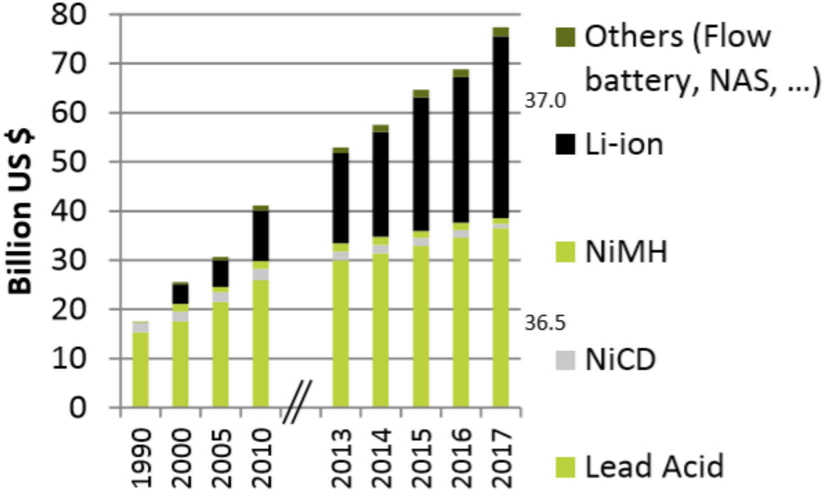

Source: Battery market share (Avicenne Energy)

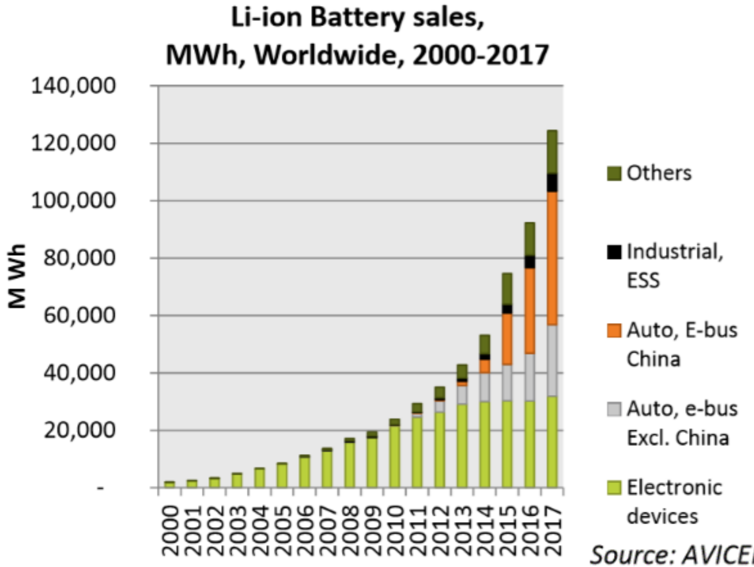
# RECHARGEABLE BATTERIES



# LITHIUM ION BATTERIES

- Largely developed in 1970s-1980s, first commercialized in 1991.
- The 2019 Nobel Prize in Chemistry are awarded to John Goodenough, M. Stanley Whittingham and Akira Yoshino “for the development of lithium-ion batteries”.

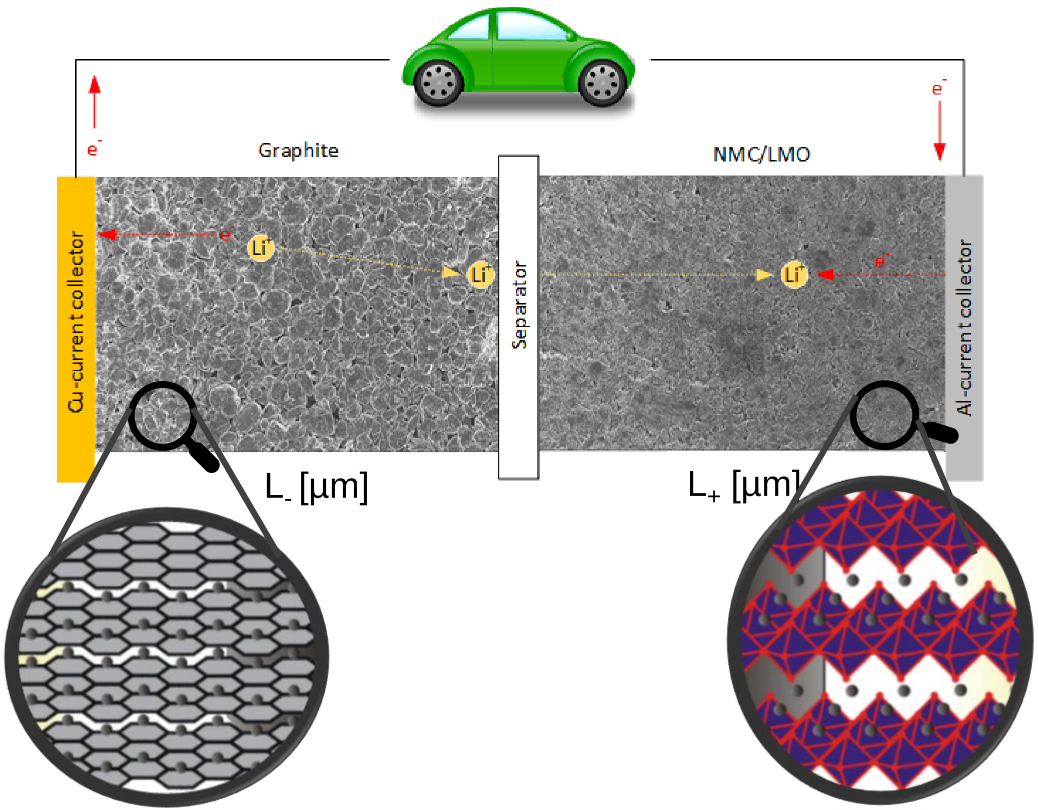



*Source: AVICENNE ENERGY, 2018*

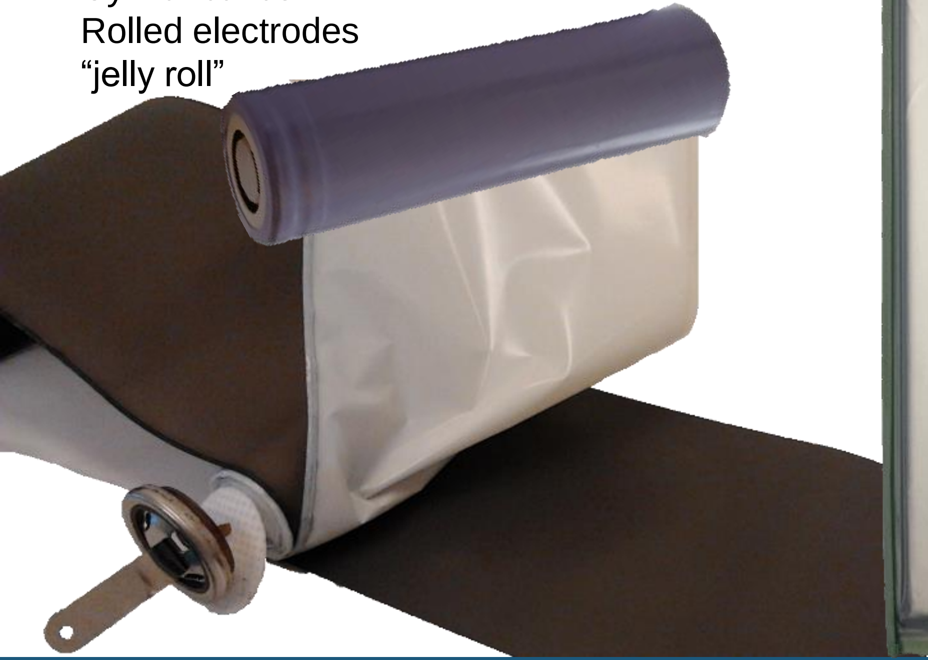
# LI-ION BATTERIES, HOW IT WORKS

- Redox reactions at the surface of the electrode materials.
- The electrodes are “host” materials that can intercalate and de intercalate Li-ion in their structurers.
- The electrolyte consists of a Lithium salt in organic solvents.
- 1-2 wt% Lithium in a cell.

