Battery Properties

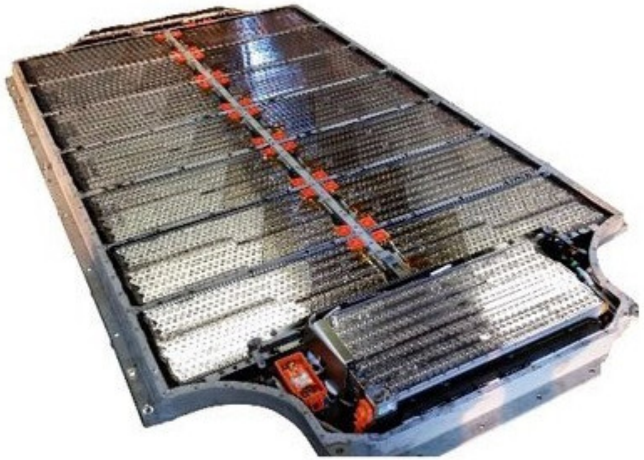
TSFS19 Battery Systems - Lecture 2

Mattias Krysander

LINKÖPINGS UNIVERSITET

Today's lecture

- Battery design and actual performance
- Current-voltage characteristics
- Battery characteristics, SOC, DOD, C-rate, OCV
- Cycling and ageing, CCCV, SOH



Charge and Energy Density

Recap

- Formulate balanced **cell reactions** given half-cell reactions.
  - Balance atomic species and charge.
- Compute the **standard potential (open circuit voltage)** of a cell given half-cell potentials: $U^0_{\text{cell}} = U^0_+ - U^0_-$
  - The lowest potential will be the negative electrode and its reaction will be reversed during discharge.
- Understand current: $I = dQ/dt$ [A = C/s]
- Use **Faraday's law** of electrolysis: $m_i = \dfrac{M_i Q}{nF}$
- Compute theoretical **charge density** for half-cells and cells:

$$\left.\frac{Ah}{g}\right|_A = \frac{F \cdot n}{M_A} \qquad \left.\frac{Ah}{g}\right|_{cell} = \left(\left.\frac{g}{Ah}\right|_{cathode} + \left.\frac{g}{Ah}\right|_{anode}\right)^{-1}$$

- Compute theoretical **energy density** of a cell = $U^0_{cell} \cdot \left.\dfrac{Ah}{g}\right|_{cell}$ [VAh/g = Wh/g]

Theoretical energy density - example ZnCu cell

- Cell reaction:

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

- Charge density:

$$\frac{Ah}{g} = \left(\overbrace{\frac{63.5\text{g}}{2 \cdot 26.8\text{Ah}}}^{Cu} + \overbrace{\frac{65.4\text{g}}{2 \cdot 26.8\text{Ah}}}^{Zn} \right)^{-1} = 0.42 \text{ Ah/g}$$

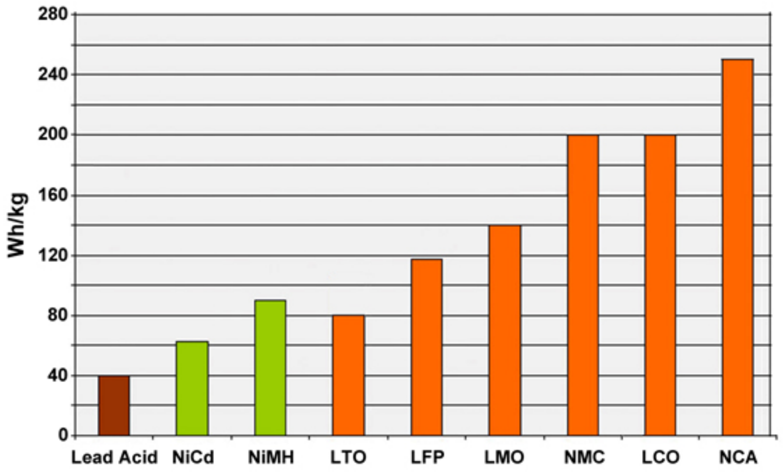
- Theoretical energy density:

$$E = V_{\text{avg}} \cdot Q_m = 1.1 \text{ V} \cdot 0.42 \text{ Ah/g} = 0.46 \text{ Wh/g} = 460 \text{ Wh/kg}$$

Battery chemistry

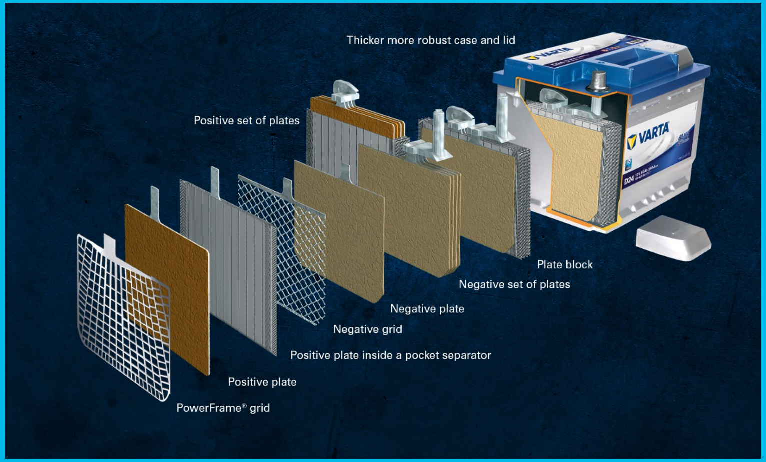
Chemical	Anode	Cathode	V	Wh/kg
Primary cells:				
Alkaline MnO_2	Zn	MnO_2	1.5	145
Li/FeS_2	Li	FeS_2(iron sulfide)	1.5	260
Secondary cells:				
Lead Acid	Pb	PbO_2	2	35-40
Nickel-cadmium	Cd	NiOOH	1.2	40-60
Nickel metal hydride	MH	NiOOH	1.2	60-120
Litium-ion (Li-ion)	Li_xC_6	$Li_{(1-x)}CoO_2$	3.6	100-265

MH - hydrogen-absorbent metal mixture



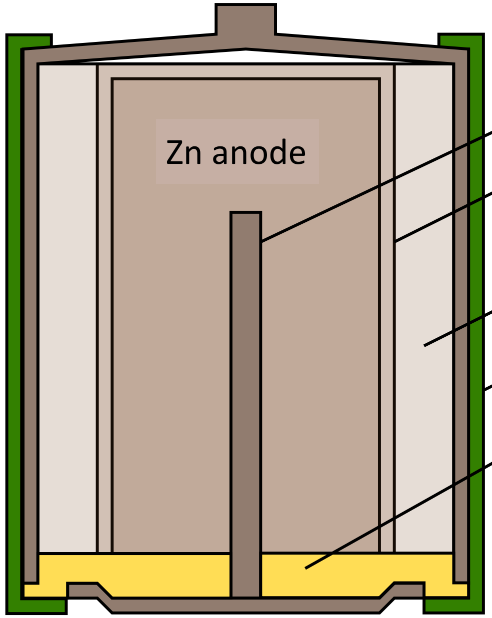
Energy density for different chemistries. Orange bars correspond to various lithium-based chemicals.

Battery Design and Actual Performance



Alkaline batteries - Construction

- Anode: $Zn(s) + 2OH^{-} \rightarrow ZnO(s) + H_2O + 2e^{-}$ Zn oxidize
- Cathode: $2MnO_2(s) + H_2O + 2e^{-} \rightarrow Mn_2O_3(s) + 2OH^{-}$ MnO_2 reduce
- Cell: $Zn(s) + 2MnO_2 \rightarrow ZnO + Mn_2O_3$
- Theoretical charge density = 0.22 Ah/g
- Actual charge density = 2.8 Ah/25 g = 0.11 Ah/g
- Why is capacity halved?
- Well, the battery contains more:
  - Anode (Zn) powder
  - Cathode (MnO_2) tablets
  - Brass conductor
  - Separator soaked in liquid KOH electrolyte



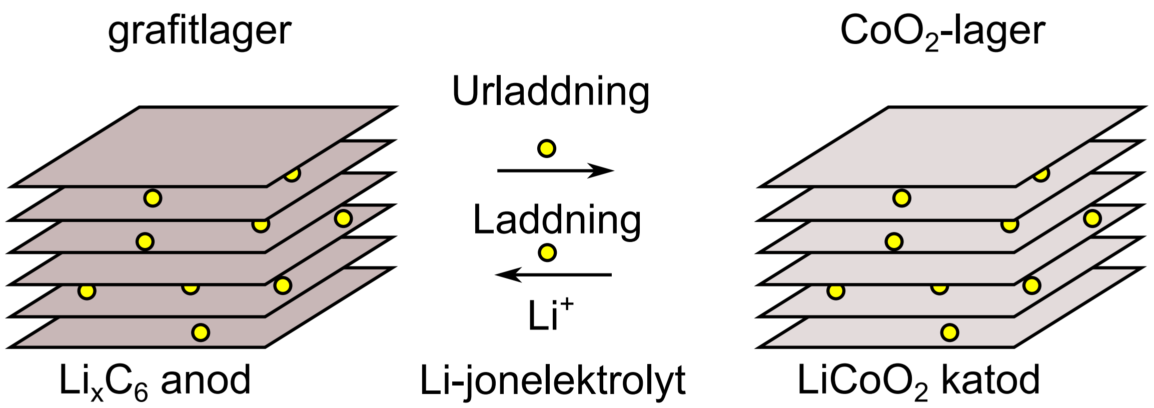
Li-ion Batteries

Discharge reaction:

Anode: $LiC_6 \rightarrow Li^+ + e^- + C_6$

Cathode: $CoO_2 + Li^+ + e^- \rightarrow LiCoO_2$

Cell: $LiC_6 + CoO_2 \rightarrow C_6 + LiCoO_2$



Li is transported in and out of the anode/cathode.

