ABSTRACT

LEE, HUN. Electrospun Nanofiber-Coated Membrane Separators for Lithium-Ion Batteries. (Under the direction of Professor Xiangwu Zhang).

Lithium-ion batteries are widely used as a power source for portable electronic devices and hybrid electric vehicles due to their excellent energy and power densities, long cycle life, and enhanced safety. A separator is considered to be the critical component in lithium-ion rechargeable batteries. The separator is placed between the positive and negative electrodes in order to prevent the physical contact of electrodes while allowing the transportation of ions. In most commercial lithium-ion batteries, polyolefin microporous membranes are commonly used as the separator due to their good chemical stability and high mechanical strength. However, some of their intrinsic natures, such as low electrolyte uptake, poor adhesion property to the electrodes, and low ionic conductivity, can still be improved to achieve higher performance of lithium-ion batteries. In order to improve these intrinsic properties, polyolefin microporous membranes can be coated with nanofibers by using electrospinning technique. Electrospinning is a simple and efficient method to prepare nanofibers which can absorb a significant amount of liquid electrolyte to achieve low internal resistance and battery performance.

This research presents the preparation and investigation of composite membrane separators prepared by coating nanofibers onto polyolefin microporous membranes via electrospinning technique. Polyvinylidene fluoride polymers and copolymers were used for the preparation of electrospun nanofiber coatings because they have excellent electrochemical stability, good adhesion property, and high temperature resistance. The nanofiber coatings prepared by electrospinning form an interconnected and randomly
orientated structure on the surface of the polyolefin microporous membranes. The size of the nanofibers is on a scale that does not interfere with the micropores in the membrane substrates. The resultant nanofiber-coated membranes have the potential to combine advantages of both the polyolefin separator membranes and the nanoscale fibrous polymer coatings. The polyolefin microporous membranes serve as the supporting substrate which provides the required mechanical strength for the assembling process of lithium-ion batteries.

The electrospun nanofiber coatings improve the wettability of the composite membrane separators to the liquid electrolyte, which is desirable for the lithium-ion batteries with high kinetics and good cycling performance.

The results show that the nanofiber-coated membranes have enhanced adhesion properties to the battery electrode which can help prevent the formation of undesirable gaps between the separators and electrodes during prolonged charge-discharge cycles, especially in large-format batteries. The improvement on adhesive properties of nanofiber-coated membranes was evaluated by peel test. Nanofiber coatings applied to polyolefin membrane substrates improve the adhesion of separator membranes to battery electrodes. Electrolyte uptakes, ionic conductivities and interfacial resistances of the nanofiber-coated membrane separators were studied by soaking the membrane separators with a liquid electrolyte solution of 1 M lithium hexafluorophosphate dissolved in ethylene carbonate/dimethylcarbonate/ethylmethyl carbonate (1:1:1 vol). The nanofiber coatings on the surface of the membrane substrates increase the electrolyte uptake capacity due to the high surface area and capillary effect of nanofibers. The nanofiber-coated membranes soaked in the liquid electrolyte solution exhibit high ionic conductivities and low interfacial resistances to the lithium electrode. The cells containing LiFePO₄ cathode and the nanofiber-
coated membranes as the separator show high discharge specific capacities and good cycling stability at room temperature. The nanofiber coatings on the membrane substrates contribute to high ionic conductivity and good electrochemical performance in lithium-ion batteries.

Therefore, these nanofiber-coated composite membranes can be directly used as novel battery separators for high performance of lithium-ion batteries. Coating polyolefin microporous membranes with electrospun nanofibers is a promising approach to obtain high-performance separators for advanced lithium-ion batteries.
Electrospun Nanofiber-Coated Membrane Separators for Lithium-Ion Batteries

by
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DEDICATION

This work is dedicated to my mother Ok-Ja Park for her support, encouragement, and love.
BIOGRAPHY

Hun Lee was born to Mr. Chae-Hwan Lee and Mrs. Ok-Ja Park in Gang-Jin, Jeon-Nam, South Korea on January 27, 1980. He began his undergraduate studies in Textile Engineering at Soong-Sil University (Seoul, South Korea) in 1998. After completing his military service, he graduated with a Bachelor of Science degree in Textile Engineering in 2005. He obtained his Master of Science degree in Organic Materials and Fiber Engineering at Soong-Sil University in 2007. After graduation, he worked as a research assistant in Soong-Sil University. He enrolled in North Carolina State University in 2010 to pursue his doctorate degree in Fiber and Polymer Science. His dissertation research was done under the direction of professor Xiangwu Zhang. His research work focused on the preparation and characterization of composite membrane separators for energy applications.
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CHAPTER 1. Introduction

1.1 Overview on battery

1.1.1 Introduction on battery

An electrical battery consists of one or more electrochemical cells that convert stored chemical energy into electrical energy. Since the invention of the first battery in 1800 [1], batteries have become a common power source for numerous domestic and industrial applications. A battery can operate as a single cell to power a cellular phone or be connected in series to deliver several hundred volts for an uninterruptible power supply system (UPS) or an electric vehicle. Each battery cell consists of at least three or four components following as [1,2]:

a) The anode is a negative electrode. It supplies electrons to external circuit with oxidation during electrochemical reaction. The half-cell with the anode has the lower electrode potential.

b) The cathode is a positive electrode. It accepts electrons from the external circuit with reduction during the electrochemical reaction. The half-cell with the cathode has the higher electrode potential.

c) The electrolyte provides the medium for the transfer of charges in the cell between the anode and cathode. The electrolyte is typically a solvent containing dissolved chemical ions which gives ionic conductivity. It should be a non-conductor of electrons to avoid self-discharge of the cell.
d) The separator should physically and electrically isolate the negative and positive electrodes.

Figure 1.1. Diagram of Galvanic cell [3].

Figure 1.1.1 schematically shows typical Galvanic cell system. It consists of two half-cells connected by a salt bridge or porous membrane that is neutral and takes no part in the reaction. Each cell has the electrode immersed in a different electrolyte containing anions and cations.

1.1.2 Working principle of battery

The battery stores energy in chemical form in its active materials and can convert this to electrical energy typically by means of electrochemical reaction. When the battery cells are fully charged, electrons are rich on the anode making a negative charge and deficient on the
cathode making a positive charge, leading to a potential difference across the cell. During discharging, the surplus electrons flow from the negatively charged anode to the positively charged cathode through the completed external circuit. Positive ions missing electrons are called cation and move toward the cathode through the salt bridge during discharge. Anions are negatively charged ions with excess electrons and attracted toward the anode through the salt bridge during discharge [1,4–6]. As shown in Figure 1.1.1, the reaction at the cathode and anode for this case are oxidation and reduction, respectively.

\[
\begin{align*}
\text{Cathode: } & \quad \text{Cu}^{2+} (aq) + 2e^- \rightarrow \text{Cu} (s) \\
\text{Anode: } & \quad \text{Zn} (s) \rightarrow \text{Zn}^{2+} (aq) + 2e^- \\
\text{Net: } & \quad \text{Cu}^{2+} (aq) + \text{Zn} (s) \rightarrow \text{Zn}^{2+} (aq) + \text{Cu} (s)
\end{align*}
\]

Both reactions simultaneously occur in the battery and are called a redox reaction. The cell voltage is the potential difference between two half-cells under standard conditions. The discharging reaction reduces the potential difference across the cell to zero until the concentration of the active chemicals is completely exhausted. The battery voltage depends on the electrode materials, electrolyte, and environmental conditions, but usually differs from the theoretical voltage [7,8].

### 1.1.3 Types of batteries

Batteries can be classified into primary and secondary batteries depending on the reversibility of the electrode reactions. Primary batteries are designed to be used once and discarded, while secondary batteries are designed to be recharged and used multiple times.
Primary batteries cannot be reliably recharged by running a current into the cell, since the chemical reactions of electrodes are irreversible. In primary batteries, the chemical reactants cannot return to their original position and form. They are useful where long periods of storage with low self-discharge rate are required, such as a smoke detector, alarm, and flashlight for emergency.

Secondary batteries, also called rechargeable batteries, can be recharged by supplying electrical energy to the cell and used again because their electrochemical reactions are electrically reversible. Secondary batteries have higher efficiency in total cost of use and lower environmental impact than disposable primary batteries. There are several different combinations of chemicals for rechargeable batteries, including lead-acid, nickel cadmium (NiCd), nickel metal hydride (NiMH), lithium-ion (Li-ion), lithium-ion polymer (Li-ion polymer) and so forth [2,9–11]. Figure 1.1.2 and Table 1.1.1 show the energy densities and characteristics of the most commonly used secondary battery systems, respectively.

The lead-acid battery invented by the French physician Gaston Plante in 1859 was the first rechargeable battery for commercial use [13,14]. In spite of very low energy-to-weight (volume) ratio, the lead-acid batteries are attractive for use in motor vehicles required to provide the high current because of its low manufacturing cost and high surge current. For example, they are still preferred for hospital equipment, wheelchairs, emergency light, and UPS systems.
The NiCd battery has been used where long life, high discharge rate, and economical price are important, including two-way radios, biomedical equipment, professional video cameras, and power tools. The NiCd battery initially had the highest share of rechargeable market, but it has replaced NiMH in most applications due to its low capacity and toxic metals [15–17].
Table 1.1.1. Characteristics of the secondary battery systems [9-11,13,15-17,19].

<table>
<thead>
<tr>
<th></th>
<th>Lead-acid</th>
<th>NiCd</th>
<th>NiMH</th>
<th>Li-ion</th>
<th>Li-ion polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Energy Density</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Wh/kg)</td>
<td>30 – 50</td>
<td>45 – 80</td>
<td>60 – 120</td>
<td>150 – 250</td>
<td>130 – 200</td>
</tr>
<tr>
<td><strong>Power Density</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(W/kg)</td>
<td>180</td>
<td>150</td>
<td>250 – 1000</td>
<td>1800</td>
<td>130 – 200</td>
</tr>
<tr>
<td><strong>Internal Resistance</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(mΩ)</td>
<td>&lt; 100</td>
<td>100 – 200</td>
<td>200 – 300</td>
<td>150 – 250</td>
<td>200 – 300</td>
</tr>
<tr>
<td><strong>Cycle Life</strong></td>
<td>500 – 800</td>
<td>1500</td>
<td>500 – 1000</td>
<td>1200 – 10000</td>
<td>500 – 1000</td>
</tr>
<tr>
<td><strong>Fast Charge Time</strong></td>
<td>8 – 16h</td>
<td>1h</td>
<td>2 – 4h</td>
<td>2h or less</td>
<td>2 – 4h</td>
</tr>
<tr>
<td><strong>Overcharge Tolerance</strong></td>
<td>High</td>
<td>Moderate</td>
<td>Low</td>
<td>Very low</td>
<td>Low</td>
</tr>
<tr>
<td><strong>Self-discharge/Month</strong></td>
<td>5%</td>
<td>20%</td>
<td>30%</td>
<td>10%</td>
<td>&lt; 10%</td>
</tr>
<tr>
<td><strong>Cell Voltage</strong></td>
<td>2.1V</td>
<td>1.25V</td>
<td>1.25V</td>
<td>3.6V</td>
<td>3.6V</td>
</tr>
<tr>
<td><strong>Operating Temperature</strong></td>
<td>-20 – 60°C</td>
<td>-40 – 60°C</td>
<td>-20 – 60°C</td>
<td>-20 – 60°C</td>
<td>0 – 60°C</td>
</tr>
<tr>
<td><strong>Toxicity</strong></td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
</tr>
</tbody>
</table>
In recent years, lithium-ion batteries have rapidly dominated the power source market for a variety of applications because of their high energy density and excellent cycle life [10,19]. Rechargeable lithium-ion batteries are used in a wide range of devices including portable electronics, medical equipment, and military uses. Currently, lithium-ion batteries are mainly used in hybrid electric vehicles and other large-capacity battery application where safety issues are critical. Figure 1.1.3 illustrates the global market shares based on revenue contributions by different battery systems.
1.1.4 Battery construction

Batteries can be built in a variety of shapes and configurations, depending on their applications. Figure 1.1.4 shows various battery types and their configurations. The battery component should be designed to accommodate a particular cell shape and its application.

Coin cells were developed to minimize battery size and solve stacking problems. Most coin cells have the same basic layout in construction as shown in Figure 1.1.4 a. They use circular discs for the electrodes with a separator between the anode and cathode. They are used for watches, calculators, and memory backup where small size, high capacity and low power are required. Although non-rechargeable type of the coin cell continues to be popular, it has no safety vent and suffers from the swelling problem if charged too rapidly [17,20].

Typical flat stacked cells have been used in lead-acid batteries over a hundred years. The electrodes are made in the form of flat plates and suspended in the electrolyte. Figure 1.1.4 b shows their construction. A separator is placed between the plates to prevent them from physical contact and short circuit. This type of battery can be scaled up to very large size and provide high currents and high storage capacity [12]. They are mainly used in automobile and back-up power supplies for alarm and small computer systems.

In a demand for higher current carrying capacity, it is necessary to increase the active surface area of the electrodes. However, the size of cell case limits the size of electrodes. In order to increase the electrode surface area, the electrode and the separator are made into spiral or cylindrical shape as shown in Figure 1.1.4 c. The cylindrical cell is the most common seen on the consumer market like AA and AAA batteries. The spiral construction provides very low internal resistance cells and increases the current carrying the capacity of
the cells [17,21,22]. It has less space for the electrolyte because the electrodes take up more space in the cell case and thus the potential energy storage capacity of the cell decreases. This cell type is used for high rate discharge applications and can be used in NiCd, NiMH, and even some lead-acid cell as well as secondary cells.

Figure 1.1.4. Battery configurations: (a) coin cell, (b) stack lead-acid cell, (c) cylindrical cell, and (d) prismatic cell.
The prismatic cell was developed in response to consumer demand for thinner pack sizes. It is most common in the lithium battery family. This cell type is used predominantly for mobile phone applications. Figure 1.1.4 d shows typical prismatic cell. The disadvantage of the prismatic cell is slightly lower energy densities compared to the cylindrical equivalent [1,9].

1.1.5 Introduction on lithium-ion battery

A lithium-ion battery is the most popular rechargeable battery for portable electronics because of high energy density, no memory effect, long cycle life, and low self-discharging. The lithium-ion battery typically doubles the energy density of the standard NiCd battery. In addition to high capacity, the load characteristics are reasonably good and show a similar shape of discharge profile to the NiCd batteries. The flat discharge provides effective and stable utilization of the stored power in a desirable voltage spectrum [21,23]. The lithium-ion battery is available in a wide variety of shapes and sizes efficiently fitting the devices used. It has lower self-discharge rate and much lighter weight than other secondary batteries. Components for lithium-ion batteries are environmentally safe due to no free lithium metal. There is no memory effect and no maintenance is required for a long battery life. However, charging forms deposits inside the electrolyte and decreases the capacity of the battery by hindering ion transport [10,24,25]. It leads to the increase in internal resistance and more pronounced in high current applications. If lithium-ion batteries are overcharged, they may suffer from thermal runaway and cell rupture [20,26]. In order to reduce this risk, lithium-ion battery packs should contain a protection circuit that can shut down the battery. This safety
device occupies useful space inside the cell and thus limits the voltage and current of the batteries [1].

Practical lithium-based rechargeable batteries were first proposed by M.S. Whittingham [7] while working for Exxon in the 1970s. Unlike primary batteries, lithium-ion batteries use intercalated lithium compounds as the electrode materials instead of metallic lithium. They were designed to overcome the safety issues associated with the highly reactive properties of lithium metal. In 1991, Sony released the first commercial lithium-ion battery [9]. Since the invention of this chemistry, it has become the most promising and fastest growing on the energy market.

For the last two decades, the rapid growth in energy demands for portable electronic devices, such as mobile phones, digital cameras, and laptop computers, has led to huge development in lithium-ion batteries that provide high energy and power densities with reliability. In addition to energy demands, environmental issue stimulates the intensive efforts to develop advanced batteries for electronic devices.

1.1.6 Working principle of lithium-ion battery

Lithium is the lightest metal and floats on water. It also has the greatest electrochemical potential which makes it one of the most reactive metals [4,27]. These properties give lithium the potential to achieve high energy and power densities in battery applications. Initially commercial cells with metallic lithium anodes were considered unsafe due to the formation of lithium dendrites during charge-discharge processes. However, modern cells are combined with other elements into more benign compounds which do not form dendrites.
Similar to the architecture of basic Galvanic cells, lithium-ion battery consists of three functional components, i.e. an anode (negative electrode), a cathode (positive electrode), and the electrolyte as ionic conductor. Typical lithium-ion batteries use porous carbon as the anode and metal oxide compound for the cathode [26,28–30]. Commercially, the most popular material for the negative electrode is graphite and for the positive electrode is one of three materials: lithium cobalt oxide (LiCoO$_2$), lithium iron phosphate (LiFePO$_4$), and lithium manganese oxide (LiMn$_2$O$_4$) [30–32]. Their properties are summarized in Table 1.1.2 and crystal structures are illustrated in Figure 1.1.5 Lithium ions are assumed to be mobile while transition metal ions are immobile at octahedral sites.
Table 1.1.2. The properties of materials for positive electrode [30,34–37].

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>LiCoO$_2$</th>
<th>LiFePO$_4$</th>
<th>LiMn$_2$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average potential  difference (V)</td>
<td>3.7</td>
<td>3.3</td>
<td>4.0</td>
</tr>
<tr>
<td>Specific capacity (mAh/g)</td>
<td>140</td>
<td>150</td>
<td>100</td>
</tr>
<tr>
<td>Specific energy (kWh/kg)</td>
<td>0.518</td>
<td>0.495</td>
<td>0.400</td>
</tr>
<tr>
<td>Life span</td>
<td>Short</td>
<td>Long</td>
<td>Moderate</td>
</tr>
<tr>
<td>Safety</td>
<td>Poor</td>
<td>Good</td>
<td>Moderate</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>Poor</td>
<td>Very good</td>
<td>Good</td>
</tr>
<tr>
<td>Crystalline structure</td>
<td>Layered</td>
<td>Olivine</td>
<td>Spinel</td>
</tr>
</tbody>
</table>

Since lithium ion violently reacts with water, the electrolyte is composed of non-aqueous organic lithium salts. The electrolyte is typically a mixture of organic carbonates, such as ethylene carbonate (EC), diethyl carbonate (DMC), propylene carbonate (PC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC), containing a complex of lithium ions.
Lithium hexafluorophosphate (LiPF₆), lithium hexafluoroarsenate monohydrate (LiAsF₆), lithium perchlorate (LiClO₄), lithium tetrafluoroborate (LiBF₄), and lithium triflate (LiCF₃SO₃) are used as a lithium salt [38–40]. The electrolyte acts as a conducting medium and takes no part in the chemical reaction.

The voltage, capacity, and cycle life of a lithium-ion battery significantly depend on the materials selected for the components [41,42]. Figure 1.1.6 shows the three participants in lithium-ion batteries during the electrochemical reactions.

![Figure 1.1.6](image_url)  
Figure 1.1.6. Schematic illustration of a typical lithium-ion battery when discharged and charged [41].
Rather than the traditional redox galvanic reaction, the reactions of lithium-ion batteries depend on an intercalation mechanism. Lithium ions are embedded into the crystalline lattice of the positive electrode in the discharged state and into the negative electrode in the charged state, which is known as intercalation [7,43,44].

When the battery is discharged, lithium ions move from the negative electrode to the positive electrode through the non-aqueous electrolyte, carrying the current. During charging, an external electrical power source applies a higher voltage than that produced by the battery, forcing the current to pass in the reverse direction. The lithium ions at this process migrate from the positive electrode to the negative electrode across the electrolyte [21,25,43,44]. For example, for charging in lithium cobalt oxide, the positive and negative electrode half-reactions are:

Cathode: \( \text{LiCoO}_2 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + n\text{Li}^+ + n\text{e}^- \)

Anode: \( n\text{Li}^+ + n\text{e}^- + \text{C} \rightarrow \text{Li}_x\text{C} \)

Net: \( \text{LiCoO}_2 \rightarrow \text{Li}^+ + \text{CoO}_2 \)

These reactions are completely reversible and backward reactions are for discharging.

1.2 Overview on the separator

1.2.1 Introduction on the separator

The separator is placed between the negative electrode and positive electrode as shown in Figure 1.1.6. In lithium-ion batteries, the essential function of separators is to prevent the
physical contact of electrodes while serving as the electrolyte reservoir to enable ionic transport. The separator does not involve itself in any cell reactions, but its structure and properties significantly influence the battery performance, including cycle life, safety, energy, and power densities. A wide variety of factors should be considered for separators used in batteries. The considerations in the selection of the best separator for a particular application include the following:

- Electrochemical stability
- Mechanical properties
- Physical and dimensional uniformity
- High temperature stability
- Electrolyte wettability and retention
- Permeability
- Ionic conductivity
- Safety
- Cost

The order of importance changes with the various criteria, depending on the battery applications. For example, highly porous and thin separators are used for batteries that require small internal resistance and little power, but one for sufficient physical strength requires thick separators. Each battery type has requirements essential for good performance.
and safety. The general requirements that should be considered for lithium-ion battery separators are given in the following section.

1.2.2 Requirements for battery separator

1.2.2.1 Chemical stability

The separators must be chemically and electrochemically stable to the electrolyte and electrode materials in lithium-ion batteries. They should be inert under the strong oxidizing and reducing conditions when the battery is fully discharged and charged. In cell reactions, they should not degrade mechanical strength and produce impurities, which can cause the interference to the function of the battery. In addition, the separators have to withstand the corrosive nature of electrolyte at high temperature.

1.2.2.2 Wettability

The wettability of liquid electrolyte is one of the most important properties for battery separators since the electrolyte absorption is required for ion transport. They have to absorb and retain a significantly amount of liquid electrolyte to achieve low internal resistance and high ionic conductivity. The fast absorption of liquid electrolyte facilitates the process of electrolyte wetting in the battery assembly. The wetting speed depends on the type of the material, porosity, and pore size of the separator [45,46]. Moreover, the cycle life of the battery increases with increasing the retention of liquid electrolyte.
1.2.2.3 Mechanical strength

Mechanical strength is evaluated by the puncture strength and the tensile strength in machine direction (MD) and the transverse direction (TD). The tensile strength is described by Yong’s modulus in machine direction because the separators must be strong enough to withstand the tension of winding operation during battery assembly. The puncture strength is defined by the maximum load required for a needle to penetrate a given separator [45]. The separator should have high puncture strength to withstand the penetration of electrode material. If particular materials from the electrodes pass through the separator, it leads to electrical short circuit and the battery will fail.

1.2.2.4 Thickness

Rechargeable batteries use the separator which is less than 25 µm in the thickness for general applications [47,48]. If the separator is thin, it shows high ionic conductivity, energy and power densities. However, thin separators may have adverse effects on the mechanical strength and safety. On the other hand, thicker separators give greater mechanical strength during cell assembly and ensure safer battery. In addition, the uniformity of thickness plays critical role in stable and long cycle life of the batteries.

1.2.2.5 Dimensional stability

The separators should be flat and not curl up when they are laid out and immersed with liquid electrolyte. The bow and skew of the separators can cause misalignment between the
separator and the electrodes during battery assembly [45,49]. Also, the separators must not shrink in high temperature.

