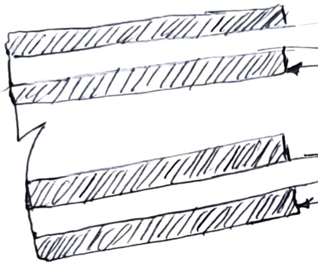
Week 5 - How cells are made & can fail

Knowing how battery cells are fabricated aids understanding of its operation basically considering Lithium-ion cell.

#1 Electrode Structure

Electrodes in lithium-ion cells are of similar form and are made by similar processes on similar or identical equipment even though they are (cells) are in different form i.e cylindrical, prismatic, pouch.

- Electrode structure starts with the current collector materials which are metal foils and both sides of the metal foils are coated with layers of the electrode materials.



By coating both sides of the current collector, there is a reduction on the total volume required for the same total capacity of the battery cell.

* Electrode Materials

The negative-electrode material is usually a form of **graphite**. Positive-electrode material is usually a **Lithium metal oxide**. Positive and negative electrodes are sing constructive, so they're usually fabricated in different rooms when the cell is being no airborne contamination

Particles are important in fabricating electrode.

- Particle size and shape are important in fabricating the electrode. Particles are desired to be small in order to maximize the surface areas to have high current cell & a high power cell.
  - Smooth spherical shapes are also desired since sharp edges are susceptible to higher electrical stresses and cause faster decomposition of their solid electrolyte interface layer.
  - Sharp edges and pointy edges can lead to premature aging and fail on the cell even possible thermal runaway after extended periods of degradation.

* Electrode Coating

When fabricating the electrodes, it begins with just foils of current-collector material that are usually delivered in large spiral reels up to ~0.5m wide

- Cu for negative and Aluminium for positive current collector.
- When coating the current-collector foil, we don't simply put on the active materials and we include with some conductive agents like carbon black perhaps, and some binding agents like PVDF in slurry form.
- From the coater, coated foil is fed directly into long drying oven to bake electrode material onto the foil. As coated foil exit oven, it is re-reeled

* Electrode Calendering

It means pressing to compress something. Roller press the electrodes down to a highly calibrated thickness. The purpose of performing this calendaring is to compress the electrodes to compact out extra spaces or voids between the particles and pressing the porosity down to a calibrated level. to ensure more consistent density of particles throughout the entire electrode.

- It also helps to ensure electronic contact between the particles that might otherwise be relatively disconnected at the end of the previous processing step.
- The electrode material then passes through a machine that slits the electrodes lengthwise and these narrower electrode strips are wind on to individual coils at the output of this machine having the final desired widths

#2 How is a Lithium Cell assembled?

* Cell Assembly

It comprises building electrode subassembly, packing filling with electrolyte, sealing and welding, inspection. Details how it is done varies on the shape of the cell

* Stacked Electrode Structure

- Pouch/~~[illegible]~~ cells often used for high-capacity battery applications to optimize use of space (inside the packaging of the cell). There's very little wasted space also when put multiple cells together to form a battery pack.
- Pouch design use stacked electrode structure in which negative and positive electrode foils are cut into individual electrode plates that are stacked alternatively and kept apart by the separator.

- Separator may be cut to the same size as electrodes but not often is a long strip wound zig-zag between alternate electrodes in the stack.
- All negative-electrode tabs are welded in parallel and to the cell's negative terminal; all positive-electrode tabs are welded in parallel and to the cell's +ve terminal.

* Cylindrical & Prismatic electrode structure
- For cylindrical cells, negative and positive electrode foils are cut into two long strip and wound on a cylindrical mandrel together with separator to hold electrodes apart, to form a jelly roll.
- Most prismatic cells are constructed similarly, by winding electrodes on a flat mandrel.
- Tabs) connects electrodes to terminals (multiple tabs for high-current cells) (welded to external terminals in order to allow more current paths and more uniform utilization of the electrodes.

* Final steps: Electrolyte Fill
Whether we are constructing a pouch or a cylindrical or a prismatic cell, after the electrode structure, the next step involves filling the cell with electrolyte.
- Safety devices like internal fusing connected, then insert the subassembly into the package, but at this point the cell is completely dry.
- The package is sealed except for a small opening. Sealing often done by laser welding. For pouch, it could be sealed by heating some materials and effectively making a hot glue connection
- Cell is first subjected to a vacuum through the small opening which removes most of the air from the inside of the cell from the pores, then a small amount of electrolyte is injected into the cell, then the vacuum is released so that the atmosphere pressure forces the electrolyte into the cell, into those small pores or opening
  - Electrolyte filling must be done on a dry room (uses very high capacity dehumidifier to remove as much moisture from atmosphere as possible)
  - This is important because the electrolyte used in lithium-ion battery cell often have salts that react chemically with water.
  - Any moisture on the electrolyte will cause the electrolyte to decompose, emitting toxic gases.
  - Lithium hexafluorophosphate ($LiPF_6$) for instance, one of the most commonly used electrolyte salts, reacts with water forming toxic hydrofluoric acid (HF)

- Finally, cell is given an ID with a label or by printing serial number on case.