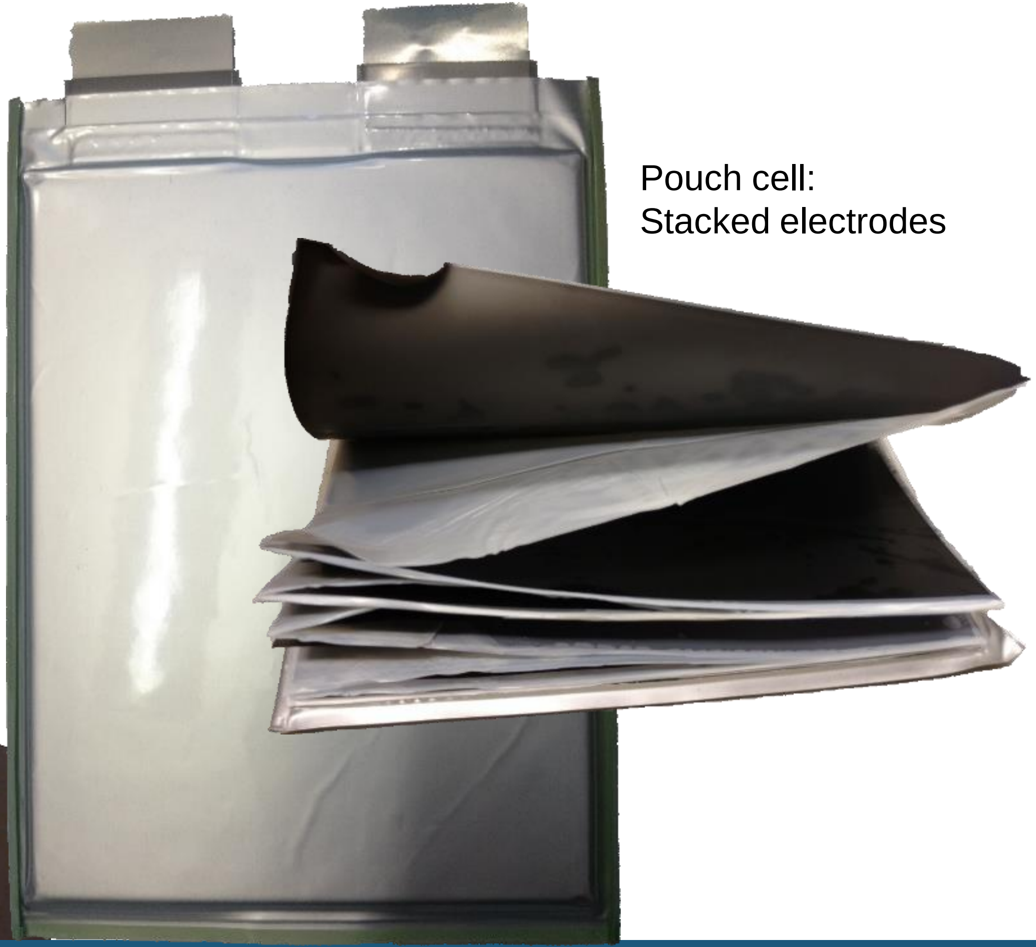


# INSIDE A LI-ION BATTERY

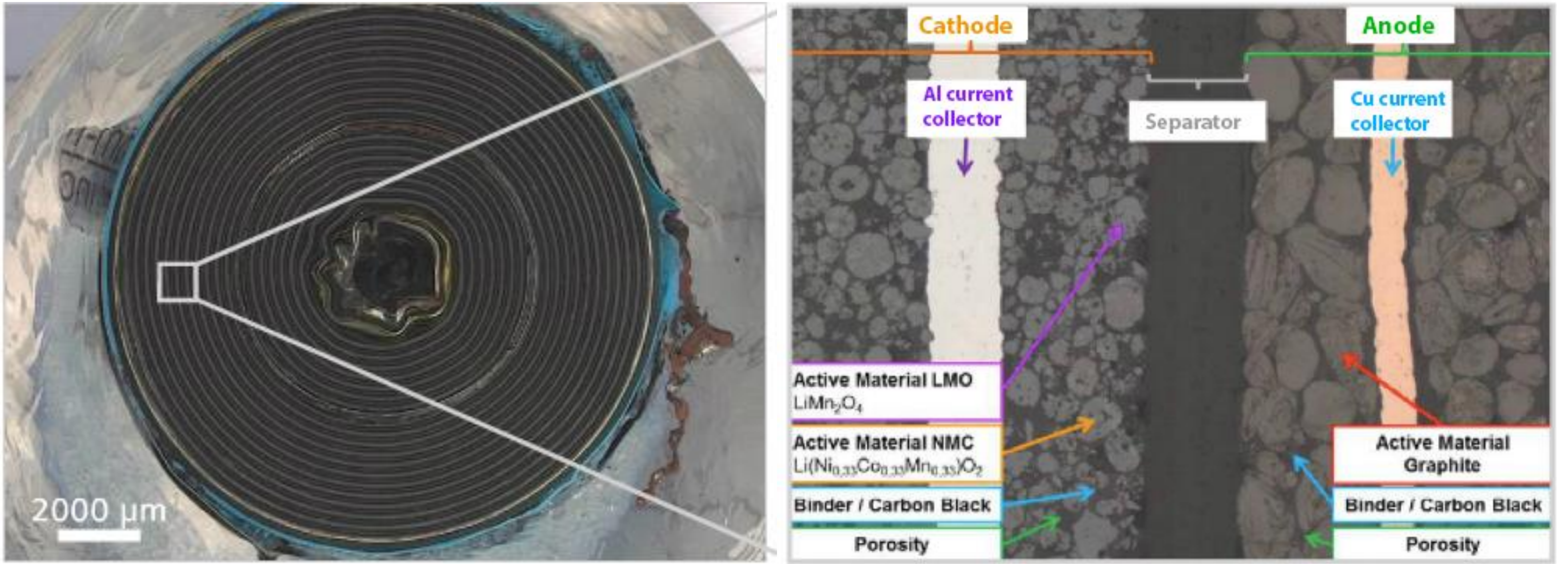
Cylindrical cell:
Rolled electrodes
“jelly roll”



Pouch cell:
Stacked electrodes



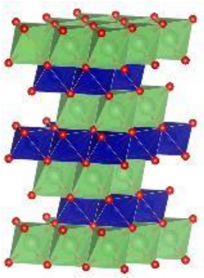
# INSIDE A LI-ION BATTERY




ZEISS Battery Solution, The Complete Guide

# PROPERTIES FOR AN APPLICATIONS

- Weight
- Volume
- Safe operation
- Temperature range
- Durability
- Cost
- Efficiency
- Energy
- Power



Material level

~500 Wh/kg

Cell level

~270 Wh/kg

Volvo cars

Pack level

~170 Wh/kg

# REFERENCE ELECTRODE

For Li-ion batteries, Li metal is used as a reference instead of the SHE.

Properties of the electrode materials, positive or negative, are tested with a Li metal reference.

| | E [V] | |
|---|---|---|
| **$Li^+ + e^- \rightleftharpoons Li$** | -3.04 | Lithium Metal |
| $Na^+ + e^- \rightleftharpoons Na$ | -2.71 | |
| $Mg^{2+} + 2e^- \rightleftharpoons Mg$ | -2.37 | |
| **$Al^{3+} + 3e^- \rightleftharpoons Al$** | -1.66 | |
| **$2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-$** | -0.83 | |
| **$Zn^{2+} + 2e^- \rightleftharpoons Zn$** | -0.76 | |
| $Fe^{2+} + 2e^- \rightleftharpoons Fe$ | -0.45 | |
| $Cd^{2+} + 2e^- \rightleftharpoons Cd$ | -0.40 | |
| $Ni^{2+} + 2e^- \rightleftharpoons Ni$ | -0.26 | |
| **$2H^+ + 2e^- \rightleftharpoons H_2$** | **0.00** | Standard Hydrogen Electrode(SHE) |
| **$Cu^{2+} + 2e^- \rightleftharpoons Cu$** | 0.34 | |
| **$O_2(g) + 2H_2O + 4e^- \rightleftharpoons 4OH^-$** | 0.40 | |
| $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ | 0.77 | |
| $Ag^+ + e^- \rightleftharpoons Ag$ | 0.80 | |
| **$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$** | 1.23 | |
| **$MnO_4^-(aq) + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$** | 1.51 | |