Intercalation - insertion in layers of a host material

- Theoretical charge density: 0.10 Ah/g
- Actual charge density = 0.94 Ah/19 g = 0.05 Ah/g
- About half of an alkaline battery, but the voltage is twice as large (4.1 V compared to 1.5 V) so the energy density is greater.

Battery Design

There is a compromise between high power density and high energy density.

- High power density requires a large contact area between the electrodes.
- High energy density requires maximum active material

Container

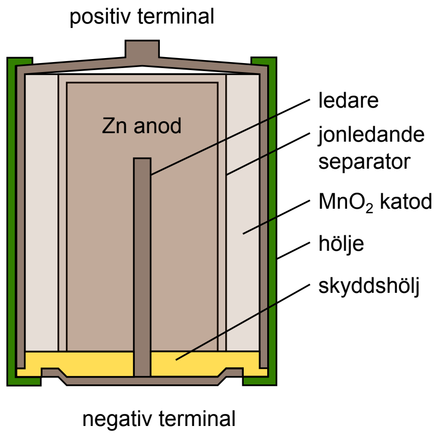
- High energy density
- Alkaline batteries

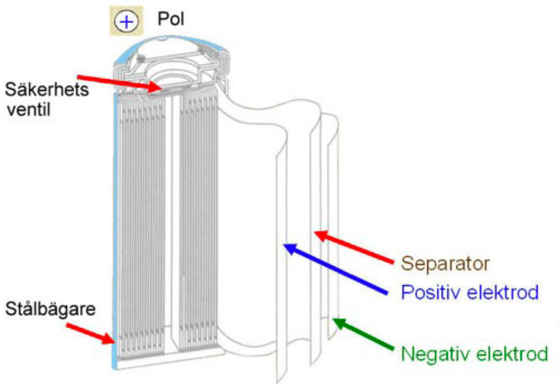
Cylindrical cell

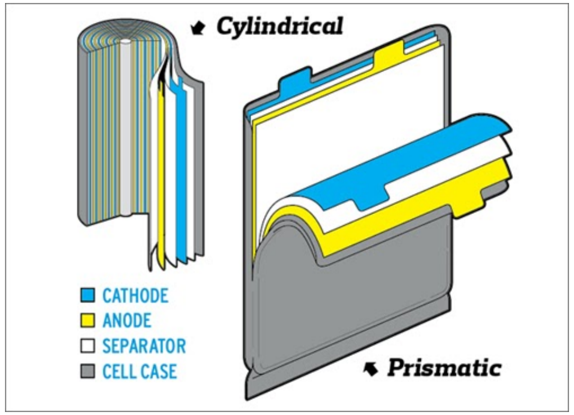
- High power, easy to construct
- Li-ion, NiMH, NiCd

Prismatic cell

- High packing density
- Easier to short circuit

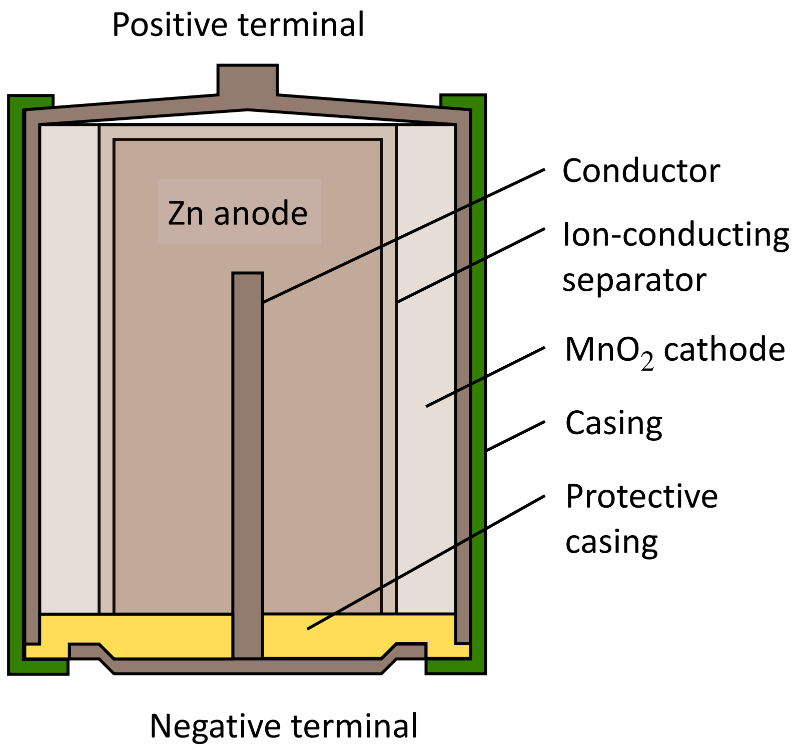






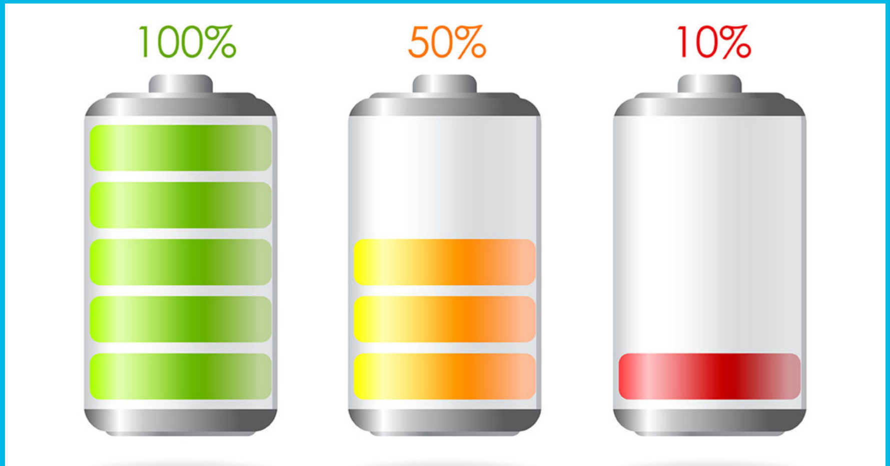
Remarks on Battery Components

- The separator is a porous film
  - Electronically isolation
  - Electrolyte fills porous to conduct ions.
- Electrodes: Typically porous structures increasing the active surface area. They contain
  - Active material for electrochemical reactions
  - Conductive material to reduce ohmic losses
  - Binder to provide structural integrity



Charge Dependent Properties (zero current)

C-rate, SOC, DOD, OCV



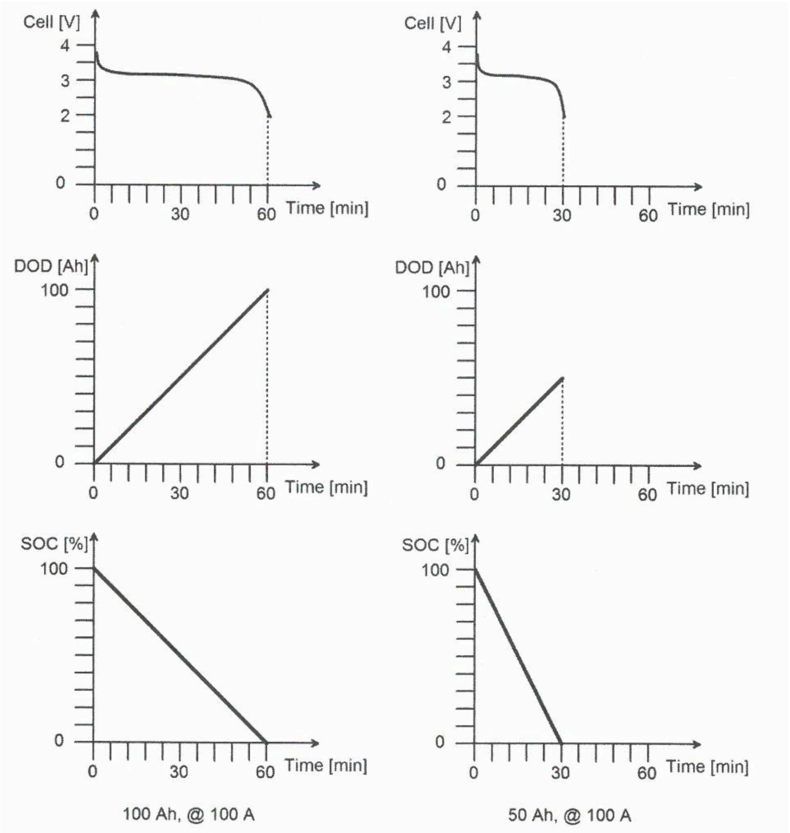
Normalized Current (C-rate)

- Battery currents are often expressed relative to battery capacity.
- Definition: 1C current discharges the nominal battery in 1 hour.
- Example: Consider a 100 Ah battery.
  - The 1C rate is 100 A for this battery since this current discharges the battery in 1 hour.
  - 2C = 200 A, discharge time 30 min
  - C/10 = 10 A, discharge time 10 h

Battery and Cell Properties

- State of charge (SOC):
- $$\mathrm{SOC} = \frac{\text{available capacity remaining}}{\text{total capacity}} \cdot 100\,\%$$
- Percentage of charge in the battery/cell
  - 100% full
  - 0% empty
- State of discharge, SOD = 100 - SOC
- Depth of discharge (DOD)
  – Ah discharge from full battery

