Adding Safety to Lithium Ion Batteries

Fascinating World of Invisible Polymers

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Rechargeable lithium ion batteries have become ubiquitous since Sony Corporation first introduced them in Japan in 1990. Today, every electronic device from a smart phone to a laptop, from a wristwatch to a medical device, from an electric car to a Boeing 777 uses lithium ion battery to store energy. The market for lithium ion batteries reached USD 12 billion in 2012 and is expected to double by 2017. These batteries are light in weight (lithium is one of the lightest metal), can store enormous amount of energy (150 watt-hours per kilogram), can hold its charge for a long time (loss of only 5% charge per month) and can be charged and discharged several hundred times without any deleterious effect.

The Insides of an LIB

Similar to any battery, a lithium ion battery (LIB) has a cathode (typically, lithium cobalt oxide, lithium cobalt phosphate etc.), an anode (a layered graphite), lithium salt (typically, LiPF6) and a liquid electrolyte (typically a ratio of 1 : mixture of ethylene carbonate and

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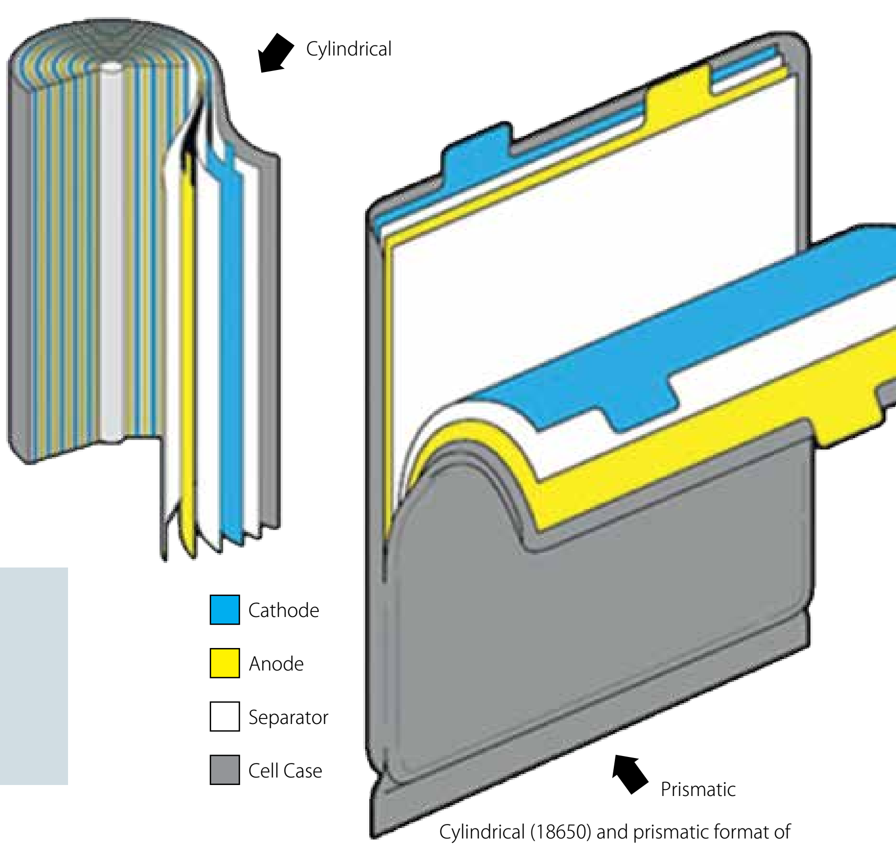

Cylindrical (18650) and prismatic format of lithium ion battery.

