

Lithium-Ion Batteries and Beyond

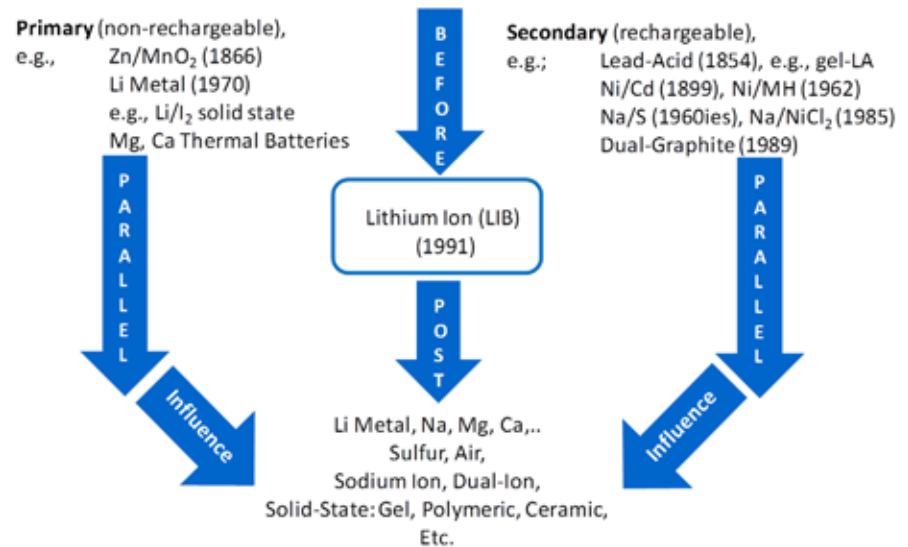
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VI. Beyond Li-Ion Batteries

1. Definitions: Beyond Lithium Ion, before Lithium Ion, and parallel to Lithium Ion
2. How to make high-energy-density (“super”) batteries?
3. Specific energy vs. energy density: a necessary look at new cell chemistries
4. Lithium/sulfur chemistry
5. Lithium/air chemistry
6. Solid electrolytes: polymeric and ceramic electrolytes
7. Alternative chemistries: Na, Na-Ion, Mg, Al, Dual-Ion

- Lithium-Ion Batteries (LIBs) were first commercialized by SONY in 1991.*
- Batteries, in general, are more than 200 years old.
- Many rechargeable and non-rechargeable (primary) battery systems have been developed since then (Before-LIB). A few are still relevant today (Parallel-to-LIB)
- Based on its unique mix of beneficial performance and cost properties, the LIB has become a benchmark for future battery systems (Post-LIBs, PLIBs).
- Past experience with LIBs and Before-LIBs will help to develop PLIBs