1.2.2.6 Shutdown

For battery safety, the separator should be able to shut the battery down when overheating occurs, such as the occasional short circuit in lithium-ion batteries. So, thermal runaway can be avoided. The shutdown function should not be achieved through mechanical integrity, which causes the direct contact of electrodes. It usually takes place when the pores are closed and it blocks ionic flows at certain temperature close to the melting point of the polymer [46,49,50]. At this temperature, the impedance of battery significantly increases and the current passage is restricted. Hence, it stops electrochemical reactions in the batteries and shuts batteries down before an explosion occurs. It can be obtained by a multilayer design of the separator, in which at least one layer melts to close the pores below the thermal runaway temperature and the other layer provides mechanical strength. For the shutdown temperature, 130 °C is desirable to control the heating and avoid thermal runaway [45,46].

1.2.2.7 Thermal stability

The separators must not shrink and wrinkle significantly when the temperature rises although pores are closed and the porosity decreases. The thermal shrinkage during drying process for battery assembly should be minimized. The requirement of thermal shrinkage is generally less than 5% after 60 min at 90 °C in a vacuum [46,49].
1.2.2.8 Porosity

The separators should have appropriate porosity to retain adequate liquid electrolyte. It is very important for the ionic conductivity of batteries. If the porosity is too low, it leads to high electrolyte resistance because of insufficient liquid electrolyte between positive and negative electrodes. However, too high porosity adversely impacts the battery performance because it causes low mechanical strength and inefficient shutdown property. Also, the separator with high porosity tends to shrink easily when temperature increases. Non-uniform porosity leads to non-uniform current density and reduces the performance of batteries because the electrodes to contact parts with non-uniform structure might work harder compared with regular parts [47,51]. The porosity of a separator is determined by the ratio of void volume to apparent geometric volume [50]. It is usually calculated by following equation:

$$ Porosity (%) = \left( 1 - \frac{\rho_M}{\rho_P} \right) \times 100 $$

where $\rho_M$ is the membrane separator density and $\rho_P$ is the polymer density. The actual porosity is determined by the weight of the separator before and after the absorption of a liquid as following equation:

$$ Porosity (%) = \frac{W/\rho_L}{W/\rho_L + W_o/\rho_P} \times 100 $$
where $W$ and $W_0$ represent the weights of the separator after and before immersing a liquid, respectively. $\rho_L$ and $\rho_P$ are the densities of a liquid and the membrane separator. In this calculation, it is assumed that the volume occupied by the liquid is equal to the porous volume of the separator. The percent of porosity for lithium-ion battery separators is typically 40% [52].

1.2.2.9 Pore size

The pore size of separators is a key characteristic. It should be small enough to block the penetration of particles, including the electrode components like active materials and conducting additives. Uniform distribution and tortuous structure of the pores contribute to the inhibition of dendritic lithium and prevent particles from penetrating the separator [46,53]. Typically, submicron pore size is desirable for lithium-ion batteries.

1.2.2.10 Permeability

The separator must not restrict the electrical performance of the batteries. The presence of the separator between the electrodes has adverse impacts on the resistance of electrolyte. The permeability of the separator is described by MacMullin number which is the ratio of the resistance of the separator immersed with liquid electrolyte to the resistance of the electrolyte alone [45]. The MacMullin number should be lower for a long cycle life and safety, especially in hybrid electric vehicles. The MacMullin number is proportional to air permeability and thus it can be expressed by the Gurley value [49,50]. The Gurley value measures the time required for air to pass through unit area of the separator under a fixed
pressure [45,47]. If the porosity and thickness of the separator are given, the Gurley value means the tortuosity of the pores. If the Gurley value is low, the separator has high porosity and lower tortuosity. In addition, the uniform permeability of a separator is critical for a long cycle life because non-uniform permeability leads to uneven distribution in current density and the dendritic formation on the electrodes [45,50,54].

1.2.3 Types of separators

Battery separators can be largely divided into three types: microporous polymer membranes, non-woven mats, and composite membranes, depending on their composition and structure. Each type respectively possesses intrinsic features to satisfy requirements as the battery separator, including thickness, porosity, thermal property, wettability, mechanical, and chemical properties. In most commercial lithium-ion batteries, microporous polyolefin membranes have been widely used as the separators because of their comprehensive advantages in operating, performance, and safety. However, there has been a variety of new developments and they can still be improved in mechanical and chemical properties as battery separators.

1.2.3.1 Microporous separators

Microporous polymer membranes are usually made of polyethylene (PE), polypropylene (PP), and their combinations such as PE/PP and PP/PE/PP. Other polymers such as isotactic poly(4-methyl-1-pentene [55], polyoxymethylene [56,57], PE-PP blend [58–61], polystyrene
(PS)-PP blend [62], and poly(ethylene terephthalate (PET)-PP blend polymers [62] have been used for preparing microporous membranes.

Bierenbaum et al. [63] reviewed the process, physical and chemical properties, and the application of microporous polymer membranes as battery separators. The commercial PP and PE microporous membranes were investigated in terms of dimensional structure, porosities, permeability, mechanical strength, thermal properties, and electrochemical properties of microporous membranes [47,64–67].

Microporous membranes can be prepared by two different manufacturing methods: wet process and dry process. The both manufacturing methods basically involve an extrusion step to prepare polymer thin film and orientation steps to form porous structure. Microporous membranes made by dry process are slit-like pores in shape, while those from wet process show interconnected and elliptical pores. Figure 1.2.1 shows the microstructures of membranes made by dry process and wet process. The membranes formed by the dry process are more appropriate for high power density batteries because of their open and straight porous structure. On the other hand, the membranes made by the wet process are more suitable in long cycle life batteries because interconnected pores and tortuous structure are benefit in preventing the growth of dendritic formation during charging and discharging.
Figure 1.2. SEM images of membranes made by (a) dry process and (b) wet process [46].

The dry process [55–57,59,60,62,65,68–79] generally consists of extruding, annealing, and stretching steps. In the initial extrusion step, the polymer melts and is extruded into polymer films with uniaxial lamellar structure. The resulting films exhibit a nonporous structure with lamellae arranged in row direction. The annealing step is the process to improve the crystalline structure of the polymer film and thus facilitates the formation of porous structure in the stretching step. The annealed films are then stretched along machine direction to form micropores. Figure 1.2.2 shows the microstructure of polymer films before and after stretching. The polymer film before the stretching process shows a stacked lamellar morphology oriented along transverse direction (Figure 1.2.2 a). After stretching, the stacked lamellae are apart from each other and form pores oriented in machine direction (Figure 1.2.2 b).
Figure 1.2.2. The microstructure of polymer films: (A) before stretching and (B) after stretching [54].

This stretching step is composed of cold stretch, hot stretch, and relaxation that is heat treatment to reduce internal stresses in the membrane. The porosity of the membrane depends on the morphology of extruded film, annealing and stretching conditions, including annealing temperature, annealing time, and drawing ratio. There are uniaxial [55–57] and biaxial stretches [59,75,80] adopted in the industry, but the uniaxial stretching method has been more successful to date. The tensile strength of membranes made by uniaxial stretches is anisotropic in machine direction and transverse direction. Also, its pore shape is oriented in machine direction because of the stretching in machine direction. It is desirable that higher tensile strength in machine direction than transverse direction for handling the separators during battery assembly. This method is technologically convenient since no solvents are used during the process. Celgard LLC [81–84] and Ube Industries [85] provide PP and PE microporous separators obtained by dry process.
The wet process [58,61,63,80,86–91] employs the same principle with the solvent extraction. This process generally includes three steps. The first step is the mixing of polymer resins, hydrocarbon liquid, and other additives and heating them to form a homogenous solution. The second step is to extrude the solution into films and finally the liquid and other additives are extracted by a volatile solvent to form the microporous structure. A stretching step can be added before or after the extraction step for high porosity and large pore size. The microstructure and properties of the membranes depend on controlling the composition of the solutions and the extraction of solvents. The SEM images of separators by wet process are shown in Figure 1.2.3. The pore structure of all the membranes exhibits distinct differences in the orientation of pores, pore size, and pore shape.

Weighall [92] reviewed the manufacturing of microporous PE membranes by wet process. Ihm et al. [93] investigated the effect of polymer blending and drawing conditions in wet process on the mechanical properties of PE separators. The mechanical strength increased with increasing the molecular weight of high density polyethylene (HDPE) and the content of ultra-high molecular weight polyethylene (UHMWPE). The membranes made by stretching after extraction showed larger pore size and the wider distribution of pore size than those prepared by stretching before extraction step.
Chung et al. [95] suggested polyethylene tetrafluoroethylene (FTFE) microporous separator by wet process. It improved the membrane performance in discharging voltage and capacity because of a unique ETFE microporous structure.

The membranes consisting of the multilayer of PP and PE have been designed as a thermal shutdown separator with safety advantage. Many patents for PE-PP bilayer [75,79,96] and PP-PE-PP trilayer [76–79,85,97–99] have been reported by separator
manufacturers. In those multilayer structures, the impedance of the separator increases with increasing temperature because the PE layer melts and fills in pores. On the other hand, the PP layer still remains their dimensional structure and mechanical strength preventing a short circuit between electrodes. Hence, such a structure can provide the assurance about safety issue and sufficient mechanical strength. It was described that trilayer structures have higher puncture strength than single layer.

Kinouchi et al. [100] investigated the effect of additives on PP-PE-PP trilayer membranes. A small amount of metal oxide particles dispersed into two PP layers of membranes and they effectively adsorbed the impurities from polymer resin during manufacturing process, leading to reducing negative impacts on battery performance. In addition, these inorganic fillers increased the wettability and retention of liquid electrolyte.

Polyolefin microporous membranes have been widely used as the separators for lithium-ion batteries due to their suitable properties such as morphologic structure, mechanical strength, and chemical stability. However, their intrinsic natures such as poor thermal stability, low wettability, poor adhesion property, and the insufficiency of high rate performance restrict the high performance in the lithium-ion batteries. To overcome these drawbacks, a variety of polymers have been used for preparing microporous membranes by phase inversion method, including poly(vinylidene fluoride) (PVDF) [101–108], poly(methyl methacrylate) (PMMA) [109–112], and polyacrylonitrile (PAN) [110,113–116].

For a microporous structure, the phase inversion is one of efficient methods using the same principle with the wet process. The phase inversion [117–119] also involves the dissolution of a polymer in a good solvent and the precipitation of the polymer to form the
microporous structure by solvent exchange, which is similar to the wet process. As a result, asymmetrical porous structure is formed by the phase separation and solidification of the polymer, depending on the type and concentration of polymers, temperature, thickness, and solvent type. The membranes made by phase inversion usually shows highly porous morphology on the top surface and distorted cross-sectional structure, whereas the surface on the bottom is a compact structure with hardly distributed pores as shown in Figure 1.2.4.

Figure 1.2.4. SEM images of microporous membranes by phase inversion: (a) Top surface and (b) Bottom surface [120].

This asymmetrical structure fairly limits the application of the membranes prepared by phase inversion because such a compact structure on bottom surface reduces the absorption of liquid electrolyte and hinders ionic flows.

Strathmann et al. [121] studied the formation of asymmetric and symmetric membranes obtained by phase inversion process. They claimed that membrane structures greatly depend
on polymer concentration, the present of additives, temperature, and evaporation time. In order to address the adverse effect in their microstructure, various polymers and solvents were attempted in phase inversion process.

In addition to polyolefin membranes, PVDF membranes have been mainly used as battery separators because they are physicochemically and electrochemically stable in lithium-ion batteries [101–108]. PVDF membranes have great wettability due to good affinity to liquid electrolyte solutions, and show good mechanical strength because of high crystallinity. However, PVDF forms stable LiF by the interaction between lithium ions and the fluorine atoms in PVDF and thus it leads to instability on lithium metal. Microporous PAN membranes can be also utilized as a separator material in lithium-ion batteries [110,113–116]. They exhibit good characteristics such as processability, thermal stability, desirable morphology for electrolyte uptake, electrochemical stability, and compatibility with electrodes. PAN-based membranes show different behavior in ion conduction compared to PVDF-based membranes. It acts as a polymer matrix to maintain liquid electrolyte and participates in lithium ion transport due to interaction between the lithium ion and the C≡N groups of PAN. Furthermore, PAN membranes minimize the formation of dendrite growth during the charging/discharging process of lithium-ion batteries. As a result, the PAN membrane shows a high ionic conductivity and electrochemical stability in lithium-ion batteries. However, it decreases ionic conductivity on long storage due to the leakage of liquid electrolyte. PMMA is commonly used as the host polymer material for the battery separators [109–112] because PMMA has good mechanical properties and high affinity to the liquid electrolyte.
In a number of literatures, the membranes prepared by phase inversion using PVDF, PAN, and PMMA were discussed in terms of the mechanism of membrane formation, its chemical structure, hydrophilicity, morphology, solubility parameters, thermodynamic properties, and polymer-solvent compatibility. Those membranes showed a high equivalent conductivity and good thermal and electrochemical stability. They exhibited high ionic conductivity and adhesion to the electrodes because of the gel phase of polymer membranes. The conductivity of microporous membrane depended on the porosity of membranes and liquid electrolyte used. The membranes provided a shut-down effect which depends on the porous volume.

Lloyd [122] prepared the microporous membranes via solid-liquid phase separation using PP, poly(4-methyl-1-pentene), poly(chlorotrifluoroethylene) (PCTFE), and PVDF. Also, the author used a mixture of isotactic polypropylene-n,n-bis(2-hydroxyethyl) tallow amine for preparing the microporous membrane by phase separation [123].

Magistris et al. investigated the microstructure of PVDF [104] and PVDF-co-HFP [124] membranes prepared by a phase inversion method. The morphologies of membranes were divided into the sponge-like and the finger-like structures. They claimed that the electrolyte solution mainly goes into the porous structure and it gives swollen gel phase in polymer membranes, increasing the ionic conductivity.

The high crystallinity of the polymer membranes is one of major factors to lower the ionic conductivity of lithium-ion batteries. Since the crystalline region of the polymer membranes hinders the migration of lithium ions, the battery cells with those membranes exhibits low charge/discharge capacity and poor C-rate value [45,46,111,114,124].
In order to address these problems, copolymers have been utilized as materials for battery separators, including poly(ethylene-co-methyl acrylate) (PE-co-MA) [125], Poly(methyl methacrylate-acrylonitrile-vinyl acetate (PMMA-AN-VAc) [126], polyacrylonitrile-methyl methacrylate (PAN-MMA) [127], poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) [124,128,129], poly(hydroxyethyl acrylate-co-acrylonitrile) (PHEA-co-AN) [130].

PVDF-co-HFP has drawn much attention as separator material for lithium-ion batteries because it has high affinity to liquid electrolyte solution, high ionic conductivity, good electrochemical stability, and desirable adhesion with the electrode. The amorphous HFP phase helps to capture large amount of liquid electrolyte while the PVDF crystalline phase acts as a mechanical support for the polymer membrane. PVDF-co-HFP also has high dielectric constant and electron withdrawing fluorine atoms in the polymer backbone. This feature is advantageous to dissociate the lithium salt to lithium ions while transforming into electrolyte [128,129,131].

Highly porous PVDF-co-HFP membranes were prepared by using phase inversion method and the microstructure and performance were reported by Shi et al. [128]. The processing conditions such as temperature and solution composition changed the porous structure of the membranes, including porosity and pore size. Small pores with narrow distribution were good in maintaining the liquid electrolyte and high porosity showed high conductivity. Shi et al. suggested that porosity should be more than 80% and pore diameter should be less than 1 µm for the ideal separator.

Wu et al. [130] prepared highly porous PHEA-co-AN membranes by the phase inversion method. The ionic conductivity of the microporous was found to be as high as $3.66 \times 10^{-3}$
S/cm. The porous structure of membranes changed from finger-like to honeycomb-like with increasing AN content, leading to high ionic conductivity. The pore size decreased and ionic conductivity was improved as the concentration of polymer solution increases.

Microporous membranes made by polymer blends have been widely reported in order to improve the ionic conductivity by decreasing the crystalline regions of the membranes. These resultant membranes can achieve the combined advantages offered by both polymers, which are mechanical properties, thermal stability, wettability, and electrochemical stability.

Subramania et al. [132] suggested the microporous membranes made by phase inversion using PVDF-co-HFP and PAN blend. It was observed that the ionic conductivity of microporous membranes increases with the increase in PAN content. These blend membranes had thermal stability up to 161 °C and higher specific capacity than the case using PAN or PVDF alone.

Jung et al. [133] prepared microporous PAN/poly(vinylpyrrolidone) (PVP) blend membranes by the phase inversion method. The asymmetric structure of the membranes on the top and bottom grew with the molecular weight of PVP increases. The permeability of membranes increased as PVP content decreases.

PVDF/PMMA blend [134,135] and poly(vinyl chloride) (PVC)/PMMA blend [136,137] were also used for preparing microporous membranes. The microporous structure was formed by casting the polymer solution and extracting additives. The tensile strengths of the membranes were improved by adding PMMA but the melting temperature of membranes decreased as PMMA content increased. The mechanical properties were stable in temperatures ranging from 20 °C to 140 °C. The amorphous phase of the membranes increased with
decreasing PMMA content, which helps the formation of polymer gel electrolytes. With 60% of PMMA in composition, it showed the most favorable ionic conductivity and lithium self-diffusion. The ion conductivity of polymer electrolyte increased with increasing PMMA content in the blend because of the good affinity of PMMA to liquid electrolyte.

The microporous membranes based on the blend of PVDF-co-HFP/poly(methyl methacrylate-co-acrylonitrile-co-lithium methacrylate) (PMAML) [138], PVDF-co-HFP/poly(ethylene oxide-co-ethylene carbonate) (PEO-co-EC) [139] and PVDF-co-HFP/poly(vinyl acetate) (PVAc) [140] were prepared and characterized. The membranes showed high ionic conductivity and good electrochemical performances.

Poly(acrylonitrile-co-butyl acrylate) (PAN-co-BuA) and PVC blend was used for the preparation of microporous membranes by the phase inversion [141]. The mechanical strength of the membranes was found to be much higher than that of pure PAN-co-BuA ones, depending on the composition ratio of blend. The ionic conductivity of membranes was higher than $1.5 \times 10^{-3}$ S/cm and electrochemical stability was up to 4.8 V. The results were attributed to PAN-co-BuA acting as a conducting channel and PVC which improves mechanical strength.

The microporous membranes based on PVDF-co-HFP and cyanoethylated cellulose derivative (DH-4-CN) were obtained and characterized by Ren et al. [142]. The tensile strength and thermal property were improved with the increase of DH-4-CN. The ionic conductivity of the membranes showed a maximum result in the ratio of 14:1 for PVDF-co-HFP/DH-4-CN, which depends on the porosity of the membrane.
One of the other advanced methods to enhance physical and chemical properties as the battery separator is to add various fillers into microporous membranes. It was reported that the nanosized inorganic fillers such as aluminum oxide (Al$_2$O$_3$) and titanium dioxide (TiO$_2$) can improve the mechanical strength, thermal stability, and ionic conductivity [143,144]. The addition of inorganic fillers into polymer membranes can also reduce their crystallinity that hinders the migration of lithium ions. Although the addition of particles leads to less homogenous in the morphology of polymer membranes, they result in excellent exceptional wettability due to high hydrophilicity and high surface area of particles.

Many researchers used magnesium oxide (MgO) [145], lithium aluminate (LiAlO$_2$) [145,146], Al$_2$O$_3$ [145], and montmorillonite clay (MMT) [111] as inorganic fillers into PVDF-co-HFP membranes. The inorganic powders were dispersed into PVDF-co-HFP solution in fixed ratio of the inorganic powder to polymer. The PVDF-co-HFP/inorganic filler solution was spread over a glass using a calibrated slit and dried to form self-standing and intrinsically porous membranes. The electrochemical stabilities and ionic conductivities of each membrane were investigated and the membrane based on PVDF-co-HFP with MgO had the best results. However, resultant membranes exhibited the formation of dense polymer phase which inevitably causes the difficulty in filling with liquid electrolyte.

To overcome this problem, phase inversion method was applied for the fabrication of microporous PVDF-co-HFP membranes filled with silicon dioxide (SiO$_2$) [147–149], TiO$_2$ [150,151], and zirconium dioxide (ZrO$_2$) [152]. They successfully produced stable porous structure, mechanically and thermally reinforced by inorganic content. The membranes attained good pore structure and uniform pore size when using acetone as the solvent and de-
ionized water as the non-solvent. The microporous membranes obtained by the phase inversion showed better properties in terms of wettability, ionic conductivity, electrochemical and interfacial stability than cast films because of highly porous structure of phase inversion membranes. In addition, the wettability of the membranes increased with inorganic particles because the crystallinity of membranes reduced with increasing inorganic content. The membranes incorporated with inorganic particles showed high ionic conductivity in the order of $10^{-3}$ S/cm.

The effects of Al$_2$O$_3$ particles were studied on the preparation of PVDF [153] and PVDF-co-HFP [154] membranes by the phase inversion. The crystallinity of the membranes decreased with the addition of Al$_2$O$_3$ particles and the amorphous phase expended. It was found that ionic conductivity and lithium ion transference number increase with increased fraction of Al$_2$O$_3$ particles because Al$_2$O$_3$ particles weaken the interaction between lithium ions and fluorine atoms in PVDF polymer chains. Moreover, the membranes containing smaller particles showed high electrolyte retention and excellent cycling performance.

Huang et al. [155] reported the preparation of microporous membranes with PVDF-co-HFP/PS blend and SiO$_2$. The porosity of the membranes increased with increasing amount of PS, leading to higher conductivity.

Sundaram et al. [156] also described the preparation of microporous membranes based on PVDF-co-HFP/PVA blend and LiAlO$_2$ through the phase inversion method. It showed the improvement in the electrolyte uptake and ionic conductivity because of the increment in porosity and pore size.
1.2.3.2 Non-woven separators

Non-woven separator is a fibrous structure that is directly manufactured from numerous fibers. It can be defined as the membrane made by bonding randomly oriented fibers through chemical and mechanical methods. The fibers for manufacturing the non-woven separators are of natural and synthetic materials, including cellulosic materials and their derivatives [157–159]. In the last few decades, many patents have been published on manufacturing methods using various synthetic materials, including polyolefin [160–165], polyamide (PA) [166,167], polytetrafluoroethylene (PTFE) [168], PET [169], polyester (PES) [170,171], PVC [172,173], PVDF [172,174] and so forth.

The fibrous membranes can be prepared by dry process such as melt-blown method [162,164,165,175–177] and wet process such as wet laid method [158,170,178–180] and papermaking process [160,172]. The melt-blown method is a binderless process which can be divided by two steps, forming a fibrous web and bonding the fibrous web. First, melted polymer is extruded through a spin net or die having holes to form a polymer web consisting of numerous fibers. In the second step, the resultant web is collected into rolls and subsequently bonded by calendaring at high temperature and pressure to form the non-woven mat with sufficient mechanical strength. The wet process uses a resin or a thermoplastic fiber as an adhesive. The adhesive is sprayed onto a fibrous web and then cured with heat and pressure to bond the base fibers with the adhesive. The properties of the final non-woven mats depend on various parameters such as polymer materials, their composition, temperature, and pressure. It is difficult to control the pore size, thickness and uniformity in
the porous structure of non-woven mats. In general, they have relatively large fiber diameter and thickness which are inappropriate for battery separator.

