Recent Development of Polyvinylidene Fluoride/Cellulose Membranes Electrolyte Separator for Lithium Ion Batteries

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Abstract. Lithium ion batteries (LIB) are an important energy storage system. As one component in a LIB, the separator has an important role in the safety of LIB. Separators have porous structures that make it possible to transfer lithium ions between anode and cathode. This paper discusses the method for making separators with the main material as PVdF and cellulose. Such as casting, phase inversion, paper making, and electrospinning. So, we found two potential methods that can be developed in preparing lithium-ion battery separators, casting and electrospinning. Casting has benefits like a simple preparation step and does not require much equipment, but the weaknesses are expensive processes. The electrospinning step has advantages such as an inexpensive process, but has the disadvantage of needing much equipment.

1. Introduction
Separator of Lithium Ion Battery (LIB) is a solid phase electrolytes membrane which separate anode and cathode [1], [2]. Separator is made by polymer, one of them is poly(vinylidene fluoride) (PVdF) [3]. Several studies have shown that the combination of PVdF and cellulose can improve separator membrane property [4]. Cellulose exhibits excellent wettability, low processing costs, high porosity, and can increase ion conductivity[5]. For sure, It will increase the thermal stability[6–10]. Every cellulose polymer combined with PVdF has shown good increasing characteristic of membrane for LIB.

Cellulose acetate has low thermal conductivity and good as an electricity isolator so it will be good as a polymer for a separator in LIB [11]. C=O and C-OH bonds on cellulose acte as polar groups on polymers with good electron affinity for electrodes and also will be a good thermal isolator [12,13]. The other advantages of cellulose acetate is very good at thermal stability and hydrophobicity [14], [15]. Good thermal stability will reduce the degree of crystallinity so the coating process on the separator membrane will be better and lead to enhancement of LIB’s performance. Blending of PVdF and cellulose acetate for coating separator membrane has shown a reduction of crystallinity degree compared with PVdF polymer without cellulose acetate [16]. Hydrophobic nature of polymer for this modification is truly important because lower hydrophobicity caused modification difficulty. Thus, promoting crystallinity which decreases the quality of separator membrane. This blending of PVdF and cellulose acetate will combine each advantage and eliminate the disadvantages. This will lead to enhancement of
LIB performance. Research has been employed regarding PVdF-Cellulose as a separator membrane polymer for LIB. Adding nanocrystalline cellulose in preparing PVdF/cellulose membrane can lead to very high thermal stable membrane and higher tensile strength membrane [17]. An application of cellulose acetate bacteria for LIB separator membrane has shown dimensionally more stable, better the conductivity of ion and comparable [18]. Cellulose can also support the charging and discharging process for LIB because of the adhesive property which is more stable for the process [19]. PVdF and cellulose acetate polymers for coating separator membranes has shown reduction of crystallinity degree compared to PVdF polymer without cellulose acetate [16,20,21]. Meanwhile, coating of separator membrane with hydroxyethyl cellulose aerogel will result in better electrolyte uptake, higher conductivity of ion and lead to enhancement performance of battery [22,23]. Advantages of PVdF and cellulose can be explored by preparing PVdF/cellulose acetate through several methods. In the following section, we will discuss some methods for preparing PVdF/cellulose acetate separator membrane.

2. Manufacturing Method of Lithium Ion Battery (LIB)

Some of the methods we have reviewed are methods that are often used by several studies in making PVDF/cellulose based separators. The method used includes casting, phase inversion, electrospinning, coating, and several other methods with varying results. The table 1. has presented research data on various methods.

2.1 Casting

In general, the manufacture of cellulose-based separator membranes can be done using the solution casting method [24]. There are several important parameters that affect the quality of the cellulose separator membrane made through the solution casting process, such as cellulose concentration to area, ratio of cellulose to dispersing media and drying process [25]. Casting itself can be said as the most standard method for making separators. Casting has a simple preparation stage and does not need too many equipment. After the material passes through the mixture, the mixture is poured into a smooth surface like a glass plate to dry to form a film. This process can be shown in this figure 1 below.

