Cellulose Based Separator for High-Performance Lithium-Ion Batteries

Akshit Vaidya
Western Michigan University, akshltmvaidya@gmail.com

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CELLULOSE MEMBRANE SEPARATOR FOR HIGH-PERFORMANCE LITHIUM-ION BATTERIES

by

Akshit Vaidya

A thesis submitted to the Graduate College in partial fulfillment of the requirements for the degree of Master of Science in Engineering Chemical Engineering Western Michigan University April 2020

Thesis Committee:

Dr. Qingliu Wu, Chair
Dr. Paul Fleming
Dr. Qiang Yang
CELLULOSE BASED SEPARATOR FOR HIGH-PERFORMANCE LITHIUM-ION BATTERIES

Akshit Vaidya, M.S.
Western Michigan University, 2020

During the past two decades, lithium-ion batteries (LIBs) have gained great success in the field of portable devices, and currently, are penetrating to the market of vehicles. Compared to the fast development of LIBs, little efforts have been dedicated to the separator, which is one of the most important components of LIBs. Primarily, the lithium-ion battery separator has two functions, one is to prevent direct contact between the positive and negative electrodes, and the other is to provide a path for effective ionic transportation. Currently, the separator market of LIBs is dominated by polyolefin materials such as polypropylene, polyethylene, and their combinations. However, the low thermal stability and poor wettability of polyolefin separators by the electrolyte result in state-of-art (SOA) LIBs with low power density, narrow range of operating temperature, and high cost. In this thesis, a novel cellulose-based membrane will be developed and be utilized as a separator of LIBs to address aforementioned issues. The well-established methods for papermaking will be adopted to fabricate two types of cellulose-based membrane separators; one is made of cellulose fibers and the other with cellulose fibers and cellulose nanocrystals (CNC). The effect of processing parameters, such as the solvents, ratio of CNC to cellulose fiber, and filtering method on the properties of membranes will be investigated. The achieved membranes will be evaluated by using advanced techniques, including force tensiometer, scanning electron microscopy, electrochemical characterizations, etc., to demonstrate superior properties of cellulose separators developed here.
I would be forever grateful to Dr. Qingliu Wu for letting me be a part of his research group. It was a huge learning experience, and this thesis proves to be an encouragement and inspiration to learn and understand every aspect of this research. Without his constant efforts, it would be very difficult to learn so much in the last two years.

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Akshit Vaidya
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CHAPTER 1
INTRODUCTION

1.1. Overview

1.1.1. Lithium-ion battery

With the advantages of high energy density and long cycle life, lithium-ion batteries (LIBs) have been considered as one of the most promising technologies to address our incremental concerns on global warming and demands on energies. Generally, a LIB could offer an energy density of >200 Wh/Kg (1), which is 4-5 times higher than that of a lead-acid battery. During the past two decades, LIBs have gained great success in the market of portable devices and, currently are penetrating to the automobile market. (2) The rapid expansion of associated commercial markets generates a growing need for LIBs with high safety, high power/energy density, and low cost. A promising approach to address these concerns is to replace components of LIBs by sustainable materials without scarifying their performance.

A typical LIB consists of four major components, i.e. negative electrode (anode), positive electrode (cathode), separator and electrolyte, as shown in Figure 1.1. The cathode acts as a reservoir with lithium source and anode as another reservoir. An intercalation mechanism will be involved in electrode materials when LIB is charged or discharged. (3) During charging process, lithium ions are extracted from the cathode, transported through separator in the medium of electrolyte and inserted into the anode. The extraction and insertion of lithium ions will happen during the discharge process but in the reverse direction. The voltage difference of lithium ions between electrode materials combining with the stored amount of lithium ions determines the energy density of LIBs. (2) Therefore anode and cathode are two crucial components in a LIB. In
the current LIB market. Graphite and LiCoO$_2$ and are the most common and widely used anode and cathode materials, respectively. Theoretically, graphite could deliver a specific capacity of 375 mAh/g (4) (5), which does not meet requirements on LIBs for vehicles. This promotes the exploration of novel electrode materials with high capacity and low cost. For instance, novel anode materials including lithium titanium oxide (LTO), silicon, titanium dioxide (TiO$_2$), silicon/carbon composites and etc. have caught a lot of interest due to their high capacity and low cost. The theoretical capacity of LiCoO$_2$ cathode is 248 mAh/g. (6) However, the utilization of Cobalt (Co) on the cathode leads to the high cost of LIBs. Therefore, tremendous efforts have been dedicated to developing low-cost cathode materials without Cobalt such as lithium iron phosphate (LiFePO$_4$), lithium manganese oxide (LiMn$_2$O$_4$), lithium- and manganese-rich composite, and etc. (7) These efforts significantly improve the energy density of LIBs with reduced cost.

Figure 1.1. Illustration of a typical lithium-ion battery structure
The electrolyte is another critical part of a LIB as a medium for the transportation of lithium ions between electrode materials. The transportation of lithium ions between electrode materials is realized through the movement of inorganic lithium salts dissolved in the solvents. To this end, the selection of an appropriate electrolyte enabling the fast transportation of lithium ions within it is pivotal for LIBs with high energy/power density. Almost all electrolytes used in current LIBs are liquid organic solutions with lithium salts dissolved in aprotic solvents. The utilization of nonaqueous electrolyte solutions, rather than aqueous electrolyte solutions, is due to the high operating voltage of LIBs, under which the decomposition of water will happen. The organic solvents most often used in LIB electrolytes include ethyl carbonate (EC), ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), tetrahydrofuran (THF), diethyl carbonate (DEC), propylene carbonate (PC). Since each solvent has its own unique contribution to the transportation of lithium ions, two or three of these solvents are usually mixed in various ratios to meet the specific cell requirements. (8) Due to its high conductivity and compatibility to organic solvents, lithium hexafluorophosphate (LiPF₆) is the most commonly and widely used lithium salt for LIB electrolytes. Other inorganic salts used are lithium tetrafluoroborate (LiBF₄), lithium bis(oxalate)borate (LiBC₄O), lithium perchlorate (LiClO₄) are also used as LIB electrolytes. (9)

Another essential and crucial part of a LIB is the separator. Separators usually are thin porous membranes that are positioned between negative and positive electrodes. Functionally, an ideal separator should effectively block the internal transport of electrons through physically isolating the direct contact between anode and cathode. (10) This requires the membrane separators of LIBs with low electrical conductivity but robust structure, that is to say, a thicker membrane is favored. However, from the aspect of energy density, a light and thin separator is preferred to
reduce the weight and thickness of the finally derived LIBs. These impose requirements on separator materials with high mechanical strength and low density. More important, an ideal separator of LIBs should have little effect on the transport of lithium ions in the electrolytes, which directly determines the power density of LIBs. This means that a separator should have excellent wettability to the electrolytes of LIBs and high structural stability to allow the continuum of electrolyte in the LIBs. Especially under extreme conditions, the shrinkage of conventional separators always results in LIB shutdown or shortcut. In addition, a desirable separator of LIBs should also have high chemical and electrochemical stability against electrode materials and electrolytes. General factors that should be considered to select an appropriate separator for practical LIBs are summarized below (1) (8):

- Good electronic insulation with minimal electrolyte resistance;
- Sufficient physical strength to allow easy handling, mechanical and dimensional stability;
- Chemical stability against electrolyte and electrode materials;
- Effective in preventing migration of particles, colloidal, soluble species between electrodes;
- Readily wettable by an electrolyte;
- Uniform thickness
- Low cost

1.1.2. Cellulose and cellulose nanocrystal

Cellulose, found in plants, fungi, bacteria, etc. is an important component to maintain the cell wall structures and provide good mechanical support simultaneously. It is the most abundantly renewable polymer available on Earth. Regardless of its source, cellulose can be characterized as
a homopolymer with a linear chain conformation. (11) The repeated unit, known as cellobiose, is composed of two anhydroglucose rings, which are linked together through an oxygen covalently bonded to C1 of one glucose ring and C4 of the adjoining ring (1-4 linkage), (12) as shown in Figure 1.2. In the presence of Van Der Waals forces and intermolecular hydrogen bonds between hydroxyl groups and oxygens of adjacent molecules, the cellulose chains pack in parallel, leading to the formation of microfibrils. (13) Depending on its source, microfibrils range with diameters between of about 2-20 nm, which further aggregate, leading to the formation of cellulose fibrils. (14) Within these cellulose fibrils, the arrangement of cellulose chains in some regions are highly ordered (crystalline) but are disordered in other regions (amorphous-like). In the presence of acids, disordered and ordered regions show different reactivities. This has been widely utilized to produce cellulose nanocrystals (CNCs) with the removal of the amorphous domains whereas leaving crystalline regions intact by using acid hydrolysis. Furthermore, plenty of hydroxyl, intra and inter hydrogen bonds play crucial roles in determining the physical and chemical properties of cellulose fibrils. The hydrogen bonding in cellulose is mainly responsible for its strength, thus tuning or restructuring these bonds can help in altering the strength or porosity for suitable purposes. (15)

Cellulose fibers could be extracted from several sources such as wood, algae, plants, tunicates, and bacteria. (16) Depending on their sources, the crystallinity of obtained cellulose fibers varies in a wide range, which results in cellulose fibers with different chemical and physical properties. (17) Cellulose fibers with high crystallinity exhibit the ability to absorb a much lower amount of moisture compared to lower crystallinity cellulose at low relative humidity. (18) For the application of LIBs, the moisture of all components is strictly controlled in an extremely low
level to avoid potential side reactions. Hence, in this thesis, we will be focusing on the cellulose fibers obtained from softwood trees because of its high crystallinity (17) and high tensile index. (19)

Figure 1.2. Structure of cellulose with atom numbering. Cellulose is a long chain polymer with repeating units of two anhydroglucose rings, which are joined by single oxygen atoms between C1 of one pyranose ring and C4 of the next ring.