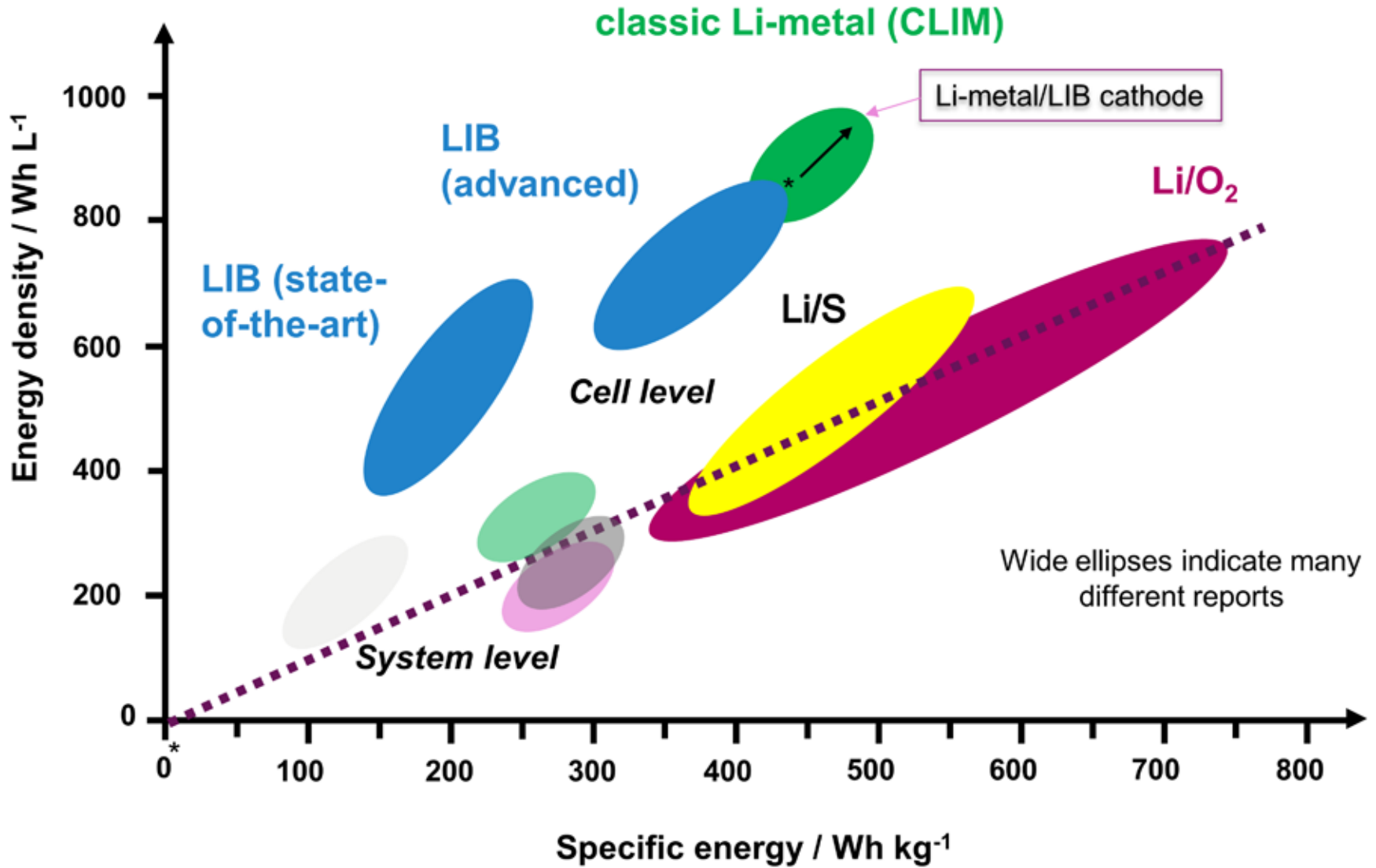
(Magnified figure on next slide)

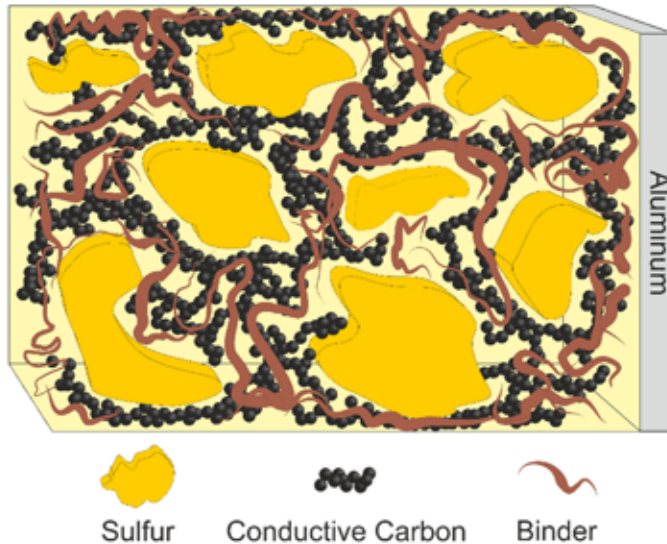
*T. Nagaura, *Progress in Batteries & Solar Cells*, 10, 218 (1991)

