

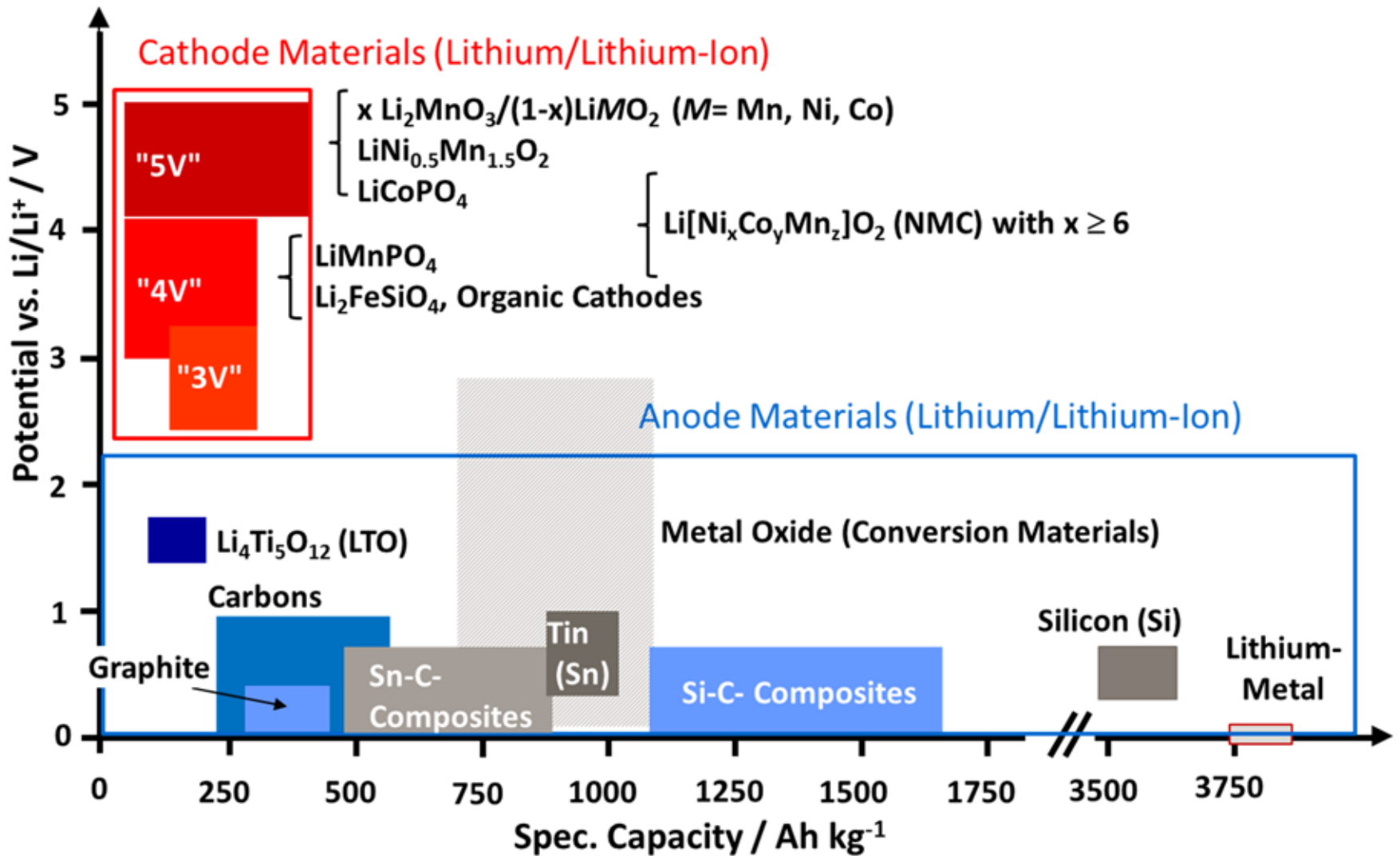
Lithium-Ion Batteries and Beyond

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II. Anodes

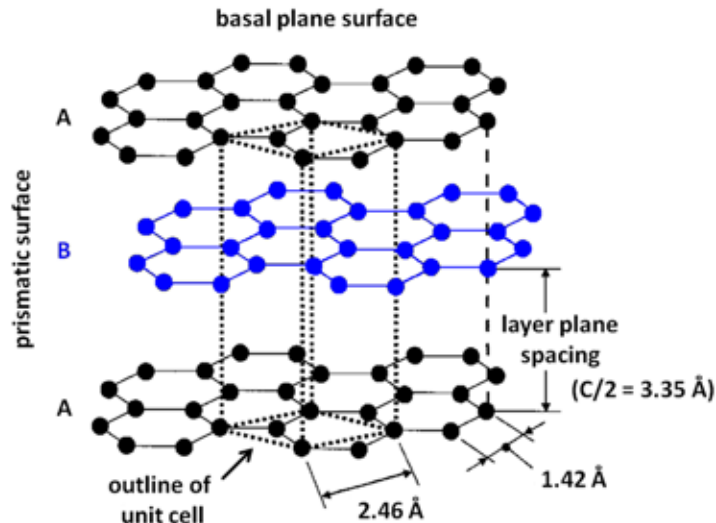
1. Introduction to Lithium-Ion battery materials
2. Carbonaceous and graphitic anodes
3. Alternatives to carbonaceous and graphitic anodes
 - i. Overview
