Fabrication of PVDF/SiO₂ Nanofiber Membrane as A Separator of Li-ion Battery by Double Jet Sprayers Electrospinning Method

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Abstract. The temperature of the lithium-ion battery while running the electric vehicle becomes a severe safety issue. One way to keep the battery work at high temperatures is by a modified battery separator. The separator was used as a component to secure the battery by preventing short circuit current between the electrodes of opposite polarity. This current research reported the high-temperature shrinkage and excellent mechanical strength membrane separator based on PVDF/SiO₂ nanofiber produced by double jet sprayers electrospinning method on rotating cylinder collectors. The independent variable in this research was the variation of a SiO₂ polymer at 0 ppm, 500 ppm, 1000 ppm, and 3000 ppm. The results of PVDF/SiO₂ nanofiber formed have beaded fiber structure with the average size of fiber's diameter of ~192 nm. The highest amount of SiO₂ addition (SiO₂ 3000 ppm) on PVDF nanofiber's membrane causes an increase of porosity up to 69%. The addition of SiO₂ also strengthens its mechanical and thermal shrinkage properties to 150°C. In the testing of the charge-discharge battery using separator PVDF/SiO₂ nanofiber, the specific capacity value is 181 mAh/g.

1. Introduction

The application of lithium-ion batteries as batteries for high operating systems such as electric cars requires modification of battery components. Fire is prone to occur in high operating systems on cells due to conditions that are high temperature. So needed a battery that has excellent electrochemical and safety characteristics. There are two ways to produce lithium-ion batteries, which have these characteristics: first, converting liquid electrolytes to solid electrolytes, second, using separators that are stable to high temperature [1].

The separator is a component of the lithium-ion battery between the cathode and the anode; its function is to prevent physical contact between the anode and the cathode. The characteristics of the separator have pores that allow lithium ions to move from both electrodes. At the same time, the separator also has functions to prevent electrons' flow from both electrodes [1] and the short-circuiting. The separator does not carry out electrochemical reactions. A suitable separator has the characteristics
of a uniform microstructure [2], high porosity, high electrolyte absorption [3], resistance to high temperatures [4], and robust mechanical properties [3].

At present, the commercial separator material uses raw materials including polyethylene (PE) and polypropylene (PP). However, PE and PP based separators have low porosity and cannot resist high temperatures. PE and PP based separators also have melting points of 135 °C and 165 °C, respectively [4]. If the two separators are used in batteries that work on high operating systems (temperature average at 150 °C), then the separators will be at a temperature condition approaching their respective melting points. This can cause the separator pores to close and inhibit the flow of lithium-ion, causing a short-circuit flow, fire and explosion in the lithium-ion battery. PE and PP based separators cannot be used as ion-lithium battery separators for high operating systems. Lithium-ion used batteries in electric cars are demanded to be able to work up to temperatures of 150 °C. This research to make a separator with characteristics having stability to temperatures above 150 °C.

Polyvinylidene fluoride (PVDF) is a polymer material that is being developed in the research of making separators. This polymer has a higher melting point than PE and PP which is 177 °C. PVDF based separators provide opportunities as battery separators that are capable of working in high operating systems. PVDF materials need to be modified to be able to be used as a battery separator. That modifies material to nanofiber membrane as a separator battery. To improve the performance of separators, the process of combining PVDF with inorganic material, are colloidal silica (SiO₂), which is carried out. SiO₂ colloids are able to increase the resistance of nanofiber membranes to high temperatures, improve mechanical properties, porosity and electrolyte absorption [2].

Electrospinning is a technique often used to produce nanofibers. However, in the production of composite nanofibers such as PVDF/SiO₂, the addition of inorganic material interferes with the electrospinning process when direct mixing is carried out between the PVDF solution and the colloidal SiO₂. Chemical interaction between both solutions will form a lump that causes the solution to become cannot be homogeneous. Homogeneity of the solution affects the electrospinning process. Therefore in this study, a modification of the electrospinning technique was carried out using double jet sprayers so that there was no direct mixing of the two solutions. PVDF/SiO₂ nanofiber membrane was synthesized at different concentrations of SiO₂ colloids. The physicochemical properties such as morphology, porosity test, thermal shrinkage ratio test and mechanical properties test of the nanofiber membrane separator, as well as the electrochemical property of the lithium-ion batteries by applying the produced separator were systematically investigated.

