Polyvinilidene fluoride (PVDF) nanofiber membrane for Li-ion rechargeable battery separator

H Widiyandari¹, A Purwanto² and S A Widyanto³

¹ Department of Physics, Diponegoro University, Jl. Prof. H. Soedarto SH, Semarang, 50275, Indonesia
² Department of Chemical Engineering, Sebelas Maret University, Jl. Ir. Sutami No. 36 A, Surakarta, Indonesia
³ Department of Mechanical Engineering, Diponegoro University, Jl. Prof. H. Soedarto SH, Semarang, 50275, Indonesia

Email: h.widiyandari@undip.ac.id

Abstract. This study reported synthesis and characterization of PVDF (polyvinilidene fluoride) nanofiber membrane using electrospinning method for Li-ion rechargeable battery separator. Electrospinning equipment system consists of a DC high voltage (HV - DC), a controllable spinner and a plate collector. The effects of the applied voltage on morphological property, porosity and thermal property were systematically investigated. The application of DC voltage at a range of 13 to 17 kV resulted the one-dimension nanostructure of the PVdF nanofiber. The produced PVdF nanofiber membrane separators are evaluated to have a higher level of porosity (86 – 93%) and a good thermal shrinkage property in comparison to Polypropylene (PP) microporous membrane separator. The produced PVdF membrane separators were assembled into the LiFePO₄ cells and demonstrated high charge-discharge capacities at room temperature with the coulombic efficiency reaching 80 %.

1. Introduction

A lithium-ion (Li-ion) rechargeable battery is an electrochemical-based energy converter device as an energy storage device as well. The main parts of the Li-ion battery include a negative electrode (anode) graphite, a positive electrode (cathode)-based on lithium, electrolyte and a membrane separator [1]. Separator is one of the most important parts in the development of Li-ion batteries. This separator must be able to get through the electrolyte ions but able to act as an electrical insulator so there is no contact between the anode and cathode. The type and material of separator are critical for enhancing the performance of Li-ion batteries such as cycling performance, power density, charge-discharge capacity, stability, and security [2]. A characteristic of a separator is determined by the chemical stability, mechanical strength, stable shape, wetability, porosity, permeability, thickness, thermal shrinkage, shut down, and cost. In general, separators in Li-ion battery are in the form of microporous membrane (pore size of less than 20 nm) made of a polymer membrane or nonwoven fabric mat. The polymer membranes made of polytetrafluoroethylene, polyethylene, polypropylene and polyvinyl chloride. Polivinylidene fluoride (PVdF) is a thermoplastic polymer crystalline that has physical properties such as high polarity, excellent thermal and mechanical properties, high affinity to...
an electrolyte solution, good chemical stability, and excellent compatibility with electrodes that make PVDF potential to be used as a membrane separator [3].

Due to some superior properties owned by nanofiber structured material such as large specific surface area, small pore size and high porosity, making the nanofiber-based membranes as a promising candidate for a separator material for Li-ion battery applications with a high performance [4]. This study aims to produce a membrane separator based on a polymeric material of PVdF nanofiber using electrospinning method.

2. Method

2.1. Materials
Polyvinylidene fluoride (PVdF, Mw 534.000, Aldrich), N-N Dimethylformamide (DMF, Merck), Acetone (Merck) and n-butanol (Merck) were used as received without further purification. 1M lithium hexafluorophosphate (LiPF6), LiFePO4, PVdF binder, acetylene black (AB), N-methyl-2-pyrollidone (NMP) were supplied by MTI corp., USA. The Celgard 2400 microporous polypropylene-commercial (PP-Comm., Celgard, USA) membrane separator was used for comparison.

