The Role of Separators in Lithium-Ion Cell Safety

by Christopher J. Orendorff

As the use of lithium-ion cells for high power applications becomes increasingly widespread, safety and reliability of these cells and battery packs is of paramount importance. While most of the targets for lithium-ion in utility storage or transportation are focused on cost, cycle life, and performance, safety will be increasingly important as these batteries continue to grow in size to meet demand. One of the most critically important cell components to ensure cell safety is the separator, a thin porous membrane that physically separates the anode and cathode. The primary function of the separator is to prevent physical contact between the anode and cathode, while facilitating ion transport in the cell. The challenge with designing safe battery separators is the trade-off between mechanical robustness and porosity/transport properties. Separator design is further complicated by additional constraints including tolerance to abuse conditions, stable at >4V, chemically inert to other cell materials, and low cost to meet the performance and cost targets. This article highlights the challenges of developing safe separators for large format cells and batteries and advances in separator technology to meet these stringent requirements.

Separators for Consumer Markets

Most commercially available non-aqueous lithium-ion separators designed for small batteries (<3 Ah) are single layer or multilayer polymer sheets typically made of polyolefins. Most commonly, these are polyethylene (PE) or polypropylene (PP) which have transition temperatures of 135°C and 165°C, respectively, but are somewhat dependent on molecular weight. Polyethylene terephthalate (PET) and poly vinylidene fluoride (PVdF) have also been used in commercial separators, but are far less commonplace than the polyolefin films. These separators are highly porous, typically >40% porosity, approximately 25 μm thick, have low ionic resistivity (1.5-2.5 Ω-cm^2), and have bulk puncture strengths >300g/mil.[1-3] Ideally separators would be much thinner than 25 μm from a performance perspective and there are examples of separators that are as thin as 12-20 μm, however a great deal of mechanical strength is lost for the very thin membranes. Separators are typically manufactured by either an extrusion processes (wet or dry) followed by a mechanical stretching process to induce porosity or from wet-laid fibers to make non-woven mats.[1-3]

A decade ago, Porisini *et al.* reported the development of composite separators made

from γ-LiAlO$_2$, Al$_2$O$_3$, and MgO ceramics and PVdF.[4] Other ceramic composites soon followed including TiO$_2$-PVdF and CaCO$_3$-polytetrafluoroethylene (PTFE).[5,6] One of the first examples of a commercialized composite separator was Separion® introduced by Degussa, which is a trilayer membrane with two layers of ceramic (SiO$_2$/Al$_2$O$_3$) supported on either side of a porous polyethylene terephthalate (PET) film.[7,8] Because of these materials choices, the composite separator has a much higher melting temperature than the polyolefin membranes (>220 °C), which will ultimately impact abuse tolerance and cell safety. Examples of other composite separators have been reported in the literature made from combinations of alumina, zirconia, and silica along with numerous polymer components including polyethylene,

polypropylene, PET, and PVdF.[9-12] A table of common commercially available separators and their properties is shown in Table I.

Abuse Tolerance of Shutdown Separators

Many of the multilayer separators are designed with a shutdown feature, where two of the layers have different phase transition temperatures. As the temperature of a cell increases, the lower melting component melts and fills the pores of the other solid layer and stops ion transport and current flow in the cell.[2] The ideal function of this shutdown activation is shown in Fig. 1.[2] In Fig. 1, a lithium cobalt oxide (LiCoO$_2$)

Table I. Commercial separator properties.*				
	Entek	**Exxon**	**Degussa**	**Celgard**
Product	Teklon	Tonen	Separion	2325
Thickness (μm)	25	25	25	25
Single/multilayer	Single layer	Single layer	Trilayer	Trilayer
Composition	PE	PE	Ceramic-PET-Ceramic	PP-PE-PP
Process	Wet extruded	Wet extruded	Wet-laid mat	Dry extruded
Porosity (%)	38	36	>40	41
Melt temperature	135	135	220	134/166