* A Critical Issue : SEI Layer

SEI - Solid Electrolyte Interface. When lithium intercalates into graphite in the negative electrode, the lithiated graphite reacts with solvents in the electrolyte and forms SEI layer.

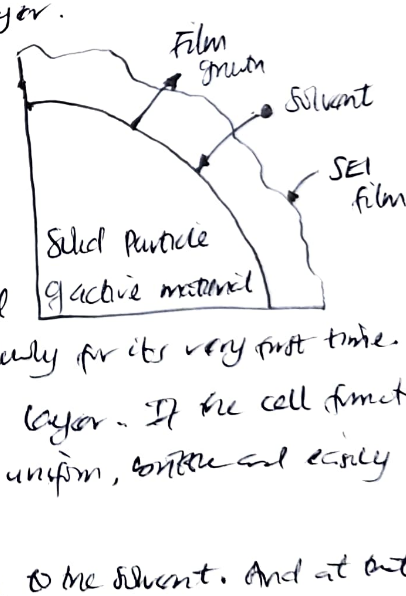
SEI layer is a film coating the particles of the negative electrode. The process of SEI formation and growth consumes lithium, so it results in capacity that's lost.

- The film also impedes ions, lithium ions, that need to travel from the electrolyte into the electrode and vice versa, which results in a higher resistance for the cell, resulting into a power loss and neither of these is desirable.

On the other hand, SEI stabilize the graphite against further reaction of the solvent, which is a positive feature. So it tends to be a self-limiting reaction.

- When the lithium-ion battery cells are assembled, they are done so in a fully-discharged state at zero volts. All of the lithium begins in the positive electrode. The negative electrode is pure graphite with no lithium in it whatsoever.
- When battery cell is built, it must be put through at least one precisely controlled charging process. During this first charging process, the graphite is lithiated for the first time, and this causes the chemical reaction that forms the SEI layer.

The first charge is termed **the formation process**



* The Formation Process

SEI layer is should be as thin as possible because we don't want to have excessive capacity loss. It is achieved if the layer is formed slowly. By charging the cell very slowly for its very first time.

Cell may also need gentle cycle to stabilize SEI layer. If the cell formation is badly done, then SEI layer will be thick and non uniform, brittle and easily break down as the battery cell is being operated.

Anytime SEI layer breaks down, it exposes more graphite to the solvent. And at that point the solvent will react with the graphite and form additional SEI products which will reduce capacity and increase resistance.

The formation process of SEI layer are used by different manufacturers are **Proprietary**, they're **trade secrets** (not simply normal CC/CV charging)

* **SEI** layer formation is due to a side reaction between the solvent, electrolyte and graphite particles in the negative electrodes

* Acceptance testing

During formation, cell performance data are gathered and recorded for quality analysis.

If high self discharge (voltage measured after rest), ~~found~~ points to some manufacturing defect and the cell will be recycled.

- If the cell has capacity that's very different from what's expected or has impedance that's higher than what's expected, that could indicate that there is a manufacturing process that's not under control and will lead to a lot of creative detective work to find and correct the process that is causing the problem.
- Even when cells do have parameters that fall within the desired tolerance band, the cells that come out of production are sorted ~~into~~ according to their capacity and resistance. This process is called cell **matching** or **binning**
- To avoid low yield, it's important to enforce tight tolerances and strict process controls.
  - Avoid contamination of raw materials, physical damage, burrs on the sharp edges on the electrodes; all of these are extremely dangerous since it can cause separator penetration, internal short circuits.
  - To reduce contamination, cells are normally manufactured in a clean room condition.

* Summary

- Cell construction comprises building electrodes subassembly, packaging, electrolyte fill, sealing and welding, Inspection.
- After construction, cell undergoes formation cycle to grow ~~thin~~ SEI layer
- By-product of formation cycle is dataset that enables acceptance testing, binning or sorting of cells for a highly-calibrated applications.
- Finally, cells are packaged and shipped (usually at a mid-range SOC)

#3 Normal Li-ion Cell Aging Processes

* Cells change as they age

Understanding causes and effects of cell aging and failure has real value when thinking about BMS algorithms. For example, it motivates the need for SOH estimation algorithms and also for computing power limits in order to slow down degradation.