![Figure 1. Illustration of casting process [26]](image1.png)

Casting itself has two quite different methods in terms of tool use, namely solvent-casting and doctor blade casting.

a. Solvent-casting

Solvent-casting is the simplest film manufacturing method and is one of the oldest methods of manufacturing. The way this method works is that the existing material is dissolved into a volatile solvent and the liquid solution that has been obtained is then poured on a flat and smooth surface so that the solvent evaporates (Figure 2) [27]. This material, referred to as dope film, is diffused using the classic cast solvent film deposition method onto a continuous roll of release media, such as paper impregnated with plastic. The coated medium is passed through a drying device, such as an oven or convection chamber, to release the solvent. The dried films are then cut into strips and individually
packed in sealed, atmosphere resistant bags. This method allows a fairly easy development of cellulosic materials by simply adding the necessary nanoparticles / particles to the solution before casting [28].

### Table 1. Cellulose Data Results in a Separator for Li-Ion Batteries

| Materials                        | Method          | Operation condition | Results                        | Ref.  |
|----------------------------------|----------------|--------------------|--------------------------------|-------|
| PVdF/HEC/PVdF GPE                | Electrospinning| T (°C) P (atm)     | Electrolyte uptake (%) Porosity (%) Ion conductivity (S cm⁻¹) |       |
| PVdF/Cellulose Nanocrystals (CNC)| Electrospinning| 25 1               | 135.4 - 94 9.68x10⁻³         | [19]  |
| PVdF/CA                          | Electrospinning| 25 1               | 768.2 - 94 2.61x10⁻³         | [30]  |
| PVdF/CA/HNT                      | Electrospinning| 25 1               | 311 86.3 1.36x10⁻³           | [31]  |
| PVdF/CA/AgTiO₂                   | Electrospinning| 25 1               | 330 88 7.7x10⁻³              | [32]  |
| PVdF/PMMA/CA                    | Electrospinning| 25 1               | 323.4 99.1 - 4.4x10⁻³       | [23]  |
| PVdF/CA/TPP                     | Electrospinning| 40 1               | 301 90 4.4x10⁻³             | [33]  |
| PVdF/CA/TPP                     | Casting         | 25 1               | 150 - 3x10⁻³               | [34]  |
| PVdF-HFP/CA                     | Casting         | 25 1               | 360 Low 5.49x10⁻⁴           | [35]  |
| PVdF/NCC                        | Casting         | 25 1               | >100 76 2.5x10⁻²            | [36]  |
| PVdF-HFP/HPMC                   | Casting         | 25 1               | 210 - 0.38x10⁻³            | [37]  |
| PVdF-HFP/CNCS                   | Casting         | 25 1               | <100 <1 -                   | [38]  |
| PVdF/CA                         | Phase Inversion | 60 1               | - 82 -                      | [39]  |
| PVdF/CA/TPP                     | Phase Inversion | 25 1               | - 83 -                      | [40]  |
| Cellulose/PVdF-HFP              | Phase Inversion | 80 1               | 310 85.3 1.89              | [4]   |
| PVdF-HFP/Celullose/C-TiO₂       | Phase Inversion | 40 1               | 210.3 63.65 1.49           | [41]  |
| PVdF-CA/Al₂O₃                   | Phase Inversion | 70 1               | 403.9 68.6 2.85x10⁻³        | [11]  |
| PVdF/CAB/SiO₂/PE                | Coating         | 25 1               | 195 42.3 2.98x10⁻³          | [9]   |
| PVdF/CAB/PE                     | Coating         | 25 1               | 180 46.3 2.48x10⁻³          | [42]  |
| Al₂O₃/PVdF-HFP/CMC/PE           | Coating         | 25 1               | 360 42.7 0.93x10⁻³          | [43]  |
| PVdF/MC/PVdF                    | Coating         | 25 1               | 138.6 - 1.5x10⁻³           | [44]  |
| PVdF/EC/(A-SiO₂)                | Coating         | 25 1               | - - 0.79x10⁻³              | [45]  |
| PVdF/MFC/SFC                    | Coating         | 25 1               | - 59 1.25x10⁻³             | [46]  |
| PVdF/MC/Alumina                 | Papermaking-Coating | 25 1               | - 56 1.2x10⁻³             | [47]  |

The most well-known approach is the Solvent-casting and particulate leaching (SCPL) procedure, in which the material is dissolved in the solvent, porogen is added to the solution (salt such as NaCl) and the mixture is poured into a mold [48]. This solvent-casting method requires a long production time because the solvent needs to be removed by evaporation (after drying films can contain trace amounts of residual solvent), which makes it less suitable for many industries and the conditions of the casting
itself can change the quality of the film, making this process unreliable for battery separation manufacturing [49].