Nanocellulose, sometimes termed cellulose nanocrystals (CNC), nanocrystalline cellulose or cellulose nanowhiskers, are rigid rod-shaped particles that are shorter than cellulose nanofibers. Compared to the naturally available cellulose, nanocrystalline cellulose shows high strength, high surface area, and various other crystalline properties. Particularly, the high aspect ratio and high surface area enable enhanced interactions with polymers, other nanoparticles, and small molecules. Therefore, CNC has been broadly applied as fillers in reinforced composites. The reinforcement of CNC strongly depends on its surface chemistry, geometry, and the dimension of nanoparticles and process methods. CNCs are generally extracted from natural cellulose sources such as wood pulp or cotton through chemical and/or mechanical methods. Mechanical processes such as pressurized homogenization, micro fluidization, etc., are used to extract microfibrils from cellulose. (20) These microfibrils are then further subjected to mechanical or chemical treatment to convert them into CNCs. The chemical treatment has proven to be more effective in converting cellulose fibrils into CNCs, and one of the most common and efficient methods is acid hydrolysis. (21) With the assistance of acids, the amorphous regions of a cellulose fibril will be preferentially
hydrolyzed, whereas the crystalline domains have a higher resistance to acid attack and remain intact, leading to the formation of CNCs. The obtained CNCs have a morphology and crystallinity similar to the original cellulose fibers. Besides its source, the properties of CNCs strongly depend on process conditions. For instance, sulfuric and hydrochloric acids have been widely used for CNC preparation. Using sulfuric acid as the hydrolysis agent, the charged sulfate esters are generated on the surface of derived nanoparticles, which could promote the dispersion of CNC particles in water. However, the flocculation rather than uniform aqueous suspension is always obtained if CNCs are produced by using hydrochloric acid as the hydrolysis agent. Furthermore, the process conditions, such as the ratio of acid to cellulosic material, reaction time, reaction temperature and so on, also play significant roles in determining the chemical and physical properties of finally obtained CNCs, including crystallinity, geometry, aspect ratio, and morphology. Owing to its ability to disperse in aqueous solution, CNC obtained through sulfuric acid hydrolysis approach will be used in this thesis to reinforce cellulose-based membranes for the separator of lithium-ion batteries (LIBs). (21)

1.2. Literature review

Because of their natural abundance, eco-friendliness, sustainability, and low cost, cellulose-based materials have been used in several battery components. (22) For instance, cellulose has been used as a binder to improve the mechanical strength of electrode materials. (23) Cellulosic materials are indistinctly insulative and have excellent wettability to the electrolyte solutions. These advantages make cellulose a promising material to be fabricated into a porous membrane and used as a separator of lithium-ion batteries (LIBs). Zhang et al. (24) demonstrated the promise of commercial rice paper, which mainly consists of cellulose fibers with a diameter of
4-50 µm, to replace commercial separators. In the studied LIB system, the rice-paper separator exhibited superior electrochemical stability and the thermal stability at high temperatures to the commercial separator. Unfortunately, due to the poor mechanical strength of rice paper, more than two layers of rice paper (the total thickness is over 200 µm) had to be used in LIBs to avoid the penetration of lithium dendrites. This greatly reduces the energy density and increases the cost of derived LIBs.

Using nanostructured fibers could effectively improve the mechanical strength of final cellulose membranes and several approaches have been developed to fabricate porous membranes composed of cellulose nanofibers. Various techniques, such as traditional coating, casting, electrospinning, phase inversion and papermaking with force spinning for nonwoven separators using cellulose, nanocellulose [cellulose nanocrystals (CNC), cellulose nanofibrils (CNF)] and its derivatives, have been employed. Using the traditional casting process, Kelley et al. (25) made films of Poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) nanocomposites with varying amounts of cellulose nanocrystals (CNC). The strength of films prepared through this approach increased in proportion to the increased CNC percentage, but further improvements in terms of its porosity for the films are needed to be used as lithium-ion battery separators. Research reported by Bolloli et al. demonstrated nanocomposite poly-vinylidene fluoride (PVdF) porous membranes reinforced with nanocrystalline cellulose (NCC/CNC) using phase inversion for lithium-ion battery separators. (26) The separator showed promising mechanical strength, but low ionic conductivity with the insertion of CNC due to lower pore interconnection. Using cellulose fibers from softwood and traditional papermaking techniques, Zolin et al. (27) demonstrated a paper sheet separator with high porosity, mechanical strength, and wettability, alongside
substantial ionic conductivity values for LIB application. But the highly porous structure of the membrane required multiple layers of separators to be used while assembling lithium-ion batteries. This inadvertently increased the overall thickness of the separator layer, which affects the energy density of the battery. By using the electrospinning process, Zhang et al. (28) reported fabrication of a porous cellulose membrane as a separator of high-performance LIBs. In this approach, a slurry composed of cellulose acetate dispersed in Dimethylacetamide (DMAc) and acetone solvent was further electrospun to form a porous membrane on the substrate. The porosity and mechanical strength of the finally obtained membrane could be tuned by dip-coating the dried membrane in a solution of Poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) dispersed in acetone. With this membrane separator, the derived LIB showed a higher rate capability and thermal stability as compared to the commercial polypropylene (PP) membrane separator. Though proven effective, electrospinning requires a lower feed flow rate, which results in several drawbacks compared to other techniques. Especially, cellulose fibers used in this thesis were obtained from softwood, which have a bigger diameter than that of general electrospinning needles and tend to make it difficult to get a continuous and strong film.

An alternative and promising approach to address the aforementioned concerns is to prepare a cellulose-based separator using a vacuum filtration process. Chun et al. (29) reported that, through vacuum filtering a cellulose nanofiber (CNF) dispersion in isopropyl alcohol (IPA)-water mixture on a funnel apparatus, a cellulose nanopaper (CNP) could be achieved. The porous structure and the mechanical properties of the CNP separators could be controlled through tuning the ratio of IPA to water as well as the solid content of CNF in the mixture. The porosity of obtained CNP separator increases with the enhancement of IPA concentration but results in the deterioration
of tensile properties. This was ascribed to the capillary action between the fibers due to the strong hydrogen bonds of polysaccharide chains and the cohesive force in the nanofibrillar structure between CNFs. The CNP separator showed excellent cycling performance up to the 100th cycle with 87% capacity remaining. Similarly, Pan et al. (30) used vacuum filtration approach to prepare separator films with Cladophora cellulose powder. The Cladophora cellulose separator showed a slight decrease in cycling capabilities as compared to a commercial polypropylene separator. Mautner et al. (31) reported the use of vacuum filtration to form nanopapers from nanocellulose. They used cellulose-based filter papers with thickness 5-13 µm and pores size of 2 um for the vacuum filtration but observed that nanocellulose passed through filter paper with such big pore size. Hence, Henriksson et al. (32) reported the use of PVDF filter papers with 0.65 µm pore size for nanocellulose retention.

The post-treatment on wet membranes obtained through various techniques also plays an important role in determining the properties of finally dried cellulose-based separators, especially their porous architecture. It is well known that the porosity of cellulose fibers obtained from softwood is usually reduced upon the conventional drying from water. (33) (34) However, this situation could be effectively alleviated by using a so-called quick drying method, in which the wet films are sandwiched between two aluminum plates and consequently dried at various high temperatures (43 – 200 °C) under vacuum. (35) The distribution of pore size in finally dried membranes could be tuned through controlling the rate of water evaporation during drying processes. The porous architecture of the finally dried cellulose membrane could be also be controlled by using a solvent exchange/inversion approach prior to the drying process. Sehaqui et al. (36) applied the solvent exchange process to a nanofiber membrane right after the vacuum
filtration step to generate a nanoporous architecture. This membrane was immersed in ethanol to exchange the residual free water within the fiber network and water in the nanofibrils. The exchange between ethanol and water helped in reducing the hydrogen bonding and subsequent capillary forces in the membrane, thus generated nanosized pores in the membrane. Henriksson and et al. (32) reported the use of other less polar liquids along with ethanol to adjust the porosity of membranes. It was observed that porosity of the finally dried films increased from 19% to 28%, 38% and 40% by use of methanol, ethanol, and acetone respectively. Obviously, the tensile strength and modulus of final cellulose membranes are also changed with varied porosity. Alongside solvent exchange, other methodologies such as CO₂ drying (36) or tert-butanol freeze-drying (37), have been reported to further increase the porosity of the films to up to 86%.

With enhanced mechanical stability, LIBs constituted of aforementioned cellulose separator demonstrated excellent durability, as well as rate capability. However, most of these membranes were made from pure CNFs, the cost of which is high. This leads to the high cost of LIBs comprised of CNF-based membrane separators. Compared with CNFs, the cost of cellulose fibers is much lower. However, none of these works present any significant insight upon the use of cellulose fibers with cellulose nanocrystals (CNC) to create a nanoporous membrane with improved mechanical strength to be used as separator in LIBs.

