Lithium-ion aging in the positive electrode

- In previous lessons, you learned about physical degradation mechanisms that occur in the negative-electrode region of a lithium-ion battery cell
- In positive electrode, as with negative electrode, aging occurs in three regions:
  - At the positive-electrode particle surface
  - Within the “bulk” of the active materials themselves
  - In the composite positive electrode

Positive electrode aging at surface of particles

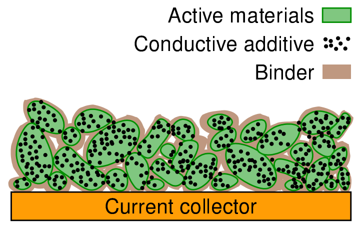
- Electrolyte oxidation and $LiPF_6$ decomposition can form surface layer on positive electrode materials as well
  - This is not as pronounced as for negative electrodes
- A bigger factor is the dissolution of metals from the electrode into the electrolyte, and products formed from these metals which can re-precipitate on the surface as high-resistance film
- Dissolution of Mn or Co into electrolyte results in capacity loss (fewer lithium storage sites), can poison negative electrode
  - Mechanism depends on which oxide is used, but tends to happen predominantly at low/high states of charge, and can be greatly accelerated by high temperature

Positive electrode aging in bulk

- Phase transitions (distortions in shape of crystal structure, without changing structure itself) can lead to cracking
  - Transitions caused by presence/absence of Li in storage sites, leading to different local molecular forces
  - Some phase transitions are normal and reversible
  - Others cause collapse (*e.g.*, overcharge layered structure), rapid capacity loss
- Can also lead to “structural disordering.” when electrode crystal structure breaks down (bonds broken, reformed to different atoms, collapsing the tunnel-like structures that allow Li movement: Li sites are lost and, Li can be trapped)
- Phase transitions near surface can lead to permanent sub-surface layers forming that do not allow Li to move freely as in unaltered crystal structure

Positive electrode aging in composite electrode

- The positive electrode also experiences degradation of the inactive components of the cell:
  - Binder decomposition
  - Oxidation of conductive particles (*e.g.*, carbon black)
  - Corrosion of the current collector
  - Loss of contact to conductive particles due to volume changes



Summary of aging at positive electrode (1/2)

- Principal aging mechanisms at positive electrode (1/2)

Cause	Effect	Leads to	Enhanced by
Phase transitions	Cracking of active particles	Capacity fade	High rates, high/low SOC
Structural disordering	Li sites lost and Li trapped	Capacity fade	High rates, high/low SOC
Metal dissolution and/or electrolyte decomposition	Migration of soluble species	Capacity fade	High/low SOC, high temperature
	Reprecipitation of new phases, form surface layer	Power fade	

Summary of aging at positive electrode (2/2)

- Principal aging mechanisms at positive electrode (2/2)

Cause	Effect	Leads to	Enhanced by
Electrolyte decomposition	Gas evolution		High temperature
Binder decomposition	Loss of contact	Power fade	
Oxidation of conductive agent	Loss of contact	Power fade	
Corrosion of current collector	Loss of contact	Power fade	High SOC