

Role of Polymorphism in the Electrochemical Behavior of Electrode Materials for Rechargeable Batteries: a First-Principles Perspective

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Energy storage technology has already proven to offer great opportunities for technological progress. A clear example of this is the indispensable role of the Li-ion rechargeable battery, making possible the revolution of portable electronics. But far away from previous achievements, energy storage technology possess a significant potential to offer a number of new economic and environmental benefits by means of replacing systems powered by fossil fuels (such as electric vehicles) and balancing the fluctuating generation of renewable power sources (the main obstacle to get an extensive penetration of clean energy sources in the electrical grid).

The quest to find new sustainable electrode materials has revealed that the electrochemical behavior of many of these compounds is strongly affected by polymorphism. Despite similar thermodynamic stabilities, different polymorphs often show different electrochemical performance in terms of voltage potential, cyclability, polarization, and reaction redox mechanisms.

From a theoretical viewpoint, here we discuss a brief selection of some of our most exciting examples of recent work in this area and the underlying physical insight and general concepts that emerge about how polymorphism affects key thermodynamic and kinetic properties in a range of systems and processes: (i) electrochemical delithiation in monoclinic and orthorhombic $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ polymorphs [1], (ii) phase transformations in layered $\text{Na}_{2/3}\text{Fe}_{2/3}\text{Mn}_{1/3}\text{O}_2$ polymorphs (Figure 1), (iii) phase stability of Na_xFePO_4 along the whole range of sodium compositions ($0 \leq x \leq 1$) [2], and (iv) electronic structure of NaO_2 bulk and nanoclusters for Na-air batteries [3,4].

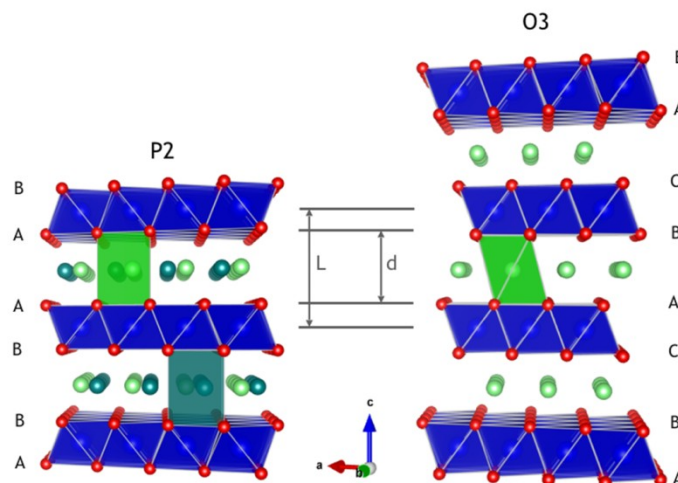


Figure 1. Crystal structures of P2- and O3- $\text{Na}_{2/3}\text{Fe}_{2/3}\text{Mn}_{1/3}\text{O}_2$ polymorphs. A, B, and C letters indicate the stacking sequence of oxygen sheets. Color code: inequivalent prismatic Na(1) and Na(2) sites in P2 phase, dark and light green, respectively; octahedral Na sites in O3 phase, light green; Fe/Mn octahedra, blue; and O atoms, red.

Bibliography

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