1.3. Statement of problem

Current separators used in commercial LIBs are primarily porous polyolefin membranes, including polyethylene (PE), polypropylene (PP) and their combinations. Polyolefin separators have the advantage of high mechanical stability, but their melting points, 130 °C for PE and 160 °C for PP respectively (8), and poor wettability to liquid electrolyte limit the wide application of
LIBs, especially when operations are exposed to some extreme environment. In addition, the hydrophobic nature and low porosity of polyolefin separators originated from currently fabricating techniques impair the electrolyte uptake, impede the ionic transportation, and consequently further limit the commercialization of LIBs. Thus, there is a critical need to develop an advanced membrane separator with high porosity, wettability, mechanical and thermal stability. (38) (39)

A Cellulose-based membrane is one of the most promising materials for separators of LIBs with the promise of low cost, sustainability, high porosity, thermal stability, and wettability. However, membranes composed of pure cellulose fibers usually have poor mechanical stability, originated from the weak Van der Waals force and weak intermolecular hydrogen bonds in cellulose fibers. To avoid the potential short cut, a thick (>200 μm) or multiple layers of thin cellulose membranes have to be used as separators, leading to the low energy density of derived LIBs. With the substitution of pure cellulose fibers with cellulose nanofibers (CNFs) could effectively improve the mechanical strength of cellulose membranes with a lower thickness. LIBs with CNF-based membrane separators also demonstrated superior, or at least comparable, electrochemical performances to those with polyolefin separators. However, the processing challenges and high cost limit the practical application of CNFs-based membrane separators in commercial LIBs. Therefore, there is a need to develop a cellulose-based membrane with high mechanical stability but low cost. (40)

To address aforementioned concerns, we propose to develop a cellulose nanocrystal (CNC) reinforced cellulose membrane with robust structure and low cost for LIB separators in this thesis. Compared with cellulose fibers, CNC has higher aspect ratio and the tendency to aggregate together. Thus, the first challenge is to fabricate cellulose membranes with uniformly dispersed
CNC particles. The introduction of CNC will increase the mechanical strength of cellulose membrane, but reduce its porosity and pore size, which will affect the ionic conductivity in LIBs. Therefore, the second challenge is to balance the physical and electrochemical properties of cellulose membrane separator with the incorporation of CNC. It has been shown that the membrane composed of pure cellulose fiber is electrochemically stable in the LIBs. However, CNC particles have a much higher surface area, leading to high reactivity. Therefore, there is a potential challenge to fabricate a cellulose membrane with high electrochemical stability in the presence of CNC.

1.4. Objective of this research

The long-term goal of this research is to fabricate a robust and low-cost cellulose membrane for high-performance lithium-ion batteries. The overall objective of this research is to establish an appropriate approach to fabricate a CNC-reinforced cellulose membrane and evaluate its performance as separator of LIBs.

Objective 1: Establish an approach to fabricate cellulose membranes with uniformly dispersed CNC.

Due to the high aspect ratio and large surface area, it is a challenge to uniformly disperse CNC in cellulose membrane. The effect of process parameters, including solid content of slurry, the ratio between cellulose fibers and CNC, method to fabricate wet filter cakes and drying conditions, on the properties of dried membranes will be investigated.

Objective 2: Demonstrate nanocellulose-reinforced membranes with superior mechanical stability to that of membrane composed of conventional cellulose fibers.
A membrane separator with high mechanical strength is essential to prevent the potential short cut in LIB. With the reinforcement of CNC, we believe that the mechanical stability of cellulose membranes will be significantly improved, even at low thickness and high porosity, compared with those composed of pure cellulose fibers.

Objective 3: Demonstrate a battery with CNC-reinforced cellulose membrane with superior electrochemical performance to that of a cellulose membrane.

One important application of the obtained cellulose membranes is to use them as separators of LIBs. The obtained membranes in this research will be assembled into LIBs with graphite and lithium metal as electrode materials. The electrochemical stability of the cellulose membrane and performances of derived LIBs will be evaluated. We believe that the cellulose membrane produced in this research will demonstrate superior, at least comparable, electrochemical performance to those with polyolefin separators.
CHAPTER 2
EXPERIMENTAL PROCEDURE

2.1. Materials/apparatus

Solvents such as Isopropanol (99.5%, ACS Reagent), Acetone (98%, ACS Reagent) were purchased from FisherSci. Cellulose fiber was supplied by Domtar Canada as softwood pulp sheets. Cellulose Nanocrystals (CNC-FD) were obtained from Cellulose Lab. All solvents/chemicals were used as received without any further treatment.

Nylon filter membranes (Hydrophobic 90 mm, 0.22 µm pore size) were obtained from Foxx Lifesciences. Cellulose filter papers (Whatman) were obtained from GE Lifesciences. Graphite anode coated on copper foil and lithium metal foil was purchased from MTI, commercial Celgard separator provided by Celgard.

2.2. Approaches for fabrication of cellulose-based membranes

2.2.1. Slurries of cellulose fiber and nanocrystal preparation

Prior to the membrane preparation, slurries containing cellulose fibers and/or nanocrystal powders were prepared. Softwood pulp dried into commercial sheets was used as a source of cellulose fibers. The solid content in the sheets was measured by drying a measured (10 grams) portion of the sheet in a commercial oven for a span of 6 hours. Weight was measured after completion of the initial 3 hours and then subsequently after equal intervals of 1 hour. Pulp sheets were found to contain the dry weight at 97.0 ± 0.5%.

\[
\frac{\text{Weight before drying}}{\text{Weight after drying}} \times 100 = \text{Dry weight of sample}
\]
To prepare the slurry of cellulose fibers in water, 30 grams of the dried cellulose pulp was soaked in 1000 mL Deionized (DI) water for 24 hours. After 24 hours, the slurry was diluted with DI water to a total volume of 2000 mL, bringing the solid consistency to about 1.5%. To enhance their fiber bonding characteristics, the prepared slurry was then disintegrated in a commercial disintegrator (Three-blade propeller) for 13000 revolutions during 20 minutes. This disintegrated fiber slurry was then vacuum filtered using regular filter paper (Whatman). The obtained filtrate was weighed and diluted further with DI water to about 300 grams bringing consistency of solids to about 10%. The diluted filtrate was then loaded onto a commercial beater (PFI laboratory beater) and subsequently beaten for about 5000 revolutions. (41) (42) The beaten filtrate was stored in a refrigerator to avoid any bacterial degradation of the cellulose fibers. Membranes fabricated from these cellulose fibers are referred to as “Generation I or Gen I” in this thesis for future reference.

To prepare slurries for fabricating cellulose nanocrystals (CNC) reinforced cellulose fiber membranes CNC powders were dispersed in DI water (with a concentration of 0.5 w/w %) using a vacuum mixer for about 15 minutes until complete dispersions were ensured. (20) These suspensions, with varying CNC concentrations, were then added to a slurry with cellulose fibers dispersed in a water/IPA base, using a mixer (Servodyne EW-50008, US). The slurry was stirred at 1000 rpm for 90 minutes until the proper dispersion of cellulose fibers was observed. Membranes prepared from these slurries will be referred to as “Generation II or Gen II” in this thesis. Typically, the finally dried Gen II membranes are composed of 0.15 g cellulose fibers and with CNC in a varied proportion of 5%, 10%, 20% & 30%.
2.2.2. Cellulose membrane preparation

Rare researches on preparing CNC reinforced cellulose membranes have been reported, hence, four well-established membrane preparation methodologies, traditional papermaking, spin coating, casting and vacuum filtration techniques, were employed here to fabricate Gen I and Gen II membranes. The obtained membranes were evaluated and the appropriate approach for fabricating battery membrane separators was identified.

2.2.2.1. Papermaking

In accordance with TAPPI T 205 sp-95, (43) hand sheets (membranes) were prepared for the Gen I membrane by loading a proportionate slurry containing cellulose fibers onto the sheet maker. To get membranes with the thickness in the range of 60-80 µm, sample sheets were prepared using varying amounts of cellulose fibers suspensions. After several trials, it was found that 5 grams (10% solid content) of the beaten pulp was optimum amount for the dried membranes with the thickness in the targeted range. Prepared sheets were first dried in a pressure press for about 20 minutes under 345kPa pressure. Further, the sheets were air-dried for about 24 hours in a room with temperature and relative humidity (RH) controlled at 23 °C and 50% respectively. The dried sheets were kept for further characterizations and applications. Weight and thickness of sheets were measured and recorded after drying for further calculations. The procedure for preparing the Gen I membrane through the papermaking is illustrated in Figure 2.1. The same approach was also employed to prepare Gen II membrane by using the slurries containing CNC and cellulose fibers.
2.2.2.2. Spin coating

Spin coating techniques have been successfully incorporated to prepare thin cellulose based films on substrates. Various substrates were used to deposit thin films previously, such as silicon (44), glass (45) etc. In this thesis, a traditional spin coater (Chemat Technology, US), with silicon wafers (MTI Corporation, US) as substrate to deposit various membranes on it. Prior to spin coating, silicon substrates were extensively rinsed with DI water and subsequently dried in vacuum oven at room temperature. 50 µL of cellulose fiber slurry was dropped on the substrate. The substrate was carefully attached on the vacuum mounted holder of spin coater. The apparatus was spun at 3000 rpm for 30s.
Figure 2.2. Photographs of top (a): Spin coater; bottom (b): Silicon substrate wafer

2.2.2.3. Casting

Casting is another technique that has been successfully used to prepare thin films with cellulose and its derivatives. Instead of the traditional film casting techniques, modifications are generally made to cast films to meet requirements for specific applications. (46) (47) (48) In this thesis, slurries made of cellulose fibers and the mixture of CNC with cellulose fibers were hand
cast on the surface of flat glass Petri dishes (90 mm) and were allowed to stand still to maintain uniformity. The Petri dishes were then placed in a temperature & humidity controlled chamber to dry at 40 °C at 50% RH. After drying in the humidifier for about 12 - 14 hours, the casted films were completely dried and could be peeled off easily. The approach to prepare membranes is shown in Figure 2.3. It has been reported that nanocellulose tends to collapse compactly during water evaporation due to the capillary action originated from the hydrogen bonds of polysaccharide groups in beaten cellulose fiber. (29) To develop porosity in the dried membrane, cellulose fibers and the mixture of cellulose fibers with CNC were dispersed in a mixture of IPA and DI water (v:v, 50:50). The same as previous approaches, the solid content of slurries here used for casting was controlled to 10 wt.% to enable resultant films thicknesses in the range of 60 - 70 µm.

