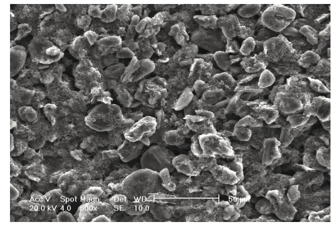
Lithium-ion aging: Negative electrode

- In the next lessons, we'll seek to describe aging <u>qualitatively</u>.[1]
- In negative electrode, aging observed at three scales:
  - At the surface of the electrode particles
  - Within the electrode particles themselves
  - Within the composite electrode structure (active materials; conductive additives; binder; current collector; porosity; etc)

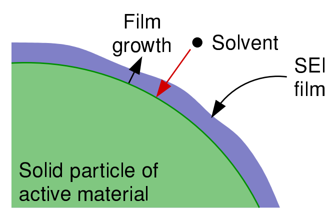


- In this lesson, our focus is on aging mechanisms that take place at particle surfaces
- We will assume that a graphitic carbon is used as the negative-electrode active material, although similar results hold for silicon as well

[1] Much of this is from: Vetter *et al.*, "Ageing mechanisms in lithium-ion batteries," *Journal of Power Sources,* 147, 2005, 269–281.

Negative electrode aging at surface of particles

- Graphitic negative electrodes operate at voltages outside electrochemical stability window of electrolyte components
- Reductive electrolyte decomposition takes place at the electrode/ electrolyte interface when the electrode (and cell) is in the charged state
- This occurs mainly—but not only—at beginning of cycling, especially during "formation" cycle
- The decomposition products form a "solid-electrolyte interphase" (SEI) surface film covering the electrode's surface

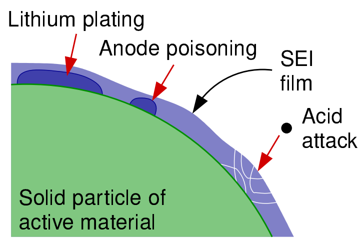


Properties of SEI

- The SEI is a passivating layer, which slows/prevents further reaction between graphite and electrolyte
  - Lithium is consumed when SEI film forms, lowering capacity of cell
  - SEI is porous, allowing de/intercalation of Li from/to graphite, but increases resistance of ion transfer
- SEI composition is complex and not uniform
  - Various products form, then decompose, then form more stable products

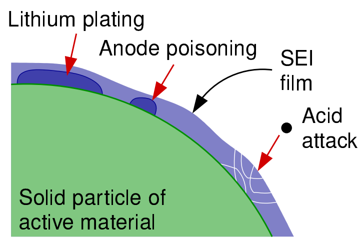
Breakdown of SEI; regrowth

- High temperatures contribute to breakdown of SEI, which can lead to new SEI forming on exposed graphite
- Pores in SEI also allow some solvent to penetrate to graphite surface, reacting and growing more SEI film
- Trace water in electrolyte combines with ionized fluorine to form hydrofluoric acid (HF), which attacks the SEI—new SEI forms
- Whenever SEI forms/grows, lithium is lost and so cell capacity decreases



Anode poisoning; lithium plating

- Products of positive-electrode degradation also end up as part of SEI (anode poisoning):
  - If not electrically conductive, increases resistance
  - Can plug pores, blocking lithium from cycling, causing capacity fade
- At low temperatures, diffusion in particles slows:
  - If charging is forced, local overpotential can attain level that causes lithium plating on particle surface
  - Capacity irreversibly lost; dendrites can form and grow, eventually leading to internal short circuit



Summary of surface effects

- Table summarizes surface effects (bold = more severe):

Cause	Effect	Leads to	Enhanced by
Continuous low-rate electrolyte decomposition builds SEI	Li loss, impedance rise	**Capacity fade, Power fade**	High temperatures, high cell SOC
Decrease of accessible surface area due to SEI growth	Impedance rise	**Power fade**	High temperatures, high cell SOC
Changes in porosity due to volume change and SEI growth	Impedance rise	Power fade	High cycling rate, high cell SOC
Metallic Li plating, subsequent electrolyte decomposition	Lithium (electro-lyte) loss	Capacity (power) fade	Low temperature, high charge rates

Credits

- Image of lithium-ion electrode on slide 1 courtesy Sangwoo Han, used with permission