In order to reduce fiber diameter and thickness with good mechanical strength, electrospinning method has been adopted to produce the highly porous non-woven separators. The polymer membrane can be also prepared by electrospinning the polymer solution. Electrospinning is fundamentally different from other mechanically driven spinning techniques. The electrospinning method is known to be a simple and efficient technique for preparing polymer membranes consisting of fibers with diameters in the range of several micrometers down to tens of nanometers. The details for the electrospinning technique are discussed in a later section. Electrospun nanofibrous membranes have many advantages as battery separators, which are high porosity, small pore size, interconnected open pore structure, high permeability, and large surface area.

As shown in Figure 1.2.5, electrospun membranes have high porosity and an interconnected open pore structure and thus the electrolyte solution can be easily absorbed and encapsulated within the membranes. Moreover, such a structure with high porosity and large pore size is very beneficial for preventing the growth of dendritic lithium in rechargeable batteries. As a result, these effects can contribute to a high ionic conductivity and good battery performance, which is suitable for lithium-ion batteries.
PVDF is an excellent material candidate for non-woven battery separators because it has good electrochemical stability and affinity for lithium ion. Kim et al. [184] proposed an electrospun PVDF nanofibrous membrane as a battery separator. The nanofiber membranes showed high electrolyte uptake and thus good ionic conductivity because of the high porosity with great surface area and the swelling ability of PVDF fibers. Figure 1.2.6 shows the SEM images of the swollen fibrous membranes with immersing in liquid electrolyte. The membranes were swollen with increasing average fiber diameters but it maintained the pore

Figure 1.2.5. SEM images of non-woven separators: (a) Wet laid [181], (b) Melt blown [182], and (c) Electrospinning [183].
structure with high porosity. Their ionic conductivity increased with decreasing the average fiber diameters of dried fibers. The author claimed that the interaction between the liquid electrolyte and the high crystalline PVDF has a minor effect on the lithium ion transfer because liquid electrolyte hardly passes through the crystalline region of the fibers.

Figure 1.2.6. SEM images of the electrospun PVDF membranes (a) before and (b) after absorbing liquid electrolyte [184].

Choi et al. [185] prepared electrospun PVDF membranes and investigated their physical and electrochemical properties. After immersing in a liquid electrolyte, the membranes were partially swollen and still supported their structure with mechanical strength because of three-dimensional network structure with fully interconnected fibers. The electrochemical properties of the electrospun membranes mainly depended on the liquid phase of electrolyte held in the porous structure and marginally swollen phase on the surface of electrospun nanofibers. Moreover, the gel phase formed by the swelling of electrospun fibers leaded to
the enhancement of the electrochemical stability. Ionic conductivity decreased with increasing the crystallinity of the membranes.

The morphology and crystal structure of electrospun PVDF membrane were investigated by Gao et al. [186] to understand the problem of poor physical properties of the membrane. The electrospun membranes exhibited the weaken crystallinity but highly oriented molecular chains which cause the increment in mechanical properties. The tensile strength of the membranes increased with decreasing fiber diameters because fibers with smaller diameters were prepared under a higher applied voltage which means high draw ratio. Since high porosity and uniform pore distribution of electrospun membranes with smaller diameters can suppress mechanically lithium dendrites, the electrospun membranes exhibited good cycling behavior.

Modified electrospinning set-up was proposed to prepare PVDF membranes. The spherical hat [187] and collector rotational [188] drum were applied in the electrospinning system instead of conventional plane collector. Resultant membranes showed high porosity and more uniformity in the thickness and fiber diameters and thus it increased the mechanical strength and improved discharge capacity. Choi et al. [188] carried out a thermal treatment on electrospun membranes to enhance their physical properties and dimensional stability. The mechanical strength of the membrane was improved by thermal treatment because the crystallinity increased. The ionic conductivities of the polymer electrolyte from the electrospun PVDF membranes were $1.6 \times 10^{-3} - 2.0 \times 10^{-3}$ S/cm.

Lee et al. [189] prepared electrospun PVDF membranes and employed hot pressing method for cell assembly to reduce the deformation in porous structure of the membranes at
high rate. They made prototype cells consisting of the electrospun PVDF membranes sandwiched between the anode and the cathode by hot pressing. Pressing membranes led to lower capacity due to the reduction of membrane porosity and electrolyte uptake.

Although the electrospun membranes based on PVDF homopolymer has high crystallinity which is beneficial for mechanical properties, such a high crystallinity causes low ionic conductivity and low stability due to the reduction in the migration rate of lithium ions. One of effective methods for lowering PVDF crystallinity is to use suitable PVDF copolymer and modified PVDF with electrospinning technique.

Kader et al. [190] suggested poly(vinylidene fluoride)-graft-poly(tert-butyl acrylate) (PVDF-g-tBA) membranes fabricated by electrospinning. The graft copolymer decreased the crystallinity of the membranes. Therefore, PVDF-g-tBA based electrospun membranes exhibited better ionic conductivity, electrochemical stability, and cycling performance.

Electrospun PVDF-co-HFP membranes were prepared and their physical and electrochemical properties were investigated for application to battery separators [191–193]. Resultant membranes formed fully interconnected porous structure with uniform morphology. The electrospun membranes showed excellent electrochemical properties of ionic conductivity at room temperature because electrolyte uptake increased with high porosity and good affinity of PVDF-co-HFP to liquid electrolyte.
Figure 1.2.7 shows the swelling behavior of electrospun PVDF-co-HFP membranes by absorbing liquid electrolyte. Similar to PVDF nanofibers, the average fiber diameter in the membranes greatly increased after immersing it in liquid electrolyte, which indicates that the liquid electrolyte well penetrated in amorphous region of polymer fibers and the membranes were swollen. The amorphous swollen phase of electrospun PVDF-co-HFP membranes can easily uptake liquid electrolyte solution and prevent its leakage. The membranes exhibited stable charge/discharge properties with little capacity fading. They claimed that it is attributed to a heterogeneous gel structure of PVDF-co-HFP based electrospun membranes formed when they absorb liquid electrolyte. As absorbing liquid electrolyte, PVDF-co-HFP polymers on the surface of electrospun fibers are swelled and formed gel phase, while the solid phase in the core of PVDF-co-HFP fibers plays the role in mechanical support to give a good cycle performance.
Kim et al. [194] also incorporated a room temperature ionic liquid (RTIL) into polymer electrolytes by using electrospun PVDF-co-HFP membranes. It is effective method to improve the electrochemical stability and compatibility of lithium metal electrodes. Moreover, the addition of RTIL relieves safety concerns because of intrinsic properties of RTIL such as negligible vapor pressure and high thermal stability. The cells based on electrospun PVDF-co-HFP membranes incorporated with RTIL exhibited good cycle stability and high discharge capacity.

Electrospun membranes of PAN have been proposed as battery separators by several research groups [195–199] because PAN has superior characteristics in mechanical stability and lithium ion transport. The studies reported that PAN based membranes provide sufficient mechanical strength due to the interaction of adjacent nitrile (C≡N) groups in PAN polymer chains. Since highly polar nitrile groups hinder the arrangement of polymer chains during electrospinning, a flexible membrane made up of nanofibers with amorphous structure was prepared with good mechanical strength and porosity. The PAN membranes showed high electrolyte uptake and high ionic conductivity because of the highly porous structure and polymer gel phase formed into amorphous region. Furthermore, the interaction between the nitrile group in PAN and lithium ion in the electrolyte contributed to high ionic conductivity. The superior cycle performance and rate capability of cells using PAN membranes was observed. The main reason was their high ionic conductivity arising from high wettability and good retention of liquid electrolyte. In addition, it was found that electrospun PAN membranes maintain their porous structure after charge-discharge tests of over 100 cycles as
shown in Figure 1.2.8. This stability in the morphology of electrospun membrane pretty contributed to stable cycling performance.

![Figure 1.2.8. SEM images of electrospun PAN membranes: (a) pristine membrane, (b) after immersing in liquid electrolyte, and (c) after charge-discharge cycles [198].](image)

In order to improve the affinity to liquid electrolyte and the physical properties, blend polymer solutions have been employed in electrospinning process. Rao et al. [200] made electrospun PAN/PMMA membranes and investigated their properties compared with
Electrospun PAN membranes. Under the same electrospinning conditions, PAN/PMMA membranes showed smaller fiber diameters than PAN membranes, leading to higher porosity. In addition, PMMA in electrospun PAN/PMMA membranes had good compatibility with the liquid electrolytes and offered a good ability to absorb liquid electrolyte. These effects resulted in higher electrolyte uptake than PAN membranes and better ionic conductivity, $3.6 \times 10^{-3}$ S/cm. Consequently, the cells using electrospun PAN/PMMA membranes showed better electrochemical stability, good cycle and rate performances.

Electrospun membranes were also prepared by using blends, such as polyimide (PI)/PVDF [201], PI/PAN [201], PVDF/PAN [202] and PVDF-co-HFP/PMMA [203]. The crystallinities of the membranes were depressed with blending two polymers. The membranes showed good electrolyte uptake, ionic conductivity, and electrochemical properties. Moreover, the mechanical properties of the blend membranes were better than that of electrospun membranes prepared by homopolymer solutions.

Raghavan et al. [204] developed a trilayer membrane consisting PAN nanofibers and PVDF-co-HFP nanofibers via electrospinning. Figure 1.2.9 shows the schematic representation of the trilayer membrane. The membranes exhibited high electrolyte uptake and good ionic conductivity in the range of $10^{-3}$ S/cm because of high porosity resulting from nanofibers. The cells assembled with the membranes showed high electrochemical stability and stable cycling performance with comparable capacity fade.
In the development of promising separators, one of attractive methods is to introduce small inorganic particles into electrospun membranes. Ding et al. [205] proposed one step method for PVDF-based electrospun membranes containing TiO$_2$. They investigated the effect of TiO$_2$ on the morphology of electrospun membranes, crystallinity, and electrochemical properties. The electrospun PVDF membranes containing TiO$_2$ particles exhibited improved ionic conductivity and cycling performance compared to the membranes without inorganic particles.

Raghavan et al. [206,207] described the preparation of electrospun PVDF-co-HFP membranes with inorganic fillers. They incorporated nano-sized particles such as barium titanate (BaTiO$_3$), Al$_2$O$_3$, and SiO$_2$ into the polymer membranes by electrospinning method. The resultant electrospun composite membranes presented good absorption of the liquid electrolyte and high electrolyte retention. Also, the addition of the inorganic particles led to

Figure 1.2.9. Schematics of the trilayer membranes [204].
positive effects on the ionic conductivity and the mechanical properties of the membranes. Moreover, the electrochemical stability and discharge capacities were enhanced by incorporating inorganic particles, especially in BaTiO$_3$. For Li/LiFePO$_4$ cells, the membranes containing BaTiO$_3$ delivered a discharge capacity of 164 mAh/g. The authors also [208] incorporated a RTIL into electrospun PVDF-co-HFP membranes containing inorganic particles. The addition of RTIL and BaTiO$_3$ resulted in high ionic conductivity of $2.1 \times 10^{-3}$ S/cm at room temperature and led to electrochemical stability. The Li/LiFePO$_4$ cells based on the membranes containing RTIL and BaTiO$_3$ exhibited high discharge capacity of 166 mAh/g.

Kim et al. [209] investigated the effect of different composition of SiO$_2$ particles on the structure and properties of electrospun PVDF-co-HFP membranes. The average fiber diameter of the membranes increased with increasing the silica content. The addition of SiO$_2$ particles inhibited the crystallization of electrospun fibers, which is beneficial for achieving higher ionic conductivity. The optimum electrochemical properties were observed in the membranes containing 6% of SiO$_2$. The membranes with 6% SiO$_2$ showed a very stable cycle property, delivering the specific capacity of 170 mAh/g in Li/LiFePO$_4$ cells.

For incorporating inorganic particles, PAN was also used for host membranes. The composite membranes were prepared by using electrospinning method with hydrophilic fumed silica and PAN [210]. The membranes with 12% SiO$_2$ resulted in smaller average fiber diameter and higher porosity. The ionic conductivity of the membranes was $1.1 \times 10^{-2}$ S/cm because of high electrolyte uptake. Furthermore, the electrospun PAN membranes
showed good electrochemical stability and performance when they were incorporated with inorganic particles, especially in 12% SiO$_2$.

Liang et al. [211] also introduced lithium lanthanum titanate oxide (LLTO) into PAN membranes by electrospinning. It was found that the membranes containing 15% of LLTO content provide great electrolyte uptake and higher ionic conductivity, $1.95 \times 10^{-3}$ S/cm. As a result, it led to high discharge specific capacity and good cycling performance.

1.2.3.3 Modified Separators

The most widely used separators in lithium-ion batteries are made of polyolefins, specifically microporous PE and PP separators. However, they provide poor thermal stability, wettability, and electrolyte retention. Various methods to modify the surface of polyolefin separators have been used for improving those properties, including patents [212–216]. Among the numerous methods, grafting the hydrophilic monomers is the simple and effective method for the surface modification, making the surface of the membranes hydrophilic. There are various techniques to modify the surface of the polyolefin membranes for grafting hydrophilic monomers, including plasma, light, chemical, and irradiation [217].

Kim et al. [218] fabricated the modified PE membranes with the plasma-induced AN on the surface of the PE membranes. As reported in many researches, the presence of hydrophilic monomers induced on the surface of the PE membranes improved the electrolyte retention and wettability.

The ultraviolet (UV) irradiation process is another promising method to graft functional polymers because of the rapid formation of active sites for initiating the chemical reaction on
the entire membranes. Tsuneda et al. [219] introduced the sulfonic acid (SO$_3$H) groups onto PE membranes by radiation-induced grafting of sodium styrene sulfonate (SSS) with hydrophilic monomers. The resultant membranes exhibited excellent hydrophilicity with the uniformity of hydrophilic monomers on the surface. It was also reported that PE membranes treated by irradiation have good thermal properties [220] and electrochemical properties [221].

Gineste et al. [222] developed microporous PP membranes with hydrophilic surface by grafting a hydrophilic monomer. The author introduced acrylic acid and diethylene glycol-dimethacrylate (DEGDM) on the surface of PP membranes by UV irradiation. The modified membranes showed better electrolyte uptake, conductivity, and cycle life than that of unmodified PP membranes, indicating that the hydrophilicity of the PE membranes increased with grafting polymers.

The hydrophilic surface of microporous PE membranes was also prepared by grafting glycidyl methacrylate (GMA) [223] and methyl methacrylate (MMA) [224] on the surface of electron beam irradiated PE membranes. The hydrophilic monomers on the surface of PE membranes improved the electrolyte capability and retention, leading to better electrochemical performances.

The grafting method by using UV irradiation was an effective on PVDF [225,226] and PVDF-co-HFP [227] membranes. They showed improved mechanical properties and electrochemical properties compared to untreated membranes.

Lee et al. proposed PE membranes grafted with poly(ethylene glycol) borate acrylate (PEGBA) [228] and 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (Siloxane) [229]
by electron beam irradiation. It was reported that the degree of grafting increased and the porosity of modified membranes decreased as the irradiation dose increased. The ionic conductivity of the grafted membrane exhibited a magnitude of $10^{-4}$ S/cm at 10 kGy irradiation dose. The cells using the grafted membranes showed better cycling performance at various current rates, especially at high voltage operating conditions.

Kim et al. [230] investigated the effect of irradiation on the morphological, thermal, and electrochemical properties of PE membranes. The PE membrane was irradiated by the dose rate of 10 kGy/h under air condition at room temperature. The irradiated membranes experienced the morphological changes because of the crosslinking of PE polymer chains by irradiation. As a result, the porosity and pore size of the membranes decreased with increasing irradiation dose. In addition, the irradiated membranes showed good thermal stability compared to non-irradiated membranes. The discharge capacities at high rate were also better than those of non-irradiated membranes due to stable morphological property.

1.2.3.4 Composite Separators

As mentioned above, a variety of separators such as non-woven, inorganic, and modified membranes show remarkable improvements in electrolyte uptake, ionic conductivity, thermal stability, and electrochemical performances. However, they still have difficult to simultaneously attain optimal properties in both mechanical strength and electrochemical performances. In an effort to overcome this problem, composite separators combined two different membrane types have been studied extensively, including the advantages from both membrane types.
The microporous polyolefin membranes can be employed as a dimensional support to enhance the mechanical strength. There are lots of patents to make composite separators by coating polyolefin membranes, including dip coating method [231–235], laminating method [236–238], slot die [239,240], gravure [241,242], phase inversion [243,244], and so forth.

Taskier et al. [235] discussed hydrophilic polymer-coated microporous membranes capable of use as a battery separator. The author coated a suitable surfactant on the hydrophobic membrane to increase wettability and electrolyte retention. However, the surfactant was unstable on the surface of the membranes because it temporarily makes the membrane hydrophilic.

Poly(ethylene terephthalate) (PET) non-woven was coated by PVDF [245] and PVDF-co-HFP [243,244,246]. The coating solution was prepared by dissolving the polymer in acetone and then coated on PET non-woven. The authors reported high wettability and good electrochemical properties such as ionic conductivity, mechanical stability, and electrochemical stability.

The composite membranes based on PE non-woven matrix were prepared by coating acrylonitrile (AN)-methyl methacrylate (MMA) copolymer [247], PVDF-co-HFP [248], and PVDF/PVAc blend [249]. The PE matrix provides good mechanical strength and a thermal shut-down property, while the polymer coating layer enhances the compatibility with the liquid electrolyte, leading to good ionic conductivity and electrochemical performance. The composite membranes containing AN-MMA coating layer of 14 µm in thickness showed a stable discharge capacity and excellent rate performance. Lee et al. [250] proposed a continuous process to make composite membranes coated by PVDF. Figure 1.2.10 showed
the schematic description of the process for preparing composite membranes based on PE non-woven matrix and PVDF coating.

![Diagram of the preparation process of the composite membrane](image)

**Figure 1.2.10. Schematic for the preparation process of the composite membrane [250].**

Many polymer membranes form gels in liquid electrolyte. The flow properties of polymer gel-based membranes at elevated temperature can lead to internal short-circuits and safety hazards. To address these problems, polyethylene glycol diacrylate (PEGDA)/PVDF-co-HFP blend [251,252], polyethylene glycol diacrylate (PEGDA)/PVDF/PMMA blend [253], PEGDA/poly(ethylene glycol) methyl ether acrylate (PEGMEA) blend [254] were used with irradiation method to form chemically cross-linked structure. Figure 1.2.11 showed the chemical structures of PEGDA and PEGMEA crosslinker, respectively. Microporous polyolefin membranes were dipped in the blend solutions with various ratios. The coated
membranes were then irradiated for crosslinking at the different rate of irradiation dose. The thermal stability of the composite membranes increased with increasing irradiation dose and PEGDA content because of the formation of cross-linked networks. It was also found that the crystallinity decreased as irradiation dose increased and PEGDA content decreased. The high ionic conductivities in order of $10^{-4}$ S/cm were obtained with the membranes coated by cross-linked polymers.

![Chemical structures of (a) PEGDA and (b) PEGMEA](image)

Figure 1.2.11. Chemical structures of (a) PEGDA and (b) PEGMEA [254,255].

When a battery is overcharged, the voltage uncontrollably climbs up and then exothermic reactions take place inside the cell. These reactions produce excessive heat and flammable gas, which can lead to a thermal runaway. In order to solve this problem, internal and self-actuating overcharge protection mechanisms have been proposed by using redox shuttles [256–260] and electroactive polymers [261–270] as safety additives in electrolyte solution. Among those, electroactive polymers obtained by the polymerization of conducting
monomers can effectively function as shutdown components to increase the overcharge tolerance of the cell [51]. As based on this idea, composite separators based on polyolefin membranes were prepared by coating electroactive polymers, such as poly(3-butylthiophene) (P3BT) [271], ploy(3-Decylthiophene) (P3DT) [272], and poly(triphenylamine) (PTPAn) [273]. The composite membranes showed the behavior to transform from conductive state to insulating state at overcharged voltage, effectively protecting the batteries from voltage runaway. The composite membranes worked reversibly and had no significant impact on charge-discharge cycling at normal conditions.

Zhang et al. [274] prepared multilayered polymer membrane by coating PVDF on both sides of PMMA membrane. The outer PVDF layers are porous and the inner PMMA layer is solid. The composite membranes having the unique porous structure of PMMA [275] and PAN [276] nanoparticle coating layer were reported. A colloidal solution of polymer nanoparticles was prepared by conventional emulsion polymerization and applied on the surface of polyolefin non-woven. The microstructures of PAN and PMMA nanoparticle array-coated membranes are shown in Figure 1.2.12. The polymer nanoparticles successfully formed close-packed coating layers on microporous membranes, forming unique porous structure. The composite membranes showed good wettability and ionic conductivity in the order of $10^{-4}$ S/cm.

In order to improve the thermal stability and wettability of microporous polyolefin membranes, nano-sized inorganic powders and hydrophilic polymers as a binder have been applied on the surface of the polyolefin membranes. PVDF-co-HFP/ poly(ethylene oxide) (PEO)/Al$_2$O$_3$ [277], PVDF/PEGDA/PMMA/Al$_2$O$_3$/BaTiO$_3$/TiO$_2$ [278], PVDF-co-HFP/SiO$_2$
poly(lithium 4-styrenesulfonate) (PLSS)/Al₂O₃ [280], and PMMA/SiO₂ [281] were used for the preparation of composite membranes. These composite membranes exhibited good thermal stability and wettability to liquid electrolytes due to the presence of hydrophilic polymer and inorganic particles with high surface area. As a result, the lithium-ion cells assembled with the composite membranes showed good capacity retention and ionic conductivities in the range from $10^{-3}$ to $10^{-4}$ S/cm.

Figure 1.2.12. SEM images of composite membranes: (a) Surface of PAN-based, (b) Cross-section of PAN-based [276], (c) Surface of PMMA-based, and (d) Cross-section of PMMA-based [275].
Jeong et al. [282] studied the effect of coating solution on the microporous structure of PE membranes. PVDF-co-HFP and Al₂O₃ particles were mixed by a composition ratio of 50/50 in acetone and coated on both sides of PE membranes. Figure 1.2.13 showed the microstructure of the composite membranes as a function of non-solvent (i.e. water) content.

![Figure 1.2.13. SEM images of the composite membranes prepared by different concentrations of non-solvent: (a) 2 % (b) 4% (c) 6 %, and (d) 8 % [282].](image)

The coating solution became immiscible with increasing non-solvent content. The microporous structure of composite membranes depended on the miscibility of the coating solution. The pore size of composite membranes increased and the microporous structure
became more developed as the non-solvent content increased. Therefore, the immiscible coating solution caused the superior electrochemical performance, whereas the miscible coating solution led to better thermal shrinkage.

A bilayer composite membrane comprised of a ceramic layer and a porous PVDF layer was proposed as shown in Figure 1.2.14 [283]. The silica dispersion was coated on the surface of the anode and then the PVDF coating was also applied onto the surface of the ceramic layer by casting method. Ionic conductivities of the membranes saturated with a liquid electrolyte were a magnitude of $10^{-3}$ s/cm. Cells with bilayer composite membranes showed stable cycling performance and excellent rate capability.

![Figure 1.2.14. Structure and morphology of the bilayer composite membrane [283].](image)
Figure 1.2.15. Schematic of trilayer composite membrane [285].

