Battery Storage Systems: What are their chemical hazards?

While consumer interest in battery storage systems continues, an issue often overlooked when discussing the pros and cons of battery storage systems is the chemical hazards associated with the battery technology and ways of managing these hazards.

An array of battery chemistries is available on the commercial market, and the range of products continues to increase. It is important to know the battery technology used by a storage system, and the technology's associated chemical hazards. Depending on the battery technology, there will be different risks when exposed to different externalities, e.g. overcharging batteries, puncturing of battery case, high ambient temperature. The resultant chemical reaction can cause severe property damage, including the possible loss of life.

There is a wide range of battery technologies included as part of a battery storage system for home energy storage. Lead acid battery technologies have historically been the most common technology used, however lithium ion technologies are becoming more popular due to their compact size compared to the amount of energy which can be delivered.

The risks of lithium-ion batteries were highlighted in GSES' article *Hoverboards, fires and residential battery storage* in response to exploding hoverboards over the festive season of 2015, and more recently by the recall of Samsung Galaxy Note 7 due to potentially explosive lithium-ion batteries contained within these devices.

This article covers risks associated with selected lead-acid battery technologies and lithium-ion battery technologies.

Figure 1 - Lead acid battery

Lead acid battery chemical risks

Lead-acid batteries are currently still the most widely used battery type for battery storage systems, having a lower up-front cost and a long track record for stand-alone system applications and other battery storage applications.

Lead-acid batteries can present significant chemical hazards. These are:

- Use of sulphuric acid - a highly acidic acid, as a electrolyte
- Use of lead - a neurotoxin, as electrodes
- Production of explosive gas when overcharged

Sulphuric acid

The electrolyte in lead-acid batteries is a very harsh acid called sulphuric acid (H2SO4). This chemical is dangerous due to its high corrosiveness and reactivity. Contact with sulphuric acid, like any other chemical acid, is not advised, due to its potential to cause damage - particular to bodily tissue. In certain circumstances, the acid may become airborne in the form of fumes. Sulfuric acid's hazard increases as a fume, as it can come in contact with eyes or be inhaled, causing significant damage to internal tissues. It will corrode and decompose other metals and release heat and fumes in the process. It is subsequently known as a dangerous chemical for the environment.

Figure 2 - Hazard symbols for corrosive substances

Hazards associated with sulfuric acid is present even in valve regulated lead-acid (VRLA) batteries such as AGM batteries or gelled electrolyte batteries, where the sulphuric acid is contained within the battery and there is less likelihood of spillage.

Lead

An obvious comment to make is the presence of lead in lead-acid batteries. Lead is a soft, dense metal which is also very toxic. When it enters the body (either by ingestion, direct contact, or inhalation) it can affect every organ and bodily system. Lead can replace metallic atoms that are very important in biological processes, such as the iron in haemoglobin, which is a major component of red blood cells, or the calcium in bones. It is what is considered a bioaccumulative substance, in that it accumulates in the body. This is a significant problem in the fishing industry, in which the lead content in fish can be passed on to humans. As the lead passes from animal to animal through the food chain, more and more lead content will accumulate and become increasingly poisonous towards the end of the food chain, which in many cases is the human population.

Lead acid battery recycling programs exist to reduce the chances of lead contamination. All countries now have regulations regarding the disposal of lead-acid batteries. Additionally, manufacturing processes are analysed to ensure that if lead is used that it does not contaminate other components. This way, lead cannot enter the food-chain easily.

Figure 3 - Hazard symbol for poisonous substances

Gassing of Hydrogen

If a lead acid battery is overcharged, it can cause a chemical reaction known as electrolysis: the splitting of water molecules into hydrogen gas and oxygen gas. This causes hydrogen gas to vent out of the battery. Hydrogen gas is highly flammable, and will combust if exposed to a spark or flame. Battery enclosures must be fitted with appropriate and safe ventilation.

Lithium ion battery chemical risks

One of the newer products for the domestic battery storage industry is the lithium battery technology. Compared to lead-acid, it has a higher energy density, meaning that it takes up less space to deliver the same amount of energy as lead acid batteries. However, this technology is more sensitive to temperature and is currently more expensive to manufacture. Lithium ion technology can also pose greater chemical risks than lead-acid.

Lithium is one of the lightest and most reactive metallic elements on the periodic table. It is also highly reactive towards water and oxygen. When lithium is exposed to water, even the humidity in the air, it readily decomposes water:

$$2Li_{(s)} + 2H_2O_{(l)} \rightarrow 2LiOH_{(aq)} + H_{2(g)}$$

This process is exothermic, meaning that it releases a lot of heat during the reaction. Hydrogen gas is highly flammable in the presence of a spark or with high concentration of heat.

Figure 4 - Hazard symbol for flammable substances.

The production of gas when a lithium ion battery experiences overvoltage and/or high temperatures will pressurise the battery container, causing it to bulge and eventually it will burst to release the gas build-up, which is why when a lithium battery explodes it is shown to release a lot of fumes.