2.2. Separator preparation
PVdF nanofiber membrane separator was prepared by electrospinning of PVdF solution. The PVdF solution was prepared by dissolving 10 wt% PVdF powder in acetone/DMF (3:7 by vol. ratio) as a solvent, which was stirred at 60 °C for 8 h. The polymer solution was fed through the syringe with the flow rate of 1.5 mL/h. The cone jet was formed at the tip of syringe by applying the DC high voltage to the body of metal syringe. The jets were then elongated toward the lower potential and the solvent was evaporated simultaneously to form the nanofiber. The tip-to-collector distance was set at 17 cm to maintain the complete evaporation of the solvent. In this research, the DC high voltage was adjusted and varied from 13 to 17 kV. The electrospinning conditions are indicated in table 1. Figure 1 shows the schematic diagram of electrospinning system.

| Sampel  | Voltage (kV) | Spinning time (h) | TCD\(^a\) (cm) | Flow rate (mL/h) |
|---------|--------------|------------------|----------------|-----------------|
| PVdF-A  | 13           | 1                | 15             | 1.5             |
| PVdF-B  | 15           |                  |                |                 |
| PVdF-C  | 17           |                  |                |                 |

\(^a\)Tip-to-collector distance

![Figure 1. Schematic diagram of electrospinning system.](image-url)
2.3. Characterization

2.3.1. Morphology of nanofiber separator. The morphology of the PVdF nanofiber separator was characterized using scanning electron microscope (SEM, JEOL JSM-6360 LA, Japan). The electron energy was adjusted at 15 keV.

2.3.2. Porosity of nanofiber separator. The porosity of nanofiber was measured by soaking the dried nanofiber with a measured weight of $W_{\text{dry}}$ into the n-butanol (Merck) for 2 h then wiped using a filter paper to obtain their wet weight ($W_{\text{wet}}$). The porosity of PVdF nanofiber separator was obtained by Eq. (1)[5].

$$\text{Porosity} = \frac{W_{\text{wet}} - W_{\text{dry}}}{\rho_b W_{\text{dry}}} \times 100\%$$

where $\rho_b$ is the density of n-butanol of 0.81 g/cm$^3$.

2.3.3. Thermal property of nanofiber separator. The thermal property of the PVdF nanofiber separator was obtained by measuring the shrinkage ratio of the nanofiber. The same dimension of nanofibers were heated at 105°C and 130°C separately in the oven for 8 h. The shrinkage ratio was calculated by Eq. 2 [5].

$$\text{Shrinkage ratio} = \frac{L_0 - L_1}{L_0} \times 10\%$$

where $L_0$ is the length before heat treatment and $L_1$ is the length after heat treatment.

2.3.4. Performance evaluation. The performance of PVdF nanofiber as a separator in the Li-ion battery was evaluated by measuring the charge-discharge test. The charge-discharge of LiFePO$_4$ cells containing liquid electrolyte-soaked membrane (PVdF and PP-commercial) were carried out using a split test cell (MTI corp. USA). The main components of a cathode is LiFePO$_4$ as an active material, acetylene black (AB) and PVdF as binders. The anode and electrolyte are carbon and LiPF$_6$, respectively. Electrochemical performance of secondary lithium battery was analyzed using the eight channel battery analyzer (MTI corp, USA).

3. Result and Discussion

3.1. Morphology and Porosity of Separator
The photographs of produced PVdF nanofiber membrane separator are shown in figure 2. Figure 3 shows the morphology of PVdF nanofiber with different DC high voltage at the range of 13 to 17 kV. Adjusting the appropriated voltage is an important condition during nanofiber formation. The applied voltage produces electrostatic force around the needle conductor which acts to overcome the surface tension of the polymer solution [6].

The performance of the cells is strongly influenced by the ionic transport through the separator. It is closely related to the pore size and porosity of the membrane separator. Separators commonly have a thickness of 10 – 30 micron and a pore size of 0.1 – 1 micron. The porosity of the PVdF nanofibers and PP microporous membranes are indicated in table 2. The porosity of PVdF prepared at 13 kV applied high voltage shows highest porosity of 93% and overall the porosity of PVdF nanofiber membrane separator is comparable and even higher than PP microporous. This high porosity is due to the nanofiber that was produced in this condition has uniform and good fiber morphology without any beads or agglomerated parts as shown on the SEM images. Porosity is a measure of the void (i.e. "empty") spaces in a material, and is a fraction of the volume of voids over the total volume.
3.2. **Thermal property**

In order to investigate the thermal stability of the nanofiber membrane separator, the PVdF nanofiber membrane and PP-Celgard microporous were heated at 105°C and 130°C for 8 h in an oven and its thermal shrinkage ratio (Table 3) was measured. PP microporous membrane often shrinks at an elevated temperature due to the crystalline of PP decreases with curliness of molecular chain. This phenomenon could lead to a serious safety concern when used as a battery separator [5]. To prevent

**Figure 2.** Photograph of PVdF nanofiber membrane separator that was spun at different high voltage, (a) 13, (b) 15, (c) 17 kV and (d) PP-comm.