**Figure 2.** Solvent-casting method for cellulose derivative membrane fabrication [49]

b. **Doctor Blade Casting**

Doctor blade (tape casting) is one technique that is widely used to produce a thin film over a large area surface. Doctor blade casting offers a fast and simple approach to continuous wide area filming [49]. Tape casting is a relatively new method that was developed in the 1940s as a method of forming thin sheets of piezoelectric materials and capacitors [50]. In the doctor blading process, a well-mixed slurry consisting of a suspension of seranyl particles together with other additives (such as binders, dispersants or plasticizers) is placed on the substrate outside the doctor blade. When relatively constant motion occurs between the blades and the substrate, the slurry spreads over the substrate to form a thin sheet which produces a gel layer after drying. Doctor blading can operate at speeds of up to several meters per minute and is suitable for coating substrates with a very wide range of wet coating thickness ranging from 20 to several hundred microns [51]. It is also said that in this process, the material is first dissolved into a certain liquid. After a fluid with sufficient fluidity has been obtained (cellulose concentration must be kept low), the mixture is stored onto a clean glass plate and spread with a doctor's knife (figure 3) [52].

**Figure 3.** Doctor blade casting method for cellulose derivative membrane fabrication [49]

Recently, several types of materials have been considered as host polymers for gel polymer electrolyte (GPE) membranes, such as poly (vinylidene fluoride) (PVdF), poly (acrylonitrile) (PAN), poly (ethylene oxide) (PEO), poly (methyl methacrylate) (PMMA), and so on. In particular, PVdF is an ideal material for GPE membranes associated with high dielectric constants (ε = 8.4), strong electron withdrawal function groups (CF), good electrochemical stability, good affinity for electrolyte solutions, and high ionic conductivity at room temperature [30]. Leng et al. Combining hexafluoropropylene (HFP) with PVdF results in lower crystallinity in the polymer and enhanced ionic conductivity. However, PVdF-HFP with the presence of more fluorine groups usually exhibit hydrophobicity, which leads to low electrolyte uptake [35].

Hydroxypropyl methyl cellulose (HPMC), one of natural celluloses, which has a perfect mechanical stability and high polarity, is used as binder, membrane material, and dispersing agent [53]. HPMC is widely used in cosmetic products and medicines because it is a gel forming agent that produces a clear gel, that easily soluble in water, and has a low oxidation rate [54]. PVdF-HFP and HPMC as mixed matrix because having high polarity so it can enhance the ionic conductivity [37]. Cellulose
Nanocrystals (CNCs) have been used to fabricate nanocomposites, aerogels, and hybrid materials [38]. CNCs represent the crystalline regions extracted from cellulose microcrystals by strong acid hydrolysis at elevated temperature. CNCs possess the unique properties of high aspect ratio surface area, mechanical strength, and one of liquid crystalline nature. The crystalline nature of the CNCs is primarily obtained naturally from cellulose fibers by the removal of amorphous segments from renewable resources via strong acid hydrolysis [55].

Cellulose acetate (CA) is a promising derivative cellulose which can be easily dissolved in organic and polar solvents. CA has a high glass transition temperature, electrically non-conductor and high affinity for organic electrolytes because acetyl (C = O) and hydroxyl groups (-OH) make it a promising candidate for LIBs [34]. In membranes, CA acts as an additive to increase the ionic wettability and conductivity of the mixed membrane. CA presents excellent performances due to its high hydrophilicity, good biocompatibility, environmental friendly, and good thermal stability (initial decomposition temperature > 270 °C) [30]. The purpose of making this separator is to develop the potential and use of CA as a separator of high-performance LIB. Meanwhile, the overall performance of many materials has also been improved by blending with CA [30]. Therefore, the polymer electrolyte membrane for lithium-ion batteries becomes a proposed material consisting of PVdF and CA, and expected to make an increase in hydrophilicity and reduce the level of crystallinity. The electrochemical characteristics and application of CA / PVdF membranes in lithium-ion batteries were also evaluated, which proves that the PVdF membrane modified by CA blending is suitable as a GPE membrane for lithium-ion batteries.

