Material Review of Li Ion Battery Separators

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Abstract. Separators for Li ion batteries have a strong impact on cell production, cell performance, life, as well as reliability and safety. The separator market volume is about 500 million m² mainly based on consumer applications. It is expected to grow strongly over the next decade for mobile and stationary applications using large cells. At present, the market is essentially served by polyolefine membranes. Such membranes have some technological limitations, such as wettability, porosity, penetration resistance, shrinkage and meltdown. The development of a cell failure due to internal short circuit is potentially closely related to separator material properties. Consequently, advanced separators became an intense area of worldwide research and development activity in academia and industry. New separator technologies are being developed especially to address safety and reliability related property improvements.

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SEPARATOR IMPACT ON LI ION CELLS

Separators are an important component within a Li ion battery cell. They need to mechanically separate anode and cathode within a cell while allowing maximum ionic conductivity of the Li ion containing electrolyte. Typically they account for 10 – 15 % of cell component costs strongly depending on the specific cell design. Separators impact cell production, cell performance, life and very importantly safety and reliability as indicated in Tab. 1.

The aim of this essay is to review and discuss the influence of the most prominent separator design parameters from a practical, industry production level point of view. Next, the currently dominating separator technology based on stretched membrane technologies is briefly presented. Comprehensive materials reviews on these materials where published in the past [1,2].

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The increasing need to boost battery safety and reliability without compromising on performance and cost brought separators back into the focus of increased worldwide research and development activities in academia and industry. It is beyond the scope and possibilities of this article to fully collect and discuss the wide range of new separator technologies. This review of advanced separator technologies will therefore emphasis novel materials that have recently been commercialized or are close to enter the battery market.

TABLE 1. Influence of selected separator properties on cell production, cell performance, reliability and life as well as safety.

	Cell production	**Cell performance**	**Reliability and Life**	**Safety**
Shrinkage	X		X	X
Modulus	X			
Drying temperature	X		X	
Wettability	X	X	X	
Thickness		X		
Weight		X		
Ionic resistance		X	X	
Porosity		X	X	
Penetration resistance			X	X
Meltdown				X

Cell Production: The separator elasticity during the winding of the cell can be described by the load that is needed to elongate the separator by a certain percentage (modulus). The load on the separator depends strongly on the speed and evenness of the tensile load profile at the beginning and during winding. It must be set low enough in order to prevent an increase in maximum pore size and/or increased sensitivity to shrinkage during the drying steps and possibly during abuse tests or internal short circuits during field service. Separators with a high modulus value are more robust to the cell production conditions. Cell production is significantly influenced by the separator shrinkage during the drying steps. Cell producing companies that work with dry room technology tend to dry the electrodes and – if needed – the separator at their respective maximum drying temperature. Then, cells are assembled in the dry room and at times conduct a final drying to assure that water uptake during dry room storage remains low and consistent. The temperature of the final drying step is governed by the weakest temperature resistant component in the cell which currently is the conventional separator. The invest and operation of dry rooms is high, so that a number of cell producers prefer air conditioned rooms as the assembly environment of the cell. In this case a final drying is mandatory. It is best in terms of production speed, cell performance and cycle life to choose the drying temperature as high as possible for the involved components. The speed and homogeneity of electrolyte impregnation is important for the production speed and cell cycle life (see below).

Cell Performance: Gravimetric and volumetric cell performance in terms of power and energy density obviously depend on the separators area weight and thickness. Thickness requirements can have a significant impact on volumetric energy density. High power cells may gain 2 % when the separator thickness is reduced from 30 µm to 20 µm, while high energy cells may gain up to 10 % under the same conditions. Especially the cell's power performance is also dependent on the ionic resistance for the movement of Li ions through the separator. As a first order approximation the resistance can be considered as an ohmic resistor under the condition of neglecting any separator surface or electrode surface effects. Thus, the true length of the ionic path and the cross sectional porosity through the separator's pore structure are most critical design parameters. Commonly the porosity value for separators is provided on a calculatory basis considering the density of the employed materials, area weight and thickness of the separator. This statement can be misleading if the porosity in *z*-direction of the separator is varying and/ or if the surface roughness of the separator is difficult to determine. The calculated porosity, however, must be considered when determining the maximum amount of electrolyte for the cell in order to reach maximum cell life and prevent drying out of the separator. Incomplete wetting out of the separator - particularly at low temperatures next to the anode- may cause Li dendrite formation with its negative consequences for capacity and safety issues. This can happen during cell production or during cell life affecting cell reliability.

Cell Reliability and Life: Cell reliability is characterized by the absence of a cause for individual cell failures which could lead to a sudden loss of capacity or the increase of cell resistance. With respect to the separator such failures can be triggered by uneven heat impact and drying during manufacturing or in the field, uneven chemical or electrochemical environments at the electrodes, mechanical pressure on the separator or combinations thereof. Uneven heat impact may negatively affect the separator pore structure and thus alter wettability and porosity, cause localized shrinkage and eventually ionic resistance. Cell reliability is highly sensitive to the homogeneity of the separator as strong local deviations of porosity, holes, closed areas, thickness variations, folds, tears, wettability, lack of adhesion to electrodes, and chemical inhomogeneities may promote conditions for dendrite formation, penetration or shrinkage. Individual, localized defects are easily found by microscopic analysis- even on materials of commercial status. Variations may also include *e.g.* thickness and porosity as well as the challenges of lot to lot variations, which can lead to cell inhomogeneities and premature cell performance fading. Cell life is considering the overall ageing process of the cell components and has similar dependences as cell reliability. It depends strongly on the evolving Joule heating through the resistance of the separator and its permanent wettability. Permanent wettability and continuously high porosity requires that the separator's pores are not filled by electrolyte decomposition products over time [3]. Even more so it requires that the separator's pore structure has a high penetration resistance and thus, is not collapsing under the cell's mechanical pressure leading to irreversible electrolyte squeeze out.