 - ii. Lithium-storage metals and alloys
 - iii. Metal oxides
4. Pre-lithiation and other measures to compensate for C_{irr}



Carbons in > 99 % of commercial LIBs

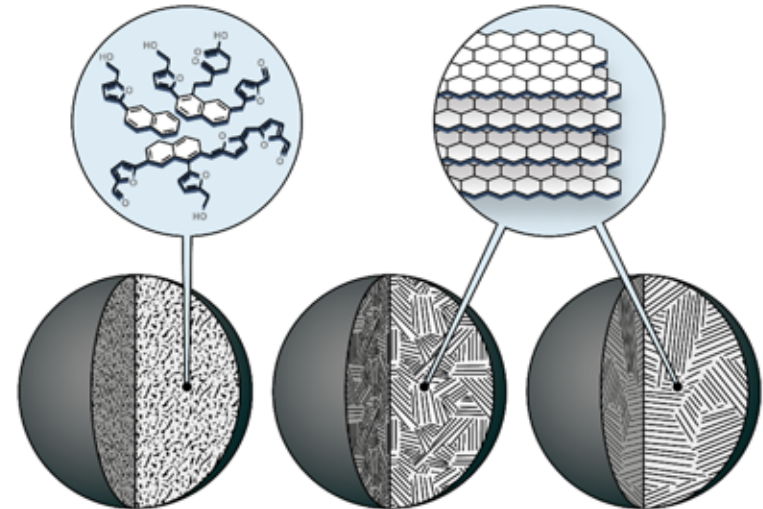
Graphitic carbons

- Natural & synthetic graphites
 - Morphologies: flakes, (micro-)beads, fibers, whiskers, mesocarbon, core/shell materials, ...