Source: https://en.wikipedia.org/wiki/File:Tallest_buildings_in_the_world.png

# LI-ION BATTERIES, MATERIALS

**Positive electrode materials:**

LMO – Lithium manganese oxide

LCO – Lithium cobalt oxide

NMC – Lithium nickel manganese cobalt oxide

NCA – Lithium cobalt aluminium oxide

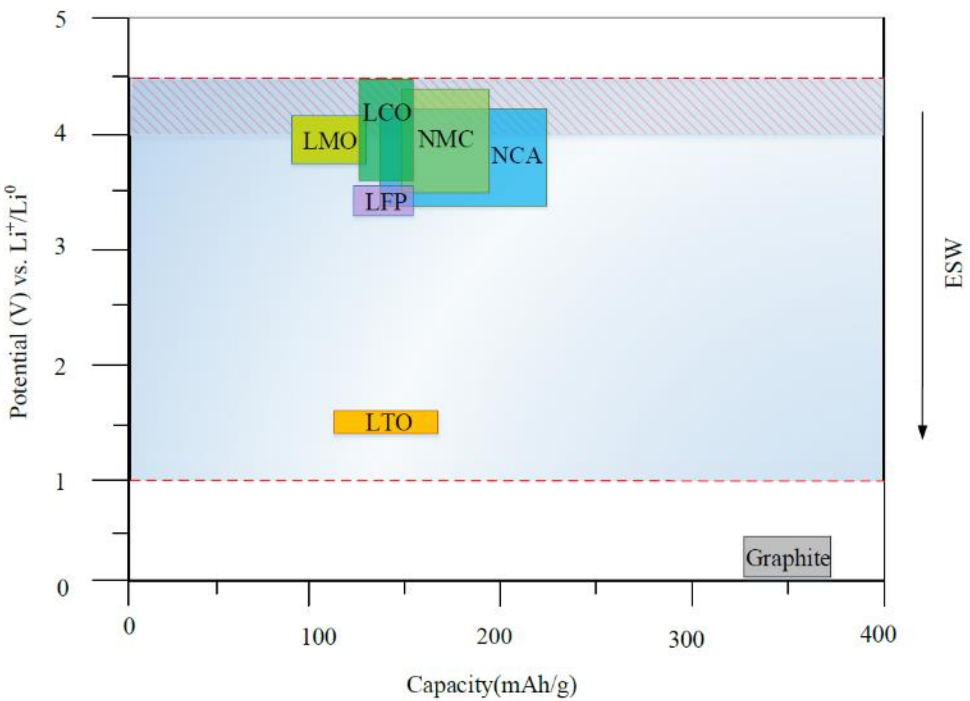
LFP – Lithium iron phosphate

**Negative electrode materials:**

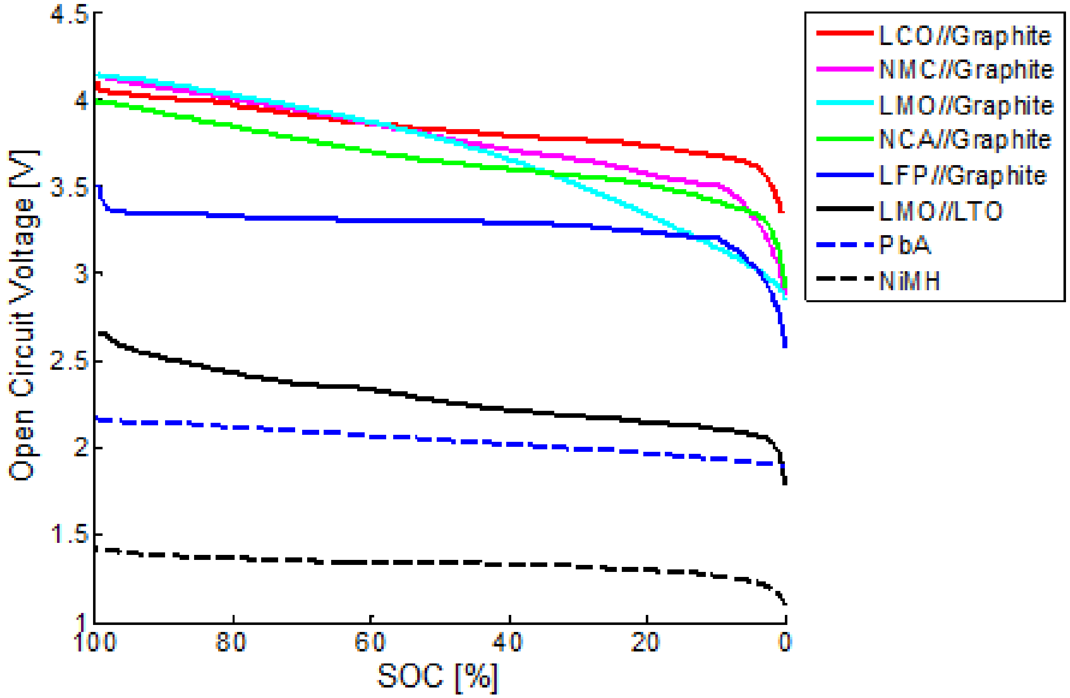
LTO – Lithium titanium oxide

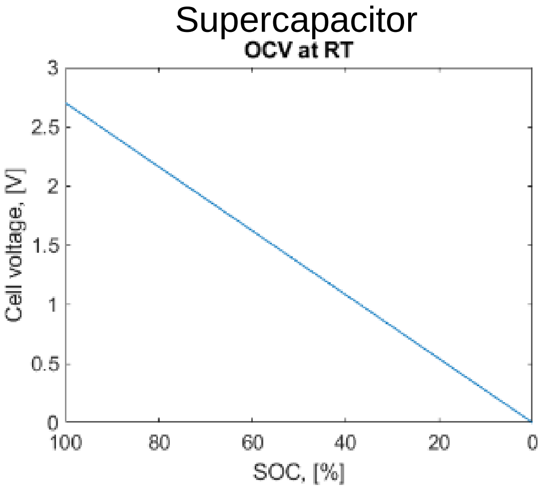
Graphite

ESW – Electrolyte stability window



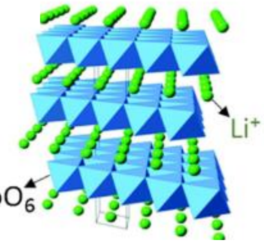
# CELL VOLTAGE



# LI-ION BATTERIES, MATERIALS

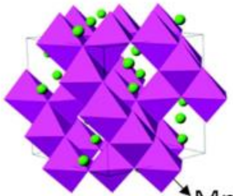
**Layered Oxides**




LCO: $LiCoO_2$

High potential
High capacity
Moderate power
Expensive
Toxic

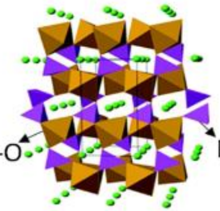
**Spinel Oxides**




LMO: $LiMn_2O_4$

High potential
Moderate capacity
Suitable for high power
Cheap
Non-toxic

**Polyanionic Compounds**




LFP: $LiFePO_4$

Moderate potential
Moderate capacity
High power
Cheap
Non-toxic

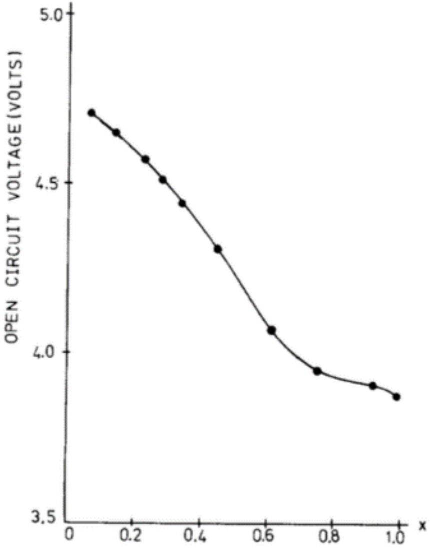
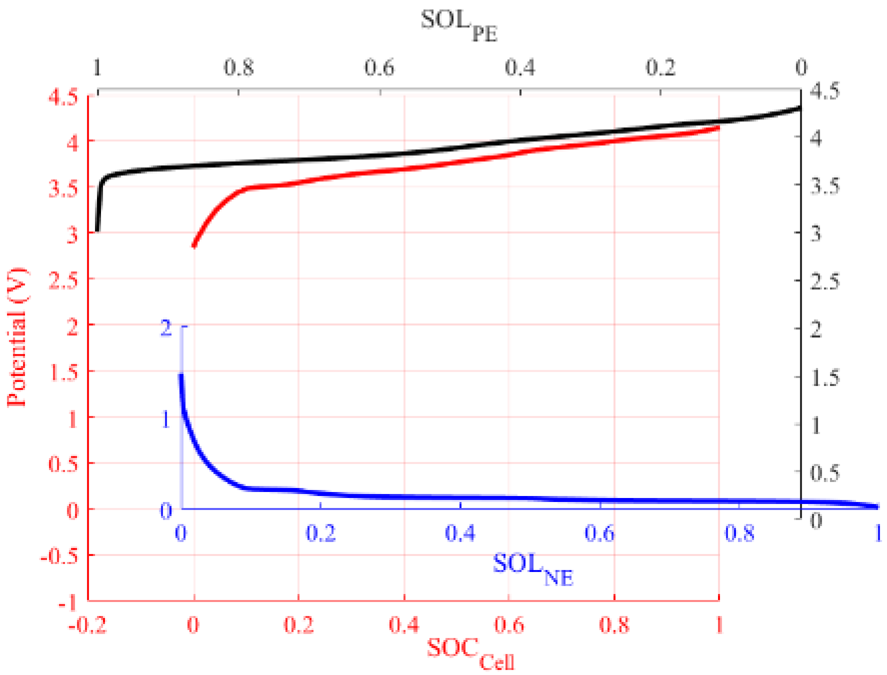
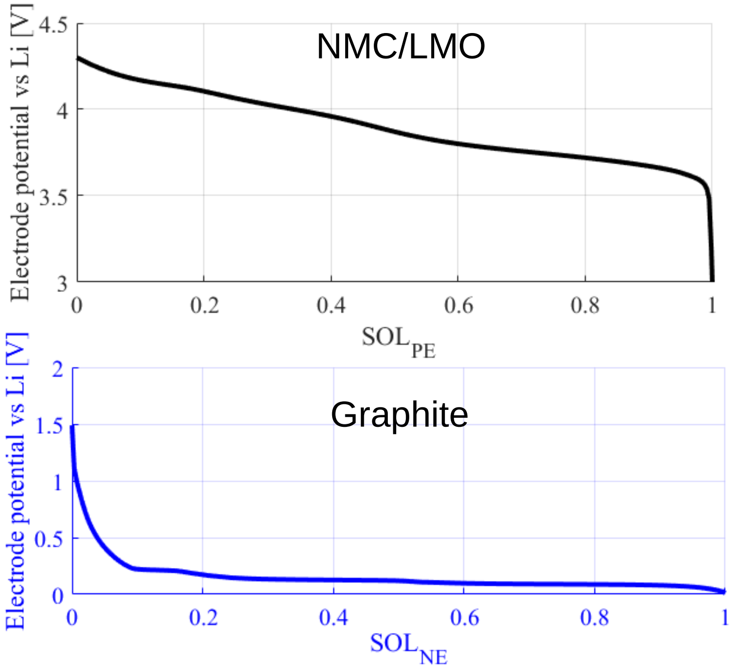