2. Experimental section

2.1. Materials
Polyvinylidene fluoride polymer (PVDF) ((C₂H₂F₂)n, Mw 534,000, Aldrich, France) as the main material for synthesis nanofiber membranes. Dimethylformamide (DMF) (C₃H₇NO, Merck, Germany) and acetone (C₃H₆O, Merck, Germany) are used as PVDF solvents. Colloid SiO₂ (PT. Dipon Indonesia) and methanol (CH₃OH, Merck, Germany). Butanol (C₆H₉OH, Merck, Germany), 1 M lithium hexafluorophosphate (LiPF₆), LiFePO₄, PVDF binder, acetylene black (AB), N-methyl-2-pyrrolidone (NMP) MTI corp, USA. Celgard 2400 microporous separator membrane (PP-Comm., Celgard, USA).

2.2. Preparation of PVDF/SiO₂ nanofiber
The PVDF/SiO₂ nanofibers were synthesized by firstly, mixing DMF and acetone in a beaker glass (volume ratio of DMF and acetone was 7: 3). Secondly, dissolved PVDF powder as much as 10% of the mass DMF and acetone at 60 °C with stirring 8 hours to get homogeneous solutions. The electrospinning system consists of a rotating cylinder collector, double jet sprayers and DC high-voltage power supplies. PVDF solution is inserted into the syringes, the metal needle is connected to positive DC high-voltage power supplies while the negative DC high-voltage power supplies are connected to a rotating cylinder collector. Collector as a place of formation of nanofiber membranes. In the same way, the SiO₂ colloids are inserted into another syringe the metal needle is connected to
positive DC high-voltage power supplies while the negative DC high-voltage power supplies are connected to a rotating cylinder collector.

PVDF solutions electrospinning process for 2 hours while the SiO$_2$ was only 1 hour, the electrospinning process was simultaneously between PVDF and SiO$_2$ colloids. PVDF solution and SiO$_2$ colloid syringe needling in 17 cm distance from the metal needle to rotating cylinder collector. The collector rotation speed was fixed at 500 rpm and the DC high-voltage used is 15,000 volts. The flow rates of PVDF solutions and SiO$_2$ colloids were controlled by 1.5 ml/h and 0.5 ml/h. The result of the PVDF/SiO$_2$ nanofiber membrane must be dried with the oven at 80 °C for 8 hours.

2.3. Physicochemical characterization

Morphological analysis of PVDF/SiO$_2$ nanofiber membranes using SEM, JEOL JSM-6360 LA, Japan, nanofiber membrane porosity test, thermal shrinkage ratio test and mechanical properties test using Strograph VG 10-E, Japan.

2.4. Electrochemical properties test

A set of coin batteries consists of several components, there is the anode (graphite with copper foil), separator (PVDF/SiO$_2$ nanofiber or PP), cathode (LiFePO$_4$ with aluminum foil) and electrolyte (LiPF$_6$). Before assembling the battery, anode, cathode and separator materials must be heated to temperature 60 °C for 8 hours. Then, all components are assembled in a Vigor Glove Box filled with argon gas with an O$_2$ concentration of less than 1 ppm. The assembly battery components consist of a cap, wave spring, steel plate, cathode, separator and electrolyte, anode and can. Components are assembled together and pressed using Compact Hydraulic Crimping. The performance lithium-ion battery charge-discharge test. The battery tested was modified by using PVDF/SiO$_2$ nanofiber separator. This test is to determine the capacity and voltage of the battery.

3. Results and discussion

3.1. Morphology of nanofiber membrane separators

Nanofibers are composed of fibers continuous and connect with one another to form pores between these fibers. Figures 1 show the morphology of the nanofiber membrane which was beaded fibers. Forming beads is not expected because it reduces the uniformity of the nanofiber microstructure. The appearance of separator nanofiber membrane beads is influenced by the electrospinning process. The emergence of beads is caused by the flow rates of the solution is not constant because a small portion of PVDF solutions forms a gel when in contact with air, and disrupts the flow of the solution because it inhibits the flow of the polymer. Gel polymer will be pushed from the syringe to the collector so that beads are formed.

![Figure 1. SEM images of nanofiber membrane (a) pure PVDF and (b) PVDF/SiO$_2$ (SiO2 3000 ppm)](image-url)

The addition of SiO$_2$ colloids affects the morphological changes of the separator nanofiber membrane. In figure 1(b) it looks different due to the addition of SiO$_2$ colloids. Seen SiO$_2$ is on the sidelines of the fiber. Based on the SEM image of the PVDF/SiO$_2$ nanofiber membrane, the average size of the fiber diameter is ~192 nm.
3.2. Thermal shrinkage ratio

The durability of the PVDF/SiO$_2$ nanofiber separator and PP (commercial) separator have been tested to a high temperature, by heating the membrane separator at 150 °C for 30 minutes. The membrane separator is cut in a circle with a diameter of 2.70 cm. Thermal shrinkage ratio calculated using equation 1. Membrane shrinkage results in Table 1.

\[
S = \frac{A_b - A_a}{A_b} \times 100\%
\]

Where $A_b$ is the surface area nanofiber membrane before heated and $A_a$ surface area nanofiber membrane before heated [6].