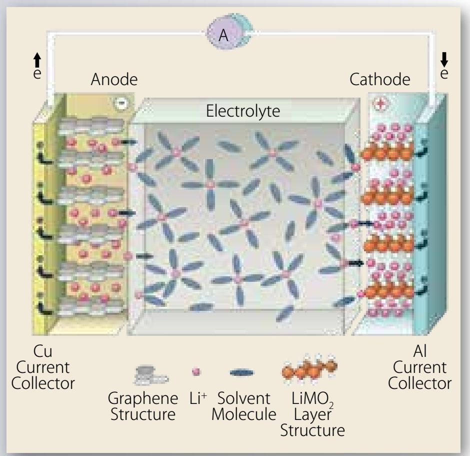

Figure 1: Schematic of a lithium ion battery consisting of the negative electrode (graphitic carbon) and positive electrode (Li-intercalation compound).

dimethyl carbonate). The cathode and the anode are separated by a thin film of a porous polymer, which is insulating, but allows the transport of lithium ions from the cathode to the anode and vice versa during the charging and discharging cycles. The porous polymer film is called a 'separator' since it prevents the direct electrical contact of the cathode and the anode.

A typical internal structure of a lithium ion battery is as shown in Figure 1. During a charging cycle, lithium ions present in the cathode migrate through the electrolyte medium to the anode where they intercalate into the layers of graphite. An external electrical power source injects electrons into the anode. At the same time, the cathode gives up some of its lithium ions, which move through the electrolyte to the anode and remain there. During this process, electricity is stored in the battery in the form of chemical energy. During the discharging cycle, the lithium ions de-intercalate from the graphite anode and migrate across the electrolyte to the cathode, enabling the release of electrons to the outer circuit to perform the electrical work.

Figure 2: Rolls of polyolefin separator films.

Lithium ion batteries are currently manufactured in three formats; one, the most familiar button cells used in small devices; second, cylindrical with a dimension of 65 mm long and 18.6 mm diameter (termed as 18650 cells) and third, flat cells called prismatic cells (Refer opening figure). For example, Tesla Motors uses 18650 standard format cylindrical cells in Model S cars. The battery pack consists 7,104 cells giving a total power of 85 kWh.

Separator – The Critical Component

The separator is a critical component of the battery and its properties have a strong impact on cell production, cell performance, life and most importantly, reliability and safety, although the separator does not 'directly' participate in any reactions[1]. It provides a physical barrier between the anode and the cathode, at the same time enabling the exchange of ionic charge carriers, namely the lithium ions, between the two electrodes to control the number of lithium ions and their mobility. The porous structure of the separator is filled with the liquid electrolyte (lithium salt dissolved in a mixture of one or more solvents). Separators currently used are made of polyolefins; either, polyethylene or polypropylene which are rendered porous by a mechanical mono- or bi-axial orientation during film extrusion. In this respect, a polyolefin derived battery separator is no different than a packaging film produced by biaxial orientation, a familiar processing technique. However, the value addition to polyolefins in a battery application is huge.

Market Share

Separator films are sold in rolls and priced by square foot and not by weight. There are just a few manufacturers of polyolefins based separator films. They are Asahi Kasei (Hipore, www.asahi-kasei.co.jp/hipore; and Celgard, www.celgard.com), Toray (Setela, www.toray-bsf.com), Ube (UPore, www.ube-ind.co.jp), Entek (Teklon, www.entek.com) and Targray (www.targray.com). All of them have a broad portfolio of products based on polyethylene and polypropylene (monolayer) and co-extruded PP/PE/PP (trilayer) films in thickness ranging from 16 to 25 microns. Hipore, Setela and Teklon are single layer PE; whereas, UPore and Targray are available in single layer PE or PP. Celgard is available as single layer or multilayer PE and PP (Refer Figure 2). Separator films are available in a range of pore sizes, a property critical to the performance of the battery.

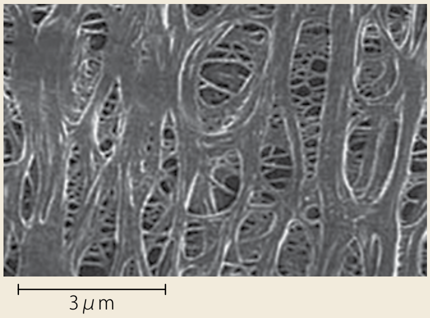

Figure 3a: Large pore diameter Hipore™.

