ME4252 Nanomaterials for Energy Engineering

ENERGY STORAGE

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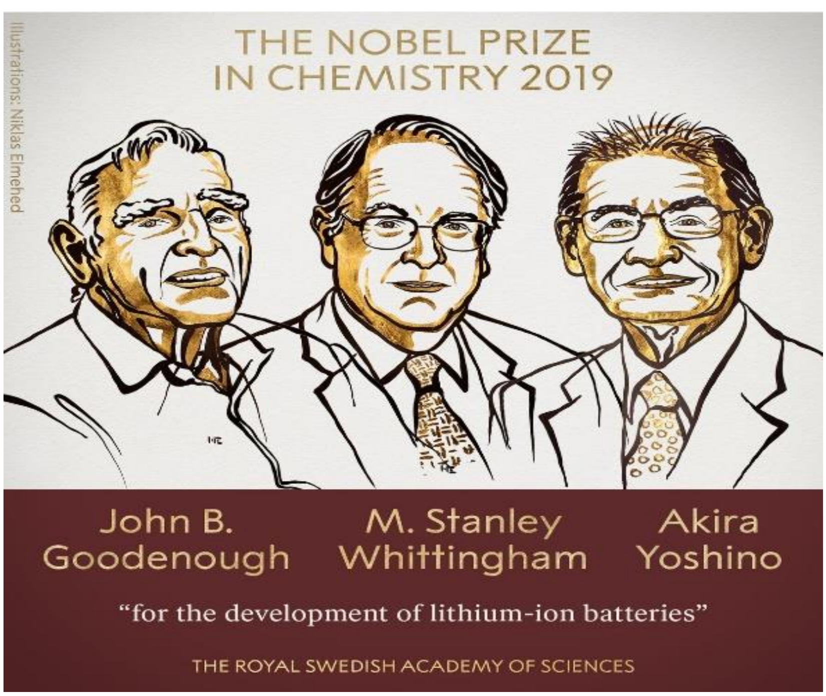

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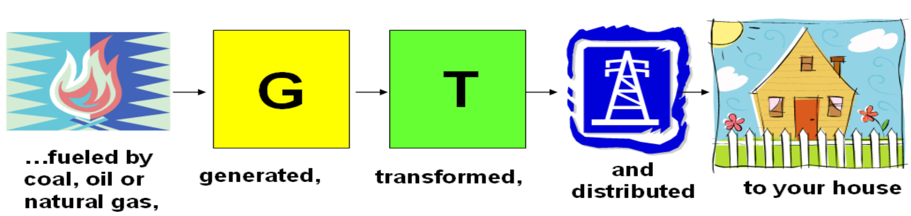
Contents

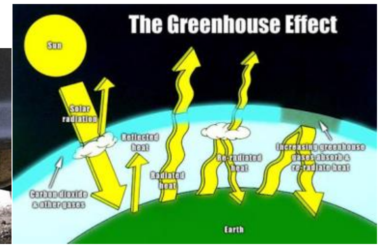
Electricity

ELECTRICITY HAS TRADITIONALLY BEEN……….



*www.aps.com/_files/renewable/**Grade4RenewableEnergySources**.pps*

Climate Change Issues



- Need to reduce CO_2 emission

Renewable Energy Options

Ref.: IPCC-Special Report on Renewable Energy for Climate Change Mitigation, 2011

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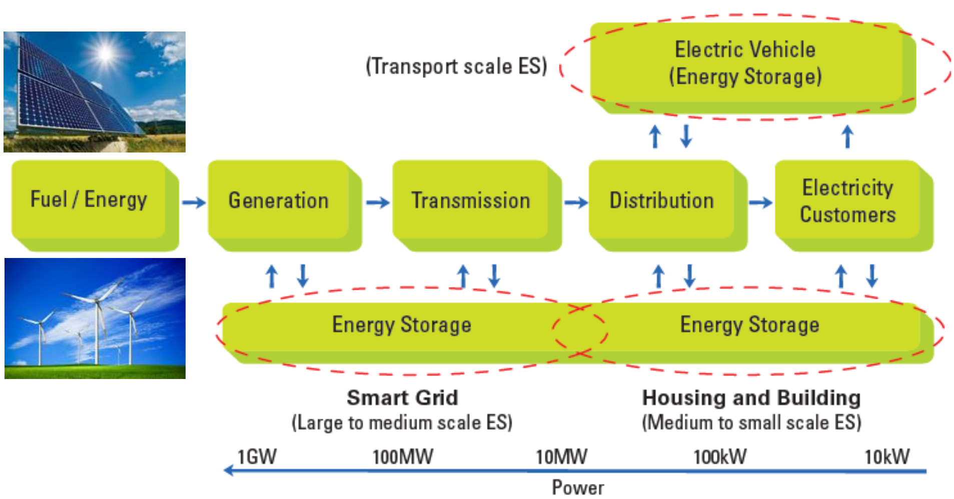
Renewable Energy: Electricity Value Chain



Electric Vehicles: 10 – 100 kWh
Nissan Leaf (fully EV): 24 kWh
Toyota Prius (hybrid): 10 kWh

Energy Storage Tech Primer, Singapore 2011

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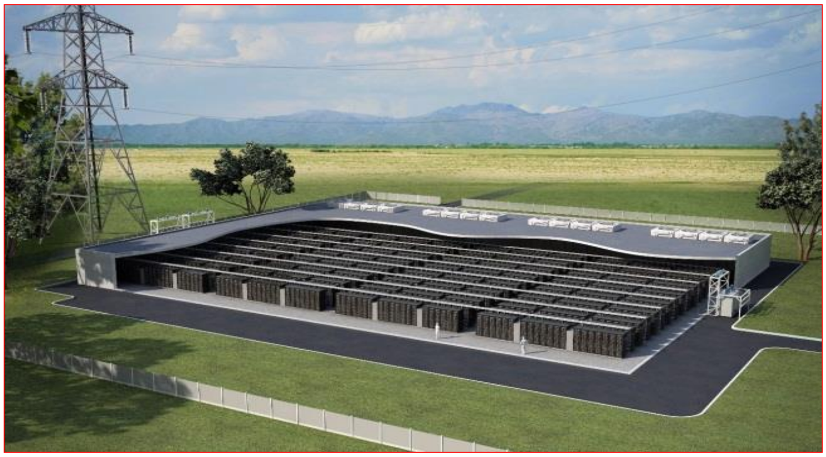
Micro-grids: Large scale storage of renewable energy



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Renewable Energy Sources…

Case study in Santa Barbara: 2700 GWh

- Wind energy: 300 GWh
- Solar farm: 80 GWh
- Wave energy: 300 GWh

With just 3 projects, 25% of demand was met!

What stops us going from 25% to 100%?

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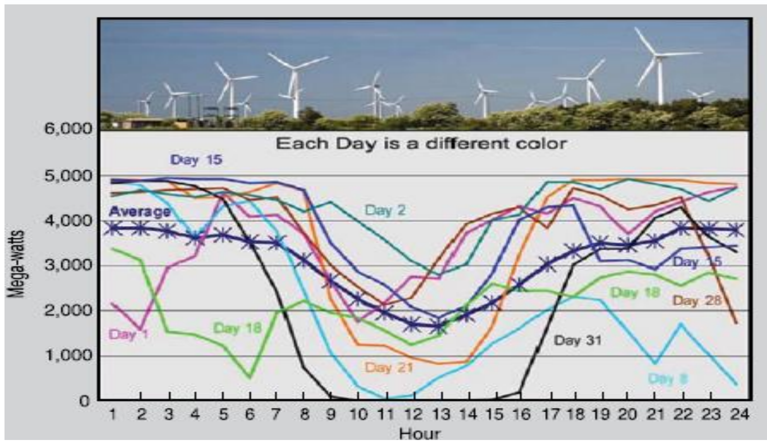
Intermittency!



California study on the irregular output of wind

http://www.megawattsf.com/gridstorage/gridstorage.htm

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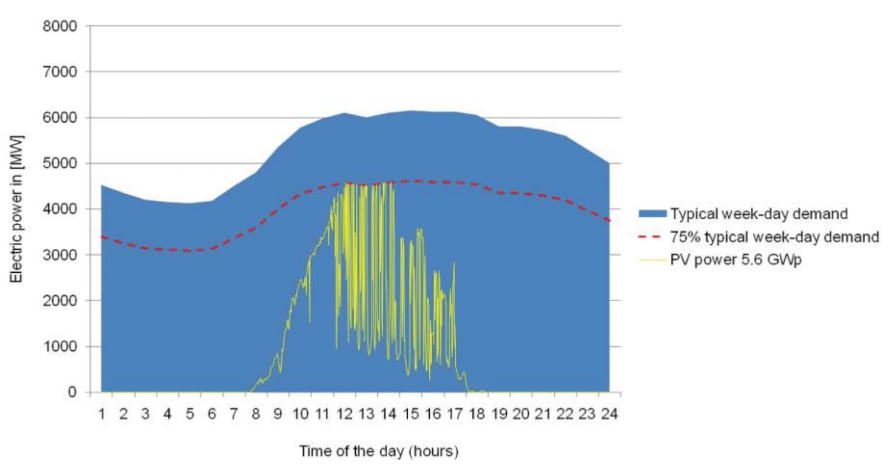
Intermittency!