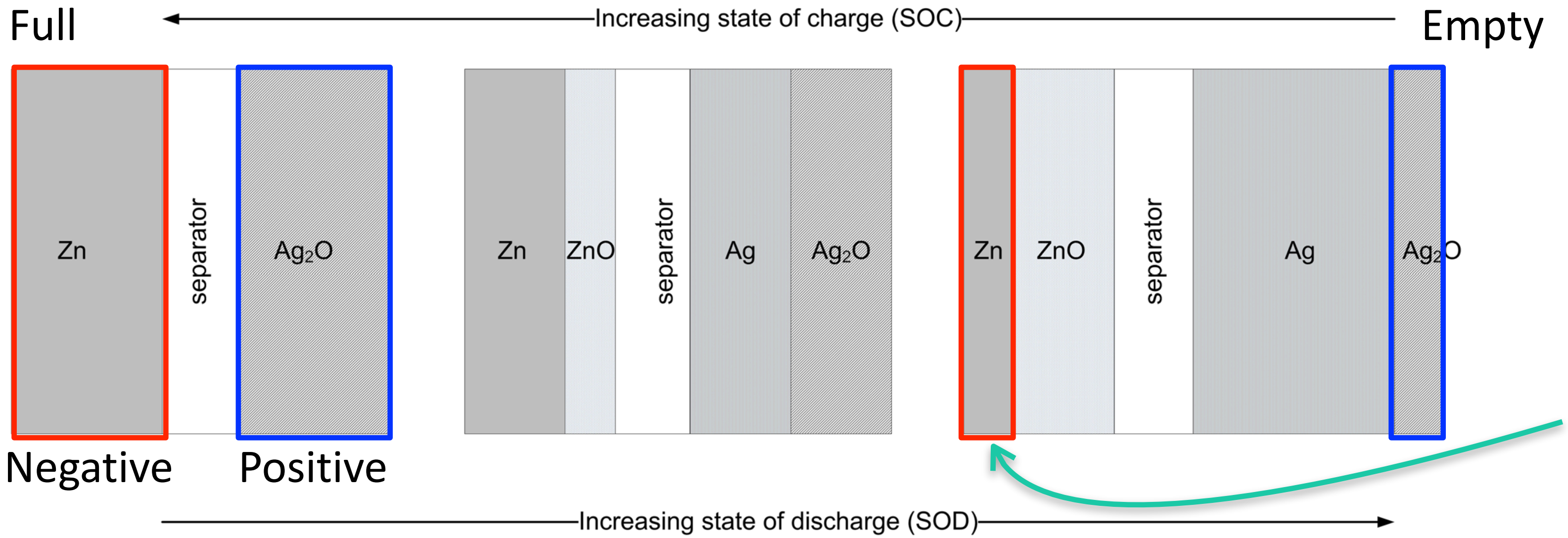
Nominal battery	Degraded battery
Capacity = 100 Ah	Capacity = 50 Ah
Discharge rate =1C	Discharge rate = 1C



State of Charge as a Conversion of Active Material

- $\mathrm{SOC} = \dfrac{\text{available capacity remaining}}{\text{total capacity}} \cdot 100\,\%$
- SOC = The fraction of active material in the initial rather than the product state.
- The two electrodes can have different capacities.
- Neither the total amount nor the unconverted amount of active material is typically not measurable!

All active material in initial state

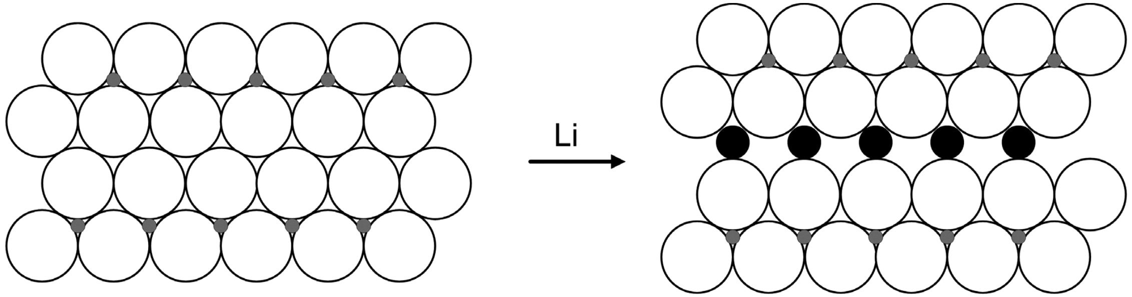


Fraction of active material in initial state

$$\mathrm{Zn + Ag_2O \rightarrow ZnO + 2Ag}$$

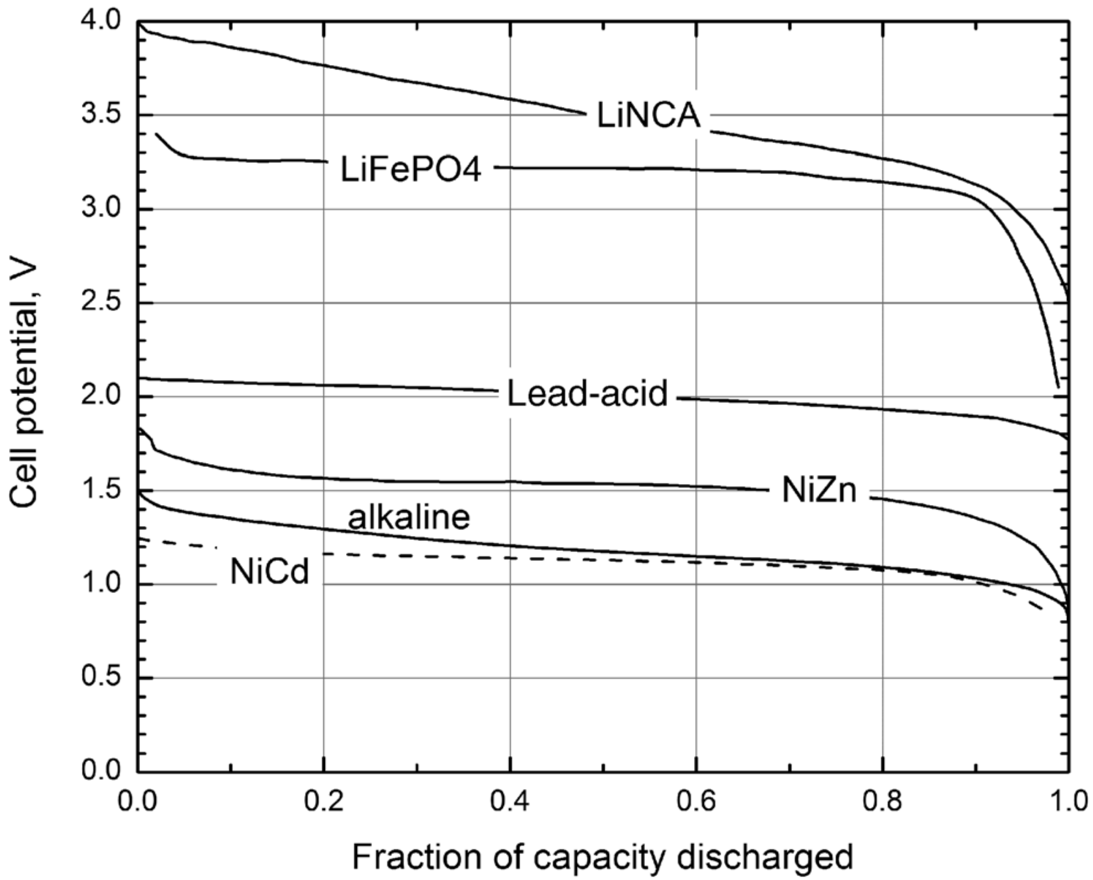
Electrode Reaction - Insertion

- Stable host material
- Guest material in unoccupied sites
- If the host is layered, insertion is called intercalation.
- Illustration of lithium into a positive electrode of titanium disulfide TiS_2.
  - $x\mathrm{Li}^+ + x\mathrm{e}^- + x\mathrm{TiS}_2 \rightarrow \mathrm{Li}_x\mathrm{TiS}_2$
- x the fraction of intercalated Li^+ in TiS_2.
- $x = \begin{cases} 0 & \text{dilithiated (charged)} \\ 1 & \text{lithiated (discharged)} \end{cases}$



Open Circuit Voltage depends on SOC

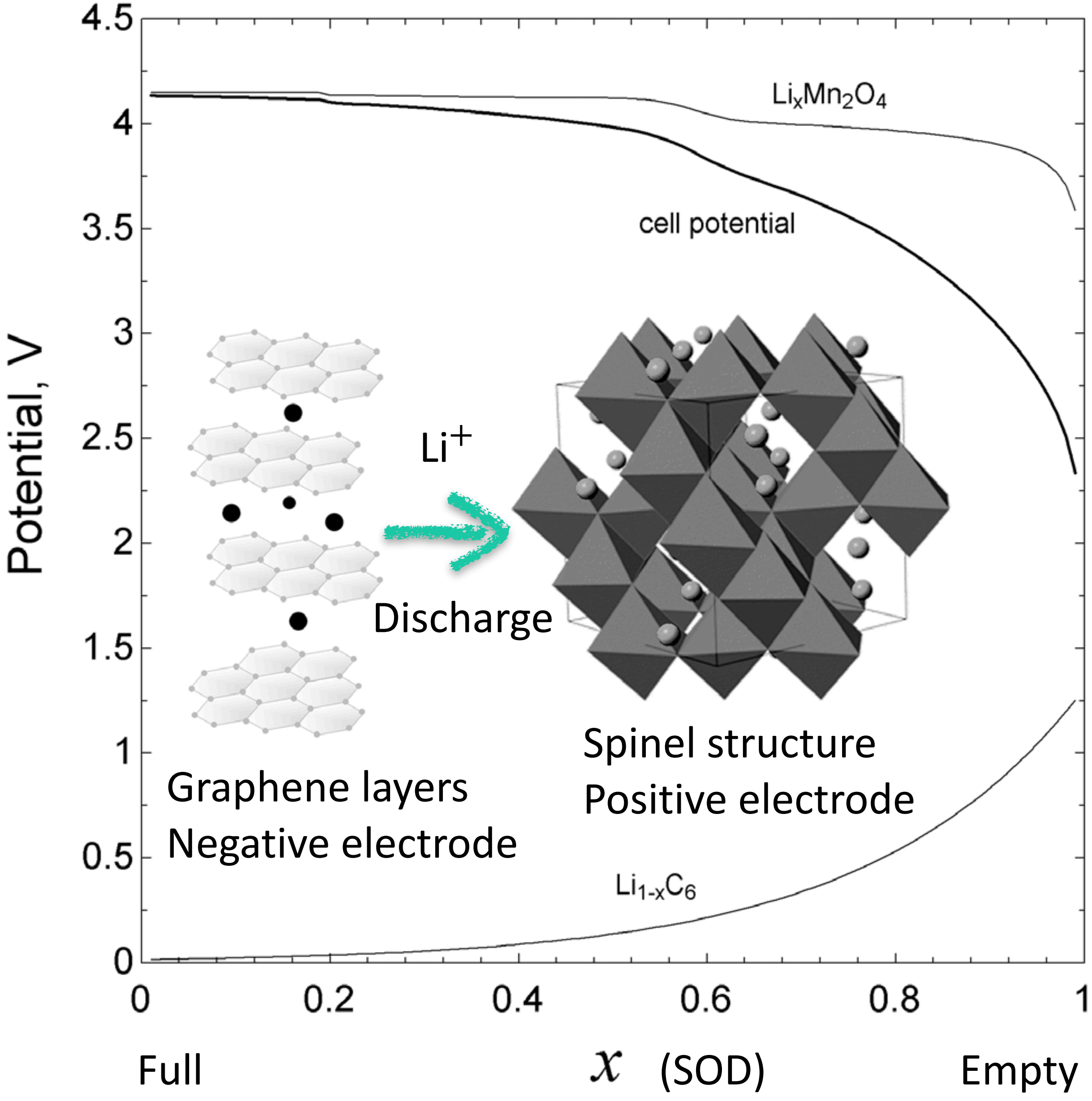
- The cell potential is increasing with increasing SOC.
- This is a consequence of concentration changes.