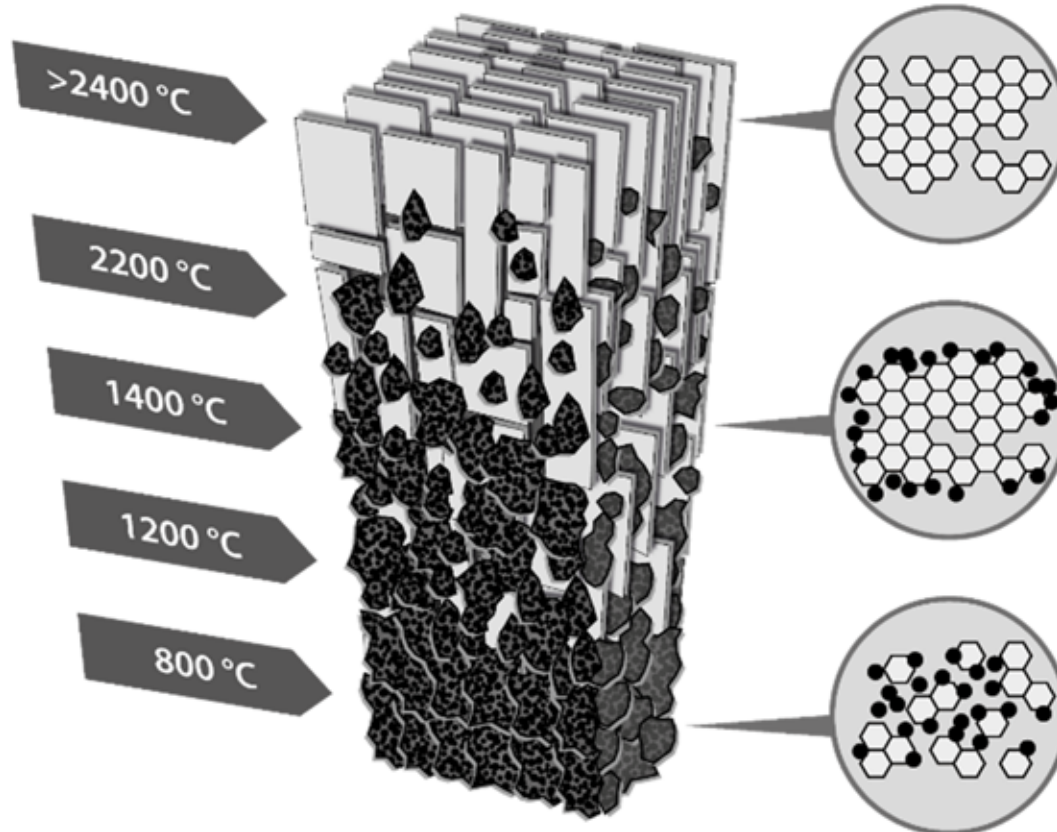


Non-Graphitic carbons

- Graphitizable (soft) carbons
- Non-graphitizable (hard) carbons
 - Other terms: amorphous carbons, carbon blacks, activated carbons, cokes, etc.



- Carbonization/graphitization leads to various intermediate forms of different crystallinity
- The transition between graphitic and graphitizable (soft) carbons is fluent

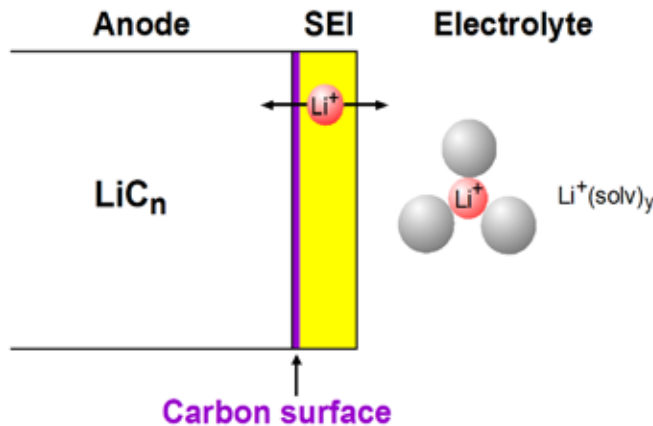
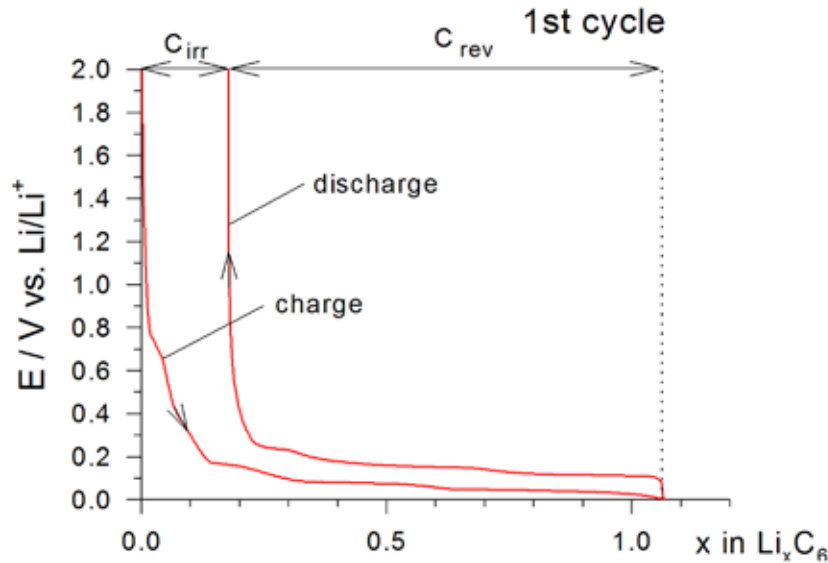


