Comment

LITHIUM-ION BATTERIES

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Limiting lithium hazards

Standards needed to protect people and marine installations

BY MARCUS JONES

Lithium-ion batteries (LiB) are increasingly used in the marine industry. Compact with high energy density and cheap, their advantages in reducing the use of fossil fuels are obvious. However, while problems are rare, when things do go wrong, they are high impact.

Invented in the 1970s, a LiB is sometimes referred to as a rocking chair. The different types are named by their cathode material chemistry with lithium iron phosphate being the most common. The current collectors are metal foils; copper (Cu) for the anode and aluminium (Al) for the cathode. A thin paste layer of carbon nano particles is spread on the Cu anode and a lithium chemical compound paste is spread on the Al cathode. Between them is a layer of organic solvent with a microns-thick polyethylene ion porous separator in the middle. This completed sandwich is then rolled or folded into a form factor called a cell and packed into casing.

Lithium cells come in three types:

1. The cylindrical cell, similar to an AA battery, such as the lithium 86/50.
2. The soft flexible pouch cell, often the size of a A4 sheet of paper but can be smaller and shaped to fit within a housing.
3. The prismatic cell with a plastic case, which is about the shape and size of six cigarette packs stacked in pairs side by side.

The cells are made into strings, connected in series and then made into modules which are connected in parallel to form the battery pack. This is packaged into a metal or plastic enclosure. The pouch cell was developed for electric vehicles.

Failure modes

LiBs can store a large amount of energy in a very small space and can be recycled many times over their life with very little loss of capacity. However, if the stored energy is released all at once, it can be very destructive.

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When things go wrong with LiB batteries, the results can be catastrophic

Lithium fields/evaporation ponds in Argentina where batteries are born

In normal operation, charged lithium ions enter the carbon particle matrix on the anode by leaving the lithium paste at the cathode to pass through the solvent and separator. Discharge is the reverse. When LiBs are made the first charge is very slow and the batteries are left for 10 or more days to form a solid electrolyte interface (SEI) or passive layer of solids around the carbon particles. Without this SEI layer the charged lithium ions chemically attack the carbon partials. This creates an exothermic reaction that creates huge amounts of heat and gas, and the cell explodes. This reaction can also be triggered if the SEI layer is damaged, leading to thermal runaway (TR) in a cell and then to thermal propagation (TP) from cell to cell, which is the big baddie.

Lithium batteries don't commit suicide. They are murdered by abuse such as physical damage, overcharging, over-discharge, short circuit, overheating or manufacturing defect.

TR occurs when the limited chemical reactions within the cell become self-sustaining. Once this state is reached it can't be stopped. Degradation of the separator can start at as low as 60°C. Heat is produced in the volume of the object, but only dissipated by its surface area. Thermal propagation heats up adjacent cells which then go into TR. No active or visual fire is required for TR or TP.

When LiBs go into TR a number of things can happen. The first is the battery simply explodes, throwing hot shrapnel around. If not, then a popping of pressure caps failing is heard, along with the hissing of gas escaping and a chemical smell. A black cloud might briefly be seen as the carbon particles are blasted out.

A building storing litium batteries in Grand-Couronne, France, caught fire early in 2023

The flammable gas escapes at high pressure and can ignite, producing jet- or rocket-like flames at 1,000°C. If ignition is delayed the gases vent, creating an explosive atmosphere with a lower explosive limit (LEL) of 11%–16%, with a risk of vapour cloud explosion composed of hydrogen, hydrogen cyanide, hydrogen fluoride, hydrogen sulphide, carbon monoxide, CO_2 and visible droplets of the solvent, which can be mistaken for smoke or steam. The danger to life and health level is well below the LEL. Hydrogen fluoride turns into acid on contact with sweat on skin.

The volume of gas boiled off is huge, in the region of 300–5,000 litres per kWh of battery capacity. There will also be two vapour clouds. One is lighter than air, the other denser than air. It's not known yet how to predict which will dominate.

But it's the vapour cloud explosion (VCE) risk that is the real problem, especially for the marine industry. Current fire-suppression systems put out active fires. But the risk is flipped with VCE because TP continues and cells continue to boil off vapour. As the cells are watertight, it's like pouring water on the roof of your house when your kitchen is on fire.

IMarEST members should look at the human factors and installation standards related to LiB. There is currently some guidance, but not defined standards. ■

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