Energy Storage

3. Batteries

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Batteries - definition

- Electrochemical devices
- Potential difference between two different metals submerged in an electrolyte solution
- Potential difference enables generation of the electrical energy
- Chemical energy is converted to electrical energy by an electrochemical process – therefore, batteries have efficient energy conversions

Basic division

- Primary or non-rechargeable – cannot be recharged after a single discharge cycle
  - Zinc-carbon
  - Zinc-chloride
  - Alkaline
  - Silver-oxide based
- Secundary or rechargeable – capable of performing multiple charging/discharging cycles

Basic division

- Reserve batteries
  - They need to be activated as one key component is isolated from the rest of the battery
  - Therefore, there is no self-discharge and battery can be in stand-by for a long period of time
  - Usually the electrolyte is isolated
  - Thermal battery – not active until heated, which causes solid electrolyte to melt and become conductive for ions
  - Reserve batteries are designed to endure long and extreme conditions, which is hard and expensive to achieve with active batteries
  - They are used in torpedos, rockets and other weapons where high power must be delivered in short time period, but also, for instance, in airplane life jackets

Basic parts

- Positive electrode:
  - electrode with higher standard electrode potencial
  - reduction or electron acceptance occurs during discharge
  - oxidation or electron release occurs during charge
- Negative electrode:
  - electrode with lower standard electrode potencial
  - oxidation or electron release occurs during discharge
  - reduction or electron acceptance occurs during charge
- Electrolyte – substance that enables ion flow between the two electrodes
- Separator – membrane that is immersed into electrolyte and used to mechanically separate electrodes

Keep in mind!

- Anode – electrode where the oxidation occurs
- Cathode – electrode where the reduction occurs
- Non-rechargeable batteries:
  - positive electrode is cathode and negative electrode is anode
- Rechargeable batteries:
  - positive electrode is cathode during discharge and anode during charge
  - negative electrode is anode during discharge and cathode during charge
  - **positive electrode and cathode, as well as negative electrode and anode, are not synonyms**

Energy flow

- Charging: electrical energy from the grid is stored in the battery in the form of chemical energy
- Disharging: chemical energy from the battery is injected into the grid in the form of electrical energy
- Outer electrical flow: electrons use the outer circuit through the grid, in order to move between the electrodes
- Inner ion flow: ions use the inner flow to move between the electrodes, either through the electrolyte (passive electrolyte) or to be stored from the electrodes to the electrolyte (active electroylte)

Battery composition

- Battery can be made of a single cell or multiple cells
- Battery cell is the smallest separable battery part which constitutes out of active parts (electrodes, electrolyte with separator)
- Cell voltage is determined by the electrochemical characteristics of the material, while capacity is determined by the size of the cell (electrode surface, amount of electrolyte…)
- Connecting multiple cells in series and/or in parallel results in a battery with higher voltage and/or capacity, respectively

Battery composition (2)

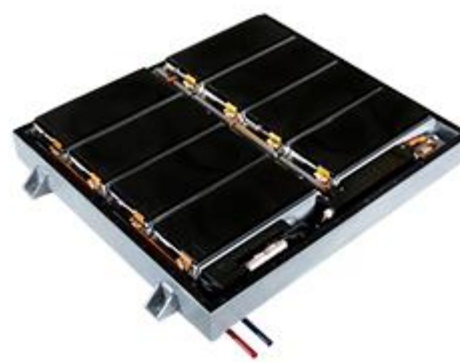
- In case of large batteries, several electrically connected cells that are enclosed in a mechanical frame are called battery module
- Mechanical frame of the battery module protects the cells against impacts, heat and vibrations
- Several modules constitute a battery or a battery pack
- Battery pack connects modules electrically and uses battery management system (BMS) to supervise, control and protect them

Battery composition – example

- Battery pack in BMW i3 consists of 96 cells, 12 cells being connected into a module and 8 modules to a pack

Battery cell

Battery module



Battery pack

Batteries

- Types of batteries:
  - Lead-acid
  - Nickel-cadmium
  - Nickel-metal-hydride
  - Lithium-ion
  - Zinc-air
  - Vanadium redox (flow battery)

Lead-acid batteries – discharging

- Two lead plates (electrodes) immersed in sulfuric acid (electrolyte)
- At 100% SOC:
  - negative electrode consists of metallic lead (Pb)
  - positive electrode consists of lead dioxide (PbO_2)
  - electroyte is concentrated sulfuric acid (H_2SO_4)
- During discharge:
  - both plates gradually transition into lead sulfate ($PbSO_4$)
  - sulfuric acid becomes ever sparser and finally transitions to water (0% SOC)

Lead-acid batteries – charging

- Two lead plates (electrodes) immersed in sulfuric acid (electrolyte)
- At 0% SOC:
  - both plates are lead sulfate ($PbSO_4$)
  - electrolyte is water
- During charge:
  - lead sulfate ($PbSO_4$) on positive electrode oxidises to lead dioxide (PbO_2)
  - lead sulfate ($PbSO_4$) on negative electrode reduces to metallic lead (Pb)
  - electrolyte becomes concentrated sulfuric acid

Lead-acid batteries – features

- In lead-acid batteries, electrolyte participates in chemical reactions when charging/discharging and its density may be used as a SOC measure
- Admixtures are often added to lead electrodes in order to improve their characteristics, e.g. antimony, calcium, tin and selenium
- One of the basic development directions of lead-acid batteries is adding carbon based materials to the negative electrode in order to reduce sulfation, increase conductivity and charge acceptance

Lead-acid batteries – pros

- High reliability
- Low price (low investment cost per power)
- High specific power (discharge power)
- Medium life-time duration
- No memory effect
- Low self-discharge rate
- Perform well at low, even negative temperatures

Lead-acid batteries – cons

- Low specific energy
- Slow charge, cannot be charged fast
- Must be stored with high SOC, as low SOC leads to sulfation

Lead-acid batteries – divison

- By type of electrolyte:
  - Flooded - non-sealed with liquid electrolyte
  - VRLA (Valve Regulated Lead-Acid) - sealed
    - AGM (Abosrbent Glass Mat)
    - GEL
- Flooded batteries produce gas if overcharged – this gas must be released
- VRLA batteries have a valve which releases gases in the extreme conditions, while during the normal operation gases recombine inside the battery
- VRLA advantages over the flooded batteries
  - Do not require regular addition of water (often advertised as ”maintenance free”)
  - Cannot spill its electrolyte when inverted

Lead-acid batteries – divison

- AGM batteries have fiberglass linings which absorbs sulfuric acid
- Higher cycle count, as well as higher charge/discharge currents in comparison to flooded batteries
- Less prone to sulfation
- Depth of discharge up to 80%, as opposed to the flodded batteries, which achieve depth of discharge up to 50%
- Higher manufacturing price and somewhat lower specific energy compared to the flooded batteries

Lead-acid batteries – divison

- GEL contains gelified electrolyte (sulfuric acid is mixed with sillicon dioxide based polymer)
- Better heat transfer compared to the AGM batteries -> longer life-time
- Slower capacity fade during working life in comparison to the AGM batteries
- Higher manufacturing costs compared to AGM batteries

Nickel-based batteries – division

- Nickel-cadmium batteries (NiCd)
- Nickel-metal-hydride batteries (NiMH)
- Nickel-cadmium batteries ruled the world of portable devices for more than 50 years
- Due to the problems with toxicity they are being replaced by nickel-metal-hydride batteries

NiCd – parts

- NiCd battery consists of:
  - Nickel oxide hydroxide ($NiO(OH)$) as positive electrode
  - Metallic cadmium (Cd) as negative electrode
  - Alkaline electrolyte (usually potassium hydroxide, KOH, in distilled water)
  - Separator

NiCd – charging/discharging

- During discharge:
  - positive electrode transitions to nickel hydroxide ($Ni(OH)_2$)
  - negative electrode transitions to cadmium hydroxide ($Cd(OH)_2$)
- During charge, the reverse reactions occur
- Electrolyte does not take part in the reactions, so it cannot be used as a SOC measure like with lead-acid batteries

NiCd – discharging

- Chemical reaction on negative electrode during discharge:

  $$Cd + 2OH^{-} \rightarrow Cd(OH)_2 + 2e^{-}$$

- Chemical reaction on positive electrode:

  $$2NiO(OH) + 2H_2O + 2e^{-} \rightarrow 2Ni(OH)_2 + 2OH^{-}$$

- Overall reaction during discharge:

  $$2NiO(OH) + Cd + 2H_2O \rightarrow 2Ni(OH)_2 + Cd(OH)_2$$

NiCd – features

- High number of cycles
- Fast charging
- Operation at low temperatures
- High profitability considering price per cycle

- Low specific energy
- Memory effect
- Toxicity of cadmium
- High degree of self-discharge
- Low cell voltage

NiMH – parts

- Positive electrode is, as in NiCd batteries, nickel oxide hydroxide (NiO(OH))
- Electrolyte is again alkaline (usually potassium hydroxide, KOH)
- Cadmium negative electrode is substituted with the hydrogen-absorbent alloy, metal hydride
- During discharge positive electrode gradually transitions to nickel hydroxide ($Ni(OH)_2$), while metallic negative electrode releases ions (OH^-) and receives hydrogen
- During charging, the reverse reactions take place

NiMH – features

- No problems with electrode toxicity
- Higher capacity
- Less prone to memory effect compared to NiCd
- Downsides:
  - Limited working life with deep discharges
  - Require complex charging algorithm (sensitive to overcharge)
  - Heat up during fast charges and discharges
  - Low cell voltage
  - High degree of self-discharge
  - Very low coulombic efficiency

Lithium-ion batteries (LIB)

- Named after lithium ions which travel among electrodes during chemical reactions of charging and discharging
- Higher capacity
- Conventional li-ion battery consists of:
  - Negative carbon electrode (e.g. graphite, C_6)
  - Positive lithium metal oxide electrode (e.g lithium cobalt oxide, $LiCoO_2$)
  - Electrolyte is lithium salt in an organic solvent
- Both electrodes allow lithium ions to go in and out of their structures

LIB charging/discharging

- During discharge, lithium ions (Li^+) and electrons travel from negative to positive electrode through electrolyte and circuit, respectively
- Discharge is possible until the negative electrode becomes pure graphite (C_6), i.e. it loses all the lithium, while in the meantime the positive electrode transitions to lithium cobalt oxide ($LiCoO_2$)
- During charging, the process is reversed and lithium ions (Li^+) and electrons travel from positive ($LiCoO_2$) to negative electrode (C_6)
- Process is possible until positive electrode loses all the lithium and becomes cobalt oxide (CoO_2)

LIB charging/discharging

- Reaction on positive electrode:

  $$CoO_2 + Li^+ + e^- \leftrightarrow LiCoO_2$$

- Reaction on negative electrode:

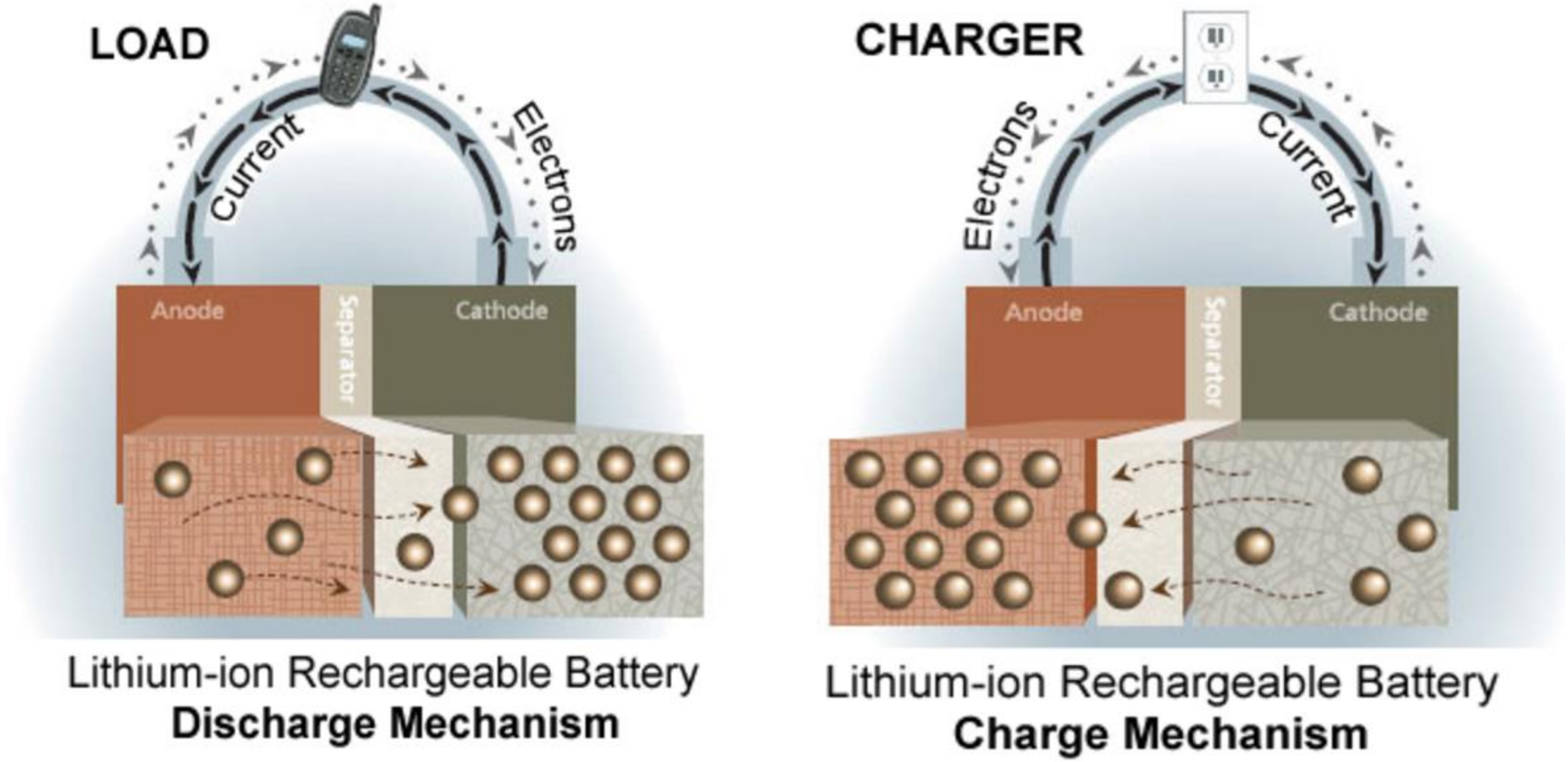
  $$LiC_6 \leftrightarrow C_6 + Li^+ + e^-$$