Cell Safety: Finally, cell safety is a sine qua non condition for increasingly larger Li ion batteries to realize the widespread utilization which they deserve based on their performance potential. Neglect or compromising on safety performance have the clear potential to severely damage this technology's growth potential. Prominent safety incidents are well documented and the recent fire problems in civilian aviation only underline the paramount importance to assure cell safety under normal and expectable abuse conditions. Many safety features have been invented, such as positive temperature coefficient devices (PTC), current interrupt device (CID), nail penetration device, overvoltage and overtemperature sensitive electrolyte additives, just to name a few. Maybe the most challenging task in battery safety is to reduce the probability for the formation of internal short circuits and – if they cannot be avoided – to handle such incidents gracefully. This means that the separator has to have a high strength to withstand the pressure which arises from the electrodes and potential electron conductive particles which may be present on the electrode surface. In case that such particles are penetrating the separator and lead to a current flow, the surrounding of the particles will begin to heat up due to Joule heating. At this stage of the cell failure the separator may not shrink in order to avoid exposure of both electrodes to each other. Last and not least the separator must still be fully functional even if larger currents are flowing and the temperature is rising to a few hundred degrees centigrade, *i.e.* the separator may not melt down [4].

MEMBRANE SEPARATORS

Almost all of today's separator market is served by polyolefine (PO) membranes. These are produced in two fundamentally different methods. About half of the global market relies on the so-called "wet process". Here, polyethylene (PE) polymer granulates and wax are melted, mixed and extruded. After a typcially bi-axial stretching step, the wax is being washed out leaving a skeleton structure behind. Finally the separator is slit to the desired roll width and length. The process is described in more detail elsewhere [1]. Figure 1(a) shows an overview scanning electron microscope (SEM) image of a commercial membrane for Li ion batteries. Figure 1(b) shows more detailed magnifications of the skeleton structure. In terms of physical parameters such membranes are available and used for large cells with thicknesses from about 15 to 32 µm with a weight of 10 – 20 g/m². Porosities are typcially between 38 – 45 %. A study of ageing batteries using high voltage cathodes revealed that the oxidation stability of PE wet membranes are limited and may shorten cell life [5].

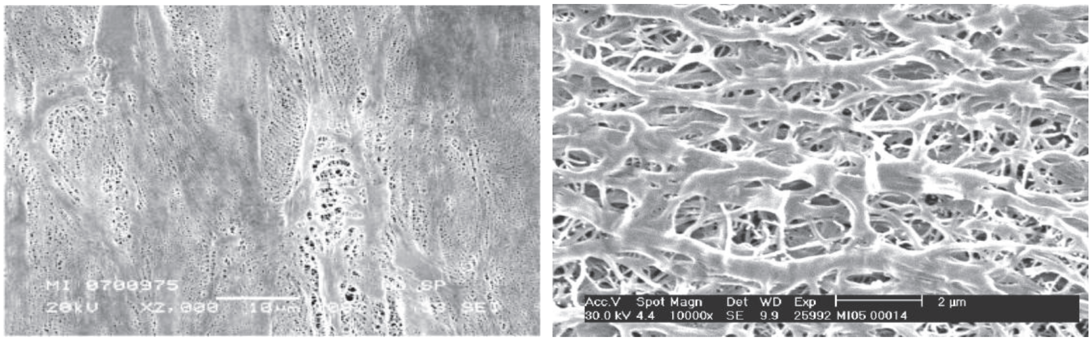

FIGURE 1. "Wet" membrane (a) left: overview SEM (b) right: detail SEM.

The second common production technology for separators is the so-called “dry process”. The process is described in the literature [1]. Here, PE or/and polypropylene (PP) are being used. The polymer granulates are melted and extruded. The granulate composition is of different crystallinity, which allows a controlled generation of porosity and slit like pores during stretching and annealing of the extruded film. Figure 2(a) displays an overview SEM image from a commercial “dry” PP membrane. As for “wet” membranes shown above areas of inhomogeneity on a level of several tens of µm become visible. Figure 2(b) has been made with higher resolution showing the slit pore structure of a dry membrane. PE and PP membranes made from wet or dry process are difficult to wet out during manufacturing or permanently with the polar electrolyte. Therefore it is not uncommon that the membranes undergo an extra finishing step of applying wetting agents or a plasma/corona treatment to generate sufficient wettability.