Electricity load profile (demand) of Singapore on a typical week-day in January 2011 (in blue)

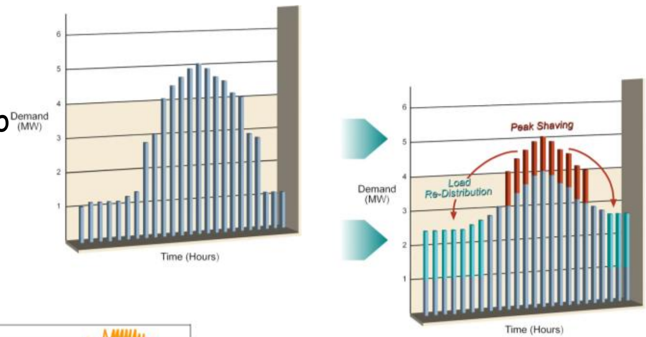


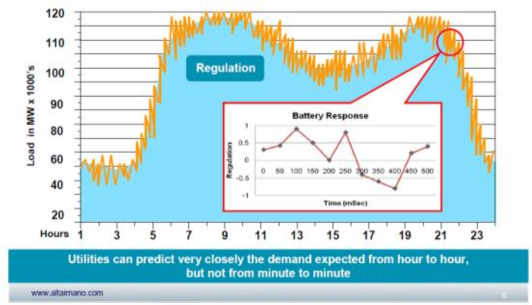
Supply seems so dynamic: supply must meet constant demand

Ref: Technology Primer on Solar Energy , 2011 (Singapore)

Micro-grid Power Management

Peak shaving or load shifting:
Load management to shift the demand from peak hours to off-peak hours

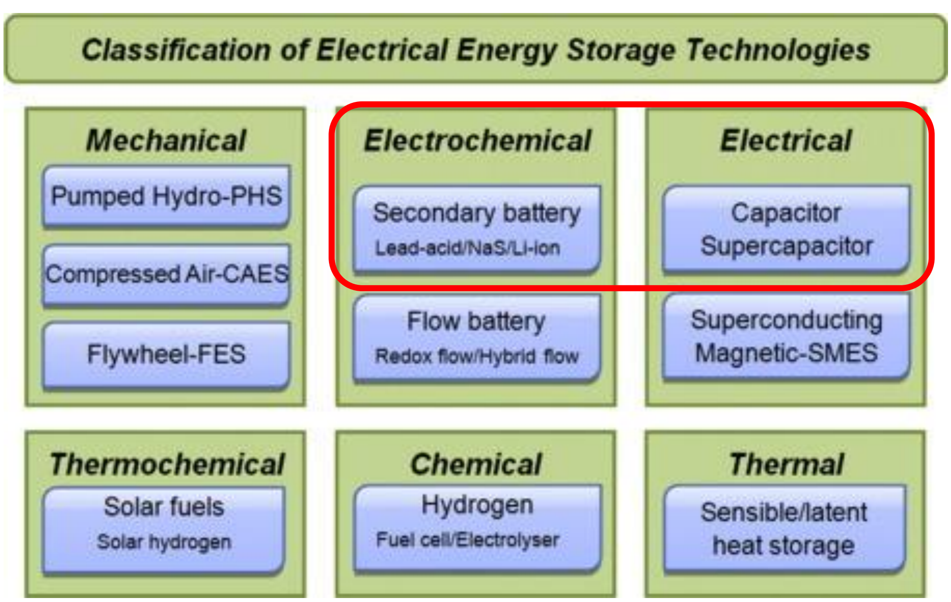




Frequency Regulation:
To smoothen and improve the quality of the grid power

[http://etap.com/smart-grid/smart- grid-demand-management.htm](http://etap.com/smart-grid/smart-grid-demand-management.htm)

Storage Type Grouped by Technology



Battery based Storage Systems

Fundamentals of Electrochemistry

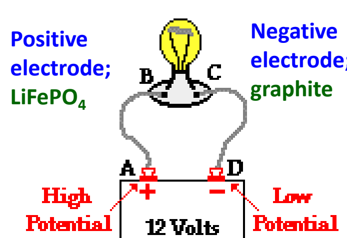
Electrical Measurements of Chemical Processes

- Redox Reaction involves transfer of electrons from one species to another.
  - **Chemicals are separated**
- Can monitor redox reaction when electrons flow through an electric current
  - **Electric current is proportional to rate of reaction**
  - **Cell voltage is proportional to free-energy change**

Anode: Is where oxidation occurs / Is where electrons are produced / Is what anions migrate toward / Has a negative sign

Cathode: Is where reduction occurs / Is where electrons are consumed / Is what cations migrate toward / Has a positive sign

cal energy to



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Fundamentals of Electrochemistry

Basic Concepts

Redox Reaction

- Reduction-oxidation reaction
- A substance is *reduced* when it *gains* electrons from another substance
  - **gain of e^- net decrease in charge of species**
  - **Oxidizing agent (oxidant)**
- A substance is *oxidized* when it *loses* electrons to another substance
  - **loss of e^- net increase in charge of species**
  - **Reducing agent (reductant)**

Fe_2O_3

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \quad \text{(Reduction)}$$

$$Cu^{+} \longrightarrow Cu^{2+} + e^- \quad \text{(Oxidation)}$$

$$Fe^{3+} + Cu^{+} \longrightarrow Cu^{2+} + Fe^{2+}$$

In order for a redox reaction to occur, both reduction of one compound and oxidation of another must take place *simultaneously*

- ***Total number of electrons is constant***

Fundamentals of Electrochemistry

Basic Concepts

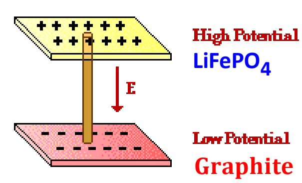
$$LiFePO_4 \leftrightharpoons Li^+ + e^- + FePO_4$$

$$6C + Li^+ + e^- \leftrightharpoons LiC_6$$

$$LiFePO_4 + 6C \leftrightharpoons FePO_4 + LiC_6$$

Electric Potential Difference (E)

- Measured in volts (V)
- Work (energy) needed when moving an electric charge from one point to another
  - **Measure of force pushing on electrons**



Relation between Gibbs free energy, work and voltage:

$$\underbrace{\Delta G = -work}_{\text{Joules}} = -\underset{\text{Volts}}{E} \bullet \underset{\text{Coulombs}}{q}$$

$$q = n \bullet F$$

The chemical driving force across the cell is due to difference in the standard Gibbs free energy change per mole of reaction, ΔG_r. This is determined by the difference between the *standard Gibbs free energies of formation* of products and reactants in the virtual chemical reaction that would occur if the *electrically neutral* materials in the two electrodes were to react chemically.

Relation between Gibbs free energy difference and electric potential difference:

$$\Delta G = -nFE$$

Nernst Equation

Describes voltage that can be generated by a chemical reaction

What Decides the Operating Voltage?

In a LIB, there is a chemical driving force as well as an electrostatic driving force; during open circuit conditions (no current flowing), the chemical driving force on the mobile ionic species within the electrolyte (lithium) is balanced by an electrostatic driving force in the opposite direction:

$$\Delta G_r = -nFE$$

ΔG_r = standard Gibbs free energy change per mole of reaction
= the *standard Gibbs free energies of formation* of products and reactants in the virtual chemical reaction that would occur if the *electrically neutral* materials in the two electrodes (lithium in our case) were to react chemically

E = open-circuit voltage between the two electrodes
n = charge number of electrons transferred/involved
F = Faraday's constant (96,485 Coulombs/mole)

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Terminologies

Coulombic Efficiency:
Coulombic efficiency describes efficiency with which charge (electrons) is transferred in a system facilitating an electrochemical reaction. For anode material in half-cell (active material vs. Li) study:

$$\text{Coulombic Efficiency} = \frac{\text{Discharge capacity}}{\text{Charge capacity}}$$

C rate:
During Galvanostatic cycling, the magnitude of current that the cell is charged and discharged. The higher the C rate, the faster the cell is charged or discharged.

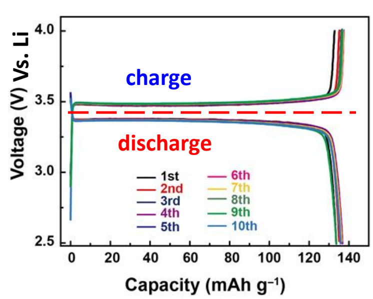
Cycling at 1C rate:
The cell will finish one charging/discharging process within 1 hour.

Cycling at 5C rate:
The cell will finish one charging/discharging process within 1/5 hour (12 mins).

charge →

$LiFePO_4 \leftrightharpoons Li^+ + e^- + FePO_4$

← discharge



$$\Delta G_r = -nFE$$

Theoretical capacity: 170 mAh g^{-1}

Linden, D., & Reddy, T. B. (n.d.). HANDBOOK OF BATTERIES.