FIG. 3
Open circuit voltage versus composition x for $Li_xCo_{1.01}O_2/Li$

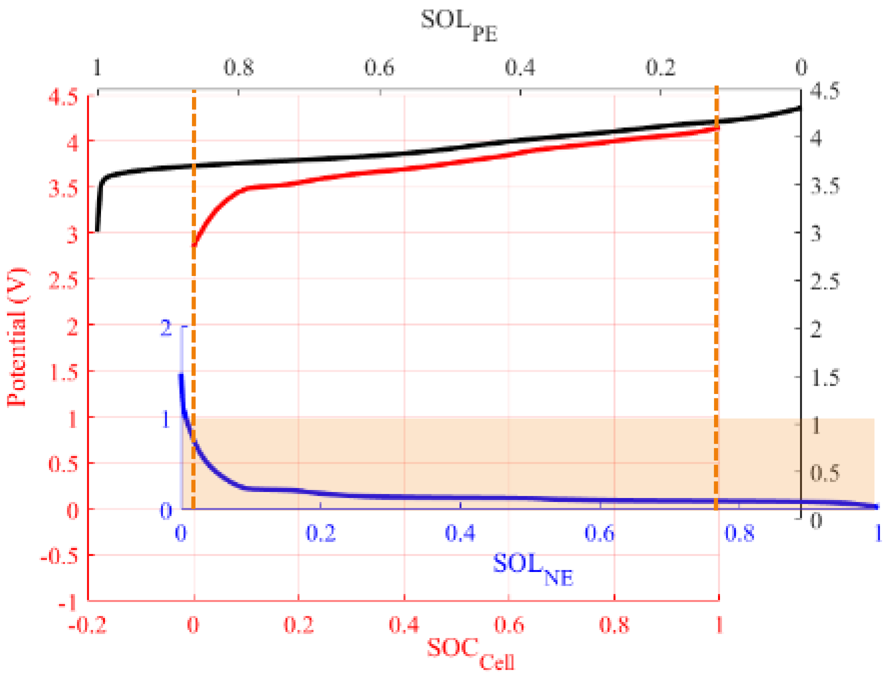
SOL – State of lithiation

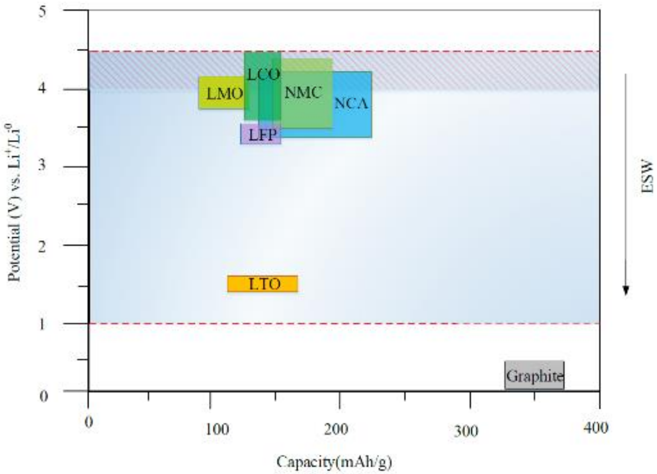
# CELL VOLTAGE



# OPERATING WINDOW




- Graphite's low operating potential causes electrolyte to degrade (the potential is outside the electrolyte stability window.)
- The battery works because the degradation products forms a passivating film, the SEI (solid electrolyte interphase), on the surface of the graphite.

# COULOMB EFFICIENCY / ENERGY EFFICIENCY

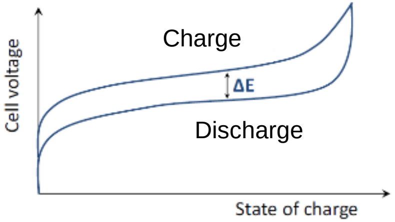
## Coulomb efficiency

- The coulomb efficiency is a measure of the electrochemical conversion efficiency.
- It is very low during the first few cycles (formation of SEI).
- It is related with side reactions.
- Typically >99.9% in a commercial Li-ion battery, influenced by T, C-rate, chemistry, age…

$$\eta_{coul} = \frac{Q_{dis}}{Q_{cha}} = \frac{\int_{dis} I dt}{\int_{cha} I dt}$$

## Energy efficiency

- Cannot be higher than the coulombic efficiency.
- The energy efficiency is rate dependent (resistive losses, $P=RI^2$).
- Higher ΔE = lower efficiency.




$$\eta_e = \frac{\int_{dis} V(t) I dt}{\int_{cha} V(t) I dt}$$

# NON-LINEAR BEHAVIOUR

Battery behaviour is dependant on temperature, SOC, current level, previous short-term history, pressure, ageing,…

Non-linearly!

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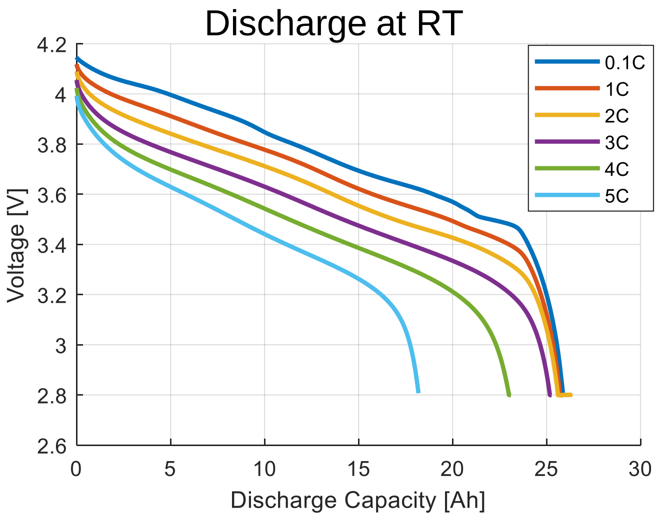
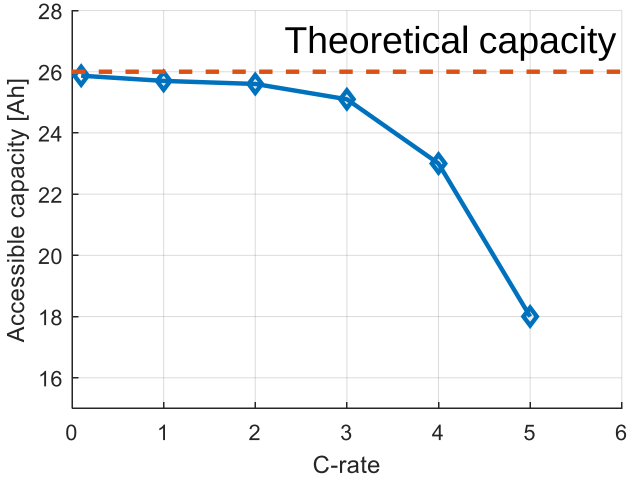
# POWER CAPABILITY

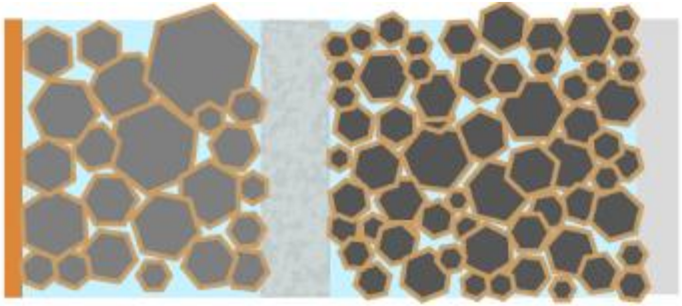
- C-rate: a measure of the rate at which a battery is being discharged.
- The constant current needed to discharge the cell for a given time (1C = 1h, 2C = 0.5h).



# ENERGY VS POWER OPTIMISED CELLS

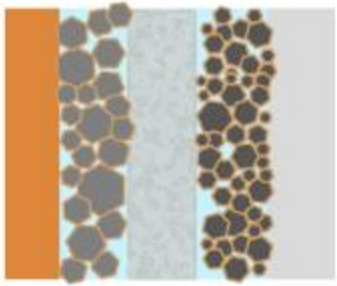
**Energy optimised**
- Thick coating
- Large particles
- Limited C-rate



Figures: Viktor Nilsson

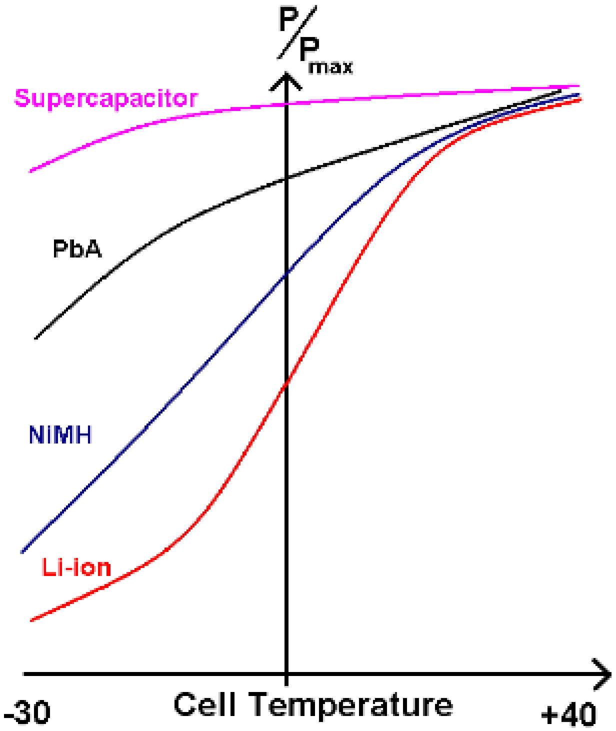
**Power optimised**
- Thin coating
- Small particles
- Thick current collectors

