Industrial gases for lithium-ion battery recycling

By Stephen B. Harrison, sbh4 consulting

Waste Electrical and Electronic Equipment (WEEE) is one of the fastest-growing recovery and recycling streams. It covers anything with a plug, power cord or battery that has been disposed of.

For environmental and economic reasons, WEEE recycling is essential. It contains toxic metals such as lead and mercury in addition to valuable gold and silver.

Furthermore, lithium-ion batteries (LIBs) are often present in WEEE. They contain strategic and critical materials such as graphite, lithium, manganese, nickel and cobalt, in addition to copper and aluminium.

Given the importance of critical materials circularity, LIB recycling is essential. However, when LIBs are damaged or intentionally crushed during recycling, there is the risk of a self-sustaining fire which burns with extreme intensity.

LIB recycling therefore requires specialised processes, which rely on industrial gases.

LIB recycling regulations

There are many types of LIBs, each with different active materials in the LIB anode. The highest energy density is achieved with Nickel, Manganese, Cobalt (NMC) LIBs. These are favoured in premium automotive applications and are displacing Lithium Cobalt Oxide (LCO) LIBs in premium mobile phones to extend their battery life.

NMC and LCO LIBs contain large amounts of cobalt, manganese and nickel. The EU regards cobalt and manganese as critical materials. Nickel is regarded as strategic. Recovery of these metals during LIB recycling is therefore of paramount importance.

In the EU, the Battery Regulation (2023/1542) states that at least 65% of the total mass of an LIB must be recycled. For critical and strategic materials, the mass percentage that must be recycled is even higher.

LIB recovery

The fire risk of LIBs is well documented. Many videos and photographs of battery-powered buses and cars have shown the intensity of the fires that can result if the battery is over-charged, or becomes damaged.

The risk is high because all three elements of the fire triangle are present in NMC and LCO battery types. Residual stored electrical energy can provide the ignition source; the battery electrolyte solvent is highly flammable; and the cathode material contains metal oxides, which release pure oxygen gas at high temperatures, resulting in thermal runaway.

During waste collection batteries are not yet sorted, so the process must be designed to cover the worst case scenario.

LIB collection takes place using boxes which are robust and sealed. They often contain an adsorbent material that ‘soaks up’ the LIB electrolyte solvent in the event of a leakage. This removes the flammable element of the fire triangle and mitigates the risk.

Liquid nitrogen freezing

On arrival at the LIB recycling facility, there is an initial sorting of the incoming batteries. Large battery packs, such as those used in battery electric vehicles are disassembled to separate steel housings and copper cabling from the LIBs. Undamaged batteries are discharged to remove residual stored electrical energy. This is intended to eliminate the ignition source from the fire triangle.

Damaged batteries can be set aside to follow a more cautious recycling pathway. They are frozen using cryogenic liquid nitrogen. This reduces the fire risk for three reasons. Firstly, the energy associated with any residual electrical charge is reduced because the electrochemical reaction is inhibited. Secondly, the solvent is frozen meaning no flammable vapour is present. Thirdly, vaporised nitrogen forms an inert gas blanket over the batteries to eliminate the presence of atmospheric oxygen.

An additional benefit of freezing the LIB with liquid nitrogen is that the batteries become brittle and are easily shredded.

In the past, the Toxco Process used cryogenics as the primary recycling process for all incoming LIBs. However, more recently, less expensive gas-based inerting has become the mainstream technology that is used at this early stage in the LIB recycling process.

Despite its higher cost, the cryogenic process is still used in exceptional cases, such as safe handling of damaged LIBs.

Gas-based inerting

After disassembly and discharging residual electricity, the next stage of the recycling process is brutally mechanical. LIBs are shredded in vicious grinding machines to open up the battery housing.

Shredding flakes the battery casing, and the polymer membrane inside the battery. The copper and aluminium foils from the anode and cathode current collectors are also flaked. Graphite from the anode and metal oxides from the cathode are released as powders.

The liquid electrolyte solvent is also released during shredding. The solvent is often a blend of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC). DMC and DEC are highly volatile and extremely flammable. EC is also flammable at elevated temperatures, but with a higher flash point. To prevent ignition of the solvents, the crushing chamber is flooded with an inert gas. This can be nitrogen, argon, carbon dioxide (CO_2) or a mixture of these gases.

These three inert gases are also used in dry fire extinguishing systems where they are filled into pressurised gas cylinders which release their contents in the event of a fire in a high-value technical area such as a data centre.