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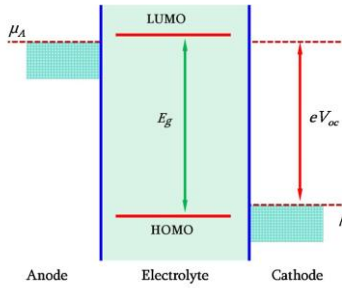
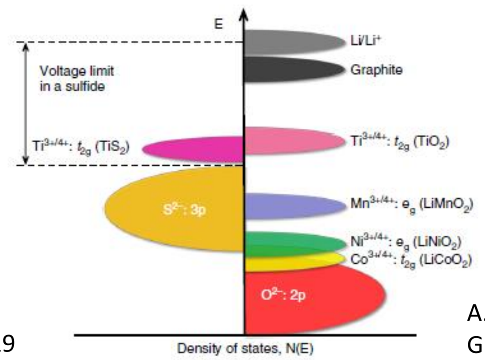
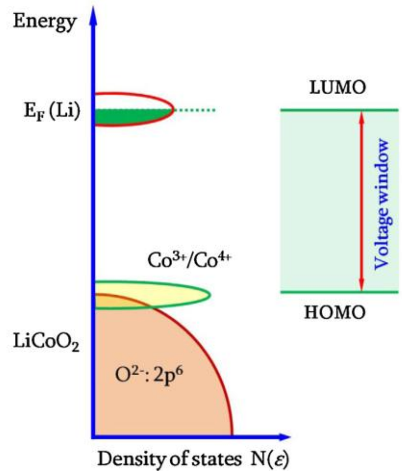
Open Circuit Voltage in a Lithium Battery







A. Manthiram, Nature Commun. (2020)
G. Cao et al., Materials Today, 19 (2016)

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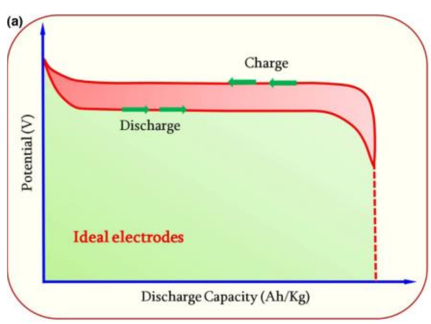
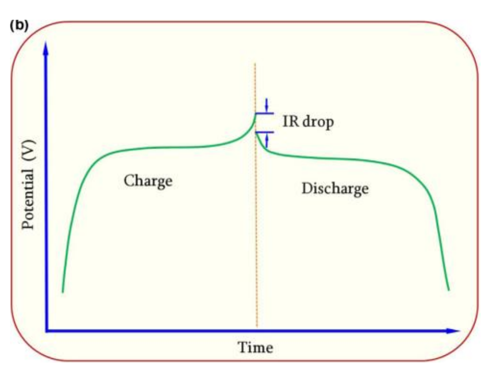
Charge/Discharge Curves in a Lithium Battery



(a) Schematic of potential hysteresis in the charge/discharge procedure of an ideal insertion electrode material.
(b) Illustration of the potential drop in the interval between charge and discharge. Internal resistances chiefly induce the IR drop, which in turn gives rise to side effects that lead to safety issues.



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Specific Energy Density

- A battery is ultimately a device to store energy
- Capacity is only one half of the equation
- Energy density stored in a battery measured in terms of Wh

Specific Energy Density (Wh/kg) =
Capacity (mAh/g)*Operating Voltage (V)

- ➢ Need high capacity electrode materials
- ➢ Need the **cathode's operating voltage to be as high as possible, while the anode's operating voltage to be as low as possible** to maximize cell voltage

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Criteria for Batteries

Several factors influence the choice of battery materials

- Voltage (V)
- Capacity (Ah)
- Rechargeability/cycle life
- Safety
- Cost
- Energy (Wh = V*Ah)
- Power (W)

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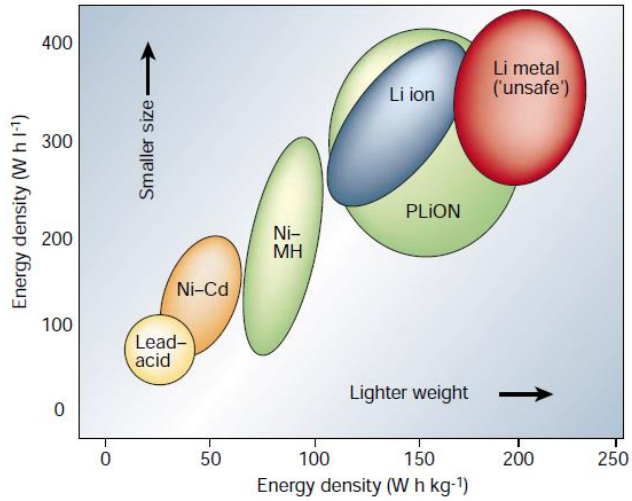
Comparison of Energy Density of Batteries



J.M. Tarascon and M. Armand, Nature, 414 (2001) 359

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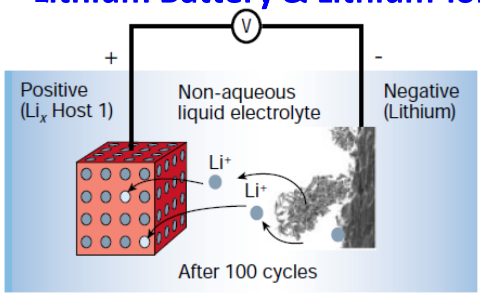
Lithium-ion Batteries (LIBs)

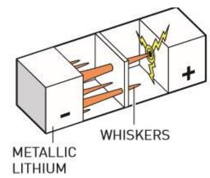
Lithium Battery & Lithium-ion Battery: Comparison



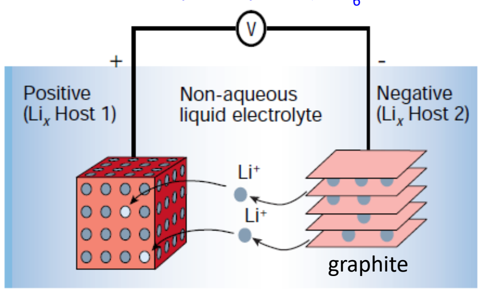
$TiS_2 + Li^+ + e^- \leftrightharpoons LiTiS_2$ (2.0V vs Li)

$LiCoO_2 \leftrightharpoons 0.5Li^+ + 0.5e^- + Li_{0.5}CoO_2$

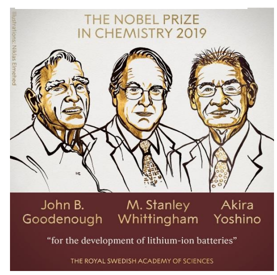
3.9V vs Li



$6C + Li^+ + e^- \leftrightharpoons LiC_6$



J.M. Tarascon and M. Armand, Nature, 414 (2001) 359



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What is a Lithium-ion Battery?

- It basically consists of two types of electrodes:

➢ Cathode (positive electrode): this is generally a lithium-based compound which is capable of "giving away" its lithium

➢ Anode (negative electrode): this is a generally a compound (not necessarily lithium based) which is capable of accepting the lithium that the cathode provides

- Electrolyte: Its function is to ensure that the lithium coming from cathode to anode can "travel" without much hindrance. An electrolyte is an ionic conductor and an electronic insulator.

✓ By this arrangement, the lithium going from the cathode to the anode is forced to travel as its ion, that is, forced to travel as a lithium-ion. The electron, in the meanwhile, travels through the external circuit, doing the required work

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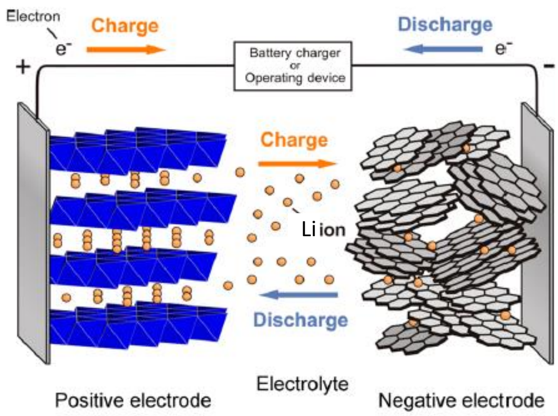
How Do LIBs Work?



Schematic Illustration of the working of a lithium-ion Battery (LIB)

During Charging:
Lithium ions travel from the cathode to the anode (through the electrolyte) with electrons travelling through the external circuit. In the fully charged state, the cathode exists as its lithium deficient phase, while the anode is lithiated. To force the lithium ions to travel, one needs to supply an external current from a battery charger. To maintain charge balance, lithium ions will be forced to depart from the cathode.

During Discharging:
The reverse occurs. That is, lithium ions leave the anode and enter back into the cathode, while the electrons travel through the external circuit from the anode to the cathode, doing work.