- Capacity and potential of the electrode materials determine the maximum achievable cell energy density of LIBs and lithium-metal batteries.
- The assignment as cathode or anode material proceeds according to the relative electrode potentials (cf. discussion on standard reference potentials).
- Specific capacity values are given in Ah/kg; volumetric capacities in Ah/L.
- The number of state-of-the-art Li-metal and LIB electrode materials is limited (next slide)
- There are numerous possible future LIB materials. The second next slide shows only a few examples.
- State-of-the-art and future LIB anode materials show significantly higher capacities than LIB cathode materials.
- Future anode materials show much higher capacities than carbon/graphite.
- Future LIB cathode materials show higher voltages than state of the art → High voltage.
- There is a mismatch in specific capacities of anode and cathode materials, even for state-of-the-art LIB materials, whereas the volumetric capacities are better balanced.
- For standard Li-metal batteries, the specific anode capacities are also misbalanced. Future cathode materials, such as S and O₂ show a better specific capacity balance.

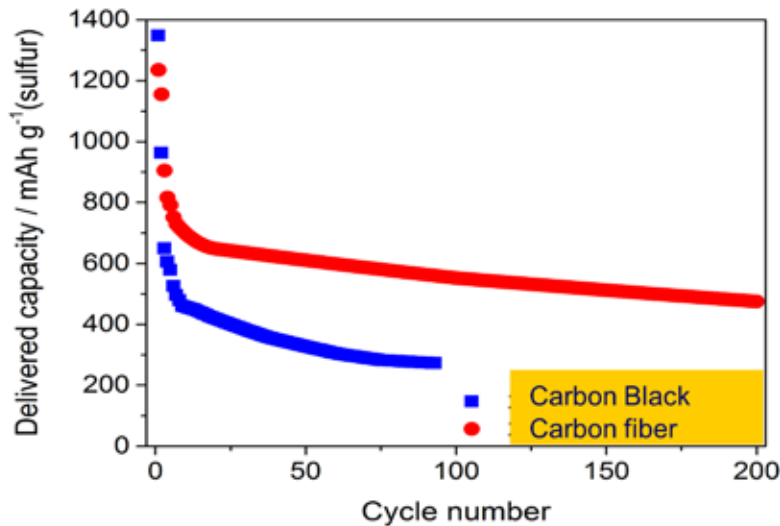
- Due to limited installation space in vehicles (as is well-known from portable consumer electronics), volumetric capacity, and energy density have gained increasing importance.
- Whereas the specific capacities of LIB and Li-metal battery materials range from 100 – 4,000 Wh/kg, the corresponding volumetric capacities only range from 500 – 2,500 Wh/L.
- Practical volumetric electrode capacities do not only depend on the capacity of the active material, but also on the used inactive materials and the electrode porosity.
- Li/S and Li/air cells need more inactive materials and show higher porosities than LIB cells → reduced practical energy densities (Wh/L).
- LIB cells show typical cell voltages of 3.5 - 4V. Li/S cells show typical cell voltages of 2V → A Li/S battery system needs more cells to achieve similar voltages as a LIB-system.
- Li/air battery system needs additional system components, such as air supply, air filter, compressor, gas purification (CO₂, H₂O removal), etc. → reduced energy densities (Wh/L).

Available with Report purchase





- Sulfur is an insulator
- Electrolyte wetting → Electrode porosity ca. 30-40%
- Electrode needs substantial amounts of conductive additive, e.g., conductive carbon
- Binder → as “glue” for the particles



- Often carbon weight and volume is disregarded in capacity and energy calculations
- Type of carbon is important for performance
- Many (fancy and expensive) carbons under investigation

- Goal 1: Higher energy density (Wh/L)
- Goal 2: Better cycle life, better efficiencies (less hysteresis)
- Goal 3: Higher safety and reliability (Li metal, air and sulfur reactivity)

Possibilities and Measures

- Less carbon content in air & sulfur electrodes (without compromising life?)
- Thinner air electrodes (→ For realization, the discharge product needs to be dissolved in the electrolyte. Eventually, aq.-solvent-based electrolytes seem to be a solution)
- Immobilized/encapsulated sulfur → reduced dissolution in the electrolyte
- Less irreversible reactions, better kinetics → better efficiencies
- Decreasing Li reactivity with electrolyte and impurities (Li_2S_x , CO_2 , N_2 , H_2O)

