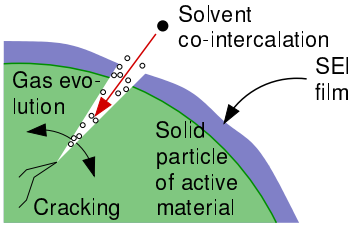
Negative electrode aging in bulk

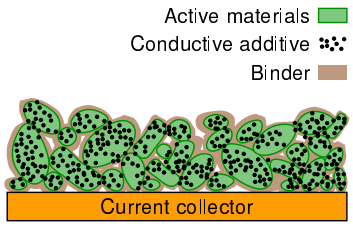
- Aging/degradation occurs inside negative-electrode particles
- Dis/charging causes (anisotropic) particle volume changes (usually less than 10 %)
  - Strain can lead to cracking of particles, more SEI formation on exposed graphite
  - Cracking of SEI itself, and more SEI formation on exposed graphite



- Graphite exfoliation (layers flaking off) due to solvent cointercalation with lithium is considered to have a bigger impact
- Solvent reacting with graphite inside particles releases gasses, accelerates cracking

Negative electrode aging in composite electrode

- Stresses and strains within electrodes can cause mechanical and electronic contact loss:
  - Between graphite particles
  - Between current collector and particles
  - Between binder and particles
  - Between binder and current collector



- Results in higher impedance and can result in capacity loss if particles become electrically disconnected from current collector
- Porosity of electrode can be reduced by volume changes and growth of SEI, impeding movement of lithium ions in electrolyte, increasing resistance

Current-collector corrosion

- At low voltages (near 1.5 V) copper current collector can corrode, releasing Cu^{2+} into electrolyte:
  - Reduced current-collector/particle contact, higher cell resistance
  - Corrosion products that deposit on electrode particles have poor electronic conductivity, giving higher film resistance
- Leads to nonuniform current and potential distributions across cell plate area, accelerates aging in parts of the cell, gives preference toward lithium plating
  - Copper also makes a metallic annealing site that can accelerate lithium plating, dendrite growth, and hence short circuits

Summary of aging in bulk, composite electrode

- Table summarizes bulk/composite effects (bold = more severe)

Cause	Effect	Leads to	Enhanced by
Solvent cointercalation, gas evolution, graphite exfoliation	Loss of active material, Li loss	Capacity fade	Overcharge
Contact loss b/w particles due to volume changes	Loss of active material	**Capacity fade**	High rate, low cell SOC
Decomposition of binder	Li loss, loss of mechanical stability	Capacity fade	High SOC, high temperatures
Current collector corrosion	Impedance rise; nonuniform current and potentials	Pwr. fade; accelerates aging	Overdischarge, low cell SOC