100 % SOC 0 % SOC

Cell Potential for Typical Li-Battery

- Negative electrode:
- $Li_{1-x}C_6 \xrightarrow{\text{discharge}} (1-x)Li^+ + (1-x)e^- + 6C$
- Positive electrode
- $xLi^+ + xe^- + Mn_2O_4 \xrightarrow{\text{discharge}} Li_xMn_2O_4$
- x from 0 to 1 during discharge.
- The potential varies with the amount of inserted lithium, see fig.
- $U^0_{\text{cell}}(x) = U^0_+(x) - U^0_-(x)$

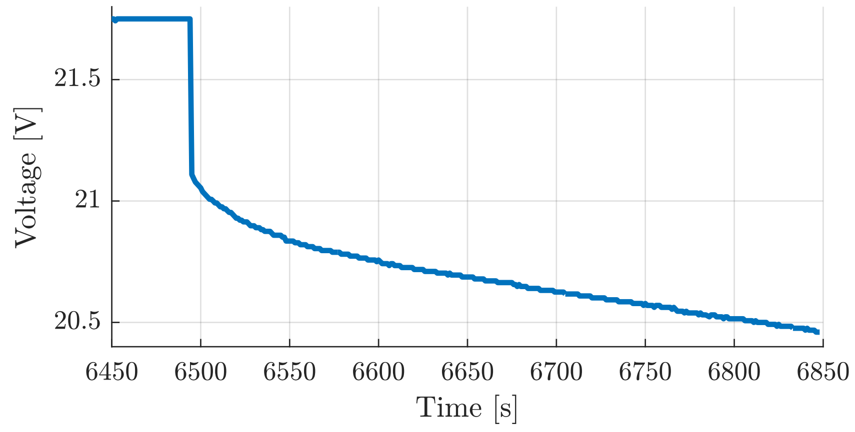


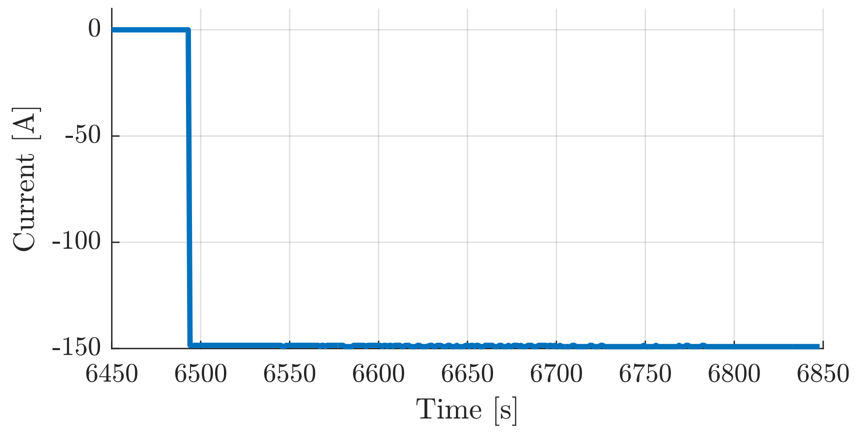
Current-voltage characteristics

A new fully charged cell

Battery Voltage at Load

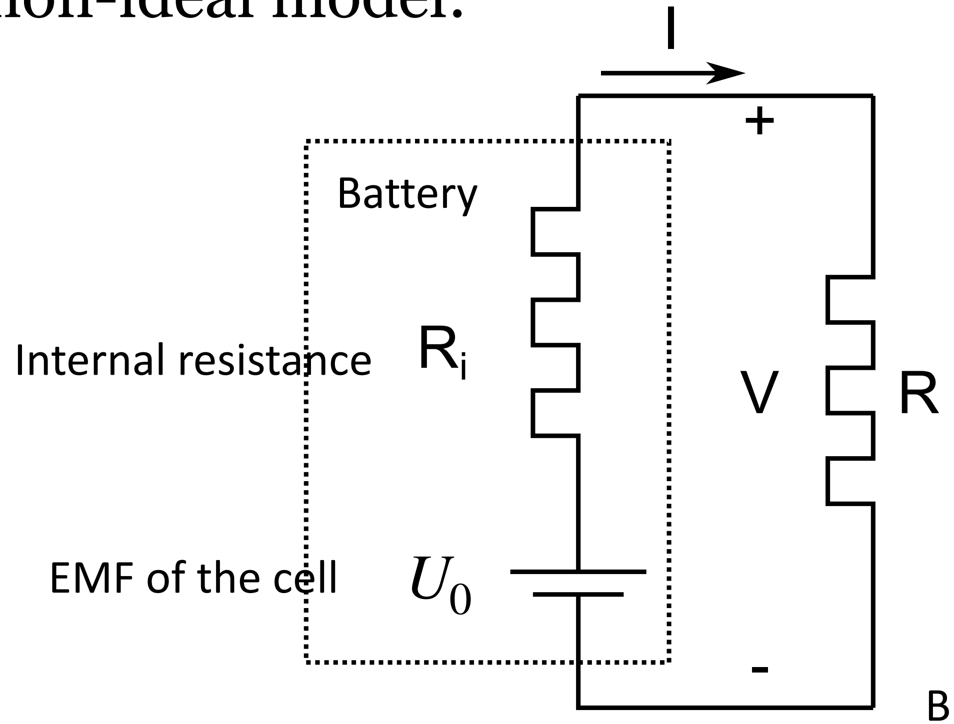
- A battery at equilibrium is started to be discharged with a 150 A current at 6500 s.
- The voltage drops instantly more than 0.5 V.
- This is partly due to internal resistance in the battery which will be discussed next.
- The change of SOC causes the almost linear voltage decrease at the scenario's end.





Battery Voltage at Load

- What does the relation between the voltage and the current look like?
- Simplest non-ideal model:

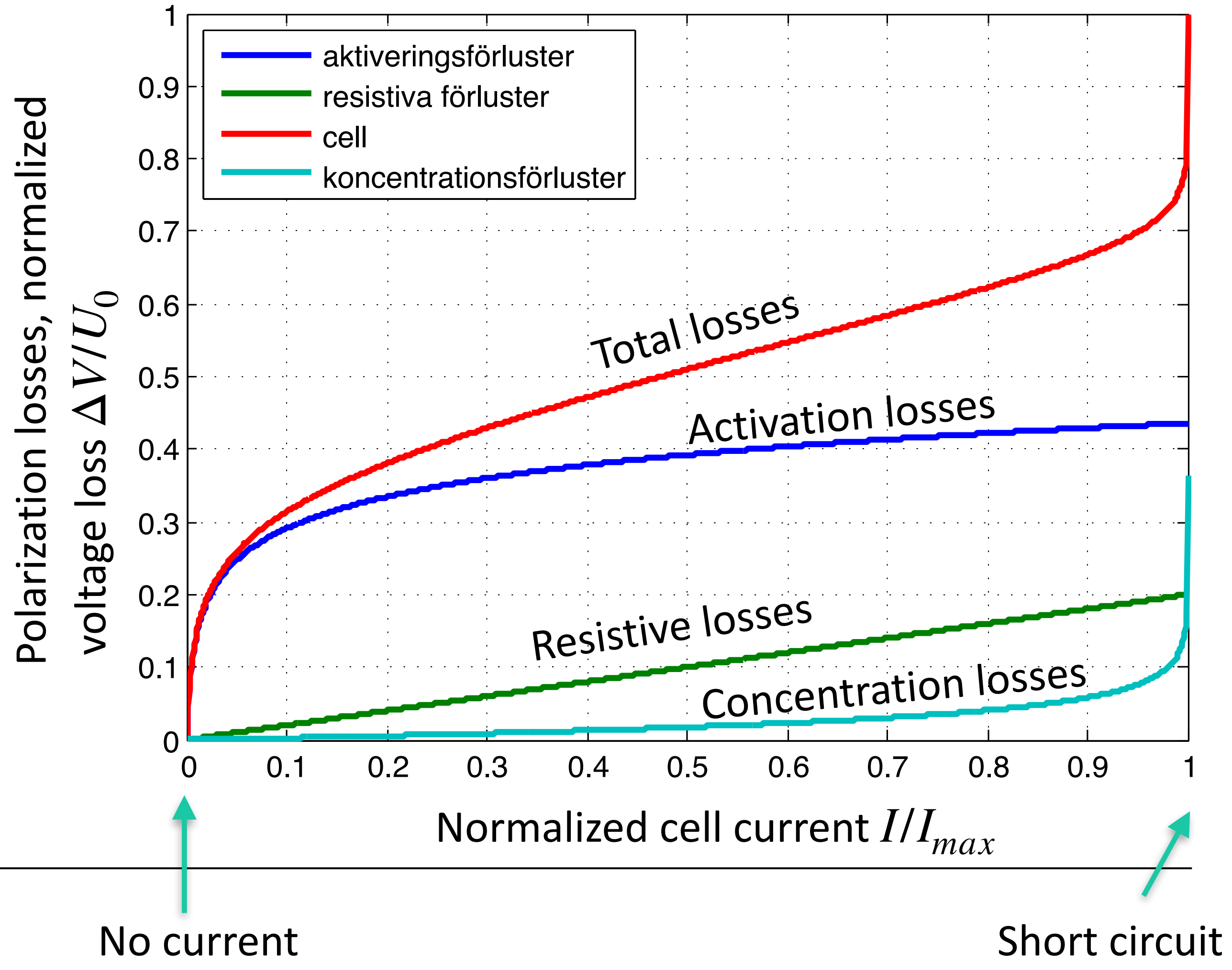


$$V = U_0 - IR_i$$

But this is a clearly simplified picture of battery losses.

Polarization losses in batteries

- The voltage drop caused by internal cell losses $\Delta V = U_0 - V$ where
  - V terminal voltage
  - U_0 OCV
- Normalized voltage loss $\Delta V/U_0$ and current I/I_{max} where I_{max} is the short circuit current.
- Low currents 0-0.2: Energy losses connected to activation of the reactions at the electrodes.
- 0.2-0.9: Energy losses linked to resistive losses in electrode contacts, ion transport in the electrolyte
- High currents 0.9-1: Losses associated with the concentration of reactants, and products are limiting



Current-voltage characteristics

Cell voltage

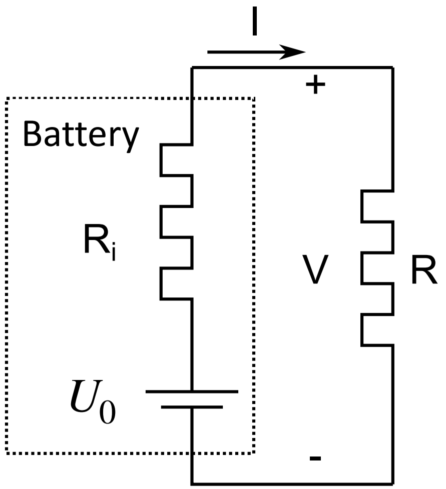
$$V = U_0 - \Delta V(I)$$

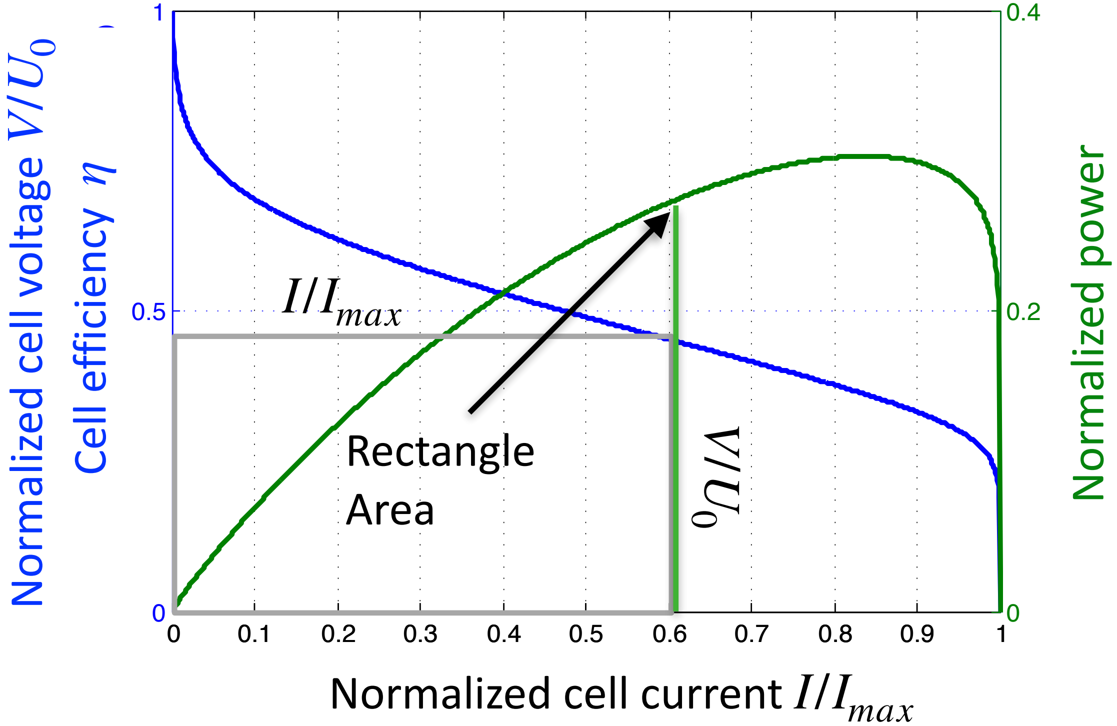
Normalized cell voltage

$$V/U_0 = 1 - \Delta V(I)/U_0$$

Instantaneous cell efficiency

$$\eta = \frac{P_{\text{load}}}{P_{\text{cell}}} = \frac{VI}{U_0 I} = \frac{V}{U_0}$$



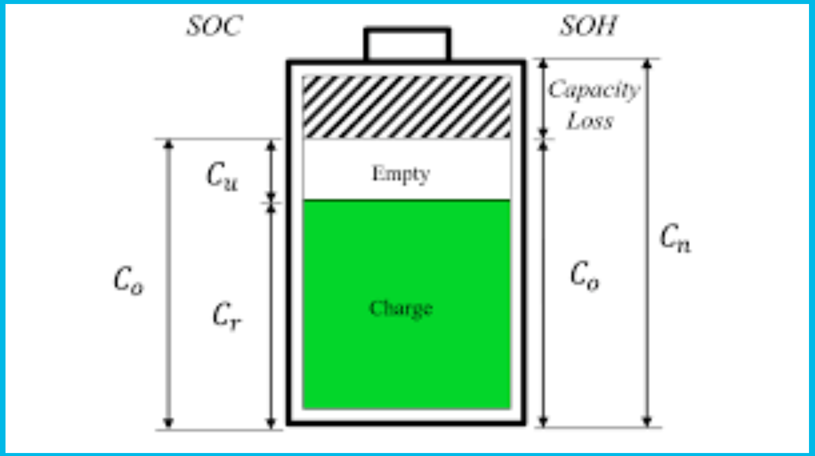


Normalized power

$$\frac{P_{\text{load}}}{U_0 I_{\max}} = \frac{VI}{U_0 I_{\max}} = \frac{V}{U_0}\frac{I}{I_{\max}} = \text{normalized voltage} \cdot \text{normalized current}$$

Battery Cycling and Aging

Charging, discharging, aging, SOH



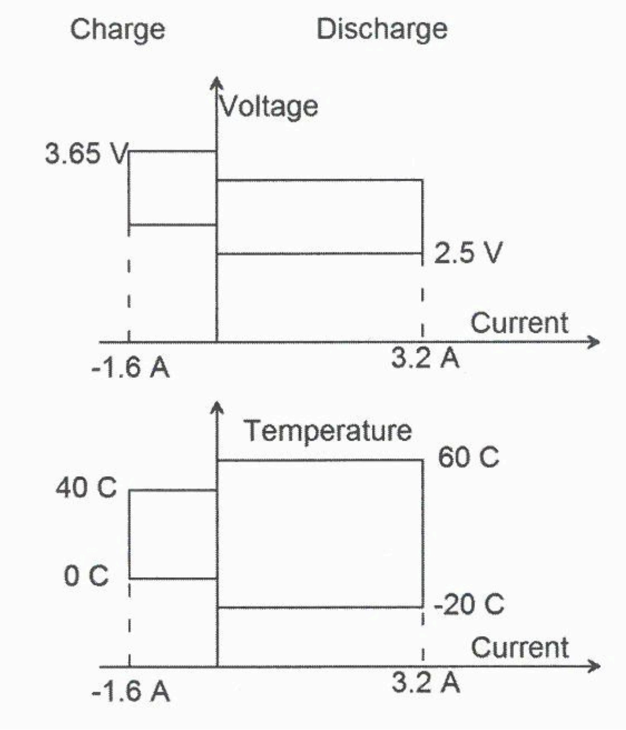
Safe operation

Reduction or damage to cell

- Over-discharge
- Charging, discharging outside certain temperature bounds
- Charging, discharging with high currents

Dangerous abuse

- Overheating cause by over-current, over-voltage, over-charging, or external heat.
- Piercing, crushing



Charging algorithm - CCCV

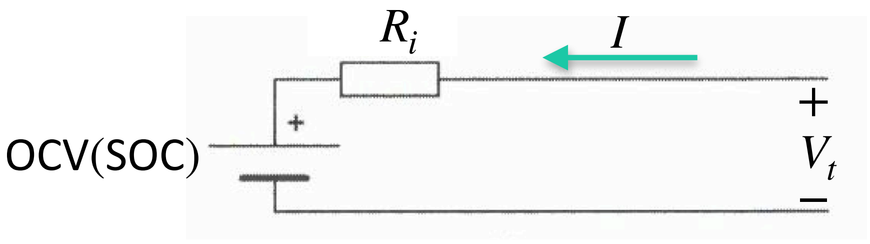
Constant current constant voltage (CCCV) charging

