

Nonwoven support material for improved separators in Li-polymer batteries

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Abstract

In the present paper, a nonwoven material is presented, which improves the mechanical behaviour and safety of current polymer electrolytes/separators in Li-polymer batteries.

The nonwoven material thereby acts as a support material of the separating polymer electrolytes. It helps to improve mechanical properties, safety and processibility of the current polymers.

The presented nonwoven material consists of fine polyester fibres and has a thickness of below 20 μm . The mechanical strength values are in the range of 20 N/5 cm with low values of elongation at tension values, which are relevant in battery production. It is electrochemically stable against a Li battery environment and can tolerate temperatures up to 180 $^{\circ}\text{C}$ with low values of thermal shrinkage. The wet-laid material is homogeneous regarding pore size distribution. Average pore sizes are in the range of 20–30 μm . On the other hand, the material's porosity is in the range of 55–65%, which is high enough to be filled with gel electrolytes also of increased viscosity. Due to the labyrinth-like structure of the nonwoven material, pin-holes do not occur.

An outlook is given, how such a material could also improve separators for proton exchange membrane (PEM) fuel cells.

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1. Introduction

Common separators used in secondary (rechargeable) batteries consist either of nonwoven materials, or of membranes. In general, nonwoven materials possess thicknesses above some 100–200 μm and maximum pore sizes typically in the range of 20–50 μm . Nonwoven materials are widely used as separators in rechargeable alkaline cells (Nickel–Cadmium cells and Nickel–Metal–Hydride cells). Due to the stochastic nature of the production process of nonwoven materials, pin-hole like pores commonly do not exist, and thus, electrical shorts caused by metallic dendrites are prevented.

Membranes commonly have thicknesses below 50 μm and pore sizes below 1 μm . In principle, they can be used in all batteries, in which the electrolyte is not a reactive partner during charging/discharging, where an “electrolyte reservoir” is

needed. Thus, membranes are widely used as separators in primary and secondary Lithium cells, in which the electrolyte is completely inert. Typical thicknesses of membranes in these cells are 25 μm and below. The thinner the membrane is, the higher the specific energy (energy per volume) of the cell is, but also the higher the risk regarding mechanical penetration, and thus, safety is.

The low pore sizes together with a necessary labyrinth-like structure prevent from metallic Li “fibres” (dendrites), which can be formed during the charging/discharging cycles. If such a dendrite reached the counter electrode, the cell would fail.

Secondary Lithium batteries can be classified roughly into two classes: “Real” Li-ion batteries containing a liquid electrolyte and “real” Li-polymer batteries containing an ion-conductive, either composite polymeric or geleous polymeric electrolyte [1–6]. Between these “extremes”, mix-types exist, in which additional liquid electrolyte is added to the electrolyte gel, mainly to improve the rate capability at high discharges and/or at low temperatures, respectively [7,8].

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Separators used in commercial Li-ion batteries are nearly exclusively polyolefine membranes. In general, such materials consist either of pure polyethylene (PE), or have sandwich structures of two layers of polypropylene (PP) and one layer of PE between. Pure PE separators have proven to cause safety problems in Lithium-polymer batteries at temperatures above 140 °C [9–11]. At these temperatures, the separator melts and internal short-circuits could be observed, if the melt does not perfectly cover the electrodes.

Three-layered separators are seen to be somewhat better from a safety point of view [10,11]. If temperature is increased, the PE layer melts (at T approximately 130 °C) and plugs the pores of the surrounding PP layers. Equipped with this so-called “shut-down mechanism”, this kind of separator prevents the cell from shorts occurring at miss-use conditions. However, temperatures above the melting point of the PP layers (some 160 °C) lead to a so-called “melt-down” of the whole membrane, which is critical from safety point of view. In any case, after releasing the shut-down mechanism once, the cell is destroyed.

Pure PP membranes exhibit a too high melting temperature, so the cell might reach the thermal runaway condition before the separator can initiate a shut-down [10,11]. Consequently, pure PP membranes commonly are not used in secondary lithium batteries.

The large difference of the polarity between the non-polar PO polymers and the highly polar Li battery electrolytes leads to a low pore wettability, and thus, to possibly high values of the inner resistance, when the pores are not filled completely with the electrolyte [4,5].

New developments use “ceramic separators”, in which either the ceramic is applied with polymeric binders (e.g. PVDF) [12–14] or in form of coated particles on a nonwoven substrate [15].