Cellulose based PVdF, both NCC, CNCs, and HPMC, electrolyte uptake, porosity, and ionic conductivity values were quite different. PVdF / NCC and PVdF-HFP / MPMC obtained high enough electrolyte uptake, with PVdF / NCC results of more than 100% and PVdF-HFP / HPMC valued at 210%. Whereas PVdF-HFP / CNCs are said to have a low electrolyte uptake that is below 100%. Porosity values in PVdF / NCC and PVdF-HFP / CNCs have high and very low values, which is 76% for PVdF / NCC and less than 1% for PVdF-HFP / CNCs. Ionic conductivity in all three studies, obtained the highest value in PVdF-HFP / HPMC 0.38x10^{-3} S cm^{-1} and the lowest value in PVdF / NCC 2.5x10^{-5} S cm^{-1} [36–38].

Some studies have found that the PVdF/CA-based membrane separator with casting solution has a variety of electrolyte uptake ranges. The highest electrolyte uptake was obtained from a separator membrane made from PVdF / CA with an additional Al(OH)₃ of 403.9%. Al(OH)₃ functions as an additive that can improve heat resistance performance, crystallization performance, adsorptive properties and processing performance. Al(OH)₃ has been investigated by mixing a little Al(OH)₃ powder with cathode material to improve electrochemical performance [11]. Meanwhile for PVdF / CA without additive, electrolyte uptake range of 150-350% is obtained. This is due to the absence of additives that can increase electrolyte uptake. In addition, Leng et al. who varied HFP with PVdF to PVdF-HFP, obtained electrolyte uptake of 360%. This is because PVdF-HFP has better wettability which is beneficial for electrolyte uptake [11,34,35].

Leng et al. mention that their results have low porosity. From these data, it can be concluded that low porosity could be caused by the absence of additives [11,35]. For the conductivity of ion, various results are obtained. It was seen that the highest ionic conductivity was obtained by Asghar et al. which uses PVdF / CA only for membrane separator material of 3x10^{-3} S cm^{-1}. For PVdF / CA with Al(OH)₃ an ionic conductivity of 2.85x10^{-3} S cm^{-1} was obtained and variation of PVdF-HFP / CA obtained ionic conductivity of 5.49x10^{-4} S cm^{-1}. It can be concluded that the highest and lowest ionic conductivity is in the membrane separator made from PVdF / CA and PVdF-HFP / CA [11,34,35].

The various data have been discussed, it was concluded that the PVdF / CA membrane separator mixed with additives in the form of Al(OH)₃ obtained greater results compared to PVdF / CA or PVdF-HFP / CA both in terms of electrolyte uptake test, porosity, and conductivity ionic. The results that it turns out that PVdF / CA with the addition of Al(OH)₃ is a suitable and good material for high performance LIB. The variations of PVdF-HFP give significant results, but still differ slightly smaller compared to PVdF / CA / Al(OH)₃. Whereas PVdF/CA without any variation gives much different results than the other two materials. This proves that PVdF/CA must developed further and also requires variations in order to have good results for high performance of LIB.
2.2 Phase inversion
Phase inversion is one of several methods that has been used in preparing membrane for battery. The concept of phase inversion method is separating the membrane from the solvent by exposing them in to high thermal or also dipping them into anti-solvent so the membrane will remain meanwhile the solvent will excuviate. By excuviating the solvent, the membranes will have porous on the surface with diameter that can be measured. This porous will be spread over the membrane which is called as porosity described by percentage. Figure 4 will representate phase inversion process.

![Figure 4. Phase inversion method [4]](image)

A porous membrane made by inversion methods containing ethyl cellulose has shown high performance. By adding ethyl cellulose on the PVdF, the wettability of membrane will increase so this membrane has good characteristic for LIB. This study also believes that preparing the membrane by phase inversion method is low cost [56]. Another study has shown that phase inversion method can be a promising method for large scale process. [36].

