LITHIUM BATTERIES
UNIQUE FIRE CHARACTERISTICS

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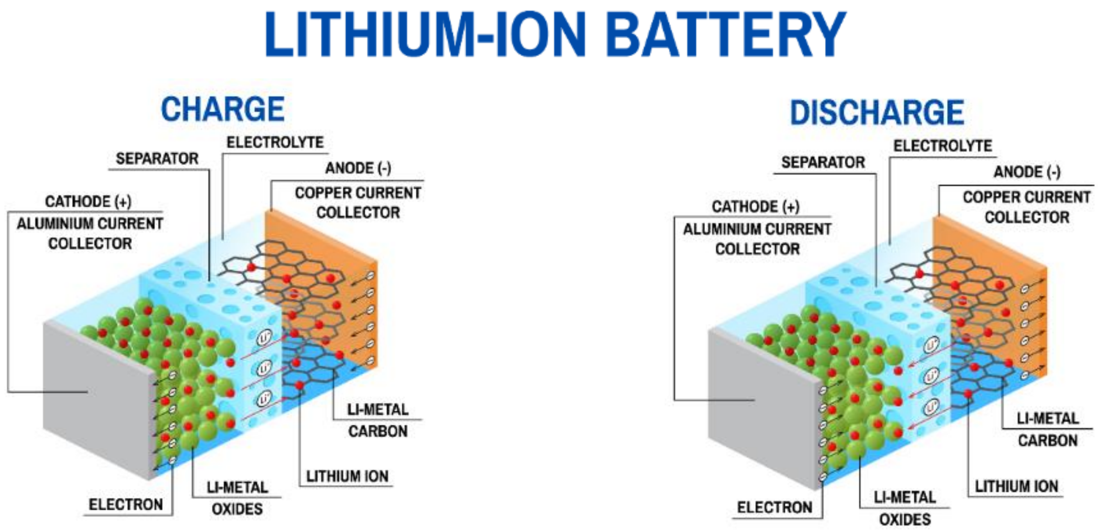
Lithium batteries are found just about everywhere in our lives, from mobile phones to flashlights to EV automobiles. Large grid-scale battery storage is touted as the answer to non-dispatchable, renewable power sources such as wind turbines and solar arrays. These batteries are lightweight, packed with energy, rechargeable and convenient, and they will become even more widespread in the future.

However, lithium batteries can burst into flame if mishandled. It is not unusual to see reported fires of electric vehicles or battery-powered buses. New York City's Chief Fire Marshall reported over 200 fires in 2022 alone from micro-mobility devices. On the other end of the size spectrum, large demonstration units of grid-scale power storage have been plagued with destructive fires. Because of their extraordinary intensity, these fires often propagate to nearby vehicles or buildings, and they are also unusually difficult to extinguish. What makes them so unique?

BATTERY DESIGN

The most common lithium battery today is the lithium-ion battery. This figure below depicts its general architecture, in both charging and discharging modes.



Such batteries can best be described as ***electrochemical cells.*** This suggests that both physics and chemistry are involved: physics to govern electricity flow within the battery case and around external circuits; chemistry because of the reversible chemical reactions that store energy within the cell.

Component parts include:

- **Anode** (negative charge) and **Cathode** (positive charge) on opposite ends of the battery. These metal connections serve as collectors of electrical current from internal reactions, and as contacts to the external world.
- **Electrolyte** is the liquid solution that allows lithium ions (Li+) to diffuse as they migrate from anode (where they have given up an electron) toward the cathode during discharge, and in the opposite direction upon charging. Electrolyte commonly contains dissolved lithium hexafluorophosphate (LiPF6) salt in organic carbonates.
- **Separator** is a thin insulating film, inserted between the anode and cathode to prevent internal short circuiting. Lithium ions diffuse through the microporous structure.
- **Lithium metal oxides** (on cathode side) and **lithium carbon compounds** (on anode side) provide lithium ions within the battery electrolyte itself.

LITHIUM BATTERY FIRES

Fires involving lithium batteries are unusually intense. From investigation and research, we observe two general stages. Initially, the fire is incandescently bright, with fast gas evolution, sparks and dense white-ish smoke. The smoke cloud has been analyzed to contain lithium hydroxides, hydrogen fluoride (HF), hydrogen cyanide (HCN) and many other reactive chemical species, including hydrogen gas (H2).

Attempting to water quench the fire during this phase is generally futile, as the burn site will quickly dry out and again burst into flame. All ingredients for combustion are still present and intimately mixed.

Once the mixed reactive ingredients are consumed, the fire enters a longer second phase during which combustible materials including residual hydrocarbon electrolyte, polymeric separator, any electronic circuitry, battery cases, etc. are burned in more conventional combustion. In this phase, the fire switches to becoming oxygen-starved, and now emits a dense dark cloud of highly-reducing gases and char. If not extinguished by fire response, this phase can burn for long periods.

COMBUSTION REACTIONS

For comparison, solid rocket propellants are cast into solid blends of oxidizer, aluminum powder and polymeric binder. All ingredients for fire are contained in a single package. Once ignited, burning does not stop until the propellant is completely consumed and the motor case is empty.

In similar fashion, a single lithium ion battery contains all ingredients for fire. Inside the battery case, lithium/ carbon compounds along with aluminum and cobalt will act as fuels when oxidized up to higher valence states, giving off considerable heat energy. These fuels along with chemical oxidizers are comingled within the battery itself.

Fluorine, a very active halogen, acts as an excellent oxidizing agent inside the battery case, as does in-situ oxygen contained within cyclic electrolyte carbonates. All that is needed to start a battery burn then is a hot spot or spark.

Later on, any remaining electrolyte will be combusted in the conventional manner that petroleum products burn, requiring oxygen from air in the surrounding environment.

IGNITION/ INITIATION

Overheating, on either a macro- or microscopic scale is the predominate means to begin the avalanche of reactions leading to thermal runaway. A handful of causes have been identified after event investigations:

- External short circuiting from anode directly to cathode
- Overcharging, from failure of control circuitry
- Mechanical damage from mishandling or external overtemperature
- Aging and repeated charge/discharge cycles which can precipitate lithium/ copper dendrites bridging internally from one electrode to its opposite. A tiny short circuit point can quickly lead to ignition.

FIRE FIGHTING

Successfully fighting lithium battery fires does not follow convention. There is no easy answer. Obviously, the first order of business is moving any people away from the area, followed by defensive cooling of nearby structures or vehicles. Generally, dowsing with copious volumes of water or flooding with dry chemicals will not be successful, particularly during the initial, intense phase.

Evolved fumes will be extremely toxic so that responders must be in full protective gear. If water quenching is attempted, runoff should be carefully controlled due to hazardous acidic contamination.

If a lithium battery fire is detected inside a closed and sealed structure, extreme caution must be observed. Flashover explosion from ignition of evolved, hot, reactive combustible gases is a serious threat to responders. Opening such a container allows air to enter and the cloud to explode.

SUMMARY

Lithium battery fires present many dilemmas. Extraordinary research is underway to make the batteries safer and more reliable, e.g., cathode formulations are being sought with lower halogen content. Meanwhile fire response organizations are working to codify best practices to safely deal with this growing threat. Successfully dealing with the many challenges of lithium ion batteries will require utmost innovation and dedication.