There is membrane shrinkage in the PP, PVDF nanofiber membrane without SiO$_2$ colloidal and PVDF/SiO$_2$ 500 ppm. The shrinkage that occurs in PP is very significant, causing membrane damage. If this shrinkage occurs inside the battery, it will cause a short circuit, a fire and an explosion. Factors that cause PP shrinkage due to the melting point PP 165 °C, so that when the temperature approaches the melting point it will cause a shrinkage of the separator. Thermal shrinkage on the PVDF nanofiber membrane separator is 5.8% and PVDF/SiO$_2$ 500 ppm is 1.4%. Depreciation that occurs in PVDF is insignificant, so it will remain safe despite minor disruptions due to shrinkage. The cause of PVDF nanofiber membrane separator shrinkage due to the PVDF melting point of 177 °C. PVDF/SiO$_2$ nanofiber membrane separator is able to maintain its shape and size due to the influence of SiO$_2$, SiO$_2$ has heat-resistant properties because SiO$_2$ has a melting point of 1710 °C [5].

Table 1. Thermal shrinkage of membranes at a temperature of 150 °C for 30 minutes

| Membrane          | $A_b$ ($\times 10^{-4}$ m$^2$) | $A_a$ ($\times 10^{-4}$ m$^2$) | $S_a$ (%) |
|-------------------|-------------------------------|-------------------------------|----------|
| PVDF              | 5.73                          | 5.39                          | 5.8 ± 0.05 |
| PVDF/SiO$_2$ 500 ppm | 5.73                          | 5.64                          | 1.4 ± 0.05 |
| PVDF/SiO$_2$ 1000 ppm | 5.73                          | 5.73                          | 0 ± 0.05   |
| PVDF/SiO$_2$ 3000 ppm | 5.73                          | 5.73                          | 0 ± 0.05   |
| PP                | 5.73                          | damaged                       | -        |

Figure 2. PVDF/SiO$_2$ nanofiber at different SiO$_2$ content (0, 500, 1000, 3000 ppm) and PP, before and after heating at 150 °C for 30 minutes

3.3. Porosity membrane separator

The test was carried out by immersing the PVDF/SiO$_2$ (0, 500, 1000 and 3000 ppm) nanofiber membrane separator and PP in the n-butanol solution. The porosity membrane calculated using equation 2. Membrane separator porosity can be seen in Table 2.
\[ P = \frac{W_b - W_k}{\rho V} \times 100\% \]  

where \( W_b \) is wet mass membrane after soaked, \( W_k \) is dry mass membrane before soaked, \( \rho \) is density n-butanol and \( V \) is volume of membrane [7]

**Table 2.** The porosity of membranes separator at room temperature

| Membrane          | Porosity (%) |
|-------------------|--------------|
| PVDF              | 52 ± 6       |
| PVDF/SiO\(_2\) 500 ppm | 58 ± 7   |
| PVDF/SiO\(_2\) 1000 ppm | 62 ± 6   |
| PVDF/SiO\(_2\) 3000 ppm | 69 ± 7   |
| PP                | 38 ± 6       |

The enhancement of the porosity of PVDF/SiO\(_2\) nanofiber separator is caused by 2 factors are fiber size and concentration of SiO\(_2\) colloids. First, the size of the fiber in the PVDF nanofiber membrane separator is ~192 nm. This size is smaller than the PP membrane whose fiber size is ~1 \( \mu \)m [1]. Nanofibers are composed of fibers that are interconnected to form porous membranes. The smaller the size of the fiber produced, the smaller the pore size that forms. The pores in the nanofiber are evenly distributed and have a winding structure. This causes an increase in the separator porosity numbers, this situation supports the ion exchange mechanism process that occurs in lithium-ion batteries. Second, concentration SiO\(_2\) colloids can increase the membrane separator porosity numbers. Increasing the porosity of the membrane separator due to the morphology of the SiO\(_2\) structure is a porous material [8]. Making it possible for electrolyte absorption to occur in pores SiO\(_2\) materials.

### 3.4. Mechanical properties of nanofiber membrane

Testing the mechanical properties of the nanofiber membrane aims to determine the resistance of the nanofiber membrane separator to the influence of forces from inside or outside the battery. The membrane sample form that was tested using a standard ASTM code D638-02A. Mechanical properties consisting of tensile strength and elongation in table 3 and table 4.