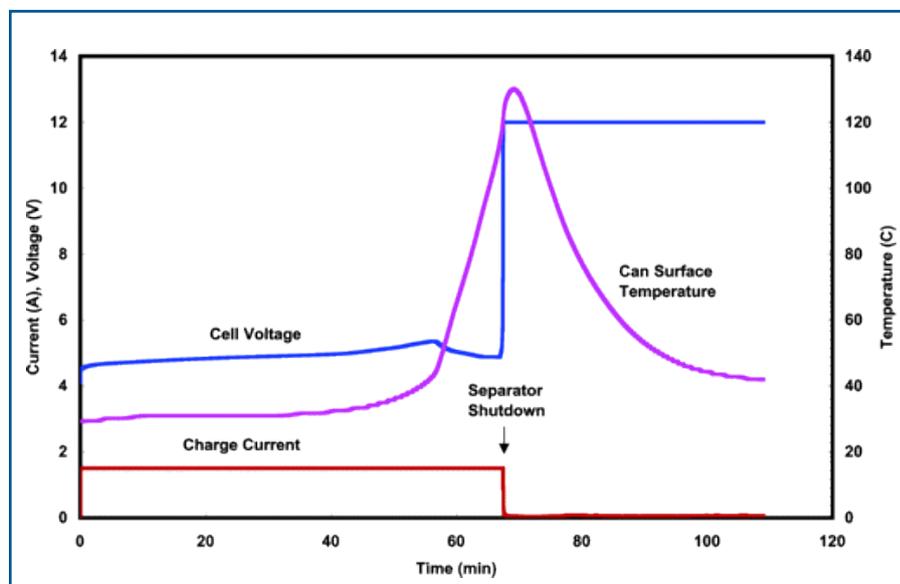*Separator specifications are found on data sheets for each product

FIG. 1. *Ideal separator shutdown function for a LiCoO$_2$ 18650 cell during a 1C rate overcharge test. (From Ref. 2) Copyright 2004 American Chemical Society. Reprinted with permission.*

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18650 cell is overcharged at a 1 C rate and the cell temperature reaches 135°C at 215%SOC. At this point, the separator shuts down as it is designed, the cell becomes resistive, and the voltage increases to the 12 V limit set for this test (typical DC voltage for a consumer product), and the cell begins to cool safely.

It is important to note that most shutdown separators were first designed for the consumer market, which are generally low voltage (<20 V), smaller battery systems (<10 A). If applied to higher voltage, larger battery systems, the abuse tolerance and shutdown function may or may not be as robust. All test results will be dependent on material choice, manufacturer, quality, design, etc. Figure 2 shows overcharge test results for cells with shutdown separators with different outcomes to those reported by Arora and Zhang (Fig. 1).[2] In Fig. 2a, a lithium nickel cobalt aluminum oxide (NCA) cell is overcharged at a 1C rate. The cell can temperature increases to 125°C at 170%SOC (approx. 135°C internal temperature) and the separator shuts down, but in this case the compliance voltage limit was set to 20 V. At this limit, the cell continues to draw current, which develops into an internal short circuit and thermal runaway. This is consistent with observations made by Roth *et al.* for shutdown separators under overcharge abuse testing.[13] Figure 2b shows a LiCoO$_2$ cell that is overcharged at a 2C rate. In this example, when the cell temperature reaches the separator shrinkage temperature (110°C), the cell shorts internally and goes into thermal runaway.