(low electronic resistance)

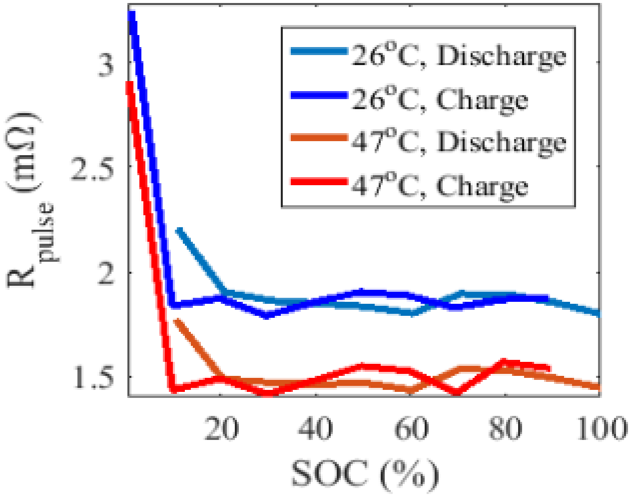


Power limiting factors:
- Electronic resistances
  - Active materials,
  - Additives,
  - Contact points between materials
- Mass (ion) transport:
  - In electrolyte
  - In active materials
- Interfacial processes:
  - Reaction kinetics
  - Surface later growth
  - Structural changes

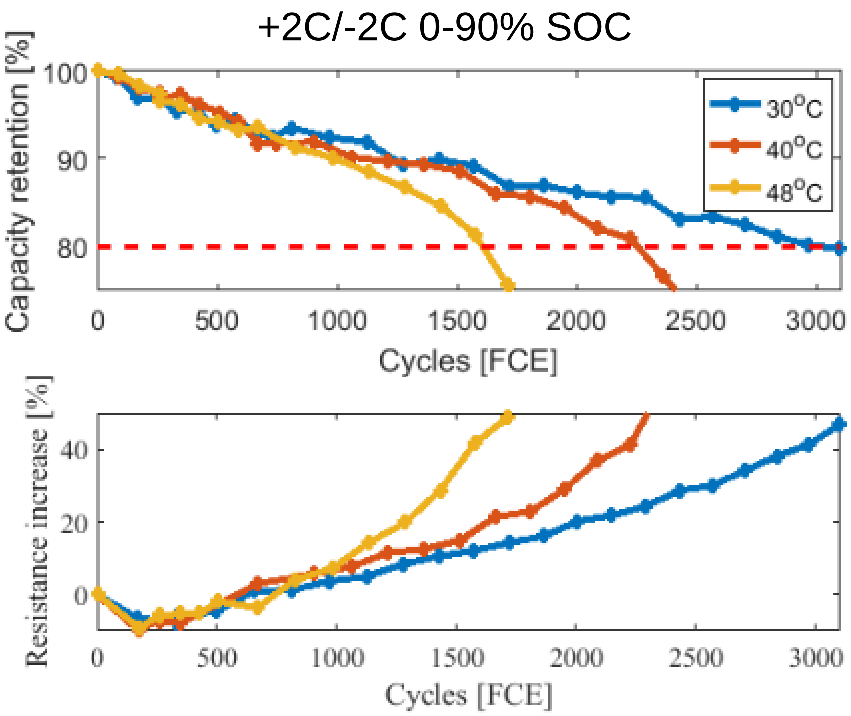
# PERFORMANCE – TEMPERATURE




Li-ion battery pulse resistance



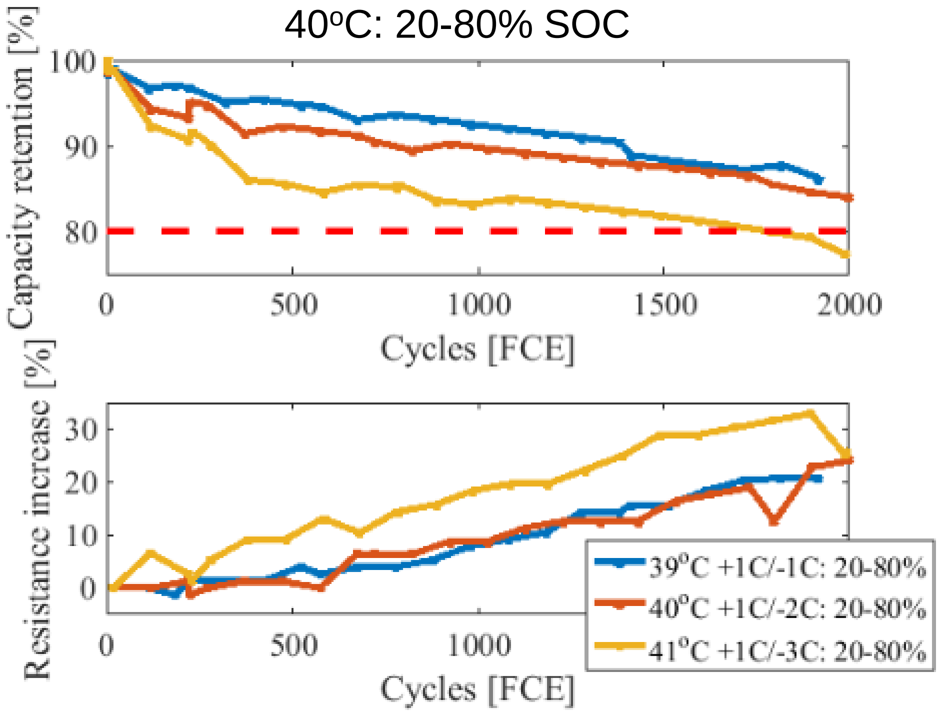
# PERFORMANCE – LIFETIME




**FCE** – Full cycle equivalent

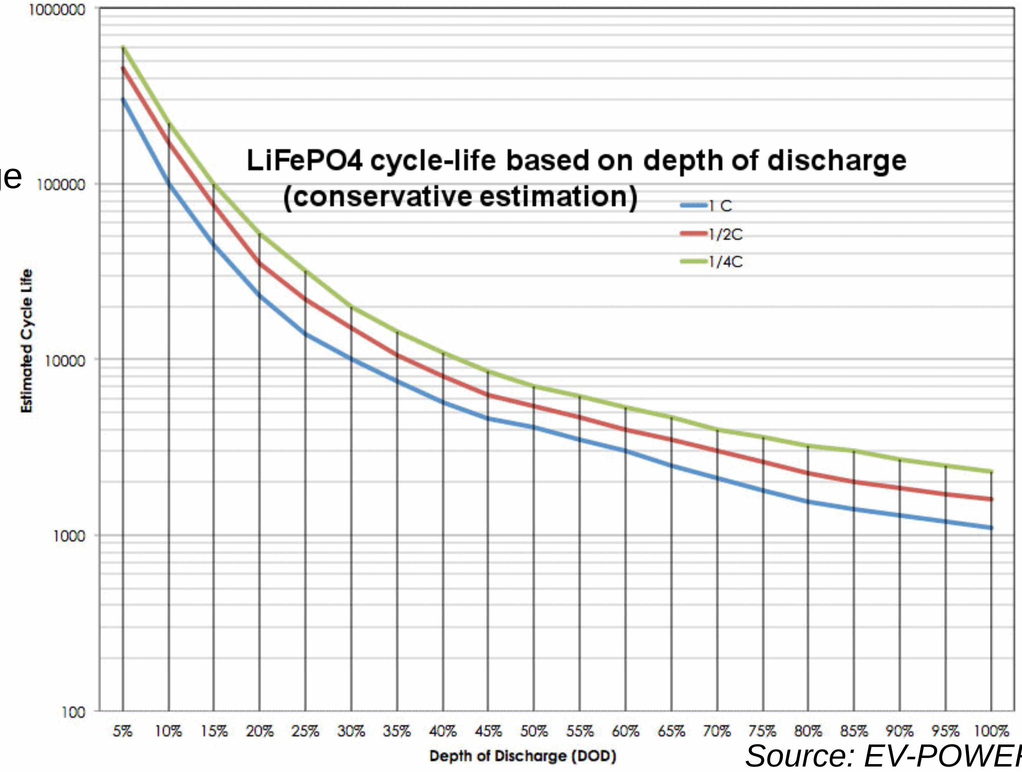
$$FCE = \frac{Current\ throughput}{2 \cdot Rated\ capacity}$$

# PERFORMANCE – LIFETIME



# PERFORMANCE - OPERATION AND DURABILITY

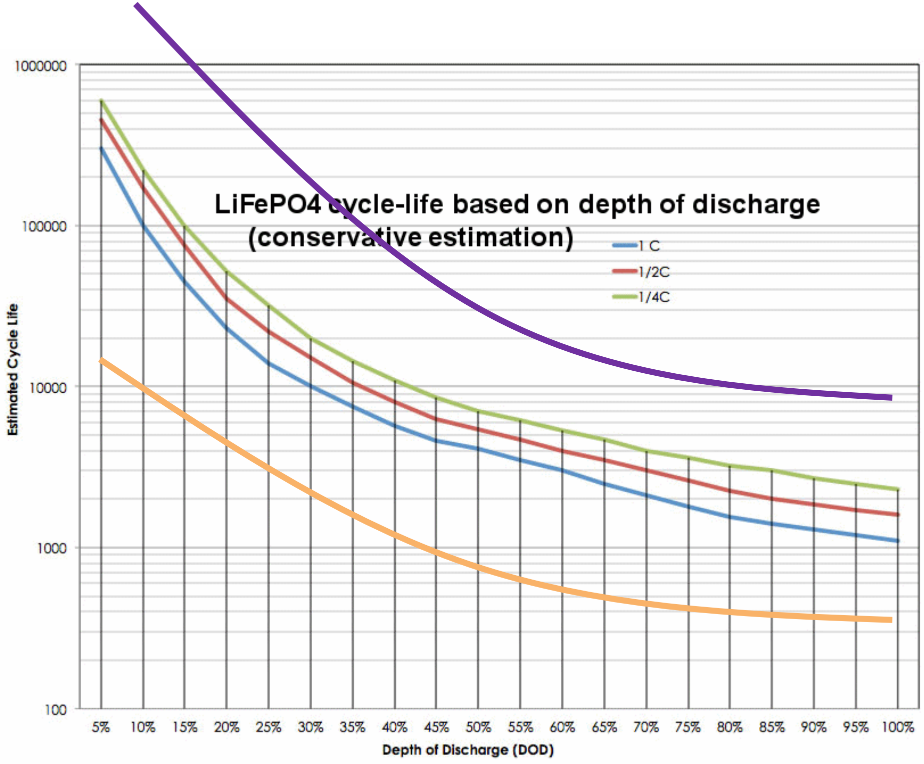
Highest energy throughput achieved at low Depth of discharge (DOD).