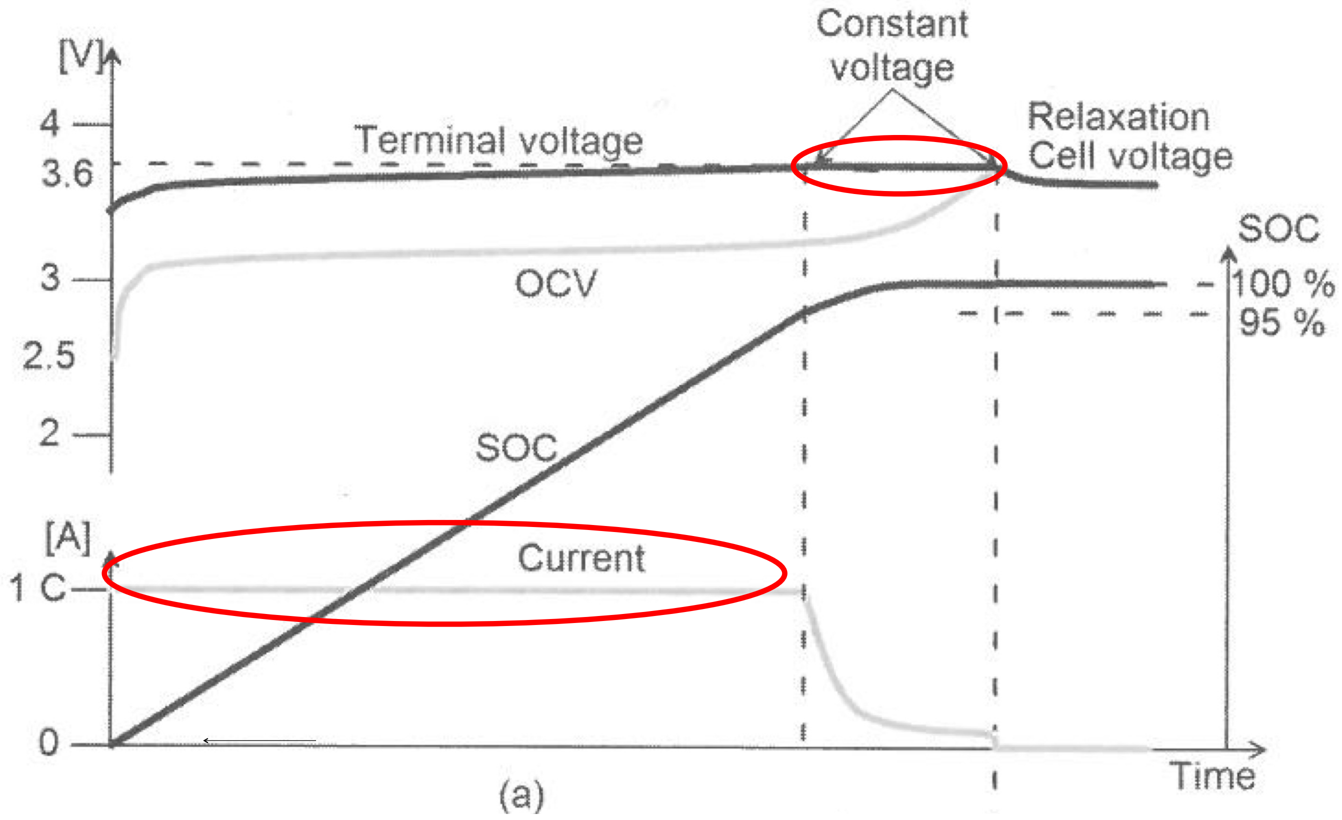
Constant current charging, I fixt:

$V_t = \text{OCV(SOC)} + IR_i$

Switch when terminal voltage V_t reaches voltage threshold V_{max} to constant voltage charging, $V_t = V_{\text{max}}$:

$I = (V_{\text{max}} - \text{OCV(SOC)})/R_i$

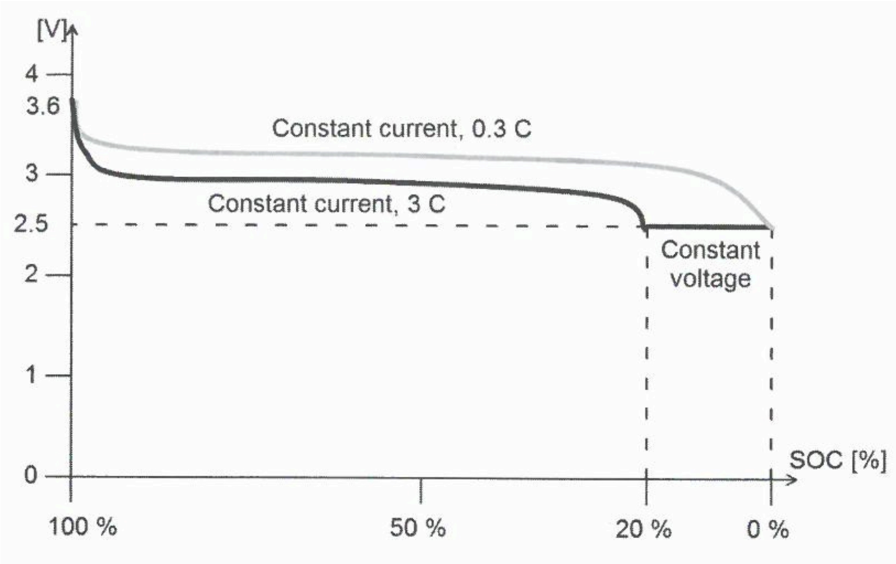


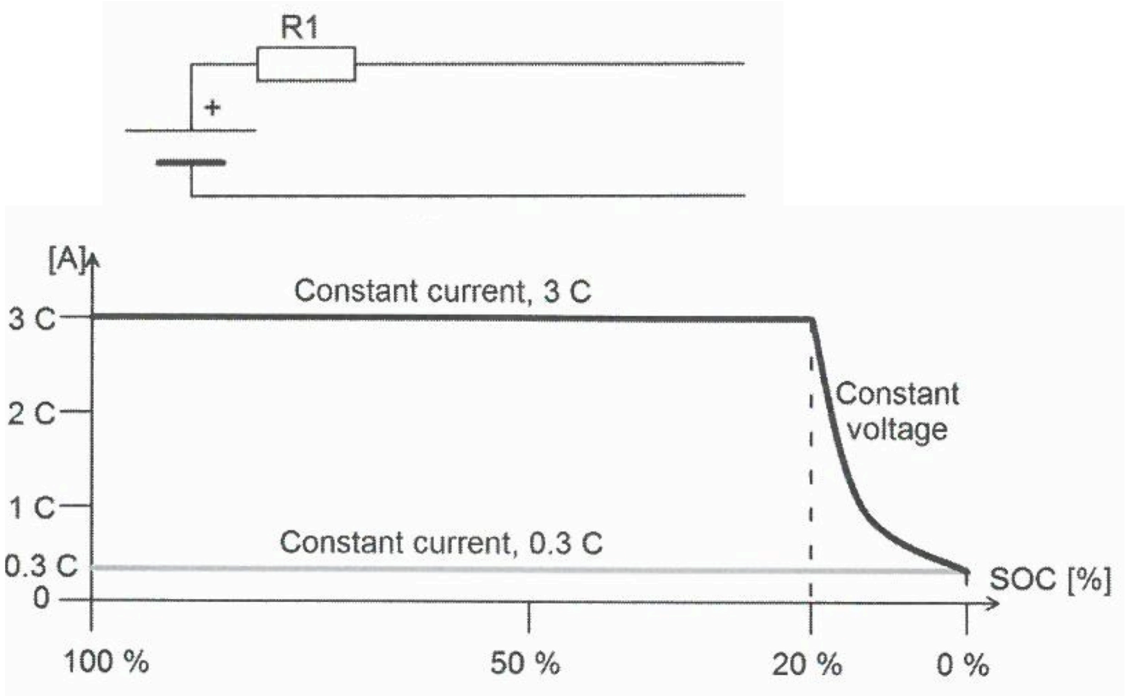


Discharging

Constant current discharge until a specified cut-off voltage V_{co} is reached.