Overcharge abuse tolerance of shutdown separators is highly dependent on the test conditions, where modest changes in the voltage limits or charge rates can have a profound impact on the separator performance and the test results. It should also be noted that the failures in these two examples occur at temperatures well below the runaway temperatures for LiCoO$_2$ (180°C) and NCA (190°C), suggesting that separator failure may contribute to premature cell failure under certain abuse scenarios. These results are consistent with results described in the literature where shutdown separators can continue to pass up to 200 mA at 20 VDC and 350 mA at 30 VDC, which can quickly develop into an internal short circuit and cell runaway (Fig. 3).[13] While this might be a low probability event, the consequences could be quite severe. This type of abuse and cell failure are unique to larger, higher voltage batteries that may not have been anticipated or designed for in scaling up from low voltage consumer electronics scale batteries, highlighting the importance of selecting the correct cell components for the application.
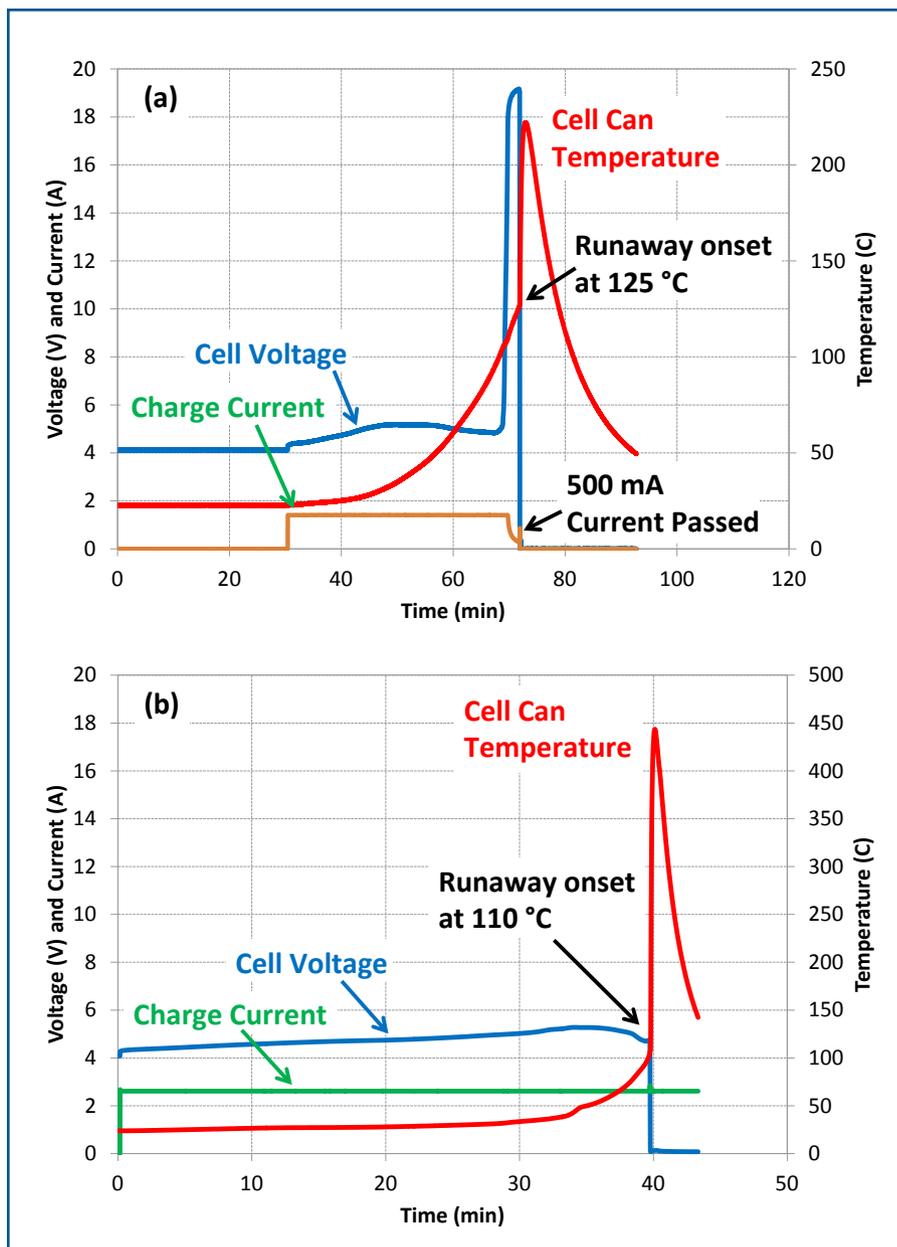