Li-polymer batteries ideally do not need an additional membrane separator, since the electrolyte gel itself prevents from dendrite growth, is not electronic conductive, and thus, fulfills all requirements of a separator. Both, Sadoway and Noda et al. summarized the “ideal” separator for Li-polymer batteries to “have the ionic conductivity of a liquid, the mechanical properties of a solid, and the formability of a commodity thermoplastic” [16,17]. In reality, the existing gels have some principle drawbacks (see also Fig. 1):

- they are not easy to apply, especially in an industrial scale production [18];

„Conventional“ Li-Polymer Cell

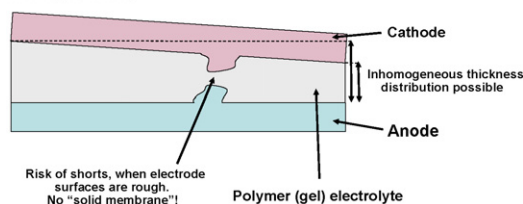


Fig. 1. Schematic cross-sectional structure of a “conventional” Li-polymer cell. Due to the flexibility of the gel separator, thickness variations and shorts caused by surface roughness may occur.

- if not applied correctly, a significant thickness variation of the gel might occur, resulting in an increased variation of the electronic parameters between the single cells, or even within one cell;
- they commonly are too soft, so during production, a complete displacement of the gel might occur, which then leads to a short of the cell;
- surface roughness might penetrate the flexible gel leading to short circuits of the battery.

To overcome these problems, the following attempts have been proposed.

- Jeong and Kim described the coating of a 25 μm thick polyethylene membrane with various gellable polymers. The total separator thickness was 30–45 μm and showed good electrical conductivity and mechanical properties [18]. A similar attempt is done by Kim et al. who paste a 2–3 μm thick layer of a gellable polymer containing ceramic particles on both sides of a membrane [19]. The resulting composite shows better wettability, a lower ionic resistance and an improved mechanical strength.
- Song et al. presented a 85 μm thick nonwoven support material, which contains the polymeric electrolyte in its pores. They found large improvement compared with “nonwoven-free” separators regarding mechanical strength and liquid electrolyte uptake (the hydrophilic nonwoven acts as an additional electrolyte reservoir). The positive results with batteries containing these separators led the authors to the conclusion that “the synergic results of the composite electrolytes are thought to be highly suitable for practical Li-ion polymer batteries” [20].
- Lee et al. recently published two papers, in which they did investigations with a nonwoven-supported PVDF separator. A solution of PVDF in NMP thereby was coated in the nonwoven material. The nonwoven is a strongly compressed PE material with relatively coarse fibres [21,22]. The thickness of the separator is 33 μm when using a 20 μm thick nonwoven base material. The authors proved the enhancement of mechanical strength when introducing a nonwoven support material. The low melting point of the PE fibres leads to a shut-down effect when the cells are heated to temperatures above the melting point of the PE (some 130 °C).

In the present study, a thin support material is presented, which

- fulfills the technical market requirements regarding thickness;
- tolerates temperatures up to 180 °C without any decomposition and with reasonable values of thermal shrinkage;
- is open enough to take up the electrolyte gel, but homogeneous enough to avoid sealed areas and thus, local differences of the electrical field;
- shows a labyrinth-like structure without pin-holes to avoid failures due to electrochemical shorts;

- mechanically supports this gel with respect to simplified processibility and improved cell homogeneity;
- is attractive from cost point of view.

2. Experimental

The development of ultra-thin, temperature-stable materials as separator support in Li batteries at Freudenberg Vliesstoffe started 2001 with a round 30 μm thick polyester nonwoven material. Following the general market requirements for “reduced thickness”, the thickness could be reduced to values below 20 μm (see below) since then.

The separator support material in the present study consists of a wet-laid polyester material. The recipe is a mixture of various polyester fibres including a binder fibre, which are mixed in an aqueous suspension and are continuously and randomly laid down on a screen belt. The fibres used possess diameters of rd. 3–4 μm . Thermobonding of the fibres is obtained by heating the material up to temperatures of 230 $^{\circ}\text{C}$ in an air-through-dryer. After thermobonding, the thickness is calibrated with the help of two oil-heated steel calander rolls. An in-line inspection system allows the continuous measurement of weight, and thickness, respectively, and the detection of defects.