(Source: http://www.asahi-kasei.co.jp/hipore/en)

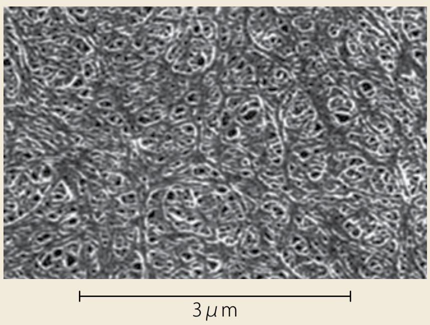

Figure 3b: Small pore diameter Hipore™.

(Source: http://www.asahi-kasei.co.jp/hipore/en)

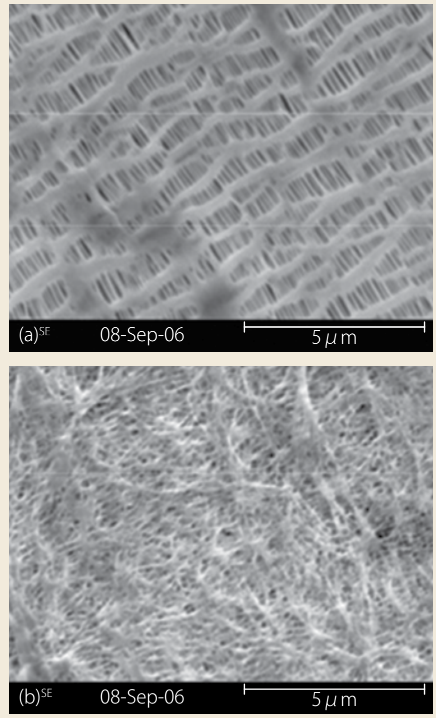

Figure 4: Morphology of PP separator film made by dry process (a) and wet process (b). (Source: NASA Glenn Research Center, 2009).

Celgard, Hipore and Setela command 26, 25 and 21%, respectively, of the market share, whereas UPore has about 7% of the market share. The rest of the manufacturers have the balance market share. Today, about 1000 billion m^2 of separator film is produced globally. The share of the value of the separator in a lithium ion battery components is about 20 - 25% with a projected value of over USD 3 billion by 2020[2].

Manufacturing Process

Separators for the lithium ion battery are usually manufactured via a 'wet' or 'dry' process. In the 'dry' process, polypropylene (PP) or polyethylene (PE) is extruded into a thin sheet and subjected to rapid drawdown. The sheet is then annealed at 10 - 25°C below the polymer melting point such that crystallite size and orientation are controlled. Next, the sheet is rapidly stretched in the machine direction to achieve slit-like pores or voids at 35 - 45% porosity. A PP/PE/PP trilayer separator can also be produced in this fashion.

Polyolefin separators based upon UHMWPE are usually produced in a 'wet' or 'gel' process involving extrusion of a plasticiser / polymer mixture at elevated temperature, followed by phase separation, biaxial stretching and extraction of the pore forming agent (i.e. plasticiser). The resultant separators have elliptical or spherical pores and porosity in the 40 - 50% range (Refer Figure 4 (a) and 4 (b)). On account of the biaxial orientation, good mechanical properties are achieved in the transverse and machine direction.

Going Forward

Separators play a critical role in defining the safety of operations of lithium ion batteries. The fire hazards inherent in lithium ion batteries have been in the news recently (phones and cars exploding in flames). Separator materials and design will play a significant role in creating more safe batteries in the future.

References

1. A review of recent developments in membrane separators for rechargeable lithium-ion batteries, H. Lee, M. Yanilmaz, O. Toprakci, K. Fu and X. Zhang, Energy Environ.Sci., Vol 7, 3857, 2014; A review on the separators of liquid electrolyte Li-ion batteries, S. S. Zhang, J. Power Sources, Vol. 164, 351, 2007.
2. Separators for lithium-ion batteries: A review on the production processes and recent developments, V. Deimede and C. Elmasides, Energy Technology, Vol.3, 453, 2015.