2.2.2.4. Vacuum filtration

An alternative and promising technique to prepare membrane separators for LIBs is the paper-making filtration technique with advantages of low amount of solvent use, and capability of varying thickness and porosities without the use of externally applied pressure and various drying methodologies. (49) Therefore, this approach has also been adopted with modifications to prepare membrane separators in this thesis. As shown in Figure 2.4, slurries prepared in Section 2.2.1 were poured onto a Nylon filter membranes. After no liquid content was observed on the filtrate, the
membrane was peeled off the funnel along with the filter paper. Since CNCs are still loosely attached to the filter paper, the membrane wasn’t peeled off immediately.

Membranes along with filter papers were then immersed in Petri dishes filled with Acetone (99.5% purity) for the subsequent solvent exchange to replace water with acetone. The solvent exchange helps in reducing the capillary action between cellulose fibers & CNC’s, to induce more porosity in the membrane. (36) After being immersed in acetone for 12 hours, the membrane with the attached filter paper was sandwiched between two normal cellulose filter papers, followed by being placed between two aluminum plates. To obtain uniform films, this apparatus was kept between two glass slabs with a weight of about 1 kg applied on top. Since pressing of membranes improves dewatering, provides higher tensile strength and better tear resistance. (50) The whole apparatus was then transferred into a vacuum oven and films were dried at 120 °C for about 4 - 5 minutes under vacuum for quick drying. Quick drying was used to reduce water evaporation time, thus limit capillary action between cellulose fibers and cellulose nanocrystals. After drying, the film was peeled off the attached Nylon filter membrane and kept for further characterizations and applications.
2.3. Characterizations

2.3.1. Physical characterizations

2.3.1.1. SEM

Morphologies of the membranes obtained were characterized using a scanning electron microscope (JEOL-JSM-IT100LA, US) with an accelerating voltage of 10 keV. To improve the conductivity, samples (2 mm x 2 mm) were coated with carbon using a vacuum sputter coating system (Agar, US) prior to the SEM observations. Coated samples were then loaded onto probes and inserted into imaging chamber under vacuum. Images were captured of both sides of membranes, as well as the cross-sectional view at different magnifications.

2.3.1.2. Tensile strength

Tensile Strength is the maximum stress required to break a single strip of membrane. Tensile index for membranes is calculated based on the tensile strength required to break a membrane with respect to its dimensions. (51) The mechanical properties of all membranes were
measured at room temperature by using the Instron universal testing machine (Instron 4301, England). The membrane samples were cut into the same dimension of 10 mm width and 80 mm length, and then were mounted on the testing equipment with both ends attached to two clamps, and the load was applied longitudinally in the opposite direction. During the testing, one of the clamps is fixed while the other clamp is driven by a servo motor with a constant crosshead speed of 1 inch/minute. The small increments of elongation of the sample and the applied load were recorded based on load-elongation values. The curve is drawn with measured tension (tensile index) against the concentration of CNC in membranes.

2.3.1.3 Electrolyte retention & uptake

To evaluate the wettability, discs with a diameter of 5/8 inch were cut from different membranes obtained from various approaches. The separator membrane discs were immersed in a 50ml electrolyte solution with 1.2 M LiPF₆ dissolved in ethyl carbonate (EC)/ethyl methyl carbonate (EMC) [w/w, 3/7] for 1 hour. Excess electrolyte was removed from the membranes using a nylon filter membrane. The weights of membrane discs before and after immersion were measured and recorded as initial reading. Weight gains were analyzed to determine the electrolyte retention characteristics of various separator samples. Infiltrated separators were treated at 50° C and weight was measured at varying intervals of time. For comparison, the same approach was also used to evaluate commercial Celgard separator. Parallel readings were recorded for different membranes under identical conditions. (52)

Effective infiltration of electrolyte into the separator was also be analyzed by testing the separator’s inherent electrolyte uptake ability. One strip of 85 mm x 10 mm dimension was cut out of each membrane hung onto a burette stand using separate paper clips. Every strip was hung into
an electrolyte solution (30 ml), ensuring 2 mm of each strip was immersed into the solution. This arrangement of membrane strips was then dipped into an equal amount of electrolyte for a span of 20 minutes. Observations were made based on the level electrolyte uptaken longitudinally on the membrane strips over the span of 20 minutes. Theoretical uptake capability was calculated by immersing separator membrane discs in the electrolyte and measuring its weight before and after.

Electrolyte Uptake and Retention of various separators was tested using the following formula: (52)

\[
\text{Electrolyte Uptake} = \frac{w_1 - w_0}{w_0} \times 100\%
\]

\[
\text{Electrolyte Retention} = \frac{w_x - w_0}{w_1 - w_0} \times 100\%
\]

Here, \(w_0\), \(w_1\) and \(w_x\) represent the mass weight of membrane before immersed in the electrolyte solution, after immersed in the electrolyte solution for 1 hour, and dried for \(x\) hours respectively.

2.3.1.4. Thermal test

To evaluate the thermal stability, cellulose membranes prepared here were cut into discs with a diameter of 5/8 inch, placed in a glass Petrich dish, and transferred into an oven. The oven was heated from room temperature to 160° C (320° F) and kept at this temperature for 30 minutes. Physical attribute (diameter) of the separator discs was measured before and after being exposed to high temperature.
2.3.1.5. Contact angle

Wettability results are further evaluated with the contact angle measurements by using DI water as a medium. Strips of membranes were equally in 70 mm x 10 mm dimensions for the test. 50 ml of DI water was loaded on to a syringe and hung on to an automated rack and pinion lift apparatus (First Ten Angstroms 125, USA). Using FTA200 Dynamic Contact Angle Analyzer software, the rack and pinion apparatus was operated to have a constant flow (2 - 2.5 ul/min) of fluid dispensed from the syringe. Once begun, the apparatus starts applying force against the lever of the syringe and dispensing of DI water begins as soon as air bubbles are pushed out of the needle attached to the syringe. Images were being captured continuously using a fixed optical system (Navitar Modular Tube Lens, US) at every 1/5th of a second. Using the FTA200 Dynamic Contact Angle Analyzer, the exact image when the first drop of DI water touches the membrane is selected. The contact angle is generated between the drop of DI and the membrane.

2.3.1.6. Thickness and porosity

The thickness of various membranes was calculated at 5 different points, and calculation was made upon averaging these 5 points and obtaining the average thickness (Technidyne, USA). The density of membrane was calculated from the ratio of weight of membrane to the volume of membrane. Porosity was calculated with following formula (53) (40):

\[
\text{Porosity} = \left[ 1 - \left( \frac{\rho_m}{\rho_{cellulose}} \right) \right] \times 100\%
\]

Here, \(\rho_m\) is the density of membranes, and \(\rho_{cellulose}\) is the density of cellulose (1.5 g cm\(^{-3}\))
2.3.2. Electrochemical characterizations

2.3.2.1. Cell assembly

To study the electrochemical performances, the membrane obtained in this thesis was cut into discs with a diameter of 5/8 inch and assembled in coin cells (CR2032). A graphite-based anode coated on Cu foil (composed of 90 wt.% active material) and lithium metal as counter electrode were cut into discs of 1.6 cm$^2$. The graphite/ Li electrodes were assembled in 2032-type coin cells with the above membrane separators. Before the cell assembly, membrane separators and graphite anodes were dried at 90 °C for 12 hours under vacuum to completely remove residual moisture. The solution containing 1.2M LiPF$_6$ dissolved in ethyl carbonate (EC)/ethyl methyl carbonate (EMC) [w/w, 3/7] was used as the electrolyte for all coin cells. The cell assembly was conducted inside a glove box, which is filled with Argon gas and has the oxygen and moisture levels controlled below 0.1 ppm.

2.3.2.2. Formation

Galvanostatic cycling tests of the assembled cells were conducted on battery testing equipment (BTS3000, Neware, China). Initially, three formation cycles with an approximated 0.1 C current were applied to all cells. The specific capacity of cells was calculated based on the voltage-current, and time of the charge/discharge curves, and weight of the active material (graphite). The exactly calculated 0.1 C current was used the baseline and applied to cells for subsequent rate capability and cycle life measurements. In addition, formation cycles of lithium-ion batteries are also necessary to grow a stable solid electrolyte interphase (SEI) on the surface of the electrodes. This protective film prevents the further decomposition of electrolyte and side reactions at the surface of the electrodes, diffusion of solvents into active materials and thus
enables long life of lithium-ion batteries. (54) The voltage window applied to all cells was 0-1.5 V.

2.3.2.3. Rate capability test

After three formation cycles, the charge capacity was measured at incrementally higher C-rate (0.1 C, 0.2 C, 0.3 C, 0.5 C, 1 C, 2C) to evaluate the rate capability. At every rate, cells went through 3 cycles and the same current of 0.1 C was applied to all discharging processes. The charge capacity retention at different C-rate was calculated from the cell capacity at the specific C-rate against that at 0.1 C.
CHAPTER 3
OBSERVATION AND RESULTS

3.1. Investigation on effect of fabricating methods on the properties of cellulose membrane

There are various approaches reported to prepare cellulose membranes, however, rare studies on the fabrication of membrane separators have been reported in the presence of CNC. Therefore, several representative methodologies for cellulose-based membrane fabrication were investigated firstly. The same approach of preparing membranes with cellulose fibers (Gen I membrane) was applied to fabricate membranes with the mixture of cellulose fibers and CNC (Gen II membrane, 5 wt.% CNC and 95 wt.% cellulose fibers in finally dried membrane). The obtained membranes were evaluated in terms of uniformity, mechanical properties, or electrochemical behaviors.