- Failure causes: cell design faults, poorly controlled manufacturing processes, aging mechanisms, or uncontrolled operation and abuse.

* Aging Processes

Li-ion cell performance generally deteriorates gradually over time due to unwanted chemical reactions that happen inside the cell and also due to physical changes to the active materials in the cell.

The processes that result in aging are usually not reversible, and eventually result in the cell reaching point of incapable of performing its duty in an application.

- Some examples of causes:
  1. **Corrosion**: can refer to corrosion (undesired chemical reaction with environment) of the current collectors in the cells for example, when the current collectors react with the electrolytes It leads to increased impedance and usually also to capacity loss.
  2. **Crystal formation**: Crystal structures have a tendency to grow over time and to join together, forming larger crystals. Electrode particles evolve as larger crystals are formed, causing effective surface area of the electrode being reduced. Reduction in surface area will reduce the amount of current that can flow in the cell.
  3. **Dendritic growth**: It is similar in a way to crystal formation, but in crystal formation, it is the active materials themselves somehow merging together and forming larger crystals. Dendrite is the growth of undesirable crystal that are not the active materials. Formation of treelike structures on electrodes, which can ultimately pierce separator and cause short circuit.
  4. **Chemical loss through evaporation**: This is very common for cells made of different chemistries eg lead-acid battery cells; solvent of electrolyte can decompose into hydrogen and oxygen gases when the cell is fully charged. These gases can escape through small openings in the packaging. This results in increased resistance of the battery cell and failure of the cell.

Chemical loss through evaporation is perhaps less common with lithium-ion battery cells but it can still happen. If Li-ion cell is overcharged or over discharged, the electrolyte can break down and form gases, including hydrogen gas and methane gas and others. These gases generally do not recombine to form the electrolyte and its solvents. So the Li-ion battery cell can dry out over time.

5. **Passivation**: one type of passivation is the formation of an SEI film layer. The film layer is known as a passivation layer because when it forms on the surface of negative electrode particle, it impedes the further formation of SEI layer. It passivates or isolates that layer from more chemical reactions.

6. **Shorted cells**: Short circuit situation of the cell. Cells that were marginally acceptable when new may have contained latent defects that become apparent only as the aging process take its toll: poor cell construction, contamination, burrs on metal parts leading to a short circuit.

7. **Electrode or electrolyte cracking**: Some Li-ion battery cells use a solid material for their electrolyte, which is some plastic like lithium polymer materials. Over time, the solid electrolyte can crack due to stresses and strains, causing resistance of the cell to increase because it is not possible for that part of the separator to conduct ions any longer.

* Undesirable Effects of Aging

1. **Increase internal impedance**: as larger crystal form, reducing effective surface area of electrodes; due to film, loss of electrolyte, corrosion of current collectors, e.t.c

2. **Reduced capacity**: When the active materials disintegrate or deteriorate, they lose vacancies that could have held lithium. Or lose charge carriers from the electrolytes when side reaction occurs.

3. **Increased Self discharge**: As electrodes swell, that increases the pressure on the separator, and as a consequence, decreases the resistance of the separator and can lead to increased self discharge rates.

Aging processes are generally accelerated by elevated temperatures but not necessarily noticed right away
- "Battery dies in the summer but you hold the funeral in the winter"

#4: Abnormal cell aging processes and failure modes

Some bad things (abuse) to do to a cell include (internal) overcharging, undercharging, and overtemperature. Violating temperature, voltage specifications causes:

- Electrolyte breakdown, Electrode plating, Penetration of separator, Gassing swelling venting, Overheating & thermal runaway.

* Failure due to physical abuse

Physical abuse may include: dropping, crushing, penetrating, impact, immersion in fluids, freezing or contact with fire.

* Failure modes

1. **Open Circuit**: it is the safest of the different failure modes. It is fail safe for the cell but not the application.
2. **Short Circuit**: i) hard short: solid connection between electrodes, extremely high current flow, complete discharge, permanent damage
   ii) Soft short: localized contact between electrodes, possibly self correcting by melting separator
3. **Explosion and/or fire**: The rate of chemical reaction tends to double for every 10°C increase in temperature. If the heat produced by short circuit can't be removed as quickly as possible, it is generated heat causing temperature increase, resulting to fire or explosion.