Figure 1.2.16. SEM images of the composite membranes with different SiO$_2$ particle size: (a) without particles (b) with particles of 530 nm, and (c) with particles of 40 nm [284].
Trilayer composite membranes were prepared by coating SiO$_2$ [284] and Al$_2$O$_3$ [285] nanoparticles with PVDF-co-HFP as a binder. The coating solution was prepared by mixing PVDF-co-HFP and inorganic particles in acetone, and a composition ratio of PVDF-co-HFP/inorganic particle was 10:90 (by weight). The coating solution was applied on microporous PE [284] and PMMA [285] membranes by dip coating method. The schematic and microstructures of the composite membranes are shown in Figure 1.2.15 and 1.2.16, respectively.

The inorganic particles bonded by PVDF-co-HFP formed unique coating layers compared to Jeong’s research [282] using different composition ratios. The membranes coated by small particles allowed higher porosity and better ionic conductivity than those with large particles. The composite membranes exhibited great thermal stability and good cell performances with stable microstructure of coating layers.

It has been widely known that hydrogen fluoride (HF) formed by the hydrolysis of lithium hexafluorophosphate (LiPF$_6$) are one of main sources on the capacity fading in the cathode materials. In order to resolve this problem, Zhang et al. [286,287] proposed alkaline calcium carbonate (CaCO$_3$) as the main component for the composite separators because it can neutralize acidic products. They prepared flexible and self-standing composite separators by thermal pressing method. CaCO$_3$ and Teflon emulsion were thoroughly mixed with a small amount of ethanol and hot-rolled for self-standing membrane. The composite membrane led to ionic conductivities as high as $2.5 - 4 \times 10^{-3} \text{ S/cm}$ at 20 °C and superior performance on high rate cycling. The author claimed that it is attributed to the alkali CaCO$_3$ which can scavenge acidic impurities such as HF.
Cho et al. [288] proposed a silica composite membrane by air-laid method using polyolefin membrane and nanosize silica power. The SiO$_2$ particles were homogeneously distributed into the membrane, filling the pore structure of the membrane. The silica composite membranes showed better wettability and cycling performance than those of silica-free polyolefin membranes. They were also thermally stable up to 150 °C.

The composite membranes reinforced by polyolefin membranes via general coating methods exhibit sufficient mechanical strength for manufacturing cells and lead to excellent electrochemical properties as well as good ionic conductivity. However, the increment in thickness and the reduction in porosity are inevitable consequences for composite membranes. In order to solve these problems, electrospinning method can be applied to coat nanofibers on the surface of polyolefin membrane.

Cho et al. [289] proposed a novel composite membrane by laminating an electrospun PAN membrane with a polyolefin membrane. The author prepared the electrospun PAN membrane and the PE/PP non-woven membrane by wet laid method. The PE/PP non-woven was filled by inorganic particles and then combined with the electrospun PAN membrane through hot roll press at 135 °C. Figure 1.2.17 shows laminating process and SEM images of the composite membrane, respectively.
The composite membranes exhibited higher porosity and air permeability than commercial separators. It was also found that the cells using the composite membrane have stable cycling performance and high rate capability. On a hot oven test at 150 °C, thermal shrinkage in the composite membrane was not observed after exposed for 1 h.

Lee et al. [290] developed a composite membrane directly coated by microfibers containing Al₂O₃ via electrospinning. The coating layer was made up of electrospun fibers with diameters of 2 – 4 µm and formed greatly porous structure with thin thickness of 5 µm as shown in Figure 1.2.18.
The inorganic particles improved the thermal stability of the membranes and the wettability of liquid electrolyte. The cells assembled with the composite membranes showed good capacity retention and high rate performance because of good retention capacity of liquid electrolyte.

### 1.3 Overview on electrospinning

#### 1.3.1 Introduction on electrospinning

Materials with a nanoscale dimension have attracted a great deal of attention over the last couple of decades. There are many kinds of nanoscale materials including nanoparticles, nanorods, nanotubes, and nanofibers. Recently, nanostructure materials have been a subject of intensive research due to their unique properties and interesting applications in many fields such as textile, filtration, biomedical technology, energy device, electronic engineering, and environmental technology.
Nanoscale materials can be prepared by various methods such as solvothermal synthesis [291–293], self-assembly [294–297], interface synthesis techniques [298], vapor-phase methods [299,300], solution-phase growth controlled by capping reagents [301], template-directed methods [302–304], and lithography [305–308]. However, most nanomaterial synthetic methods involve multiple steps and have limitations such as material restriction, complex set-up, and high cost.

On the other hand, electrospinning has attracted significant attention because it is a simple, versatile and inexpensive technique for the fabrication of fibrous nanostructure materials in continuous process. This method can be used to prepare nanofibers, nanotubes, nanobelts, and porous membranes. When the diameter of fibers decreases from micrometer (i.e. $10^{-1} – 10^{2}$ µm) to submicron or nanometer (i.e. $10^{-2} – 10$ µm), the fibers have amazing characteristics, such as large surface area to volume ratio, flexibility in surface functionalities, superior stiffness, and tensile strength, compared with other forms of materials [309–312].

In 1600, W. Gilbert [313] first observed electrostatic interaction on the smooth surface of a water droplet. Although the term “electrospinning” was used recently, its fundamental idea was first described by G.M. Bose in 1745 [312,313]. He was the first to describe the generation of aerosols by the application of high electric potentials to drops of fluids. The process was then studied by many researchers including L. Rayleigh in 1882 [313], W.J. Morton in 1902 [314], J.F. Cooley in 1902 [315] and 1903 [316], and J. Zeleny in 1914 [317,318]. In 1930s, A. Formhals [319–321] patented the first invention related to the process and the apparatus for producing artificial filaments using electric charges.
In 1969, G.I. Taylor [322] studied the effect of electrostatic interaction on a polymer droplet from conducting tubes. He reported that the droplet deforms into a conical shape and the jets are ejected from vertices of the cone, which later is referred as the “Taylor cone” (Figure 1.3.2). He derived the condition for the critical electrical potential to transform the liquid droplet into a conical shape. He determined the balance angle of 49.3 degrees required between the surface tension of the polymer and the electrostatic force.

Despite early discoveries, the electrospinning technique was not received academic attention from researchers and not utilized commercially. In the early 1990s, several research groups had interest in this technique in order to fabricate thin fibers from a wide range of polymers [323–325]. After that time, the term electrospinning was coined and it triggered numerous researches related to electrospinning. In these days, the number of publications in this field has been grown exponentially due to remarkable simplicity, versatility, and potential uses. Recent research on this technique has been focused on exploring various materials, apparatus, and theoretical study.

1.3.2 Working principle of electrospinning

Electrospinning is a unique approach using electrostatic forces to produce fine fibers. The electrospinning setup essentially consists of three major parts: a grounded collector, a spinning needle filled with polymer solution, and a voltage supply connected between the collector and the spinneret. Figure 1.3.1 shows a schematic illustration of the typical setup for electrospinning.
Figure 1.3.1. Schematic illustration of the basic setup for electrospinning. (a) Formation of Taylor cone in an applied electric field, (b) Taylor cone ejects spinning jet, and (c) Surface tension causes cone shape to relax [326].

First, polymer solution is slowly fed by the syringe pump into the spinneret. A high voltage potential is applied to the polymer solution inside syringe needle, increasing free charges in the polymer solution. These charged ions move towards the electrode of opposite
polarity in response to the applied electric field. The interaction between the electrical charges in the polymer solution and the external electric field forms the droplet with a conical shape which is known as Taylor cone (Figure 1.3.1 a). When the applied potential reaches a critical value required to overcome the surface tension of the polymer solution, the droplet becomes unstable and spinning jet is ejected from the surface of the polymer solution (Figure 1.3.1 b). Subsequently, the surface tension causes the droplet shape to relax again, but the spinning jet continues to be ejected in a steady state (Figure 1.3.1 c).

Figure 1.3.2. Photographs illustrating the unstable region of spinning jet [330,331].
Although the spinning jet is stable near to the tip of the spinneret, the jet is distorted and undergoes stretching and whipping because it is subjected to a variety of forces during traveling, including electrostatic repulsion between charged ions and Coulombic force by the external electric field [313,327–329]. The optical images of the unstable jet formation are shown in Figure 1.3.2. The solvent evaporates while the spinning jet travels from the spinneret to the collector and finally electrospun fibers are solidified on the collector.

1.3.3 Parameters

A variety of materials including natural polymers, synthetic polymers, ceramic precursors, and metal oxides can be electrospun in different fiber morphologies such as beads [332–334], aligned [335–338], flat ribbon [332,339–341], core-shell [342–345], hollow [346–348], and porous [349–352] as shown in Figure 1.3.3.

However, the creation of nanofibers via electrospinning technique requires the careful consideration of electrospinning parameters. There are a lot of parameters affecting the formation of nanofibers by electrospinning process [328,346,354]. These parameters can be divided into three groups: operating variables, material variables, environmental variables. The parameters that can influence the creation of nanofibers by the electrospinning are classified in Table 1.3.1.
Figure 1.3.3. Different electrospun fiber morphologies: (a) beads [333], (b) aligned [336], (c) flat ribbon [332], (d) core-shell [345], (e) hollow [347], and (f) porous [353].
Table 1.3.1. The classification of parameters affecting the electrospinning process.

<table>
<thead>
<tr>
<th>Operating variables</th>
<th>Solution variables</th>
<th>Environmental Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Applied voltage</td>
<td>Polymer molecular weight</td>
<td>Temperature</td>
</tr>
<tr>
<td>Solution feed rate</td>
<td>Solution concentration</td>
<td>Humidity</td>
</tr>
<tr>
<td>Spinning distance</td>
<td>Conductivity</td>
<td>Air velocity</td>
</tr>
<tr>
<td>Spinneret design</td>
<td>Viscosity</td>
<td></td>
</tr>
<tr>
<td>Collector design and arrangement</td>
<td>Surface tension</td>
<td></td>
</tr>
<tr>
<td>Electrode design and arrangement</td>
<td>Solvent evaporation</td>
<td></td>
</tr>
</tbody>
</table>

1.3.4 Applications on energy devices

Since electrospun nanofibrous membranes have light weight, uniform diameter distribution, small pore size, and high permeability, they are considered to be promising materials for a wide range of applications including textile, medical, filtration, energy conversion and storage devices [324,326,346]. The applications of electrospun nanofibers are summarized in Figure 1.3.4.
The use of electrospun materials in energy devices and electronic components has been recently reviewed [355–358]. The unique properties such as high porosity and very large surface area to volume ratio make electrospun nanofibers to be considered as materials for batteries. Figure 1.3.5 shows that recent energy issues related to environmental problems and high energy demand have accelerated growth in the number of scientific publications [355,358].
1.3.4.1 Lithium-ion batteries

Lithium-ion batteries are composed of three primary components: a cathode, an anode, and the electrolyte (Figure 1.1.6). Electrospinning provides great opportunities to develop new materials with improved properties for all three components in lithium-ion batteries. Recently, metal oxide materials have low self-discharge, high specific energy density, and excellent cycle life, but slow solid state diffusion of Li$^+$ cations [23,30,37,42]. Carbon and graphite which are the most popular anode materials have stable capacity during cycling, but the theoretical capacity is very limited [28,29,37]. Commercial separators used in the
electrolyte of lithium-ion batteries have good properties such as mechanical strength and chemical stability. However, they show poor thermal stability, low wettability, and poor adhesion property [40,45,64,65,92]. Electrospun nanofibers can improve these problems as well as electrochemical performance because of their unique morphology.

1.3.4.2 Fuel cells

A fuel cell is an energy conversion device which converts the electrochemical oxidation of hydrogen or hydrogen-rich fuel into electrical energy. Fuel cells are different from conventional electrochemical cell batteries. Fuel cells require a flow of chemicals like hydrogen and oxygen that react in the presence of catalysts, rather than rely on static stores of chemicals that should be periodically recharged [359–361]. Electricity is generated through the reaction and conducted to an external circuit. If the essential reactions are maintained, fuel cells can theoretically continue the operation.

There are many types of fuel cells such as proton exchange membrane (PEM) fuel cells, phosphoric acid fuel cells, molten carbonate fuel cells, alkaline fuel cells, and solid oxide fuel cells [361]. PEM fuel cells have attracted a great research attention due to their high power density and low operating temperature. The PEM fuel cells typically consist of two graphite plates, assisting components such as gaskets, and five-layer membrane electrode assembly (MEA) which includes a proton exchange membrane, two catalyst layers, and two gas diffusion layers. Figure 1.3.6 shows a schematic of PEM fuel cells.
The catalyst material is the key component that facilitates the reaction of oxygen and hydrogen in a PEM fuel cell. Pt nanoparticles have been commonly used as catalyst for commercial PEM fuel cells, but these catalysts suffer from poor durability in the harsh operating conditions of PEM fuel cells. Electrospinning technique has been used to prepare novel catalysts with high activity, good durability, and high poisoning resistance [363–365]. For the catalysts activity, the catalysts should be uniformly dispersed on supporting materials. Electrospinning is also used for the fabrication of supporting materials with high surface area, large pores, and good electrical conductivity [366–368]. The proton exchange membrane is the critical element of the PEM fuel cells. The membranes should absorb water and conduct hydrogen ions and protons, but not electrons and gas []. It is also required to have sufficient mechanical strength to withstand normal operating process. The membranes
prepared by electrospinning method exhibited high proton conductivity, good chemical resistance, thermal stability, and low gas permeability [369–371].

1.3.4.3 Dye-sensitized solar cells

Electrospun materials can also be utilized in the preparation of solar cells. The solar cells directly convert the energy of sunlight into electrical energy through the photovoltaic effect. The dye-sensitized solar cell (DSSC) is a relatively new class of solar cell in the group of thin film solar cells, which can be described by an artificial photosynthesis process. The use of electrospun materials in DSSC photoelectrodes and electrolytes has been discussed in many publications [372,373].

In DSSCs, the dye on the surface of TiO$_2$ particles gathers solar energy and loses an electron to the conduction band of the TiO$_2$. However, particle-based TiO$_2$ layers have low diffusion efficiency due to the high density of grain boundary between particles. Electrospun nanofiber electrode can provide high specific surface area and large pore size [372–374]. In addition, traditional liquid electrolytes in DSSCs have poor durability and retention. Electrospun polymer membranes have interconnected porous structure which is desirable for long-term stability and the encapsulation of electrolyte solution [373,375,376].
1.4 References


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CHAPTER 2. Research Motivation and Objectives

2.1 Motivation

A separator is the essential component in a lithium-ion battery, which is placed between the positive and negative electrodes to prevent electrical short circuits. Although polyolefin microporous membranes are commonly used as the separator for lithium-ion batteries due to the excellent mechanical strength and good chemical stability, their intrinsic characteristics such as low wettability to the liquid electrolyte, poor adhesion property, and thermal stability can still be improved. In order to improve these intrinsic properties, commercial polyolefin membrane separators can be combined with a nanoscale fibrous polymer coating. Nanofibers have very high surface area which is beneficial for wettability to liquid electrolyte and adhesion properties, leading to better electrochemical performance.

Electrospinning is a simple and efficient method to prepare nanofiber coatings. The morphology of electrospun nanofibers can be controlled by many experimental parameters such as solution concentration, applied voltage, electrode type, electrode-to-collector distance, and solution feeding rate. The electrospun nanofibers can be homogenously coated on the surface of membrane substrates through the controlled parameters of electrospinning. The electrospun nanofiber coatings can improve the wettability and adhesion property while maintaining the advantages of base membrane substrate, which is highly desirable for developing high performance lithium-ion batteries.
Furthermore, the good adhesion between the separator and the battery electrode is required for high performance lithium-ion batteries. Although it is well recognized that adhesive polymers would enhance the adhesion strength between the separator and the battery electrode, the adhesion properties have not been studied by using standard test method.

2.2 Objectives

The primary objectives of this research work are to optimize electrospinning parameters and achieve controlled nanofiber coatings onto microporous membrane separators in order to improve the properties of lithium-ion battery separators. In this research, novel approaches are proposed to prepare nanofiber-coated membrane separators using commercial membrane separators. Figure 2.1 shows schematic for the preparation of nanofiber-coated membrane separator.

![Figure 2.1. Schematic for the preparation of nanofiber-coated membrane separator.](image)
The resultant nanofiber-coated membrane separators have the potential to combine the advantages of both polyolefin membranes and electrospun nanofibers. The polyolefin microporous membrane serves as a substrate providing mechanical strength to withstand the stress inherent in manufacturing process of lithium-ion batteries. The morphologic structure, electrolyte uptake, and adhesion properties of nanofiber coatings were investigated. The electrospun nanofibers form nanoscale fibrous polymer coatings with interconnected and randomly oriented structure on the surface of the polyolefin microporous membranes. The nanofiber coatings increase the electrolyte uptake capacities of the membranes. A modified version of standard test methods was used in order to examine the adhesion property of nanofiber-coated membranes on the electrode. The nanofiber-coated membranes have improved adhesion properties to the battery electrode. Those studies are discussed in Chapters 3 to 5. More specifically, the fabrication and characterization of nanofiber-coated membranes by two different electrospinning methods with various parameters are discussed in Chapter 3. The preparation and properties of electrospun nanofiber-coated membranes using different polymer blends are studied in Chapter 4. Coating nanofibers onto different types of membrane substrates is discussed in Chapter 5. In addition, electrochemical properties and cycle performances of the cells assembled with nanofiber-coated membranes are investigated in Chapter 6. Figure 2.2 shows the illustration of this research.
Figure 2.2. Illustration of this research.
CHAPTER 3. Nanofiber-Coated Membranes for Battery
Separators via Single Nozzle and Nozzle-Less Electrospinning

Methods

Abstract

An electrospun nanofiber-coated Celgard® 2400 polypropylene microporous battery separator was prepared using polyvinylidene fluoride (PVDF) and polyvinylidene fluoride-co-chlorotrifluoroethylene (PVDF-co-CTFE). The coating of PVDF and PVDF-co-CTFE nanofibers was carried out using single nozzle and nozzle-less electrospinning methods. The nanofiber coating prepared by the nozzle-less electrospinning method was found to have better adhesion to the separator microporous membrane than the nanofiber coating prepared by single nozzle electrospinning. The PVDF and PVDF-co-CTFE nanofiber coatings increased the electrolyte uptake capacity in a secondary lithium ion battery, with PVDF-co-CTFE co-polymer nanofiber-coated microporous membrane showing higher electrolyte uptake capacity than PVDF homopolymer coated microporous membrane. In addition, the PVDF and PVDF-co-CTFE nanofiber coatings improved the adhesion of the porous microporous membrane to a battery electrode. It was also found that nanofiber coatings prepared by the nozzle-less electrospinning method have better adhesion properties and higher electrolyte uptake capacity than those by single nozzle electrospinning.
3.1 Introduction

Lithium-ion batteries are widely used as a power source for portable electronic devices and hybrid electric vehicles due to their excellent energy and power densities, long cycle life, and enhanced safety [1-5]. A critical component of lithium-ion batteries is the microporous separator membrane which is placed between the positive and negative electrodes of the battery. The main function of the separator is to prevent the physical contact of electrodes while serving as the electrolyte reservoir to enable ionic transport.

Polyolefin microporous membranes are commonly used as separators for lithium-ion batteries due to their excellent performance properties, such as good chemical stability and high mechanical strength [4,6-8]. Recently, researchers have modified polyolefin microporous membranes using different coating methods to improve surface properties of the membrane. Numerous patents have been published on technologies which use a variety of coating methods to deposit functional polymers on the surface of the separator membranes. Common coating methods are dip coating [9-12], laminate [13-15], slot die [16-17], gravure coating [18-19] and curtain coating [44-45]. The coated layer applied by these methods must not compromise the performance properties of the battery and should be designed to enhance both the porous and tortuous structure of the membrane and to improve the battery electrolyte uptake capacity.

In order to address these challenges, several research groups have used electrospinning method to prepare nanofiber-based porous separators with a variety of polymers, such as polyacrylonitrile (PAN) [20-23], polyvinylidene fluoride (PVDF) [24-29], polyvinylidene fluoride-co-hexafluoropropylene (PVDF-co-HFP) [30-32], and polymethyl methacrylate
(PMMA) [33]. These nanofiber membranes have high porosities, which is beneficial for increasing the electrolyte uptake capacity. Electrolyte uptake capacity is an important property for battery separators since they have to absorb a significant amount of liquid electrolyte to achieve low internal resistance and sufficient cell performance [34-35]. In addition, nanofiber separator membranes have improved adhesion to the battery electrodes that can help prevent the formation of gaps between the separators and electrodes during prolonged charge-discharge cycles, especially in large-format batteries. Even a small failure of the interfacial adhesion between the separator and the electrode can increase battery impedance and cause uneven current distribution leading to the formation of lithium dendrite growth [43]. Many of these nanofiber membranes can provide adhesion to a battery electrode by using polymers such as PVDF and PVDF co-polymer such as PVDF-co-HFP. The type of polymer for electrospinning is important as some electrospun nanofiber membranes are typically weak and can be easily damaged during the assembling of lithium-ion batteries [4, 6].

This paper reports the preparation of a composite separators prepared by coating a Celgard® 2400 polypropylene (PP) monolayer microporous membrane separator with PVDF and polyvinylidene fluoride-co-chlorotrifluoroethylene (PVDF-co-CTFE) nanofibers. PVDF and PVDF-co-CTFE were selected due to their excellent electrochemical and thermal stabilities, good adhesion properties, and high mechanical strength. The resultant nanofiber-coated membranes have the potential to combine advantages of both polyolefin separator membrane (e.g., good chemical stability and high mechanical strength) with a nanoscale fibrous polymer coating (e.g., high porosity and high surface area). The coating of nanofibers
was carried out using single nozzle and nozzle-less (or up-spinning) electrospinning methods. The results of this study show that a coating of PVDF and PVDF-co-CTFE nanofibers applied to a PP microporous membrane separator can improve electrolyte uptake capacity and the adhesion of the separator membrane to a battery electrode in a lithium ion secondary battery. The PVDF polymer type, the electrospinning method and electrospinning process parameters can impact the structure and properties of the nanofiber-coated microporous battery separator membranes.

3.2 Experimental

3.2.1 Materials

Microporous PP membrane separator (Celgard® 2400, Celgard LLC), with a porosity of 41% and thickness of 25 µm, was used as the base substrate membrane for the deposition of nanofibers. PVDF (Kureha W#9100) and PVDF-co-CTFE (Solvay® Solef 32008), both with a molecular weight of 280,000 g/mol, were used for preparing the electrospun nanofiber coatings. The basic properties of these two polymers are summarized in Table 3.1. Electrospinning solutions (15 wt%) were prepared in a solvent mixture of N,N-dimethylformamide (DMF) and acetone (7:3 by weight).
Table 3.1. Molecular structure, monomer, molecular weight and melting temperature of polymer materials.

<table>
<thead>
<tr>
<th>Molecular Structure</th>
<th>Monomer</th>
<th>Molecular Weight (g/mol)</th>
<th>Melting Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>Homopolymer</td>
<td>CH₂=CF₂</td>
<td>280,000</td>
</tr>
<tr>
<td>PVDF-co-CTFE</td>
<td>Copolymer</td>
<td>CH₂=CF₂ and ClCF=CF₂</td>
<td>280,000</td>
</tr>
</tbody>
</table>

3.2.2 Preparation of nanofiber-coated separator

Nanofiber coatings were prepared by two different electrospinning methods. In the first method, electrospun nanofibers were deposited by using the single nozzle, lab scale electrospinning device shown in Figure 3.1. A high voltage was applied between the electrospinning solution contained in a syringe and the grounded metallic collector. When the voltage reached a critical value, the electrostatic force overcame the surface tension of the pendant drop of the polymer solution at the tip of the nozzle and a liquid jet was ejected. Nanoscale fibers were deposited on surface of the PP base membrane accumulating and forming a nanofibrous coated layer. Nozzle electrospinning parameters can be easily
controlled however, the production rate of nanofibers is low and the sample size obtained is relatively small (typically, 11 - 12 cm in diameter).