3.1.1. Papermaking

The traditional papermaking method is a well-established technique to fabricate nonwoven membranes. The nonwoven membranes prepared through this technique with various celluloses and their derivatives have also been successfully utilized as separator membranes for lithium-ion batteries. (55) (56) (57). Hence, the papermaking technique was the foremost methodology and firstly adopted to prepared cellulose membranes in this thesis.
Under visual inspection, both Gen I and II membranes show smooth surfaces without agglomerates observable (Figure 3.1). Both Gen I and Gen II membranes exhibit uniform thickness measured to be in the range of 55 – 65 μm. This implies that using the traditional papermaking approach could fabricate uniform membranes regardless of introducing CNC into slurries or not. These membranes were then cut into discs and assembled in coin cells acting as separators and, coupled with graphite and Li-metal electrodes. Results from the electrochemical characterizations demonstrated that, in the presence of one layer of Gen II membrane separator, the cell could only run one cycle, and, the voltage stopped at ~0.15 V during the second charge process, indicative of the occurrence of short circuit in the cell (Figure 3.2). The electrical short circuit in the coin cells might be the result of cellulose membrane separator with high porosity and weak mechanical strength, which is incapable of preventing the contacts between graphite electrode and Li-metal counter electrode. Increasing the layer of separator could effectively enhance the lifetime of the cells. With two layers of separator, the cell similarly also failed in the second formation cycle.
(Figure 3.3). However, all three formation cycles could be successfully completed when three layers of separator were used in the cell (Figure 3.4).

Figure 3.2. Electrochemical formation charge/discharge curves of Li/Graphite cell with one layer of Gen II membrane separator prepared with papermaking methodology.

Figure 3.3. Electrochemical formation charge/discharge curves of Li/Graphite cell with two layers of Gen II membrane separator prepared with papermaking methodology.
These observations imply that Gen II membranes prepared through traditional papermaking approach have little improved mechanical strength, compared with Gen I membrane. It is highly possible that CNC was not incorporated into the cellulose membrane, due to the large pore size of the filter screen on the sheet making machine, which allowed nanosized CNCs to flow through. Thus, though showing great promise of easy process and low cost, the papermaking technique was unable to fabricate CNC reinforced membrane, and hence will not be studied further in this thesis.

3.1.2. Spin coating

Spin coating is another approach well adopted to fabricate thin films. Unfortunately, the wet film with cellulose fibers being concentrated irregularly on various parts of substrate was produced by using this method (Figure 3.5). Changing coating conditions, such as the solid content of the slurry and the spin speed, has little effect on the distribution of the cellulose fibers at the surface of substrate. For instance, the agglomeration of cellulose fibers on the substrate was
inevitable under various spin speeds. Hence, the spin coating proved to be an unviable option to prepare cellulose based membranes.

![Image](image.png)

**Figure 3.5. Cellulose fibers agglomeration on silicon substrate wafers**

3.1.3. Casting

Cellulose-based membranes were also prepared through casting the slurry containing cellulose fibers with or without CNC onto the surface of the petri dish followed by a drying process. It was observed that, regardless of CNC, the thickness of both dried membranes was nonuniform with cellulose fibers seen rich in some regions of the membrane, while poor in other regions (Figure 3.6). This non-uniform distribution of cellulose fibers might be ascribed to the aggregation propensity of cellulose fibers in the course of natural evaporation of the solvents. Using this membrane as the separator, cells with one layer of either Gen I or Gen II failed during 1\textsuperscript{st} cycle (Figure 3.7), and so did cells with two layers of separators (Figure 3.8).
Based on these observations, it is not a viable approach to fabricate membranes by using casting method in the presence of cellulose fibers and CNC.

Figure 3.6. Photographs of Gen I and Gen II membranes obtained through the casting method.

Figure 3.7. Electrochemical formation charge/discharge curves of Li/Graphite cells with one layer of Gen II membrane separator prepared with casting methodology
3.1.4. Vacuum filtration

The vacuum filtration is another promising approach and well adopted to fabricate porous membranes. Results from our preliminary experiments showed that uniform membranes with homogeneously distributed cellulose fibers could be obtained in the absence or presence of the CNC (Figure 3.9). It is worth to note that, before the vacuum filtration, cellulose fibers with and without CNC were dispersed in DI water, and after the filtration, the drying process was applied to the wet cake directly. However, it was also observed that our preliminarily prepared Gen I and Gen II membranes, though uniform, possess highly nonporous structure when DI water was used as the sole solvent for the slurry preparation. The nonporous structure is attributed to the hornification among cellulose fibers occurring during the evaporation of water from cellulose fibrils. (58) (14) (59) Obviously, these nonporous membranes could not be used as separators in LIBs, and it is necessary to modify this approach to produce uniform membranes with porous structure for LIB applications.

Figure 3.8. Electrochemical formation charge/discharge curves of Li/Graphite cells with two layers of Gen II membrane separator prepared with casting methodology.
Figure 3.9. Photographs of Gen I (a) and Gen II (b, 5 wt.% CNC) membranes prepared through the vacuum filtration process.

It has been reported that the substitution of water with IPA could effectively reduce the hornification of cellulose fibers through creating the flocculation, rather than uniform dispersion, of cellulose fibers in slurries, while the function of water is to interrupt the hydrogen bonds amongst cellulose fibers and thus enable their uniform dispersion in the solvents. The flocculation might result in finally dried membranes with porous structures. (60) (61) In light of this, the mixture of IPA and DI water was used as the solvent for slurry preparation. It is worth to note that having cellulose fibers homogeneously distributed in the slurry, under visual inspection, is critical to enable membranes with uniform thickness, although the flocculation of fibers exists. Table 3.1 demonstrates the effect of varying ratios of IPA/ DI water on the homogeneity of slurries in the absence of CNC. Apparently, it is difficult to have a slurry with cellulose fibers homogeneously distributed in the solvent when more than 80% IPA is used in the solvent.
### Table 3.1. Effect of IPA on the homogeneity of slurries with cellulose fibers in DI water

<table>
<thead>
<tr>
<th>Sr No.</th>
<th>Material</th>
<th>Percentage of IPA in solvent (%)</th>
<th>Homogeneous Slurry Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cellulose Fibers</td>
<td>10</td>
<td>Yes</td>
</tr>
<tr>
<td>2</td>
<td>Cellulose Fibers</td>
<td>20</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
<td>Cellulose Fibers</td>
<td>30</td>
<td>Yes</td>
</tr>
<tr>
<td>4</td>
<td>Cellulose Fibers</td>
<td>40</td>
<td>Yes</td>
</tr>
<tr>
<td>5</td>
<td>Cellulose Fibers</td>
<td>50</td>
<td>Yes</td>
</tr>
<tr>
<td>6</td>
<td>Cellulose Fibers</td>
<td>60</td>
<td>Yes</td>
</tr>
<tr>
<td>7</td>
<td>Cellulose Fibers</td>
<td>70</td>
<td>Yes</td>
</tr>
<tr>
<td>8</td>
<td>Cellulose Fibers</td>
<td>80</td>
<td>No</td>
</tr>
<tr>
<td>9</td>
<td>Cellulose Fibers</td>
<td>90</td>
<td>No</td>
</tr>
</tbody>
</table>

The effect of IPA could be observed on the mechanical property of finally dried cellulose-based membranes. It should note that this measurement was performed on the Gen II membranes with 10 wt.% CNC to demonstrate the effect of IPA. Figure 3.10 shows that, with 25% IPA in the solvent, the tensile index of the obtained membrane with 10 wt.% CNC is about 22 Nm/gram. The tensile index of the obtained membranes decreases along the enhancement of IPA in the solvent, and it is reduced to about 14 Nm/gram at 50%, 12 Nm/gram at 75%, and finally reaches to 8 Nm/gram at 90% IPA. The reduction of tensile index might be ascribed to the increased porosity of membrane obtained with higher IPA percentage in solvent. Therefore, the introduction of IPA could effectively create a porous structure in the obtained cellulose membrane, but, surplus IPA could lead to a nonuniform membrane with poor mechanical strength. In addition, using a high amount of IPA in solvent will tend to increase the cost of membrane preparation. Therefore, 50%
IPA was used to prepare the cellulose-based membrane in this thesis, considering the balance among porous structure, uniformity and cost of finally dried membrane.

![Figure 3.10. Effect of the amount of IPA in solvent on tensile index of cellulose membranes with 10 wt. % CNC](image)

3.2. Advantages of CNC reinforced cellulose membrane

Aforementioned results show that the vacuum filtration process is an appropriate approach to prepare cellulose membranes in the presence and absence of CNC. Therefore, Gen II membranes with 5 wt.% CNC were initially obtained through this method and evaluated in terms of their physical and electrochemical properties. For comparison, the same approach was applied to prepare membranes without CNC (Gen I) for evaluations.

3.2.1. Physical characterizations

3.2.1.1. Tensile index

The introduction of CNC could benefit the cellulose-based membranes with strong mechanical strength. Figure 3.11 summarizes the force required on the cellulose-based membranes
to reach a breaking point. As seen from the graph, the tensile index of the Gen II membrane with 5 wt.% CNC is about 12 Nm/gram, which is almost 50% higher than that of Gen I membrane with pure cellulose fibers (~8 Nm/gram). The enhanced mechanical strength in Gen II membrane is ascribed to the CNC particles filled in the pores of the cellulose fibers forming bonds with cellulose fibers and leading to dense and robust structure. It is worth to note that the same approach was employed to evaluate the mechanical property of commercialized Celgard membrane separator and the plastic deformation without rupture was observed within the force range applied in this thesis.