- Overall reaction (charged state is on the left, discharged on the right):

  $$LiC_6 + CoO_2 \leftrightarrow C_6 + LiCoO_2$$

- Too deep discharge causes oversaturation of lithium cobalt oxide and formation of lithium oxide Li_2O
- Overcharge causes cobalt(IV) oxide to synthesize

LIB charging/discharging



LIB positive features

- High specific energy
- Good discharge possibilities
- Long working life, no need for maintenance
- Low internal resistance
- Good coulombic efficiency
- Simple charging algorithm
- Short charging time
- Low self-discharge

LIB negative features

- Need for Battery Management System (BMS)
- Degradation at high temperatures and voltages
- Hard or impossible charging at low temperatures

LIB – positive electrode

- LIB batteries can be divided by electrode materials
- Positive electrode (underlined are commercially available):
  - <u>Lithium cobalt oxide – $LiCoO_2$ (LCO, ICR)</u>
  - Lithium nickel oxide – $LiNiO_2$ (LNO)
  - <u>Lithium nickel cobalt aluminum oxide – $LiNi_xCo_yAl_zO_2$ (NCA, NCR)</u>
  - Lithium manganese dioxide – $LiMnO_2$ (LMO)
  - Lithium nickel manganese oxide – $LiNi_{0.5}Mn_{0.5}O_2$ (NMO)
  - <u>Lithium nickel manganese cobalt oxide – $LiNi_xMn_yCo_zO_2$ (NMC, CGR, INR)</u>
  - <u>Lithium manganese oxide – $LiMn_2O_4$ (LMO, IMR)</u>
  - <u>Lithium iron phosphate – $LiFePO_4$ (LFP, IFR)</u>

LIB – negative electrode and electrolyte

- Negative electrode (underlined are commercially available):
  - <u>Graphite – C_6</u>
  - Hard carbon
  - <u>Lithium titanate – $Li_4Ti_5O_{12}$ (LTO)</u>
  - Silicon/carbon alloy
- Electrolyte – lithium salts in organic solvent (this division does not alter features like various electrode materials):
  - Organic solvent is most commonly ethylene carbonate ($(CH_2O)_2CO$), dimethyl carbonate ($OC(OCH_3)_2$) or diethyl carbonate ($OC(OCH_2CH_3)_2$)
  - Lithium salts can be lithium hexafluorophosphate ($LiPF_6$), lithium hexafluoroarsenate monohydrate ($LiAsF_6$), lithium perchlorate ($LiClO_4$), lithium tetrafluorborate ($LiBF_4$) or lithium trifluoromethanesulfonate ($LiCF_3SO_3$)

LIB – separator

- Immersed in electrolyte is separator, a thin porous plastic sheet, the function of which is electrical separation of the electrodes
- Separator allows lithium ion flow, but prevents electron flow through the electrolyte
- Besides being thin and very porous, separator must be able to soak up in electrolyte
- Separator can be made of polyethylene (PE), polypropylene (PP) or their combination

LIB – separator

- LIB can be:
  - Conventional Li-ion
  - Li-polymer
- Conventional LIB uses separator with bigger pores which is immersed in a liquid electrolyte
- Li-polymer uses gel electrolyte with a micro-porous separator
- The amount of electrolyte is about the same
- Upside of Li-polymer batteries is somewhat higher specific energy and fact that cells can be produced thinner than those with conventional separator
- Downside is higher price

LIB – basic cell parts

- Besides active electrochemical parts, LIB cell contains:
  - Positive terminal – conductive material which connects positive battery pole with the positive pole of the outer circuit, i.e. with the positive pole of the electric load (or grid)
  - Negative terminal – conductive material which connects negative battery pole with the negative pole of the outer circuit, i.e. with the negative pole of the electric load (or grid)
  - Positive current collector – thin metal sheet used to electrically connect positive electrode with the positive terminal, usually made of aluminum alloys
  - Negative current collector – thin metal sheet used to electrically connect negative electrode with the negative terminal, usually made of nickel alloys or copper alloys

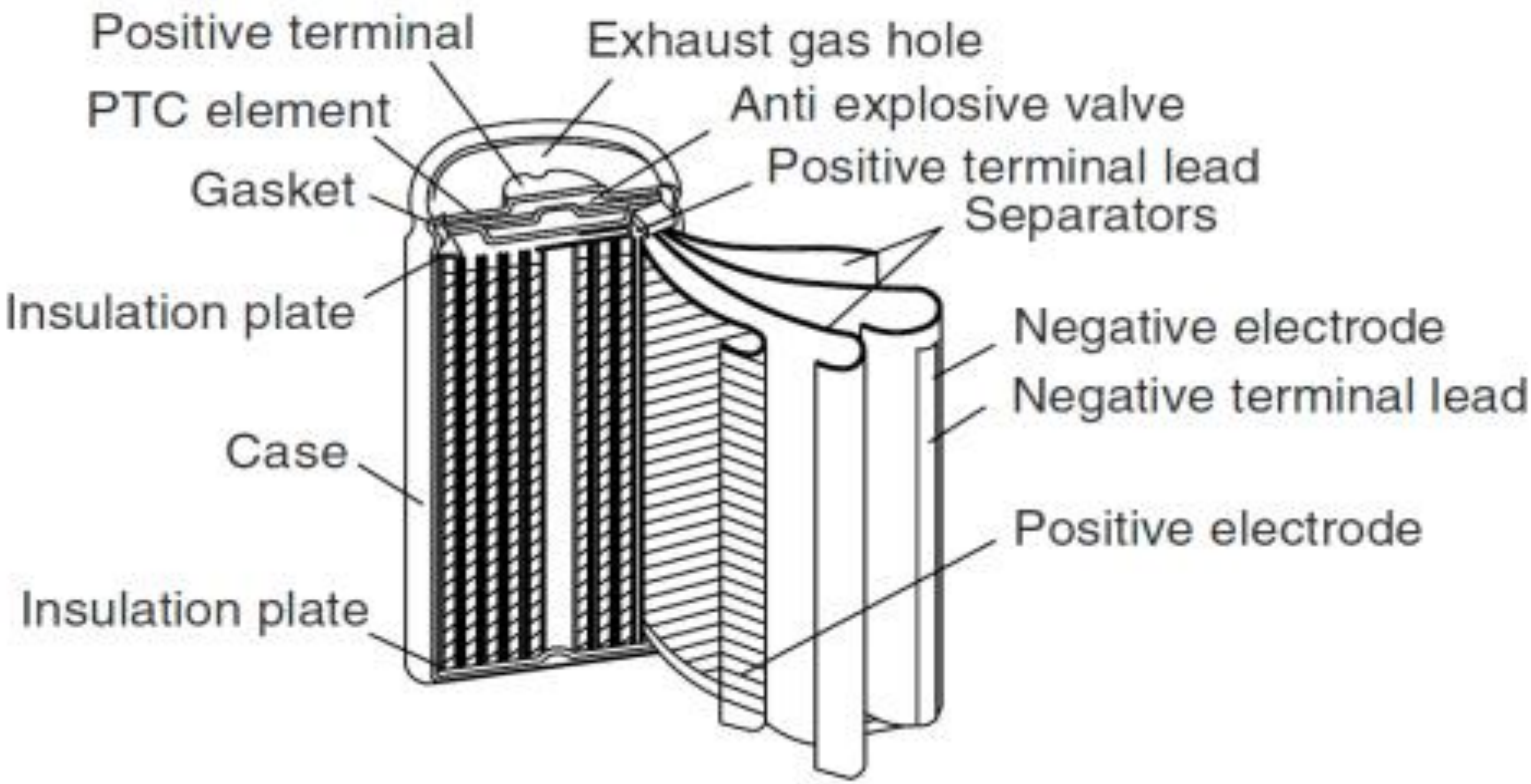
LIB – integrated cell protection

- Metal frame
  - Used to cover active cell parts, thus providing mechanical protection and facilitating its transport
- Isolation plates
  - Thin plastic sheets which electrically isolate conductive cell parts thus preventing short circuit occurrence
- Insulation gasket
  - Insulation material which fills the space between the metal frame (negative terminal) and positive terminal
- Positive temperature coefficient element (PTC element)
  - Conductive materal used for limiting currents at high temperatures

LIB – integrated cell protection (2)

- Anti-explosive valve
  - Mechanical device used to prevent explosion of the battery
  - When pressure inside the cell rises significantly, anti-explosive valve breaks due to activity of the inner pressure forces
  - Circuit disconnects and the battery can no longer be used
  - Usually placed between the PTC element and isolation plate
- Exhaust gas hole
  - Mechanism for venting gases surplus when anti-explosive valve is opened
  - Holes are placed on the positive terminal of the battery
  - Gases within the battery can appear due to improper operation, e.g. cell overcharge, physical damage or inner short circuits

LIB – cell parts



LIB – cell shape

- Cylindrical solid frame

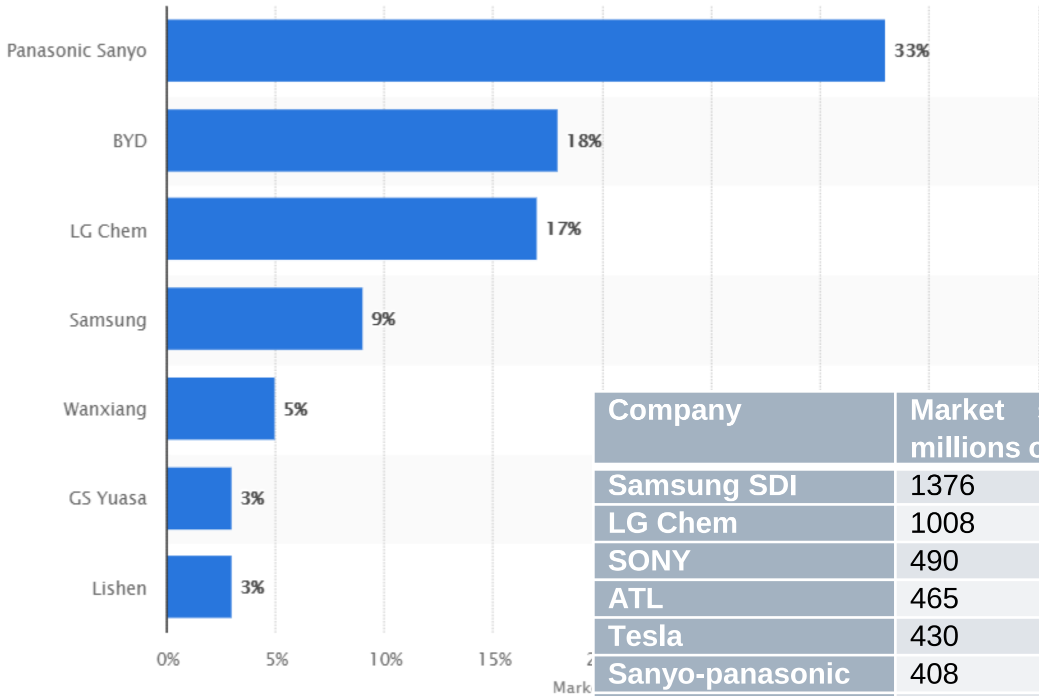
- Prismatic solid frame

LIB – cell shape

- Pouch cell
  - Cells can be constructed in any shape, but they are most commonly prismatic