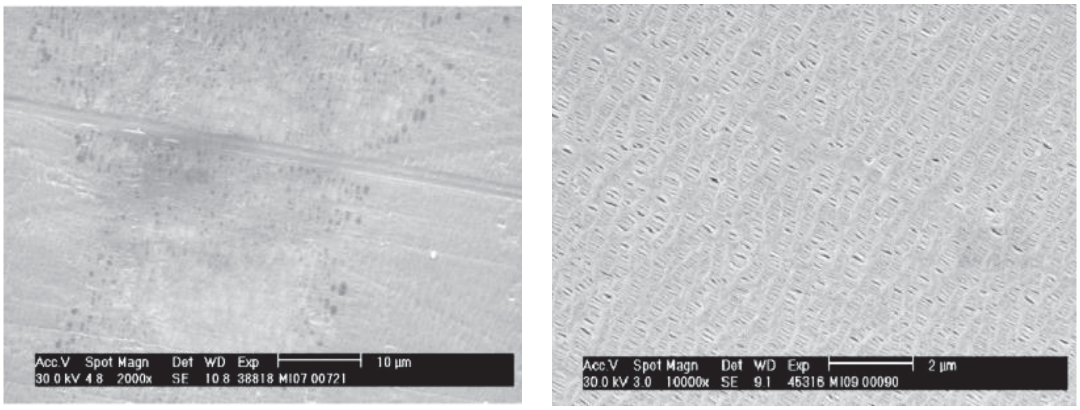

FIGURE 2. “Dry” membrane (a) left: overview SEM (b) right: detail SEM.

Both technologies provide established standard materials for the Li ion battery industry and as such are successful. In the meantime, however, emerging applications for stationary energy storage systems and the trend to increase the electrification of the automotive drive train up to a pure electric vehicles lead to a detailed review of the current state of the art separator performance. Eventually worldwide research and development activities with the aim to invent and commercialize better performing and / or lower cost lithium ion battery separators have started.

The commonly used electrolyte salt LiPF6 tends to dissociate into LiF and PF_5. PF_5 is reacting with residual moisture in the cell leading to the formation of HF and OPF_3. Especially HF is causing detrimental reactions mainly to the electrode materials which leads to a loss of power and capacity [6,7,8]. Therefore, the residual remaining moisture in the complete battery must be reduced to a low ppm level in a way that fits to the available process route. As explained above the drying condition is limited by the material of the lowest temperature tolerance. Currently these are the membrane separators with drying temperature limits around 70 – 90 °C. The maximum drying temperature of separators may be defined as the temperature where the air flow of the microporous structure is unchanged. Air flow can be determined by the Gurley method which measures the time for a given volume of air to pass through the separator. The high shrinkage of membrane separators thus limits the possibility of drying the electrodes as needed for optimum life performance. Drying temperatures up to 150°C may be desirable depending on the choice of the electrode binder system and may lead to longer cell life and/or lower production cost by reducing drying times. In today's cell manufacturing the impregnation process of membrane containing cells is a slow and therefore expensive step, which may take hours or days. The task is to evenly distribute the electrolyte throughout all of the cell's electrodes, which becomes particularly challenging for high energy carrying large format cells. If wetting out of the cell components during manufacturing or during field life is incomplete, then the likelihood for reduced cycle life and early cell failure is increased. The electrolyte mainly has to be carried through the electrodes in this process, since membranes are difficult to wet out. Thus, an improvement of lateral electrolyte wetting can help to speed up the impregnation process and therefore reduce manufacturing costs.

Recent literature is investigating the long term mechanical stability of membranes in Li ion batteries [9,10] under normal operating and storage conditions, such as external pressure on the cell stack combined with internal pressure generated through the expansion of the electrodes depending on their state of charge. If, for instance, the anode has an initial coating thickness of about 100 µm and is increasing its thickness by about 10 % upon charging then the mechanically weakest element in cell will have to compensate this expansion. Depending on the separator and cathode material and assuming fixed outer dimensions of the cell housing a separator thickness reduction of 25 – 50 % can be expected. Under this pressure the investigated PP/PE/PP membranes undergo permanent mechanical deformation and collapse of porosity which leads to reduced or non- ion conducting areas of the separator. Thus, depending on state of charge, temperature, time and pressure the membranes undergo mechanical creep which leads to strong impedance increase and eventually shortened cycle life and early field failure.

The limited mechanical stability of the membrane separator also gives rise to some field failures. The image in Fig. 3(a) is taken from a membrane separator of a commercial 1.2 Ah pouch cell (flat jelly roll design). The cell could not be charged anymore after about 100 charge/discharge (1C/1C) cycles. The picture identifies a hole in this "dry" membrane. The countering anode side of the separator had a dark, presumably conductive electrode particle, laying on top of the regular coating. A similar hole in a "wet" separator piece is shown in Fig 3(b), which was also taken from a cell that was produced under commercial conditions and suddenly failed the cycling test. In both cases we can assume that conductive debris on the surface of the electrodes was pushed through the separator over time resulting in an internal short circuit. The Joule heat of the internal short circuit leads to the shrinkage of these stretched membranes. Eventually the temperatures are high enough to cause the membranes to flow under pressure or to melt. Precursors of such internal short circuits are extremely difficult to identify and avoid during production. Despite strongest efforts to produce in clean room environments and actively avoiding or removing particles with all technically possible scrutiny there will always remain a significant likelihood for µm-sized, internal short circuit precursor to get wound into the cells. The review of field failures revealed that this internal short circuit must be considered to be the main reason for battery failure in the field, in part with catastrophic cell and cell pack failure [11].

