CHARACTERISATION OF NANOFIBROUS SEPARATORS FOR LITHIUM-ION BATTERIES

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Abstract. Nano fibred materials ensure high porosity and relative surface area of separators. These parameters are important to improve ionic mobility between electrodes and ensure sufficient electrolyte volume in battery. These advantages make electrospinning very promising method of nanofibrous separators mass production. In this paper are described electrospinning fabrication process and discussed results of separator's electric and electrochemical properties measurements compared with Celgard 3401.

Keywords: spinning, battery, separator, impedance measurement

CHARAKTERYSTYKA SEPARATORÓW Z NANOWŁÓKIEN DLA BATERII LITOWO-JONOWYCH

Streszczenie. Nanostruktura materiałów wykorzystywanych jako separatory zapewnia ich wysoką porowatość, a co za tym idzie dużą powierzchnię właściwą. Parametry te są ważne w kontekście podwyższenia mobilności jonów (Ion mobility) i zagwarantowania wystarczającej ilości elektrolitu w baterii. Korzyści te pozwalają upatrywać w elektro wirowanie bardzo obiecującą metodę masowej produkcji separatorów z nanowłókien. W niniejszym artykule opisany zostaje proces produkcji separatorów. Omawia się również wyniki pomiarów elektrycznych i elektrochemicznych w porównaniu do Celgrad 3401.

Słowa kluczowe: wirowanie, bateria, separator, pomiar impedancji

Introduction

Battery separators play very important role in rechargeable lithium-ion batteries and determine the battery performance. The main function of these is to keep the positive and negative electrodes apart to prevent electrical short circuits while enabling free ionic transport.

Microporous separators based on polypropylene and polyolefine are the most used ones in contemporary commercial li-ion batteries. The reason is its properties suitable for this purpose. These separators demonstrate high chemical stability, appropriate thickness, tensile strength and toughness. As a negative properties of commercial separators occur low porosity, low thermal stability, wettability and ability to uptake electrolyte. Low wettability and ability to uptake electrolyte are both caused by polarity difference between non-polar separator (polyolefine) and highly polar electrolyte containing solvent. This fact may lead to increase in battery cell resistance and subsequently to battery capacity drop [5].

Wettability increase can be ensured by the surfactant addition. Nevertheless, surfactants may affect electrolyte and electrodes in a negative way. Usage of nanofibred separators prevents from that negative factors. Nanofibred separator production is realized by electrospinnig or forcespinning [3].

Nafigate nanofibred separators were fabricated by electrospinning method. Fibres were spinned from the free surface of polymer. Thanks to higher porosity of nanofibred separators, dissociated ions exhibit higher mobility between cathode and anode. It results in better electrochemical properties. Chemical resistance depends on the used material [7].

1. Separator fabrication

Experimental samples of nano fibred separators are fabricated in the laboratory machine Nanospider™ NS LAB 500 equipped with EMW (Endless Motion Wire) technology. This EMW technology is based on spinning by the string electrode with usage of a small amount of polymer solution. Polymer solution is applied (the rate of application is set) on the string (spin electrode). Intensive electrostatic field, which results from potential difference between spin and collecting electrodes, forms Taylor's cone. This cone is fibre source. Drawn fibre is subsequently elongated, surface area increases and solvent evaporates simultaneously. Properly adjusted Nanospider (electrodes position, solvent selection) produces sub-micron wide dry fibres. Electric charge carried by the produced fibres has the same polarity as the spin electrode. This charge is drained onto collector and usually grounded [7]. Nanospider scheme is shown in Figure 1.
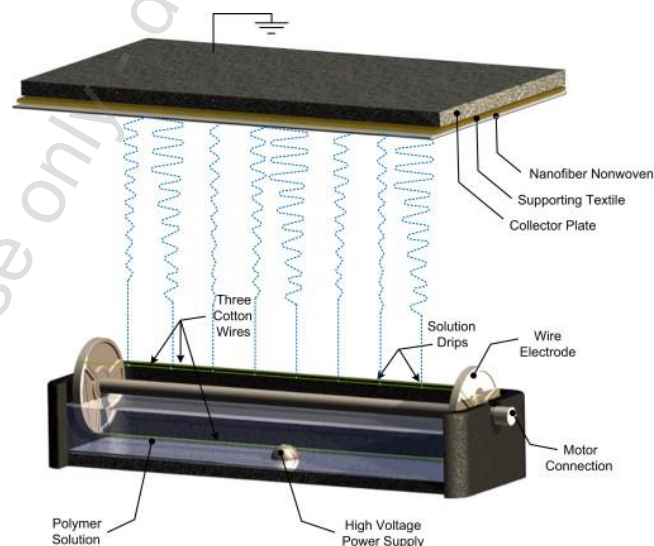