Fig. 2. *Overcharge abuse test of (a) NCA and (b) LiCoO$_2$ 18650 cells showing cell failure coinciding with the separator shutdown and shrinkage temperatures, respectively.*

Challenges for Separators in Large Scale Lithium Ion

In general, there is a migration toward the production of large format lithium-ion cells (>10 Ah) for transportation and utility storage. There are several reasons for this trend including reducing production cost, minimizing cell packaging material in a battery, and optimizing cell stack configuration in a battery. While these large capacity cells include both cylindrical and flat (stacked or wound prismatic) designs, much of the discussion in this article will focus on the flat cell geometry. It is important that the separator choice made for these large format cells be made to meet the requirements and potential abuse scenarios that exist for these large battery systems. For example, strategies and materials used for a separator in a 2 Ah 18650 cell in a 50 Wh laptop battery may or may not be appropriate or even relevant to 50 Ah z-fold stacked cell in a 15 kWh battery. In fact, small cell separator designs may even be detrimental to battery safety for large systems. Operating voltage, variability in thermal profiles, storage capacity, operating environments, and potential abuse scenarios are all very different in large scale lithium-ion batteries.

One important difference between small cylindrical cells and large format cells are the thermal profiles during normal use and abuse conditions. Electrochemical/thermal modeling research by Kim *et al.* and Gerver *et al.* have shown large format cells are heated heterogeneously across the area of the cell during normal use charging or from the development of an internal short circuit.[14-16] For a large format pouch
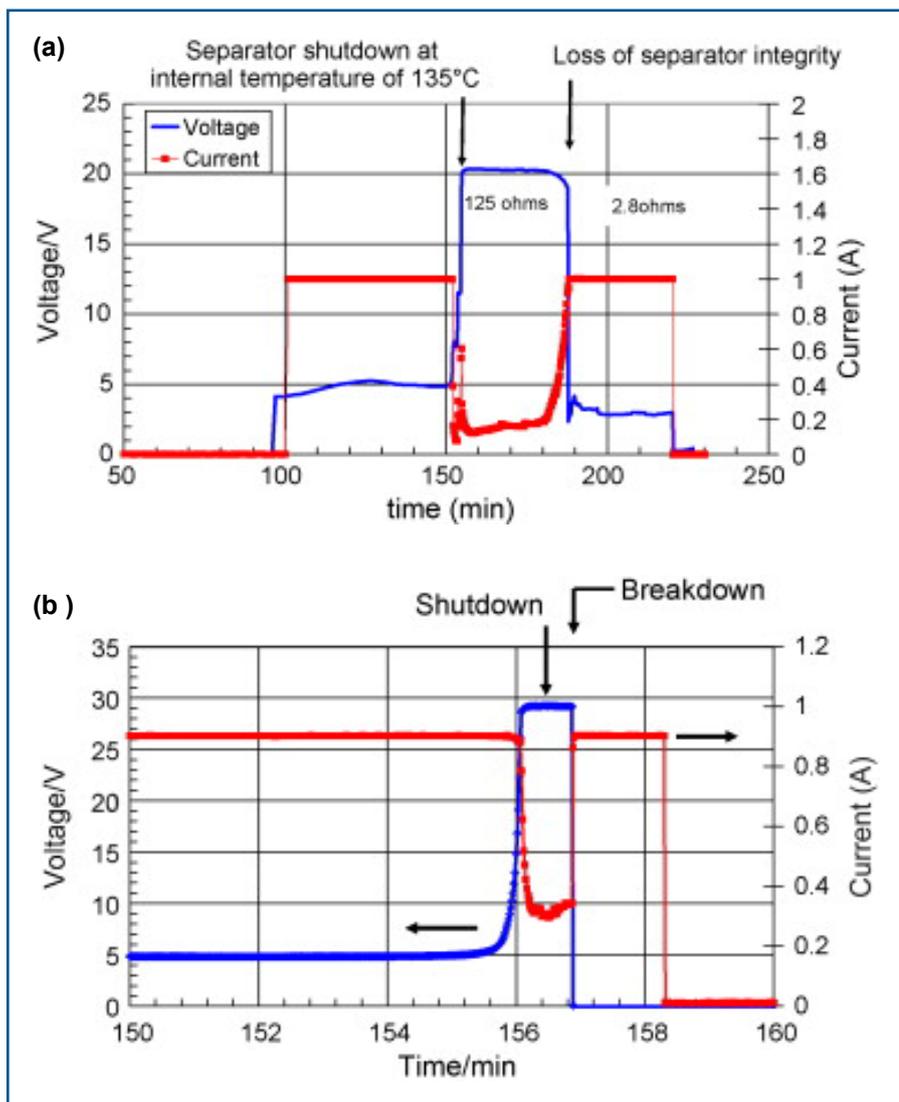
Fig. 3. *Leakage current through separators that are shutdown at 20 and 30 VDC stand-off. (From Ref. 13) Copyright 2007 Elsevier. Reprinted with permission.*