Table 1
Technical data of ultra-thin PES nonwoven materials

	FS 2200/047	FS 2200/060
Production	631702	637495
Weight (g m^{-2})	12	8
Thickness (μm)	19	16
Mechanical strength machine direction (N/5 cm)	22	16
Elongation at break (%)	5	7
Mechanical strength cross direction (N/5 cm)	9	5
Air permeability at 100 Pa ($\text{L m}^{-2} \text{s}^{-1}$)	350	900
Porosity (%)	55	63
Average pore size (μm)	20	35
Thermal shrinkage (180 $^{\circ}\text{C}$ /10 min) (%)	<3	<3

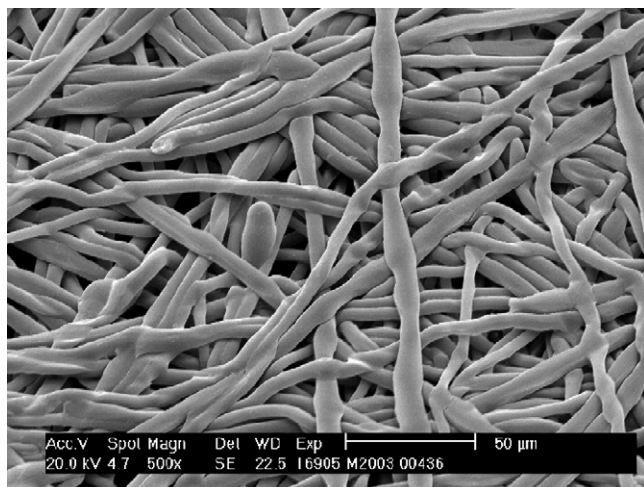


Fig. 2. SEM pictures of FS 2200/047: top section (0.5 k \times).

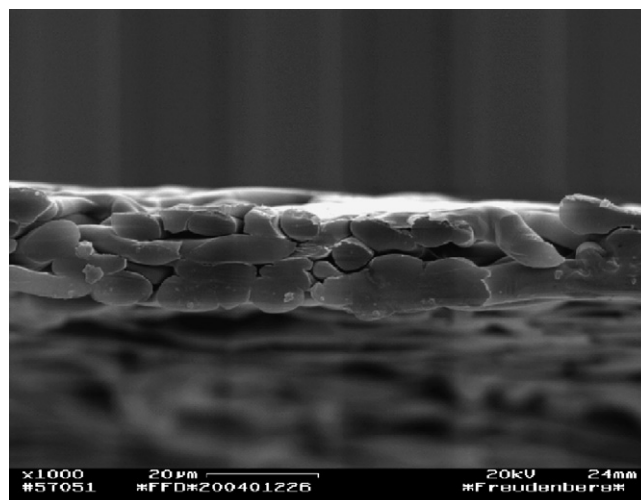


Fig. 3. SEM pictures of FS 2200/047: cross section (1 k \times).

Two materials have been specified yet: FS 2200/047 with 12 g m^{-2} and FS 2200/060 with 8 g m^{-2} . The technical characteristics of both materials are listed in Table 1. Scanning electron microscope (SEM) pictures of FS 2200/047 are shown in Fig. 2 (top section) and 3 (cross section). Material FS 2200/060 can be seen in Fig. 4 (top section) and 5 (cross section). It can be seen that the structure of the lighter material FS 2200/060 is significantly more open compared with that of the heavier derivate FS 2200/047.

Pore size detection was performed after ASTM 1294 with a PMI Capillary Flow Porometer (Poreous Materials Inc., USA). Thermal shrinkage tests were done with the help of a Labdryer (Mathis, CH). Thickness measurement is done after the standard EN 20534 with a test area of 2 cm^2 and a test pressure of 100 kPa (DM 2000/U; Schmitt Prüftechnik, Germany).

3. Discussion

As mentioned above, there seems to be an urgent need for a “thin, stable and easy to handle” separator for Li–polymer batteries. The current gel materials might perform well from an electrochemical point of view, but have some essential drawbacks regarding safety and handling (see Fig. 1).

To overcome these problems, attempts have been made by a combination of the real polymer separator together with a “Li-ion” membrane separator [18,23]. In this attempt, not only the advantages of the both technologies are combined, but also their disadvantages. Due to the relatively low membrane’s porosity of rd. 40% and the low pore sizes of below 1 μm , the gel is mostly deposited on the membrane surface and not in its pores. Thus, the thickness of the total separator is increased significantly, the same way its resistance, and also its costs.

The introduction of a nonwoven support material containing the real polymer electrolyte within its lattice offer some fundamental advantages over the polymer electrolyte alone (see introduction and schematically drawing in Fig. 6).