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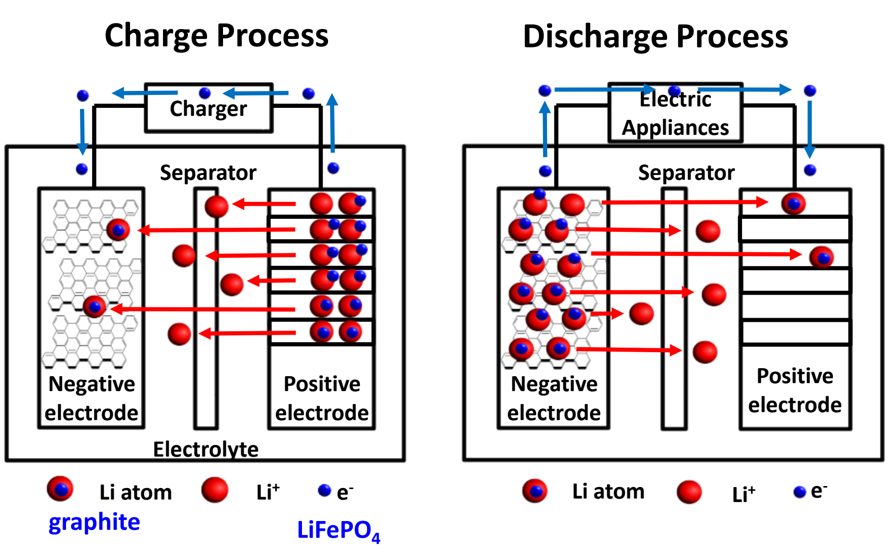
Lithium-ion Battery



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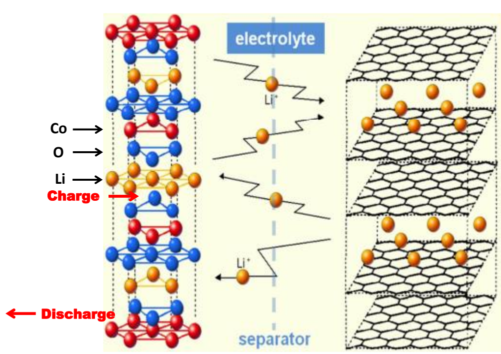
Performance Metrics of LIBs

Commercial Li-ion Battery

Cathode **Anode**



$LiCoO_2$
Layered structure
($R\bar{3}m$ space group)

Graphite

137 mAh/g (4.1 V vs. Li/Li^+)
370 mAh/g (0.2V vs. Li/Li^+

$$LiCoO_2 + C_6 \underset{discharge}{\overset{charge}{\rightleftharpoons}} Li_{1-x}CoO_2 + C_6Li_x$$

$(0 \le x \le 0.5)$

Specific Capacity

- It can be seen that the working principle of LIBs is fairly straight-forward
- To obtain a long-lasting battery, one needs the cathode to supply more lithium, while one needs the anode to be able to accept this lithium (or lithium-ions really, which actually means electric charge as electrons will be travelling simultaneously from the external circuit)
- Hence, one needs high capacity cathode/anode materials. Capacity is nothing but the amount of charge that can be stored in a cathode/anode

Specific Capacity (mAh/g) =
Charge stored (mA*h)/Mass of electrode (g)

- The higher is the specific capacity of cathode and anode, the longer the battery can last before it needs to be recharged

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Specific Energy Density

- A battery is ultimately a device to store energy
- Capacity is only one half of the equation
- Energy density stored in a battery measured in terms of Wh

Specific Energy Density (Wh/kg) =
Capacity (mAh/g)*Operating Voltage (V)

- Need high capacity electrode materials
- Need the cathode's operating voltage to be as high as possible, while the anode's operating voltage to be as low as possible to maximize cell voltage

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Round Trip Energy Efficiency (RTEE)

- The RTEE is a product of the coloumbic efficiency (CE) and the voltage efficiency (VE). Coulombic efficiency (CE) is defined as the ratio of the discharge capacity to the charge capacity:

$$Coulombic\ Efficiency, CE = \left(\frac{Discharge\ Capacity}{Charge\ Capacity}\right)$$

- The voltage efficiency (VE) is essentially the difference in the discharging voltage to that of the charging voltage. It is hence, interchangeable with polarization:

$$Voltage\ Efficiency, VE = \left(\frac{Discharge\ Voltage}{Charge\ Voltage}\right)$$

RTEE = (CE * VE) * 100

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Polarization

- If battery delivers current at a voltage different from the theoretical voltage predicted by $\Delta G_r = -nFE$, then this phenomenon is called Polarization

- To overcome this polarization, the battery discharges at a voltage lower than the theoretical voltage and this difference is called the overvoltage, η

- Likewise, during charging of a rechargeable battery, one needs to supply an extra voltage to see the effects of the reverse chemical reaction

- This leads to low efficiency and needs to be minimized

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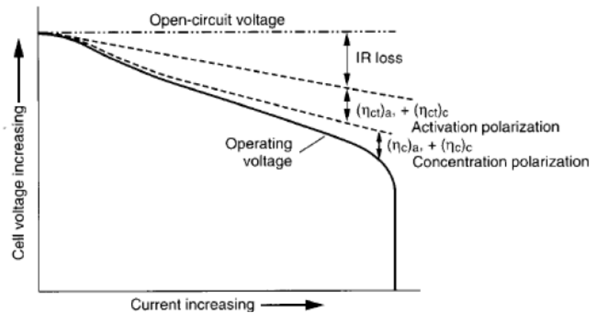
Polarization

- **Theoretical values drop because of inidealities, e.g. charge transfer limitations, contact resistance, etc = *Polarization* effects**

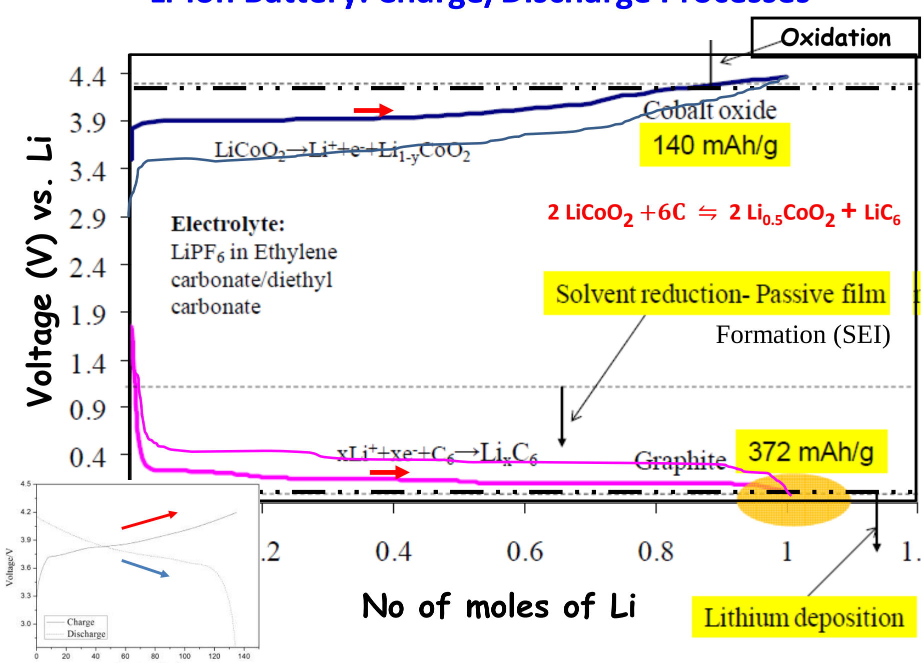
When connected to an external load R, the cell voltage E can be expressed as

$$E = E_0 - [(\eta_{ct})_a + (\eta_c)_a] - [(\eta_{ct})_c + (\eta_c)_c] - iR_i = iR$$

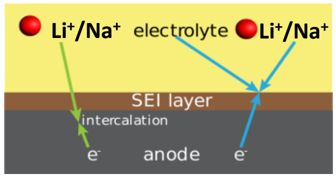
where
E_0 = electromotive force or open-circuit voltage of cell
$(\eta_{ct})_a, (\eta_{ct})_c$ = activation polarization or charge-transfer overvoltage at anode and cathode
$(\eta_c)_a, (\eta_c)_c$ = concentration polarization at anode and cathode
i = operating current of cell on load
R_i = internal resistance of cell



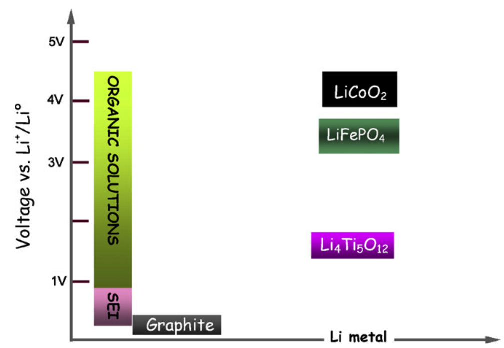
Li-ion Battery: Charge/Discharge Processes



Electrolyte: Electrochemical Stability Window



LiPF6 in EC:DEC:DMC



Solid Electrolyte Interphase (SEI):

The solid electrolyte interphase (SEI) is a protecting layer mostly formed on the negative electrode (anode) of batteries as a result of electrolyte decomposition, mainly during the first cycle.

Battery performance, irreversible charge "loss", safety are highly dependent on the quality of the SEI.

