

Supporting Information

Leveraging valuable synergies by combining alloying and conversion for lithium-ion anodes

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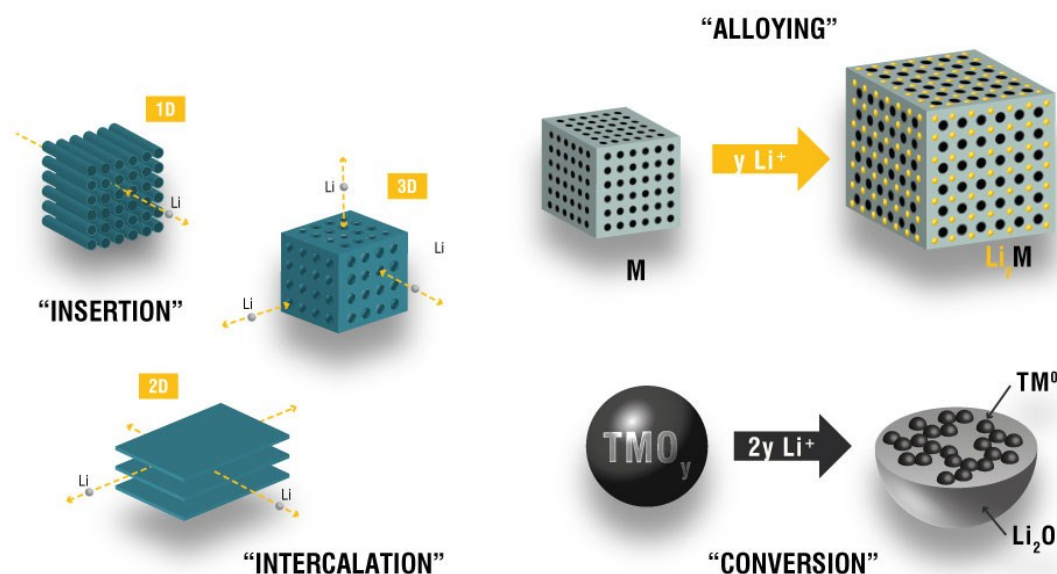


Figure S1. Schematic illustration of the different reversible lithium storage mechanisms; from the top to the bottom and from the left to the right: insertion (1D and 3D) & intercalation (2D), alloying, and conversion.

From metallic lithium to lithium-ion host structures

The first generation of rechargeable lithium batteries comprised a sheet of metallic lithium as anode coupled with an intercalation-type layered cathode as, for instance, TiS_2 or MoS_2 . The non-even lithium plating upon continuous cycling and the resulting formation of dendrite-like lithium deposits led in some cases to an accidental short-circuiting of the cells, accompanied by rapid heat evolution and, in some cases, fire incidents. To overcome this safety issue, researchers proposed to replace the metallic lithium anode by host materials, reversibly storing lithium ions in their open structure, similar to the cathode side but hosting lithium at lower electrochemical potentials. Such batteries were initially called ‘rocking chair batteries’ and are nowadays commonly referred to as ‘lithium-ion batteries’. Depending on their crystalline structure and the lithium storage mechanism, such host materials can be roughly classified in ‘insertion’, ‘intercalation’, ‘alloying’, or ‘conversion’ materials. Insertion and intercalation materials are characterized by a crystalline lattice, which provides open channels (1-dimensional (1D) or 3-dimensional (3D) → insertion; e.g., $\text{Li}_4\text{Ti}_5\text{O}_{12}$, LiFePO_4 , or LiMn_2O_4) or layers (2-dimensional (2D) → intercalation; e.g., graphite, LiCoO_2 , TiS_2 , or MoS_2) within which lithium ions can easily migrate, while the crystalline structure remains unaffected once the lithium ions are removed again (e.g., $\text{Li}_4\text{Ti}_5\text{O}_{12} + 3 \text{Li}^+ + 3 \text{e}^- \leftrightarrow \text{Li}_7\text{Ti}_5\text{O}_{12}$) or re-inserted (e.g., $\text{LiCoO}_2 \leftrightarrow \text{Li}_{1-x}\text{CoO}_2 + x \text{Li}^+ + x \text{e}^-$). Alloying materials, in contrast, are commonly pure metals or metalloids (e.g., Sn, Pb, Al, Zn, Ge, Sb, or Si) within which lithium enters the metallic lattice forming an intermetallic compound or, simply, an alloy (e.g., $\text{Sn}^0 + 4.4 \text{Li}^+ + 4.4 \text{e}^- \leftrightarrow \text{Li}_{4.4}\text{Sn}$). Such reactions may occur via the formation of new phases including also the breakdown of the initial long-range order, i.e., the amorphization of the “host” metal. While these two reversible lithium storage mechanisms have been studied already for several decades, conversion materials host lithium by a reversible displacement reaction necessitating a reversible bond cleavage and reformation upon (de-)lithiation (e.g., $\text{Co}_3\text{O}_4 + 8 \text{Li}^+ + 8 \text{e}^- \leftrightarrow 3 \text{Co}^0 + 4 \text{Li}_2\text{O}$).