Polymers
Critical to Safer Lithium Ion Batteries

Fascinating World of Invisible Polymers

From a materials point of view, two issues become important. One, the nature of the separator and second, a need for an electrolyte which is non-flammable. Polymers are key to realising both these objectives.

In a previous article (POLYMERS Communiqué, October - November, 2016 issue), I addressed the role of polymer (polyolefin) separators on the functioning of a lithium ion (Li-ion) battery and its role in battery safety. Battery safety has been much in the news lately.

Analysing Battery Failure

There are many reasons why a battery overheats and catches fire. Any mechanical damage to the battery can cause the battery to discharge rapidly which is accompanied with evolution of heat. Any damage to the separator film or a manufacturing defect (pinhole) can increase the risk of shorting, which is release of energy. When a battery is overcharged, some cathode materials release oxygen, which causes the liquid electrolyte to burn. The liquid electrolytes are composed of organic carbonates, which can degrade during charging, releasing carbon dioxide. Batteries are hermetically sealed; so any pressure generation inside the battery causes the battery to explode. The organic carbonates are also flammable. Lithium hexafluorophosphate is dissolved in organic carbonates and is the source of mobile Li-ions. Traces of moisture causes a breakdown of the salt to generate fluoride ions which decompose the organic carbonate, thus generating gases. Overcharging can also drive more lithium from the cathode to the anode, beyond its capacity to hold. This generates a needle-like dendritic form of lithium, which pierces through the separator and causes shorting. Many particulate impurities are inadvertently introduced in the battery during its manufacturing in spite of the scrupulously clean environment under which batteries are assembled. Such particles can

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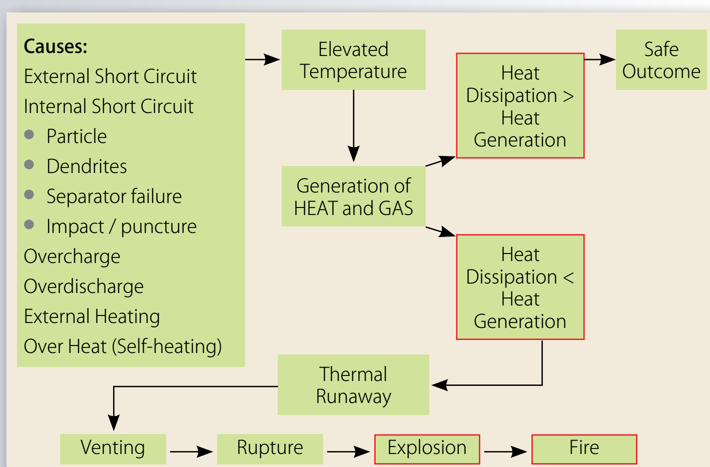

Figure 1: Anatomy of a battery failure.

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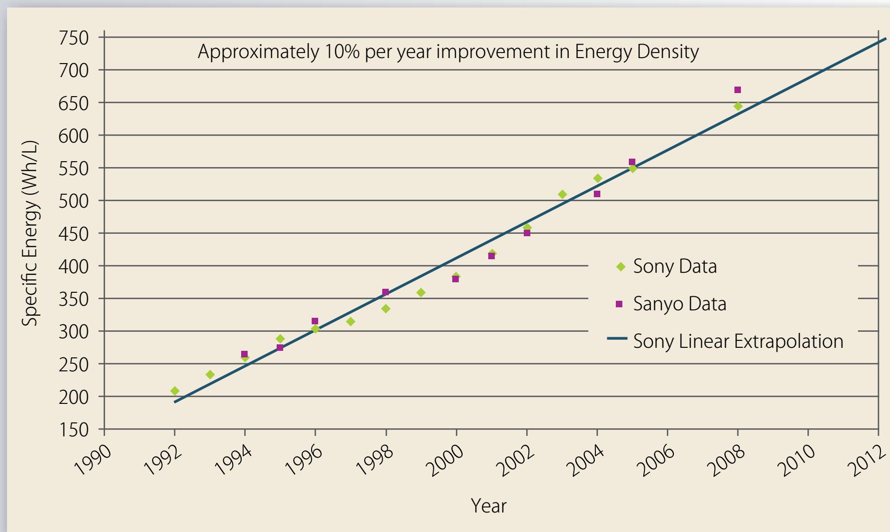

Figure 2: Energy density trends for commercial Li-ion batteries.

(Source: Vehicle Battery Road Map, NREL Report, USA, 2012)

cause short circuit by providing a conductive contact between the cathode and the anode. In short, many chemical reactions occurring in a lithium ion battery are heat liberating; and the cornucopia of chemicals and materials used are flammable and combustible, a perfect recipe for disaster.

In fact, one should really wonder why in spite of such a complex mixture of reactive chemicals present in a battery, the reports of accidents with lithium ion battery have been so far and few in between. This is due to the maturity of the manufacturing process perfected over two decades. Statistically, the batteries are very reliable and failure rates are better than six sigma defect levels (about one in 10 million).