B. Scrosati and J. Garche, J. Power Sources, 195 (2010) 2419

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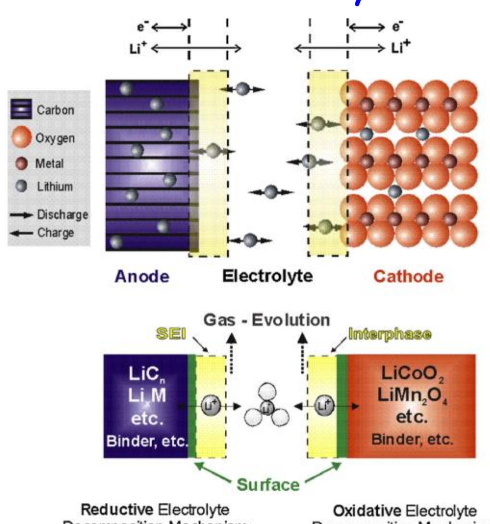
Formation of Solid Electrolyte Interface



Operational principle of SEI formation in a C/LiCoO2 lithium ion battery. Taken from "Report of the Basic Energy Science Workshop on Electric Energy Storage",
Department of Energy, USA, http://www.sc.doe.gov/bes/reports/files/EES rpt.pdf.

B. Scrosati and J. Garche, J. Power Sources, 195 (2010) 2419

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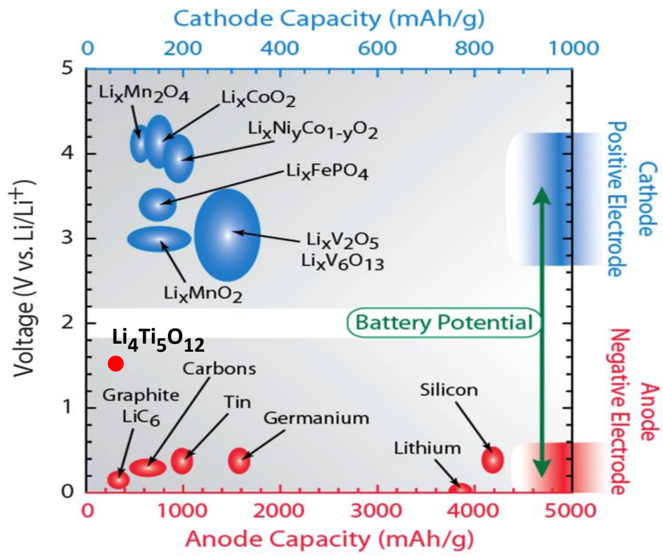
Potential Cathodes and Anodes for Lithium-ion Battery



Landi, B.J., et al., *Carbon nanotubes for lithium ion batteries.* Energy & Environmental Science, 2009. **2**(6): p. 638-654.

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Commercial Type Lithium-ion Battery

18650

A123
2.5 Ah

Pouch

A123
20 Ah

Prismatic

Samsung S7
3.6 Ah

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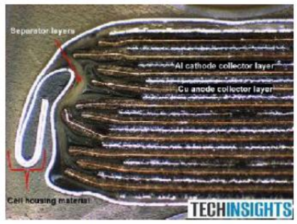
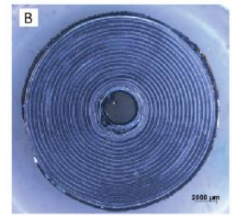
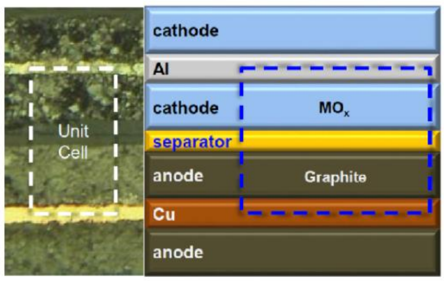
Commercial Type Lithium-ion Battery



Jelly Roll





Metal Foil - Current Collector

Cathode

Separator

Anode

Metal Foil - Current Collector

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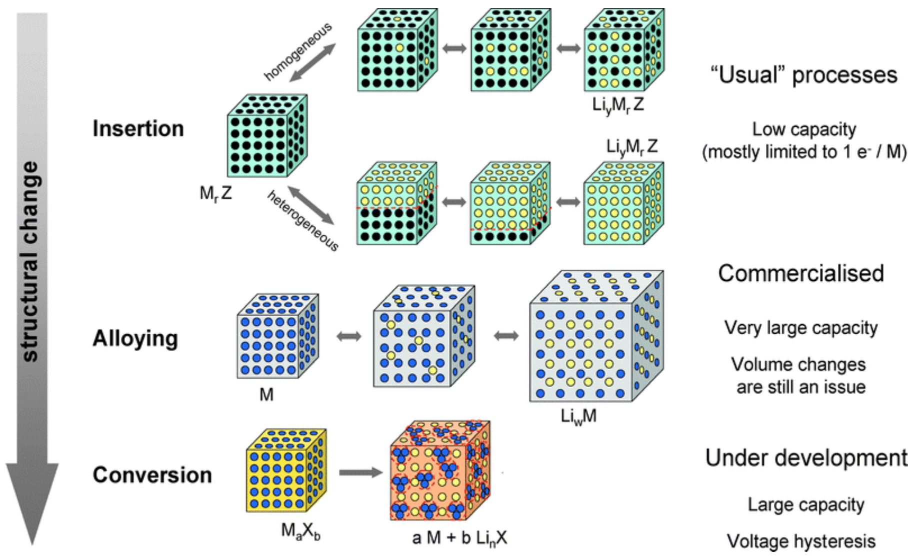
Major Types of lithium Storage Mechanisms in Cathodes and Anodes

Mechanisms of Lithium Storage in Cathodes and Anodes



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Insertion Reactions

- lithium atoms are inserted within/extracted from the empty spaces (within tunnels or layers, as the case may be) of the crystal structure of the anode/cathode. Within this, there could be 2 possibilities:

➢ The original electrode phase and the (de)lithiated phase are essentially the same phase -> **Solid-solution reaction mechanism** => sloping voltage profiles

➢ The original electrode phase and the (de)lithiated phase are different -> **Two-phase reaction mechanism** => constant voltage profile

- Examples: Almost all cathode materials, all lithium titanates anodes, etc.
- Major advantages: Less volume change upon lithium storage. Hence, generally demonstrate long cycle life and less polarization (high efficiency)
- Limitations: Capacity is typically moderate, not exceeding 200 mAh/g

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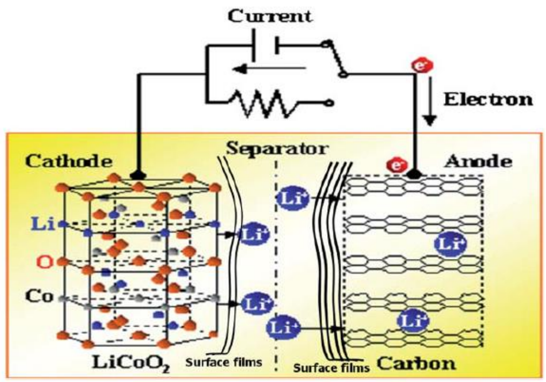
Insertion Reactions



137 mAh/g (4.1 V vs. Li/Li⁺)
370 mAh/g (0.2V vs. Li/Li⁺

$$LiCoO_2 + C_6 \underset{discharge}{\overset{charge}{\rightleftharpoons}} Li_{1-x}CoO_2 + C_6Li_x$$

$(0 \le x \le 0.5)$

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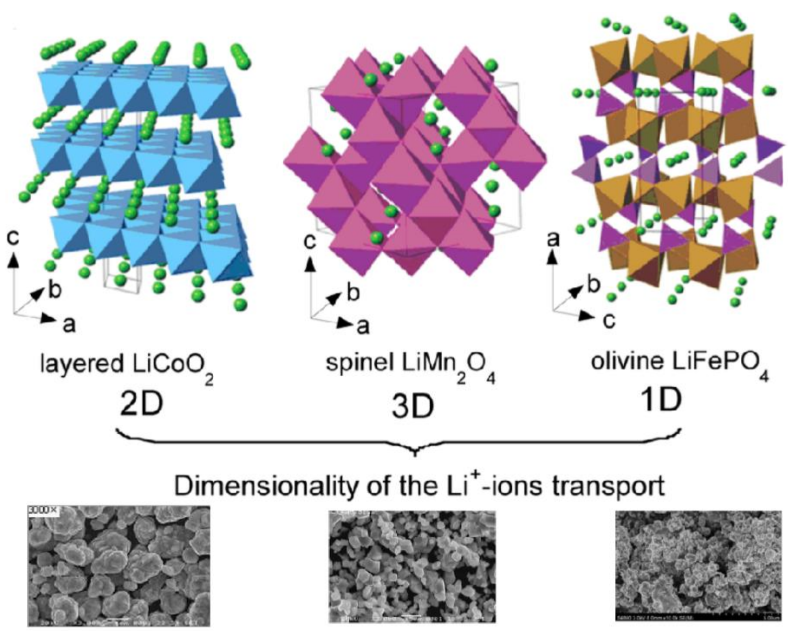
Cathodes