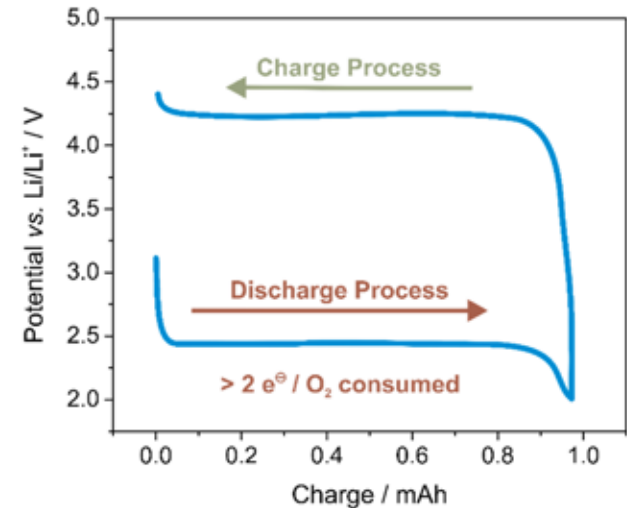
Current electrolytes are problematic

- Large potential gap between charge and discharge curve (= 'Potential hysteresis')
 - Search for catalysts to reduce hysteresis
- More charge is measured than what is calculated for the $\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$ reaction indicates side reaction
- Side reactions involve the (irreversible) reduction and oxidation of the electrolyte
- (Intermediate) reaction species lithium superoxide LiO_2 is highly reactive with electrolyte
 - continuous electrolyte decomposition causes the cell to dry out

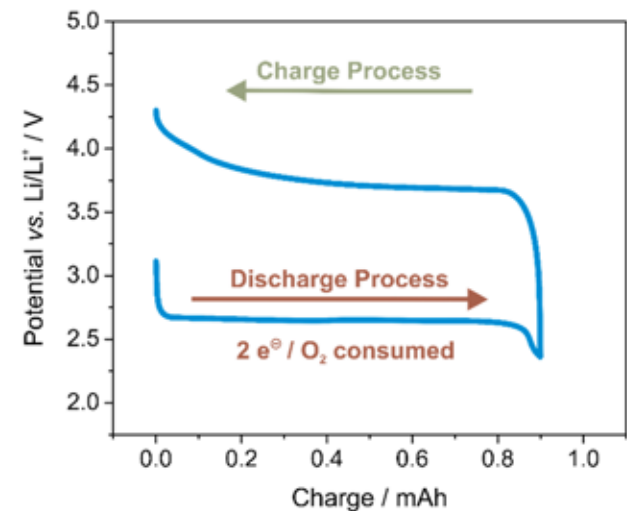
→ **Alternative electrolytes are investigated. In general, electrolytes are needed that:**

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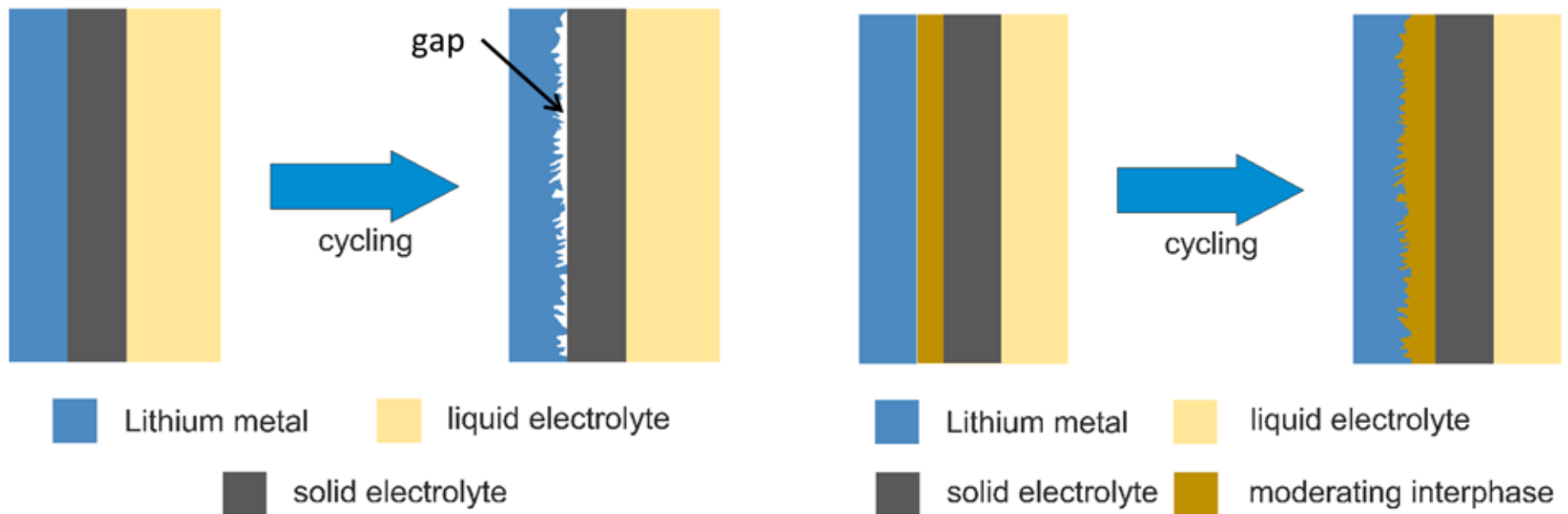