- Button Cell
  - Solid frame

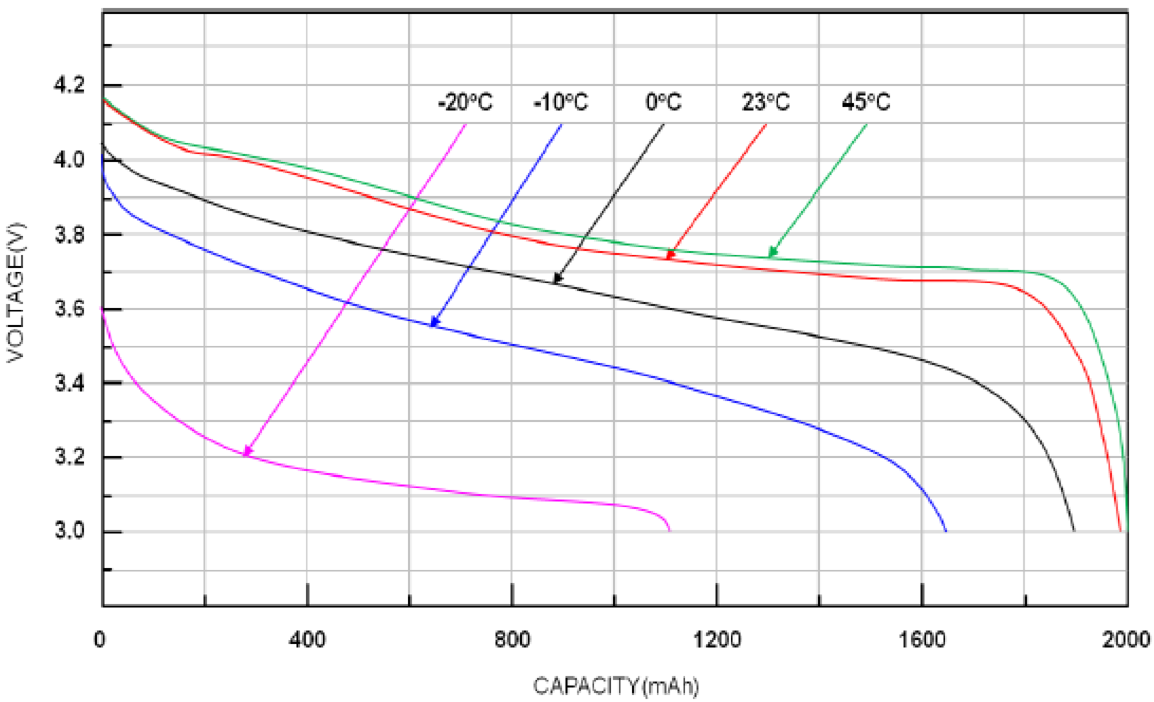
LIB cell market



Company	Market share (in millions of cells)	Company	Market share (in millions of dollars)
Samsung SDI	1376	Samsung SDI	3000
LG Chem	1008	LG Chem	2530
SONY	490	ATL	1490
ATL	465	Sanyo-panasonic	1125
Tesla	430	BYD	1120
Sanyo-panasonic	408	SONY	1040
Lishen	290	Tesla	970
Coslight	185	Lishen	850
BYD	180	NEC	520
Maxell	76	Coslight	450
BAK	67	GS Yuasa	210
Others	625	Others	3395
In total	5600	In total	16700

Capacity and environment temperature

- LIB capacity drops with temperature



Storage of LIB

- When storing LIB, losses occur for two reasons:
  - Self-discharge of the battery (energy loss)
  - Overall battery capacity reduces as the time passes, the so called ”calendar aging”
- LIB should not be stored completely empty, because the battery voltage can drop below the minimum allowed value due to self-discharge
- On the other hand, storing LIB at high SOC values leads to faster calendar aging of the battery
- Optimal SOC for storaging LIB is 30-50%

Battery cell features

Battery	Nominal voltage	Efficiency	Specific energy
Lead-acid	2 V	50-85%	35-40 Wh/kg
NiCd	1.2 V	70-90%	40-60 Wh/kg
NiMH	1.2 V	70-90%	60-120 Wh/kg
Li-ion	3.2-3.7 V	80-95%	100-265 Wh/kg
Zinc-air	1.65 V	?	450 Wh/kg
Vanadium	1.4 V	75-80%	100 Wh/kg

Battery selection

1. *Battery type:* Primary, secundary or reserve
2. *Electrochemical system:* Harmonize pros and cons of the battery technology with the usage requirements
3. *Voltage:* Nominal or operating voltage, high and low voltage limits, voltage control, profile of the discharge curve, start-up time
4. *Load current profile:* Constant current, constant resistance or constant power; current value, fixed or variable load, pulsating load
5. *Cycling:* Permanent or occasional, cycling schedule
6. *Temperature requirements:* Operating temperature span

Battery selection

7. *Working life:* Required operating duration
8. *Physical requirements:* Size, shape, mass, connectors
9. *Standing time:* Active or reserve battery, change in SoC during standing, temperature and humiditiy influence
10. *Charge and discharge cycle:* Requirements on charging and discharging, degradation, charging efficiency
11. *Environment:* Vibration, atmospheric conditions (pressure, humidity)
12. *Safety and reliability:* Number of failures; usage of potentially flammable and toxic materials; gas exhaust and leakage; ecological acceptability

Battery selection

13. *Special requirements:* Long-term storage; extreme temperatures; high reliability for special applications; fast activation in case of reserve batteries; special packaging; special mechanical requirements like resistance to impacts or acceleration, non-magnetism etc.
14. *Maintenance:* Simple installation; simple replacement; availability of chargers; requirements on transport and disposal
15. *Price:* Investment costs; operation costs; usage of exotic (expensive) materials

Batteries pros and cons

Advantages	Limitations
Independent electrical power source	High electrical energy price compared to the electric power system
Adaptability to the user: • Small size and mass • Various voltages, sizes and configurations	Usage of expensive materials
Efficient conversion for various applications	Low energy density
Reliability, safety, no moving parts	Limited standing time

Battery degradation

- State of Charge (SoC)
- Depth of Discharge (DoD)
- SoC + DoD = Capacity
- Repeated deep discharges have a negative influence on batteries' working life, as they reduce the available capacity more quickly than moderate discharges
- The deeper the discharging cycles, the more capacity is lost

Battery degradation

- Experiments are conducted by subjecting batteries to charge/discharge cycles with the same DoD
- Process is repeated until the useful battery capacity drops below certain percentage of the initial capacity, usually 80%, which is considered to be battery's end-of-life

Example 3.1

- An isolated telecommunication plant has a constant load of 2.5 kW. It is powered by a wind turbine, whose normalised production is given in the table. What is the minimum installed capacity of the wind turbine to supply the load at all times? How much wind energy is curtailed?

Hour	Wind	Hour	Wind	Hour	Wind	Hour	Wind
1	0.2	7	0.2	13	0.6	19	0.1
2	0.3	8	0.2	14	0.3	20	0.1
3	0.4	9	0.4	15	0.3	21	0.4
4	0.5	10	0.3	16	0.3	22	0.6
5	0.4	11	0.5	17	0.2	23	0.6
6	0.2	12	0.7	18	0.1	24	0.7

Example 3.1

- What installed power and capacity of the battery storage are needed in order to avoid wind curtailment? Battery efficiency is 100%.

Hour	Wind	Hour	Wind	Hour	Wind	Hour	Wind
1	0.2	7	0.2	13	0.6	19	0.1
2	0.3	8	0.2	14	0.3	20	0.1
3	0.4	9	0.4	15	0.3	21	0.4
4	0.5	10	0.3	16	0.3	22	0.6
5	0.4	11	0.5	17	0.2	23	0.6
6	0.2	12	0.7	18	0.1	24	0.7

Example 3.2

- Independent fotovoltaic system consists of PV modules, battery and load. Load consists of 4 energy saving light bulbs working on DC current and voltage of 12 V. Three light bulbs have power of 7 W, while one has power of 11 W. Light bulbs are on 4 hours per day.
- Calculate capacity of the battery which could secure necessary energy in case of 5 consecutive cloudy days during which battery would be the only source.
- Efficiency of the battery is $\eta_1 = 0{,}8$, efficiency of the charging controller $\eta_2 = 0{,}92$, and efficiency of the PV system $\eta_3 = 0{,}85$.

Laboratory testing

- Basic battery cell features:
  - Voltage (V)
  - Capacity (Ah)
- Battery which has 10 Ah capacity can deliver:
  - Current of 1 A for 10 h
  - Current of 2 A for 5 h
  - Current of 10 A for 1 h
  - Current of 20 A for 0,5 h
  - ….
- Each charge/discharge cycle reduces battery capacity

Laboratory testing

- C-rate designates charge/discharge speed of the battery
- 1C corresponds to nominal capacity
- For instance, for 10 Ah battery:
  - 1C designates current of 10 A
  - 2C designates current of 20 A
  - 0.5C designates current of 5 A
  - …
- State of charge (SoC) is a measure for the amount of energy stored in a battery (fully charged battery has 100% SoC)

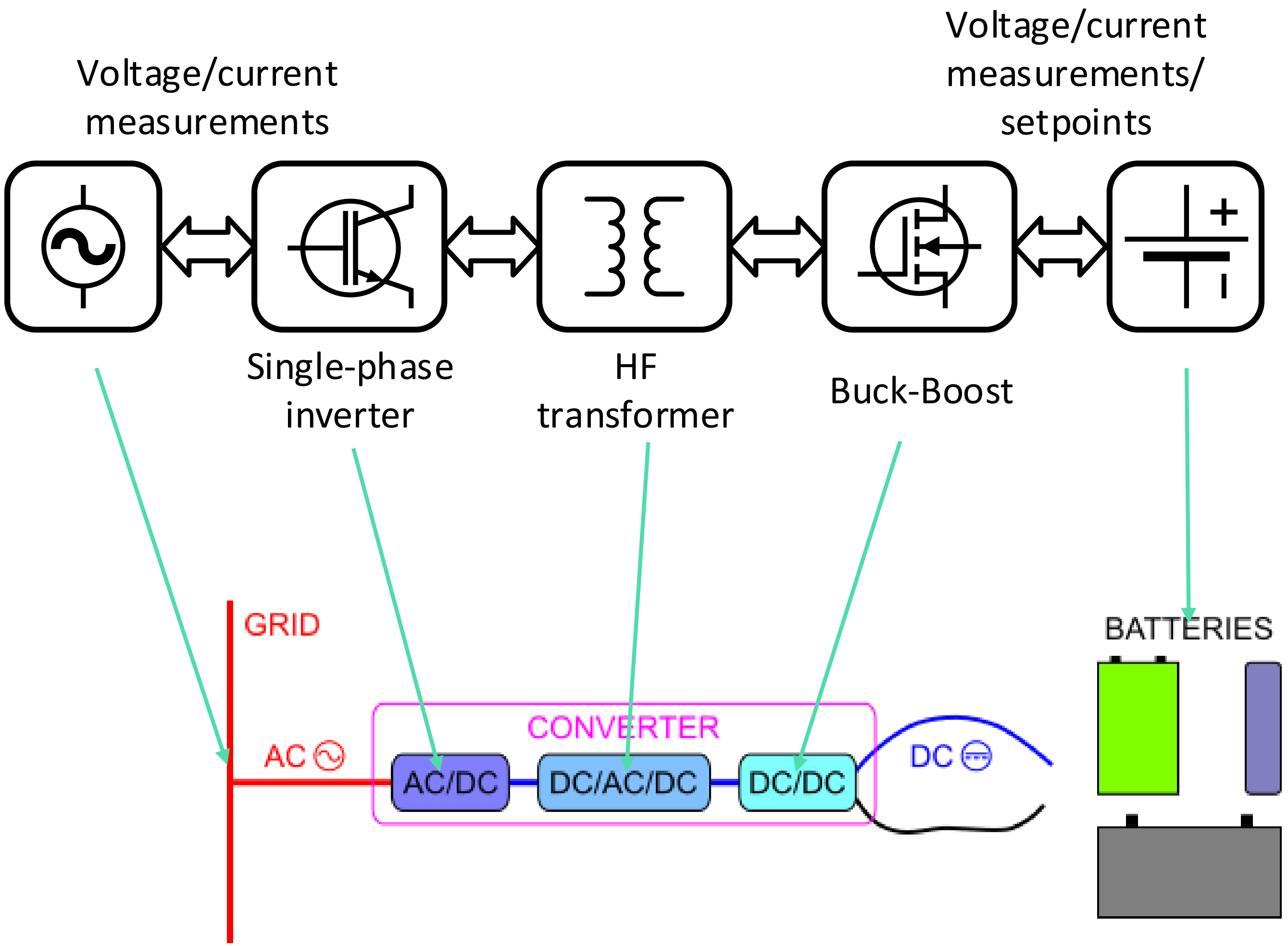
Laboratory testing

- State of health (SoH) is a measure for the overall battery condition
- SoH can include
  - Capacity
  - Internal resistance
  - Self-discharge rate
- New, healthy battery has 100% SoH
- Unambiguous determination of SoC and SoH is not straightforward

