Nanofiber Based Battery Separator

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A separator is a porous membrane placed between electrodes of opposite polarity, permeable to ionic flow but preventing electric contact of the electrodes (Figure 1). A variety of separators have been used in batteries over the years. Starting with cedar shingles and sausage casing, separators have been manufactured from cellulosic papers and cellophane to nonwoven fabrics, foams, ion exchange membranes, and microporous flat sheet membranes made from polymeric materials. As batteries have become more sophisticated, separator function has also become more demanding and complex. Separators play a key role in all batteries. Their main function is to keep the positive and negative electrodes apart to prevent electrical short circuits and at the same time allow rapid transport of ionic charge carriers that are needed to complete the circuit during the passage of current in an electrochemical cell. They should be very good electronic insulators and have the capability of conducting ions by either intrinsic ionic conductor or by soaking electrolyte. They should minimize any processes that adversely affect the electrochemical energy efficiency of the batteries. Therefore, selection of an appropriate separator is critical to the battery performances, such as energy density, power density, cycle life, and safety. For high energy and power densities, the separator is required to be very thin and porous while still remaining mechanically strong. For battery safety, the separator should be able to shut down when overheating occurs, such as in an occasional short circuit, so that thermal runaway can be avoided. The shutdown function can be obtained by a multiplayer design of the separator, in which at least one layer melts to close up the pores below the thermal runaway temperature and the other layer provides mechanical strength to prevent physical contact of the electrodes [1].



Figure 1. Schematic of lithium ion battery (Source: HowStuffWorks)

The battery industry has seen enormous growth over the past few years in portable, rechargeable battery packs. The majority of this surge can be attributed to the widespread use of cell phones, personal digital assistants (PDA's), laptop computers, and other wireless electronics. Batteries remained the mainstream source of power for systems ranging from mobile phones and PDA's to electric and hybrid electric vehicles. Lithium-ion storage batteries have been the main power supply for mobiles, laptops and digital electronic products since the commercialization of lithium-ion batteries by Sony in 1991. Lithium-ion battery are featured with the high energy density, power density, no memory effect, little self-discharge and a long circling life. Therefore, it becomes a main choice for automobile power supply. Currently lithium-ion battery powered electric vehicles are being developed by many famous auto manufacturers such as Ford and Chrysler in America, Toyota, Mitsubishi and Nissan in Japan, Korean Hyundai, Courreges and Ventury in France, etc. Governments and enterprises of many countries multiply their efforts in R&D of lithium batteries for HEV and EV. Japan has presented New Sun Plan. The participants include Hitachi, GS-Yuasa and Panasonic. Toyota has acquired the operation right of Ni-MH battery for HEV. Meanwhile, the company has invested for its own production line of power lithium-ion storage barriers. It is also making effort to apply power lithium-ion storage barriers in HEV. NEDO disclosed new development plan on storage barriers for electric vehicle in February, 2007. Moreover, LG in Korea begins to develop high-power polymer lithium-ion batteries. Two types -- 6Ah-144Wh/kg and 10Ah-158Wh/kg have been released. United States

Department of Energy (USDOE) has supported the R&D of three-generation lithium-ion storage batteries. SAFT of France has already developed two types of high-power lithium-ion batteries, with power mass ratio of 1500W/kg and 350W/kg respectively [2]. Recent market reports have predicted that the global market for large format lithium-ion batteries will see a substantial overcapacity in the coming years, with some predicting an excess of more than 100% in 2015 (Figure 2). Sanyo Electric Co. expects the global lithium-ion battery market will more than triple to 5 trillion yen (\$60 billion) in 10 years, driven by demand from power companies and electric cars [3]. The continued growth in lithium-ion battery market has led to a strong demand for battery separators. According to industry insiders, by 2011 the global need for lithium-ion battery separator will reach 353 million square meters and will reach 1.126 billion U.S. dollars in sales. The market demand will be 1.8 times the current market, and sales will be 2.3 times the current.



Figure 2. Market size of lithium ion battery

These separators play an important role by regulating cell kinetics, allowing ionic flow, preventing electronic contact between the two electrodes. However, nonpolar polyolefins have a hydrophobic surface with low surface energy and exhibit poor affinities to polar organic electrolytes. It usually gives rise to resistance increases, which is responsible for the shortening of the battery lifetime and severely affect the battery performance, e.g., cycle life. Rate capabilities of these separators are not enough for high power application, such as electric

vehicles (EV) and hybrid electric vehicles (HEV). The microporous membrane separators have some disadvantages to be improved such as low wettability and low porosity of about 40% (Figure 3). This nature of polyolefin separators would restrict the performance of the lithium-ion batteries.



Figure 3. Typical structure of PP microporous membrane

Recently, electrospinning has been developed to fabricate microporous PVDF, PVDF-HFP and PAN membranes as separators for lithium ion batteries (Figure 4). The remarkable characteristics of nanofiber webs such as large surface area to volume ratio and high porosity, which are crucial to increase the ionic conductivity of membrane full of liquid electrolyte, in this aspect, electrospinning is prior to the other methods, such as dry and wet method. Therefore, nanofiber-based battery separator by electrospinning is potential and promising. DuPont has introduced the first nanofiber-based polymeric battery separator that boosts the performance and safety of lithium ion batteries. DuPont Energain battery separators can increase power 15 to 30 percent, increase battery life by up to 20 percent and improve battery safety by providing stability at high temperatures. DuPont Energain battery separators are produced into a web using a proprietary spinning process that creates continuous filaments with diameters between 200 and 1,000 nanometers. The separators exhibit stability and low shrinkage in high temperatures and are highly saturable in electyrolyte liquids.



Figure 4. Nanofiber based PVDF separator

Electrospinning is a novel process for producing superfine fibrous and porous membranes by forcing a polymer solution through a spinneret with an electric field. The average diameter of the fibers produced by electrospinning is between 50-500 nanometers. In a typical process, an electrical potential is applied between a droplet of a polymer solution, or melt, held at the end of a capillary tube and a grounded target. When the applied electric field overcomes the surface tension of the droplet, a charged jet of polymer solution is ejected from the tip of the Taylor cone and the discharged polymer solution jet undergoes an instability and elongation process, which allows the jet to become very long and thin. Meanwhile, the solvent evaporates, leaving behind a charged polymer fiber. In the case of the melt the discharged jet solidifies when it travels in the air. With small fiber diameter, low density, large specific surface area, small pore size, interconnected pore structure, and high porosity, electrospun nanofibers have been successfully applied in various fields, such as, nanocatalysis, tissue engineering scaffolds, protective clothing, air and liquid filtration, biomedical, pharmaceutical, optical electronics, healthcare, biotechnology, defense and security, solar and fuel cells, battery and environmental engineering.

References

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