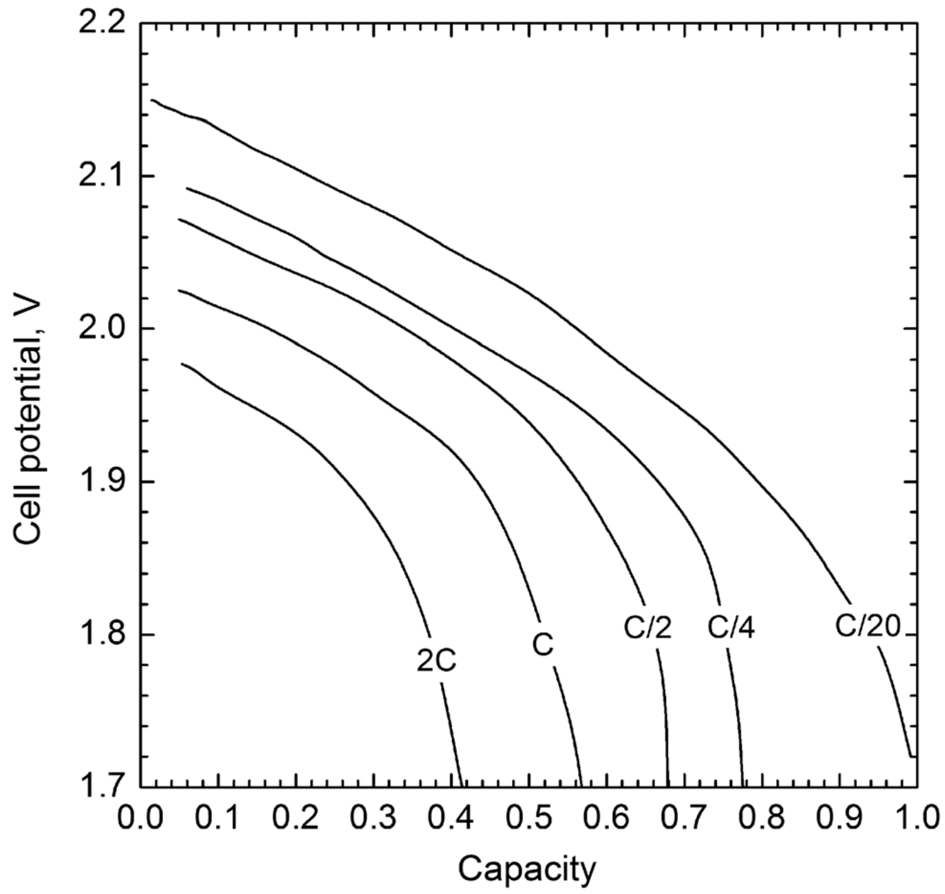
The available capacity depends on the required current (discharge rate)





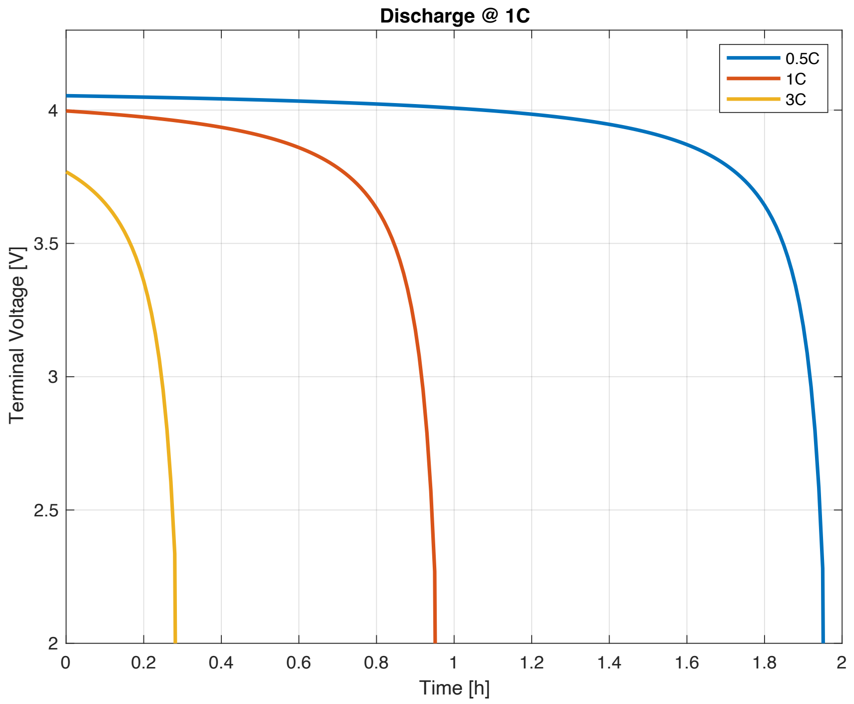
Effect of Current Rate on Cell Voltage and Available Capacity

- Cell voltage as a function of fractional capacity for a lead-acid battery discharged at different constant currents.
- At low currents C/20 all capacity is available.
- At higher currents, the cut-off voltage is reached at a fractional capacity much smaller than 1.



Shepherds Equation

- Empirical model for terminal voltage at constant discharge current I:
- $$V(t) = U - IR_{\text{int}} - K\left(\frac{Q}{Q - It}\right)I + Ae^{BIt/Q}$$
- Q [Ah] battery capacity
- It = DoD [Ah] depth of discharge
- U [V], R_{int} [Ω], A [V], B [-], K [V] are empirical constants.
- A model to empirically fit discharge curves and evaluate how available charge and energy depend on the discharge current.

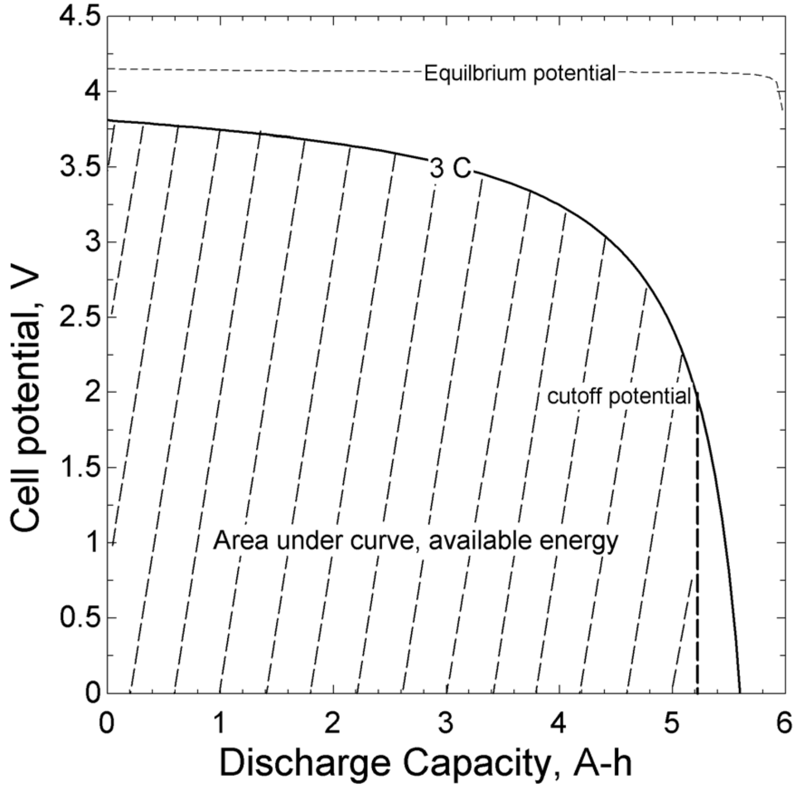


Available Charge and Energy for Different Discharge Currents

- The available charge Q_{avail} for a given discharge current I can be computed as:
- The discharge ends at $t = t_{\text{end}}$ when the cut-off voltage is reached $V(t_{\text{end}}) = V_{\text{co}}$.
- $Q_{\text{avail}} = I \cdot t_{\text{end}}$
- Available energy is given by
- $E_{\text{avail}} = \int_0^{t_{\text{end}}} p(t)dt = \int_0^{t_{\text{end}}} V(t)Idt =$

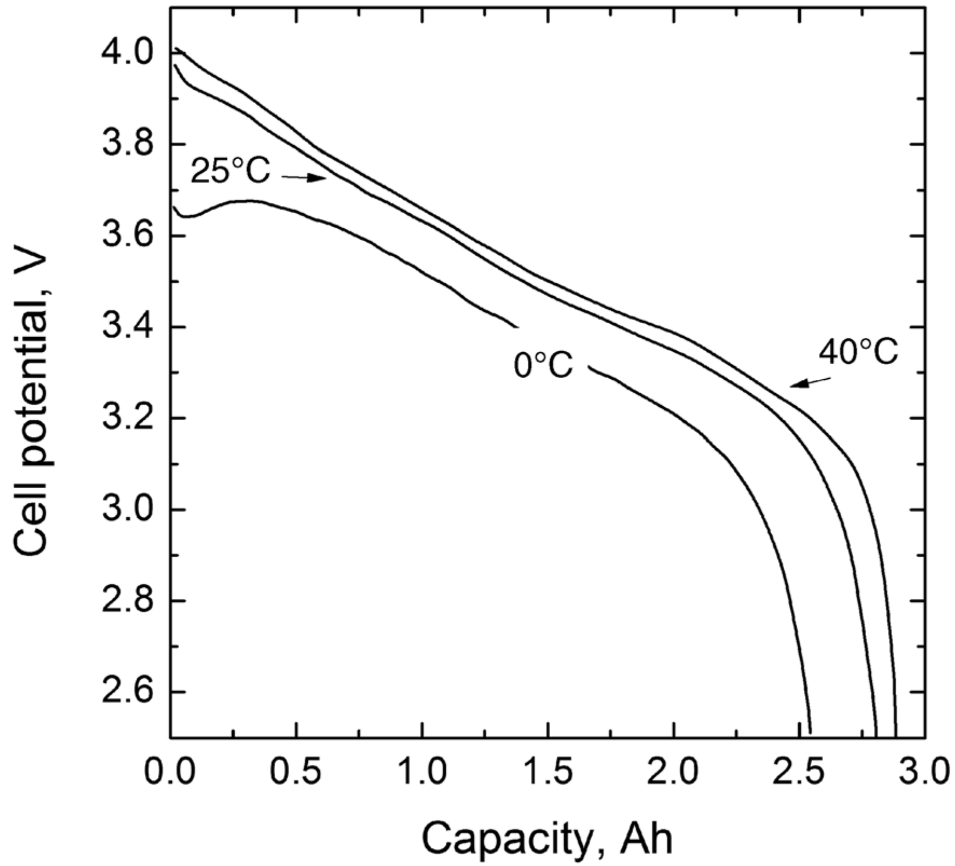
  / Variable substitution Q = It, dQ = I dt, Q: 0 → Q_{avail} /

  $= \int_0^{Q_{\text{avail}}} V(Q)dQ$



Capacity Dependence on Temperature

- The thermodynamic potential is not much dependent on temperature.
- Higher temperature reduces resistance and polarization, increasing the available capacity for a specific discharge current.
- Temperature effect on cell voltage during discharge of a lithium-ion cell.