M. H. Razzaghi et al used phase inversion method in their research in 2014, they dissolved PVdF and CA onto DMAc so they contained 18% wt of PVdF/CA in solution. This is because we can only casting solution with concentration about under 20% wt, over 20% wt concentration, the solution would have high viscosity and can not be casted. Then, let them within 24 h at 60°C without stirring. As the result, the membrane can reach 83% of porosity with contact angle of 60°[40]. On another research in 2018, M. H. Razzaghi et al had used the phase inversion method too. In this research, were preparing PVdF/CA membrane by adding PVdF 80% wt and CA 20% wt onto DMAc as solvent. Once they had homogenous solution after being stirred for a day at 60°C then the casting solution were ready. Next, they casted the casting solution onto a glass and let it dry. They used deionized water as antisolvent. For the result, 82% porosity was reached with contact angle of 60.1° [39].

Membrane developed through the non solvent phase inversion cycle have outstanding mechanical properties [57]. For an increasing CA content in the membrane matrix, the contact angles of water decreased. The contact angle of water is determined not only by the membrane content but also by the porosity of the surface [58]. CA can be used as a hydrophilic additive by phase inversion process to improve the efficiency of PVdF microfiltration membranes. XPS tests confirmed CA enrichment on membrane surfaces, suggesting that the CA segments surface concentrations are higher than in the membrane matrix [59]. For adding cellulose nanocrystall (CNC) on the casting solution of preparing PVdF membrane by phase inversion method especially while exchanging the solvent and non solvent step, there is hydrophilic character of CNC that influences the porosity of membrane compared with pure PVdF membrane. The more CNC was added, the porous will be larger [60]. Phase inversion method for polymers such as PVdF consists of mechanism of liquid-liquid mixing and crystallization [39]. The composition of coagulation bath and its conditions of phase inversion method can affect to what mechanism will be more dominant [39]. The most usual use of a non solvent as coagulation bath is water, which is potential for PVdF membranes coagulation bath [61].

2.3 Electrospinning
Electrospinning is one of the efficient methods to make a separator which provides high porosity, large surface area, good surface adhesion and three-dimensional structure that results in increased electrolyte
uptake, ionic conductivity, discharge capacity and cycle-life of LIB. The schematic of the electrospinning process can be shown in figure 5.

Weimin et al. made PVdF/CA membrane by electrospinning method. This membrane was intended for polymer electrolyte gels. The performance of the membrane was affected by the ratio of CA and PVdF. It was found that membrane from the mixture CA: PVdF = 2: 8 has the best performance with the property-strength to 11.1 MPa, electrolyte uptake of 768.2 %, thermal stability (no shrinkage under 80 °C without tension), and ionic conductivity of $2.61 \times 10^{-3} \text{ S cm}^{-1}$ [30].

Manufacturing PVdF/CA membranes with the electrospinning method is difficult to achieve, because of the large difference in electricity on the two surfaces. So, a lot of research has been done to overcome this problem and also improve the performance of PVdF/CA membranes. Suo Wang et al. add inorganic filler, halloysite nanotube (HNT) to the PVdF/CA membrane. HNT has silanol and Al-OH on its surface, so HNT will form hydrogen bonds with those compounds [31].

Monali V. Buthe et al. try a new approach to improve the performance of PVdF/CA membranes with doped silver titania (AgTiO$_2$) as a nano filler. The addition of nano filler has been proven in a number of studies that can increase the ion conductivity, stabilize interphase, and reduce overall resistance of lithium-ion batteries due to reduction in ion pairing which give a positive impact on lithium ion transport properties [32]. The average fiber diameter of PVdF/CA and PVdF/CA/AgTiO$_2$ membrane are 250 nm and 160 nm respectively. The smaller fiber diameter of the membrane, the higher viscosity of electrospinning solution that will produce the better electrolyte uptake, porosity and discharge capacity of the battery [32].