**Figure 3.1. Schematic of single nozzle electrospinning device.**

In the second method, the nozzle-less electrospinning device (NanoSpider™ NS200, Elmarco) shown in Figure 3.2 was used. The electrospinning polymer solution was placed in an open bath. To form stable polymer jets, multiple patterned wires were attached to a wire electrode as shown in Figure 3.2, and were rotated in bath to be wetted by the electrospinning solution. A high voltage was applied to the solution and multiple jets were ejected from the patterned wire surface in an ‘up-spinning’ fashion. Dry fibers were deposited onto the PP membrane which was moved continuously at a fixed speed passing over a grounded collector. Compared with the single nozzle-based approach, nozzle-less electrospinning has
higher production rate with multiple jets simultaneously generated. In this work, the nozzleless electrospinning generated a continuous nanofiber coating with a width of 16 - 17 cm on the Celgard® 2400 PP microporous membrane separator.

![Diagram of nozzle-less electrospinning device]

**Figure 3.2. Schematic of nozzle-less electrospinning device.**

In both single nozzle and nozzle-less methods, the electrospinning process conditions were controlled so that nanofibers produced had comparable morphology and nanofiber loading (0.8 - 1.0 g/m²). The process conditions used for the single nozzle electrospinning of the PVDF polymer were: 1) applied voltage = 15 kV, 2) nozzle-to-collector distance = 25
cm, 3) flow rate = 0.75 ml/h, and 4) deposition time = 3 min, while those for PVDF-co-CTFE were: 1) applied voltage = 25 kV, 2) nozzle-to-collector distance = 20 cm, 3) flow rate = 0.25 ml/h, and 4) deposition time = 5 min.

For nozzle-less electrospinning, the conditions used for both PVDF and PVDF-co-CTFE were: 1) applied voltage = 40 kV, 2) electrode-to-collector distance = 15 cm, 3) electrode rotational speed = 6 r/min and 4) membrane movement speed = 0.26 m/min.

3.2.3 Structure characterization and property measurements

The morphology of both uncoated and nanofiber-coated PP membranes was evaluated using a scanning electron microscopy (JEOL 6400F Field emission SEM at 5 kV). Samples prepared for SEM analysis were coated with Au/Pd by a K-550X sputter coater to reduce charging. The diameters of electrospun fibers were obtained by measuring fifty fibers randomly selected in SEM images using Revolution v1.6.0 software.

Liquid electrolyte uptake capacities were measured by soaking pre-weighed nanofiber-coated separator membrane samples for a fixed time at room temperature in a liquid electrolyte which consisted of 1 M lithium hexafluorophosphate (LiPF₆) dissolved in 1:1:1 (by volume) ethylene carbonate/dimethylcarbonate/ethylmethyl carbonate. The electrolyte was absorbed both on the surface and in the pores of the microporous membrane. The excess electrolyte solution adhering to the separator membrane surface was removed by gently wiping with filter paper. The electrolyte uptake capacities of nanofiber-coated separator membrane were determined using the following equation:
**Uptake Capacity** \((\text{mg/cm}^2) = (W_t - W_0) / A\)

where \(W_t\) was the weight of the electrolyte-immersed separator, \(W_0\) the weight of dried separator, and \(A\) the immersed area of the test sample.

The adhesion strength of nanofiber coatings to the PP membrane substrate was evaluated by using the ASTM D 1876 standard method, which is a modified ASTM D 2261 standard tongue tear test method using an Instron® Tensile Tester. Figure 3.3a depicts the modified peel test method used to evaluate the adhesion strength of nanofiber coating layer on the membrane substrate. In this method, the test was carried out on a T-type specimen of two adherends, which were the nanofiber coating and PP membrane. A test sample measuring \(2.5 \times 7.5\, \text{cm}^2\) was held in the two jaws of the Instron with the nanofiber coating layer clamped to the movable upper jaw and substrate membrane layer attached to the fixed lower jaw. A tape (3M Scotch® Magic™ Tape 810) was placed on the backside of the nanofiber coating and the membrane to prevent them from stretching and slippery. The jaws were set at an initial separation distance of 2.5 cm. With the upper jaw moving at a constant rate of 50 mm/min, the nanofiber coating layer was peeled away from the membrane surface at a 90 degree angle. A 100 N load cell was used for measuring the adhesion strength of the coating through the entire sample length.

The adhesion between the nanofiber-coated membrane and a battery electrode was also evaluated by conducting peel tests on the nanofiber-coated membrane/electrode laminated assemblies, i.e., peeling the electrode away from the nanofiber-coated membrane, as shown in Figure 3.3b. The electrode used was a LiFePO₄ cathode (MTI Corporation). The nanofiber-coated membrane/electrode assemblies \((2.5 \times 7.5\, \text{cm}^2)\) were prepared by hot
pressing the test sample using press plate method (Carver Model C) at 100 °C and 70 psi for 5 min. The peel tests were performed with a 5 N load cell.

The reproducibility of electrolyte uptake capacity and adhesion results was ensured by conducting all measurements on at least eight samples.

**Figure 3.3.** Schematic of peeling tests for measuring (a) the adhesion between nanofiber coating and PP membrane, (b) the adhesion between nanofiber-coated PP membrane and battery electrode.
3.3 Results and discussion

3.3.1 SEM images

Figure 3.4 shows SEM images of an uncoated Celgard® PP microporous membrane separator. Its morphology presents a microporous structure with uniform distribution of small slit-shaped rectangular pores, approximately 0.04 µm in diameter. In this work, PVDF and PVDF-co-CTFE nanofibers were coated onto the PP microporous membrane separator by using single nozzle and nozzle-less electrospinning methods.

![SEM images](image)

Figure 3.4. SEM images of an uncoated PP membrane. Magnification: 1,000 × (a), 20,000 × (b).

In both single nozzle and nozzle-less electrospinning, there are many process parameters which can influence the formation and morphology of electrospun nanofibers. These parameters include, but are not limited to, solution concentration, applied voltage, nozzle-to-collector distance, solution flow rate, and electrode rotating speed [36-39]. In order to
optimize the processing parameters, electrospinning experiments were carried out under various electrospinning conditions to obtain nanofiber coatings with uniform fiber diameters and well-defined morphology. The optimized electrospinning conditions are shown in the experimental section, and nanofiber-coated PP membranes reported here were prepared based on these conditions.

Figure 3.5. SEM images of (a,b) PVDF and (c,d) PVDF-co-CTFE nanofiber-coated PP membranes prepared by single nozzle electrospinning. Magnification: 1,000 × (a,c), 20,000 × (b,d).
Figure 3.5 shows SEM images of PVDF and PVDF-co-CTFE nanofiber-coated PP membranes produced by the single nozzle electrospinning method. The electrospun nanofibers form a random fiber orientation and are adequately interconnected on the surface of the PP membrane to form a 3-D fibrous network. Figure 3.6 shows PVDF and PVDF-co-CTFE nanofiber-coated PP membranes produced by the nozzle-less electrospinning method. The electrospun nanofibers prepared by this method also show a randomly-oriented and interconnected morphology.

Figure 3.6. SEM images of (a,b) PVDF and (c,d) PVDF-co-CTFE nanofiber-coated membranes prepared by nozzle-less electrospinning. Magnification: 1,000 × (a,c), 20,000 × (b,d).
Figure 3.7 shows average nanofiber diameters PVDF and PVDF-co-CTFE nanofiber-coated PP membranes produced by the single nozzle and nozzle-less electrospinning methods.

Figure 3.7. Fiber diameter distributions of (a) PVDF by single nozzle electrospinning, (b) PVDF-co-CTFE by single nozzle electrospinning, (c) PVDF by nozzle-less electrospinning, and (d) PVDF-co-CTFE by nozzle-less electrospinning.
The average fiber diameter produced by single nozzle electrospinning is 198 nm for PVDF nanofibers and 186 nm for PVDF-co-CTFE nanofibers. However, in the case of nozzle-less electrospinning, average fiber diameter is 138 nm for PVDF nanofibers and 129 nm for PVDF-co-CTFE nanofibers. Therefore, nanofibers deposited by nozzle-less electrospinning have smaller diameters than those by single nozzle electrospinning. The smaller diameters may be attributed to the higher voltage used in nozzle-less electrospinning (40 kV), as compared to that in nozzle electrospinning (15 or 25 kV). Higher voltage leads to greater electrostatic force, which is more effective in stretching the spinning jet and is beneficial for forming thinner diameter nanofibers. In addition, due to the use of high-polarity co-monomer (ClCF=CF₂), PVDF-co-CTFE has higher conductivity than PVDF homopolymer and is more sensitive to the electric force, especially in the high-voltage nozzle-less electrospinning [38,40]. In both cases of electrospinning, the high polarity factor of the co-monomer contributed to PVDF-co-CTFE nanofibers having smaller fiber diameters than PVDF homopolymer nanofibers.

3.3.2 Adhesion between nanofiber coating and membrane substrate

The PVDF homopolymer and PVDF-co-CTFE copolymer nanofiber-coated PP membrane separators were found adhere to the PP microporous membrane substrate. Peel tests were carried out to examine the adhesion peel force between the nanofiber coating and the PP membrane substrate. Figure 3.8a compares the peeling loads of PVDF homopolymer
nanofiber coatings prepared by single nozzle and nozzle-less electrospinning. The PVDF nanofiber coatings formed by the nozzle-less electrospinning were found to have greater adhesion to the PP membrane than those prepared by single nozzle electrospinning. In Figure 3.8b, nozzle-less electrospinning method also produced PVDF-co-CFTE nanofibers with higher adhesion than single nozzle electrospinning.

![Graph a](image1.png) ![Graph b](image2.png)

**Figure 3.8.** Peeling load as a function of length for peeling (a) PVDF and (b) PVDF-co-CFTE nanofiber coatings from the PP membrane.

The adhesion of nanofiber coatings to the PP membrane substrate depends on the nanofiber formation process during electrospinning. In single nozzle electrospinning, the polymer solution is contained in a syringe and evaporation of the solvent occurs after the jet is ejected from the nozzle tip. Since only one jet is present, the amount of evaporated solvent is low within the spinning region while the rate of solvent evaporation from the jet is high.
Hence, the fibers deposited on the membrane surface are relatively dry and poorly stick to the PP membrane substrate. In nozzle-less electrospinning, multiple jets are generated simultaneously while the spinning solution in the liquid bath is exposed to the spinning environment, and as a result, a larger amount of solvent vapor is present. This causes a slower evaporation of solvent from the spinning jets and slower drying of the nanofibers formed. The nanofibers may contain some residual solvent which helps the adhesion of the fibers to the substrate. In addition, the higher voltage in nozzle-less electrospinning leads to a higher flying speed of the spinning jets and a shorter time for the solvent to evaporate before reaching the membrane substrate. Therefore, when the fiber jets arrive at the membrane surface, they have more residual solvent, which results in the formation of nanofibers with improved adhesion to the membrane. Furthermore, nanofibers prepared by nozzle-less electrospinning have smaller fiber diameters than those prepared by single nozzle electrospinning, and thus they have larger contact area with the membrane substrate, which may also contribute to the better adhesion of these nanofibers to the membrane substrate.

### 3.3.3 Electrolyte uptakes of nanofiber-coated membranes

Electrolyte uptake capacity is an indication on how much battery electrolyte solution can be absorbed by the unit area of a separator membrane. For lithium-ion batteries, the separator should be able to absorb a significant amount of liquid electrolyte in order to achieve a low internal resistance and sufficient cell performance [4, 41]. Figure 3.9 shows the electrolyte uptake capacities of PVDF and PVDF-co-CTFE nanofiber-coated Celgard® PP microporous
membranes prepared by single nozzle electrospinning and nozzle-less electrospinning, respectively. For comparison, the electrolyte uptake capacities of uncoated PP microporous membrane are also shown. The electrolyte uptakes increase quickly for all membranes and less than 60 sec is required for saturated absorption of liquid electrolyte in separators. Rapid absorption of electrolyte is desirable in the lithium-ion battery assembly process. As shown in Figure 3.9, the PVDF and PVDF-co-CTFE nanofiber coating layers increases the electrolyte uptake capacities. Due to the presence of polar groups, PVDF and PVDF-co-CTFE can absorb liquid electrolyte to form polymer gels [30-31, 42] contributing to increased electrolyte uptake capacity. When prepared by nozzle-less electrospinning method, the electrolyte uptake capacities of both PVDF and PVDF-co-CTFE nanofiber-coated membranes are significantly higher than those of uncoated membranes.

In the case of single nozzle electrospinning, PVDF and PVDF-co-CTFE nanofiber-coated membranes have comparable electrolyte uptake capacities due to their similar morphology (Figure 3.5). On the other hand, PVDF-co-CTFE nanofiber-coated membranes prepared by nozzle-less electrospinning have higher electrolyte uptake capacities compared with PVDF homopolymer nanofiber-coated membranes. The difference in electrolyte uptake capacities is attributed to PVDF-co-CTFE nanofibers with smaller fiber diameter than PVDF homopolymer nanofibers.
Figure 3.9. Electrolyte uptake capacity as a function of time for (a) PVDF and (b) PVDF-co-CTFE nanofiber-coated PP membranes prepared by single nozzle electrospinning and nozzle-less electrospinning.

3.3.4 Adhesion of nanofiber-coated membrane on the electrode

Good adhesion between the separator membrane and the battery electrode is desired for high-performance lithium-ion batteries. Nanofiber-coated separator membrane/electrode assemblies were prepared by hot-pressing a nanofiber-coated membrane onto a battery LiFePO₄ cathode material using the plate press method at 100 °C and 70 psi. The adhesion between nanofiber-coated membrane and the battery electrode was evaluated by conducting peel tests. Figure 3.10 shows the peel test results for removing PVDF and PVDF-co-CTFE nanofiber-coated membranes from the battery electrode. For comparison, the results for peeling the uncoated membrane from the battery electrode are also shown.
The adhesion of the uncoated membrane to the battery electrode is low. However, the PVDF and PVDF-co-CTFE nanofiber coatings improve the adhesion between the separator and the electrode. Electrospun nanofibers in membrane/electrode assemblies contribute to enhanced adhesion because they provide a fibrous 3-D polymer network which can bind the PP membrane substrate to the battery electrode during lamination.

Figure 3.10. Peeling load as a function of length for peeling (a) PVDF and (b) PVDF-co-CTFE nanofiber-coated PP membranes from the battery electrode.

As shown in Figure 3.10, the PVDF and PVDF-co-CTFE nanofiber-coated PP membrane separators produced by nozzle-less electrospinning have better adhesion to the electrode than those prepared by the nozzle electrospinning method. The smaller diameters of the fibers making up the nozzle-less electrospun nanofiber coating resulted in a larger contact area of the fibers to the surface of the electrode which may be contributing to enhanced adhesion.
To further demonstrate the improved adhesion between nanofiber-coated membrane and the electrode, SEM images were taken on the membranes after they were peeled off from the electrode surface. Figure 3.11 shows SEM images of the uncoated membrane after the peel test. It is seen that the uncoated membrane is clear and only a few small cathode particles were removed from the electrode surface and were left on the membrane, indicating insufficient adhesion between the uncoated membrane and the electrode. Figures 3.12 and 3.13 show the SEM images of PVDF and PVDF-co-CTFE nanofiber-coated membranes after the peel tests. The SEM micrographs show the presence of cathode particles adhered to the PVDF nanofibers indicating that the electrospun nanofiber coating adhered both to the PP membrane substrate and to the surface of the electrode. This confirms that the nanofiber coating can significantly improve the adhesion of the separator membrane to the electrode.

Figure 3.11. SEM images of uncoated membrane after being peeled off from the electrode. Magnification: 1,000 × (a), 20,000 × (b).
Figure 3.12. SEM images (a,b) PVDF, and (c,d) PVDF-co-CTFE nanofiber-coated membranes after being peeled off from the electrode. Nanofiber coatings were prepared by single nozzle electrospinning. Magnification: 1,000 × (a,c), 20,000 × (b,d).
Figure 3.13. SEM images of (a,b) PVDF and (c,d) PVDF-co-CTFE nanofiber-coated membranes after being peeled off from the electrode surface. Nanofiber coatings were prepared by nozzle-less electrospinning. Magnification: 1,000 × (a,c), 20,000 × (b,d).

3.3 Summary

PVDF and PVDF-co-CTFE nanofiber-coated Celgard® 2400 PP membrane separators were prepared by single nozzle and nozzle-less electrospinning methods. Compared with single nozzle electrospinning, the nozzle-less electrospinning produced nanofibers with smaller diameters and better adhesion to the membrane substrate. The electrolyte uptake
capacities and separator-electrode adhesion of nanofiber-coated PP membranes was evaluated. The nanofiber-coated membranes exhibited higher electrolyte uptake capacities and stronger separator-electrode adhesion than uncoated membranes. Among the polymer nanofiber coatings evaluated, the PVDF-co-CTFE nanofiber-coated Celgard® PP microporous membrane separators prepared by nozzle-less electrospinning presented the highest electrolyte uptake capacity and the strongest nanofiber-coated separator-electrode adhesion.
3.5 References


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CHAPTER 4. Electrospun Nanofiber-Coated Membranes Using Different Polymer Blends for Battery Separators

Abstract

Nanofiber-coated polypropylene (PP) separator membranes were prepared by coating a Celgard® microporous PP membrane with electrospun polyvinylidene fluoride-co-chlorotrifluoroethylene (PVDF-co-CTFE) and PVDF-co-CTFE/polyvinylidene fluoride-co-hexafluoropropylene (PVDF-co-HFP) nanofibers. Three PVDF polymer solutions of varying compositions were used in the preparation of the nanofiber coatings. Two of the polymer solutions were PVDF-co-CTFE blends made using different types of PVDF-co-HFP copolymers. The PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP blend nanofiber coatings have been found to have comparable adhesion to the PP microporous membrane substrate. The electrolyte uptakes and separator-electrode adhesion properties of nanofiber-coated membranes were evaluated. Both the electrolyte uptake and the separator-electrode adhesion were improved by the nanofiber coatings. The improvement in electrolyte update capacity is not only related to the gelation capability of the PVDF copolymer nanofibers, but also attributed to the increased porosity and capillary effect on nanofibrous structure of the electrospun nanofiber coatings. Enhancement of the separator-electrode adhesion was due to the adhesion properties of the copolymer nanofiber coatings. Compared with the PVDF-co-CTFE/PVDF-co-HFP blend nanofiber coatings studied, the PVDF-co-CTFE coating was more effective in improving the electrolyte uptake and separator-electrode adhesion.
4.1 Introduction

In recent years, there have been intensive efforts to develop advanced battery separators for lithium-ion rechargeable batteries for use in different applications such as portable electronics, electric vehicles, and other electronic devices [1-3]. A battery separator is considered to be the critical component in a lithium-ion rechargeable battery. The role of the separator is to prevent physical contact between the positive and negative electrodes of the battery and to prevent internal short while allowing the transportation of ions [4-5]. In most commercial lithium-ion rechargeable batteries, separators are made out of polyolefin microporous membranes such as polyethylene (PE), polypropylene (PP), and their combinations. Polyolefin microporous membranes have excellent mechanical strength and good chemical stability [5]. However, increasing demands for higher-performance lithium-ion rechargeable batteries require separators to have excellent electrolyte uptake capacity and enhanced separator-electrode adhesion. High electrolyte uptake is required for the purpose of reducing the cell resistance and enhancing the cell kinetics, while excellent separator-electrode adhesion is critical for ensuring the long-term performance and safety of lithium-ion cells [6-8]. Therefore, there is a need to further explore methods which improve the electrolyte uptake and separator-electrode adhesion of polyolefin microporous membranes in lithium-ion rechargeable batteries.

Various approaches have been used to modify porous polyolefin membranes using coatings of thin layers of different materials. Examples of these approaches include, but are not limited to, lamination [9-12], dip coating [13-18], electrospinning [12,19], spraying [20-21], casting [22-25], and gravure [26-28]. Among these various coating methods,
Electrospinning provides a simple and efficient technique to prepare nanofiber-based porous coatings [19,29-31]. Polymer nanofiber-based coatings prepared by electrospinning are composed of nanoscale fibers with diameters in the range of several micrometers to tens of nanometers. The electrospun nanofibers are formed by applying electrostatic forces generated from the interaction between the charged polymer fluid and an applied electric field. The morphology of the electrospun nanofibers can be controlled by many experimental parameters such as solution concentration, applied voltage, collector type, electrode-to-collector distance, and solution feeding rate [30-31]. Due to the adhesion property of PVDF copolymers and the high surface-area-to-volume-ratio of electrospun nanofibers, nanofiber coatings are expected to have better adhesion to the substrate with adjustment of electrospinning process parameters. In addition, the excellent capillary effect and the affinity of electrospun PVDF copolymer nanofibers may contribute to improved electrolyte uptake capacities.

This paper presents an investigation of the adhesion properties and electrolyte uptake capacities of electrospun nanofiber-coatings on microporous separator membranes. The nanofiber-coated separator membranes were prepared by coating a commercial Celgard® 2400 PP microporous separator with thin layers of electrospun nanofibers of polyvinylidene fluoride-co-chlorotrifluoroethylene (PVDF-co-CTFE) and polyvinylidene fluoride-co-hexafluoropropylene (PVDF-co-HFP). The PVDF copolymers were selected because they are excellent polymer materials for battery separators and they can provide good adhesion between the separator and the electrode [6,31-32]. A comparison was made between the morphologies of the PVDF copolymer nanofiber coatings, specifically looking at the
diameter and the overall appearance of the coatings. The electrolyte uptake and separator-electrode adhesion properties of PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP nanofiber-coated membranes were also investigated. The results confirm that both the electrolyte uptake and separator-electrode adhesion are improved by coating microporous PP battery separator membranes with electrospun PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP nanofibers.

4.2 Experimental

4.2.1 Materials

Microporous PP membrane Celgard® 2400 (Celgard LLC), with a porosity of 41% and thickness of 25 µm, was used as the base substrate. PVDF-co-CTFE (Solvay, Solef#32008), PVDF-co-HFP (1) (Solvay, Solef#21508), and PVDF-co-HFP (2) (Arkema, Kynar#2801) were used for preparing polymer nanofibers. PVDF-co-HFP (1) has lower molecular weight and melting temperature than PVDF-co-HFP (2). The basic properties of these three PVDF copolymers are summarized in Table 4.1.