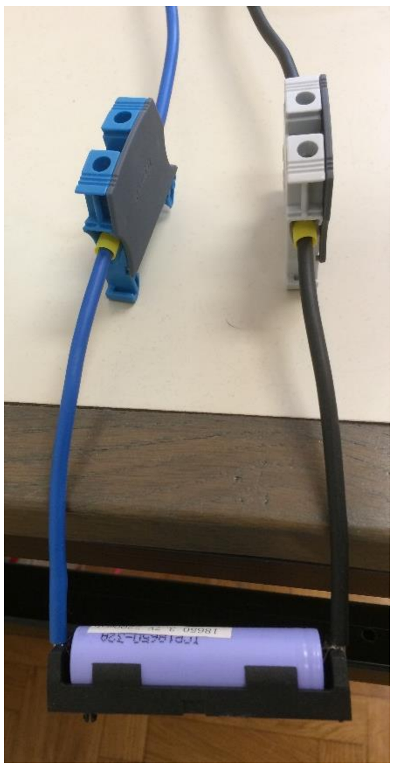
Laboratory testing

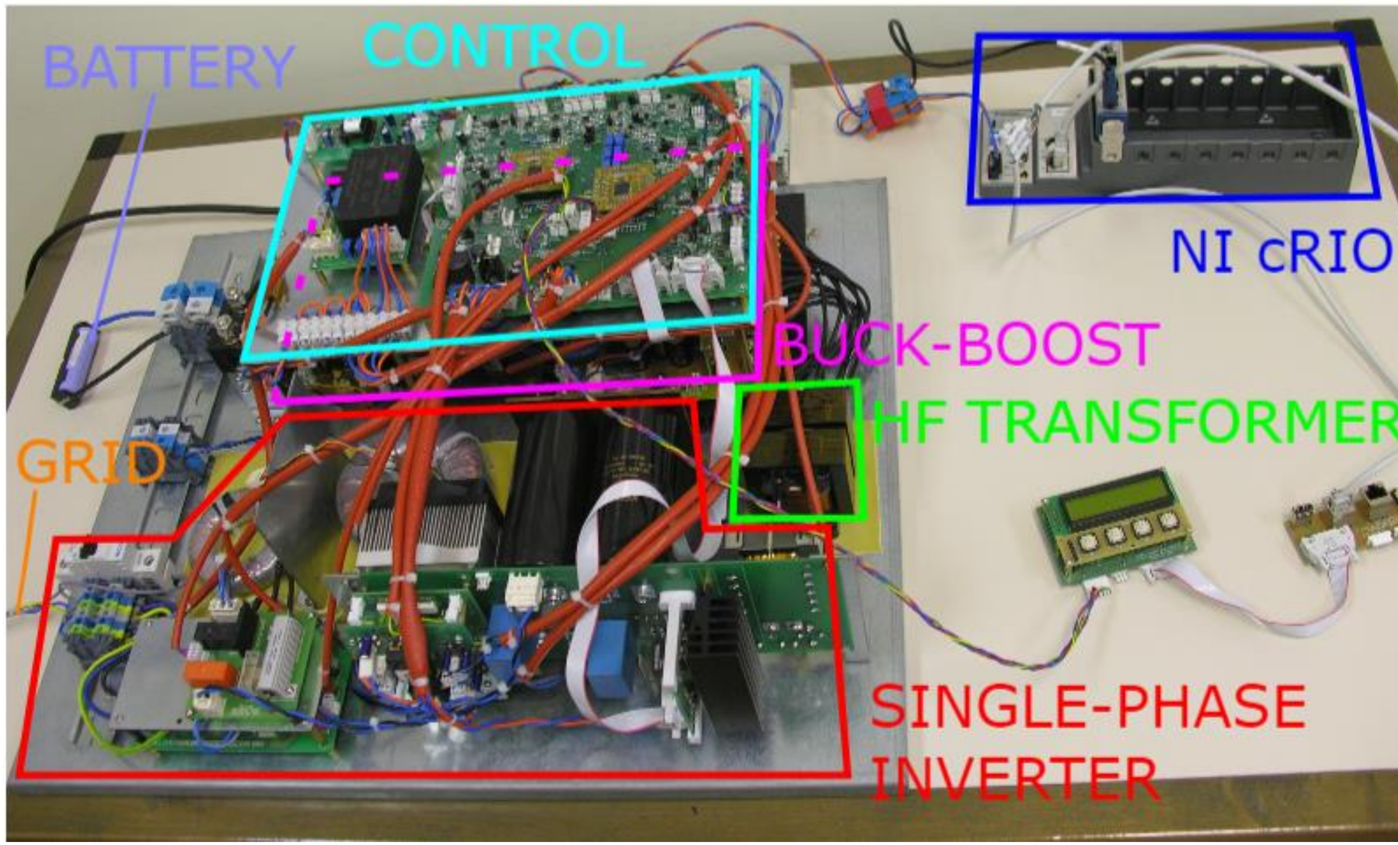
- How to test a battery?
- An AC/DC converter is required
- Features:
  - Nominal power: 1 kW
  - Output voltage: 0 to 20 V DC
  - Output current: -50 to 50 A DC
  - Input: 50 Hz, 230 V AC
  - Input/output current and voltage measurements
    - Analog signals: 0 – 10 V DC
    - Digital signals: isolated USB or RS-485
  - Remote battery voltage sensing for improved accuracy
- Communication, supervision and control: NI LabVIEW

Laboratory testing

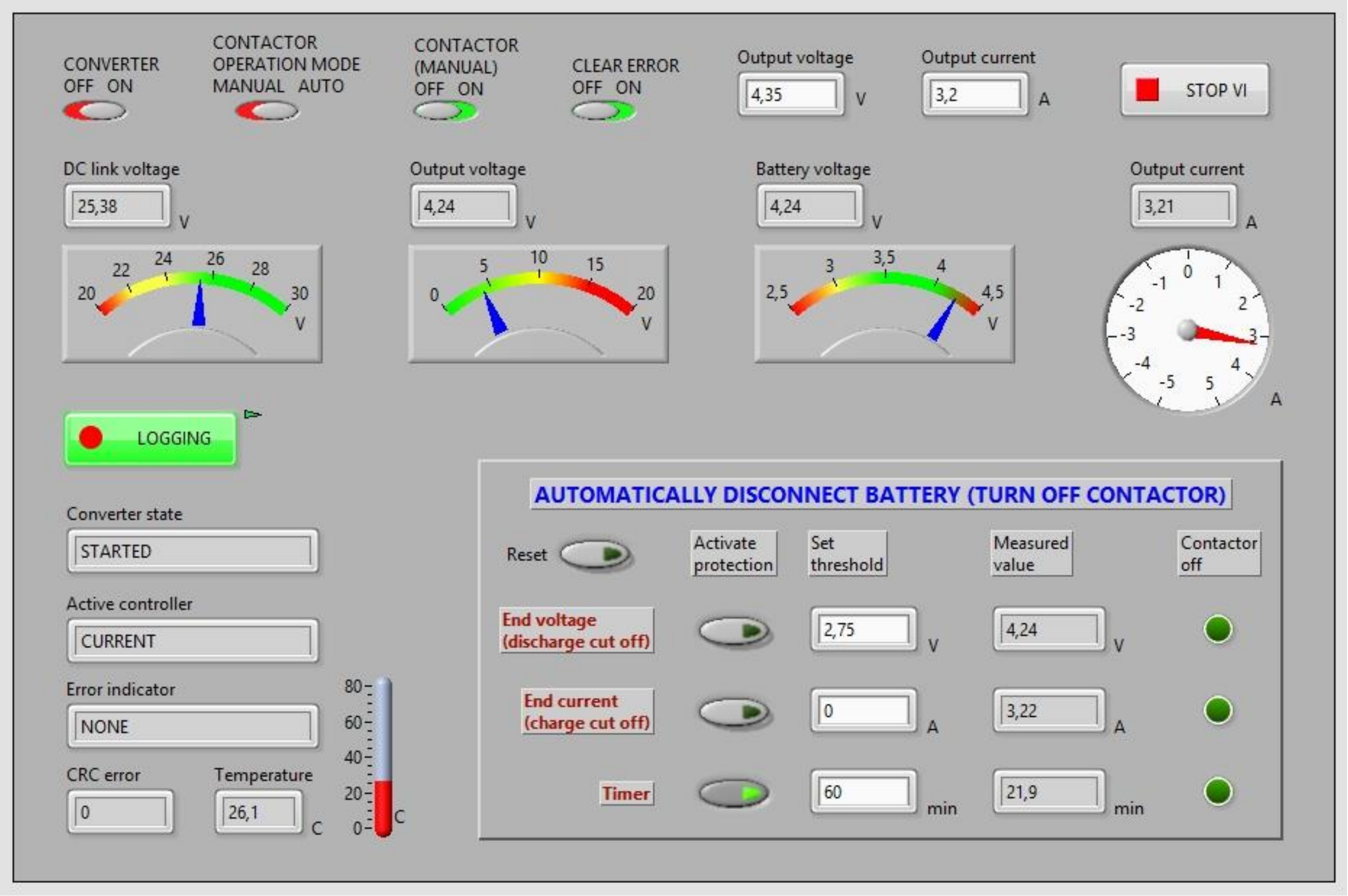


Laboratory testing





Laboratory testing

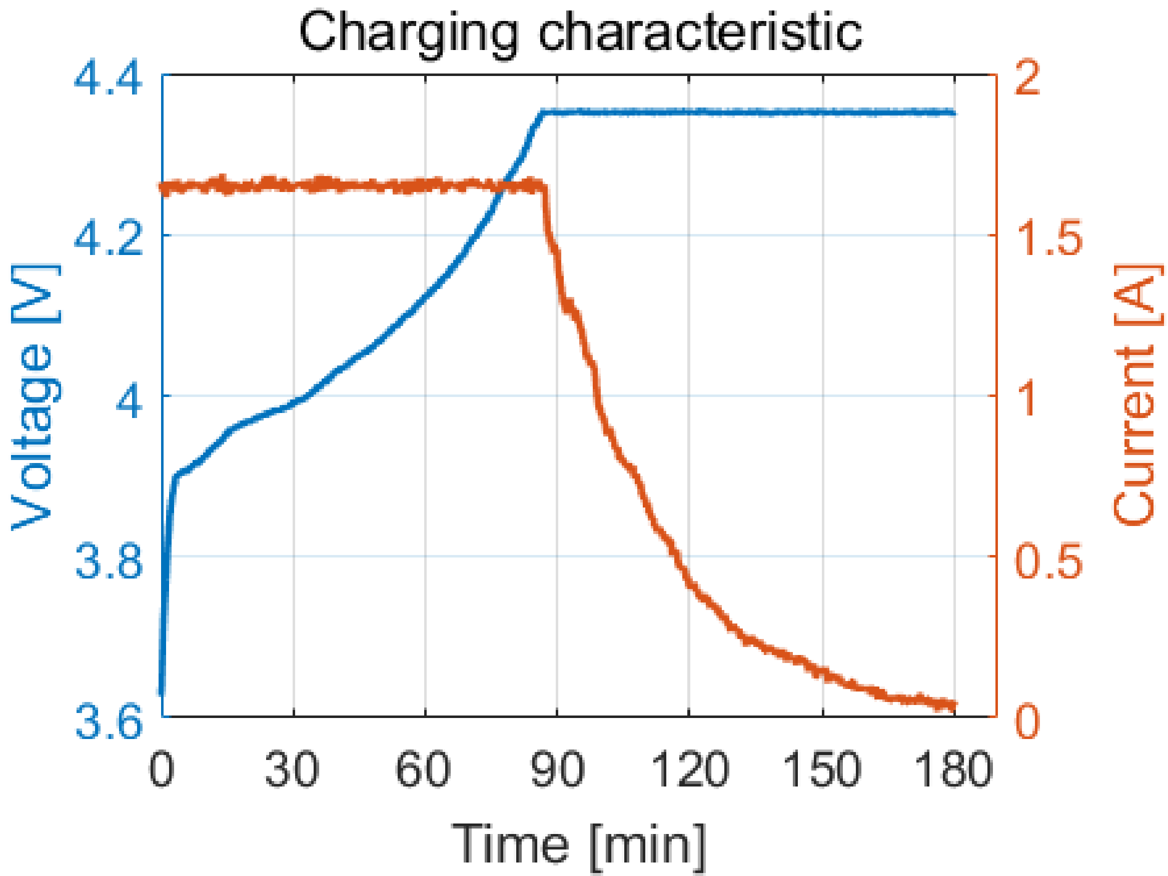


Laboratory testing

- Samsung ICR18650-32A
  - Lithium cobalt oxide ($LiCoO_2$) – LCO
  - Nominal voltage: 3.75 V
  - Nominal capacity: 3.2 Ah
  - Minimal capacity: 3.1 Ah