*Source: EV-POWER.EU (GWL/Power group)*

# PERFORMANCE - OPERATION AND DURABILITY

Large variation between different cells



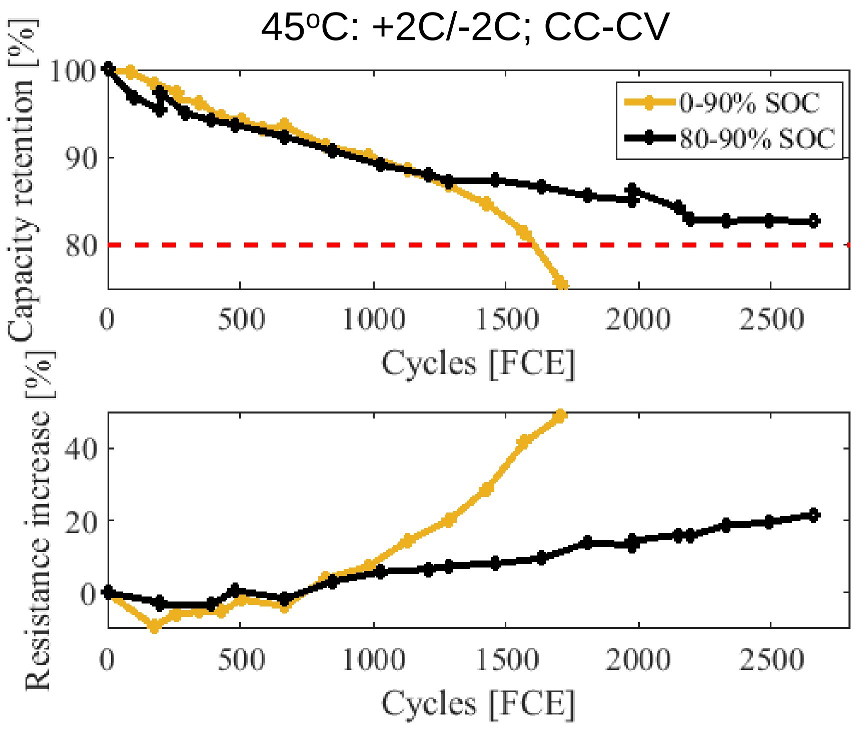

Cells optimised for cycle life

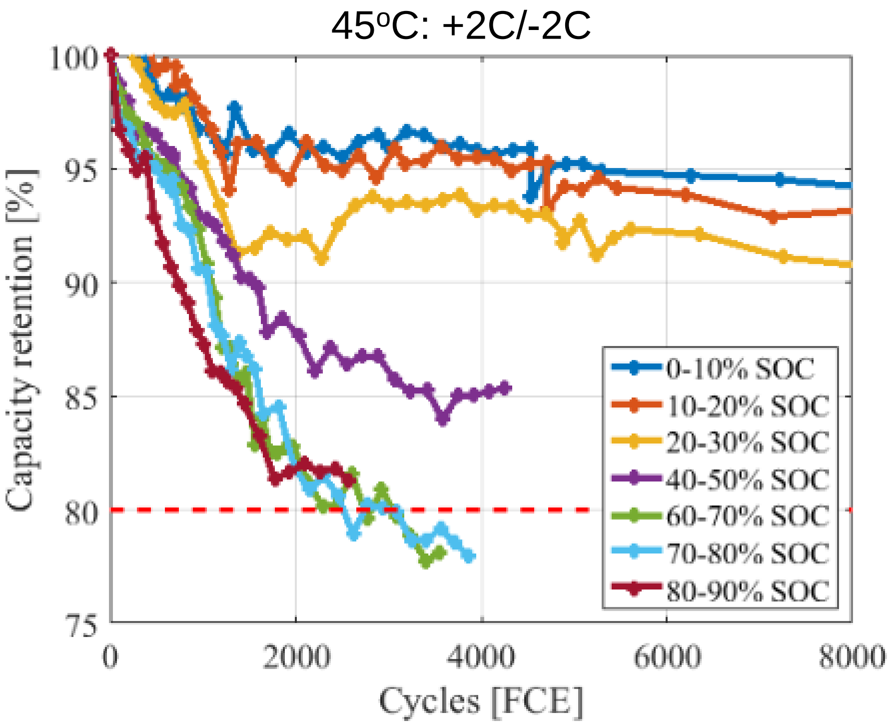
Cells optimised for compromise between cost and cycle life

Cells optimised for cost

*Source: EV-POWER.EU (GWL/Power group)*

# PERFORMANCE – DOD AND SOC



# SUMMARY - SUPERCAPACITORS AND BATTERIES

- Cell design and material selection critical for both batteries and supercapacitors

- Supercapacitors have longer cycle life higher, power density, but lower energy density than batteries.
- Generally, supercapacitors have higher efficiency and better low temperature performance than batteries.

- Batteries is a large group of different type of technologies.
- Lead acid battery is the most common battery, but Li-ion batteries is the second and fastest growing battery technology.
- Li-ion batteries is a large family of different types.
- The application determines what battery to use, combination of materials and design.
- The battery performance is dependent on temperature, SOC, current level, previous short-term history, pressure, ageing,…

- Only using part of the available energy is beneficial for the lifetime.

# LI-ION BATTERY MODELLING

Physics based

Empirical

More versatile

More accurate

Faster execution

Theoretical;
linked to electrochemical processes

Black box;
Based on battery testing

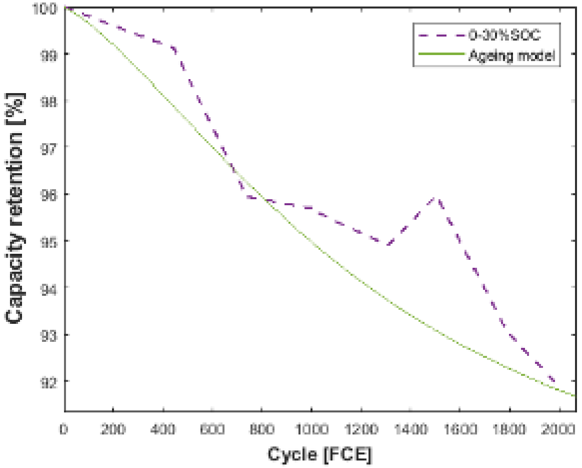
# LI-ION BATTERY MODELLING - EMPIRICAL

Based on measurement data.

- Analytical models
  - based on stochastic approaches and empirical equations to describe the basic electrochemical and performance characteristics of the battery.

- Equivalent circuit models (ECM)
  - Based on electrical components to simulate the behaviour of a battery

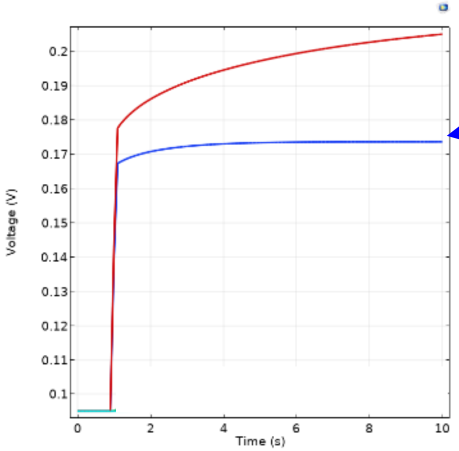
$$Cap(SOC, C\text{-}rate, T) = a \cdot e^{(b \cdot FCE)} + c \cdot e^{(d \cdot FCE)}.$$

