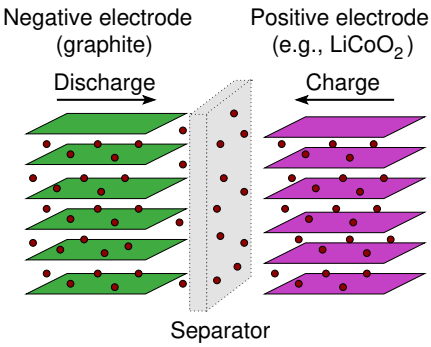
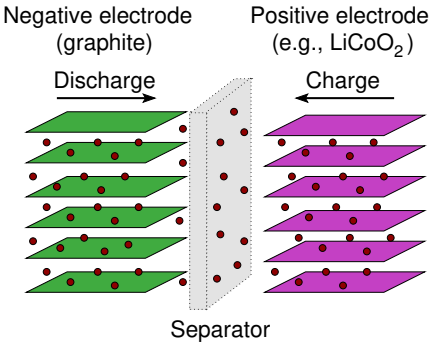
The process of intercalation

- Lithium-ion cells work differently from the electrochemical cells we looked at last week
- Both electrodes depend on an intercalation mechanism rather than redox reactions
- Lithium is stored in the electrodes much like water is stored in a sponge
- Li is stored in the electrodes, and Li^+ moves through the electrolyte
- Li^+ enters an electrode, becoming Li when an electron is available; Li exits an electrode and becomes Li^+ when it can give up an electron



Requirements of the electrode structure

- Intercalation involves insertion of lithium ions into crystalline lattice of host electrode without changing its crystal structure
- These electrodes have two key properties:
  - Open crystal structures, allowing insertion or extraction of lithium ions in the vacant spaces
  - Ability to accept compensating electrons
- Within the electrode, the lithium atom's electron is loosely shared with neighboring atoms
- The lithium is not tightly bonded in one place; it is actually quite free to move around



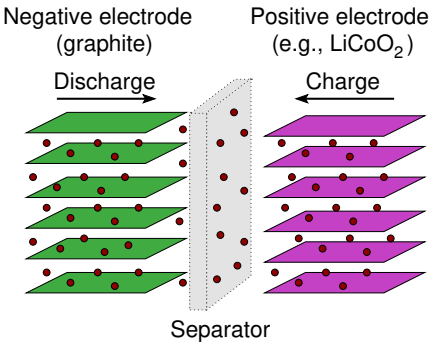
The discharge process

- During discharge, Li exits the surface of the negative-electrode particles, gives up an electron, becoming Li^+ in the electrolyte
- Li diffuses outward from center of negative-electrode particles to equalize concentrations, replenishing Li at particle surface (over time)
- Meanwhile, electron travels through external circuit to positive electrode

- Li^+ joins with the electron, and Li enters positive-electrode particles at their surface
- Li diffuses into positive-electrode particles to equalize concentration (over time)

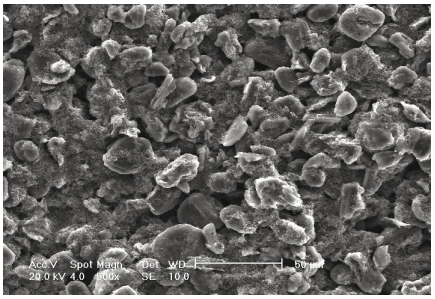
The charge process

- The process is completely reversible; thus lithium passes back and forth between electrodes during charging and discharging
- During charge, Li exits surface of positive-electrode particles, gives up an electron, becoming Li^+ in the electrolyte
- Meanwhile, the electron is forced (by charger) through external circuit to negative electrode
- Li^+ joins with the electron, and Li enters negative-electrode particles at their surface
- Diffusion of Li in both electrodes equalizes internal concentrations (over time)

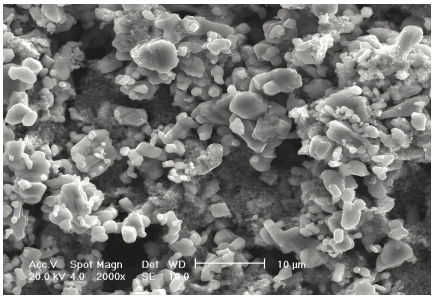


Particle nature of electrodes

- It is critical to understand that the electrodes are not homogeneous blocks, but rather millions of small particles



Mesophase carbonaceous spheres (graphite)

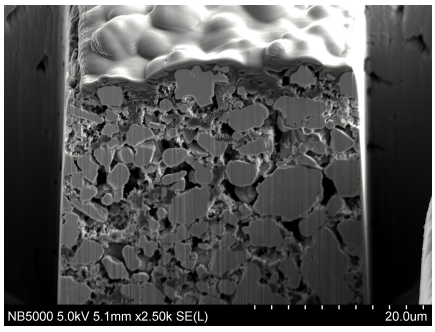


Lithium manganese oxide

- Increases surface area, decreases cell resistance, enhances power capability

Polished electrode cross section

- The photo shows a polished cross-sectional slice of electrode to further illustrate its particle nature (with voids for electrolyte)
- Mixed in with primary electrode materials are:
  - Binders (to glue things together) and
  - Conductive additives (to enhance electron conduction, which is otherwise poor in positive-electrode materials)
- These are not “active” portions of the cell, so are not often mentioned, but are always present
- Electrolyte often also has additives to inhibit side reactions and extend life



Summary

- Lithium-ion cell electrodes are made of small particles to increase surface area (and therefore power capability)
- Particles are made from compounds having open crystalline structure that can accept lithium without changing crystal structure
- Lithium intercalates into and deintercalates out of particle from surface
- Within particles, diffusion equalizes lithium concentrations over time
- During discharge, Li moves from negative-electrode to positive-electrode particles, via intermediary electrolyte (where it is Li^{+}); during charge, the opposite occurs
- Electron moves through external circuit to compensate

Credits

- Images of lithium-ion electrodes on slides 5–6 courtesy Sangwoo Han, used with permission (images on slide 5 captured using scanning electron microscope (SEM), and image on slide 6 milled using focused ion beam (FIB))
- Diffusion image on slide 3: By BruceBlaus (Own work) [CC BY 3.0 (`http://creativecommons.org/licenses/by/3.0`)], via Wikimedia Commons, `https://commons.wikimedia.org/wiki/File:Blausen_0315_Diffusion.png`