Fig. 1. Nanospider scheme with main parts description [7]

This method is convenient for spinning organic and inorganic polymers and biopolymer materials. Electrospinning is widely spread in the industry because of its simple machine design, with no need of sophisticated jet systems. It brings quality production improvement simultaneously. Nanofibres produced by spinning from the free surface exhibit better uniformity in diameter. Applied nanofibred layers are more homogenous. Diameter of produced nanofibers are usually in range from 50 to 500 nm (according to used material). Electrospinning process exhibits productivity from 0.1 to 1 g h^{-1}. Nanospider^{TM} system exhibits productivity according to individual properties of used material. Fabrication process is dependent on critical parameters optimization. It means machine configuration (distance between electrodes, potential voltage), polymer solution properties (concentration, viscosity, conductivity), appropriate substrate type and surrounding environment properties. Modern technologies enable us to set fabrication properties very simply, but exactly. Up to date methods allow nanofibres production from in water soluble polymers, from polymers dilutable in organic solvents and from polymer melts. We are capable to spin more than 30 polymer types [4, 7].

2. Results and discussion

2.1. Ageing and liquid uptake in the aprotic electrolyte

Separators must be resistant to carbonate aprotic solvents without limits, and must not lose neither its tensile strength not its toughness. Analyzed samples were long period aged in 1 mol l^{-1} LiBF$_4$ in EC/DMC electrolyte. Samples were checked on mechanical properties and structural changes dependent on time. Furthermore, mass changes during time period were studied. Weight of samples did not change during time. It proves very promising inertness of Nafigate separators soaked in carbonate solvents.

The liquid electrolyte uptake is one of the most important parameters. Separators should have high ability to uptake and retain electrolyte in long-term. Each of the Nafigate samples was measured on this property. Separators were measured by soaking them in a liquid 1 mol l^{-1} LiBF$_4$ in EC/DMC (1:1 wt.) electrolyte for 4 h at 20 °C to reach the equilibrium state. The residual electrolyte on the surface of each separator was wiped off with filter paper. [1, 6, 9]. The liquid electrolyte uptake EU (%) was calculated according to:

$$EU = \frac{m_w - m_d}{m_d} \times 100\% \tag{1}$$

where m_w a m_d are weights of the electrolyte-soaked separator and dry separator, respectively.
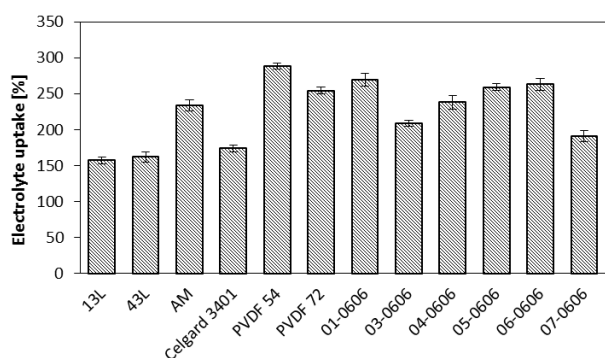

Fig. 2. Electrolyte uptake of Nafigate and Celgard separators, 20°C

Figure 2 shows the liquid electrolyte uptakes of Nafigate fibrous membranes. The majority of liquid electrolyte is distributed in the open pores. Commercial separator Celgard 3401 uptakes slightly higher amount of electrolyte in contrary to 13L and 43L types. Other Nafigate types prove EU over 200%. These characteristics correlate with the PVP content in Nafigate separators.