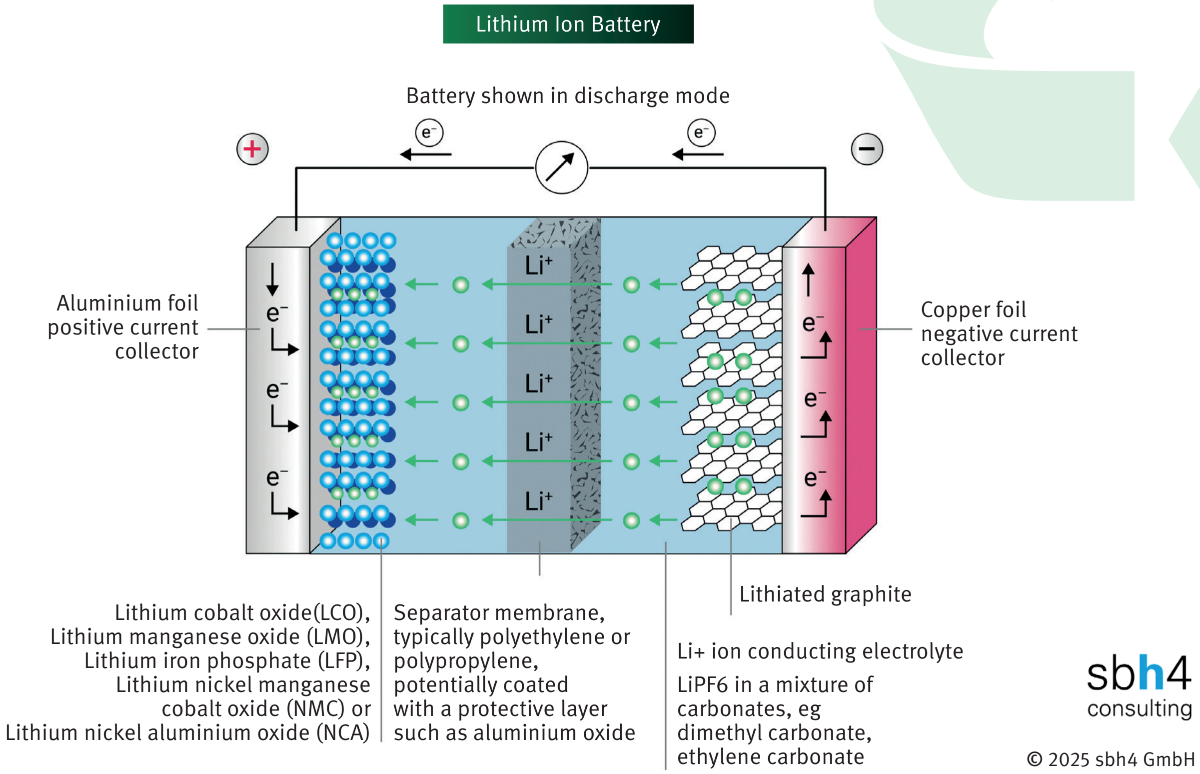
Cryogenic solvent recovery

LIB electrolyte solvents are valuable chemicals that can be re-used. During LIB recycling, they are recovered from the gas vent leaving the inerted crushing chamber. In addition to enabling their re-use, their recovery prevents emissions of these volatile organic compounds to the atmosphere where they are harmful to the environment and human health.

EC, DMC and DEC are condensed out of the vent gas using cryogenic solvent recovery. Liquid nitrogen provides the extreme cold in this process. Cryogenic solvent recovery is used in many pharmaceutical and chemical processes. It is uniquely able to achieve an exceptionally high solvent recovery rate.

Floating flakes

Plastic flakes, shredded copper and aluminium foils are then separated from the powders using a Zig-Zag Classifier. In this equipment, a gas is ▸



blown upwards through a chamber with multiple inclined stages. Through these zig-zag stages, the flakes and powder fall to the base of the classifier tower. The gas continues to blow upwards and is recycled around the classifier. The gas used in the classifier tower can either be air, or an inert gas such as nitrogen. The choice depends on the effectiveness of the previous solvent vaporisation stage and the safety protocol in place in the recycling plant.

Separation of the plastic flakes from the metal foil shreds can be performed using an electrostatic separator.

Subsequently, copper and aluminium foils can be separated with a densimetric table or fluidised bed, exploiting the vastly different densities of these two metals. In these machines, gravity and flotation work in harmony to achieve the separation of the two metallic foils.

The resulting powder, called black mass, is a mixture of anode and cathode materials. It is composed of cobalt, nickel and manganese oxides, lithium and graphite.

Graphite separation

By weight, black mass powder is approximately half mixed metal oxides and half graphite. A small amount of lithium is also present as lithium carbonate.

Pyrometallurgical or hydrometallurgical techniques can be used to recover critical materials from the black mass to enable their recycling. During pyrometallurgical processing, the black mass is heated and molten. The nickel, cobalt and manganese metal oxides react with the graphite to yield a metal alloy and carbon monoxide and CO_2 (carbon dioxide) gases. Lithium is released in the slag from pyrometallurgical processing. It can be recovered using additional hydrometallurgical steps.

Hydrometallurgy is coming to the fore because it enables the high recovery rates of graphite and other LIB materials. These higher recovery rates are required by current and future regulations in the EU.

During hydrometallurgical processing, graphite separation can be achieved by flotation in an aqueous liquor. This is effective because graphite is hydrophobic whilst the metal powders are hydrophilic. When gas bubbles are sparged into the liquor the graphite is floated out, whilst the metal powders remain suspended.

Alternatively, an acidic liquor is used to dissolve the metallic compounds and the insoluble graphite is filtered from the solution.

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Lithium carbonation

Depending on the hydrometallurgy process pathway that is used, lithium is either dissolved in an aqueous broth or a strong acid solution.

To precipitate the lithium, CO_2 gas is injected into the liquor which converts the lithium to a carbonate salt. This lithium carbonate can be extracted using evaporative crystallisation to drive off moisture. Lithium carbonate crystallises and can be filtered from the liquor.

From the initial stages of LIB recycling to the very last step, industrial gases are integral to the process. gw