During carbonization, layers of condensed carbon hexagons (= graphene layers) grow.

The edges of the condensed carbon layers contain foreign atoms (•), that are removed during carbonization at higher temperatures.

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Some carbon precursors cannot be graphitized → Hard carbons

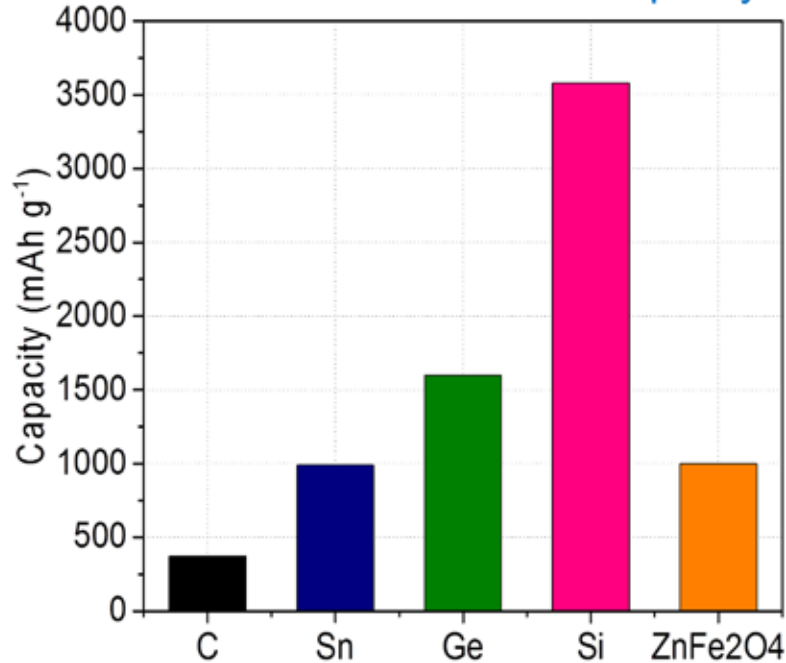


- LIB cells are assembled in the discharged state, i.e., with a lithium-free anode and a lithiated cathode.
- During the first charge processes (mainly in the 1st cycle), the Li⁺ insertion process into carbon/graphite is accompanied by electrolyte decomposition and SEI formation → a part of the charge city is irreversible (**C_{irr}**), associated with loss of material (electrolyte decomposition and Li⁺-immobilization). The other (main) charge capacity part is reversible (**C_{rev}**)
- Charge capacity – Discharge capacity = **C_{irr}**
Discharge Capacity = **C_{rev}**