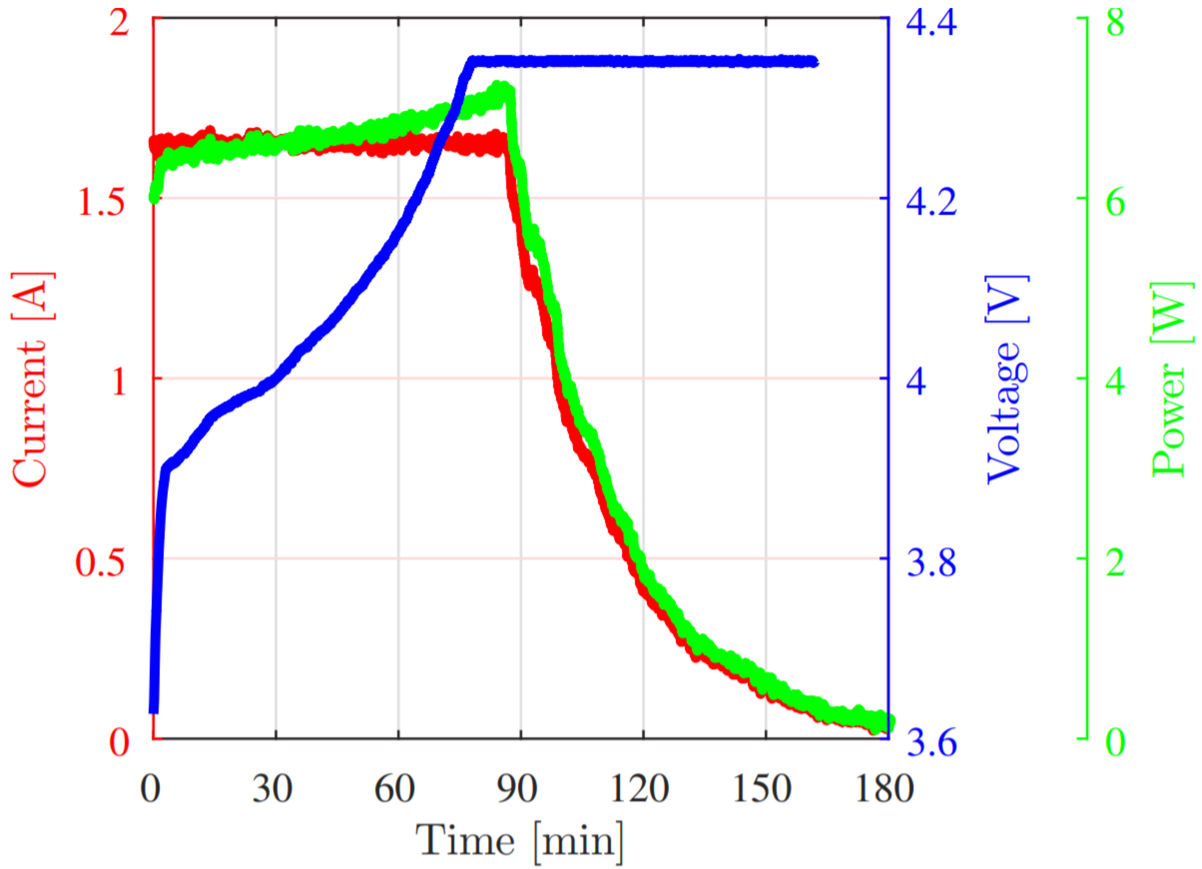
Charging characteristic

- Constant current constant voltage (CC/CV)

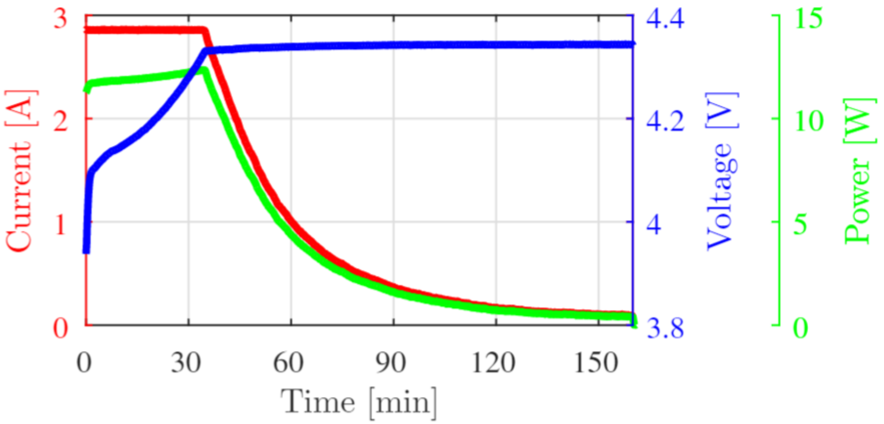


Charging characteristic

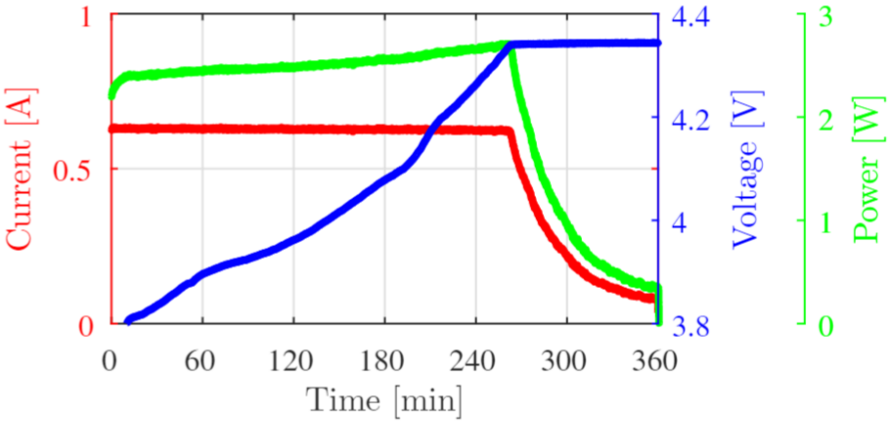
- Power



Charging characteristic



(a) Charging current 2.8 A (1C)



(b) Charging current 0.56 A (0.2C)

?

$$s_t = s_{t-1} + p_t^{\mathrm{ch}} \cdot \Delta^{\mathrm{T}} - p_t^{\mathrm{dis}} \cdot \Delta^{\mathrm{T}}, \quad \forall t \in \Omega^{\mathrm{T}}$$

$$s_t \leq SOC^{\max}, \quad \forall t \in \Omega^{\mathrm{T}}$$

$$p_{t,}^{\mathrm{ch}} \leq P^{\mathrm{bat}}, \quad \forall t \in \Omega^{\mathrm{T}}$$

$$p_t^{\mathrm{dis}} \leq P^{\mathrm{bat}}, \quad \forall t \in \Omega^{\mathrm{T}}$$

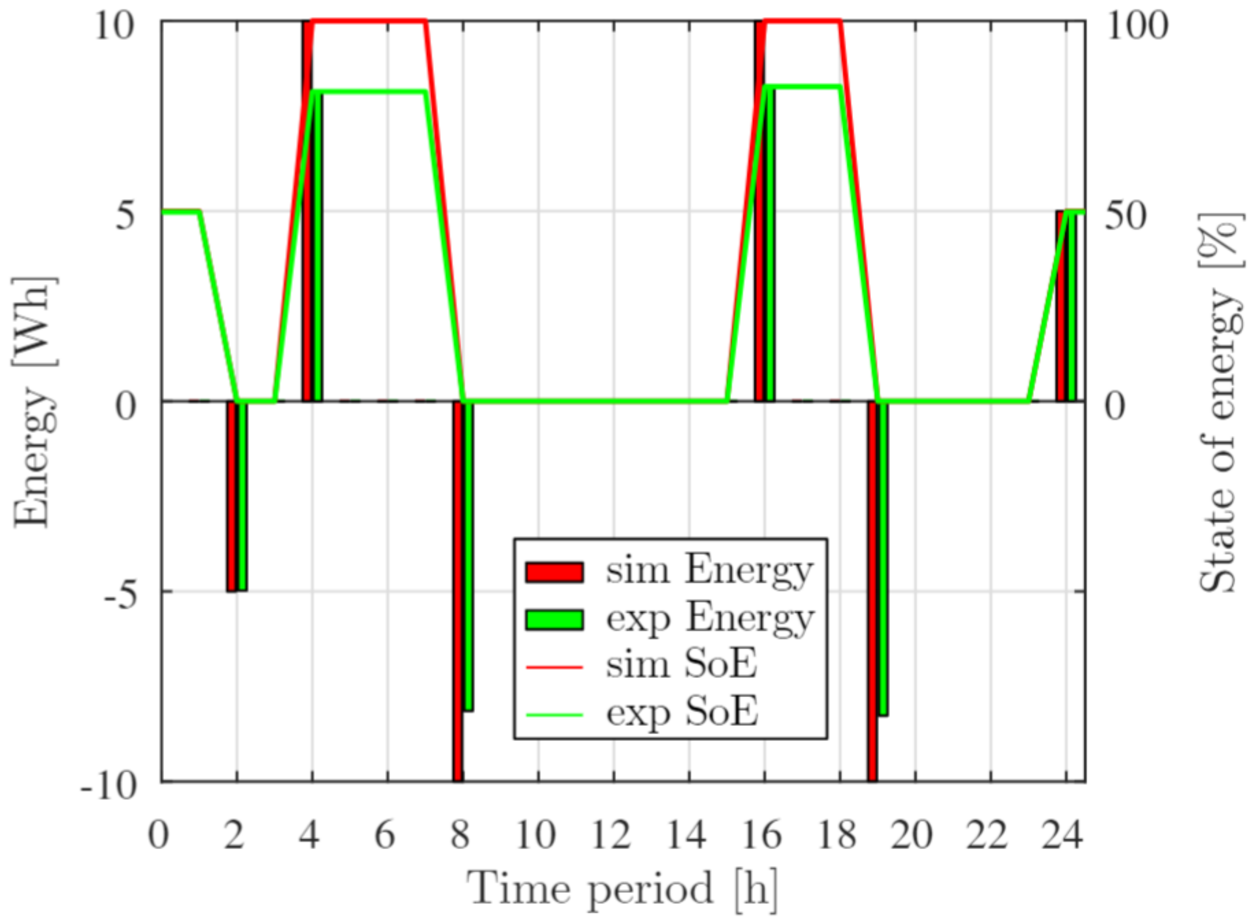
Charging power

- This limitation is not correct

$$p_{t,}^{\mathrm{ch}} \leq P^{\mathrm{bat}}, \quad \forall t \in \Omega^{\mathrm{T}}$$

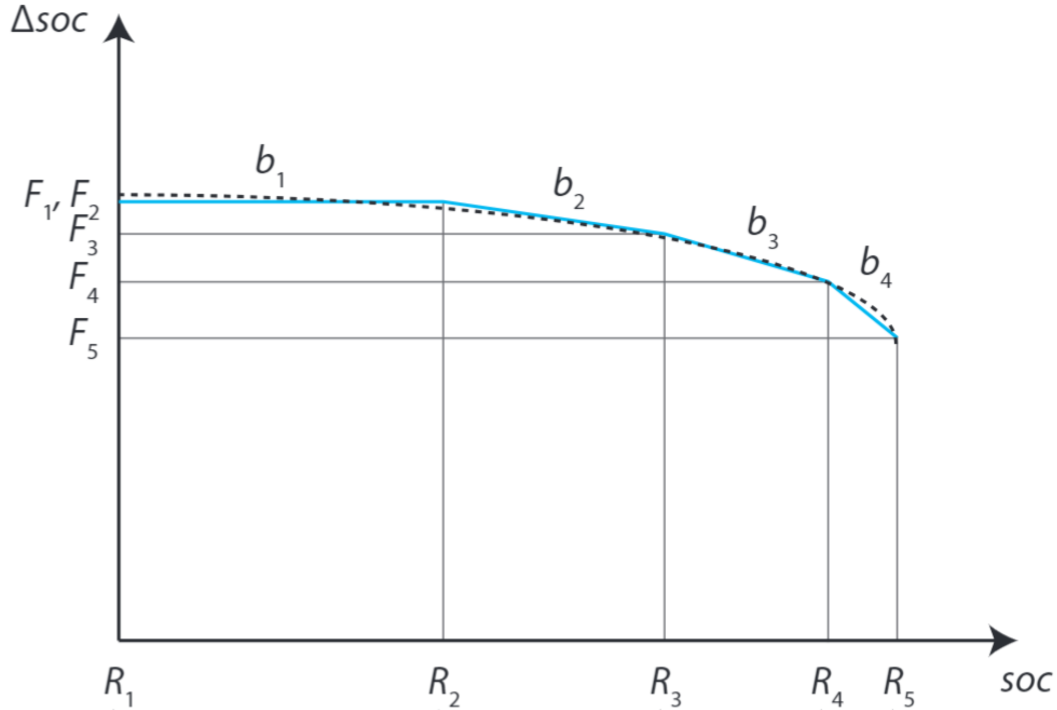
Charging power

Consequences

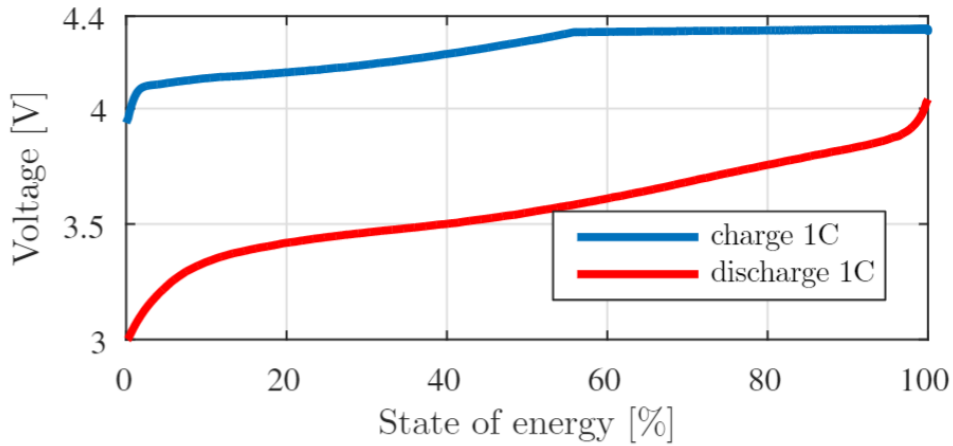


Charging power

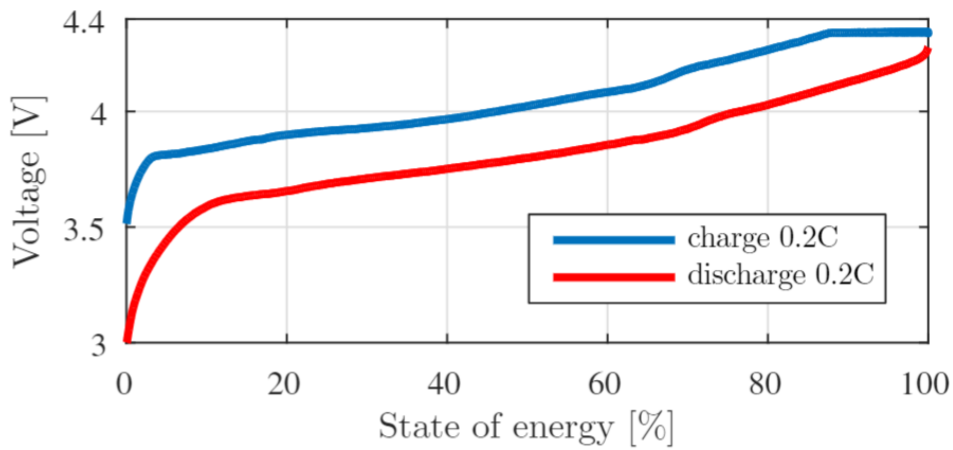
- It is necessary to know how much energy can be charged to a battery in a single time step (1 hour) for every SoC