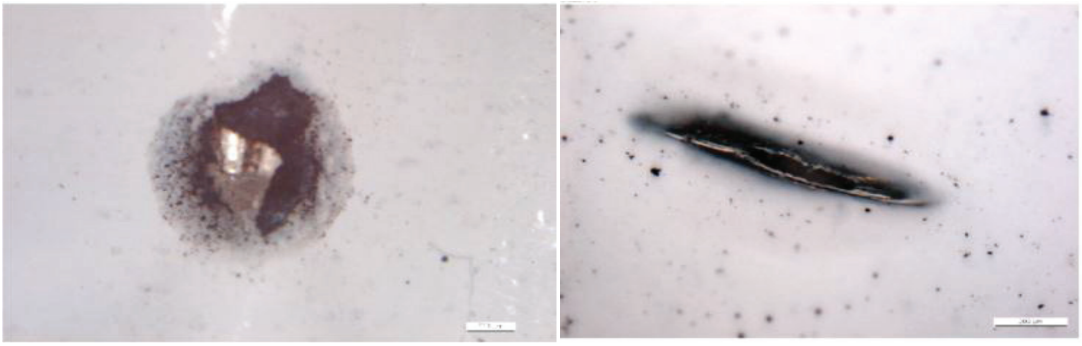

FIGURE 3. (a) left: penetrated “dry” membrane during cycling (b) right: penetrated “wet” membrane during cycling.

A well known feature of PO separators is the so-called shutdown function. The basic idea is that as the temperature increases components of the separator begin to melt and thus lock up the pores and stop ionic flow, while the mechanical separation function remains intact through higher melting point components. In case of “dry” membranes this structure is accomplished with a trilayer construction of PP membrane material sandwiching an intermittent layer of PE membrane. In case of “wet” membranes this property is engineered into the material through the selection of the employed PE grades. Once dendrite formation happens at the anode, the current density near the tip of the growing dendrite is increasing. It is conceivable that the local heat may lead to a collapse of the PE structure and thus stop ionic flow locally and permanently. It is obvious that the described shut down feature has little relevance in case of mechanical penetration of the separator through conductive debris. Roth *et al.* [12] investigated the performance of shut down separators under overcharge conditions in 18650 cells. Despite the shutdown feature of the employed Li cells it was found that cells went into thermal runaway. The finding was explained by the inhomogeneity of the temperature distribution causing an incomplete shutdown of the separator. However, since the non-affected separator has to carry all of the ionic current the heat evolution may happen even faster, leading to shrinkage, localized rupture and eventually melt down of the separator. Such findings suggest that the conventional shut down feature is of limited use with increased temperature variations under abuse conditions. Therefore the shutdown mechanism may not improve safety overall especially for large cell designs. Prevention of separator penetration, shrinkage and meltdown appear to be governing design criteria for new advanced separator technologies.

In summary of the previous sections, important variables of separator properties were discussed and their impact on cell production, performance, reliability and life as well as safety has been described. Membrane separator technology is dominating the Li ion battery market today. However, some important performance limitations are identified which are inherent to this technology and arise from the PO material selection and the stretching process to create the desired porosity. Significant improvements regarding drying temperature, wettability, permanent porosity, mechanical penetration resistance, shrinkage and melt down are in due need. In light of the emerging new applications in stationary energy storage and electric drive train support in automotive environment the requirements for Li ion cells will change considerably compared to the more consumer oriented applications today. Such Li ion battery systems will consist of many more cells where each cell becomes significantly larger. Thus, the increased concentration of energy in a confined space may not be compromised by a lack of safety measures against failures under normal operating or foreseeable potential abuse scenarios. Furthermore, also the high initial investment cost requires a strong performance boost towards more reliable, longer lasting and safer batteries. The separator is a key component on the path to reach these goals. The need to improve overall separator performance has triggered exciting worldwide research and development activities that has lead academia and industry to a technical and commercial competition of new technologies.

ADVANCED SEPARATORS

Advanced separators are in development and production worldwide. Traditional separator producers, newcomer activities from established chemical companies, separator start up companies and cell makers with in-house production of value added separators and research institutions are involved. The following companies in alphabetical order are known to the author to conduct development or already commercial activities in the field of advanced separators: Asahi Chemical, ATL, Dreamweaver, DuPont, Evonik Litarion, Entek, Freudenberg, Goretex, Hirose, Japan Vilene Company, Kuraray, Leclanché, LG Chemical, Mitsubishi Chemical, Nippon Kodoshi, Panasonic, Polypore, Porous Power, Samsung DI, Senior, SK Energy, Sony, Sumitomo Chemical, Targray, Teijin Aramide, Toray Tonen, Treofan, W-Scope, Ube Chemical. This list may not necessarily be complete and may underrepresent cell makers in-house solutions. Table 2 is classifying the development activities by technology and provides an indication of their approximate status in 2013.

TABLE 2. Advanced separator technologies.