2.2. Surface morphology

Morphology was studied by the environmental scanning electron microscope (ESEM, TESCAN, a.s., Vega 3 XMU) which was operated at 30 kV. Small samples (area 1 sq. cm) were cleaned with compressed air duster and dried at 30 °C for 24 h before observation. Micrographs were taken at resolutions 5 000× at 30 kV in the inert argon atmosphere (low pressure set to 100 Pa).

During nanofibred materials fabrication, some basic defects may occur. Fabrication process is continuously optimized. Figure 3a and 3b shows ESEM images of studied membranes. Sample 01_0606 (a) exhibits material conglomerations (beads) in the bulk of the separator. Separator type 03_0606 (b) contains visibly wider fibres (ropes). Rope – effect occurs in 05_0606 (c) too. Nanofibred separator 7_0606 (d) contains considerable beads. Items of each sample pairs PVDF 54 (e) - PVDF 7209 (f) and 43L (g) - 13L (h) were fabricated in the same way. Differences are only in the amount of used crosslinker. Samples (e) and (f) are single-layer types, where conglomerations and lack of uniformity

may occur. Samples (g) and (h) are represented by three-layer laminates. 43L and 13L separators prove higher tensile strength. In the 13L sample higher amount of particles appeared, nevertheless beads did not occur. Used electrostatic electrospinning fabrication method advantages are in splashes a droplets defects elimination [2, 11].
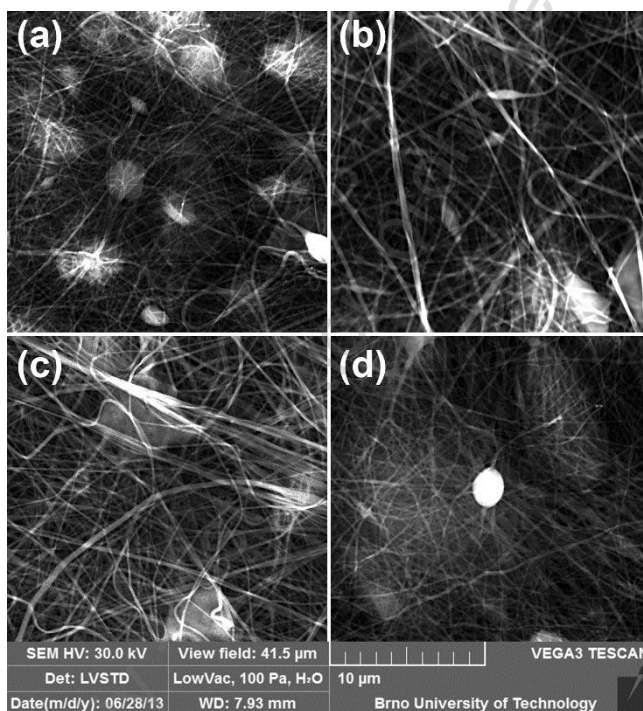