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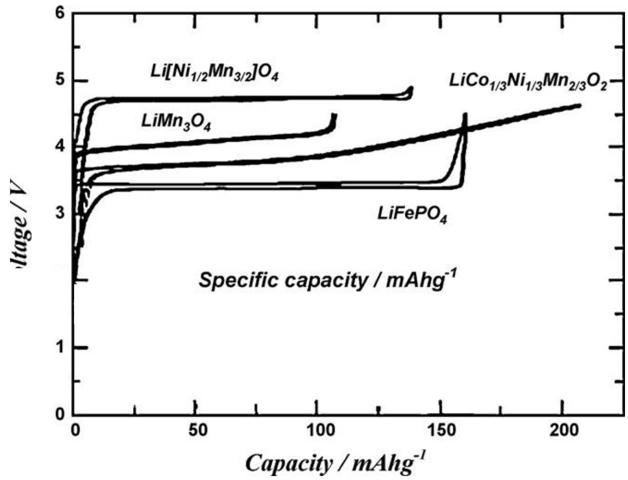
Cathode Storage Performance against Li Metal



B. Scrosati and J. Garche, J. Power Sources, 195 (2010) 2419

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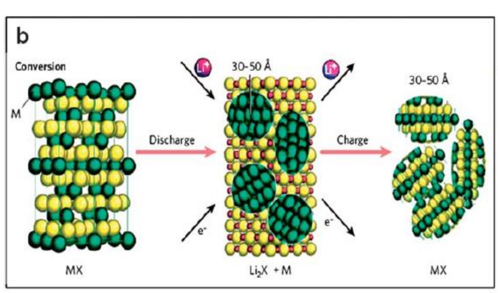
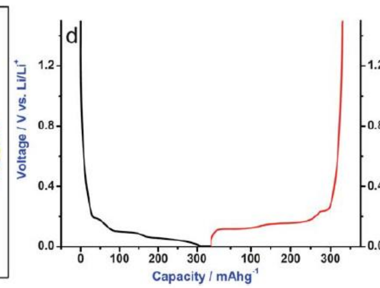
Conversion Reactions

- Involve **significant bond breaking** of the parent phase
- General equation is $Li^+ + e^- + BX = LiX + B$, where BX generally is a metal oxide such as MoO_3 or Fe_2O_3
- Examples: Generally binary metal oxide anodes operating at low voltages
- Major Advantages: Due to the possibility of storing many atoms of lithium per formula unit, capacity can be very high (300 – 1000 mAh/g)
- Limitations: Generally display poor voltage efficiency. Cyclability is also an issue due to huge volume change (100%) hence electrode pulverization





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Alloy Reactions

- Lithium is stored by **forming an alloy** with the host material
- Examples limited to anodes, such as Sn, P, Sb etc.
- Major advantages: Similar to conversion reactions, possibility of very high capacities (up to 1,800 mAh/g possible)
- Limitations: Enormous volume change (200-300%) during lithium storage can limit cyclability and poor voltage efficiency

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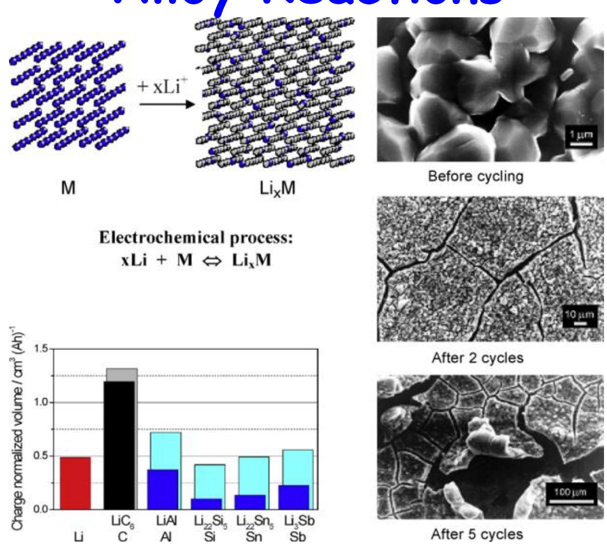
Alloy Reactions



Volume change effects associated to the charge/discharge process of metal alloy electrodes in lithium cells. The figure shows: scheme of Li ion insertion and related volume change during discharge (upper left); comparison of volume changes: pristine material (dark coloured columns) Li+ intercalated material (light coloured columns) (low left) and SEM image of LiM before and after cycling (right).

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Specifications of Various Li-ion Batteries

Cell Chemistries	$LiCoO_2$	$LiFePO_4$	$LiMn_2O_4$
Rate Voltage	3.7V	3.2V	3.8V
Charging Voltage	4.2V	3.7V	4.2V
Discharging end Voltage	3.0V	2.0V	2.5V
Energy Density (Wh/L)	447	222	253
Energy Density (Wh/Kg)	140-145	90-110	105-115
Cycle Life	>700	>1800	>500
Self-Discharge Rate (Month)	1%	0.05%	5%
High Temperature Performance (55+/-2)	Good	Excellent	Acceptable
Low Temperature Performance (-20+/-2)	Good	Good	Good
High-rate Discharge (10C)	Good	Acceptable	Best
Safety & Environmental Concern	Poor	Excellent	Good

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Li-ion Battery for Electric Vehicle Application

Grid-to-Vehicle

The five-passenger vehicle with a 24 kWh lithium-manganese vs. graphite battery for 100 miles range and **recharges in 5-7 hr**

- **Fast charging ?**

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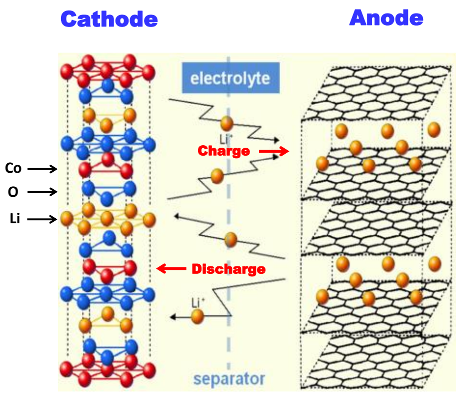
Commercial Li-ion battery

137 mAh/g (4.1 V vs. Li/Li$^+$)
370 mAh/g (0.2V vs. Li/Li$^+$

$$LiCoO_2 + C_6 \underset{discharge}{\overset{charge}{\rightleftharpoons}} Li_{1-x}CoO_2 + C_6Li_x$$

$(0 \leq x \leq 0.5)$

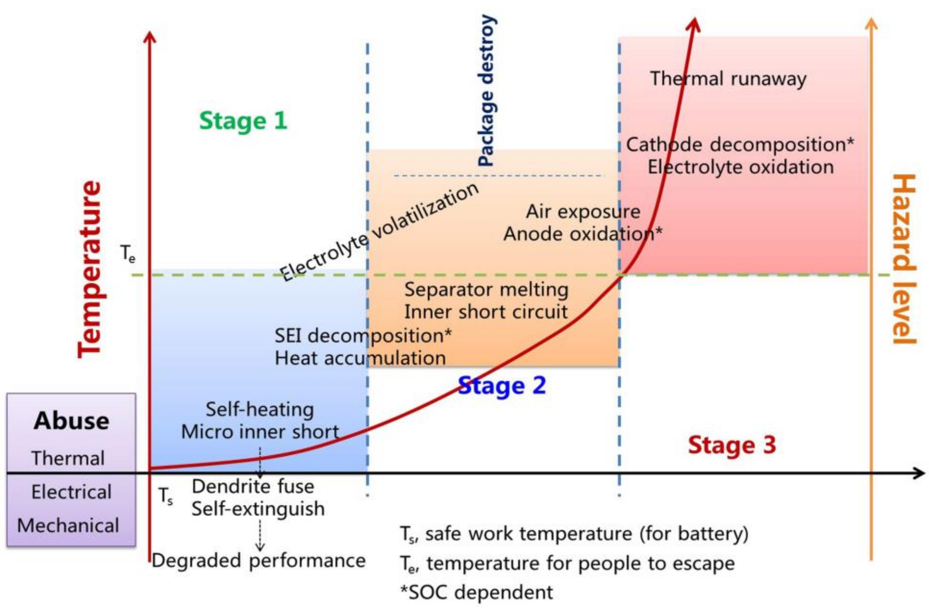


LiCoO$_2$
Layered structure
($R\bar{3}m$ space group)

Graphite

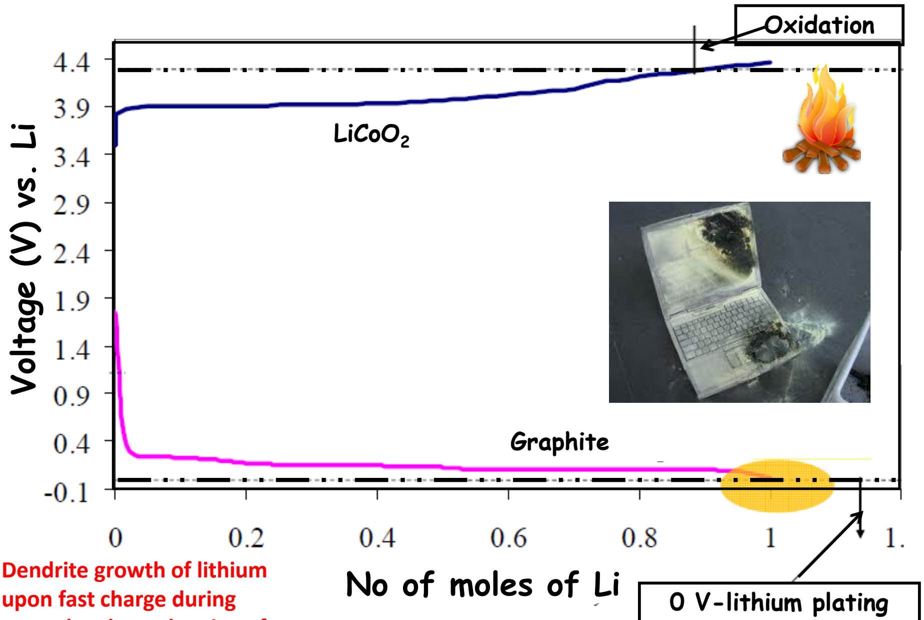
Explosive Safety ?