A PVdF/HEC/PVdF GPE sandwich is an alternative electrolyte and separator that has many advantages. The combination of PVdF/HEC/PVdF GPE sandwiches may integrate the benefits from different components and overcome the problems individually. The electrolyte uptake of PVdF/HEC/PVdF membrane is 135.4% with ion conductivity about $0.88\times10^{-3} \text{ S cm}^{-1}$. The higher the percentage of electrolyte uptake the higher the ion conductivity [19].

The studies of the addition of PMMA in pure PVdF membrane has been explored and effective to the improvement of PVdF membrane. Due to environmental concerns, a separator that is made or blended with biodegradable polymer is one of the alternative separators for LIB. Therefore, Tussimire Yvonne investigated the effects of addition cellulose acetate (CA) which has biodegradability and renewability to PVdF/PMMA membranes. The different weight ratio of PVdF: PMMA: CA is made and tested for its performance. The highest melting point (Tm) and percentage of crystallinity are obtained at a weight ratio of 90: 0: 10. The highest porosity and percentage of electrolyte uptake also is in the membrane at a ratio of 90: 0: 10 [23].

Separator is playing an important role in safety hazard of LIB, but unfortunately there are still many accidents of explosion electronic devices due to the membrane battery failure [63]. Therefore, it needs improvement of the separator which has good mechanical properties and even high temperature or flame resistance. Triphenyl phosphate (TPP) is one of the popular materials in making separators with good flame resistance. Yuen Chen makes PVdF/CA/TPP and compares the properties with various membranes. The tensile stress of PVdF/TPP/CA membrane more strength than the other membranes which strength to 8.5 Mpa and elongation rate to 155%. Moreover the addition of TPP to PVdF/CA membrane induced flame resistance and produce membrane with higher porosity, stable cycle performance and better electrolyte uptake. So, the PVdF/CA/TPP could be one of the promising
separator for LIB [33]. Besides TPP, green hydrophilic polymers such as cellulose nanocrystals (CNC) can be mixed with PVdF. CNC is one of the most plentiful renewable resources. The blended of CNC and PVdF has a good performance with porosity up to 94% and ion conductivity of 9.68x10^{-3} \mu\text{S}\cdot\text{cm}^{-1} [29].

2.4. Coating
Coating is one method commonly used in the manufacture of LIB separators. Commercial separators have disadvantages such as low melting temperature, poor electrolyte wettability, thermal shrinkage, and mechanical strength low electrolyte uptake, and poor ionic conductivity [64–66]. To solve these disadvantages, this method is used by coating the surface with a thin layer with a modification of a commercial separator.

Coating methods have several types including dip coating, gravure coating, and coating machine. Some studies on average use dip coating as a method of making PVdF/cellulose based separators because dip-coating methods are frequently employed to produce thin films from sol-gel precursors for research purposes, where it is generally used for applying films onto flat or cylindrical substrates. Dip coating can improve electrolyte wettability, ionic conductivity, and cycle performance at a high rate when measured in a battery test [65]. The method of manufacturing a separator using the dip coating method consists of four steps: immersion of the substrate into the solution, removal of the solution layer, drainage during and after processing, and evaporation and drying during and after sampling. After drying, heat treatment is also used to complete the dehydrating process and extract organic residues[67]. The schematic of the coating process can be shown in Figure 6.

![Figure 6. Schematic illustration of the stages of the dip-coating [67].](image)

Electrolyte uptake, porosity, and ionic conductivity in PVdF/CAB/SiO\textsubscript{2}/PE and PVdF/CAB/PE without any addition of SiO\textsubscript{2} obtain different values but only have a small difference. In PVdF/CAB/SiO\textsubscript{2}/PE and PVdF/CAB/PE respectively, the electrolyte uptake values were 195% and 180%, porosity values were 42.3% and 46.3%, and ionic conductivity values were 2.98x10^{-3} \text{S}\cdot\text{cm}^{-1} and 2.48x10^{-3} \text{S}\cdot\text{cm}^{-1}. From the data obtained, the PVdF/CAB/SiO\textsubscript{2}/PE based separator has higher electrolyte uptake and ionic conductivity than the PVdF/CAB/PE based separator, while it is inversely proportional to its porosity. The difference in data may be caused by the addition of additives in the form of SiO\textsubscript{2} which affect these values [9,42].