**Figure 3.** The membrane sample at ASTM code D638-02A standard form

**Table 3.** Tensile strength test

| Membrane          | Tensile strength (N/mm\(^2\)) |
|-------------------|------------------------------|
| PVDF              | 29.96                        |
| PVDF/SiO\(_2\) 500 ppm | 19.54                        |
| PVDF/SiO\(_2\) 1000 ppm | 38.32                        |
| PVDF/SiO\(_2\) 3000 ppm | 75.79                        |
The nanofiber membrane with the greatest tensile strength in the composition of the 3000 ppm PVDF/SiO$_2$ nanofiber membrane separator. The increase in nanofiber membrane strength is due to an additional increase in the concentration of SiO$_2$ colloid. The addition of SiO$_2$ colloids was able to strengthen the mechanical properties of nanofiber membranes because colloidal SiO$_2$ entered the pore crevices of nanofibers thereby reducing pore size and causing the nanofiber membrane to become tighter. The tight structure of the nanofiber membrane, causing an increase in physical resistance of the PVDF/SiO$_2$ nanofiber membrane separator [9].

The value of elongation ability determines the elasticity of a material. In table 4, the elongation value of the nanofiber membrane separator increases with the addition of SiO$_2$ colloids. The greatest elongation ability in the composition of 3000 ppm PVDF/SiO$_2$, along with the greater resistance to tensile strength, the elongation percentage also increases. Increased membrane elongation is due to an increase in density in the material due to the addition of SiO$_2$ colloids material so that the bond between the molecular chains increases.

**Table 4.** Elongation of nanofiber membranes separator at room temperature

| Membrane           | Elongation (%) |
|--------------------|----------------|
| PVDF               | 4              |
| PVDF/SiO$_2$ 500 ppm | 3              |
| PVDF/SiO$_2$ 1000 ppm | 4              |
| PVDF/SiO$_2$ 3000 ppm | 8              |

3.5. **Lithium-ion battery performance**

This performance test is to determine the value of the discharge capacity (usage) and spare capacity of lithium-ion batteries. Tests are carried out with a fixed current when charging or discharging so will get data charge and discharge obtained each cycle. Battery capacity will decrease with the duration of usage [9]. The lower capacity of the battery decreases during use, the battery is considered to have good quality. The test was carried out using PVDF/SiO$_2$ nanofiber membrane separator (SiO$_2$ 3000 ppm)

**Figure 4.** Testing of lithium-ion battery charge-discharge using a PVDF / SiO$_2$ (SiO$_2$ 3000 ppm) nanofiber separator

The charge-discharge test that was carried out showed that the battery with PVDF/SiO$_2$ nanofiber membrane separator was able to work for 11 charge-discharge cycles, meaning that the battery was able to survive when charging and discharging the battery 11 times. From Figure 4 the test results of the lithium-ion battery charge-discharge with a PVDF/SiO$_2$ (SiO$_2$ 3000 ppm) nanofiber separator obtained a specific battery capacity value of 1.81 mAh/g. This specific capacity value is the value that appears from the first cycle.
The battery performance test also shows the stability of the battery’s specific capacity for 11 cycles. The stability parameter can be seen from the decrease in specific capacity from the 1st cycle to the 11th cycle. Decreased battery specific capacity is shown in table 5. During the testing process, the lithium-ion battery charge-discharge decreased its specific capacity to only 0.53 mAh/g. This value is a reduction in specific capacity between cycle 1 and cycle 11. Decreased capacity in one cycle of normal battery usage occurs. A good quality battery is one that has the lowest specific capacity reduction value.

Table 5. Decreased battery specific capacity for 11 cycles

| Cycle number | Specific capacity (mAh/g) | Cycle number | Specific capacity (mAh/g) |
|--------------|---------------------------|--------------|---------------------------|
| C₁           | 1.81                      | C₇           | 1.33                      |
| C₂           | 1.54                      | C₈           | 1.33                      |
| C₃           | 1.50                      | C₉           | 1.28                      |
| C₄           | 1.46                      | C₁₀          | 1.28                      |
| C₅           | 1.41                      | C₁₁          | 1.28                      |
| C₆           | 1.37                      |              |                           |

4. Conclusion

It was concluded that the PVDF nanofiber membrane has a structure of beaded fibers with an average size of fiber diameter of ~ 192 nm. SiO₂ is on the sidelines of the fiber, increasing porosity up to 69%, strengthening mechanical properties and stable to temperatures of 150 °C for 30 minutes. The specific capacity of the PVDF/SiO₂ nanofiber separator is 1.81 mAh/g with a lifetime of 11 charge-discharge cycles.

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