Fig. 3a. ESEM images of Nafigate fibrous membranes (a) 01_0606, (b) 03_0606, (c) 05_0606, (d) 07_0606
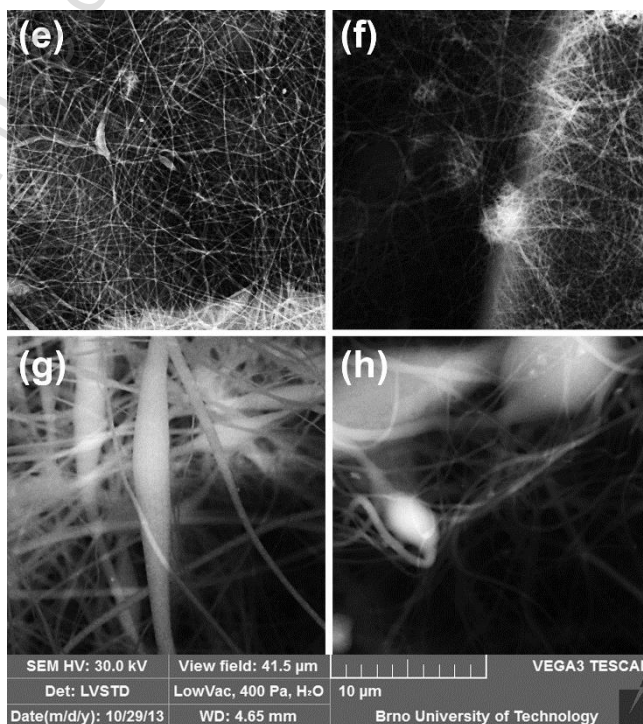

Fig. 3b. ESEM images of Nafigate fibrous membranes (e) PVDF 54, (f) PVDF 7209, (g) 43L, (h) 13L

2.3. Impedance behavior of nanofibrous separators and ionic conductivity

Impedance spectroscopy was run on potentiostat VSP Biologic. All samples were immersed in 1 mol l^{-1} LiBF$_4$ in EC/DMC electrolyte and tempered in the climate chamber with temperature set at 20 °C simultaneously. Separator circles

(16 millimeters in diam.) were measured in electrochemical test cells EL-CELL at frequency range 0.5 Hz – 1 MHz with amplitude 10 mV. All the process took place in the inert argon atmosphere [8, 10]. Ionic conductivity measurement results are shown in the Nyquist plot (see Figure 4a and 4b below).

Ionic conductivity (σ) was calculated according to the equation below:

$$\sigma = \frac{d}{R_b S} \qquad (2)$$

where R_b is the bulk resistance, d and S are thickness and area of the sample [7].
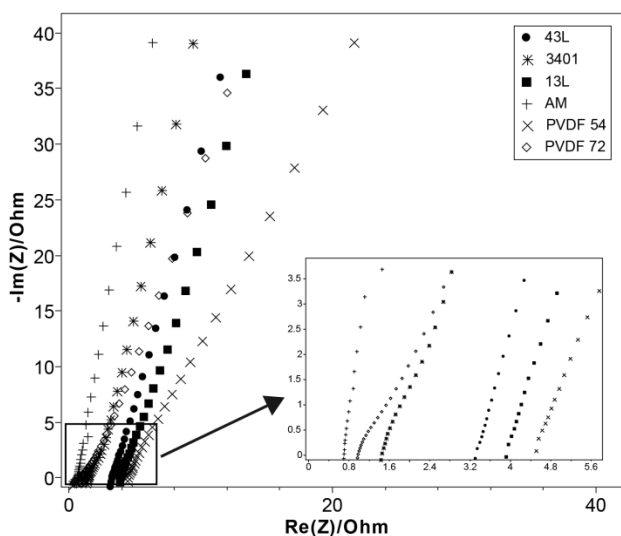

Fig. 4a. Membrane impedance spectra, 1 mol l^{-1} LiBF$_4$ in EC/DMC electrolyte, 20 °C
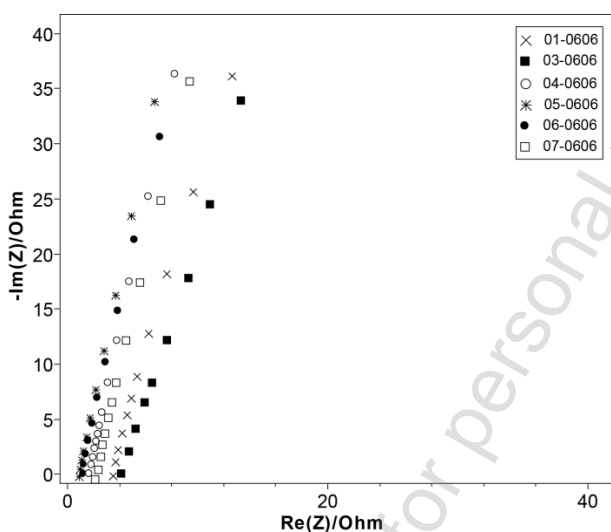