Safety of Li-ion Battery: Thermal Runaway (3 stages)



X. Wu et al., Front. Energy Res., Vol 7 (2019) Article 65

Conventional Li-ion Battery (unsafe during fast charging)



Dendrite growth of lithium upon fast charge during several cycles – shorting of cathode and anode

http://berc.lbl.gov/venkat/files/batteries-for-vehicles.pdf

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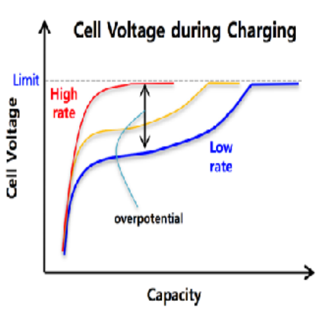
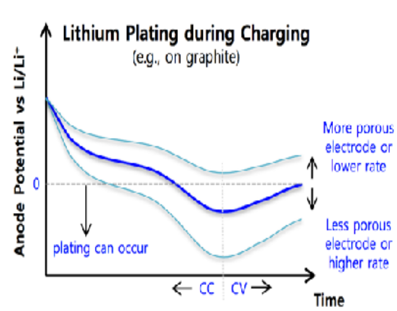
Limitations of Fast Charging of Li-ion Battery using Graphite Anode

- Fast-charge Practically Limited by:
  - Tradeoff between energy density and rate
  - Increased degradation at higher rates
  - Thermal & safety concerns
  - Additional charging-specific concerns, e.g., lithium plating

Lithium plating is a significant concern:
- Carbon anodes very close to Li+/Li potential
- Safety concerns (dendrites) + capacity loss
- Depends strongly on electrode structure/design
- Temperature plays significant role





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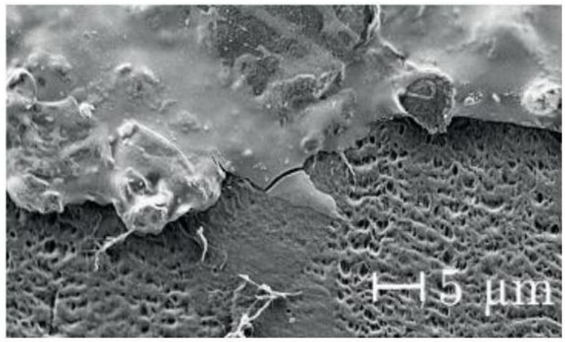
Effects of Vibrations and Shocks on 18650 Li-ion Cells (1.95Ah):

SEM image of the Separator



Evidences for internal shorts in 18650 cell shaken in z-direction for 186 days:
SEM image with partly melted separator layer.

M.J. Brand….A. Jossen, *J. Power Sources* **288** (2015) 62.

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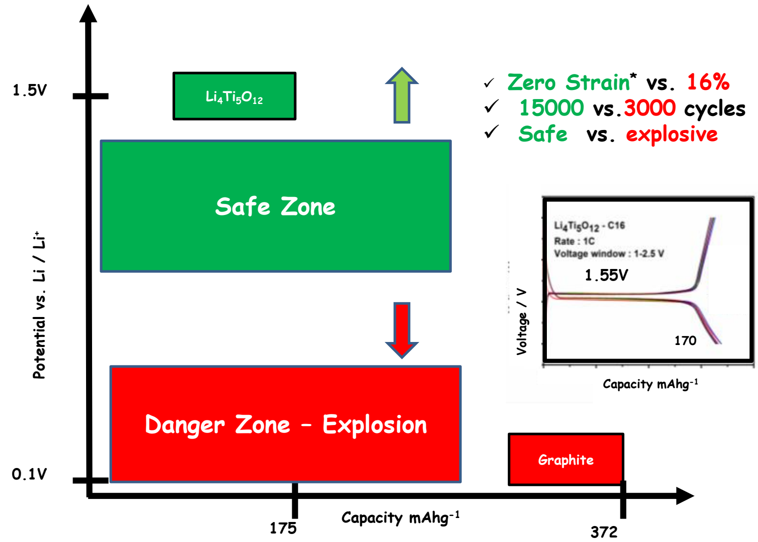
Anode Material:
$Li_4Ti_5O_{12}$

Safer Anode for Fast Charging



$$Li_4Ti_5O_{12}(spinel) + 3Li^{+} + 3e^{-} \Leftrightarrow Li_7Ti_5O_{12}\ (rock\text{-}salt)$$

*T. Ohzuku, A. Ueda, N. Yamamoto, *J. Electrochem. Soc.* **142** (1995) 1431.

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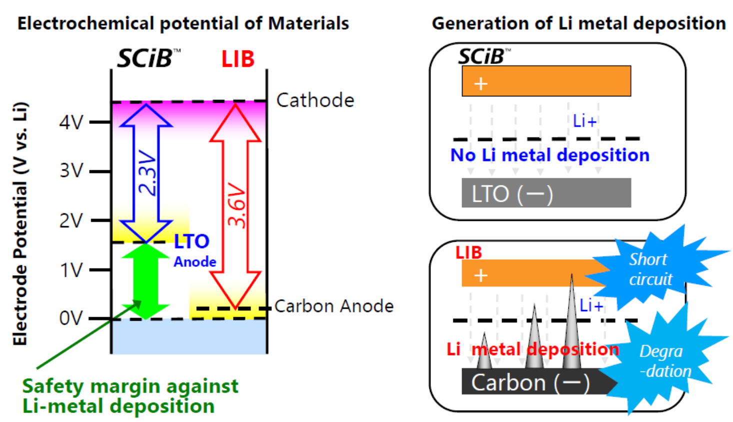
Safety - SCiB™ Design with safety margin

The margin of Electrode potential prevents Lithium-metal deposition even high rate charging in cold conditions



Toshiba, Japan

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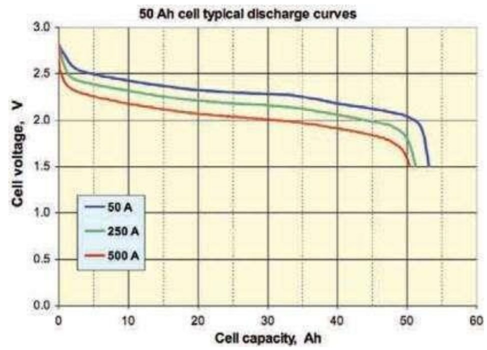
$Li_4Ti_5O_{12}$ Cells

Toshiba, Japan



- **$LiNiMnCoO_2$ against $Li_4Ti_5O_{12}$**
- 60-70Wh/kg (18650)
- Charge/Discharge: 10-15 min.
- **Suitable for addressing intermittency**
- More than 15,000 cycles
- **Cost: Expensive, ~ $500-600/kWh**

For reference:

$LiFePO_4$ vs graphite (18650): 105 Wh/kg
$LiFePO_4$ vs graphite: $100-125/kWh

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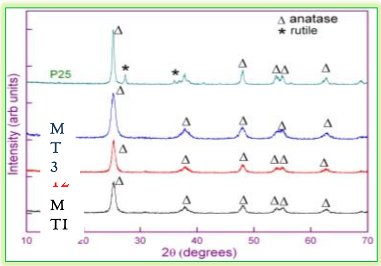
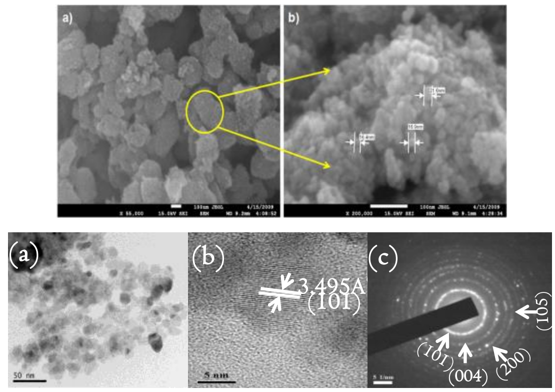
Anode Material for Li-ion Battery
Mesoporous TiO_2

Characterization of Mesoporous TiO_2





- All samples exhibit four distinct peaks (2θ = 25.3, 38.2, 48.1, 55.6): anatase TiO_2
- Average crystallite size : ~ 20 nm