![Graph showing the effect of CNC on tensile index of cellulose membranes](image_url)

**Figure 3.11. Effect of CNC on tensile index of cellulose membranes**

3.2.1.2. Thickness and porosity

Besides the improved mechanical strength, the introduction of small amount of CNC has little impact on the thickness and porosity of final cellulose-based membranes. As shown in Table 3.2, the thickness of Gen I membrane without CNC is about 83 μm, and it increases slightly to 85
μm when 5 wt.% CNC is integrated into the membrane. More importantly, the porosity of obtained Gen I membrane is about 77%, and, with 5 wt.% CNC, the porosity of obtained Gen II is still as high as ~75%, which is 2 times higher than that of commercial Celgard membrane (~37%).

Table 3.2. Calculated porosity of various separators

<table>
<thead>
<tr>
<th></th>
<th>Average Thickness (µm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gen - I</td>
<td>83.0 ± 1.5</td>
<td>76 ± 3</td>
</tr>
<tr>
<td>Gen - II</td>
<td>85.0 ± 1.8</td>
<td>74 ± 3</td>
</tr>
<tr>
<td>Celgard</td>
<td>18</td>
<td>36.6</td>
</tr>
</tbody>
</table>

3.2.1.3. Microstructure

The slightly changed porous structure originated from the presence of CNC could be verified through the observations on the microstructure of the membranes. Under visual inspection, the dried Gen I membranes exhibit rough top (interface between slurry and filtering cake) and bottom (interface of filtering cake and filtering paper) surfaces. The dried Gen II membranes also show a rough top surface, but a relatively smooth bottom surface. Observations from the scanning electron microscopy (SEM) confirm that the fiber feature and porous structure are apparently shown on the top surface of Gen I membrane (Figure 3.12 a). However, the fusion of fibers and thus pores with reduced size are found on the bottom surface of Gen I membrane (Figure 3.12 e). This indicates the formation of an asymmetrical porous architecture in cellulose-based membrane obtained through the vacuum filtration process. The introduction of CNC does not change this asymmetrical porous structure but facilitates the fusion of adjunct fibers and reduction of pore size in the membrane. Figure 3.12 b shows that, besides fiber feature, a very thin layer of film could be observed at the top surface of Gen II membrane. Furthermore, a relatively densified thin film,
rather than a porous structure, is found at the bottom surface of Gen-II membrane, and the fiber feature could only be found under this thin film (Figure 3.12 f). This asymmetric structure observed from cellulose-based membranes might be attributed to the unique filtration process. Herein, the bottom side of membranes in contact with filter paper bear the weight of the whole wet cake, leading to the relatively densely packed cellulose fibers, while the top side exposed to air, leading to relatively loosely packed cellulose fibers. The interconnection, fusion, and growth might occur among cellulose fibers during the following drying process. Therefore, relatively larger pores formed on the top side of the dried membrane with rough surface, while more small pores observed on the bottom side with relative smooth surface. Compare to Gen I membrane, the only difference in the course of fabricating Gen II membrane is that a small amount of 5 wt.% CNC was introduced into the slurry before the filtration. Therefore, it is reasonable to consider that this compact thin film settled on the bottom part of membrane is a substantial portion of CNC added to the slurry. This presence of CNCs layer on the bottom side of the membranes can attributed to inability of partial CNCs to bond with cellulose fibers initially as observed during papermaking methodology and flocculating on the filter paper after removal of solvent during vacuum filtration. Furthermore, the absence of CNC on filter paper after vacuum filtration and subsequent vacuum drying cements the theory of CNC binding to bottom surface cellulose fiber membrane. (62)
3.2.1.4. Electrolyte retention & uptake

Wettability behavior of the membrane is an important factor for the filling up success of electrolyte because the electrolyte absorption is necessary for ion transport. Figure 3.13 shows the electrolyte retention behavior of Gen I, Gen II, and Celgard membranes, which could be divided
into two stages. During the initial 60 minutes, the weight of electrolyte held in Celgard membrane dramatically dropped to about 50% and decreased slowly to 22% after 240 minutes. However, there are ~63% and ~57% electrolyte remained in Gen I and Gen II membranes respectively after initial 60 minutes. Even after 240 minutes, >37% electrolyte could be held in both Gen I and Gen II membrane. The high electrolyte retention in cellulose-based membranes is ascribed to the affinity of cellulose towards the electrolyte originated from the hydroxyl groups in the cellulose. (8)

![Figure 3.13. Electrolyte retention of Celgard, Gen I and Gen II (5 wt.% CNC) membranes.](image)

Electrolyte uptake capability calculated on basis of weight differential before and after the exposure of membranes to the electrolyte is demonstrated in Table 3.3. It shows that Gen I membrane possesses the highest electrolyte uptake capability (208%), compared to that of Gen II with 5 wt. % CNC (195%) and Celgard membrane (85%).
Table 3.3. Electrolyte Uptake capability for various membranes

<table>
<thead>
<tr>
<th>Sample (CNC %)</th>
<th>Uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gen I</td>
<td>208</td>
</tr>
<tr>
<td>Gen II</td>
<td>195</td>
</tr>
<tr>
<td>Celgard</td>
<td>85</td>
</tr>
</tbody>
</table>

The strong affinity of cellulose membranes to the electrolyte could be further confirmed through the observation of the longitudinal travel of the electrolyte on membrane strips. Figure 3.14 shows, after a span of 20 minutes, Gen I membrane has the highest electrolyte uptake, Gen II membrane has a slightly lower value and Celgard membrane has the lowest value. This uptake capability of cellulose membranes indicates their excellent ability to absorb a large amount of electrolyte. The poor uptake capability of the Celgard membrane implies its lower porosity and poor affinity to the electrolyte used in LIBs. (63) The excellent uptake capability of cellulose-based membrane to the electrolyte is a beneficial factor in derived LIBs with high rate capability.
Figure 3.14. Photographs of Celgard (a, b), Gen I (c, d) and Gen II (e, f) membrane strips before (a, c and e) and after (b, d, f) the exposure to the electrolyte solution for 20 min.
3.2.1.5. Contact angle

Figure 3.15 shows the contact angle between the DI water and the measured membranes. As expected, Celgard membrane showed poor wettability to the DI water and the contact angle was measured to be a high value of 96.83°. The poor wettability of Celgard separator arises from the hydrophobic nature of polyolefin polymer. (64) To the contrary, the cellulose has the hydrophilic nature and demonstrated excellent wettability to polar solvents. Given the asymmetrical porous structure, the contact angle between the DI water and membranes was measured for top and bottom surfaces of the membranes respectively. The DI water spread out immediately when it touched the top surface of Gen I membrane, and the contact angle was measured to be 2.78°, while 13.13° for the bottom part. The introduction of CNC into the cellulose membrane slightly increase the contact angles for both top and bottom surface. The contact angle on the top side of Gen II membrane was measured to be 3.74°, while 18.27° for bottom part. The higher value of contact angle might be related to the reduced pore size. Compared to the top surface, Gen I membrane possesses more smaller pores on the bottom side due to its asymmetric structure. We deduce from the observation that introduction of CNC could reduce the pore size of both sides of cellulose membranes leading to higher contact angles of Gen II membranes.
Figure 3.15. Photographs of contact angle of DI water on surface of Celgard (a), top (b) and bottom (c) of Gen I, top (d) and bottom (e) of Gen II with 5% CNC membranes.

3.2.2. Electrochemical characterization

The cellulose-based membranes obtained through the vacuum filtration process were cut into discs and assembled into coin cells as separators, coupling with graphite and lithium metal electrodes. It is worth to note that only one layer of separator was used in the assembled coin cells here. In addition, only formation and rate capability measurements were performed on all cells to
evaluate the electrochemical performance of cellulose-based membrane separators for the sake of saving test time.

3.2.2.1. Formation

Voltage profiles of cells with various membrane separators during initial three formation cycles are shown in Figures 3.16 to 3.19. Regardless of membrane separators used, all cells demonstrate almost identical curves with three plateaus below 0.2 V (vs. Li/Li\(^+\)), characteristics of graphite anodes in LIB. Most importantly, the irreversible capacity loss (ICL) for all cells is between 8 – 11 % during the initial cycles (Table 3.4). This indicates that there are no additional reactions occurred when Celgard membrane separator was substituted by cellulose-based membrane separators. In addition, all cells delivered almost the same reversible capacity of around ~334-338 mAh/g at the end of third cycle (Fig. 3.19, and Table 3.4). All these observations confirm that cellulose-based membranes have the same, at least comparable, stability as Celgard membrane as separators in LIBs against electrode materials and electrolyte.
Table 3.4. Performance summary of cells with various separator membranes during the initial formation cycles

<table>
<thead>
<tr>
<th>Separator Membrane</th>
<th>Cycle</th>
<th>Discharge (mAh/g)</th>
<th>Charge (mAh/g)</th>
<th>ICL (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Celgard</td>
<td>1st</td>
<td>336.2</td>
<td>307.3</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>335.3</td>
<td>331.7</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>3rd</td>
<td>338.3</td>
<td>335.9</td>
<td>0.7</td>
</tr>
<tr>
<td>Gen I</td>
<td>1st</td>
<td>338.3</td>
<td>319.6</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>332.4</td>
<td>329.1</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>3rd</td>
<td>335.2</td>
<td>332.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Gen II</td>
<td>1st</td>
<td>336.6</td>
<td>300.1</td>
<td>10.9</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>332.8</td>
<td>328.9</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>3rd</td>
<td>334.4</td>
<td>331.9</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Figure 3.16. Electrochemical formation charge/discharge curves of Li/Graphite cells with Celgard membrane separator.
Figure 3.17. Electrochemical formation charge/discharge curves of Li/Graphite cells with Gen I membrane separator.