Fig. 4b. Membrane impedance spectra, 1 mol l^{-1} LiBF$_4$ in EC/DMC electrolyte, 20°C

Bulk resistance R_b was read from the low frequencies of impedance spectra in Nyquist plot. It is clarified in Figure 5.
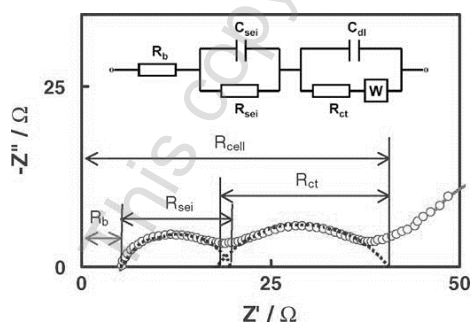

Fig. 5. EIS and equivalent circuit of Lithium Ion batteries

In Table 1 are summarized R_b and σ values of all measured separators.

Table 1. Thickness and relative conductivity of membrane, frequency range 0.5 Hz - 1 MHz, 20°C

Sample	R_b [Ω]	Conductivity σ [mS cm^{-1}]
13L	3.91	1.97
43L	3.34	2.89
AM	0.69	1.35
Celgard 3401	5.31	0.23
PVDF 54	4.52	0.70
PVDF 72	0.97	4.17
01-0606	2.75	0.28
03-0606	2.08	0.45
04-0606	1.61	0.61
05-0606	0.81	1.61
06-0606	0.87	0.95
07-0606	2.05	0.36

2.4. Dielectric properties of separators

Dielectric properties were determined by a dielectric properties tester (Agilent 4285A, Precision LCR Meter). Measurements were carried out with frequencies 100 Hz and 1 kHz. Results are summarized in Table 2. It was not possible to determine dielectric properties of sample 01-0606. Pressure between measuring electrodes always affected tears on the surface.

Table 2. Relative permittivity (100 Hz and 1 kHz respectively) of fibrous separators, 20°C

Sample	Relative permittivity ε_r[-]	
	100 Hz	**1 kHz**
13L	8.24	4.32
43L	2.62	2.03
AM	4.62	2.05
Celgard 3401	2.61	2.01
PVDF 54	1.77	1.67
PVDF 72	1.62	1.53
01-0606	-	-
03-0606	1.11	1.19
04-0606	1.28	1.28
05-0606	2.82	1.41
06-0606	1.23	1.29
07-0606	1.11	1.12

Values of permittivity at frequency 100 Hz correspond to tabulated values (samples 3401 and 13L). Separator 43, which is mainly made from polyethersulfone (PES), practically corresponds to tabulated value (ε_r = 3.5 at frequency 100 Hz). Permittivity values of 01-0606 – 07-0606 depends on different concentration of added polyvinylpyrrolidine additive. Differences are caused by non-homogeneousness and high porosity of the separator's surface.

2.5. Performance of Nafigate separators in half-cell

Separator influence on battery performance was measured in three electrode electrochemical test cell EL-CELL (diameter 18 mm). Test cells representing lithium ion half-cell consisted of metallic lithium counter (CE) and reference (RE) electrodes. As a working electrode (WE) was chosen anode. Negative electrode in commercial lithium ion batteries is made from materials based on carbon. We prepared our WE from graphite COND CR 5995. Test cells were assembled in the inert argon atmosphere. We employed common liquid electrolyte 1 mol/l LiBF$_4$ in EC/DMC (50:50 wt. %) in test cells.