4.2.2 Preparation of nanofiber-coated separator

Three different electrospinning solutions were prepared: PVDF-co-CTFE, PVDF-co-CTFE/PVDF-co-HFP (1) blend (9:1 by weight), and PVDF-co-CTFE/PVDF-co-HFP (2) blend (9:1 by weight). The solvent used was a mixture of N,N-dimethylformamide (DMF) and acetone (7:3 by weight).
Nanofiber coatings were prepared using the nozzle-less electrospinning device (NanoSpider™ NS200, Elmarco) shown in Figure 4.1. The electrospinning polymer solution was contained in the open solution container. An electrode connected with 6 parallel stainless steel patterned wires was rotated at a fixed speed of 6 r/min in order to wet the steel wires with the polymer solution. A high voltage was applied to the polymer solution to form multiple polymer jets which were ejected (up-spinning) from the solution carried on the wire surface. A 3-D network of nanofibers was deposited onto the PP membrane as it moved continuously at a fixed speed under the grounded collector. This up-spinning of multiple jets is also known as nozzle-less electrospinning. Using the NanoSpider™ NS200, a 16 - 17 cm wide nanofiber coating was deposited on the continuously moving PP microporous substrate.
The electrospinning conditions were controlled so that nanofibers were produced with comparable morphology at nanofiber coating loadings of 0.9 - 1.1 g/m². The process conditions used for electrospinning of PVDF-co-CTFE nanofibers were: i) applied voltage = 40 kV, ii) electrode-to-collector distance = 15 cm, iii) electrode rotational speed = 6 r/min, and iv) membrane movement speed = 0.26 m/min, and those for PVDF-co-CTFE/PVDF-co-
HFP (1) and PVDF-co-CTFE/PVDF-co-HFP (2) blend nanofibers were: i) applied voltage = 38 kV, ii) electrode-to-collector distance = 15 cm, iii) electrode rotational speed = 6 r/min, and iv) membrane movement speed = 0.26 m/min.

4.2.3 Structure characterization and property measurements

The morphology of both uncoated and nanofiber-coated PP membranes was evaluated using a scanning electron microscopy (JEOL 6400F Field emission SEM at 5 kV). Prior to SEM observation, membranes were coated with Au/Pd by a K-550X sputter coater to reduce charging. The diameters of electrospun fibers were obtained by measuring fifty fibers randomly selected in SEM images using Revolution v1.6.0 software. To evaluate the surface areas of electrospun nanofibers, nitrogen isothermal adsorption-desorption measurement was carried out using Gemini surface area and pore size analyzer (Micromeritics Instrument Corp.).

Liquid electrolyte uptakes were measured by soaking weighed membranes for a fixed time at room temperature in the liquid electrolyte of 1 M lithium hexafluorophosphate (LiPF₆) dissolved in 1:1:1 (by volume) ethylene carbonate/dimethylcarbonate/ethylmethyl carbonate. Prior to weighing, any excess electrolyte solution adhering to the membrane surface was gently removed by wiping with filter paper. The electrolyte uptake capacities were determined by using the following equation:

\[
\text{Uptake Capacity (mg/cm}^2\text{)} = \frac{(W_i - W_0)}{A}
\]
where $W_t$ was the weight of the electrolyte-immersed membrane, $W_0$ the weight of dried membrane, and $A$ the immersed area.

The adhesion strength of nanofiber coatings to the PP membrane substrate was evaluated using a peel test method. The peel test experiments were performed on an Instron® Tensile Tester by using the ASTM D 1876 standard method, which is a modified ASTM D 2261 standard tongue tear test method. Figure 4.2A depicts the modified peel test method for evaluating the adhesion strength of nanofiber coatings on the PP membrane substrate. In this method, the test was carried out on a T-type specimen of two adherends, which were the nanofiber coating and PP membrane. 2.5 × 7.5 cm$^2$ samples were prepared and positioned by the two jaws of the Instron testing apparatus. The nanofiber coating was clamped to the movable upper jaw and substrate membrane was attached to the fixed lower jaw. A piece of tape (3M Scotch® Magic™ Tape 810) was placed on the undersides of the nanofiber coating and the PP membrane to prevent them from stretching or slipping during testing. The jaws were set at an initial separation distance of 2.5 cm. The upper jaw speed moved at a constant rate of 50 mm/min peeling the nanofiber coating away from the membrane surface. A 100 N load cell was used for measuring the adhesion strength through the entire sample length.

The adhesion between the nanofiber-coated PP membrane and a battery electrode was evaluated by conducting similar peel tests on membrane/electrode laminated assemblies, i.e., the electrode was peeled away from the nanofiber-coated membrane as shown in Figure 4.2B. The electrode used in this study was a LiFePO$_4$ cathode (MTI Corporation). The membrane/electrode assemblies (2.5 × 7.5 cm$^2$) were prepared by hot pressing (Carver Model
at fixed temperature (100 or 120 °C) and pressure (70 or 85 psi) for 5 minutes. The peel tests on the membrane/electrode laminated assemblies were performed using a 5 N load cell.

The reproducibility of electrolyte uptake and adhesion results was ensured by conducting measurements of a minimum of eight samples.

![Schematic of peeling tests](image)

**Figure 4.2.** Schematic of peeling tests for measuring (A) the adhesion between nanofiber coating and PP membrane, (B) the adhesion between nanofiber-coated PP membrane and battery electrode.

### 4.3. Results and discussion

#### 4.3.1 SEM images

Figure 4.3 shows SEM images of uncoated Celgard® 2400 PP microporous membrane at magnifications of 1,000x and 20,000x. The microporous structure membrane shows
uniformly distributed slit-shaped pores approximately 0.03 - 0.04 um in diameter. The microporous PP membrane was used as the substrate for deposition of electrospun PVDF-co-CTFE, PVDF-co-CTFE/PVDF-co-HFP (1), and PVDF-co-CTFE/PVDF-co-HFP (2) nanofibers.

Figure 4.3. SEM images of an uncoated PP membrane. Magnification: (A) 1,000 ×, (B) 20,000 ×.

SEM images of the three nanofiber-coated PP membranes (see Figure 4) show randomly oriented electrospun nanofibers with an interconnected network morphology. The nanofibers on the surface of membrane substrates were produced with comparable nanofiber coating loadings. The loading densities of PVDF-co-CTFE, PVDF-co-CTFE/PVDF-co-HFP (1), and PVDF-co-CTFE/PVDF-co-HFP (2) nanofibers were 1.11, 0.94, and 1.07 g/m², respectively.
Figure 4.4. SEM images of (A,B) PVDF-co-CTFE, (C,D) PVDF-co-CTFE/PVDF-co-HFP (1), and (E,F) PVDF-co-CTFE/PVDF-co-HFP (2) nanofiber-coated membranes prepared by electrospinning. Magnification: 1,000 × (A,C,E), 20,000 × (B,D,F).
Although nanofiber-coated membranes show a few beads on the surfaces of all three substrates, the microporous membrane substrates are visible between the fibers, indicating that the sizes of the nanofibers and beads formed in the coating are on a scale that does not interfere with the micropores in the membrane substrates.

Figure 4.5. Diameter distributions of (A) PVDF-co-CTFE, (B) PVDF-co-CTFE/PVDF-co-HFP (1), and (C) PVDF-co-CTFE/PVDF-co-HFP (2) nanofibers.
Figure 4.5 shows the distributions of fiber diameters. The average fiber diameter is 129, 167, and 188 nm, respectively, for PVDF-co-CTFE, PVDF-co-CTFE/PVDF-co-HFP (1), and PVDF-co-CTFE/PVDF-co-HFP (2) nanofibers. PVDF-co-CTFE nanofibers were found to have a smaller diameter than PVDF-co-CTFE/PVDF-co-HFP (1) and PVDF-co-CTFE/PVDF-co-HFP (2) nanofibers. Furthermore, the PVDF-co-CTFE/PVDF-co-HFP (1) nanofibers were observed to have a smaller diameter than PVDF-CTFE/PVDF-HFP (2) nanofibers. This is mainly due to the lower viscosity of PVDF-co-CTFE/PVDF-co-HFP (1) solution since PVDF-co-HFP (1) has a lower molecular weight than PVDF-co-HFP (2). The BET surface areas of nanofiber coatings were measured by the nitrogen isothermal adsorption-desorption method. The surface areas of electrospun nanofibers were measured to be 2.99, 2.37, and 1.39 m$^2$/g, respectively, for PVDF-co-CTFE, PVDF-co-CTFE/PVDF-co-HFP (1), and PVDF-co-CTFE/PVDF-co-HFP (2). Results show that smaller fiber diameter leads to higher surface area and the presence of beads does not change that trend.

4.3.2 Adhesion between nanofibers and PP substrate

To make a commercially viable nanofiber-coated battery separator, the nanofiber coating must adhere adequately to the surface of microporous PP membrane substrate. Inadequate adhesion results in gaps forming between the coating and the membrane which adversely affect the charging and discharging cycling performance of a battery. Since PVDF copolymers have excellent adhesive properties [32-34], they may be able to adhere to the microporous membrane substrate. In this study, peel tests were carried out to examine the
adhesion properties of copolymer nanofiber coatings on the PP membrane substrate. Figure 4.6 shows the results of the peel testing as the loads (or force) needed to peel PVDF-co-CTFE, PVDF-co-CTFE/PVDF-co-HFP (1), and PVDF-co-CTFE/PVDF-co-HFP (2) nanofibers from the porous PP membrane samples. A load of at least 2.0 N/cm is needed to peel the nanofiber coatings from the PP membrane substrate, indicating that these nanofibers adhered well to the microporous PP membrane substrate. PVDF-co-CTFE, PVDF-co-CTFE/PVDF-co-HFP (1), and PVDF-co-CTFE/PVDF-co-HFP (2) nanofiber coating shown in Figure 4.6 indicate that these three types of coatings have comparable adhesion to the PP membrane substrate.

![Figure 4.6. Peeling load as a function of length for peeling nanofiber coatings from the PP membrane.](image)

Figure 4.6. Peeling load as a function of length for peeling nanofiber coatings from the PP membrane.
As shown in Figure 4.7, electrospun nanofibers on the surface of membranes are completely peeled off from the membrane substrates after peel test. The SEM images confirm that the peeling load is an appropriate indication of the adhesive property between nanofibers and membrane surface.

![Figure 4.7. SEM images of the membrane substrate after peeling off the nanofiber coatings. Magnification: 1,000 × (A), 20,000 × (B).](image)

### 4.3.3 Electrolyte uptake of nanofiber-coated membranes

During the manufacturing process of lithium-ion rechargeable batteries, the microporous separator membrane should readily absorb liquid electrolyte in a short period of time [5-6]. Figure 4.8 shows the electrolyte uptake measured on the uncoated and nanofiber-coated PP microporous membranes included in this study. All samples were observed to absorb liquid electrolyte rapidly after they were immersed in the liquid electrolyte. Furthermore, the electrolyte uptake leveled off after less than 60 sec, as shown in the inset of Figure 4.8. From
Figure 4.8, it is seen that the three nanofiber-coated membranes have higher electrolyte uptakes than the uncoated membrane. The improvement in electrolyte uptake by the PVDF nanofiber coatings should be caused mainly by the increased porosity and capillary effect on nanofibrous structure. The formation of beads does not have apparent negative effect on the electrolyte uptakes. In addition, the improvement in electrolyte uptakes might be also related to the gelation capability of the nanofibers, which is attributed to the affinity of PVDF copolymers to the polar organic electrolyte solution [8,35].

Figure 4.8. Electrolyte uptake as a function of time for nanofiber-coated PP membranes. For comparison, uncoated membrane is also shown.

For comparison, the electrolyte uptake property of self-standing PVDF-co-CTFE films (thickness = 55 µm) was measured, and the electrolyte uptake capacity reached 3.53 mg/cm² in 60 sec, indicating that PVDF copolymer has excellent absorption property to liquid
electrolyte solution. This excellent wettability of PVDF copolymer should help to improve the electrolyte uptake capacity of PP microporous membranes.

Among the three nanofiber-coated PP membranes studied, PVDF-co-CTFE nanofiber-coated membranes have the highest electrolyte uptakes. Since the PVDF-co-CTFE nanofibers have the smallest average diameters (see Figure 4.5), these smaller fiber diameters provide higher surface area and capillary effect of nanofiber coatings, leading to improved electrolyte uptake.

### 4.3.4 Adhesion of nanofiber-coated membranes to the battery electrodes

Excellent adhesion between the microporous separator membrane separator and the battery electrodes is important for improving the battery performance and safety [6,33]. To investigate the adhesion properties of both uncoated and nanofiber-coated PP membrane separators to battery electrodes, peel tests were carried out on membrane/electrode assemblies which were prepared by hot-pressing a nanofiber-coated membrane onto a LiFePO₄ electrode using the plate press method at different temperatures and pressures. The membrane/electrode assemblies were prepared at 100 °C and 70 psi.

Figure 4.9 shows the loads needed to peel the uncoated and nanofiber-coated PP membranes away from the LiFePO₄ electrode. The adhesion between uncoated membrane and the electrode was observed to be low with a load of around 0.005 N/cm needed to peel the uncoated membrane from the electrode. Figure 4.9 shows the PVDF copolymer nanofiber coatings improved the adhesion of the membranes to the electrode. The presence of beads does not have apparent negative effect on the adhesive properties. In addition, compared with
PVDF-co-HEP, PVDF-co-CTFE has higher polarity and strong adhesion property owing to the presence of CTFE comonomers. As a result, among all samples studied, PVDF-co-CTFE nanofiber-coated membrane has the highest adhesion to the electrode. For comparison, the adhesion between the self-standing PVDF-co-CTFE film and the electrode was also measured and it was found the load needed to peel the self-standing PVDF-co-CTFE film from the electrode was around 0.09 N/cm. This high loading value demonstrates that the good adhesion property of PVDF copolymer is the main reason for the improved separator-electrode adhesion.

Figure 4.9. Peeling load as a function of length for peeling uncoated and nanofiber-coated PP membranes from the battery electrode. Membrane/electrode assemblies were prepared at 100 °C and 75 psi.
Figure 4.10. SEM images of (A,B) uncoated membrane, (C,D) PVDF-co-CTFE, (E,F) PVDF-co-CTFE/PVDF-co-HFP (1), and (G,H) PVDF-co-CTFE/PVDF-co-HFP (2) nanofiber-coated membranes after the peel test. Magnification: 1,000 × (A,C,E,G), 20,000 × (B,D,F,H).
To further demonstrate the improved adhesion between the nanofiber-coated membrane and the electrode, the morphology of the membranes was examined after they were peeled off from the electrode. Figure 4.10 shows SEM images of uncoated and nanofiber-coated membranes after the peel tests. The SEM micrographs provide evidence that after peel testing, some cathode particles are pulled off the surface of the cathode by the nanofiber coating, indicating the good adhesive property of the PVDF copolymer nanofiber coatings studied. However, only a few small particles can be found on the uncoated membrane after the peel test due to the absence of nanofiber coating. SEM results confirm that the adhesion between the separator membrane and the electrode has been improved by the deposition of nanofibers on the membrane surface.

Figure 4.11. Peeling load for peeling (A) PVDF-co-CTFE and (B) PVDF-co-CTFE/PVDF-co-HFP (1) nanofiber-coated PP membranes from the battery electrode.

Membrane/electrode assemblies were also prepared at a series of different temperatures and pressures, and the peel test results are shown in Figure 4.11. Increasing temperature and
pressure from $T = 100 \, ^\circ C$ and $P = 70 \, \text{psi}$ to a $T = 120 \, ^\circ C$ and $P = 85 \, \text{psi}$ for both PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP (1) nanofiber-coated PP membranes, increased the separator-electrode adhesion. Under the conditions studied, the PVDF copolymers are better softened and have higher bonding capability at elevated temperature and pressure [36-37].

4.4 Summery

Electrospinning technology was used to prepare PVDF copolymer nanofiber-coated microporous PP membranes for use as separators in rechargeable lithium-ion batteries. Interconnected nanofiber coatings were obtained on the surface of PP membrane substrate for PVDF-co-CTFE, PVDF-co-CTFE/PVDF-co-HFP (1), and PVDF-co-CTFE/PVDF-co-HFP (2). All three nanofiber coatings have comparable adhesion to the PP membrane substrate. Due to increased porosity and capillary effect of PVDF copolymer nanofibers, the electrolyte uptake capacities were improved by incorporating nanofiber coatings on the surface of the PP membrane substrate. Because PVDF copolymers have good adhesion properties, PVDF copolymer nanofiber-coated membranes exhibit stronger separator-electrode adhesion than uncoated membranes. In addition, PVDF-co-CTFE nanofiber-coated membranes show higher electrolyte uptakes and better separator-electrode adhesion than PVDF-co-CTFE/PVDF-co-HFP (1) and PVDF-co-CTFE/PVDF-co-HFP (2) nanofiber-coated membranes since PVDF-co-CTFE has higher polarity and stronger adhesion force which are attributed to the presence of CTFE comonomers. The separator-electrode adhesion can be further improved by
increasing the temperature and pressure used during the preparation of separator-electrode assemblies.
4.5 References


CHAPTER 5. Electrospun Nanofiber-Coated Membranes Using different Types of Membrane Substrates for Battery Separators

Abstract

Nanofiber-coated composite membranes were prepared by electrospinning polyvinylidene fluoride-co-chlorotrifluoroethylene (PVDF-co-CTFE) and PVDF-co-CTFE/polyvinylidene fluoride-co-hexafluoropropylene (PVDF-co-HFP) onto six different Celgard® microporous battery separator membranes. Application of a PVDF-based copolymer nanofiber coating onto the surface of the battery separator membrane provides a method for improving the electrolyte absorption of the separator and the separator-electrode adhesion. Peel tests showed that both PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP nanofiber coatings have comparable adhesion to the membrane substrates. Electrolyte uptake capacity was investigated by soaking the nanofiber-coated membranes in a liquid electrolyte solution. PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP nanofiber-coated membranes exhibited higher electrolyte uptake capacities than uncoated membranes. It was also found that PVDF-co-CTFE nanofiber-coated membranes have higher electrolyte uptakes than PVDF-co-CTFE/PVDF-co-HFP nanofiber-coated membranes due to the smaller diameters of PVDF-co-CTFE nanofibers and higher polarity of PVDF-co-CTFE. The separator-electrode adhesion properties were also investigated. Results showed PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP nanofiber coatings improved the adhesion of all six membrane substrates to the electrode.
5.1 Introduction

Lithium-ion rechargeable batteries have been considered as one of the most promising candidates for large-scale power source and energy storage devices for the near future. A critical component of lithium-ion batteries is the separator. The separator provides a physical barrier between the positive and negative electrodes in order to prevent electrical short circuits. The separator serves as a medium for transport of ions during the charging and discharging cycles of a battery. In addition, the separator must be electrochemically inert in the battery. It is well recognized that the separator greatly influences the electrochemical performance of lithium-ion batteries [1-3]. Currently, polyolefin microporous membranes are the most commonly used separator for lithium-ion rechargeable batteries. However, polyolefin microporous membranes can still be improved in terms of the adhesion of separator to electrode and wettability for the higher performance of lithium-ion batteries [4-6].

A variety of approaches have been used in the development of novel porous membrane separators, including phase inversion membranes [7-10], electrospun nonwoven separators [11-14], inorganic composite materials [11,12-18], surface-modified membranes [19-21], and multilayered separators [22-23]. The nanofiber membranes prepared using electrospinning methods have high porosity enabling them to host a large amount of liquid electrolyte which contributes to good electrolyte retention and high ionic conductivity.

Various polymers including polyethylene oxide (PEO) [24-26], polyacrylonitrile (PAN) [11-13,27], polymethyl methacrylate (PMMA) [27-29], polyvinylidene fluoride (PVDF) [30-31], polyvinylidene fluoride-co-chlorotrifluoroethylene (PVDF-co-CTFE) [32],
polyvinylidene fluoride-co-hexafluoropropylene (PVDF-co-HFP) [13-14,28], polyvinyl chloride (PVC) [29,33], and polyethylene glycol (PEG) [26,34] have been used for electrospun nanofiber membranes. Among them, PVDF copolymers, such as PVDF-co-CTFE and PVDF-co-HFP, are particularly promising due to their good affinity to the electrolyte solution and excellent electrochemical stability in lithium-ion batteries. However, most electrospun nanofiber stand-alone membranes are inherently weak and do not have sufficient mechanical properties to withstand the winding forces during the battery assembling process. In addition, when they are soaked in liquid electrolyte solution, they can form polymer gels and the flow properties of these gels can lead to internal short-circuits and safety hazards, especially at elevated temperatures [1-2,13,35]. An alternative approach uses electrospinning technology to apply nanofibers onto a microporous supporting substrate which provides the required mechanical strength. The resultant composite membrane can then withstand the stresses inherent in the manufacturing process of lithium-ion batteries.

This paper presents the preparation and properties of PVDF copolymer nanofiber-coated microporous membranes prepared using a nozzle-less electrospinning technique. Six different Celgard microporous polyolefin membranes were used as the supporting substrate. Electrospun PVDF copolymer nanofiber coatings were found to improve the wettability of the separator by liquid electrolyte, which is highly desirable for the development of lithium-ion batteries with high ionic conductivity and good cycling performance. The results presented in this paper also demonstrate that PVDF copolymer nanofiber-coated microporous separator membranes had improved adhesion properties to the battery electrode.
5.2 Experimental

5.2.1 Materials

Microporous separator membranes (Celgard\textsuperscript{\textregistered} LLC) were used as the base substrate for the deposition of nanofibers.

Table 5.1. Material type, thickness, porosity, and pore size of membrane separators.

<table>
<thead>
<tr>
<th>Membrane material</th>
<th>Thickness (\textmu m)</th>
<th>Porosity (%)</th>
<th>Pore size (\textmu m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolayer 1</td>
<td>PP</td>
<td>25</td>
<td>41</td>
</tr>
<tr>
<td>Monolayer 2</td>
<td>PP</td>
<td>20</td>
<td>41</td>
</tr>
<tr>
<td>Monolayer 3</td>
<td>PP</td>
<td>15</td>
<td>74</td>
</tr>
<tr>
<td>Trilayer 1</td>
<td>PP/PE/PP</td>
<td>12</td>
<td>38</td>
</tr>
<tr>
<td>Trilayer 2</td>
<td>PP/PE/PP</td>
<td>16</td>
<td>35</td>
</tr>
<tr>
<td>Trilayer 3</td>
<td>PP/PE/PP</td>
<td>14</td>
<td>38</td>
</tr>
</tbody>
</table>

In order to investigate the effect of substrate type on the morphology and properties of PVDF copolymer nanofiber coatings, six membrane separators, referred to as Monolayer 1, Monolayer 2, Monolayer 3, Trilayer 1, Trilayer 2, and Trilayer 3, were selected for this
study. Monolayers 1 through 3 are single-layer and polypropylene (PP) microporous membranes made by using dry process technique. The trilayer microporous membranes consist of a PE monolayer membrane between two outer PP monolayers in a PP/PE/PP configuration. Table 5.1 summarizes the basic separator properties of polymer type, thickness, porosity, and pore size of the six Celgard® microporous membranes included in this study. The selected microporous membranes have pore sizes ranging from 0.026 to 0.096 µm, thicknesses of 12 - 25 µm, and porosities of 35 - 74%.

Table 5.2. Chemical structure, molecular weight and melting temperature of PVDF copolymers.

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Molecular Weight (g/mol)</th>
<th>Melting Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF-co-CTFE</td>
<td>280,000</td>
<td>168</td>
</tr>
<tr>
<td>PVDF-co-HFP</td>
<td>115,000</td>
<td>135</td>
</tr>
</tbody>
</table>

PVDF-co-CTFE (Solvay® Solef#32008) and PVDF-co-CTFE/PVDF-co-HFP (Solvay® Solef#21508) blend (9:1 by weight) dissolved in mixed solution of acetone and N,N-
dimethylformamide (3:7 by weight) were used to prepare the electrospun nanofiber coatings. Table 5.2 shows the basic properties of the PVDF copolymers included for this study.