Technology	Anode	Stage
Ceramic blended “wet” PE membrane	Graphite	Advanced development.
Ceramic/PVDF casted or sprayed layer	Graphite	Commercial. Lamination or electrode coating with tight process interdependence on electrodes and cell making process.
Ceramic filled nonwovens	Graphite	Established in EV. Beginning widespread commercialization.
Ceramic/Polymer coated PO membranes	Graphite	Established in HEV and selected consumer applications. Beginning widespread commercialization.
Nanofiber separators	Graphite	Beginning commercialization
Cellulose/ polymer paper	Lithium Titanate	Commercial.
PET Nonwoven	Lithium Titanate	Advanced development

Ceramic blended PE membranes based on “wet” membrane technology are being reported in the literature with claimed improvements in power performance, safety and life [13,14]. Casted films or sprayed layers are in a commercial stage especially for laminatable separators. These materials are used in tight process interdependence with the cell’s electrodes and cell making processes. An independent performance evaluation outside of the final cell is not possible. Nonwoven separators, *e.g.* from Freudenberg, and cellulose or polymer papers are becoming available for lithium titanate (LTO) systems and are in close link to separators for capacitor applications. Ceramic filled nonwovens, ceramic/polymer coated membranes and nanofiber separators can generally be applied for Li ion cells and are becoming recently available on the market. In the remaining sections of this essay the focus is on a discussion of these three technologies, their production steps and their comparative evaluation particular in the light of the needed performance improvements of conventional membrane separators identified above.

Ceramic filled nonwovens: Ceramic filled nonwovens are made in a two-step process. First, the nonwoven is produced from a careful selection of microfibers in a wet laid process and fixed through a hot treatment process near the melting point of the employed polymers. For instance, Freudenberg favors a Polyester (PET) based nonwoven, which is produced at temperatures well above 200 °C without a stretching step to increase porosity. The major challenge is to maintain high possible production speeds without compromising the high demands on low weight, thickness, modulus, homogeneity and defect freeness. Second, a paste of inorganic particles is applied onto and into the nonwoven and subsequently the solvents are dried off leaving a solid structure with defined porosity behind. An important design requirement is that the adhesion of the particles to the substrate is sufficient to allow for the separator to be used independent of cell design requirements, as in cylindrical, jelly flat, z-fold or separator stack design. Freudenberg’s technology accomplishes this task by use of organic, highly flexible binder systems. An overview surface SEM image of Freudenberg ceramic filled polyester nonwoven separator is shown in Fig. 4(a). The fibers are completely and evenly covered. The microporous ceramic structure is shown in Fig. 4(b). Typical pore sizes are in the range of 100 – 300 nm, which is well comparable to the measured pore sizes of membrane separators. Figure 4(c) displays a cross sectional view showing the cut through the nonwoven fibers and the filling with ceramic particles in between and on the separator surfaces. Desirably high levels of ceramic coatings up to 30 g/m² Alumina are within the scope of such technologies. Obviously, this separator design does not have a layered structure to itself, so that in direction through the separator the porosity remains essentially constant. A horizontal layer of collapsed pores as described in the discussion of membranes is by the nature of this separator design not possible.

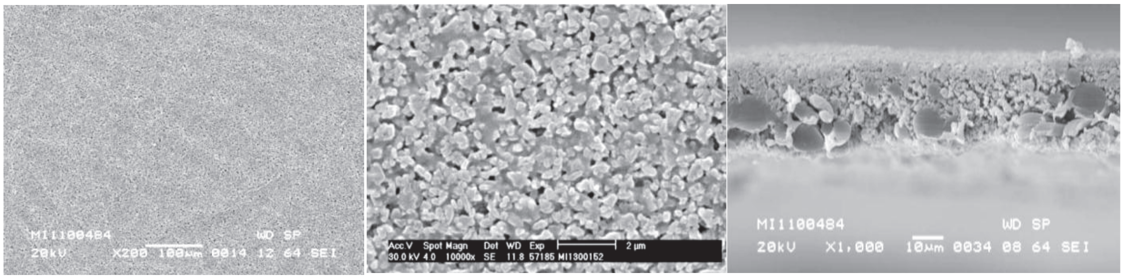

FIGURE 4. Freudenberg Separator (a) left: overview (b) middle: detail image (c) right: cross section.

Coated PO membranes: Coated membranes are produced in a two step process. The basic processes for "dry" and "wet" membranes are discussed above. In the coating process the membrane is lined with an inorganic layer either single or double sided. Coating weight based on Alumina is up to 10 g/m². Figure 5(a) is an overview surface SEM image of a coated membrane, followed by Fig. 5(b) which shows a cross sectional view and an indication of the coating variations present in the commercial product analyzed. Clearly a critical aspect of delivering a reliable product is the generally poor adhesion of the inorganic layer with the nonpolar nature of the membranes (Fig. 5(c)). Mechanical interlocking may aid to overcome some of the difficulties but the trade off is the limited porosity near the membrane/coating interface. Nevertheless, in the group of advanced separators this design has clearly reached significant commercial status by now due to the high availability of PO membranes and the straightforward approach of a thin ceramic coating.

