A Novel Separator Membrane for Safer Lithium-ion Rechargeable Batteries

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Introduction

Since their first introduction by Sony in the early 1990s [1, 2] Lithium-ion rechargeable batteries have become the preferred power source for portable electronic devices such as cellular phones and notebook computers due to their much higher energy density. As their performance is improving and cost dropping, they are beginning to penetrate other applications such as hybrid electric vehicles and power tools that require higher power. A lithium-ion cell, as most of the other electrochemical cells, is constructed with positive electrode, negative electrode, and separator membrane. These components are generally soaked with organic electrolyte. Typical configuration of lithium-ion battery and its components are described in Figure 1.

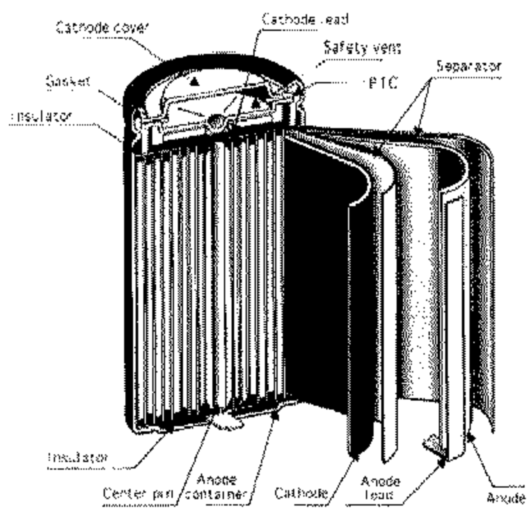


Figure 1. Typical configuration of lithium-ion battery and its components.

The separator is a micro porous membrane placed between two electrodes. The main functions are to physically isolate a cathode and an anode so that no electrons can flow in between and to allow rapid transport of ionic charge carriers during the passage of electric current [3-5]. Among these two requirements, the electrical isolation of electrodes is considered to be most critical as far as battery safety is concerned. Internal short-circuits caused by protrusions on the electrode surface either by unavoidable metallic impurities or by dendritic lithium growth during battery operation has been the most fatal to battery safety. Such safety concerns have become even deeper as energy density and performances of lithium-ion batteries are continually improving.

Furthermore it is well known that thermal shrinkage of the separator membrane or its mechanical rupture can lead to an abnormal heating, which may cause fire or explosion eventually. This so-called thermal runaway is likely to take place as local heat generation accelerates electrolytes and electrode materials to decompose. If separator membrane can prevent the internal short-circuit, the separator can be engineered as a safety device in lithium-ion batteries.

In general the separators in lithium-ion batteries are based on polyolefins, especially polyethylene (PE), and polypropylene (PP). Though polyolefin-based separators have many advantages in chemical and electrochemical stability, high porosity, low costs, and so on, they still have limitations in preventing the fore-mentioned internal short-circuit between electrodes due to the poor dimensional stability and mechanical strength. Therefore, it goes without saying that a technical breakthrough that can overcome these drawbacks contributing to safer lithium-ion cells is extremely awaited.

In this study we have developed a novel separator membrane that can significantly improve battery safety. Basic membrane-related properties are investigated and its relationship with electrochemical performances in lithium-ion batteries is discussed. And finally, its contribution to the safety improvement is given.

Experimental

Sample preparation.
The separator was prepared by the LG Chem's proprietary technology. The separator was incorporated into various kinds of batteries covering cylindrical cells, prismatic cells, and polymer cells. In addition to the separator, lithium metal oxide-based cathodes, carbon-based anodes, and carbonate-based electrolytes with lithium-based salts were assembled into the cells. The detailed chemistry and structures in each cell can vary, depending on the cell capacity and other related performances. For comparison, conventional polyolefin-based separators (REF) are included in the same experimental conditions.

Characterization.
The basic membrane properties of the separator were examined and compared with conventional polyolefin-based separators. Air permeability, pore size, porosity, ionic conductivity, thermal shrinkage, and z-directional penetration resistance are the major variables to monitor carefully. The electrochemical performance including capacity, C-rate performance, and cyclability of cells were measured in the voltage range of between 3.0 V and 4.2 V. To investigate the effect of separator on the cell safety, various abuse tests were carried out, which includes hot-oven, overcharge, nail penetration, bar crush, and so on. The detailed test conditions were based on the Underwriters Laboratory (UL) requirements.

Results and discussion

Separator Properties.
It is useful to characterize the separator in terms of its structural and functional properties and to establish a correlation with its performance in batteries. The overall transport property of the new separator membrane is represented by the air permeability and was found to be comparable to the conventional ones. The dimensional stability was measured at various temperatures. Both a hot-oven thermostat test and a thermomechanical analysis (TMA) revealed that the new separator has remarkably improved in thermal stability compared to the conventional ones (Figure 2 and 3).

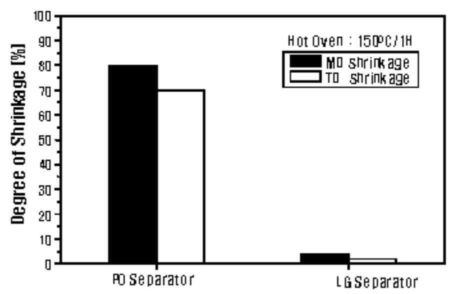


Figure 2. Thermal shrinkage of separators (after storage in hot-oven for 1hr at 150°C).