As described in the work of Song et al., and Lee et al., respectively, a mechanically stable Li–polymer separator can

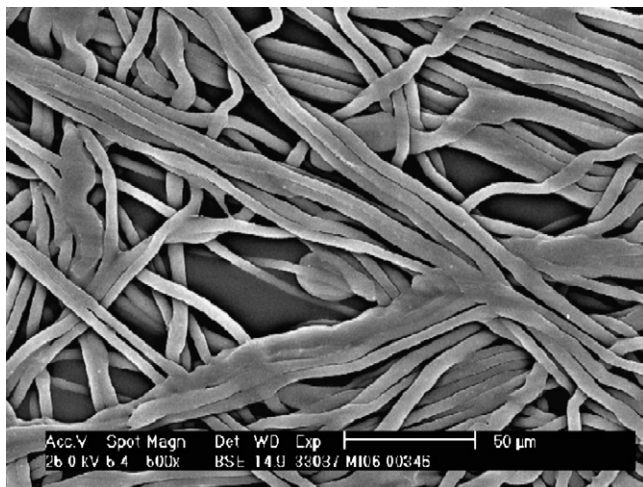


Fig. 4. SEM pictures of FS 2200/060: top section (0.5 k \times).

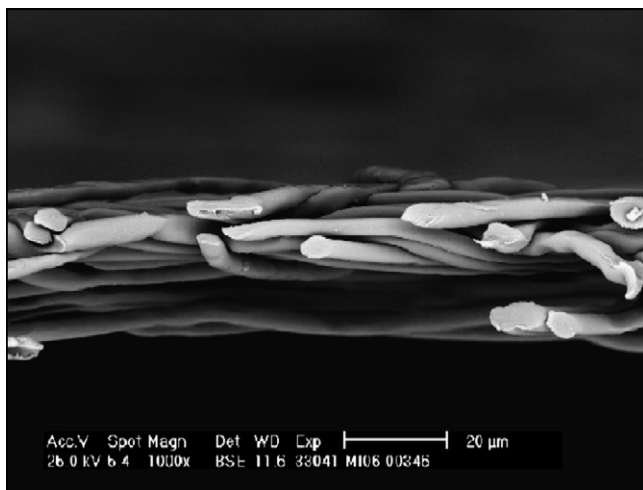


Fig. 5. SEM pictures of FS 2200/060: cross section (1 k \times).

be obtained by coating the polymer electrolyte into the nonwoven lattice [22]. However, the nonwoven materials used in these two studies offer significant potential for improvement.

Song et al. used a very thick nonwoven support (85 μm) [20]. The group has proven the suitability of such a separator for Li–polymer batteries. However, the thickness of the total separator is out of scope for most commercial Li battery applications.

Li-Polymer Cell containing “coarse-fibred” support material

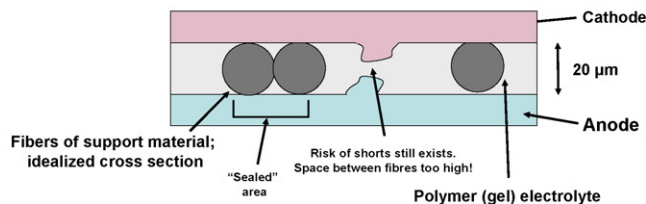


Fig. 6. Schematic cross sectional structure of a “supported” Li–polymer cell containing coarse fibres. Here, the gel separator supporting function is guaranteed, but the coarse fibres lead to a high inhomogeneity. “Sealed” areas might exist. In neighbored “open areas”, the occurrence of pin-holes and thus, a risk of shorts caused by electrode surface roughness, still exists.

Currently, the thickness of polyolefine membrane separators for consumer batteries is in the range of some 20 μm , with tendency towards 15 μm or even lower. In order not to lose one of the most important advantages of Li batteries – their high energy density – the thickness of the total separator has to be reduced to values below at least 30 μm .

Lee et al. applied a 20 μm nonwoven support material, containing relatively coarse fibres [21,22]. If fibre diameters were in the range of the nonwoven thickness, there would only be space for one layer of fibres. Such a structure might contain either locally sealed areas, when two or more of these coarse fibres are neighbored. Further, pin-holes in “open” areas might occur, which cannot prevent perfectly from shorts caused by surface roughness. The effect of such a material is schematically illustrated in Fig. 6.

The effect of pin-holes in a separator on dendrite growth and thus, the risk of electrical shorts, can be explained as follows: Dendrites generally grow along the gradient of the electrical field. If pores had the same “direction”, dendrite growth is fast and cannot stop within the pores.

Therefore, it is extremely important for a battery separator, that its pores do not show pin-holed structures. Pores ideally should be labyrinth-like. In such structures, dendrite growth is hindered since they break within the labyrinth. Thus, dendrite growth is suppressed by use of labyrinth-like separator structures.

Transformed to a nonwoven material, this means that dendrite growth is avoided the better:

- the higher the material’s homogeneity is and
- the lower the thickness of the fibres compared with the thickness of the whole material is (how much fibre diameters “fit” into the total thickness of the nonwoven).