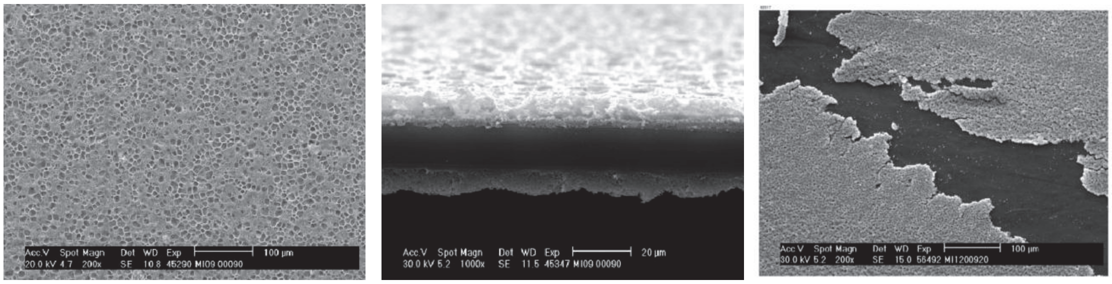

FIGURE 5. Coated Membrane (a) left: overview (b) middle: cross section (c) right: overview image of damaged area.

Nanofiber separators: Technically, nanofibers are having diameters of 100 nm and less but in the textile industry this term is more freely used and includes fibers up to 1000 nm. Nanofibers are produced by meltblown technology or more commonly electrospinning technologies. Pure electrospun separators were investigated in detail and showed very good potential for specialized high power requirements [15]. Nowadays, nanofiber separators oftentimes include micro- or fine fibers for mechanical stability next to nanofibers. They can either be included in wet laid nonwoven forming processes or applied as a fine layer on top of a nonwoven in a second step. Figure 6(a) shows a cross sectional view of a nanofiber layer (lower section of the picture) which has been applied onto a previously produced fine fiber nonwoven (upper section of the picture). The nanofibers have the function to mechanically separate the electrodes by reducing the maximum pore size and still maintain a high overall porosity.

Figure 6(b) shows the top view of the nanofiber side of this separator. Figure 6(c) is the top view of a nanofiber separator which has the fibers being intermixed with fine and microfibers. Surface densification from a calibration process are clearly visible also in this image of a commercial product. The chemical composition of the nanofibers is flexible. Polyimide, polyacrylnitrile, polyvinylalcohol, polyvinylidendifluoride and polyester [16] are being developed or produced.

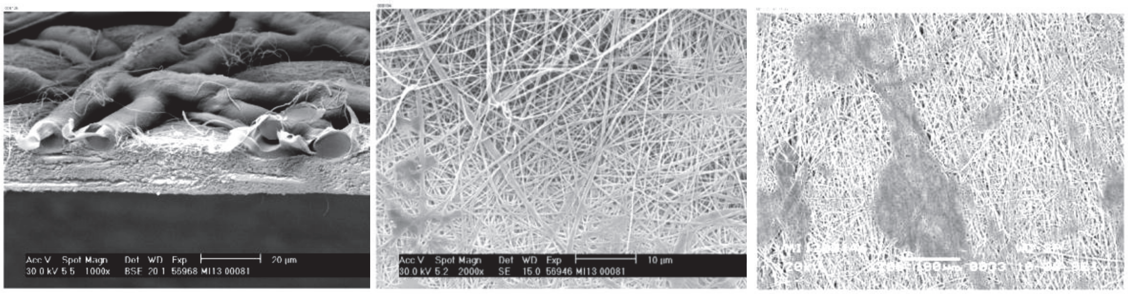

FIGURE 6. Nanofiber separator: (a) left: cross section of wet laid nonwoven with nanofiber layer below (b) middle: view of nanofiber layer (c) right: top view of micro and nanofiber based separator.

As worked out in the previous sections the main goals for advanced separators are to improve their performance in terms of drying temperature, wettability, permanent porosity, mechanical penetration resistance, shrinkage and melt down without compromising other performance characteristics such as modulus, thickness, weight, resistance, homogeneity.

Table 3 compares material characteristics of advanced separator versus conventional membrane technologies. At this stage of development advanced separators have not yet reached the minimum thickness values as they are known from membranes and are heavier in weight. This results in reduced volumetric and gravimetric energy and power densities. However, separator thickness requirements below 20 µm are rare in high end, large cell applications of emerging markets at least for cell reliability reasons. The module values for membranes and coated membranes are the highest compared to their fiber based alternatives. Difficulties in high speed winding processes may be possible, but standard winding machines for jelly flat, z-fold and wide cylindrical cells proof to be able to work with a minimum level of expertise in machine adjustments. Ionic resistance values are the benchmark set by membranes and are within reach of advanced separator technologies. The maximum drying temperature can be significantly increased by some of the advanced separators. However, with the introduction of ceramic particles and non polar polymer surfaces the separators may become a source of humidity as well. Thus, the total humidity resulting from all cell materials must be lowered in order for the higher drying temperature to be an advantage. In terms of porosity fiber based advanced separators have clear benefits for allowing more electrolyte to be stored between the electrodes and are expected to be less prone to the cold creep phenomena of (coated) membranes as identified above. As documented in the material descriptions, separator homogeneity does not seem to be fully resolved as it is easily possible to identify material defects in new and aged material by microscopic methods. Such defects or variations are and will remain difficult to detect on a continuous basis of each square meter of separator since a full analysis will be extremely costly to implement through the analysis equipment and potential negative effects on production speed.