cell with tabs collocated on the same side of the cell, the temperature variance can be as great as 10°C during normal use.[14,15] Under abusive conditions or field failure, for example, the temperature variability across the cell is much greater. Kim *et al.*[16] have also modeled the effects of internal short circuits on the thermal profile in small (0.4 Ah) and large (20 Ah) format cells. Results show that the heating profiles for small cells (35 x 40 mm) are much more uniform after initiation of an internal short while the temperature distribution in a larger cell (140 x 200 mm) is much more heterogeneous across the area of the cell (Fig. 4). These examples of heterogeneous heating of large cells under normal use or field failure can lead to localized separator degradation, separator shrinkage (~110°C for polyolefins) or incomplete separator shutdown (~135°C for a polyethylene shutdown design). Separator shrinkage or degradation can lead to exposed electrodes and internal shorting of a cell. Incomplete separator shutdown refers to the condition where only a fraction of the separator pores are filled and the other

half remain open. This can inadvertently increase the current density in the remaining open pores in the cell (far fewer in number), resulting in additional localized heating, degradation, and potentially accelerate cell failure.[13]

In addition to considering the abuse tolerance of separators in single cells, it is also important to consider the cell-to-cell interactions within a large battery system, such as an EV battery. For the battery performance standpoint, if cells connected in parallel become out of balance, the higher voltage cell will charge the lower voltage cell to reach equilibrium. Similarly, changes in the state-of-health of a cell or failure of a cell can affect neighboring cells and the entire battery. Consider the scenario where all the cells in a battery pack have shutdown separators and that battery is heated. Not all of the separators will shutdown at exactly the same time, because of temperature heterogeneity within the battery. This sets up a situation where some of the cells shutdown and others are not. The shutdown cells instantly become the most resistive

elements in the circuit and the voltage of the remaining cells in the battery is dropped over that shutdown cell or cell group.

Safety Advances and Opportunities

R&D efforts are very active in the area of lithium-ion cell separators. Much of the work is aimed at improving performance characteristics including ionic conductivity, porosity, surface modification to improve wetability, and gel or solid state separators to reduce or eliminate liquid electrolyte.[17-19] There are several approaches to design and engineer safety into lithium-ion cell separators. One argument is that conventional lithium-ion cells are not useful (will suffer from significant energy fade, life, etc.) at temperatures >80°C and separators should shutdown at or below 80°C before the autocatalytic degradation of electrode materials begins.[20] While this would significantly reduce the probability of a high consequence failure event in a cell, it may not be as effective for batteries with large numbers of cells because of the leakage current that can be passed under modest standoff voltages (Fig. 3).[13] If this low temperature shutdown operates using a different mechanism that does not pass any appreciable current, it could be advantageous. The other approach is eliminating the shutdown feature of the separator and to improve the thermal stability. This approach closes the gap between the separator shrinkage/shutdown/degradation temperature (110/130/165°C for polyolefins) and the cell runaway temperatures (in general >200°C, depending on cell chemistry).[21] There are advantages and trade-offs to both strategies and these are the areas of active research in the battery safety community. For the purposes of this article, this discussion will focus on the non-shutdown, thermally stable separator design approach.