Small hysteresis



Step 1: Li⁺-ion conducting solid electrolyte protects the reactive Li vs. the electrolyte.

Step 2: For the use of “thick” Li electrodes and in order to keep the contact between the firm solids during cycling, an (also Li⁺-ion conductive) “moderating” interphase is needed.

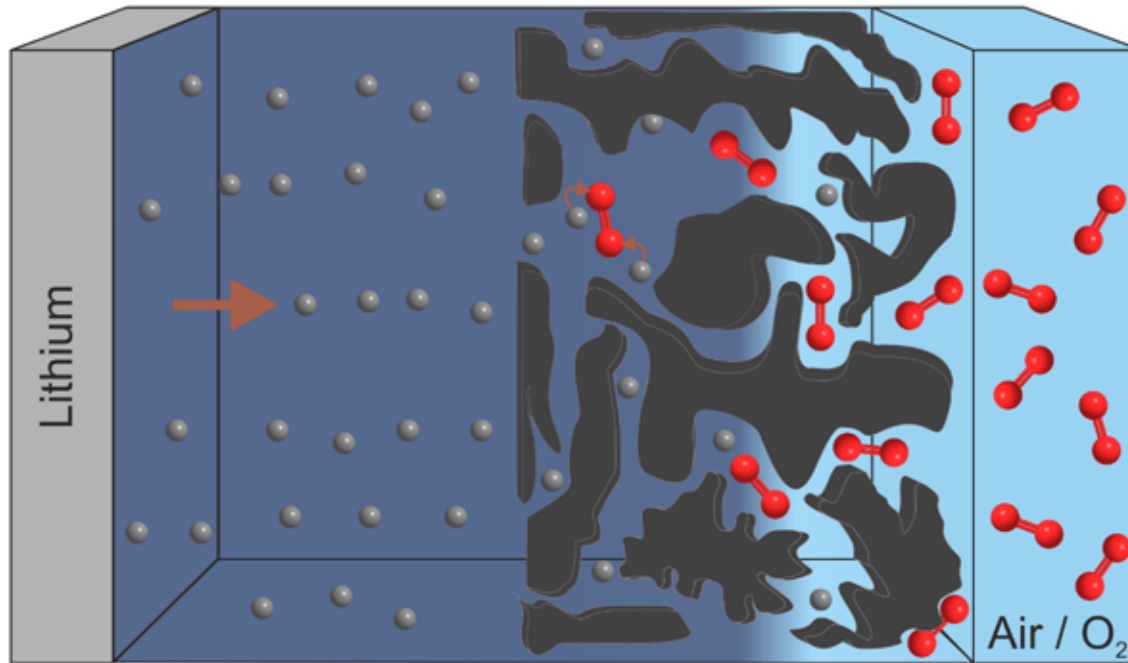


Summary: Can work:

- if the moderating interphase is flexible and durable
- if the solid electrolyte does not dissolve and is mechanically stable
- if the electrolyte is electrochemically stable vs. anode and cathode

Ultimate goal: All Solid State Battery (ASSB, no liquid-cell component)

Solid State Li/Air Cell



All-solid-state battery (AASB):
No liquid component

Ceramic electrolyte is thermally stable and non-flammable

Unknowns:

Solubility of oxygen in the SE?