TABLE 3. Properties of conventional and advanced separators (Status 2013).

	PO Membranes	**Ceramic filled Nonwovens**	**Freudenberg Ceramic filled PET Nonwoven**	**Ceramic coated Membranes**	**Nanofiber Separators**
Thickness [µm]	15 - 35	25 - 35	23 - 35	23 - 28	25 - 35
Weight [g/m^2]	10 - 20	20 - 40	22 - 35	20 - 25	15 - 25
Theo. Porosity [%]	38 - 45	45 - 55	50 - 60	50 - 55	45 - 55
Modulus at 2 % Elongation [N/cm] [1]	3 - 8	3 - 6	4 - 5	3 - 6	2 - 4
Wetability [cm^2][2]	1 - 2	10 - 15	10 - 15	10 - 15[3] (1 - 2)	10 - 25
Ionic resistance [mOhm*cm^2/µm][4]	125 - 150	125 - 250	125 - 215	115 - 140	100 - 215
Maximum Drying Temperature [°C][5]	70 - 90	100 - 170+	120 - 170+	80 - 110	100 - 170+
Mixed Penetration Force [N]	250 - 500	500 - 700	650 - 800	300 - 500	200 - 400
Mixed Penetration Force [N/µm]	15 - 20	18 - 23	25 - 30	18 - 23	9 -14
Free Shrinkage after 160°C/ 1 hrs [%]	destroyed	PET – NW[7]: <1% PO - NW: ~15%	<1%	PP memb.: 5 – 40 % PE memb.: destroyed	PO - fibers: 15% Imide/Aramide: <1%
Free Shrinkage after 200°C/ 1 hrs [%]	destroyed	PET - NW: <1% PO - NW: destroyed	<1%	PP memb.: destroyed PE memb.: destroyed	PO - fibers: destroyed Imide/Aramide: <1%
Melt down[6]	destroyed	intact	intact	destroyed	PO - fibers: destroyed Imide/Aramide: intact

[1] Measured at 25 °C with unwetted separators.

[2] Wetted area 1 hrs after placing 50 µl of 1 M LiPF6/DEC:EC 1:1 onto an unsupported, horizontally positioned separator at 25 °C.

[3] Visual inspection of separator surface. No statement possible regarding wetting out of membrane itself. In Brackets the wettability of the membrane after coating removal is provided.

[4] High frequency electrolyte resistance of 1 M LiPF6/EC:EMC 1:1 electrolyte soaked into separator measured at 25 °C.

[5] Determined by constant Gurley value before and after drying or by cell producer and separator suppliers recommendations.

[6] 415 °C soldering tip placed on separator for 10 s.

[7] Nonwoven = NW

The key properties to add safety against internal short circuits in their order of need to prevent thermal runaway are penetration resistance, shrinkage and eventually melt down. They will be discussed now in detail due to their extreme importance to reach improvements in safer and more reliable batteries.

Penetration resistance: Mechanically robust and tough separators are needed to be resistant against conductive debris that collected on the electrode surfaces and that apply pressure points against the separator due to external forces or the electrode expansions during charging and discharging. At times the room temperature characterization of maximum tensile strength at its breaking load and the penetration resistance of an unsupported, free standing separator is used in membrane separator specifications in order to represent quantitative values for mechanical robustness. However, it has been recognized [1,17] that such tests are not simulating the real situation in a battery abuse situation and therefore it is proposed to introduce the "mixed penetration resistance" as a better predictor of separator safety in batteries. In the mixed penetration test a separator is pressed in between a steel ball and a steel plate with increasing pressure until a short circuit occurs. Pinch tests on flat jelly battery levels are reported to have lead to reproducible and relevant test results [18].

The authors have further refined the mixed penetration test by sandwiching the separator between a commercially produced NMC cathode and Graphite anode. The aim for this alteration was to provide a more real life but still reproducible testing environment to the separator. The sandwich structure was placed on the 63 Rockwell hardness polished steel block and a 65 Rockwell hardness steel ball (6 mm diameter) which was pressed from top onto the dry sandwich structure. The set up was located in an air conditioned room at room temperature. The force was measured continuously until a short circuit occurred between the two dry electrodes through the separator. This force was determined by an ohm- meter. The results of the separators and their normalized value based the µm thickness of the separator are shown in Table 3. Clear improvements in mixed penetration resistance are seen by advanced separators except for nanofiber based separators. The best performance in this test has been reached with PET Nonwovens and inorganic/organic composite filling as realized in the Freudenberg design.

Free Shrinkage: The mechanical penetration of a particle through the separator and the initial stages of battery abuse tests mostly lead to localized heat evolution inside the cell. A critical stage on the pathway to thermal runaway is reached when the charged electrodes are not kept apart anymore by the separator. Then, Joule heating from internal short circuit in addition to the exothermic, electrochemical reactions can happen. Thus, the robustness of a cell against heat depends greatly on a minimized thermal shrinkage resistance of the separator. Simulations of 18650 cells show that the thermal energy of an internal short is sufficient to increase the local temperatures by 200 °C in less than a second [4]. Therefore free shrinkage tests of 15 cm (machine direction) by 5 cm (cross direction) were conducted with conventional and advanced separators. The obtained data are included in Tab. 3. The results show that strong performance improvements have been realized through advanced separators. Inorganic reinforcements help to extend the stability range of PO containing materials. Best performance is being reached through the use of polyester or speciality polymers.