Battery voltage characteristic



(a) Charging/discharging current 2.8 A (1C)

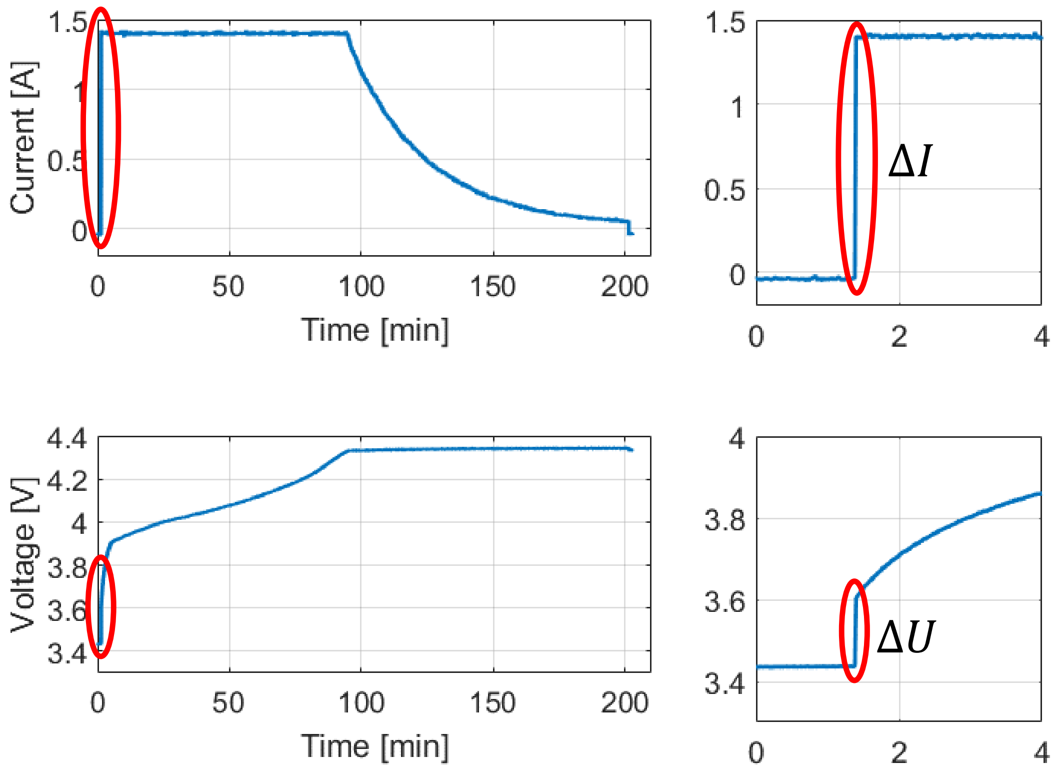


Battery cycle efficiency

- Losses are caused by the internal resistance of electrodes and electrolyte
- Types of efficiencies:
  - Coulombic (Ah)
  - Voltaic (V)
  - Energy (Wh) – includes the former two

Internal resistance

- Charging characteristic

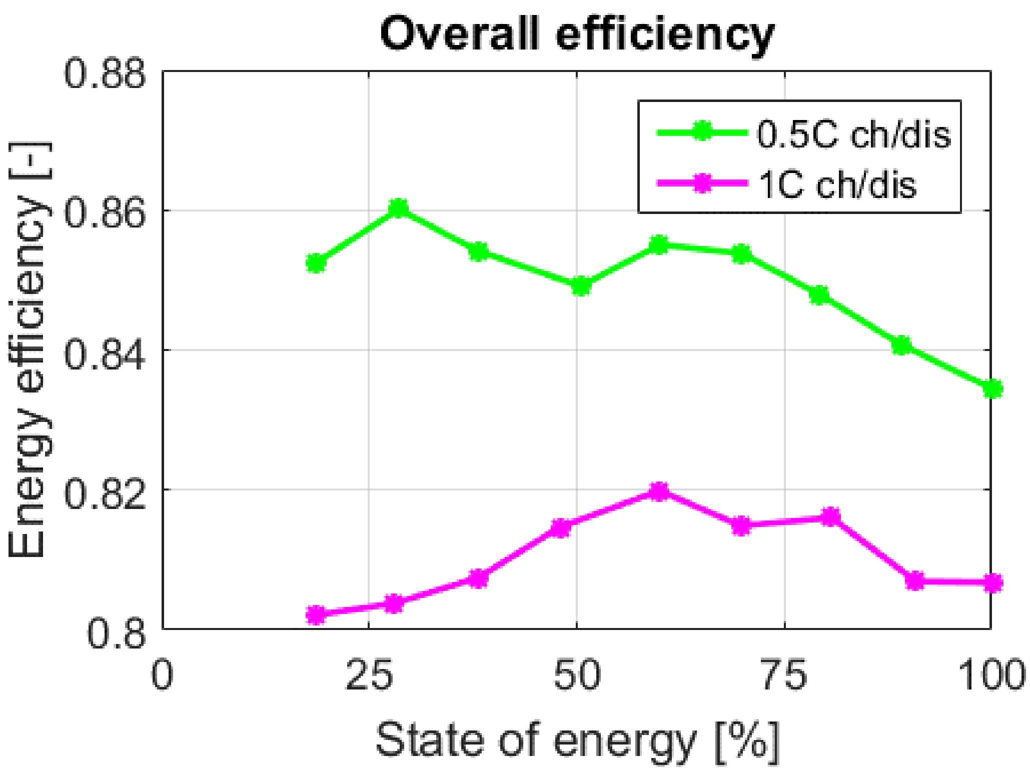


Internal resistance:

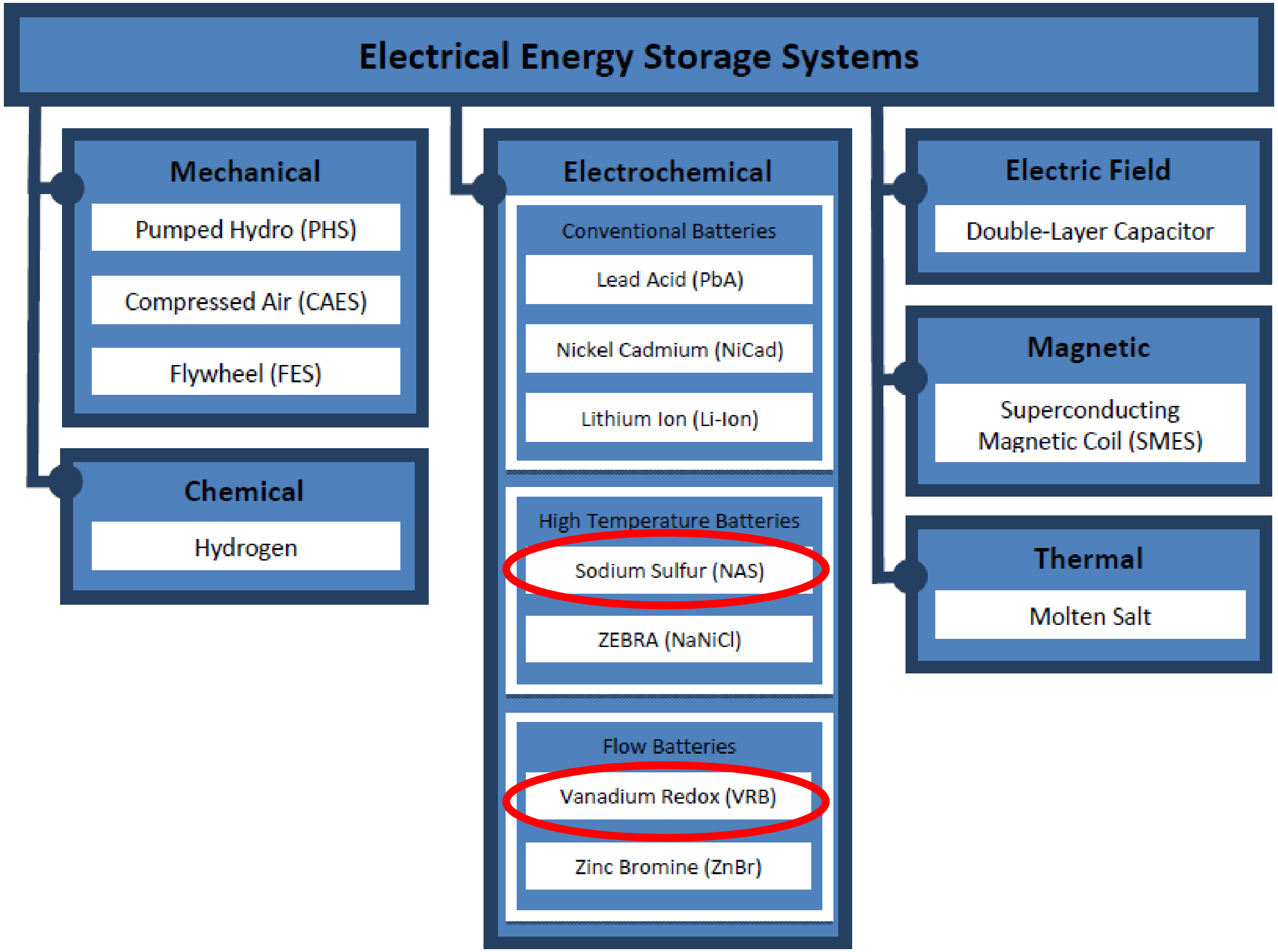
$$R = \frac{\Delta U}{\Delta I}$$

Battery cycle efficiency

- Dominantly dependant on charging/discharging currents

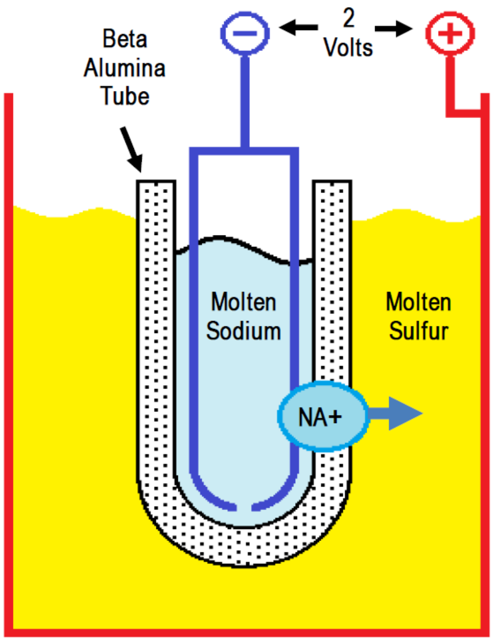


Classification of ES

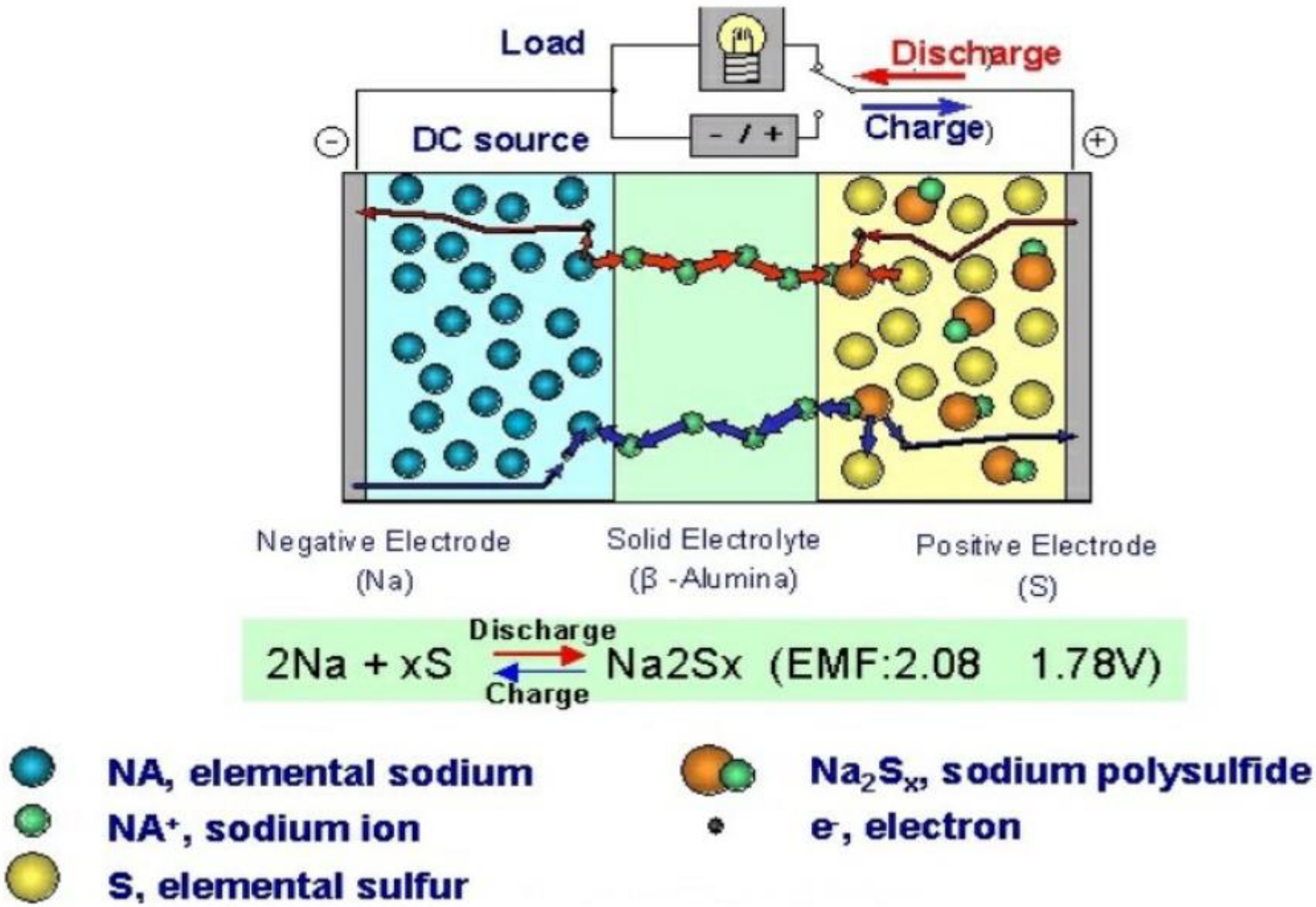


Sodium-sulfur battery

- Battery cells contain:
  - a molten sodium (Na) negative electrode
  - a molten sulfur (S) positive electrode
  - a solid ceramic electrolyte - Beta-Alumina Solid Electrolyte (BASE) - allows only positively charged sodium-ions to pass through
- Operating temperature:
  - 300-350 °C
- Stationary ES applications
- Lifespan between 10 and 15 years, depending on frequency of use and depth of discharge



Charging/Discharging process



Charging/Discharging process (2)

- Reaction on positive electrode:

$$xS + 2e^{-} \underset{CHARGE}{\overset{DISCHARGE}{\rightleftarrows}} S_x^{-2}$$

- Reaction on negative electrode:

$$2Na \underset{CHARGE}{\overset{DISCHARGE}{\rightleftarrows}} 2Na^{+} + 2e^{-}$$

- Overall reaction:

$$2Na + xS \underset{CHARGE}{\overset{DISCHARGE}{\rightleftarrows}} Na_2S_x \; (x = [3,5]),\; E_{celije} = [1.78, 2.076]\,\mathrm{V}$$

Charging/Discharging process (3)

- As discharge proceeds, sodium passes from the negative electrode to the positive one, and sodium polysulfide is formed at the operating temperature
- During charge this process is reversed

NaS batteries – pros

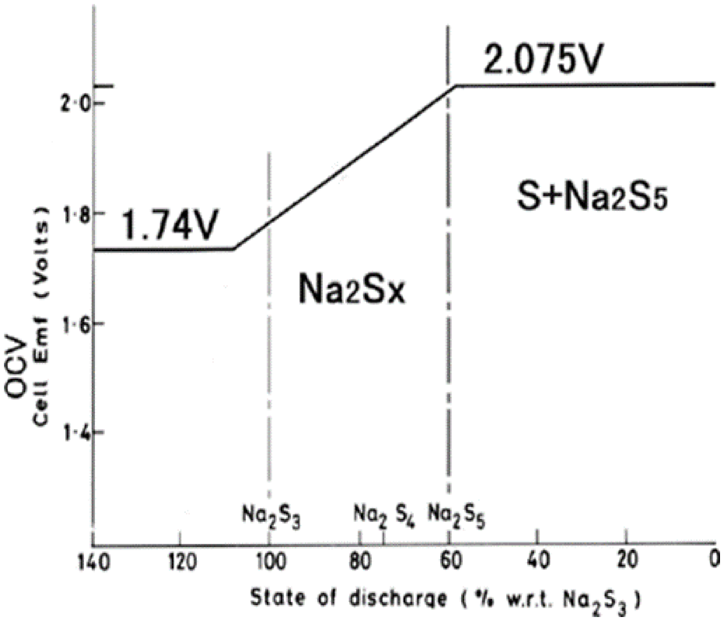
- Relatively high energy densities (150–300 Wh/l)
- Almost zero daily self-discharge
- Higher rated capacity than other types of batteries
- Battery type: “Energy” – ability of discharging up to 6 hours
- Uses inexpensive, non-toxic materials leading to high recyclability (99%)

NaS batteries – cons

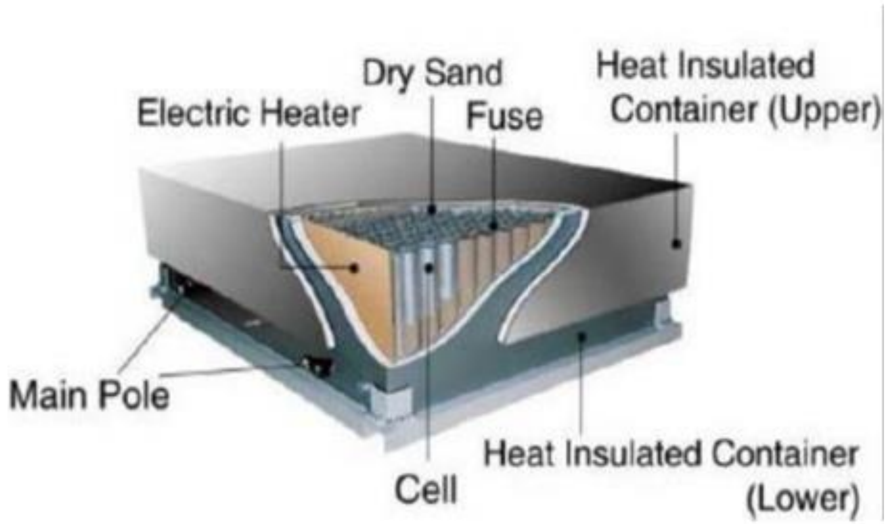
- High annual operating cost (80 $/kW/year)
- An extra system required to ensure its operating temperature

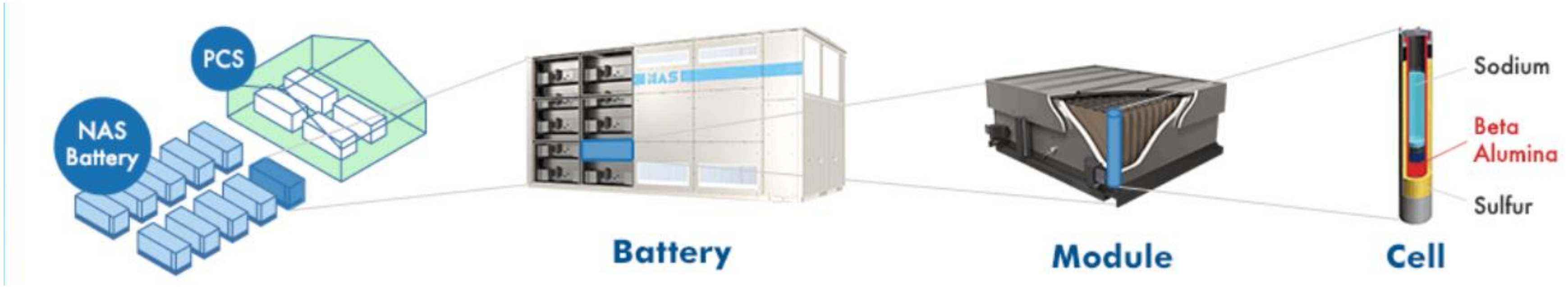
Voltage characteristics

- At 100% SOC:
  - Voltage (OCV) is constant over 60 to 75% of discharge – 2.075 V
  - The positive electrode consists of two liquids: sulfur (S) and sodium polysulfide
- At 0% SOC:
  - Voltage – 1.74 V
  - Sodium polysulfide: Na_2S_x with x less than 5



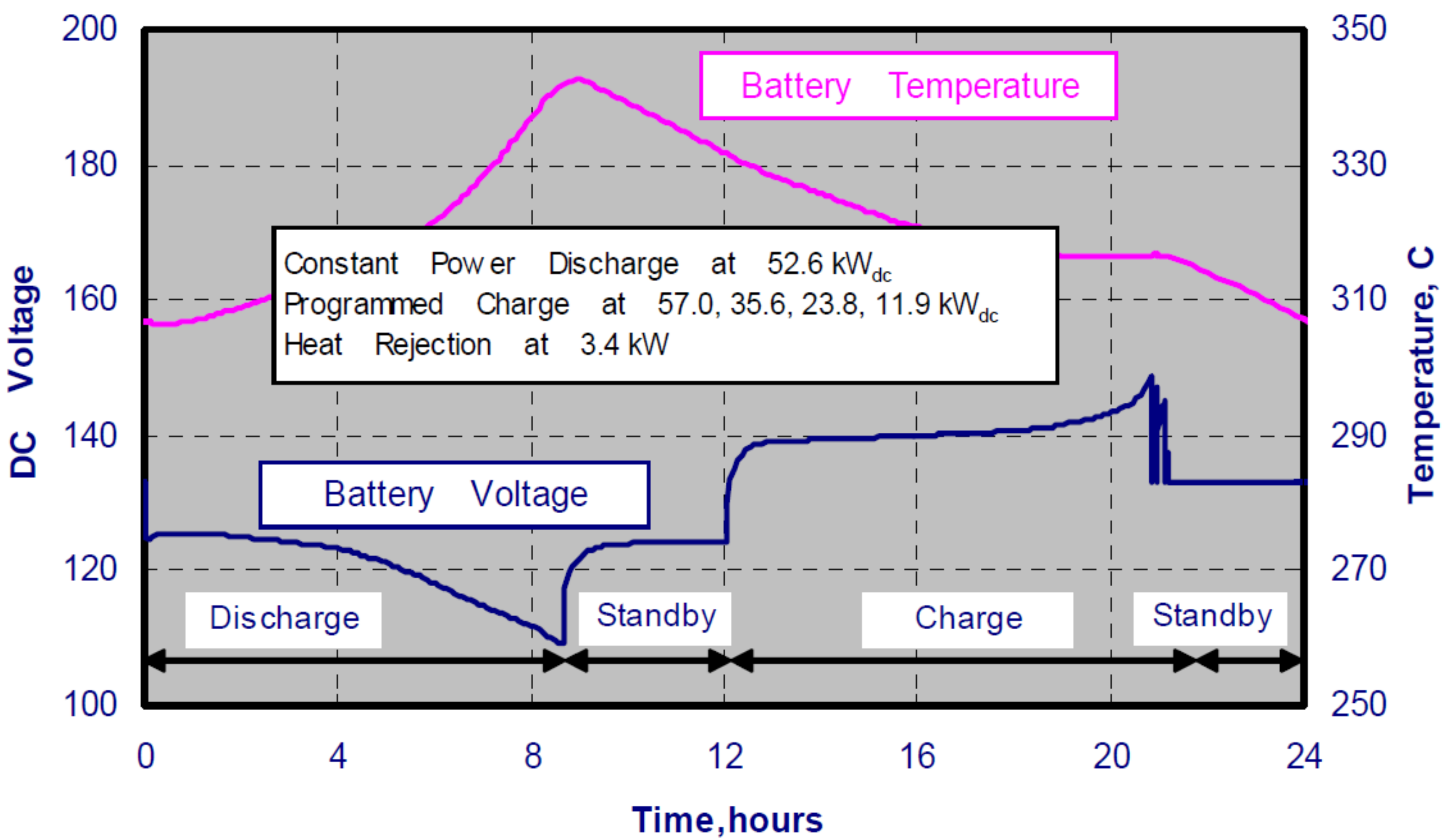
The module design





Link: https://www.ngk.co.jp/nas/specs/

Temperature vs. Voltage in Peak Shaving Cycle



Temperature vs. Voltage in Peak Shaving Cycle (2)