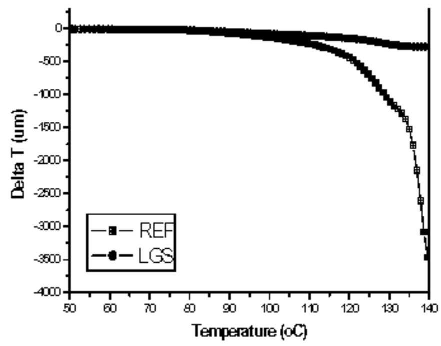


Figure 3. Plots of dimensional change with temperature (constant stress = 0.05 N, scan rate = 5°C/min).

Considering the fact that the shrinkage of separator in both machine and transverse directions is a major indicator for the possibility of internal short-circuits, such an enhancement in the thermal shrinkage is expected for the new separator to help cells remain safe even when the cells are exposed to abnormally high temperatures or during abnormal heating.

Z-directional penetration resistance is related to the mechanical force that prevents internal short-circuit across the separator. Figure 4 shows that the z-directional penetration strength of our new separator is much larger than that of conventional one.

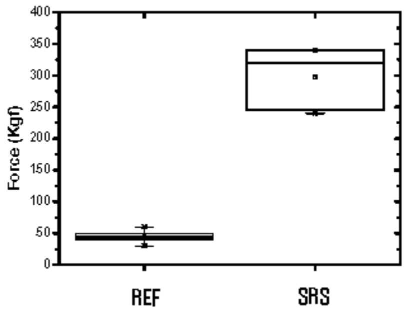
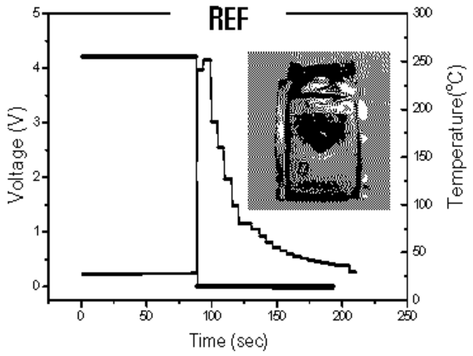


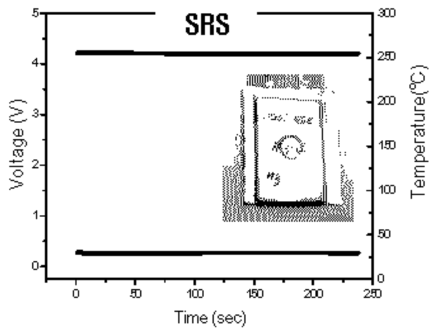
Figure 4. Z-directional penetration strength for conventional polyolefin-based separator (REF) and LG's new separator (LGS).

Effect of Separator on Cell Safety.

Based on the previous characterization of separators, its influence on the cell safeties was examined. In order to simulate the real safety issues, we adopted various abuse conditions with the details described in the experimental section. Among the various kinds of abuse tests, crush test is most employed to estimate the internal short-related safety issues. When the applied compression force onto a cell exceeds a certain level that the separator can tolerate, it causes the cathode and the anode to contact each other, which lead to sudden discharge and heating, which may result in fire or explosion. Figure 5 exhibits the voltage and temperature profiles for the conventional separator and the new one. The conventional one showed a typical behavior. When the applied force reached to a critical value to cause mechanical damage to the separator, the cell voltage dropped instantly, reflecting an electrical contact between cathode and anode, which led to cell rupture and fire.



(a)



(b)

Figure 5. Voltage and temperature profiles for (a) conventional polyolefin-based separator (REF) and (b) safety-reinforced separator (SRS). The inset represents a cell after crush test.

In contrast, quite a different safety behavior was observed in the new separator. Surprisingly, there was no voltage drop and temperature rise, even after the applied force reached to a maximum value of measurement. This suggests that the cells with the LGS are much more tolerant against the internal short caused by the separator break-down. Such a noticeable enhancement in the cell safety is attributed to the larger z-directional strength of safety-reinforced separator as discussed in Figure 4. Including the crush test, the more details on the other abused tests such as nail penetration, hot-box, overcharge, and so on will be discussed in the oral presentation.

Conclusions

The novel separator that can overcome the drawbacks of conventional polyolefin-based separators was presented. The LG Chem's advanced technology made it possible to develop the safety-enhancing separator particularly with the improved thermal shrinkage and penetration resistance. The cells employing this separator provided noticeable safety improvement in the various abuse tests..

References

[1] Tarascon, J. M., Armand, M. *Nature* **2001**, *414*, 359.
[2] Thomas, J. *Nature Materials* **2003**, *2*, 705.
[3] Arora, P., Zhang, Z. *Chemical Reviews* **2004**, *104*, 4419.
[4] Lee, Y. M., Kim, J. W., Choi, N. S., Lee, J. A., Seol, W. H., Park, J. K. *J. Power Sources* **2005**, *139*, 235.
[5] Venugopal, G., Moore, J., Howard, J., Pendalwar, S. *J. Power Sources* **1999**, *77*, 34.