Melt Down: In the event that the separator has been penetrated and heat is evolving the final barrier that the separator may provide is to remain in place even though the temperatures are going beyond the aforementioned 200 °C. Several hundred degrees Celsius can be reached [4]. In order to mimic the thermal stability of the separator under extreme conditions a soldering iron was mounted in a mechanical holder such that the soldering iron can be moved towards a piece of separator. The soldering iron tip temperature was monitored with a thermoelement. During the tests the tip was at a temperature of 410 – 420 °C. The soldering iron was lowered and kept on the separator for 10 sec and then moved back. The choice of substrates was copper foil and glass. Both substrates gave the same results which are presented in Tab. 3. Membrane, coated membrane separators and nanofiber separators containing PO were destroyed by these tests. The combination of slight mechanical pressure and high temperatures leads to a melting of the polymer and a flowing away under the given pressure. The other advanced separators yielded an intact separation of the electrodes. The separators remained in place. It is noteworthy that this has been true for polyolefin and polyester nonwovens alike even though their respective melting points are far below the 420 °C test temperature. This finding can be explained by two to four times higher amounts of ceramic volume within such separators compared to coated membranes. Speciality polymer nanofiber separators also showed good results in this test, as the test temperature has not reached the charring temperature of these materials.

The discussion of the results for the mixed penetration resistance, shrinkage and meltdown tests provide an overview of the technology performance of conventional versus advanced separators. Their results depend on the underlaying process technology, the chemical nature of the employed polymeric materials and the amount of inorganic loading.

SUMMARY AND CONCLUSIONS

In the previous sequences the most relevant separator properties to influence cell production, cell performance, reliability and life, and safety were discussed. In Fig. 7 the performance parameters of conventional membranes and a selection of advanced separator technologies is presented on a semi-quantitative basis.

For many of the emerging applications 25 µm – 35 µm separator thicknesses are requested, which can be served by conventional and advanced separators. The desire to continuously increase energy and power density will drive the need for lower weight and thickness to levels that conventional membranes have already reached. Nonwoven technology developers are currently working towards reaching lower thicknesses than 25 µm and correspondingly lower weight. Coated membranes are a well targeted improvement to reduce major disadvantages of non-coated membranes in terms of shrinkage, meltdown and penetration resistance. However, the basic character of membranes remains also in safety characteristics. Their set back on homogeneity due to flaking off of the coating is severe today. Further improvements are needed. Nanofiber separator have their strengths in porosity, meltdown, shrinkage and wettability. At the current state of their development their mechanical properties are critically weak. Ceramic filled nonwovens, from Freudenberg and other companies, meet the basic requirements for thickness and ionic resistance, while maintaining sufficient mechanical strength for the necessary production steps. Based on the data presented this new separator technology offers a highly competitive set of performance improvements in terms of drying temperature, porosity, penetration resistance, meltdown, and shrinkage.

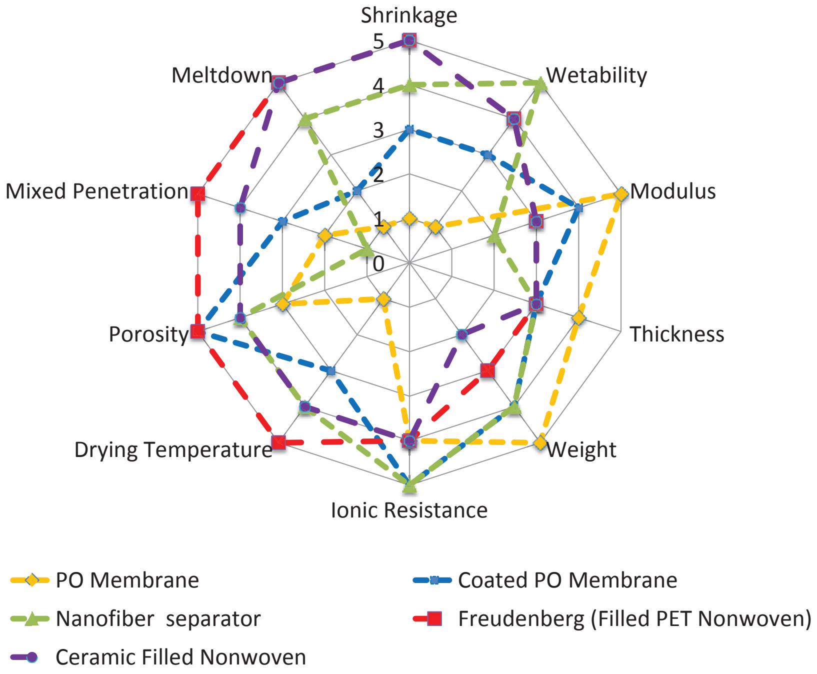

FIGURE 7. Semi-quantitative comparison of separator technologies (Status 2013). 1 = very low, 2 = low, 3 = sufficient, 4 = high, 5 = very high performance level.

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