Wetting of the air electrode with the SE?

Conformation of Li/SE interface during cycling?

Conformation of the air electrode/SE interface during cycling?



Flammability, Leakage, Gas formation



Low and high temperature performance



Dissolution of electrode materials



Drying out by decomposition



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No/Less Flammability, Leakage, Gas, Dissolution, Drying out



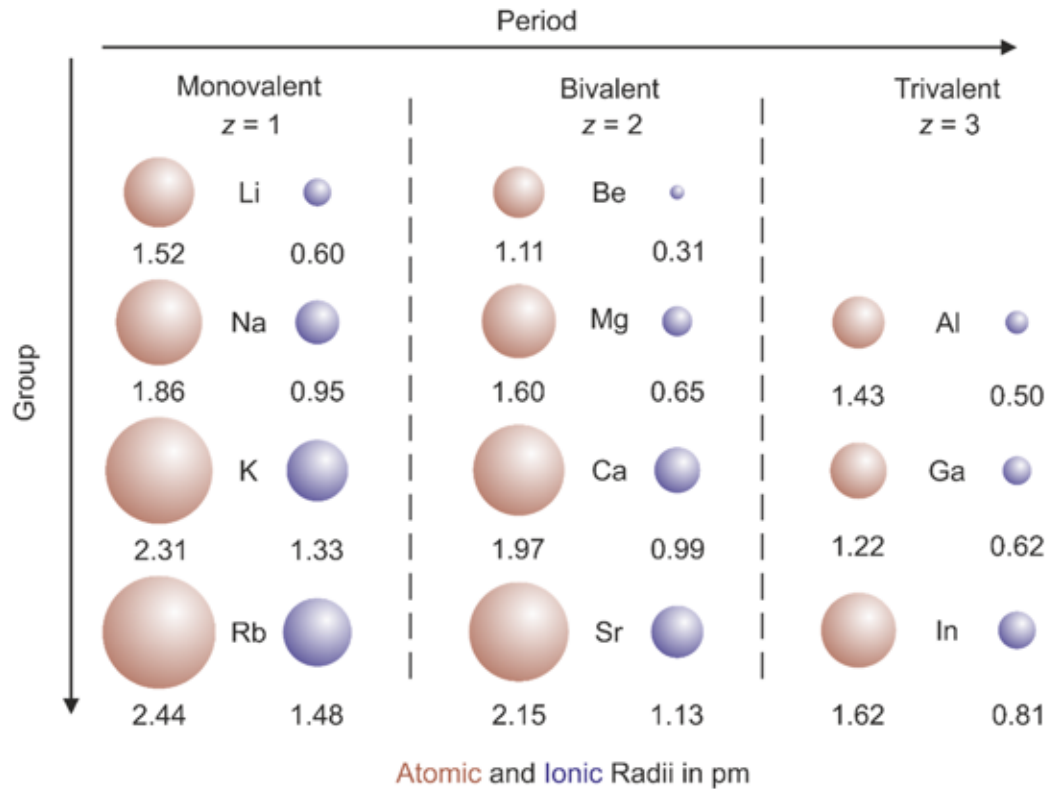
High temperature stability



Single ion conduction



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Metals that can be oxidized to multivalent cations offer higher capacity (in Ah) than monovalent cations (Li⁺, Na⁺).

As a rule of thumb, ion mobility in solids* decreases with a higher ionic charge, in particular, when this higher charge is concentrated on the same ion volume (proportional to ion radius).

* The term 'solid' covers:
Insertion electrode materials, solid electrolytes, SEI, and CEI.

- Larger ions need more space.
- There is a larger electrostatic repulsion between multivalent than monovalent ionic guests in insertion host materials.
- Both influences lead to lower capacities; e.g. max. capacity of Li in graphite: LiC₆ and K in graphite: KC₈.