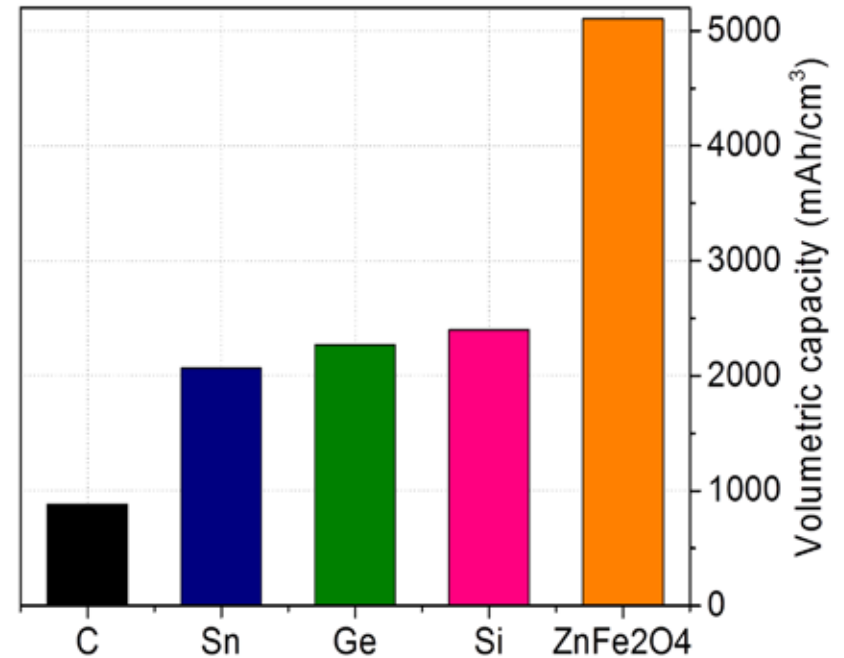
$$\text{Coulombic Efficiency (CE)} = \frac{\text{Discharge capacity}}{\text{Charge capacity}} (\%)$$

- 1st cycle, CE of graphite is typically 90 – 98%
- In the later cycles, CE: > 99.8%
- The 'Li losses' by Li⁺-immobilization in the SEI do reduce the practical cell capacity.
- The extent of **C_{irr}** depends on the anode material (surface area, morphology, chemistry) and the composition of the electrolyte.

