Preparation of Polyimide Nanofiber Membranes and Their Application as Li-ion Battery Separator

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With the rapid development of modern electronic industry, especially the portable devices and the electric or hybrid electric vehicles and tools, more and more attentions have been focused on developing high-performance rechargeable lithium-ion batteries with the characteristics of large energy capacity, long cycle life, high working voltage and excellent safety guarantee. As the "third electrode" in a lithium-ion battery, the separator plays a determining role in the safety performance of the battery and plays a key role in improving its energy density, since the separator functions as both an "insulator" to prevent the direct contact of the anode and cathode, and meanwhile as a "sieve plate" to provide channels for the lithium ions in the electrolyte to move through freely between the two electrode. [1, 2]

Currently, most of the commercially available lithium-ion battery separators are polyolefin micro-porous membranes derived from polyethylene (PE) and polypropylene (PP) via either a dry or a wet process. Polyolefin separator bears excellent chemical stability, good mechanical strength and low cost, and therefore used as the major commercial product in various lithium ion batteries. [1,3,4] However, the polyolefin separator encounters severe limitations when being used in lithium-ion batteries for high-power consumption equipment such as electric vehicles, where high-temperature safety and high rate capability are required. Due to the low thermal stability, the polyolefin separator has been proven to cause safety problems above its meting temperature (PE, 135 ºC; PP, 165 ºC) in lithium ion batteries. [1] On occasion internal electric short circuit or high power discharge leading to the rapid rising of temperature happens, the polyolefin separator can't stand for a long time, and will melt and rupture above its melt temperature, causing battery explosion disaster. Besides, the polyolefin separator has relatively low porosity (ca. 40%) and nonpolar chemical structures, therefore leading to inferior wetting behavior, high cell resistance and low rate capacity, consequently restricting its application in high-energy density batteries. Therefore, the research and development of new separators possessing high temperature stability, high porosity, high rate capability and high safety is strongly demanded.

Among numerous approaches to overcome these shortcomings of polyolefin micro-porous separators, the use of electrospun polyimide-based nanofiber nonwovens [4, 5] has drawn substantial attention because of their superior thermal properties, high porosity and electrolyte uptake, sufficient electrolyte wettability and chemical stability performances for high power lithium-ion battery. However, the nanofiber nonwoven is usually prepared with rather low mechanical properties since the nanofibers in the as-prepared nonwovens are only loosely and randomly overlapped together with no strong interactions, which make it inadequate to meet the requirement for the winding process in industrial battery assembly. Besides, due to the loose architectures, the nanofiber nonwovens will always generate not so desirable pore structures which are too open when being used as separator, leading to some potential safely hazard during long-term applications.

To overcome these drawbacks and problems, preparation of nanofiber nonwovens with cross-linking topographies was suggested to be an effective approach. In our recent works, by introducing cross-linking micro-structures, either chemically or physically, cross-linked polyimide nanofiber nonwovens with strong mechanical strength and well-improved pore structures have been successfully produced. Several different methods were developed in our recent work for forming cross-linked architectures in the polyimide nonwoven. Figure 1 shows the SEM morphologies of the as-prepared and cross-linked nanofiber nonwovens fabricated via two different strategies, i.e., chemical welding process and micro-melting process.

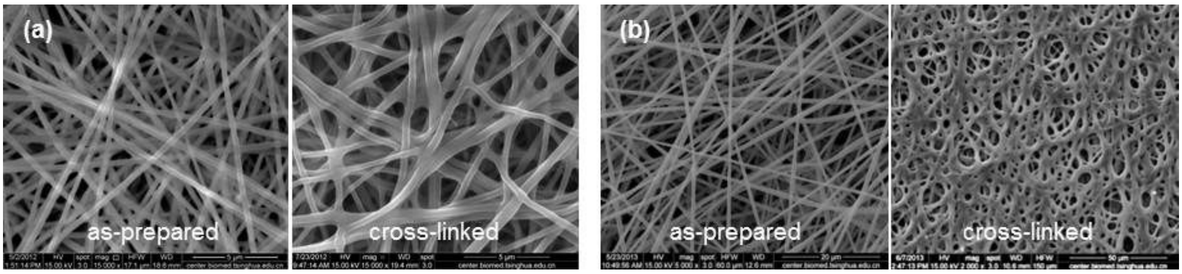

Figure 1. The SEM morphologies of the as-prepared and cross-linked nanofiber nonwovens fabricated via (a) chemical welding process and (b) micro-melting process.

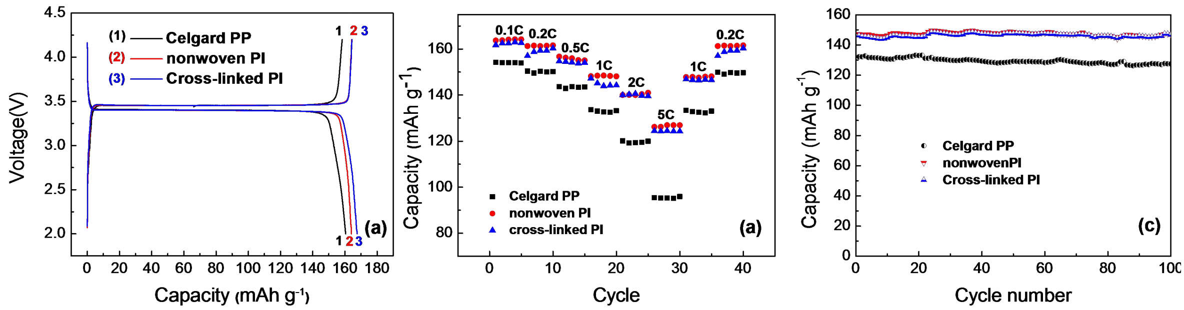

Figure 2. The (a) charge-discharge curves, (b) rate capability and (c) cycling performances for the lithium ion cells with Celgard PP membrane, polyimide nonwoven and the cross-linked polyimide nonwoven as the separator, respectively.

The cross-linked structures formed in the nonwovens have significantly enhanced the interactions between the neighboring nanofibers, making the nonwovens mechanically rather more robust and dimensionally more stable, as will be shown in our presentation. Cell tests indicate that the lithium ion batteries using the cross-linked polyimide nonwoven as the separator exhibit better charge-discharge properties, comparable long cycle life and cycling performances with perfect capacity retention ratio, and considerably higher rate capacity as compared to the commercial Celgard PP separator, especially at high rate, as displayed in Figure 2, demonstrating the advantages of the cross-linked polyimide nonwoven as advanced material for the new-generation lithium ion battery separators

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