As mentioned above, one method of improving the thermal and mechanical stability of lithium-ion separators is to use ceramic composite-base materials. In general these composite separators are multilayer films where the ceramic layer is supported on one or both sides of a polymer membrane substrate.[7,8] Work by Choi *et al.* has shown layered Al_2O_3-PE composite separators to have better wetability and ionic conductivity than a commercial PE separator by a factor of 2.[22] In addition, the Al_2O_3-PET ceramic shows as little as 4% shrinkage compared to 14% shrinkage for PE separators measured at 105°C for 1 hr, which implies a more abuse tolerant material for the composite relative to PE.[22]

Entek Membranes have developed another composite separator strategy where the ceramic is embedded in an ultra-high molecular weight polyethylene (UHMWPE)
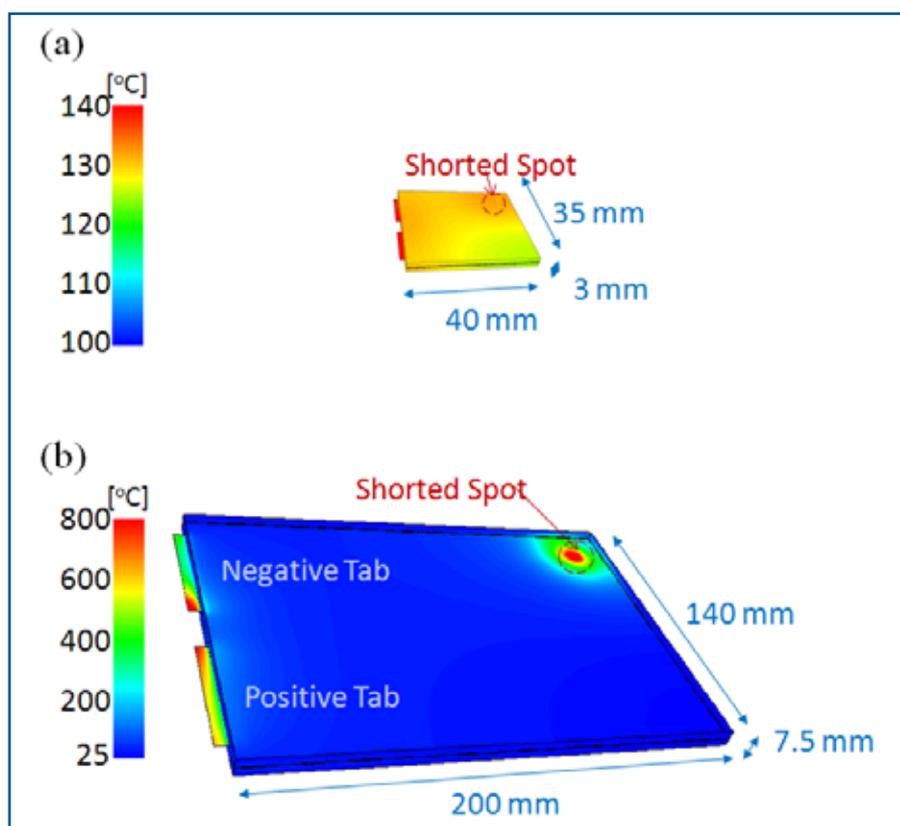
Fig. 4. *Electrochemical/thermal modeling of the initiation of an internal short, showing (a) homogeneous temperature distribution of a 0.4 Ah 35 x 40 mm cell, and (b) heterogeneous temperature distribution of a 20 Ah 140 x 200 mm cell after initiation of an internal short. (From Ref. 16) Copyright 2012 Elsevier. Reprinted with permission.*

impedance measurements of these separators show good thermal stability to >210°C, consistent with DSC measurements of the bulk materials (Fig. 5b),[24] work to improve processing techniques to decrease thickness, scale up, and demonstration of abuse response in lithium-ion cells, are all currently underway.