Half-cell was measured on Galvanostatic Cycling with Potential Limitation (GCPL). This method enabled us to control electrochemical half-cell potential at cycled charge and discharge. In first two cycles was half-cell formatted (double layer on the interface electrode-electrolyte was stabilized). Formatting is linked to electrode characteristics changes – irreversible capacity of the half-cell, impedance of both electrode and electrode material; coulombic efficiency.
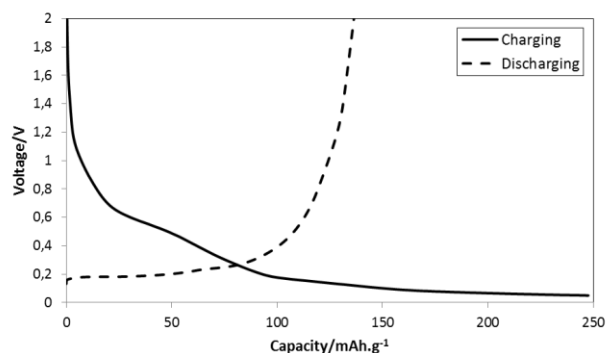
Fig. 6a. First cycle charge and discharge performance of the half-cell with Nafigate separator 05-0606 soaked in 1 mol l^{-1} LiBF$_4$ electrolyte, 20 °C
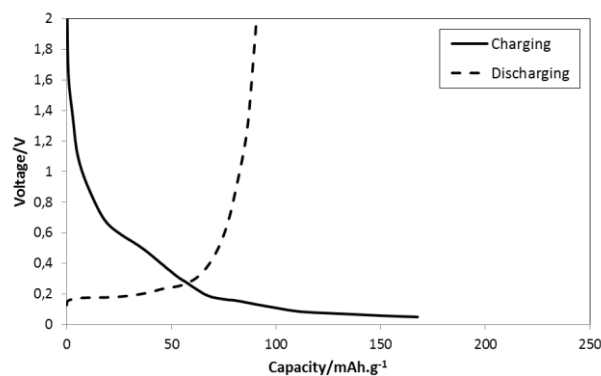

Fig. 6b. First cycle charge and discharge performance of the half-cell with Nafigate separator 06-0606 soaked in 1 mol l^{-1} LiBF$_4$ electrolyte, 20 °C

In figure 6a and 6b are shown charge and discharge characteristics of the lithium-ion half-cells equipped with separator 05-0606 and separator 06-0606 respectively. It is obvious, that half-cell with Nafigate separator 05-0606 proves higher first charge capacity in comparison with half-cell with 06-0606 type. It may by caused by the lower porosity of 06-0606 sample. In the bulk of the 06-0606 separator runs glomer formation process. Glomer consists of solvent components, which are affiliated to separator fibres. Measurement was performed in the potential range from 0 V to 2 V and current set on C/10. Measurement was carried out at 25 °C and relative humidity 49%. Furthermore, half-cell with 05-0606 separator reached first cycle charge capacity 249 mAh g^{-1} in contrast to 06-0606 half-cell with only first cycle capacity of 167 mAh g^{-1}.

3. Conclusion

This report is focused on measuring properties of non-commercial separators from the Nafigate Corporation stock company. Properties of separators are compared with on the market widely spread separator Celgard 3401. Nafigate separators were prepared by electrospinning. Samples were tested on ionic conductivity and influence on characteristic of lithium-ion half-cell. These Nafigate separators (especially AM model) have all the important parameters comparable with the world production. Further work will be focused on development of very promising AM types with internal sandwich structure. Moreover, we are in co-operation with Nafigate focused on trimming fabrication time of new separators.

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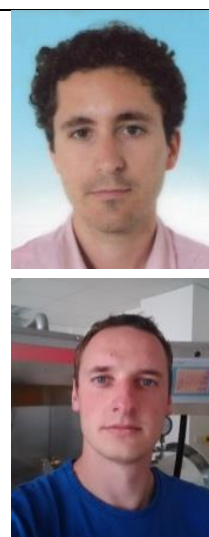
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