5.2.2 Preparation of nanofiber-coated separators

Nanofiber coatings were prepared by using a nozzle-less electrospinning device (NanoSpider™ NS200, Elmarco), as shown in Figure 5.1. The electrospinning polymer solution was placed in an open solution container (not shown in Figure 1). An electrode connected with 6 parallel stainless steel patterned wires was rotated at a fixed speed of 6 r/min in order to wet the steel wires with the polymer solution. A high voltage was applied to the polymer solution to form multiple polymer jets which were ejected (up-spinning) from the solution carried on the wire surface. A 3-D network of nanofibers was deposited onto the membrane substrate as it moved continuously at a fixed speed under the grounded collector. A continuous nanofiber coating with a width of 16 - 17 cm was deposited on the surface of the microporous membrane substrate.

The electrospinning conditions were controlled so that nanofibers were produced having comparable morphology and uniform fiber diameters. The optimal conditions used for electrospinning of PVDF-co-CTFE nanofibers were: i) applied voltage = 40 kV, ii) electrode-to-collector distance = 15 cm, iii) electrode rotational speed = 6 r/min, and iv) membrane movement speed = 0.26 m/min, while those for PVDF-co-CTFE/PVDF-co-HFP were: i) applied voltage = 38 kV, ii) electrode-to-collector distance = 15 cm, iii) electrode rotational speed = 6 r/min, and iv) membrane movement speed = 0.26 m/min. The electrospinning for PVDF-co-CTFE/PVDF-co-HFP was also carried out at 40 kV, but it did not produce uniform
nanofibers. Similarly, the electrospinning for PVDF-co-CTFE was carried out at 38 kV, but no uniform nanofibers were obtained. Therefore, 40 kV was selected for the electrospinning of PVDF-co-CTFE and 38 kV was selected for PVDF-co-CTFE/PVDF-co-HFP.

Figure 5.1. Schematic of nozzle-less electrospinning device. For simplicity, the solution container is not shown.

5.2.3 Structure characterization and property measurements
The morphology of the uncoated and nanofiber-coated membranes was evaluated using a scanning electron microscopy (JEOL 6400F Field emission SEM at 5 kV). The samples for SEM observation were pre-coated with Au/Pd by a K-550X sputter coater to reduce charging. The diameters of electrospun nanofibers were obtained by measuring fifty fibers randomly selected in SEM images using Revolution v1.6.0 software.

Liquid electrolyte uptake capacities were measured by soaking pre-weighed nanofiber-coated composite membrane samples for a fixed time at room temperature in a liquid electrolyte. The electrolyte consisted of 1 M lithium hexafluorophosphate (LiPF₆) dissolved in 1:1:1 (by volume) ethylene carbonate/dimethylcarbonate/ethylmethyl carbonate. The excess electrolyte solution adhering to the surface of the composite membrane was removed by gently wiping with filter paper. The electrolyte uptake capacities were determined using the following equation:

\[ \text{Uptake Capacity (mg/cm}^2\text{)} = (W_t - W_0) / A \]

where \( W_t \) was the weight of the electrolyte-immersed composite membrane, \( W_0 \) the weight of dried composite membrane, and \( A \) the immersed area of the test sample.

The adhesion strength of nanofiber coatings to the membrane substrate was evaluated by using the ASTM D 1876 standard method, which is a modified ASTM D 2261 standard tongue tear test method using an Instron® Tensile Tester. Figure 2a depicts the modified peel test method used to evaluate the adhesion strength of nanofiber coating layer on the membrane substrate. In this method, the test was carried out on a T-type specimen of two adherends, which were the nanofiber coating and the membrane substrate, respectively. A test sample measuring \( 2.5 \times 7.5 \text{ cm}^2 \) was held in the two jaws of the Instron machine, with
the nanofiber-coated layer clamped to the movable upper jaw and the membrane substrate attached to the fixed lower jaw. A tape (3M Scotch® Magic™ Tape 810) was placed on the undersides of the nanofiber coating and the membrane substrate to prevent stretching and slipping. The jaws were set at an initial separation distance of 2.5 cm. With the upper jaw moving at a constant rate of 50 mm/min, the nanofiber coating layer was peeled away from the membrane substrate surface at a 90 degree angle. A 100 N load cell was used for measuring the adhesion strength of the coating layer through the entire sample length.

Figure 5.2. Schematic of peeling tests for measuring (a) the adhesion between nanofiber coating and membrane, and (b) the adhesion between nanofiber-coated membrane and battery electrode.
The adhesion between the nanofiber-coated composite membrane and a battery electrode was also evaluated by conducting peel tests on the nanofiber-coated membrane/electrode laminated assemblies, i.e., peeling the electrode away from the nanofiber-coated composite membrane, as shown in Figure 2b. The electrode used was a LiFePO₄ cathode (MTI Corporation). The nanofiber-coated membrane/electrode assemblies (2.5 × 7.5 cm²) were prepared by hot pressing (Carver Model C) the test sample using the press plate method at 120 °C and 85 psi for 5 minutes. The peel tests were performed with a 5 N load cell. The reproducibility of electrolyte uptake capacity and adhesion results was ensured by conducting all measurements on at least eight samples.

5.3 Results and discussion

5.3.1 SEM images

Figures 5.3 and 5.4 show SEM images of uncoated Monolayer and Trilayer membranes, respectively. All six membranes have uniform distribution of pores with pore sizes ranging from 0.026 to 0.096. Monolayer 1 and Monolayer 2 membranes have comparable pore sizes and show typical morphology of dry process separator membranes. Monolayer 3 has unique pore structures of a different shape and size. Figure 5.4 shows the SEM micrographs of Trilayer membranes having similar morphology, but with smaller pore sizes than those of Monolayer membranes. The six membranes were selected for this study in order to investigate if membrane morphology, specifically pore size, porosity, and thickness can affect the electrolyte uptake capability and the adhesion properties of electrospun nanofiber-coated microporous membranes.
Figure 5.3. SEM images of uncoated (a,b) Monolayer 1, (c,d) Monolayer 2, and (e,f) Monolayer 3 membranes. Magnification: (a,c,e) 1,000 ×, and (b,d,f) 20,000 ×.
Figure 5.4. SEM images of uncoated (a,b) Trilayer 1, (c,d) Trilayer 2, and (e,f) Trilayer 3 membranes. Magnification: (a,c,e) 1,000 ×, and (b,d,f) 20,000 ×.

It is difficult to produce nanofiber coatings with exactly the same loading density and coating thickness. However, the processing conditions were carefully controlled so that
nanofibers on the surface of membrane substrates were produced with comparable coating loadings and thicknesses. The loading densities of PVDF-co-CTFE nanofibers were 1.0, 0.8, 0.7, 0.7, 0.7, and 0.7 g/m² for Monolayer 1, Monolayer 2, Monolayer 3, Trilayer 1, Trilayer 2, and Trilayer 3, respectively. The loading densities of PVDF-co-CTFE/PVDF-co-HFP nanofibers were 0.9, 0.9, 0.7, 0.7, 0.8, and 0.8 g/m² for Monolayer 1, Monolayer 2, Monolayer 3, Trilayer 1, Trilayer 2, and Trilayer 3, respectively. The thicknesses of PVDF-co-CTFE nanofiber coatings produced on membrane substrates were 3–4, 2–4, 2–3, 2–3, 2–3, and 2–4 µm for Monolayer 1, Monolayer 2, Monolayer 3, Trilayer 1, Trilayer 2, and Trilayer 3, respectively. The thicknesses of PVDF-co-CTFE/PVDF-co-HFP nanofiber coatings produced on membrane substrates were 3–4, 3–4, 2–4, 1–3, 2–3, and 1–3 µm for Monolayer 1, Monolayer 2, Monolayer 3, Trilayer 1, Trilayer 2, and Trilayer 3, respectively. Figures 5.5 and 5.6 show the SEM images and fiber diameter distribution of PVDF-co-CTFE nanofiber-coated membranes prepared by electrospinning. PVDF-co-CTFE nanofiber coatings on all six membrane substrates were found to have similar fiber diameters and interconnected fiber arrangement regardless of membrane type. The electrospun PVDF-co-CTFE nanofibers coated on both Monolayer and Trilayer membrane substrates show comparable average diameters in the range of 127 - 134 nm.
Figure 5.5. SEM images and fiber diameter distributions of PVDF-co-CTFE nanofiber-coated (a,b,c) Monolayer 1, (d,e,f) Monolayer 2, and (g,h,i) Monolayer 3 membranes. Magnification: (a,d,g) 1,000 ×, and (b,e,h) 10,000 ×.

(c) Average diameter = 129 nm

(f) Average diameter = 132 nm

(i) Average diameter = 134 nm
Figure 5.6. SEM images and fiber diameter distributions of PVDF-co-CTFE nanofiber-coated (a,b,c) Trilayer 1, (d,e,f) Trilayer 2, and (g,h,i) Trilayer 3 membranes. Magnification: (a,d,g) 1,000 ×, and (b,e,h) 10,000 ×.
Figure 5.7. SEM images and fiber diameter distributions of PVDF-co-CTFE/PVDF-co-HFP nanofiber-coated (a,b,c) Monolayer 1, (d,e,f) Monolayer 2, and (g,h,i) Monolayer 3 membranes. Magnification: (a,d,g) 1,000 ×, and (b,e,h) 10,000 ×.
Figure 5.8. SEM images and fiber diameter distributions of PVDF-co-CTFE/PVDF-co-HFP nanofiber-coated (a,b,c) Trilayer 1, (d,e,f) Trilayer 2, and (g,h,i) Trilayer 3 membranes. Magnification: (a,d,g) 1,000 ×, and (b,e,h) 10,000 ×.

The SEM images and fiber diameter distribution of PVDF-co-CTFE/PVDF-co-HFP nanofiber-coated membranes are presented in Figures 5.7 and 5.8. The electrospun PVDF-co-CTFE/PVDF-co-HFP nanofibers also formed an interconnected network of randomly oriented fibers on the surfaces of both Monolayer and Trilayer membrane substrates. A
comparison of electrospun PVDF-co-CTFE nanofibers with the PVDF-co-CTFE/PVDF-co-HFP nanofibers shows that the latter has larger fiber diameters, with the average fiber diameter ranging from 165 to 183 nm. The larger fiber diameters may be attributable to the lower voltage of 38 kV used in the electrospinning of the blended PVDF-co-CTFE/PVDF-co-HFP nanofibers as compared to the 40 kV voltage used for PVDF-co-CTFE nanofibers.

5.3.2 Adhesion between nanofiber coatings and membrane substrates

PVDF copolymers have been widely used as a binder for lithium-ion battery electrodes because of their excellent adhesive property [13-14,32]. The adhesion of the PVDF copolymer nanofibers to the base substrate membrane was investigated in this study. Peel tests were conducted on nanofiber-coated membranes to determine the adhesion force between the nanofiber coatings and the membrane substrates.

The surfaces of substrate membranes were examined by SEM after peeling off the electrospun nanofiber coatings (Figure 5.9). It is seen that electrospun nanofibers were completely peeled off from the membrane substrates after the peel test. The SEM images confirm that the peeling load is determined by the adhesive property between nanofibers and membrane surface.
Figure 5.9. SEM images of PVDF-co-CTFE nanofiber-coated (a) Monolayer 1, (b) Monolayer 2, (c) Monolayer 3, (d) Trilayer 1, (e) Trilayer 2, and (f) Trilayer 3 membranes after peel test. Magnification: 20,000 ×.
Figures 5.10a and 5.10b show the loads in N/cm needed to peel the PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP nanofiber coating layers away from the membrane substrates. Both PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP nanofiber coatings were found to produce good adhesion to the selected membrane substrates in this study with the exception of Monolayer 3. The adhesion of electrospun nanofiber coatings on Monolayer 3 was much lower than those on other membranes. This weak adhesion may be related to the unique morphologic structure of Monolayer 3. As shown in Table 5.1 and Figure 5.3, Monolayer 3 has significantly higher porosity and larger pore size than the other membranes in this study, which resulted in a smaller contact area between the nanofibers and the membrane substrate. It is also seen in Figure 5.10 that the adhesions of PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP nanofibers to membrane substrates are comparable.

Figure 5.10. Peeling load of (a) PVDF-co-CTFE and (b) PVDF-co-CTFE/PVDF-co-HFP nanofiber coatings from the membrane substrates.
5.3.3 Electrolyte uptakes of nanofiber coated membranes

Electrolyte uptake capacity is a measurement indicating the amount of liquid electrolyte solution absorbed by the unit area of a membrane separator. For lithium-ion rechargeable batteries, the separator should rapidly absorb liquid electrolyte solution to accelerate the battery assembly process and to achieve a low internal resistance and good battery performance [1-2,27].

A comparison of the electrolyte uptake capacities of uncoated membranes (a), PVDF-co-CTFE nanofiber-coated membranes (b) and PVDF-co-CTFE/PVDF-co-HFP nanofiber-coated membranes (c) is shown in Figure 5.11. The absorption of liquid electrolyte was quick in the first 60 seconds, as shown in the inset of Figure 5.11. The electrolyte uptake capacity of membranes depends on the basic membrane properties such as thickness, porosity, and pore size. As shown in Table 5.1, Monolayer membranes are thicker and have higher porosity and pore size than Trilayer membranes, and hence they can have higher electrolyte capacity than that of Trilayer membranes. From Figure 5.11, it is seen that Trilayer 1 showed the lowest electrolyte uptake because it has the lowest thickness and smallest pore size. On the other hand, Monolayer 3 has the highest electrolyte uptake due to its highest porosity and largest pore size in spite of thinner thickness.

Compared with uncoated membranes, electrospun PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP nanofiber-coated membranes have higher electrolyte uptake capacities. Monolayer 1 coated with PVDF-co-CTFE showed better improvement in electrolyte uptake capacity than other nanofiber-coated membranes due to slightly higher thickness and loading density of nanofibers.
Figure 5.11. Electrolyte uptake capacity as a function of time for (a) uncoated, (b) PVDF-co-CTFE nanofiber-coated, and (c) PVDF-co-CTFE/PVDF-co-HFP nanofiber-coated membranes. Inset shows the uptake capacities within 60 sec.
Since the large amount of nanofiber coating on membrane substrate leads to higher improvement of electrolyte uptake, higher thickness and loading density of nanofiber coatings can contribute greater electrolyte uptake capacity. In this work, the nanofiber coatings were prepared to have comparable thicknesses and thus further work is required to study the effects of coating thickness, loading density, and nanofiber diameter on the electrolyte uptake capability of nanofiber-coated separators.

The improvement in electrolyte uptake by nanofiber coatings should be caused mainly by the increased porosity and capillary effect on nanofibrous structure. Furthermore, PVDF-co-CTFE and PVDF-co-HFP polymers have significant amounts of polar groups and show good affinity to liquid electrolyte solutions [10,14,36], leading to improved electrolyte uptakes. In this work, to investigate the effect of chemical structure of PVDF copolymer on the electrolyte uptake capacity of nanofiber coatings, PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP blend solutions were used for the preparation of electrospun nanofibers on membrane substrates. Since PVDF-co-HFP has low molecular weight and HFP monomers on their polymer chains, they form electrospun nanofibers with lower crystallinity [14,28]. The initial purpose of using PVDF-co-CTFE/PVDF-co-HFP blend nanofibers was to achieve higher adsorption of liquid electrolyte solution. However, it was found that the use of PVDF-co-CTFE/PVDF-co-HFP blend nanofibers did not improve the electrolyte uptake capacity.

The type of membrane substrate is shown to have an influence on the electrolyte uptake capacities. For example, the Trilayer membrane substrates had smaller electrolyte uptake capacities than Monolayer membrane substrates likely due to their smaller porosity and pore size (see Table 5.1).
5.3.4 Adhesion of nanofiber-coated membranes on the electrode

Excellent adhesion between the membrane separator and the electrode is required for desirable lithium-ion battery performance. In order to evaluate the adhesive properties of nanofiber-coated membranes to the battery electrode, PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP nanofiber-coated membranes were laminated to a LiFePO₄ battery electrode to form membrane/electrode assemblies. The lamination conditions involved hot pressing the coated membranes to an electrode at 120 °C and 85 psi for 5 min. Peel tests were then performed to evaluate the comparative efficacies of the PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP nanofiber-coatings to the electrode during lamination.

Figure 5.12. Peeling load of (a) PVDF-co-CTFE nanofiber-coated, and (b) PVDF-co-CTFE/PVDF-co-HFP nanofiber-coated membranes from the battery electrode. For comparison, loads for peeling uncoated membranes are also shown.
Figure 5.12 shows the load in N/cm required to peel the PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP nanofiber-coated membranes away from the battery electrode. For comparison, the load from the peel test of the uncoated membranes is also shown. The uncoated membranes were observed to have the lowest adhesion to the battery electrode under the test lamination conditions. The coatings of PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP nanofibers were found to improve the adhesion between the membrane substrate and the surface of the battery electrode. The electrospun nanofiber coating layer provides an effective adhesive property to bond the membrane and electrode together. As shown in Figure 5.12, among all samples, Monolayer 1 coated with PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP nanofibers showed the highest separator-electrode adhesion properties because the nanofiber coating on Monolayer 1 has slightly thicker and higher loading density of nanofibers than others. The larger amount of nanofibers on the surface of membrane substrate leads to higher contact area between the nanofibers and the electrode, which may be contributing to enhanced separator-electrode adhesion. To investigate the thickness effect of nanofiber coatings on adhesion property, further work should be required to establish nanofiber-coated membranes with the different thicknesses of nanofiber coatings. Except for Monolayer 1, the adhesion properties of nanofiber-coated Monolayer 2, Monolayer 3, Trilayer 1, Trilayer 2, and Trilayer 3 exhibited comparable peeling strength. The results demonstrate that there is no correlation between the separator-electrode adhesion and the thickness of membrane substrate. The initial purpose of using PVDF-co-CTFE/PVDF-co-HFP blend copolymer was to enhance the adhesion properties.
Figure 5.13. SEM images of (a) uncoated, and PVDF-co-CTFE nanofiber-coated (b) Monolayer 1, (c) Monolayer 2, (d) Monolayer 3, (e) Trilayer 1, (f) Trilayer 2, and (g) Trilayer 3 membranes after peel test. Magnification: 20,000 ×.
However, it was found that the adhesion of PVDF-co-CTFE nanofiber-coated membranes to the electrode was higher than that of PVDF-co-CTFE/PVDF-co-HFP nanofiber-coated membranes. Therefore, using PVDF-co-CTFE/PVDF-co-HFP blend polymer solution has no improvement on the separator-electrode adhesion.

Figure 5.13 shows SEM images of uncoated and nanofiber-coated membranes after they were peeled off from the electrode surface. After performing the peel tests, a large amount of electrode particles were moved from the electrode surface and were attached onto the nanofiber-coated membranes due to the good adhesive properties of nanofiber coatings. However, on the uncoated membrane, only a few small electrode particles were found because of the absence of nanofiber coatings. These SEM images further confirm that the adhesion between the separator membrane and the electrode has been improved by the deposition of nanofiber coatings on the membrane surface.

5.4 Summary

A nozzle-less electrospinning method was used to prepare PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP nanofiber-coated battery separator membranes. The nanofiber composite membranes were prepared by electrospinning PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP blended polymers onto a series of Celgard® microporous battery separator membranes. Six different types of Celgard® microporous membrane substrates were used to study the effect of substrate type on the structure and performance properties of PVDF nanofiber coatings. Electrospun PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP nanofiber coatings showed comparable adhesion to the membrane substrates, except for
Monolayer 3 which has the highest porosity and largest pore size. Electrospinning nanoscale fibrous coatings onto the surface of microporous membranes provided an effective method for improving the absorption of liquid electrolyte by the separator membranes. The improved electrolyte uptake capacity of the PVDF nanofiber-coated membranes observed in this study is due to high affinity of PVDF copolymers and the capillary effect of the electrospun nanofibers deposited on the surface of the membrane substrates. Regardless of types of microporous membrane substrate used in this study, the PVDF copolymer nanofiber coatings were found to provide improved adhesion to the LiFePO$_4$ electrode during lamination. The properties of separator membrane material did not have a significant effect on the level of electrolyte uptake capacity and separator-electrode adhesion obtained for the series of membranes studied. Based on the results, it can be concluded that the adhesion of PVDF-co-CTFE nanofibers to Monolayer 1 provided the strongest nanofiber coating among all samples and PVDF-co-CTFE nanofiber-coated Monolayer 1 presented the highest electrolyte uptake capacity and separator-electrode adhesion property.
5.5 References


[22] X. Huang, J. Power Sources 196 (2011) 8125-8128


CHAPTER 6. Electrochemical Properties and Cycle Performance of Electrospun Nanofiber-coated Membrane Separators for Lithium-Ion Batteries

Abstract

Nanofiber-coated membrane separators were prepared by electrospinning polyvinylidene fluoride-co-chlorotrifluoroethylene nanofibers onto three different microporous membrane substrates. The nanofibers on the membrane substrates showed uniform morphology with average fiber diameters ranging from 129 to 134 nm. Electrolyte uptakes, ionic conductivities and interfacial resistances were studied by soaking the nanofiber-coated membrane separators with a liquid electrolyte solution of 1 M lithium hexafluorophosphate in ethylene carbonate/dimethylcarbonate/ethylmethyl carbonate (1:1:1 vol). Compared with uncoated membranes, nanofiber-coated membranes had greater electrolyte uptakes and lower interfacial resistances to the lithium electrode. It was also found that after soaking in the liquid electrolyte solution, nanofiber-coated membranes exhibited higher ionic conductivities than uncoated membranes. In addition, the coin cells using nanofiber-coated membranes were evaluated with LiFePO₄ cathode for charge-discharge capacities and cycle performance. The cells containing nanofiber-coated membranes as the separator showed high discharge specific capacities and good cycling stability at room temperature. Results demonstrated that
coating nanofibers onto microporous membrane substrates is a promising approach to obtain new and high-performance separators for rechargeable lithium-ion batteries.
6.1 Introduction

Recently, high energy demands have encouraged the development of high-performance lithium-ion batteries for portable electronic devices and electric vehicles [1-2]. The separator is a critical component for achieving high performance for lithium-ion batteries. The role of the separator is to prevent the physical contact between the positive and negative electrodes of the battery while allowing the transportation of ions [3-4]. Polyolefin microporous membranes are the most commonly-used separators for lithium-ion batteries because of their excellent mechanical strength and good chemical stability [5-6]. However, polyolefin microporous membranes can still be improved in aspects such as electrolyte wettability, interfacial resistance, etc., so as to achieve higher performance for lithium-ion batteries.

In recent years, electrospinning technique has been developed to generate nonwoven membranes with controlled structure and morphology [7-9]. Many researchers have used the electrospinning method to prepare electrospun nanofiber membranes with large porosity and high electrolyte uptake for lithium-ion batteries [10-12]. However, self-standing electrospun membranes have insufficient mechanical strength and they are easily damaged during battery assembly.