Figure 3.18. Electrochemical formation charge/discharge curves of Li/Graphite cells with Gen II membrane separator (5 wt.% CNC).
Figure 3.19. Electrochemical formation charge/discharge curves of Li/Graphite cells with Celgard, Gen I and Gen II (5. wt.% CNC) membrane separators in the 3rd formation cycle.

3.2.2.2. Rate

Rate capabilities of cells assembled with various separators are shown in Figure 3.20. At low rates of < 0.3 C, cells with Gen I membrane separator demonstrated superior rate capability to both Celgard and Gen II membrane separators. Even at 0.5 C, the Gen I membrane separator could deliver a specific capacity of ~338 mAh/g, which is almost same as that from Celgard separator (340 mAh/g). However, the capacity delivered by Gen I membrane dropped gradually to ~331 mAh/g at 1 C and ~319 mAh/g at 2 C, which are slightly lower than those from Celgard separator at the same rates. In the presence of CNC, the capacity delivered by Gen II membrane is almost identical to that from Celgard membrane separator at 0.1 C, but gradually decreases along the enhancement of rate and reaches to ~319 mAh/g at 2 C, which is same as that of Gen I membrane. This indicates that cellulose-based membrane separators have the comparable rate capability to the commercial separator in LIBs.
3.3. Effect of CNC concentration on the properties of cellulose membranes

In section 3.2, an approach involving the vacuum filtration process was successfully established to fabricate both Gen I membranes with only pure cellulose fibers and Gen II membranes with 95 wt.% cellulose fibers and 5 wt.% CNC. The Gen II membrane with a low amount of CNC demonstrates significantly improved mechanical strength and successfully inherits the advantages of the original cellulose membranes, such as high porosity, excellent electrolyte uptake, and promising electrochemical performance. Therefore, this vacuum filtration approach for cellulose-based membranes preparation was extended to fabricate Gen II membranes with higher CNC concentrations. The same methods for characterizing Gen I and Gen II with 5 wt.% CNC were used in this section to evaluate the Gen II membranes with high CNC concentrations.
3.3.1. Physical characterization

3.3.1.1. Tensile index

Figure 3.21 summarizes the force required on the cellulose-based membranes to reach a breaking point. As seen from the graph, the tensile index of the Gen II membrane increases essentially linearly along the enhancement of CNC amount in the membranes. With 10 wt.% CNC, the tensile index of the Gen II membrane is about 13 Nm/gram, which is almost 75% higher than that of Gen I membrane (~8 Nm/gram), ~20 Nm/gram at 20 wt.% CNC, and finally reaches to ~26 Nm/gram at 30% CNC, which is 225% higher than that of Gen I membrane. As previously noted, the enhanced mechanical strength in Gen II membrane is ascribed to the CNC particles filled in the pores of the cellulose fibers forming bonds with cellulose fibers and leading to a dense and robust structure. With more CNC integrated into the membrane, more bonds between cellulose fibers will be formed, leading to stronger mechanical stability.

Figure 3.21. Tensile index of cellulose membranes with various amount of CNC.
3.3.1.2. Thickness and porosity

The success of integrating the CNC in the slurry into the cellulose membrane could be confirmed from the thickness and porosity measurements, as shown in Table 3.5. With 10 wt.% CNC, the thickness of Gen II membrane is ~88 µm, and it increases slightly to 96 µm at 20 wt. % CNC. The thickness further increases to ~103 µm when CNC was increased to 30%. To the contrary, the porosity of Gen II membranes decreases gradually with increasing the CNC amount. The porosity of obtained Gen II membrane is about 73% with 10 wt. % CNC, about 72% with 20 wt.% CNC, and finally reaches to about 68% with 30 wt.% CNC, which is still much higher than that of commercial Celgard membrane (~37%). The reduced porosity of Gen II might be ascribed to the increased number of filled pores and/or smaller pores when more CNC is integrated into the cellulose membrane, which could be corroborated through microstructure observations in Figure 3.22.

Table 3.5. Calculated porosity of Gen II membranes with various amount of CNC

<table>
<thead>
<tr>
<th>Percentage of CNC in membrane</th>
<th>Average Thickness (µm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>88.0 ± 1.4</td>
<td>73 ± 3</td>
</tr>
<tr>
<td>20%</td>
<td>96.0 ± 2.3</td>
<td>72 ± 3</td>
</tr>
<tr>
<td>30%</td>
<td>103.0 ± 1.8</td>
<td>69 ± 3</td>
</tr>
</tbody>
</table>

3.3.1.3. Microstructure

Observations from the scanning electron microscopy (SEM) show that similar Gen II membrane with 5 wt.% CNC, a very thin layer of film could also be observed at the top surface of Gen II membrane with 10 wt. % CNC (Fig. 3.22 a), besides the fiber and porous feature. The thickness of this film increases when the amount of CNC increases (Fig. 3.22 d and g). When the
membrane possesses 30 wt.% CNC, it seems that fibers are buried in this film (Fig. 3.22 g). As discussed previously, this thin film comes from the CNC integrated into the cellulose membranes. It is more obvious to observe the thickness increase of this CNC film from the bottom (Fig. 3.22 c, f and i). In conjunction with the observations made in section 3.2.1.3, a similar densified thin film, rather than a porous structure, is found at the bottom surface of the membrane, and the fiber feature could be found under this thin film when 10 wt.% was introduced into the slurry for membrane fabrication (Figure 3.22 c). With increasing the amount of CNC, the thickness of this film increases (Fig. 3.22 f), and only a dense film without any fiber-like feature could found at the bottom side of the membrane with 30 wt.% CNC (Fig. 3.22 i). This further confirms that the introduction of CNC could not change the formation of an asymmetrical porous architecture in cellulose-based membranes obtained through the vacuum filtration process, even with high amount of CNC. Furthermore, the introduction of CNC facilitates the fusion of adjunct fibers and reduction of pore size. This is consistent with the results obtained from thickness and porosity measurements.
Figure 3.22. SEM images of Gen II membranes with 10 wt.% (a, b and c), 20 wt.% (d, e and f) and 30 wt.% (g, h and i) from top surface (a, d and e), cross-section (b, e and h) and bottom (c, h and i) surface.

3.3.1.4. Electrolyte retention & uptake

Figure 3.23. shows the electrolyte retention behavior of Gen II membranes with high amount of CNC, which, similar to those with 5 wt.% CNC, could also be divided into two stages.
During initial 60 minutes the weight of electrolyte held in Gen II membrane with 10 wt. % CNC dropped quickly to about 72% and decreased gradually to 42% after 240 minutes. Similar trend was observed on Gen II membrane with 20 wt. % CNC. However, the electrolyte retention of Gen II membrane with 30 wt. % CNC fell dramatically to ~ 60%, and gradually dropped to 37% after completion of 240 minutes.

![Graph](image_url)

**Figure 3.23. Electrolyte retention of Gen II membranes with various amount of CNC.**

Electrolyte uptake capability calculated on basis of weight differential before and after the exposure of membranes to the electrolyte is demonstrated in Table 3.6. It shows that the electrolyte uptake capability decreases when the amount of CNC in Gen II membranes increases. With 10 wt. % CNC, the electrolyte uptake capability of Gen II membrane is ~193%, decreases to ~159% at 20 wt. % CNC and finally reaches to 134% at 30 wt. % CNC.
Table 3.6. Electrolyte uptake capability of Gen II membranes with various amount of CNC

<table>
<thead>
<tr>
<th>Percentage of CNC in Gen II membranes</th>
<th>Uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>193</td>
</tr>
<tr>
<td>20%</td>
<td>159</td>
</tr>
<tr>
<td>30%</td>
<td>134</td>
</tr>
</tbody>
</table>

The reduced electrolyte uptake in Gen II membranes with high CNC amount could be further confirmed through the observation on the longitudinal travel of the electrolyte on membrane strips. Figure 3.24 shows, after a span of 20 minutes, Gen II membranes with 10 wt. % CNC have the highest electrolyte uptake, Gen II membrane with 20 wt. % CNC shows a lower value and 30 wt. % CNC has the lowest value, which is still much higher than that of Celgard membrane. This uptake capability of Gen II membranes indicates their excellent ability to absorb large amount of electrolyte, which is a beneficial factor to be used as separators in LIBs with high rate capability. The reduction of the electrolyte uptake capability might be ascribed to the low porosity of Gen II membranes with high CNC, especially when the amount of CNC is above 30 wt. %.
Figure 3.24. Photographs of Gen II membrane strips with 10 wt.% (a, b), 20 wt.% (c, d) and 30 wt.% (e, f) CNC before (a, c and e) and after (b, d, f) the exposure to the electrolyte solution for 20 min.
3.3.1.5. Thermal stability

Figure 3.25 demonstrates the excellent thermal stability of cellulose-based membranes with Celgard membrane as a baseline sample. After the exposure to a high temperature of 160 °C for 30 minutes, all cellulose-based membranes showed no visible shrinkage or dimensional instability, while commercial Celgard separator was totally deformed at the end of 30 minutes. Though deformity of Celgard membrane at 160°C could lead to inherent battery shutting down, in case of overheating, it also possesses the risk of electrodes coming in contact with each other, leading to an internal short circuit. Especially when LIBs have to be operated under some extreme conditions, such as high temperature, the high thermal stability offers cellulose-based membrane separators great viability for these practical applications. Thus, it can be argued that thermally stable cellulose membranes do prove as better alternatives for high temperature battery applications.
3.3.2. Electrochemical characterizations