Conclusion

Although separators are electrochemically inactive components in a lithium-ion cell, they play very active role in determining cell safety. Separator designs for ensuring safety should be considered for a specific battery size, application, and potential abuse scenarios. Separators that are acceptable for 5 Wh mobile phone batteries may or may not be the correct choice to ensure safety in a 15 kWh PHEV battery or a 3 MWh utility storage battery. New designs, detailed modeling, and robust testing are all essential to ensure separators selected to meet both the performance and safety requirements for a given application. Ceramic/polymer composites and high melting point polymer materials offer some improvement in thermal stability and abuse tolerance for lithium-ion cell separators but, in general, there needs to be more evaluation work dedicated to quantifying the safety impact of new separators. With the challenges of separator safety performance comes R&D opportunities to advance and improve the technology to meet the needs as lithium-ion applications continue to expand.

Acknowledgment

About the Author

Christopher J. Orendorff is Principal Investigator of the Battery Safety R&D Program at Sandia National Laboratories. This program at Sandia is focused on developing inherently safe lithium-ion technologies for the transportation market through materials development, mechanistic understanding of battery abuse and failure, and full spectrum testing of cells and battery
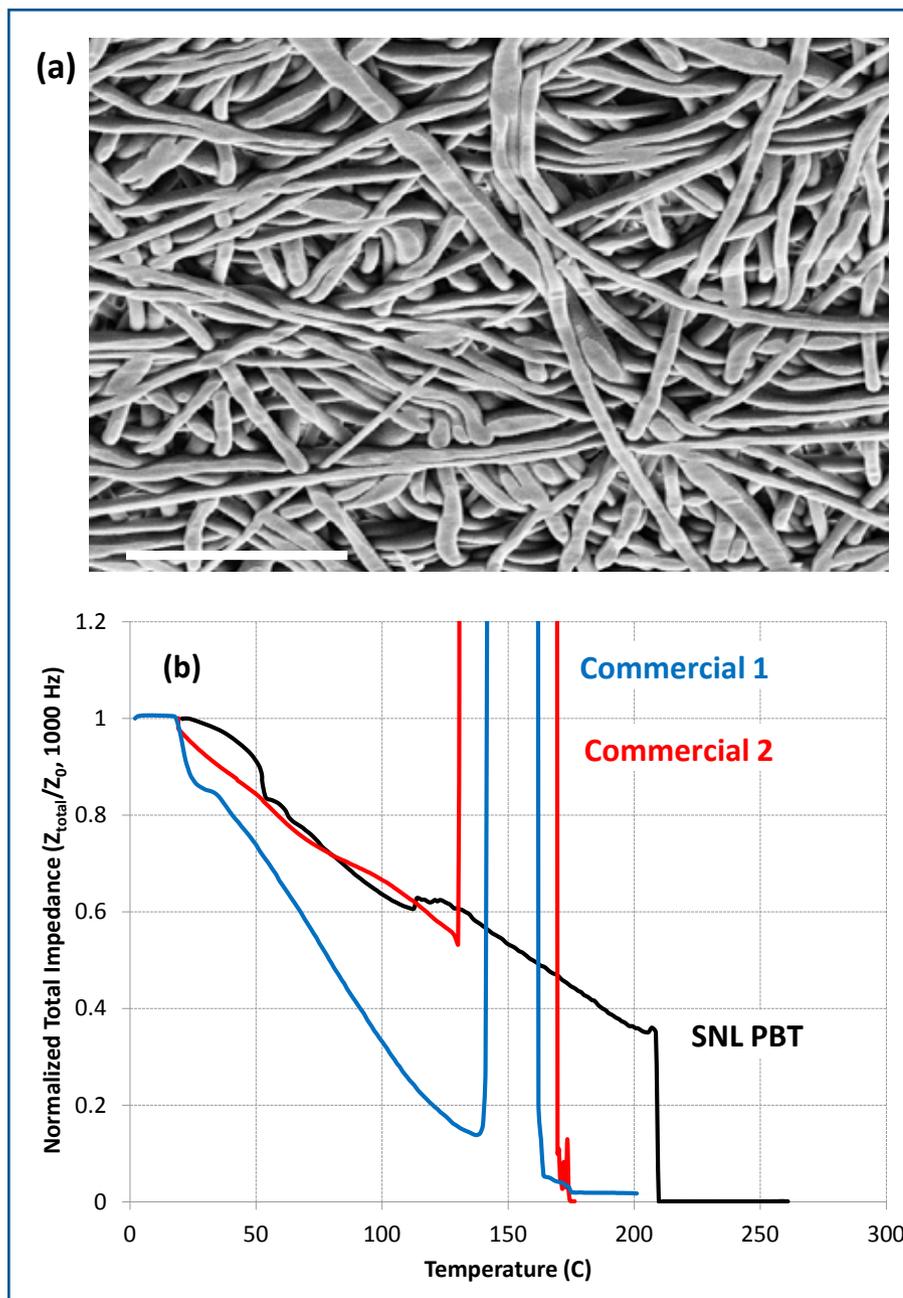
matrix.[23] These are generally high ceramic content membranes (>60%) and this approach may offer some advantages over the layered composites since they avoid delamination of dissimilar layers and may be less susceptible to mechanical cracking. More abuse and safety testing data on this class of separators is needed to determine their added value to improving cell and battery safety.