**Figure 3.** Low and high magnification SEM images of PVdF nanofiber membrane separator that were spun at different high voltage, (a, b) 13, (c, d) 15 and (e, f) 17 kV.

**Table 2.** Porosity properties of PVdF nanofiber.

| Sample         | Porosity (%) |
|----------------|--------------|
| PP-commercial  | 87           |
| PVdF-A         | 93           |
| PVdF-B         | 89           |
| PVdF-C         | 86           |
the internal short circuit failure, it is necessary that some separators with no or minimal thermal shrinkage which could be found at PVdF nanofiber membrane. Therefore the PVdF nanofiber membrane has a good potential as a separator of Li-ion battery.

| Sample       | at 105°C (%) | at 130°C (%) |
|--------------|--------------|--------------|
| PP-commercial| 5            | 24           |
| PVdF-A       | 3            | 11           |
| PVdF-B       | 1            | 10           |
| PVdF-C       | 0            | 4            |

3.3. Cycling performance

The cycling performance (i.e., discharge capacity of cells as a function of cycle number) of LiFePO₄ battery using PVdF nanofiber and PP microporous were investigated, in which the cells were cycled at constant charge/discharge current density (1C = 170 mA g⁻¹) rate. Figure 4 shows the charge (a) and discharge (b) of LiFePO₄ battery using PVdF nanofiber and PP microporous at first three cycles. The discharge capacity decay of LiFePO₄ battery using PVdF membrane separator is better than PP-microporous due to the ionic transport in PVdF membrane separator is better than PP-microporous. In addition, the coulombic efficiency of the Li-ion battery using PVdF separator reaches 80%, whereas PP-microporous of about 60% [figure 5]. The battery characteristic such as charge-discharge performance depends on the type of materials for the cathode and the anode. Separator membrane can perform in the ion transporting. The measurement to the battery performance shows that the PVDF nanofiber based- membrane has a good potential to be used as separator in the Li-ion battery.

![Figure 4](image_url)

Figure 4. (a) Charge capacity and (b) discharge capacity of LiFePO₄ cells containing PVdF nanofiber and PP-microporous at 1C rate.
4. Conclusion
The PVdF nanofiber was successfully prepared using electrospinning method for membrane separator of secondary Li-ion battery. The applied DC high voltage influenced the properties of produced nanofiber. The produced PVdF nanofiber showed high level of porosity (86-93%) in comparison to PP-commercial separator. The important point is that the PVdF nanofiber membrane separator provided substantial improvement in the thermal shrinkage. In the cell test at 1C rate, LiFePO₄ battery using PVdF nanofiber membrane separator gave a good performance. The discharge capacity decay in the first three cycling measurements showed that PVdF membrane separator relatively stable than PP-microporous membrane separator and it exhibited high coulombic efficiency at about 80%.

Acknowledgement
This research was supported by The Ministry of Research Technology and Higher Education Republic of Indonesia via Research Grant of Penelitian Unggulan Perguruan Tinggi (PUPT) with contract number: 176-07/UN7.5.1/PG/2016. The author also thanks to Iqbal Firdaus for conducting experiment in the some part.

References
[1] Goodenough J B and Kim Y 2010 Chem. Mater. 22 587
[2] Zhang S S 2007 J. Power Sources 164 351
[3] Costa C M, Gomez Ribelles J L, Lanceros-Méndez S, Appetecchi G B, Scrosati B 2014 J. Power Sources 245 779
[4] Zhang X, Ji L, Toprakci O, Liang Y, Alcoutlabi M 2011 Polym. Rev. 51 239
[5] Zhang F, Ma X, Cao C, Li J and Zhu Y 2014 J. Power Sources 251 423
[6] Navarro N H, Gonzalez V G, Moreno-Cortez I E, Garza-Navarro M A 2016 Mater. Lett. 167 34

Figure 5. Coulombic efficiency of LiFePO₄ cells containing PVdF nanofiber and PP-microporous at 1C rate.