In addition to the two materials above, the Al\textsubscript{2}O\textsubscript{3}/PVdF-HFP/CMC/PE based separator gets the highest uptake electrolyte values reaching 360% and PVdF/MC/PVdF of 138.6%. The highest porosity values were obtained by PVdF/MFC/SFC 59%, and Al2O3/PVdF-HFP/CMC/PE 42.7%. The highest ionic conductivity values are PVdF/MC/PVdF with values of 1.5x10^{-3} \text{S}\cdot\text{cm}^{-1}, PVdF/MFC/SFC with values of 1.25x10^{-3} \text{S}\cdot\text{cm}^{-1}, Al\textsubscript{2}O\textsubscript{3}/PVdF-HFP/CMC/PE with values 0.94x10^{-3} \text{S}\cdot\text{cm}^{-1} and PVdF/EC/(Al-SiO\textsubscript{2}) with a value of 0.79x10^{-3} \text{S}\cdot\text{cm}^{-1} [43,44], [45], [46]. In this case PVdF-HFP showed good electrolyte uptake. Based on the 'like dissolves like' principle, the carbon chains of the macromolecular PVdF-HFP could stretch sufficiently in the standing process, which was advantageous to the expansion
of molecular chains and formed colloidal PVdF-HFP, binding more Al₂O₃ nanoparticles to flowing PVdF-HFP to improve the hardness of LIBs [43].

2.5 Vacuum Assisted Filtration
Vacuum filtration is one of the easy methods to build a membrane as a separator. The concept is about to take solid part from the liquid by pouring them onto a filter, so the solid will be trapped on the filter while the liquid will be aspirated by flask below[68–70]. Figure 7 below is picturing how vacuum filtration process

![Figure 7. Schematic Vacuum Filtration Method][71]

There are several example of vacuum assisted filtration method that have been done to make separator for LIB. Cellulose nanofibers have processed to be separator of LIB by this kind of method and results to a satisfying mechanical properties[72], cellulose based separator improved ionic conductivity and electrolyte uptake[73], cellulose based trilayer separator shows an effective thermal shutdown[74]. After gaining membrane on the filter, this process could also followed by freeze drying and lead to enhancement of porosity[75]. This method is possibly scaled up for making cellulose based membrane for LIB[76].

2.6 Others method
Non-woven material separators have been commonly used in various batteries because of their high porosity, high chemical resistance, and good thermal stability. Nevertheless, there are still some barriers to use that separator, but the major are their large porosity and the difficulty in making them thin and uniform nonwoven membranes. To overcome this problem, Xiaosong Huang et al. made composite separators consist of cellulose fibers namely Celish micro-fibrillated cellulose (MFC) and ceramic particles namely alumina. The ceramic particles was used to conveniently control the permeability of the composite separators and increase the performance of the separator. The preparation of the MFC/alumina membrane was done with low cost wet-laid (paper-making) process. The highest performance is generated in the MFC / alumina ratio = 1 / 1.5 with the porosity of 68% and the effective conductivity of 1.28 mS cm⁻¹. Then, the MFC / alumina membrane was coated with PVDF to augment the mechanical separator strength, keep ceramic particles from falling off, and improve the uniformity of the separator’s surface. The addition of PVdF only slightly changes the membrane performance with the porosity of 56% and the effective conductivity of 1.2 mS cm⁻¹. The slightly decreased in ionic conductivity caused by some of the pores in PVdF that filled the MFC / alumina membrane [47].

Summary
LIB separator can be made by various methods, such as casting, phase inversion, paper making, and electrospinning. PVdF and cellulose are gaining attention and the favorite material for high-performance LIB. Separators made from PVdF/Cellulose have better properties compared to commercial Celgard separators or PE/PP separators. PVdF has advantages such as good electrochemical and thermal stability, high ionic conductivity, and good electrolyte wettability. While cellulose has advantages such as high porosity, good thermal and chemical stability, and good electrolyte wettability. There are two potential methods that can be developed in making lithium-ion battery separators, casting and
electrospinning. Casting has advantages such as a simple preparation step and does not require a lot of equipment, but the disadvantages are expensive processes. Whereas electrospinning has advantages such as a cheap process, but has the disadvantages of requiring much equipment.

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