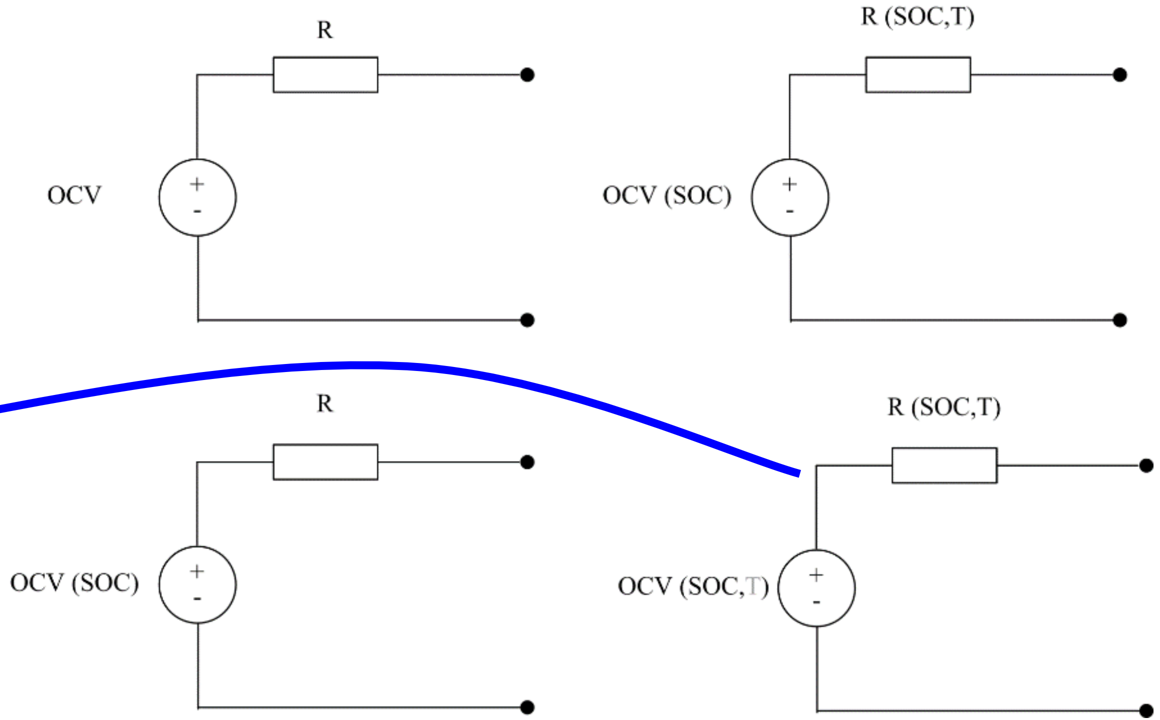



*Appl. Sci.* **2018**, *8*(10), 1825; https://doi.org/10.3390/app8101825

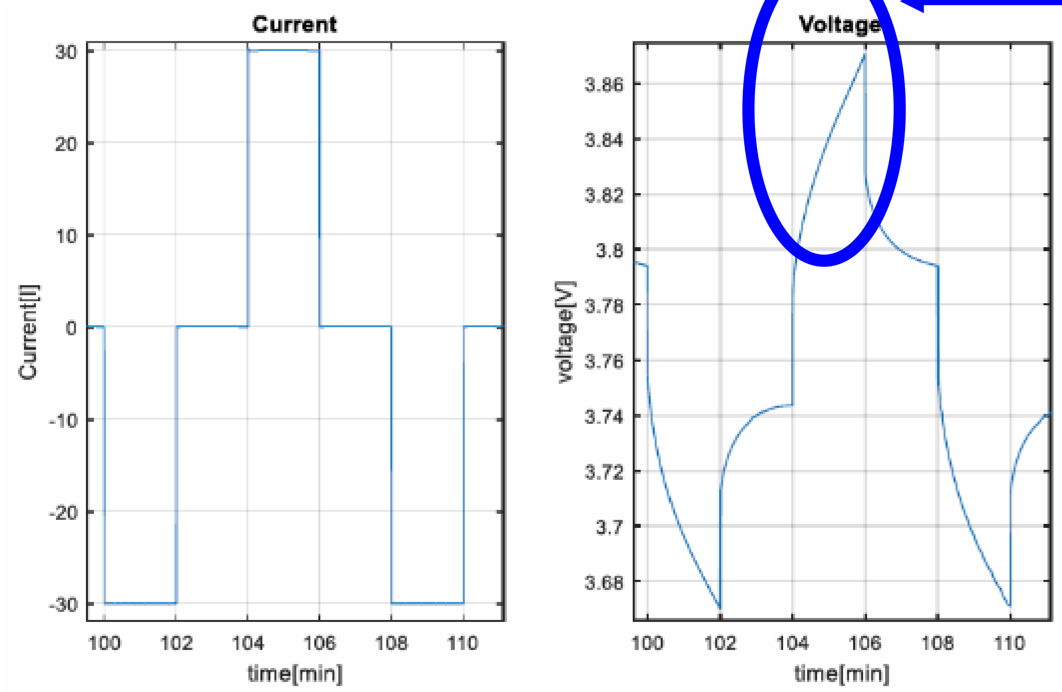
# LI-ION BATTERY MODELLING - ECM

This is the most common empirical model and consisting of different level of simple to complex electric circuits.

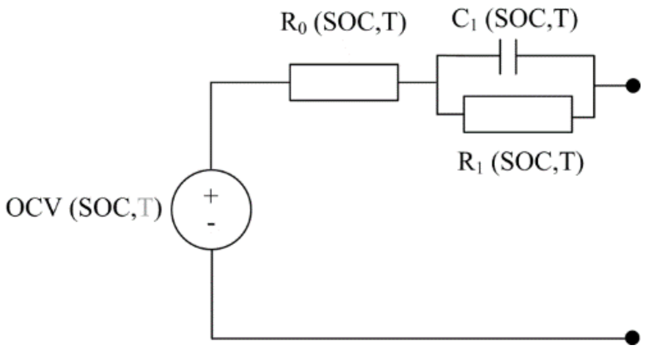


# LI-ION BATTERY MODELLING - ECM




Next step,
add RC link



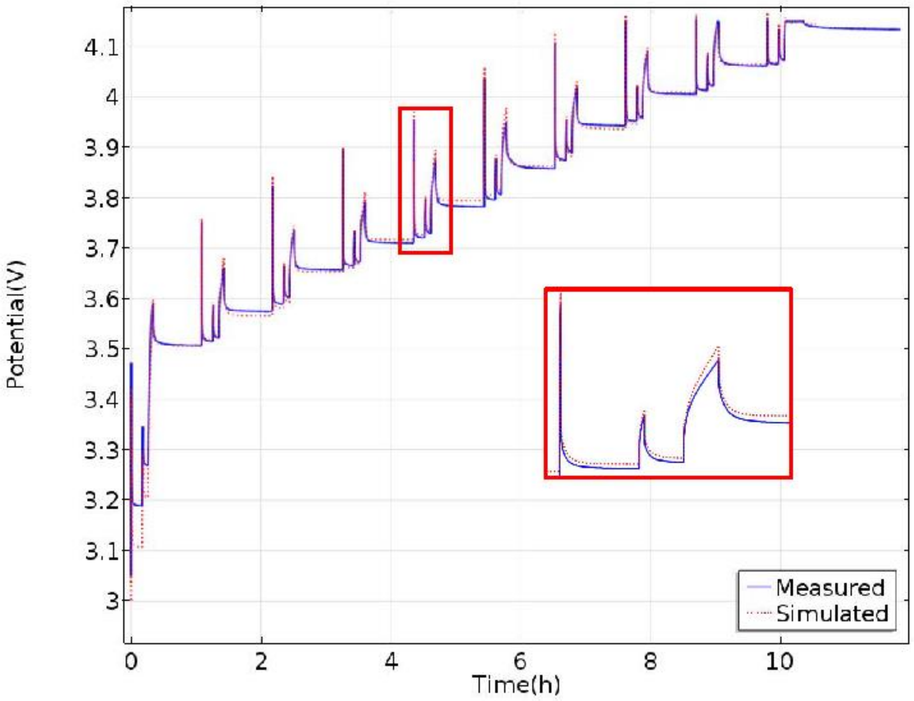
# LI-ION BATTERY MODELLING – PHYSICS BASED

Physics based or pure electrochemical models are based on theory of the electrochemical processes in the battery. These processes are described by non-linear differential equations

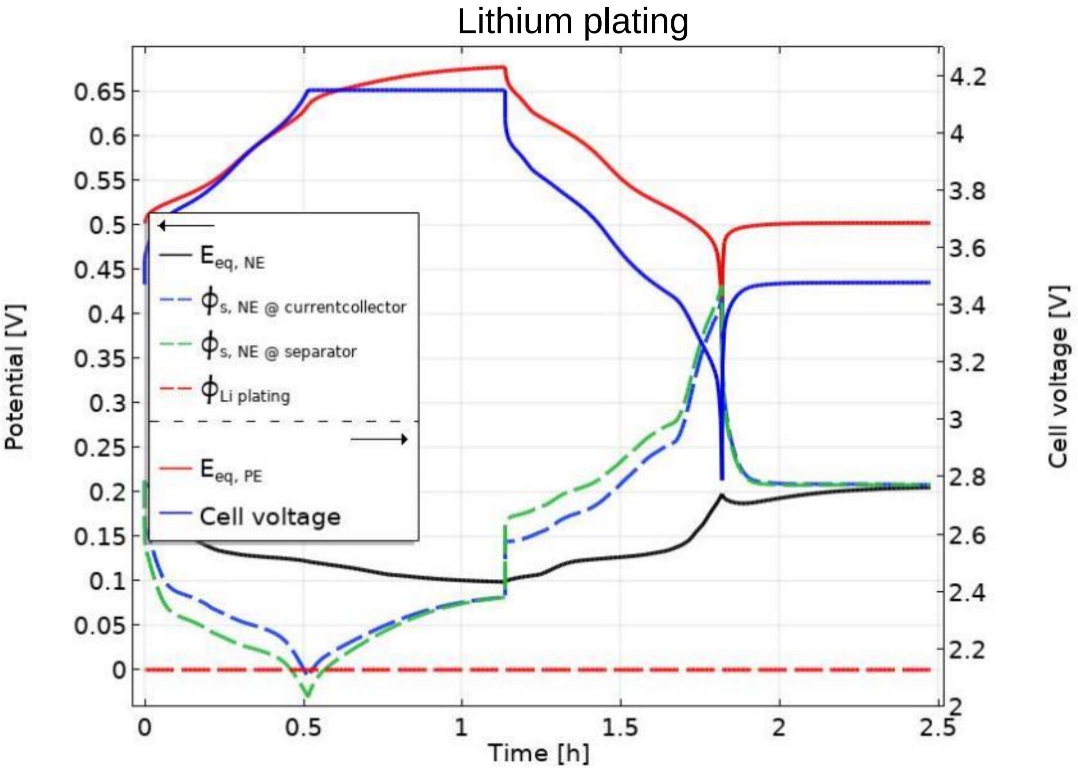
$\Rightarrow$ This is computationally heavy. Several coupled differential equations needs to be solves simultaneously.