3.3.2.1. Formation

Voltage profiles of cells with various Gen II membrane separators during initial three formation cycles are shown in Figures 3.26 to 3.30. All cells demonstrate almost identical curves with three plateaus below 0.2 V (vs. Li/Li+) during the initial formation cycles, characteristics of graphite anodes in LIBs. Additionally, the ICL in the initial cycles for all cells is in small range of 11 - 13 % (Table 3.4). These observations imply that increasing the amount of CNC does not reduce the compatibility of Gen II membranes to the electrode materials and electrolyte in LIBs. However, the same specific capacity of around 333-334 mAh/g could be delivered at the end of
the third cycle by all cells with CNC is < 30 wt.%, while a lower capacity of ~292 mAh/g was observed for cells with 30 wt.% CNC (Fig. 3.30, and Table 3.7). The lower capacity might be ascribed to the higher resistance of cells originating from the smaller pore size of Gen II membrane with 30 wt.% CNC. This could be verified from the higher overpotential of cell with 30 wt.% CNC, compared with other cells with <30 wt.% CNC (Fig. 3.31).
Table 3.7. Irreversible capacity loss (ICL) for cells prepared with various separator membranes

<table>
<thead>
<tr>
<th>Percentage of CNC in Gen II membranes (%)</th>
<th>Cycle</th>
<th>Discharge (mAh/g)</th>
<th>Charge (mAh/g)</th>
<th>ICL (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1st</td>
<td>336.6</td>
<td>300.1</td>
<td>10.9</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>332.8</td>
<td>328.9</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>3rd</td>
<td>334.4</td>
<td>331.9</td>
<td>0.8</td>
</tr>
<tr>
<td>10</td>
<td>1st</td>
<td>307.1</td>
<td>267.4</td>
<td>12.9</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>325.4</td>
<td>320.7</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>3rd</td>
<td>333.5</td>
<td>330.7</td>
<td>0.8</td>
</tr>
<tr>
<td>20</td>
<td>1st</td>
<td>362.8</td>
<td>322.7</td>
<td>11.1</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>321.3</td>
<td>314.8</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>3rd</td>
<td>333.3</td>
<td>330.1</td>
<td>1.0</td>
</tr>
<tr>
<td>30</td>
<td>1st</td>
<td>419.0</td>
<td>369.2</td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>258.3</td>
<td>248.5</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>3rd</td>
<td>292.0</td>
<td>285.1</td>
<td>2.3</td>
</tr>
</tbody>
</table>
Figure 3.26. Electrochemical formation charge/discharge curves of Li/Graphite cell with Gen II membrane separator with 5 wt. % CNC.

Figure 3.27. Electrochemical formation charge/discharge curves of Li/Graphite cells with Gen II membrane separator with 10 wt. % CNC.
Figure 3.28. Electrochemical formation charge/discharge curves of Li/Graphite cells with Gen II membrane separator with 20 wt. % CNC.

Figure 3.29. Electrochemical formation charge/discharge curves of Li/Graphite cells with Gen II membrane separator with 30 wt. % CNC.
Electrochemical formation charge/discharge curves at 3rd cycle of Li/Graphite cells with Gen II membrane separators with various amount of CNC.

3.3.2.2. Rate

Rate capabilities of cells with Gen II membrane separators are shown in Figure 3.32. Regardless of the amount of CNC in Gen II membranes, the capacity retention decreases gradually with increasing the current density applied to the cells. The Gen II membrane separator with 10 wt. % CNC demonstrates an almost identical rate capability to the membrane with 5 wt. % CNC at all rates. However, the rate capability decreases slightly with further increasing the amount of CNC. At 0.1 C, the capacity delivered by Gen II membrane separator 10 wt.% CNC is ~343 mAh/g, and it drops to ~328 mAh/g when the amount of CNC in Gen II membrane was increased to 20 wt.%. However, Gen II membrane with 20 wt.% CNC possesses the higher capacity retention than that of membrane with 10 wt.% CNC. At 1C, the capacity delivered by Gen II membrane with 20 wt.% is ~ 318 mAh/g, which is close to that of Gen II with 10 wt.% CNC (~327 mAh/g). At 2 C, Gen II with 20 wt.% CNC shows the capacity of 308 mAh/g, while 311 mAh/g for Gen II
with 10 wt.% CNC. Therefore, increasing the amount of CNC in Gen II membrane could render cells higher capacity retention, although accompanied with some reduction of specific capacity.

Figure 3.31. Rate performance curves of Li/Graphite cells with Gen II membrane separators with 10% and 20% CNC and Celgard separator.
CHAPTER 4
CONCLUSIONS

This thesis offers significant conclusive results and analyses for the requirements necessary to fabricate economic, stable and sustainable cellulose-based membranes for separators of lithium-ion batteries (LIBs) with high performance. The first part of this thesis is focusing on exploring various methodologies for the preparation of cellulose-based membranes, while simultaneously reinforcing them with cellulose nanocrystals (CNCs). The high hydrophilicity of cellulose surface should be noted as the key factor in the manufacturing process, which has a great impact on the physical attributes of finally obtained membranes, such as pore structure, mechanical strength, moisture content, chemical processability, etc. The cellulose-based membranes achieved from various methods were characterized in terms of the physical and electrochemical properties, and the vacuum filtration process was evaluated to be the most suitable technique to fabricate CNC reinforced cellulose membranes with CNC well distributed among cellulose fibers in this thesis. In addition, to address the issue of low pore size, the traditional vacuum filtration process for membrane preparation was modified by using a combination of different solvents and inculcating post-fabrication solvent exchanges. The ratio of IPA to DI water on the properties of the final dried cellulose membranes was studied and the favorable condition was identified to fabricate the CNC reinforced membranes. Compared with the commercial separator used in LIBs, the cellulose-based membranes demonstrated significantly improved porosity of >70%, electrolyte uptake and retention, and comparable electrochemical performance. Observations from electronic microscopy show that membranes fabricated this vacuum filtration process possess an asymmetrical porous structure with rougher surface and large pores on top side, while smoother surface and small pores
on bottom side, of obtained membranes. The introduction of a small amount of CNC (5 wt.%) could effectively increase the mechanical strength of cellulose membranes, and all aforementioned advantages of the original cellulose membrane were inherited in the CNC reinforced membranes.

The second part of this thesis is focusing upon the investigations on the effect of cellulose nanocrystal, specifically, the ratio of cellulose nanocrystals to fibers, on the properties of CNC reinforced cellulose membranes, which were fabricated by using the modified vacuum filtration approach established in the first part of this thesis. The results from the mechanical strength measurement demonstrated that the tensile index of CNC reinforced membranes increases almost linearly with escalating the CNC amount. The tensile index of the cellulose membrane without CNC is about 8 Nm/gram, increases gradually with increasing the amount of CNC, is ~12 Nm/gram at 5 wt.% CNC and reaches to ~26 Nm/gram at 30 wt.% CNC. The porosity of the cellulose membrane decreases slightly as the amount of CNC is increased, however, even at 30 wt.% CNC, the porosity of reinforced membrane is as high as ~68%, which is slightly lower than twice of commercial separator. The same trend as effect of CNC on the porosity was observed on other properties, such as electrolyte retention and uptake, microstructure, and thermal stability, of CNC reinforced cellulose membranes. Results from the electrochemical characterizations show that, when the amount of CNC is less than 20 wt.%, all cells with CNC reinforced membrane separators exhibited almost identical specific capacity and rate capability, while lower capacity and higher capacity retention were observed on cells with 20 wt.% CNC reinforced membrane separator.
CHAPTER 5
FUTURE WORK

A viable approach has been established to fabricate cellulose-based membranes in the presence of cellulose nanocrystal, and the achieved membranes showed the promise to substituting the conventional polyolefin separators used in lithium-ion batteries. To further improve the properties of cellulose-based membranes for practical applications in lithium-ion batteries, studies including fundamental investigations and applications will be conducted in the future.

Fundamental studies on the affinity of CNC to the cellulose fibers will be carried out in the initial stages i.e. slurry preparation. As seen in this study, cellulose nanocrystals could bond with cellulose fibers after the effective removal of solvents during filtration and solvent exchange processes. But the separation of a portion of CNC from cellulose fibers happened, leading to condensed film formed on the bottom side of Gen II membranes. Obviously, fundamental studies on the affinity of CNC to cellulose fibers will provide in-depth understanding the formation mechanism of porous structure in the CNC reinforced cellulose membranes. Based on this understanding, various methods will be developed to fabricate cellulose membranes with desirable mechanical strength and porosity for LIB applications.

Optimization of current approaches to fabricate CNC reinforced membranes with uniform porous structure across the membrane will be carried out to further improve the distribution of CNC and porous structure of the cellulose membranes. Several approaches are under consideration for this optimization. Firstly, modifying the surface chemistry of cellulose fiber or CNCs enables effective bonding between the two cellulose variants. Secondly, changing the source of cellulose fibers to ensure they disperse more efficiently in solvents and bind with CNCs. The effective
dispersion of cellulose fibers in slurries proved a challenge in this thesis, with various combinations of polar solvents being utilized to avoid agglomeration of fibers. The use of fibers from other sources, pretreating fibers to reduce their length could prove beneficial and serve as an alternative to overcome this challenge. Similarly, additional processes were undertaken in this thesis to maintain uniformity of membranes. In addition, various methods will be employed to prepare slurries with well-dispersed cellulose fibers and CNC, given that effective dispersion could help in obtaining highly uniform films. Based on these understandings the problem with smaller or diminishing pore sizes might be addressed by use of additives during the fabrication process, but also ensuring its effective removal once bigger pore sizes are induced on both sides of membranes. In addition, approaches to prepare CNC reinforced cellulose membranes with controllable porous structure will be investigated.
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