This study reports the preparation and characterization of composite membrane separators by depositing electrospun nanofibers onto polyolefin microporous membranes (Figure 6.1). Nanofiber coatings were prepared on three different Celgard microporous polyolefin membranes by using nozzle-less electrospinning. Polyvinylidene fluoride-co-chlorotrifluoroethylene (PVDF-co-CTFE) was used for the preparation of electrospun nanofiber coatings because it has excellent electrochemical stability, good adhesion property,
and high temperature resistance [9,13-16]. The morphology of electrospun nanofiber coatings on the surface of membrane substrates and the electrolyte uptake capacities of nanofiber-coated membranes were investigated. The ionic conductivities were measured by soaking nanofiber-coated membranes with a liquid electrolyte solution. In addition, the lithium-ion cells were assembled with nanofiber-coated membranes to evaluate electrochemical properties and cycling performance. In this paper, the effect of nanofiber coatings on the performance of membrane separators for lithium-ion batteries was discussed by comparing the properties of nanofiber-coated membranes with uncoated membranes.

Figure 6.1. Process for the preparation and cell assembly of electrospun nanofiber-coated membrane.
6.2 Experimental

6.2.1 Materials

Commercial microporous separators (Celgard LLC) were used as the base substrate for the deposition of nanofibers. In order to investigate the effect of base membrane structure on the properties of nanofiber coatings, three different microporous membranes were selected and they were referred as: Membrane 1, Membrane 2, and Membrane 3. The basic properties on the material type, thickness, porosity, and pore size for all three membranes are summarized in Table 6.1. Both Membranes 1 and 3 are made of polypropylene (PP), but Membrane 2 is made of polyethylene (PE). Membrane 1 has the largest thickness and smallest pore size. Membrane 3 has the smallest thickness and largest porosity and pore size.

Table 6.1. Material types, thicknesses, porosities and pore sizes of membrane separators.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Material</th>
<th>Thickness (μm)</th>
<th>Porosity (%)</th>
<th>Pore size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane 1</td>
<td>PP</td>
<td>25</td>
<td>41</td>
<td>0.043</td>
</tr>
<tr>
<td>Membrane 2</td>
<td>PE</td>
<td>16</td>
<td>40</td>
<td>0.060</td>
</tr>
<tr>
<td>Membrane 3</td>
<td>PP</td>
<td>15</td>
<td>74</td>
<td>0.096</td>
</tr>
</tbody>
</table>
Electrospun nanofibers were prepared from 15 wt% polymer solutions of poly(vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-co-CTFE) (Solvay® Solef®32008) dissolved in mixed solutions of acetone and N,N dimethylformamide (3:7 by weight).

6.2.2 Preparation of nanofiber-coated separators

Nanofiber coatings were prepared by using a nozzle-less electrospinning device (NanoSpider™ NS200, Elmarco), as shown in Figure 6.2. The electrospinning polymer solution is placed in an open polymer container. An electrode connected with 6 parallel stainless steel patterned wires was rotated at a fixed speed of 6 r/min in order to wet the steel wires with the polymer solution. A high voltage was applied to the polymer solution and multiple polymer jets were ejected (up-spinning) from the solution carried on the wire surface. The nanofibers were deposited onto the PP membrane which was moved continuously at a fixed speed under the grounded collector. Using the NanoSpider™ NS200, electrospun nanofiber coatings of 16 - 17 cm in width were deposited on the membrane substrates.

The electrospinning conditions can be controlled so that they produced nanofiber coatings with comparable morphology and uniform fiber diameter. To achieve this, the conditions used for electrospinning of PVDF-co-CTFE nanofibers were: 1) applied voltage = 40 kV, 2) electrode-to-collector distance = 15 cm, 3) electrode rotational speed = 6 r/min, and 4) membrane movement speed = 0.26 m/min.
6.2.3 Structure characterization and property measurements

The morphology of both uncoated and nanofiber-coated membranes was evaluated using a scanning electron microscopy (JEOL 6400F Field emission SEM at 5 kV). The samples for SEM observation were coated with Au/Pd by a K-550X sputter coater to reduce charging. The diameters of electrospun nanofibers were obtained by measuring fifty fibers randomly selected in SEM images for each sample using Revolution v1.6.0 software.

Liquid electrolyte uptake capacities were measured by soaking pre-weighed uncoated and nanofiber-coated separator membrane samples for a fixed time at room temperature in a liquid electrolyte which consisted of 1 M Lithium hexafluorophosphate (LiPF₆) dissolved in 1:1:1 (by volume) ethylene carbonate (EC)/dimethylcarbonate (DMC)/ethylmethyl carbonate.
(EMC). The electrolyte was absorbed both on the surface and in the pores of the membranes. The excess electrolyte solution adhering to the membrane surface was removed by gently wiping with filter paper. The electrolyte uptake capacities of uncoated and nanofiber-coated separator membranes were determined using the following equation:

\[
\text{Uptake Capacity (mg/cm}^2\text{)} = \frac{(W_t - W_0)}{A}
\]

where \(W_t\) was the weight of the electrolyte-immersed membrane, \(W_0\) the weight of dry membrane, and \(A\) the immersed area of the test sample.

For the ionic conductivity measurement, uncoated and nanofiber-coated membranes were completely soaked in the liquid electrolyte of 1 M LiPF\(_6\) in EC/DMC/EMC and then sandwiched between two stainless-steel plate electrodes. The ionic conductivities of liquid electrolyte-soaked membranes were measured by electrochemical impedance spectroscopy (EIS) using Potentiostat/Galvanostat/ZRA (GAMRY Reference 600). The measurement was carried out at amplitude of 10 mV over a frequency range of 1Hz to 1MHz at a temperature range between 25 and 100 °C. The temperature was controlled in a temperature/humidity chamber (Ransco RTH-600-S). The conductivity (\(\sigma\)) was calculated by following equation:

\[
\sigma = \frac{d}{R_b \times A}
\]

where \(d\) is the membrane thickness, \(R_b\) the bulk resistance of liquid electrolyte-soaked membrane, and \(A\) the cross-sectional area of the membrane.

The interfacial resistance between liquid electrolyte-soaked membranes and the lithium electrode was measured by EIS using the Potentiostat/Galvanostat/ZRA (GAMRY Reference 600). The liquid electrolyte-soaked membranes were symmetrically sandwiched
with two lithium electrodes. The measurement was performed over a frequency range of 0.01 Hz to 65 kHz under open circuit conditions.

The electrochemical performance of lithium/lithium iron phosphate (LiFePO$_4$) cells containing liquid electrolyte-soaked membranes was evaluated using an Arbin automatic battery tester. The cells were prepared with the electrolyte-soaked membrane sandwiched between the lithium and LiFePO$_4$ electrodes. Charge and discharge cycles were conducted in the potential window of 2.5 - 4.2 V at 0.2 C rate.

6.3 Results and discussion

6.3.1 SEM images

Figure 6.3 shows SEM images of uncoated and nanofiber-coated Membrane 1, Membrane 2 and Membrane 3, respectively. Membrane 1 and Membrane 3 were made by dry process using polypropylene, but Membrane 2 was made by wet process using polyethylene. As shown in Figure 6.3, three membranes have different pore structures. Membrane 3 has significantly larger pores and higher porosity compared to the other two membranes. The membrane morphology including pore size, porosity, and thickness could affect the electrolyte uptake capability and electrochemical properties of both uncoated and nanofiber-coated membrane separators.
Figure 6.3. SEM images of (a) uncoated Membrane 1, (b) nanofiber-coated Membrane 1, (c) uncoated Membrane 2, (d) nanofiber-coated Membrane 2, (e) uncoated Membrane 3, and (f) nanofiber-coated Membrane 3. Magnification: 10,000 ×.
Figure 6.4. Diameter distributions of electrospun nanofibers on (a) Membrane 1, (b) Membrane 2, and (c) Membrane 3.
From Figure 6.3, it is also seen that in nanofiber-coated membranes, the electrospun nanofibers were randomly deposited with interconnected network morphology on the surface of membrane substrates. The processing parameters were selectively adjusted to produce nanofiber coatings with comparable thickness. The thicknesses of PVDF-co-CTFE nanofiber coatings are in the range of 3 – 4 μm for all three nanofiber-coated membranes.

Figure 6.4 shows fiber diameter distributions of PVDF-co-CTFE nanofibers on the surfaces of membrane substrates. Electrospun PVDF-co-CTFE nanofibers on three different membrane substrates have comparable average fiber diameters, ranging from 129 to 134 nm.

**6.3.2 Electrolyte uptake capacity**

Electrolyte uptake capacity indicates the amount of liquid electrolyte solution that can be absorbed by the unit area of a separator membrane. For lithium-ion batteries, the separator should easily absorb and retain large amount of liquid electrolyte solution to achieve a low internal resistance and good battery performance [2,5-6].

Figure 6.5 shows the electrolyte uptake capacities of electrospun nanofiber-coated Membrane 1, Membrane 2, and Membrane 3, respectively. For comparison, the electrolyte uptake capacities of uncoated membranes are also presented. The nanofiber-coated membranes have higher electrolyte uptake capacities than the uncoated membranes due to the presence of electrospun nanofiber coatings. The improvement in electrolyte uptakes should be attributed to the capillary effect of nanofibers and the good affinity of PVDF-co-CTFE to polar electrolyte solution [6,14].
Figure 6.5. Electrolyte uptake capacities of uncoated and nanofiber-coated membranes.

6.3.3 Ionic conductivity

Figure 6.6 shows the ionic conductivities of liquid electrolyte-soaked uncoated and nanofiber-coated membranes at various temperatures. For all liquid electrolyte-soaked membranes, the ionic conductivities increase with increasing temperature because the mobility of ions increases as the temperature increases [17-18]. The ionic conductivities of microporous membranes are affected by their electrolyte uptakes which are dependent on the membrane structure, such as thickness, porosity, and pore size. Since Membrane 1 has the highest thickness and lowest pore size, it shows the lowest ionic conductivity. On the other hand, Membrane 3 shows the highest ionic conductivity due to its lowest thickness and highest porosity and pore size (see Table 6.1).
From Figure 6.6, it is also found that nanofiber-coated membranes exhibit higher ionic conductivities than uncoated membranes. For example, at 25 °C, the ionic conductivities of liquid electrolyte-soaked nanofiber-coated Membrane 1, Membrane 2, and Membrane 3 are $4.63 \times 10^{-4}$, $7.26 \times 10^{-4}$, and $7.51 \times 10^{-4}$ s/cm, respectively. On the other hand, the ionic conductivities of liquid electrolyte-soaked uncoated membranes at the same temperature are $2.31 \times 10^{-4}$, $4.02 \times 10^{-4}$, and $4.01 \times 10^{-4}$ s/cm for Membrane 1, Membrane 2, and Membrane 3, respectively. The presence of nanofiber coatings on the surface of membrane substrates leads to higher ionic conductivities because they can help membranes entrap more liquid electrolyte. Among all membranes, nanofiber-coated Membrane 3 exhibits the highest ionic conductivities.
conductivity due to its lowest thickness and highest porosity as well as improved electrolyte uptake.

### 6.3.4 Interfacial impedance

The interfacial resistances between the liquid electrolyte-soaked membranes and the lithium electrode were measured using impedance spectra. Figure 6.7 shows the Nyquist plots for uncoated and nanofiber-coated membranes in the range of 0.01 Hz to 65 kHz. The real axis intercept of the Nyquist plot at high frequency determines the bulk resistance ($R_b$) of the liquid electrolyte-soaked membrane. The diameter of semicircle represents the interfacial resistance ($R_i$) between the liquid electrolyte-soaked membrane and the electrode [19-20].

As shown in Figure 6.7, the electrode-electrolyte interfacial resistances of nanofiber-coated membranes are smaller than those of uncoated membranes. PVDF-co-CTFE nanofiber coatings on the surface of membrane substrate can easily absorb liquid electrolyte and swell in electrolyte solution due to the good affinity of PVDF-co-CTFE to polar electrolyte solution and the excellent capillary effect of electrospun nanofibers. As a result, nanofiber-coated membranes exhibit smaller interfacial resistances than uncoated membranes. Furthermore, nanofiber coatings can improve the adhesive strength between the membrane and the electrode during charge-discharge cycles, which may also help lower interfacial resistance.
6.3.5 Cell performance

Figure 6.8 shows the charge-discharge curves of the 1st, 2nd, and 3rd cycles of the lithium-ion half cells assembled with the uncoated and nanofiber-coated membranes. Based on the LiFePO$_4$ active material for the cathode, the cells exhibit initial discharge capacities of 143, 151, and 147 mAh/g, respectively, when uncoated Membrane 1, Membrane 2, and Membrane 3 are used as the separator. The initial discharge capacities of the cells assembled with nanofiber-coated Membrane 1, Membrane 2, and Membrane 3 are 157, 160, and 159 mAh/g, respectively. The cells using nanofiber-coated membranes have higher discharge capacities than those using uncoated membranes probably because of their higher ionic
conductivity and lower interfacial resistance. After initial cycling, all the cells show stable charge and discharge curves.

Figure 6.9 presents the discharge capacities in 50 cycles for cells assembled with uncoated and nanofiber-coated membranes. The discharge capacities of the cells with uncoated Membrane 1, Membrane 2, and Membrane 3 are 142, 149, and 140 mAh/g, respectively, at 50th cycle. For nanofiber-coated Membrane 1, Membrane 2, and Membrane 3, the discharge capacities of the cells are 149, 154, and 155 mAh/g, respectively, at 50th cycle. Therefore, all membranes have good capability of maintain their capacities during cycling and the introduction of nanofiber coatings onto the microporous membranes does not change the cycling stability. In addition, since nanofiber-coated Membrane 3 has the highest ionic conductivity and lowest interfacial resistance, the cell using nanofiber-coated Membrane 3 shows highest discharge capacity of 155 mAh/g at the 50th cycle, which is 92% of the theoretical capacity of LiFePO$_4$ (167 mAh/g). The results demonstrate that coating polyolefin microporous membranes with electrospun nanofibers is a promising approach to obtain high-performance separators for advanced lithium-ion batteries.
Figure 6.8. Charge and discharge curves of Li/LiFePO$_4$ cells containing liquid electrolyte-soaked membranes: (a) uncoated Membrane 1, (b) nanofiber-coated Membrane 1, (c) uncoated Membrane 2, (d) nanofiber-coated Membrane 2, (e) uncoated Membrane 3, and (f) nanofiber-coated Membrane 3.
Figure 6.9. Cycle performance of Li/LiFePO$_4$ cells containing liquid electrolyte-soaked membranes at 0.2 C rate.
6.4 Conclusion

Composite membrane separators were prepared by coating PVDF-co-CTFE nanofibers on the surface of three different microporous membrane substrates using the electrospinning technique. The nanofiber coatings on the substrates formed an interconnected fibrous structure with average fiber diameters in the range of 129 – 134 nm. The nanofiber-coated membranes showed higher electrolyte uptake capacities than uncoated membranes. The ionic conductivities of liquid electrolyte-soaked membranes were also improved by the coating of nanofibers on the membrane substrates. In addition, the cells assembled with nanofiber-coated membranes exhibited lower interfacial resistance than those with uncoated membranes. The nanofiber-coated membranes also showed improved discharge capacities of Li/LiFePO₄ cells compared to uncoated membranes. Therefore, coating nanofibers onto microporous membrane substrates is a promising approach to obtain new and high-performance separators for rechargeable lithium-ion batteries. Among all membranes studied, nanofiber-coated Membrane 3 provided the highest ionic conductivity, lowest interfacial resistance, and best electrochemical performance.
6.5 References


CHAPTER 7. Summery and Conclusions

This research has demonstrated the fabrication and characterization of nanofiber-coated membranes prepared by electrospinning method using PVDF polymers and copolymers. The major results and discussion of each chapter in this dissertation are summarized as follows.

I) Nanofiber-coated membranes for battery separators via single nozzle and nozzle-less electrospinning methods.

Nanofiber-coated membrane separators were prepared by two different electrospinning methods which are single nozzle electrospinning and nozzle-less electrospinning. PVDF and PVDF-co-CTFE electrospun nanofibers were deposited on Celgard PP membrane separators. In both single nozzle and nozzle-less electrospinning methods, the electrospinning process conditions were controlled to obtain comparable morphology and nanofiber loading.

The morphology of membranes and the diameter of electrospun fibers were evaluated using SEM images. Liquid electrolyte uptake capacities were measured by soaking pre-weighed nanofiber-coated separator membrane samples for a fixed time at room temperature in a liquid electrolyte which consisted of 1 M lithium hexafluorophosphate (LiPF$_6$) dissolved in 1:1:1 (by volume) ethylene carbonate/dimethylcarbonate/ethylmethyl carbonate. The adhesion between the membrane and a battery electrode was evaluated by conducting peel tests on the nanofiber-coated membrane/electrode laminated assemblies.
The results of this study showed that a coating of PVDF and PVDF-co-CTFE nanofibers applied to a PP microporous membrane separator improved electrolyte uptake capacity and the adhesion of the separator membrane to a battery electrode in a lithium-ion secondary battery. The electrospinning method and electrospinning process parameters impacted the structure and properties of the nanofiber-coated microporous battery separator membranes. Nanofiber coatings prepared by the nozzle-less electrospinning method had better adhesion properties and higher electrolyte uptake capacity than those by single nozzle electrospinning.

II) Electrospun nanofiber-coated membranes using different polymer blends for battery separators.

Composite membrane separators coated by electrospun nanofibers were fabricated using different polymer blends. This study addressed the effect of electrospun PVDF-co-CTFE and PVDF-co-CTFE/PVDF-co-HFP nanofiber coatings on the morphology, adhesion properties, and electrolyte uptake capacity of membrane separators.

In this work, the nozzle-less electrospinning was used to generate a continuous nanofiber coating with an uniform width on the Celgard PP microporous membrane separators. The electrospun nanofibers on the surface of membrane substrates showed randomly interconnected network morphology with small fiber diameters. Although nanofiber-coated membranes had a few beads on the surfaces of membrane substrates, the microporous membrane substrates were visible between the fibers, indicating that the sizes of the nanofibers and beads formed in the coating are on a scale that does not interfere with the
micropores in the membrane substrates. In addition, the BET surface areas of nanofiber coatings were measured by the nitrogen isothermal adsorption-desorption method. The nanofiber coatings on the membrane substrates had high surface area. The electrolyte uptake capacities of membrane separators were investigated and improved by incorporating nanofiber coatings on the surface of membrane substrates. The nanofiber-coated membranes also showed better separator-electrode adhesion than uncoated membranes. Moreover, the separator-electrode adhesion was further improved by increasing the temperature and pressure used during the preparation of separator-electrode assemblies. Consequently, PVDF-co-CTFE nanofiber-coated membranes showed higher electrolyte uptakes and better separator-electrode adhesion than PVDF-co-CTFE/PVDF-co-HFP nanofiber-coated membranes.

III) Electrospun nanofiber-coated membranes using different types of membrane substrates for battery separators.

This work reported the preparation of PVDF copolymer nanofiber coatings on different types of membrane substrates and the properties of nanofiber-coated microporous membranes via electrospinning method.

The electrospinning processing conditions were carefully controlled so that nanofibers on different types of membrane substrates produced comparable coating loadings and thicknesses with uniform morphology. Electrolyte uptake capacity was investigated by soaking the nanofiber-coated membranes in a liquid electrolyte solution. The electrospun
nanofiber coatings improved the wettability of different membrane separators to the liquid electrolyte solution. Regardless of types of microporous membrane substrate used in this study, the PVDF copolymer nanofiber coatings were found to provide improved adhesion to the LiFePO₄ electrode. In conclusion, application of a PVDF copolymer nanofiber coating onto the surface of the battery separator membrane provided a method for improving the electrolyte absorption of the separator and the separator-electrode adhesion.

IV) Electrochemical properties of electrospun nanofiber-coated membrane separators for lithium-ion batteries.

This study discussed the fabrication and characterization of composite membrane separators by depositing electrospun nanofibers onto polyolefin microporous membranes. The nanofiber coatings were prepared on microporous membrane substrates by nozzle-less electrospinning technique using PVDF-co-CTFE.

The morphology of electrospun nanofiber coatings on the surface of membrane substrates and the electrolyte uptake capacities of nanofiber-coated membranes were investigated. The nanofibers on the membrane substrates produced fibrous polymer networks and high surface areas. Moreover, the nanofiber-coated membranes exhibited better wettability to the liquid electrolyte solution than uncoated membranes. The ionic conductivities were measured by soaking nanofiber-coated membranes with a liquid electrolyte solution. The ionic conductivities of liquid electrolyte-soaked membranes were also improved by the coating of nanofibers on the membrane substrates. Furthermore, the ionic conductivities of liquid
electrolyte-soaked membranes increased with increasing temperature. In addition, the lithium-ion cells were assembled with nanofiber-coated membranes to evaluate electrochemical properties and cycling performance at room temperature. The cells containing nanofiber-coated membranes as the separator showed low interfacial resistance to the lithium electrode. The nanofiber-coated membranes also led to improved discharge capacities of Li/LiFePO₄ cells compared to uncoated membranes. Therefore, coating microporous membrane substrates with electrospun nanofibers is a promising approach to obtain new and high-performance separators for advanced lithium-ion batteries.
CHAPTER 8. Recommendation Works

In order to further the research for the membrane separator, the recommendations for future research are include in the following:

I) Incorporation of inorganic particles into electrospun nanofibers coated on membrane substrates.

In order to improve the thermal stability and wettability of polyolefin microporous membranes, coating the membrane substrates with nano-sized inorganic particles is an attractive method for obtaining advanced membrane separators for lithium-ion batteries.

Many researchers have studied the incorporation of inorganic particles into electrospun nanofibers [1-7]. They used various inorganic particles (e.g. TiO$_2$, BaTiO$_3$, Al$_2$O$_3$, and SiO$_2$) and investigated the effect of inorganic particles on the morphology of electrospun membranes and electrochemical properties. The electrospun nanofiber membranes incorporated with inorganic particles showed improved properties compared to the membranes without inorganic particles. Therefore, electrospun nanofiber coatings containing inorganic particles can be obtained on the polyolefin membrane substrates via nozzle-less electrospinning. The resultant composite membranes coated with inorganic particle-added nanofibers may show improved wettability and thermal stability due to the present of inorganic particles. Also, the incorporation of the inorganic particles can lead to positive effects on the ionic conductivity and the electrochemical properties.
II) Fabrication of composite membranes coated with inorganic materials via atomic layer deposition (ALD).

ALD is a chemical vapor deposition method based on sequential, self-limiting surface reactions [8]. In this method, the chemical precursors are transported in the vapor phase and decompose on the substrate to form a thin layer with angstrom level thickness under high temperature and vacuum conditions.

The advantages of ALD are to obtain continuous and pinhole-free deposition and to control the thickness of the layer by repeating sequential reactions. The use of traditional ALD process to deposit inorganic materials demands a temperature that is higher than the glass-transition temperatures of most polymers. However, the method for the deposition of inorganic materials on polymeric substrates at low temperatures has been reported for several inorganic materials [9-10]. For example, SiO$_2$ is an important inorganic material useful in lithium-ion battery applications. A thin layer of SiO$_2$ can be obtained on the surface of polymeric substrates by ALD method using silicon tetrachloride (SiCl$_4$) and H$_2$O [11-12].

Therefore, composite membrane separators with inorganic layers can be prepared via ALD method under low temperature. The introduction of the inorganic layer can improve the electrolyte uptake and temperature resistance of membrane separators so that contribute to enhanced electrochemical properties of membrane separators for advanced lithium-ion batteries.
8.1 References


