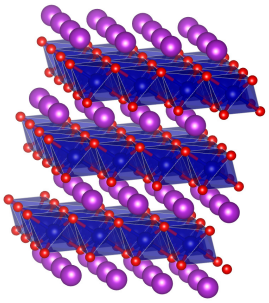
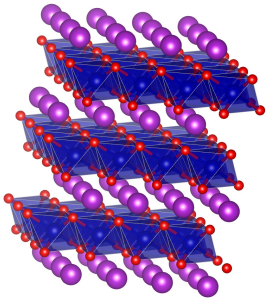
Lithium cobalt oxide (LCO)

- Last lesson, we looked at different materials that could be used in negative-electrodes in lithium-ion cells
- Now, we look at materials for positive electrodes instead, for which there are more options from which to choose
- In 1980, John B. Goodenough discovered that Li_xCoO_2 (LCO) was a viable material for lithium intercalation
- Li intercalates between the layers of CoO_6 octahedra
- LCO has layers, somewhat like graphite, so it is often called a "layered cathode"



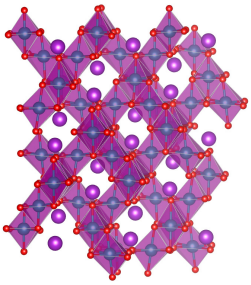
LCO and other layered cathodes

- LCO is commonly used in portable-electronics cells, but suffers some problems when trying to scale up:
  - Cobalt is rare, toxic, and expensive;
  - Only about half its theoretic capacity is useable ("x" can be in $[0.5 \ldots 1]$), else cell ages rapidly
- Ni can substitute Co, giving higher energy density (higher voltages, same capacity), but is not very thermally stable
  - Al, Cr, and Mn can be substituted as well, resulting in somewhat different properties
- NCM (a.k.a. NMC) is a blend of Ni, Co, and Mn, which retains the layered structure, and has properties from all three constituent metals; NCA is a blend of Ni, Co, and Al



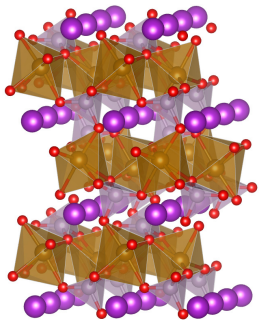
Spinel cathodes

- In 1983, Goodenough and Thackery proposed $Li_xMn_2O_4$ (LMO) as an alternate intercalation material: Mn sits in the octahedral sites, Li in the tetrahedral
- This material has a cubic "spinel" structure. It allows 3D diffusion (vs. 2D for layered and 1D for olivine)
- Value of "x" typically varies between 0...1, but can go as high as 2 (LMO unstable in acidic conditions when $x > 1$)
- LMO is cheaper and safer than LCO, but can have short lifetime due to the manganese dissolving into the electrolyte under some conditions
- Additives can be added to help prevent this, but this "art" is presently well guarded by trade secrets



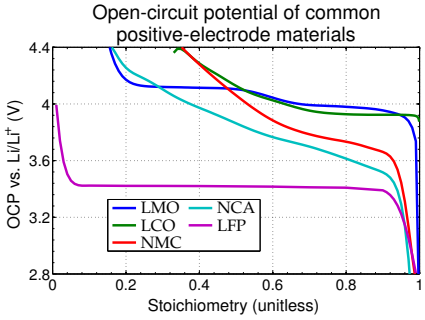
Olivine cathodes

- In 1997, Goodenough proposed olivine-style phosphates as a third major category of positive-electrode material
- Li_xFePO_4 (LFP) is the most common in this family
- This material is low cost, and low toxicity, but also has low energy density due to a low open-circuit potential and low specific energy due to heaviness of Fe
- 1D structure tends to have high resistance, which can be overcome in part by using very small particles and including conductive additives
- There are other candidate positive-electrode materials, but they are mostly mixtures of the above.



Summary

- Since essentially all lithium-ion cells presently in use have graphitic negative electrodes, lithium-ion cell cells are often referred to simply by their positive-electrode chemistry (e.g., an “LFP cell”, etc.)
- The open-circuit potential curves for different positive electrode chemistries are drawn
  - Layered cathodes (LCO, NMC, NCA) can use only around half their theoretic capacity
  - Olivine cathodes (LFP) have low voltage (and very little state information in their voltage)
  - Spinel cathodes (LMO) are inexpensive and non-toxic, but can degrade rapidly



Credits

Credits for images in this lesson:

- LCO structure on slides 1–2 drawn with VESTA. See, Momma, K. and Izumi, F., “VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data,” *Journal of Applied Crystallography*, 44, 1272–1276 (2011)
- LMO structure on page 3 also drawn with VESTA: See, reference above
- LFP structure on page 4 also drawn with VESTA: See, reference above