

Lithium ion batteries chemical composition

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Lithium-ion batteries have become an integral part of our daily life, powering the cellphones and laptops that have revolutionized the modern society^{1,2,3}. They are now on the verge of transforming the transportation sector with electric cars, buses, and bikes. They are also anticipated to be critical for enabling a widespread replacement of fossil-fuel-based power generation with renewable energy sources like solar and wind, providing a cleaner, more sustainable planet. The award of the 2019 Nobel Prize in Chemistry to John Goodenough, Stanley Whittingham, and Akira Yoshino emboldens this assertion.

The top of the $S_{2-}3p$ band lying at a higher energy limits the cell voltage to ~ 2.5 V with a sulfide cathode. In contrast, the top of the $O_{2-}2p$ band lying at a lower energy enables access to lower-lying energy bands with higher oxidation states and increases the cell voltage substantially to ~ 4 V.

Layered $LiCoO_2$ with octahedral-site lithium ions offered an increase in the cell voltage from ~ 2.5 V in TiS_2 to ~ 4 V. Spinel $LiMn_2O_4$ with tetrahedral-site lithium ions offered an increase in cell voltage from 3 V for octahedral-site lithium ions with $Mn^{3+/4+}$ couple to ~ 4 V, with an accompanying cost reduction. Polyanion oxide $Li_xFe_2(SO_4)_3$ offered yet another way to increase the cell voltage through inductive effect from ~ 2.5 V in a simple oxide like Fe_2O_3 to 3.6 V, with a further reduction in cost and improved thermal stability and safety. Oxford and UT Austin, refer, respectively, to the University of Oxford and the University of Texas at Austin.

a Two-dimensional lithium diffusion from one octahedral site to another octahedral site in the lithium plane through a neighboring empty tetrahedral site in the O_3 layered $LiMO_2$ cathodes. b Three-dimensional lithium diffusion from one 8a tetrahedral site to another 8a tetrahedral site through a neighboring empty 16c octahedral site in the spinel cathodes.

a Lowering of the redox energies of the $Fe^{2+/3+}$ couple and the consequent increase in cell voltage on going from a simple oxide Fe_2O_3 to a polyanion oxide $Fe_2(MoO_4)_3$ and then to another polyanion oxide $Fe_2(SO_4)_3$ with a more electronegative counter-cation S^{6+} vs. Mo^{6+} , i.e., with a more covalent S-O bond than the Mo-O bond. b Molecular orbital energy diagram illustrating the lowering of the $Fe^{2+/3+}$ redox energy in $Fe_2(SO_4)_3$ compared to that in the isostructural $Fe_2(MoO_4)_3$, due to a weakening of the Fe-O covalence by a more covalent S-O bond than the Mo-O bond through inductive effect.

The ability to increase the voltage drastically to as high as ~5 V in polyanion oxide cathodes^{39,40}, for example, in LiMPO_4 even with lower-valent couples like $\text{Co}^{2+/3+}$ or $\text{Ni}^{2+/3+}$ illustrates the power of the inductive effect imparted by the changes in metal-oxygen bonding in tuning the operating voltages. Accordingly, the polyanion oxide class with sulfates, phosphates, and silicates has become diverse compared to the first two classes of oxide cathodes (layered and spinel oxides) in terms of versatility and number of materials, not only for lithium-ion batteries, but also for sodium-ion batteries⁴⁰. For example, polyanion oxides like $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, and LiFePO_4 have become appealing cathodes for lithium-ion or sodium-ion batteries^{40,41,42,43}.

However, the polyanion class of cathodes offer an important advantage of high thermal stability and better safety than the layered and spinel oxide cathodes as the oxygen is tightly bound to P, S, or Si with strong covalent bonds⁴⁵. Also, the polyanion cathodes with optimally small particles coated with carbon can sustain high charge-discharge rates due to good structural integrity, despite a lower volumetric energy density. Moreover, polyanion cathodes are known with abundant transition metals like Fe, unlike the layered and spinel oxides, offering sustainability advantages; therefore, they are appealing for grid storage of electricity produced from renewable energy sources like solar and wind.

a Schematic illustration of the dissolution and migration of transition-metal ions from the cathode to the graphite anode and the consequent catalytic formation of thick SEI layers on the graphite anode. (b) Substitution of transition-metal ions with a small amount of inert ion like Al^{3+} that makes the lattice robust by perturbing the long-range metal-metal interaction and increasing the metal-oxygen bond strength and thereby suppressing metal-ion dissolution.

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