Gravimetric Capacity



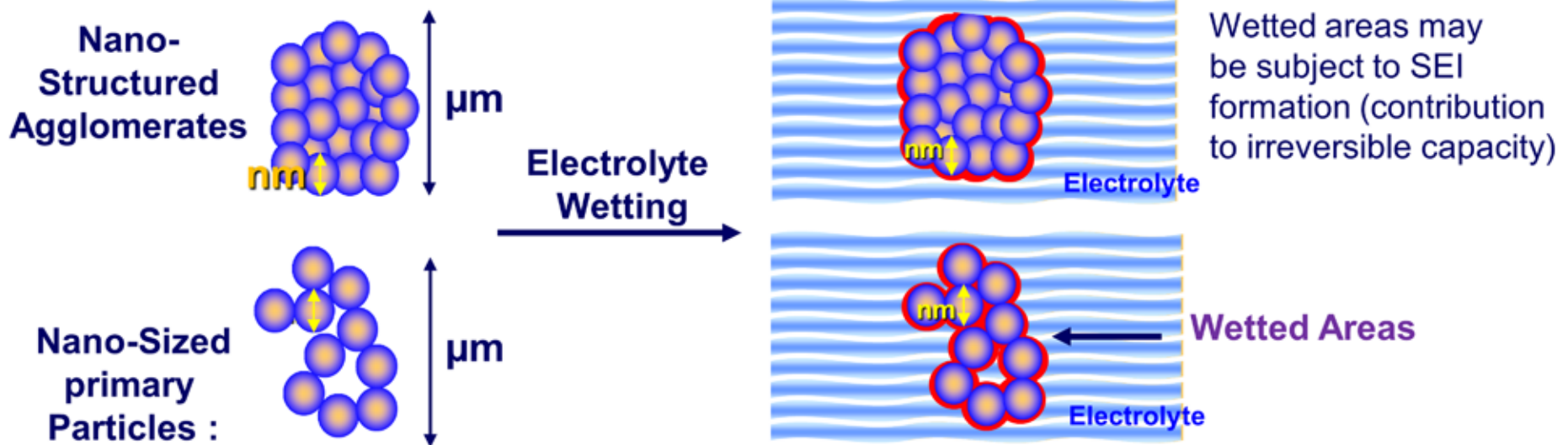
Volumetric Capacity



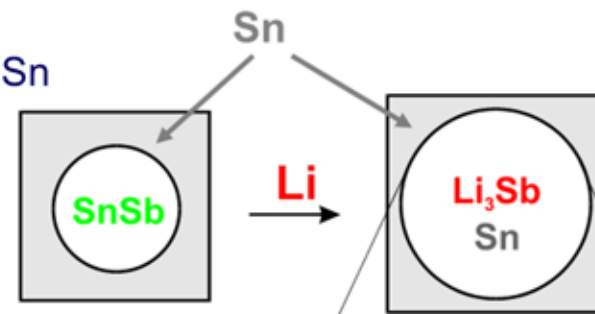
- Many anode materials with higher capacity than graphite
- ‘Alloying’ and conversion materials are heavily investigated
- Practical volumetric capacities depend on material, electrode, and cell design and may change during cycling
- Capacity C ≠ Energy E

Relationships between primary particles, agglomerates, and aggregates

- Single particles → Primary particles in various geometrical forms.
- By weak physical interactions (adhesion), the primary particles do agglomerate to larger units. Consequently, agglomerates are not fixed units, but could change their size and shape.
- Aggregates are an assembly of primary particles that have grown together. The total specific surface area is less than the sum of the surface areas of the primary particles.



- **SnSb**: Intermetallic of Sn and Sb
 - Nano-structured composite: SnSb is embedded in Sn
 - During lithiation → mosaic structure is formed (= further nano-structuring)
 - SnSb/Sn is an active/active multiphase: Both Sb and Sn are active to Li:
- Overall better cycling stability than pure Sn and SnSb



Two-step reaction mechanism:

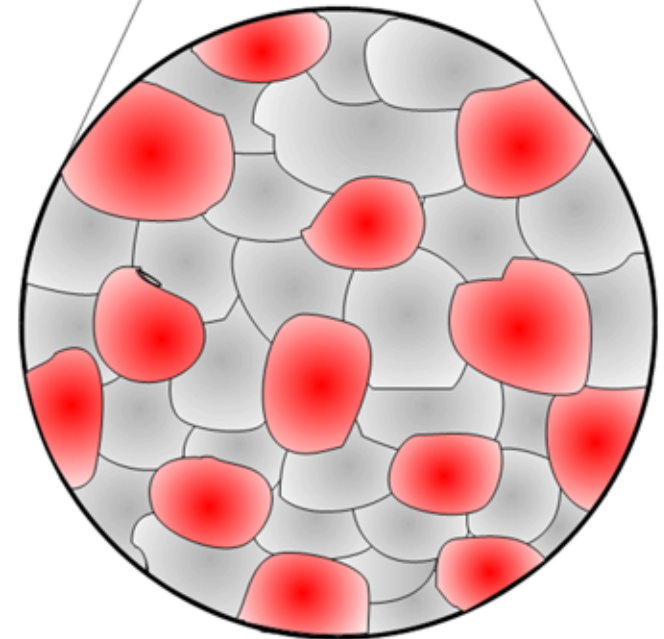


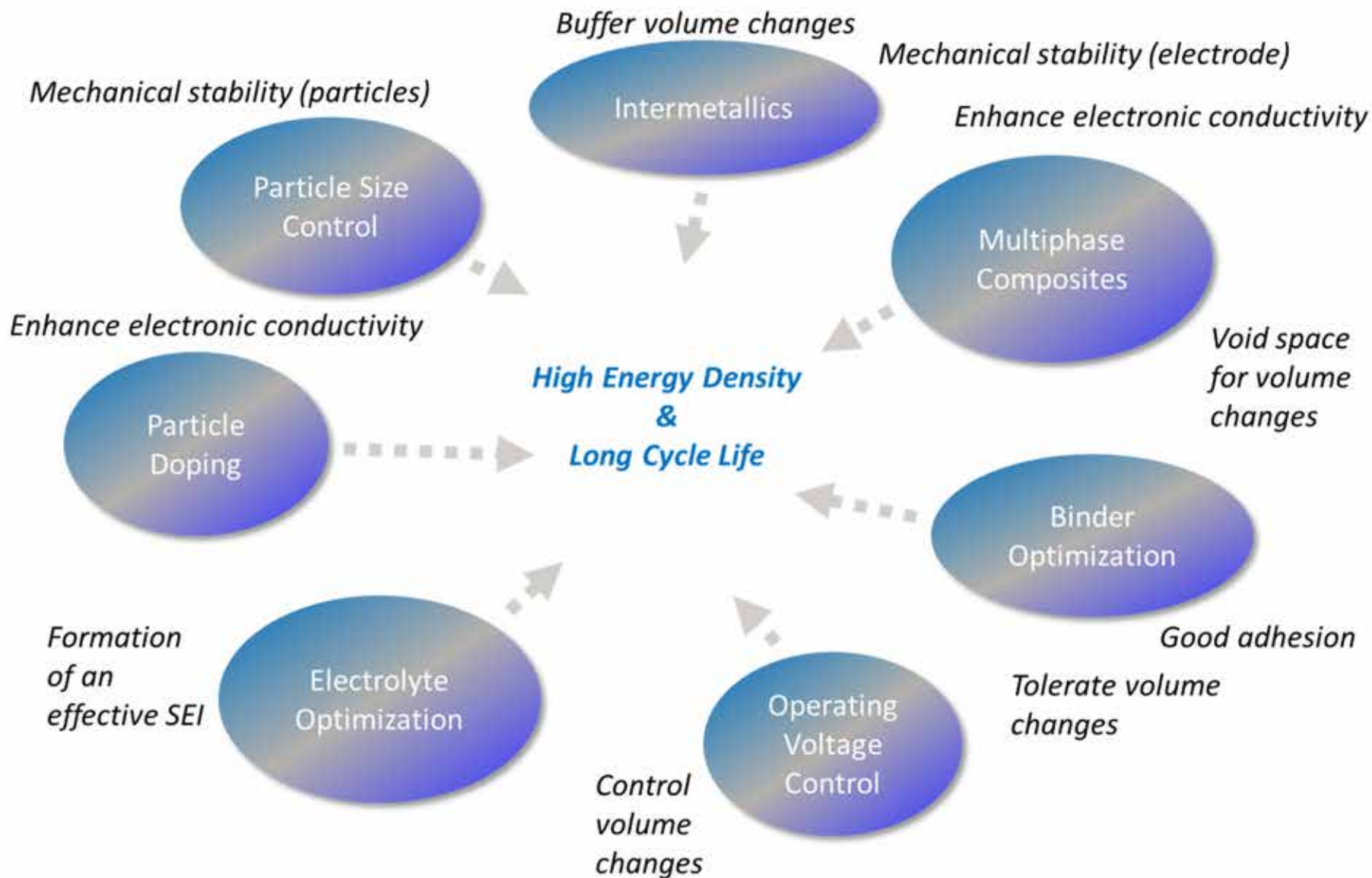
Further example: Sony's Next Era Lithium-Ion (**Nixelion**) Battery:

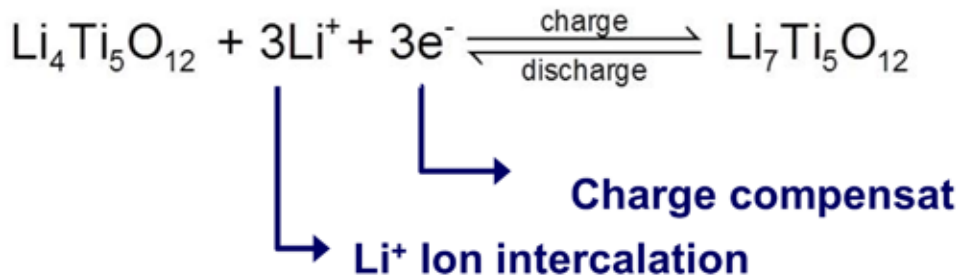
50% more anode capacity, 30% more cell capacity