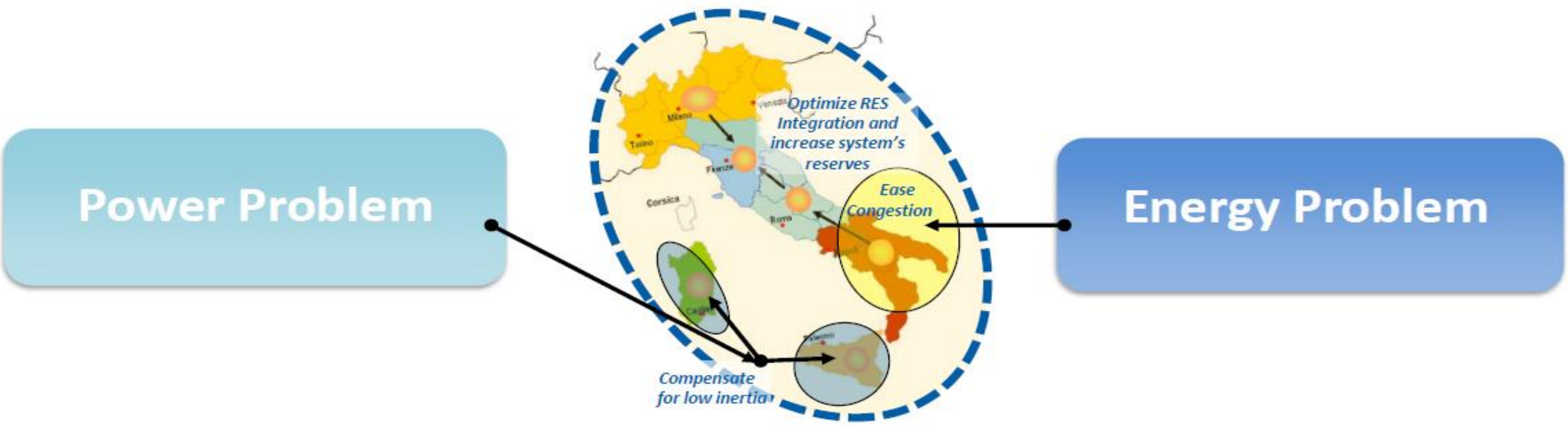
- Temperature sensors are located on the inner side and bottom surfaces of the enclosure and are insulated from cells by the sand filler; hence, temperature data lag duty cycle events due to the rate of heat transfer from cells to the sensor location
- The internal temperature of the module is observed to increase steeply during discharge mode due to the combined effects of **ohmic heating** and **the exothermic cell reaction**
- During the charge mode, ohmic heating combines with the cell endothermic reaction to effect a gradual cooling

NaS applications

- Stabilizing renewable energy output
- Providing ancillary services
- Peak shaving
- Backup power
- Firming wind capacity

TERNA project

- 35 MW NaS battery project
- Applications:
  - Frequency regulation: primary and secondary
  - Voltage support
  - Peak shaving
  - Reducing grid congestion



TERNA project (2)

Rated Output	1,200kW and 8,640kWh
Configuration	40 NAS modules, each rated at 30kW and 216kWh.
Dimension	10.2W x 4.4D x 4.8H (m)
Weight	132tonnes

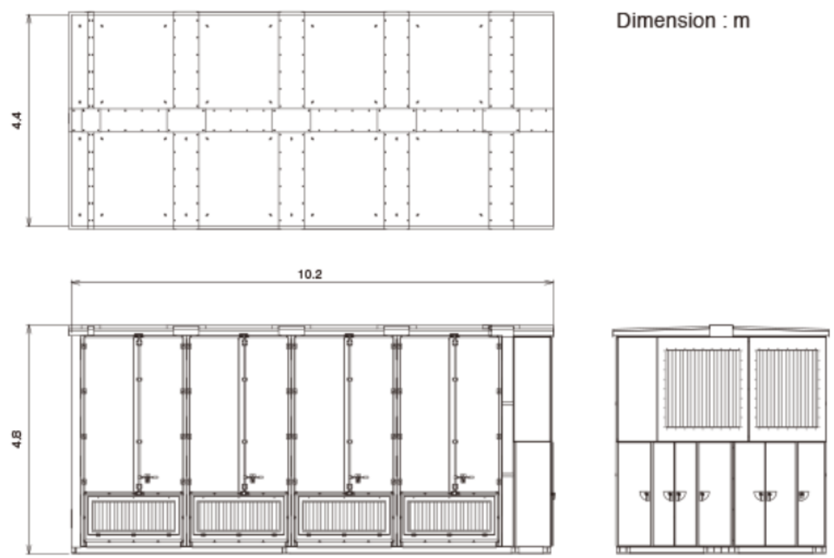
Energy Intensive

- **Mission :** reduce grid congestions
- **Total Power:** ≈35 MW
- **Solution:** NaS *Sodium Sulfur*
- **Number of sites:** 3
- **Investment Size: 160 €mln;**

Site 1: Ginestra
- **Total Capacity:** ≈ 12 MW
- **Status: operational**

Site 2 Flumeri
- **Total Capacity:** ≈ 12 MW
- **Status: operational**

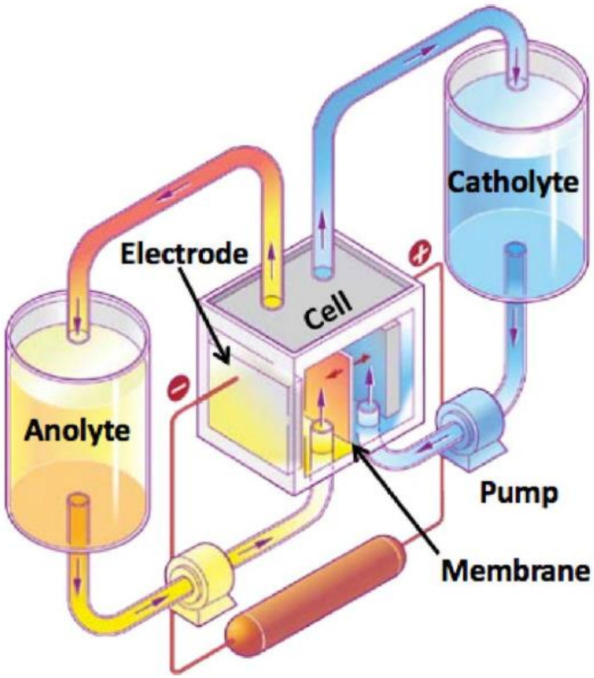
Site 3 Scampitella
- **Total Capacity:** ≈ 10.8 MW
- **Status: operational**



VANADIUM REDOX FLOW BATTERIES (VRFB)

Vanadium Redox Flow Batteries (VRFB)

- The main components:



  - A liquid electrolyte
  - A carbon felt electrode
  - An ion exchange membrane that separates the electrolytes
  - A bipolar plate that separates cells
  - Electrolyte tanks (2 or 4), pumps, and piping

Vanadium Redox Flow Batteries (VRFB)

- The redox cell means: reduction–oxidation
- VRFB employs vanadium ions in **four** oxidation states to store chemical potential energy
- Reaction on positive electrode:

$$VO^{2+} + H_2O \underset{pražnjenje}{\overset{punjenje}{\rightleftharpoons}} VO_2^{+} + 2H^{+} + e^{-}$$

- Reaction on negative electrode:

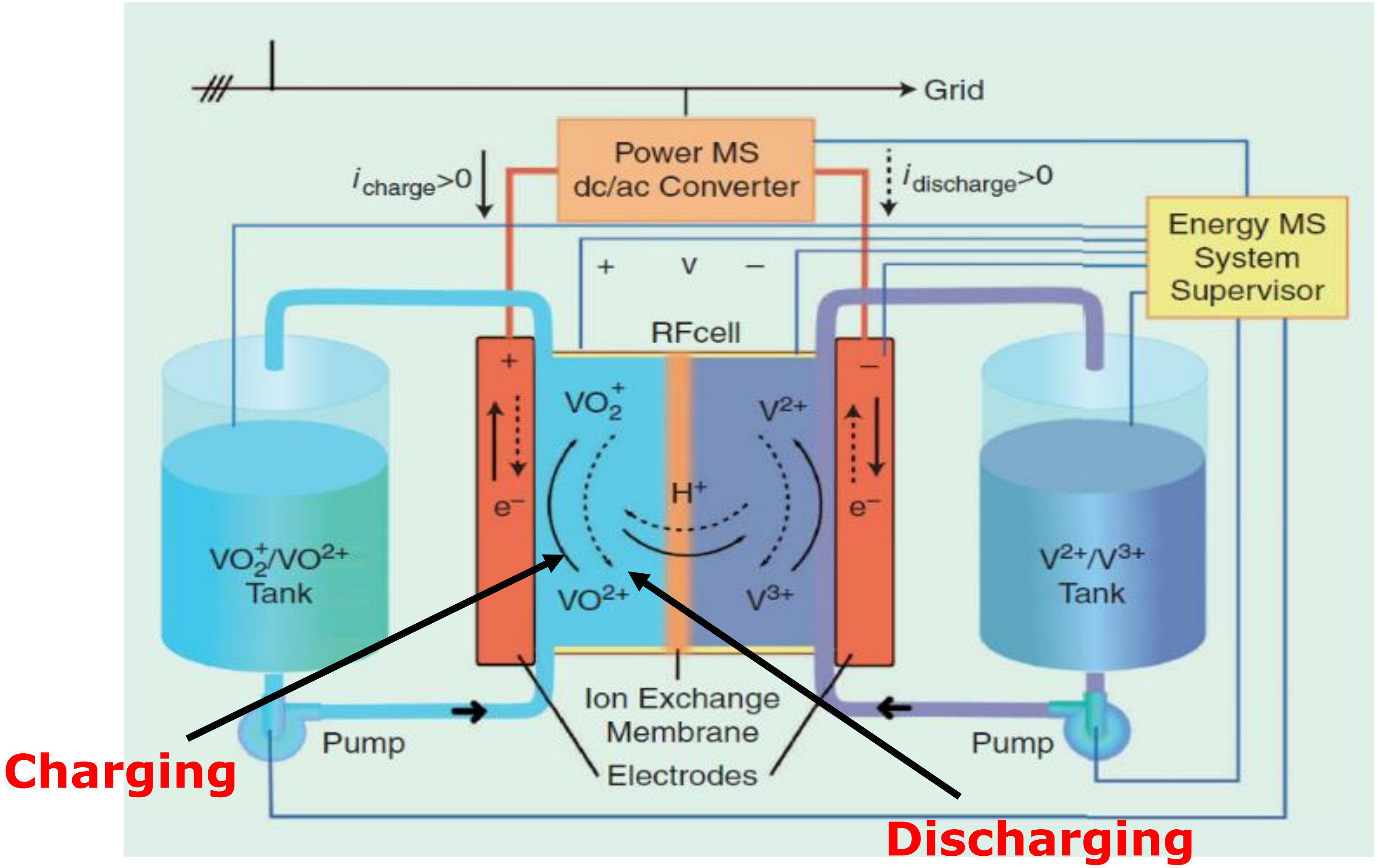
$$V^{3+} + e^{-} \underset{pražnjenje}{\overset{punjenje}{\rightleftharpoons}} V^{2+}$$

- The operating temperature: 10-40 °C

How does the Flow Battery work?

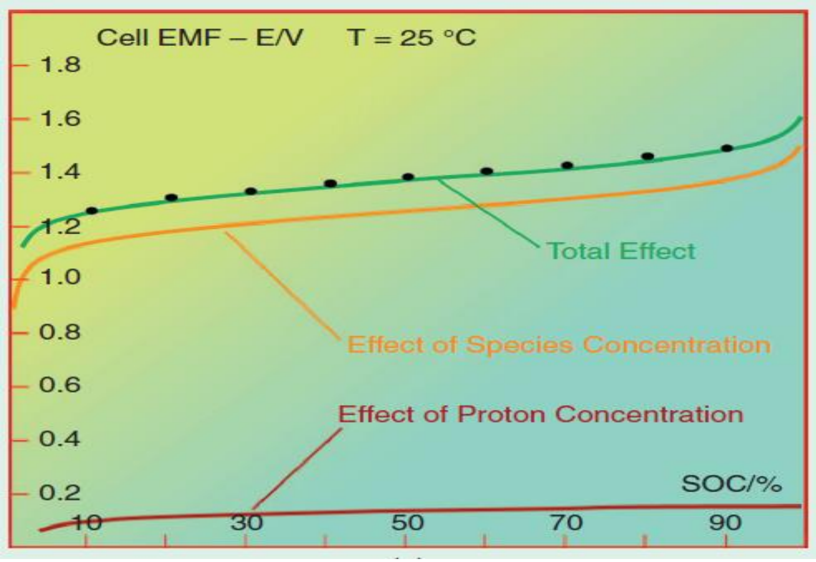
- Liquid electrolyte of metallic salts is pumped through a core that consists of a positive and negative electrode, separated by a membrane
- The ion exchange that occurs between the cathode and anode generates electricity
- Viable choice for energy applications requires discharge durations <u>greater than 5 hours</u>
- The ability to independently <u>vary energy and power capacity</u>

Charging/Discharging process



Vanadium Redox Flow Batteries (VRFB)

- The energy capacity is a function of the electrolyte volume - amount of liquid electrolyte
- The power is a function of the surface area of the electrodes
- The voltage is lower than other types of batteries: 1.15–1.55 V



VRFB batteries – pros

- Long cycle life – 10-15 years with 1000 cycles/year
- Quick response times
- No harmful emissions
- Can operate at much higher current and power densities
- Roundtrip efficiency ranges between 60 and 70 %

VRFB batteries – cons

- The energy densities vary considerably but are <u>lower</u> compared to portable batteries, such as li-ion batteries
- Cost and construction complexity
- Efficiency losses accrued by auxiliary equipment

VRFB applications

- Load shifting (peak shaving)
- Firming capacity
- Transmission and distribution operational support:
  - Frequency regulation
  - Voltage support
  - Spinning reserve
- Power quality and reliability (especially long duration)