There are various lithium ion battery technologies, utilising lithium ions as electrolyte with different chemistries and electrode. The resultant chemical substances can add to the risks present. Due to the inherent risks of the material, battery manufacturers put a lot of attention in the casing design to make it as rigid as possible. But that does not mean that the risks are eliminated completely. For this reason, installers must strictly follow manufacturers' instructions to ensure the longevity of the battery installation and its safe operation at all times.

Chemical Hazards of Lithium hexafluorophosphate ($LiPF_6$)

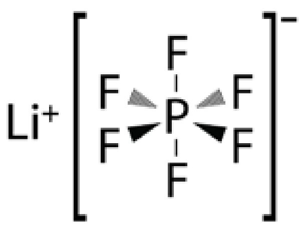

Figure 5 - Chemical diagram of $LiPF_6$

Some high capacity nickel, manganese oxide, and/or cobalt cathode based lithium technologies use LiPF6 as part of the electrolyte fluid material. While lithium itself is a metal, it is usually in the form of an electrolyte solution or plating surface on the electrodes. The chemical hazard of this substance presents itself when the electrolyte leaks from the battery casing, such as through a puncture of the battery casing.

$LiPF_6$ is a flammable, hygroscopic (absorbs water), and corrosive compound usually in a liquid state. It reacts very easily with mucous tissues and is explosively reactive to water due to the lithium ion present in the electrolyte. It causes burns to the skin, eyes and gastrointestinal and respiratory tracts. Severe organ damage, possibly leading to death, from contact with the substance is possible.

Under conditions where $LiPF_6$ is at relatively high temperatures, around 70°C or above, it can cause hydrolysis. But unlike lead-acid, this hydrolysis can prove much deadlier. The following chemical reaction shows the formation of hydrofluoric acid after hydrolysis:

$$LiPF_{6(aq)} + H_2O_{(l)} \rightarrow HF_{(aq)} + PF_{5(g)} + LiOH_{(aq)}$$

Hydrofluoric acid is a very dangerous acid, and it will react corrosively with almost anything, even glass. It can damage lung tissues severely if inhaled, and is damaging to the skin and eye tissues. It is known for causing systemic toxicity, respiratory failure, cardiac arrest, and death even with little physical contact with the compound. If a battery with $LiPF_6$ were to be damaged and spill electrolyte, $LiPF_6$ will start to react with water in the environment and create a dangerous fume. It would be incredibly dangerous to be near the spillage without any personal protective equipment.

Due to the severity of the hazards present, batteries using $LiPF_6$ are designed to contain all the internal components and ensure that any chemical reactions are contained inside the battery casing safely. However, care must be taken to avoid crushing, perforation, or careless disassembly of the battery casing.

Figure 6 - Hazard symbol for Irritants

Lithium Percholate ($LiClO_4$)

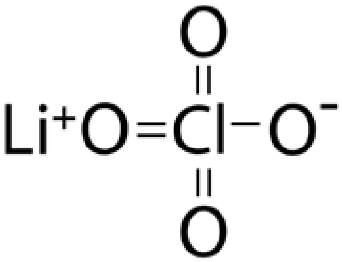

Figure 7 - Chemical diagram of $LiClO_4$

Lithium perchlorate is a salt compound that is used in the electrolyte material of lower capacity silver chromate and manganese oxide batteries. Compared to $LiPF_6$, lithium perchlorate is a more soluble, conductive, and chemically stable compound. However, when exposed to a source of heat, $LiClO_4$ breaks down to release oxygen and even larger amounts of heat. This is why $LiClO_4$ is used in rocket propellants and fireworks.

$LiClO_4$ is a very strong oxidant, which causes it to react with its own solvent in the electrolyte under high temperature situations or high discharge currents. This will cause the cell to heat up further, degrade and ignite, causing the battery casing to bulge. For such reasons this chemical compound only used in small capacity applications.

Chemically speaking, the perchlorate ion is a very reactive, oxidizing species that can cause severe harm if it makes its way into body tissues. It can cause irreversible eye damage and irritation or burns to the skin and respiratory tract. In large amounts, it is also toxic to the central nervous system. Although it is not flammable, it can cause explosions in the presence of combustible materials.

Figure 8 - Hazard Symbol for oxidising agents

Issues regarding chemical safety, first responders, and lithium batteries

Research on control methods for accidents involving lithium batteries is not extensive, and therefore not yet conclusive. Fire-fighters in many developed countries have encountered issues addressing the control of battery fires. Due to the chemical hazards involving the components of the electrolyte, first response teams are advised to wear self-containing breathing apparatus and full protective gear when approaching lithium battery fires, and to avoid contact with any battery material.

Over-saturating the ignited batteries with water is the best way to deal with a battery experiencing extreme thermal runaway. However, it does not stop the chemical reaction within the battery material. The chemical breakdown of the battery will continue until there are no more reactive materials.

This initial guide is intended to provide enough information for installers and customers to appreciate the safety concerns associated with these technologies. While batteries are safe during normal operation, they can become unstable and dangerous during accidents. It is important to install the battery systems correctly and ensure that they are housed in compliant fire-resistant enclosures. Battery systems should last as long as possible and provide energy to the customer with minimum associated risk.

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