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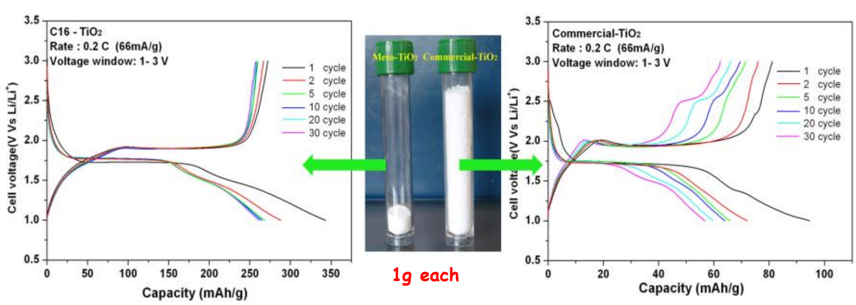
Comparison: Mesoporous TiO_2 vs Commercial TiO_2 Nanopowder



K. Saravanan, A. Krishnamoorthy and P. Balaya, *Energy & Environ. Sci.* **3** (2010) 939

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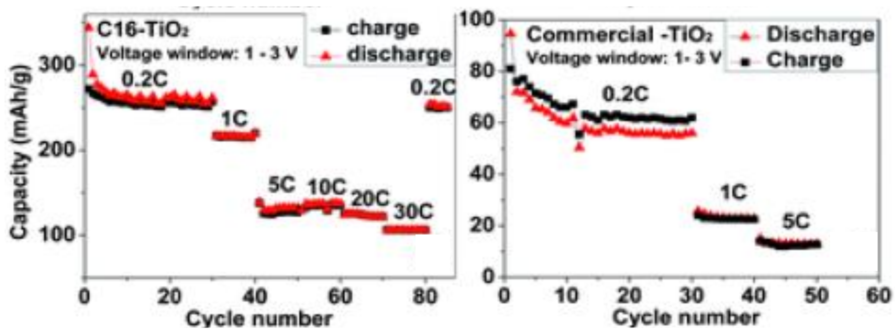
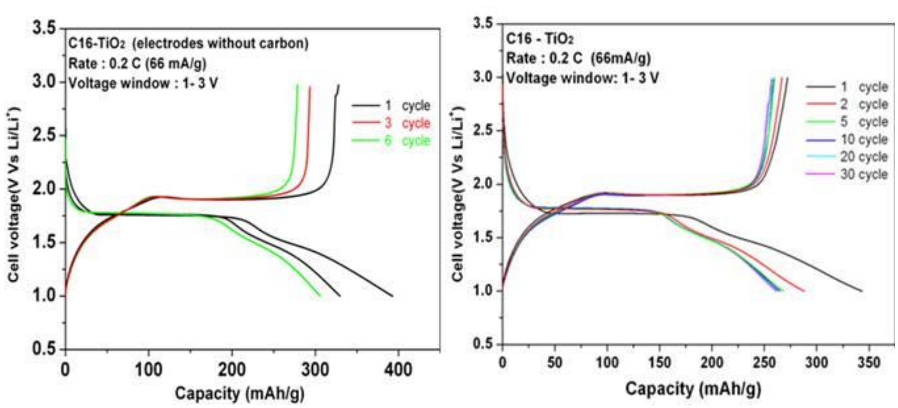
Rate Capability of Mesoporous TiO_2 and Commercial TiO_2



Storage Performance of Mesoporous TiO_2 Electrodes without Carbon Additive

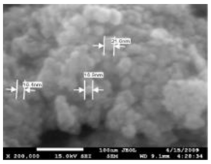


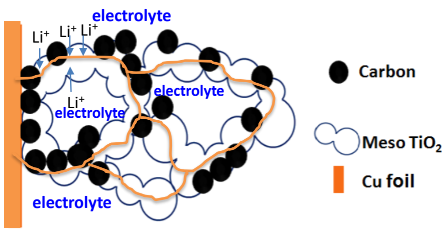
90 : 10
Active materials : binder

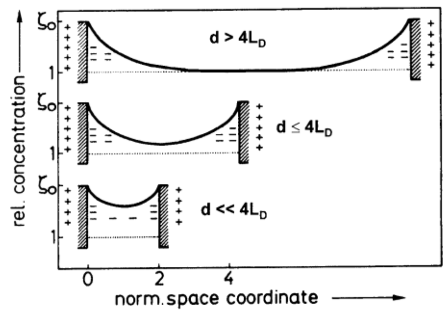
80 : 10 : 10
Active materials: Conductive carbon: binder

Size Effect on Electrical Conduction of TiO_2

$$Ti_{Ti}^{x} + 2O_{O}^{x} \leftrightarrow Ti_{i}^{\cdot\cdot\cdot\cdot} + 4e' + O_2(g)$$







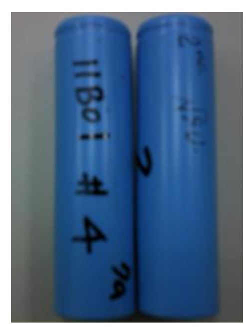
Defect profiles in structures with dimension, d. The build defect concentration is not reached when d **<<** 4L, where L, is the Debye length

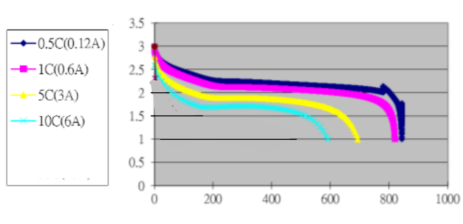
C D. Terwilliger and Y.-M. Chiang *J, Am. Cream. Sac.*, **78** (1995) 2045.

18650 Li-ion Battery Fabricated using Meso-TiO_2 vs $LiMn_2O_4$

Up scale the production of mesoporous TiO_2 (LHS)

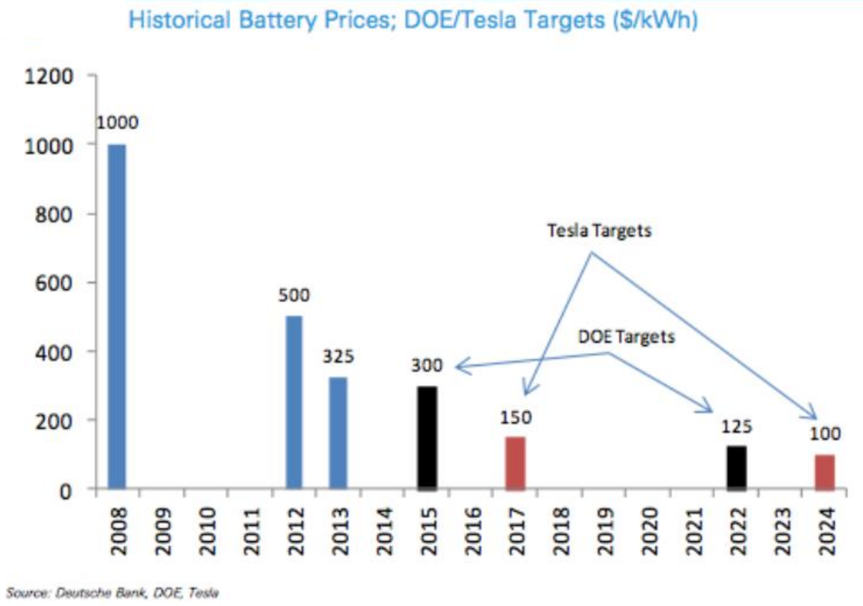
18650 Li-ion battery cells using commercial $LiMn_2O_4$ cathode and mesoporous TiO_2 anode (RHS)





Discharge curves of 18650 cell at various rates (cell fabrication by MOLICEL, Taiwan)

Li-ion Battery: Target of Cost - Projection



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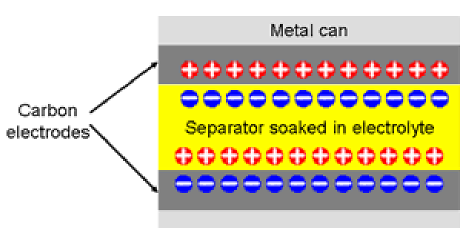
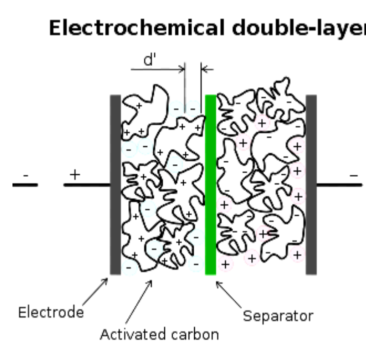
Electrochemical Capacitors (10-20 Wh/kg)



Double Layer Capacitor



- High efficiency
- Large cycle life (close to 0.1 Mil)
- High rate performance (10000W/kg)
- No need of special circuit
- Very high voltage – design
- Battery + supercapacitor enable the full regenerative charge to be captured

$Q = (A\varepsilon V / 4\pi d)$

- Low energy density (10-20 Wh/kg)
- High capital cost per unit of energy
- Limited to short duration power boost applications – UPS etc.,

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Thank you