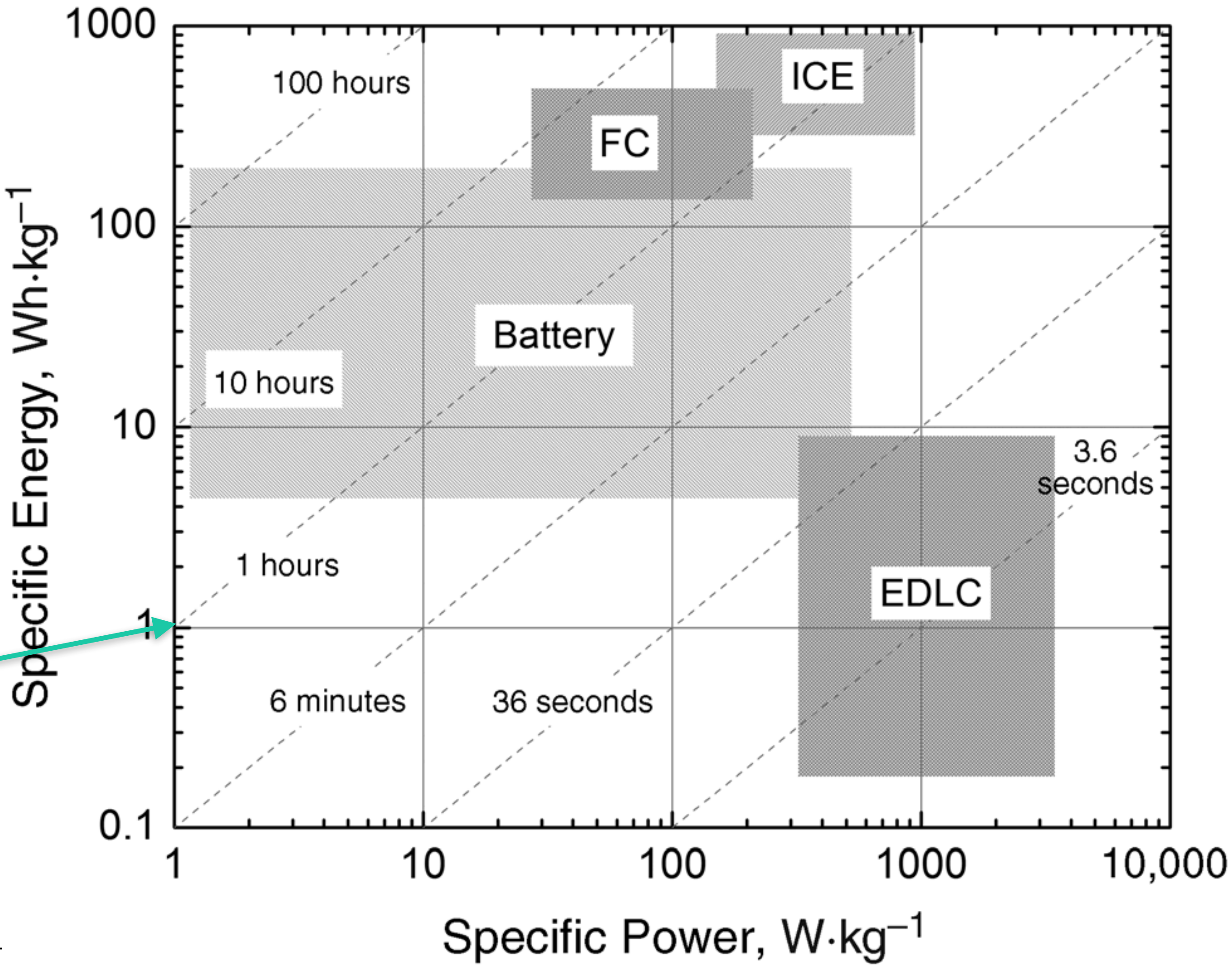


Ragone Plots

- Ragone plots show the trade-off between power and energy
- 45˚ - lines correspond to a specific runtime
- Ex:
  - E = 1 Wh
  - P = 1 W
  - => Runtime =E/P = 1h
- Shows the potential for different technologies

Fuel Cell

Internal Combustion Engine



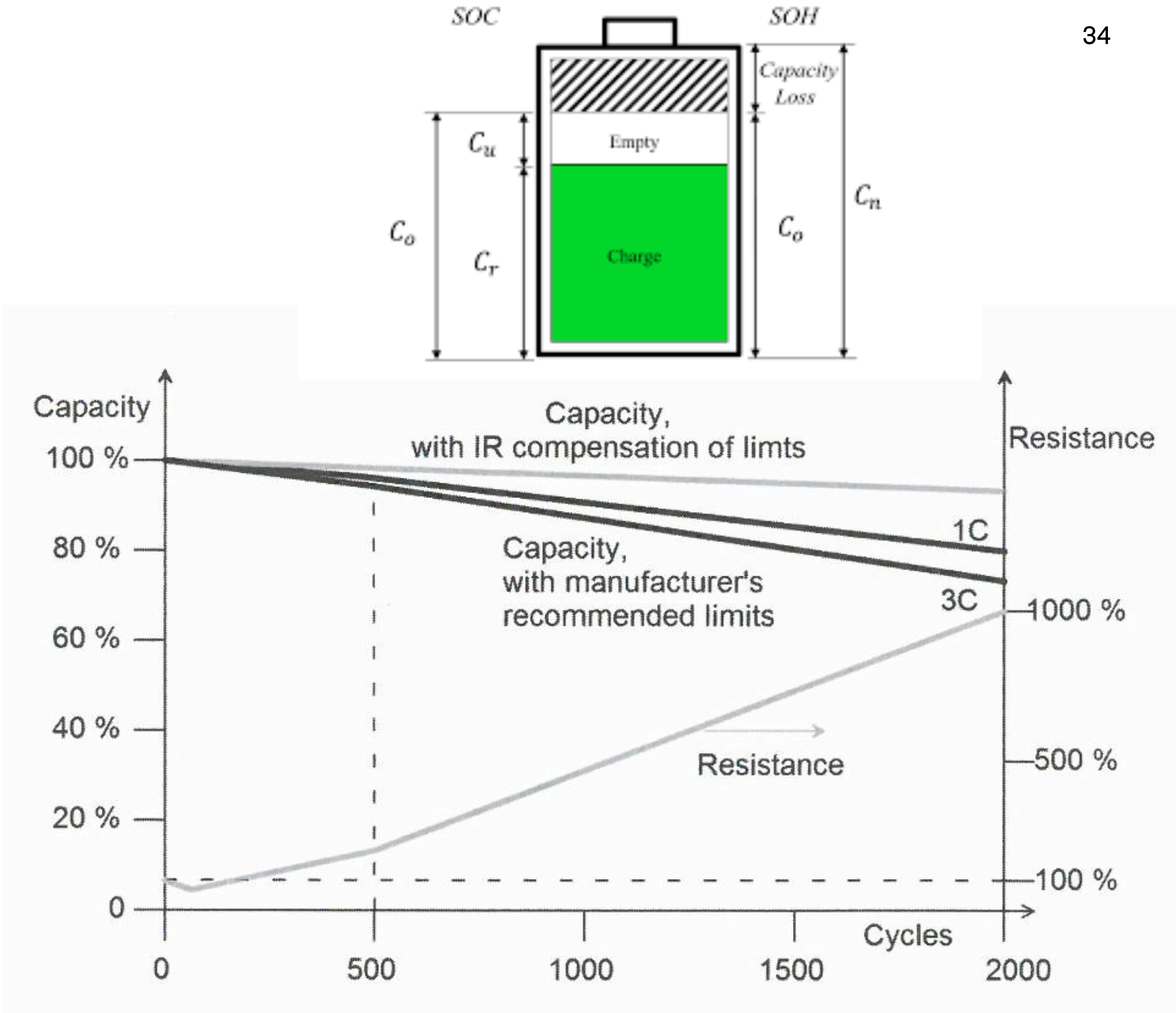
Electrochemical Double-Layer Capacitors = Supercapacitors

Efficiency of Rechargeable Cells

- The following efficiencies are defined for a complete charge-discharge cycle:
- Coulombic efficiency: $\eta_{\text{coul}} = \dfrac{\text{Number of Coulombs on discharge}}{\text{Number of Coulombs on charge}} \times 100\,\%$
- Voltage efficiency: $\eta_V = \dfrac{\text{Average discharge voltage}}{\text{Average charge voltage}} \times 100\,\%$ (depends on I)
- Energy efficiency : $\eta_{\text{energy}} = \dfrac{\text{Energy out}}{\text{Energy in}} \times 100\,\%$ (depends on I)
- The energy (round-trip) efficiency is $\eta_{\text{energy}} = \eta_{\text{coul}} \cdot \eta_V$

Ageing

- Aging factors
  - Usage e.g. number of charging/discharging cycles
  - Calendrical ageing
- Aging effects
  - Energy capacity decreases
  - Internal resistance increases causing power loss
  - The end of battery life is usually considered as falling below 80% of nominal capacity.
- The **state of health (SOH)** refers to capacity fade and/or resistance increase and goes from 100 % for a new cell to 0 % at the end of life.



Learning Outcomes

- Battery design, sketch the parts, explain types such as cylindrical, prismatic, …
- Be able to use C-rate, SOC, SOD, DOD, OCV as a function of SOC
- Safe operation regions and the risks of being outside them, e.g., upper and lower cut-off voltage.
- CCCV-charging.
- Effect of current rate and temperature on cell voltage and available discharge capacity
- Shepherds equation
- Round-trip Coulombic, voltage, and energy efficiency
- Aging effects: capacity fade, resistance increase
- SOH, end-of-life is often considered to be at 80% remaining capacity.

TSFS19 Battery Systems - Lecture 2

Mattias Krysander

www.liu.se

LINKÖPINGS UNIVERSITET