- Needs several material specific parameters that can be difficult to determine.

\+ High accuracy and versatility



# LI-ION BATTERY MODELLING – PHYSICS BASED



# SUMMARY - BATTERY MODELLING

- Electrochemical battery models are accurate but not suitable for use in applications with limited computational power, such as vehicles.
- Simple equivalent circuits can only be used in a narrow range of temperature, voltage and SOC.
- Advanced models can be used for a wider operating range.
- All models must be validated for the specific application.

- “All models are wrong, but some are useful”  - George Box

# ENERGY STORAGE SYSTEMS

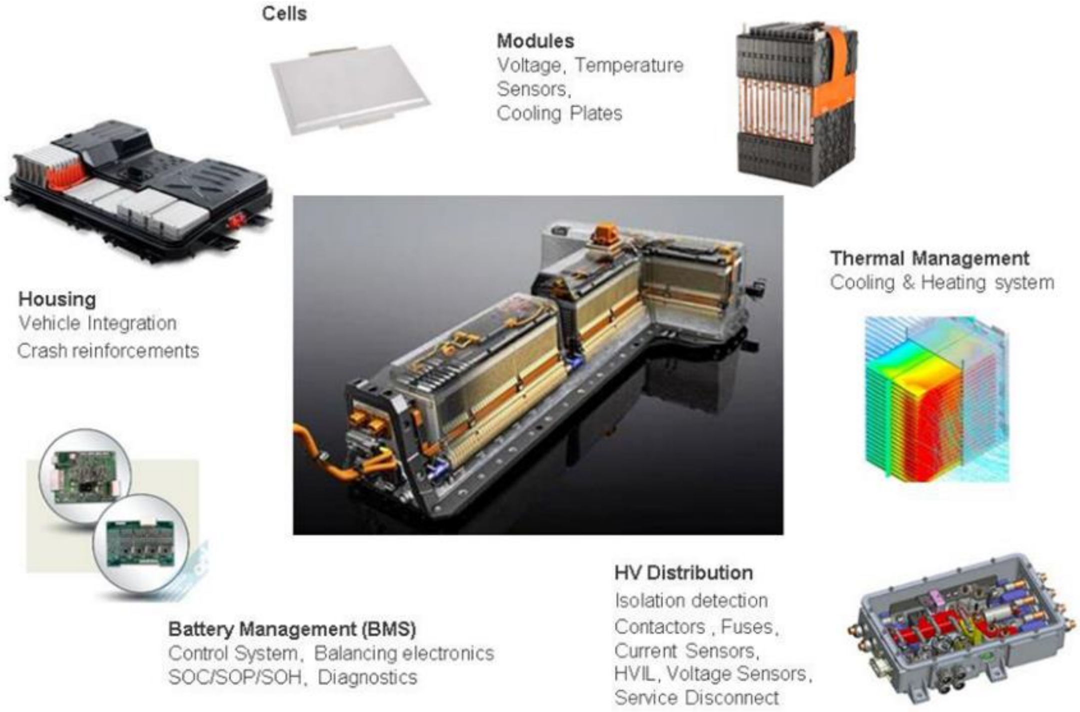
100 MW/129 MWh Powerpack system

https://www.tesla.com/sv_SE/blog/tesla-powerpack-enable-large-scale-sustainable-energy-south-australia

# ENERGY STORAGE SYSTEMS

Integrated System Components:

- Cells: Batteries or Supercapacitors
- Cooling System
- Contactors
- Pre-charge Circuit
- Sensors; voltage and temperature
- Isolation Detection
- Connectors
- Control System – Estimation of SOC and maximum power
- Fuse(s)
- Housing

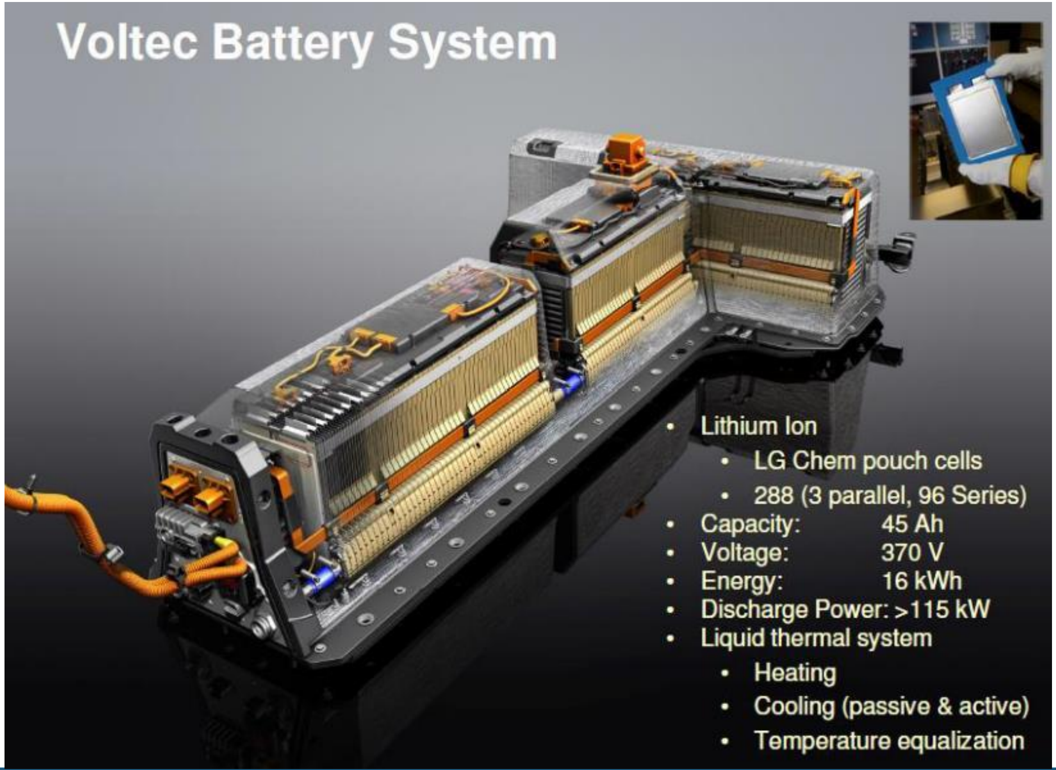


# ENERGY STORAGE SYSTEMS

## Safety

- **Key issue: thermally instable material**
- **Solutions**
  - Material selection
  - Passive safety: additives
  - Active safety mechanisms
  - System safety

# ENERGY STORAGE SYSTEMS



# ENERGY STORAGE SYSTEMS


**SIRIUS ENERGY STORAGE MODULE**
**TECHNICAL DATA SHEET**
**Part Number: 3550-48-A-1.35C-M-A-G**

| | | |
|---|---|---|
| Nominal Voltage | 48VDC | |
| Voltage Range | 44VDC – 54VDC | |
| Capacity | 3550Wh | |
| Maximum Charge Rate (0% -100% SOC) | 100A (short time withstand 300A consult Arvio for times) | |
| Maximum Discharge Rate (100% - 0% SOC) | 100A (short time withstand 300A consult Arvio for times) | |
| Maximum Charging Voltage | 54VDC | |
| Internal Resistance | ≤6mΩ | |
| DC to DC Roundtrip efficiency (@100A) | 99.1% (at caps) (tested to 96% at terminals) | |
| Operating Temperature | -30°C to 85°C (at caps) -10°C to 55°C (recommened for design life) | |
| Galvanic Isolation | 1500V | |
| Projected Cycle Life of capacitors [3] | 1,000,000 | |
| Projected Calendar Life[1,3] | Supercap cell (capacitors) | 45 years |
| | Module Control Electronics | 10 - 15 years |
| Shelf Life[2] | 10 years | |
| Warehousing | Can be stored at any SOC without affecting cycle life | |
| Communication Port | TCP/IP RJ45 Ethernet | |
| Monitoring Data | Temperature, Voltage, Current, Energy, Supercap Balancing | |
| Remote Control Input | Battery Self-Check | |
| Terminal Type | F12 | |
| Module Casing Material | Aluminium | |
| Dimensions (w x d x h) | 600mm x 534mm x 200mm (+/-2%) | |
| Weight | Approx.75kg | |
| Self-discharge[4] | 5% after 25 days | |

https://www.solarquotes.com.au/blog/arvio-supercapacitor-battery-review/

# SUMMARY - ENERGY STORAGE SYSTEMS

- System components and system design are equally important to the choice of cells.
- System safety is determined by both system design and cell design.

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