Designing the Modern Battery

There has been considerable understanding gained on the root cause of overheating (Refer Figure 1) and many safety systems have been built into the design of a modern battery. Yet exceptions can still be dangerous. Although the probability is small, greater and greater use of battery increases the chances of mishaps. Heavy duty uses such as in electric cars and airplanes are examples where even one accident can erode the confidence in technology.

Lithium ion batteries have been in use since mid-nineties. However, we have become aware of its safety as a hazard only since 2013. The reason is the need to pack more and more power in smaller and smaller sized batteries to meet the humongous power needs of new devices that are powered by them (Refer Figure 2). A consumer likes a battery that charges fast, runs longest between charge, can handle demanding tasks like downloads of audio, video, high-resolution images and view a movie uninterrupted on a smart phone for three hours. This has led the battery manufacturers to make many design changes that appear to have had an adverse effect on safety.

One of the key design changes made is downguaging the thickness of the polyolefin separator films to less than 20 microns. Thinner films permit faster lithium ion transport across the separator membrane, leading to faster charging. Thinner the film, greater the risk of pinholes formation during manufacture and puncturing due to dendritic lithium formation on the anode.

The Materials Evaluation

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Are we responsible for battery hazards?

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become important. One, the nature of the separator[4] and second, a need for an electrolyte which is non-flammable[2]. Polymers are key to realising both these objectives.

Most of the current separators are made of polyolefins, which are semi-crystalline and have melting points in the range of 140°C to 165°C. One of the earliest innovations was to sandwich a layer of lower melting PE between two outer layers of higher melting point PP in a tri-layer porous membrane. When the temperature of the cell rises and approach about 130°C, PE will begin to melt and plug the pores; cutting off the transport of lithium ion from the cathode to the anode. This shuts down the cell, letting it cool safely. One of the problems with semi-crystalline polyolefins of this type is that near their crystalline melting point, they undergo volume shrinkage. This causes changes in dimension and increases the risk of shorting. Methods to control extent of shrinking in semi-crystalline polymers are an area where more studies are needed. However, device shutdown is not a guarantee of safety. The principle reason is that, after shutting down, the internal temperature of the battery is often high enough to cause residual stress and reduced mechanical properties leading to shrinkage, tearing or pinhole formation.

Another way of improving safety is to enhance the thermal properties of polyolefins by incorporating a ceramic layer in PE or PET substrate (Refer Figure 3)[4,5]. Entek has developed a membrane where a ceramic is embedded in UHMWPE with ceramic content as high as 60%.

Another approach to safety has been to coat anodes with microspheres of low molecular weight polyethylene or paraffin wax[6]. In the event of a temperature increase inside the cell, the microspheres of PE or wax melt, flow and coat the battery surfaces rendering the surface ion insulating.

Use of speciality polymer materials with high thermal stability has been explored as battery separator materials. DuPont reported separators based on non-woven films of electrospun nanofibres of polyimides (Energain™)[7]. Porous films made from polyetherimides (Ultem™)

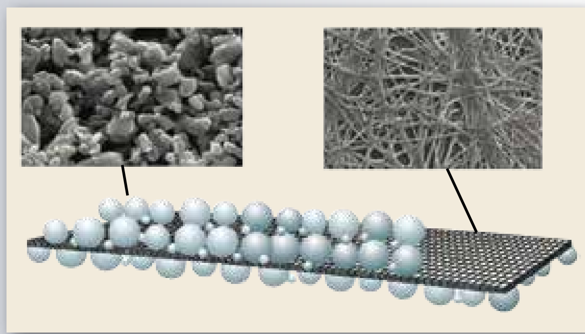

Figure 3: Schematic of a ceramic (alumina or zirconia) coated on a non-woven PET film[5].

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have also been reported by scientists in General Motors Corporation to be useful as battery separators[8]. These materials are amorphous and have high glass temperatures and polymer degradation temperatures. Consequently, no dimensional changes are anticipated. Non-woven fibre mats prepared from electrospun PET have also been found to exhibit excellent performance[4]. These materials have the potential of making the battery inherently safer. However, the benefit comes at a cost. These polymers are substantially more expensive than polyolefins.

Up Next

In a future article, we will explore how electrolytes can be rendered non-flammable and safe using polymers.

Lithium ion batteries are here to stay since they offer an optimum performance at reasonable cost. Much investment has been sunk for their large-scale manufacture. Li-ion battery technology has the benefit of longest experience curve in terms of technology development and manufacturing amongst all competing battery technologies. Therefore, it is unlikely that this technology will disappear or be disrupted very soon. Recent unfortunate incidents have spurred even more R&D towards enhanced battery safety. Greater understanding of chemistry and polymer material science coupled with more reliable battery management electronics will certainly lead to safer batteries with even far fewer incidents of hazards.

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