SnCo/C hybrid anode; combination of:

- Nano-structure
- Sn as reactive phase
- Dilution by Co, inactive to Li
- Dilution by less active C, with limited capacity and volume change
- SnCo is an active/inactive multiphase

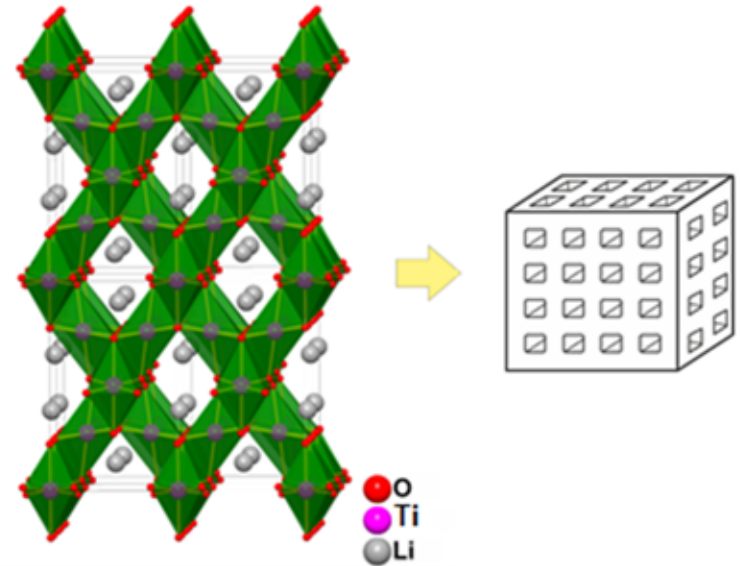












takes up to 3 Li⁺ ⇒ Li₇Ti₅O₁₂
 ≈175 Ah/kg_{theoretical} at 1.55V vs. Li/Li⁺

3D - Spinel Crystal Lattice



-  **Very long cycle life:** 10,000 deep cycles
-  **High charge/discharge rate,** in particular nano-LTO
-  **Very temperature tolerant**

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-  **Low cell voltage** (1.9 – 2.6V)
-  Lower energy density than C-Anodes
-  Higher **costs** per kWh

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- Addition of a compound that compensates for irreversible Li losses.
Addition to the electrode (anode [1] or cathode [2]) or to the electrolyte [3])
The compound reacts after assembly or during formation and provides additional Li^+
- [1] Metallic Li added to the anode → Anode lithiation and SEI formation after electrolyte addition
Disadvantages: High reactivity of Li metal with the electrolyte → heat
Incomplete Li-metal consumption → metallic Li remains in the LIB cell → safety risk
- [2] Addition of Li-rich compounds, such as Li_5FeO_4 (LFO) to the cathode; LFO capacity: 867 Ah/kg
LFO does provide substantial Li^+ during the first charge, but does react irreversibly
Disadvantages: Increase of dead weight in the cathode, eventual dissolution of LFO
- [3] Sacrificial Li salts, that during the 1st charge of the LIB cell decompose to gases and Li^+
Disadvantages: Gas formation increases internal cell pressure,
Gas needs to be separated from the cell after formation
- Caution: Anode and cathode capacities in LIB cells are balanced so that an excess of anode sites for Li^+ storage is provided → Risk of plating of metallic Li on the anode surface is reduced → better safety
- Pre-lithiation and other measures will create additional Li^+ that changes this balance
→ Impact on safety

[1] Z. Wang et al., Journal of Power Sources 260 (20146) 57 - 61

[2] X. Su et al., Journal of Power Sources 324 (2016) 150 - 157

[3] D. Shanmukaraj et al., Electrochemistry Communications, 12 (2010) 1344–1347