While actual safety or abuse studies on separators are limited in the literature, a report by Roth *et al.* highlights the safety advantages of using ceramic separators.[13] This work evaluates the abuse tolerance of commercial ceramic composite separator compared to polyolefins. Under thermal abuse, the polyolefin shutdown separator shuts down at 135°C due to the polyethylene melt and degrades and short circuits between the electrodes at 165°C, measured by the separator impedance at 1000 Hz. The impedance of the ceramic-PET separator remains stable to >220°C, at which point the PET begins to soften and the separator impedance increases. These two separators are also evaluated for overcharge abuse tolerance in 18650 cells with NCA/graphite (GDR) electrodes in 1.2 M LiPF$_6$ in EC:PC:DMC (1:1:3). At 1C constant current

overcharge, the cell with the polyolefin separator reaches 135°C at 170% SOC and immediately shorts circuits and goes into thermal runaway. By contrast, the cell with the composite separator reaches the cathode decomposition temperature (180°C) at 300% SOC and goes into thermal runaway. Results from this work suggests that ceramic composite separators offer some improvement in thermal stability along with improved overcharge abuse tolerance under higher voltage test conditions (>20 VDC).[13]

Work from our laboratory has focused on improving the thermal stability of all polymer separators and closing the gap between separator softening/degradation temperatures and cell runaway temperatures. The first separators developed with improved thermal stability are polyester fiber non-woven mats.[24] Fiber mats are prepared by electro-spinning polyesters from solution at ambient temperature and the resulting fibers are ~500-1000 nm in diameter (Fig. 5a). Mats are processed into separator membranes by hot pressing or rolling to give membranes that are ~50 μm thick. Although this preliminary work gives separators that are much thicker than conventional separators, they show excellent performance and electrochemical stability. Moreover,

Fig. 5. *(a) Scanning electron micrograph image of an electro-spun polyester separator (scale bar = 20 m) and (b) normalized AC impedance of these separator mats as a function of temperature compared to commercial polyolefin separators.*

systems. Before joining Sandia in 2006, Dr. Orendorff earned BS degrees in chemistry and biochemistry from Purdue University in 1999, his PhD in analytical chemistry from the University of Arizona in 2003, and was a post-doc at the University of South Carolina. He may be reached at corendo@sandia.gov.

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