Nonwovens produced in a wet-laid production process by nature show a high homogeneity. Holes, which are primarily formed, when the fibre suspension is laid down on the screen belt generate an increased suspension flow and thus, are immediately plugged [24]. This, together with the stochastic orientation of the fibres themselves, guarantees the best possible structure.

The typical values of thickness, fibre diameter and the ratio of both parameters for separators used in different rechargeable battery systems are summarized in Table 2.

Assuming the same homogeneity of the separator material, dendrite growth should be suppressed as better, as higher the ratio thickness divided by fibre diameter is.

Note that in NiCd and NiMH, the separator is the nonwoven alone, while for the LiP separators, also the gel acts as separator.

Summarized, it means that a support material must not only have the right thickness, but also the right morphology. High homogeneity and thin fibres are necessary to generate the desired labyrinth-like structure. Such a support material, as it is illustrated in Fig. 7, can help to prevent from shorting and is has a positive impact on the cycle life and the safety of the cell.

Thermal shrinkage is another important safety item. Support materials showing high values of thermal shrinkage might destroy the separator structure, if the cell is exposed to elevated

Table 2

Typical values of thickness, fibre diameter and the ratio of both parameters for separators used in different rechargeable battery systems

	NiCd	NiMH	LiP support material after Lee et al.	LiP support material; present study
Thickness (μm)	180–200	100–150	20	20
Fibre diameter (μm)	11–18	8–13	20 ^a	4
Fibres per thickness ^b	10–20	12–18	1	5

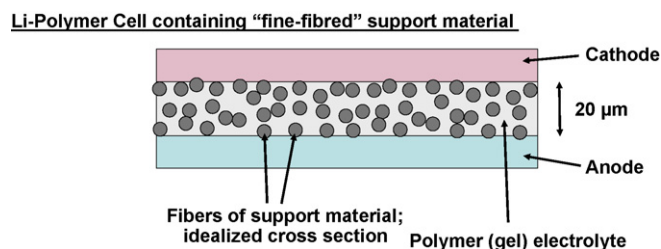
^a Value estimated after SEM pictures in the study.^b Ratio thickness divided by fibre diameter.

Fig. 7. Supported Li-polymer cell containing fine fibres: In this case, the rigid separator support forces the gel electrolyte, and thus, prevents from the disadvantages of the conventional cell structure. Due to the good homogeneity of the support material, neither “sealed” nor “open” areas exist, leading to the beneficial behaviour explained in the text.

temperatures. The thermal shrinkage values of PE nonwoven materials, when exposed to temperatures of 120 °C for a time of 10 min are in the range of 10%. Consequently, separator materials reinforced with such a support would lose its mechanical stability even below the melting point of the support material. As result, the two counter electrodes might come in contact and the cell enters a critical state.

The PES material described in the present study has low values of shrinkage up to 180 °C (see Table 1). Therefore, it can also support the gel material also at temperature ranges, where a PE support would melt. This means that the temperature range, in which the separator is “safe” is expanded towards clearly higher temperatures.

By application of polyethylene waxes or particles, a shut-down effect might also be obtained. In this case, the polyethylene might melt and plug the pores. To prove this idea, further research has to be done.

4. Outlook to other applications

From an electrochemical point of view, “thin and homogeneous support materials” are limited not only to Li battery separators. Similar requirements exist e.g. in proton exchanging membrane (PEM) fuel cells, where ion-conducting polymers are used as the separating membrane [6]. Again, handling of the mostly brittle materials – an important issue for commercialization of such membranes – can be supported by a material described in the present paper. It can be assumed that this item becomes more and more important for the application “fuel cells”, since cost reduction is one of the major items for commercialization.

It will be an item of further research to prove this idea.

5. Summary

In the present study, a thin separator support material is presented. This material consists of a porous nonwoven, which up-takes the separating gel electrolyte. The nonwoven material contains fine polyester fibres and offers a high porosity in combination with a good homogeneity. Due to the labyrinth-like and stochastic fibre structure, it neither shows “sealed” nor “pin-holed” areas. Porosity values of rd. 60% and pores, which are open enough, allow an efficient uptake of the separating polymer gel.

It is explained how such a support material could improve the current Li-polymer separators: it improves their mechanical behaviour and handling, equalizes the separator gel and minimizes the risk of shorts caused by either dendrites, or surface roughness, or by the release of conductive particles from the electrode surfaces due to the considerable absence of pin-holes.

The presented material is thermally stable up to 180 °C without significant thermal shrinkage; the so-reinforced separator has no thermal melt-down under these conditions. This could lead to an improved safety of so-equipped Li batteries.

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