Processing and characterisation of water hyacinth cellulose nanofibres-based aluminium-ion battery separators

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Abstract — Water hyacinth is an invasive plant that can be converted to high value cellulose nanofibers. This study presents battery separators prepared from water hyacinth cellulose nanofibres (WHCNF) via a freeze-thawing crosslinking method, using polyethylene glycol as a binder. The separators consist of 95 wt.%, 90 wt.%, 85 wt.% and 80 wt. % WHCNF. The thickness, wettability, electrolyte uptake, porosity and thermal stability of the separators are studied and compared with Celgard 2325, a commercial tri-layer separator. Also, tensile tests are carried out and an aluminium-ion cell is made to compare the performance of the different WHCNF separators using Nyquist plots and battery discharge curves. The results show that WHCNF separators have high thermal stability and wettability, making it a promising sustainable alternative material to petroleum-based polymeric commercial separators.

Keywords- battery; separators; cellulose nanofibres; water hyacinth; nanofibres membrane; aluminium-ion battery

I. INTRODUCTION

Cellulose is an organic polymer (C_{6}H_{10}O_{5})n found in wood, plants, bacteria and algae. Water hyacinth is a rapid growing weed on the surface of water in tropical regions [1]. Nano-cellulose is cellulose with one dimension in the nanometre range, with interesting characteristic including high specific surface area, mechanical strength, barrier properties and orientation ability [2]. Battery research has risen exponentially primarily driven by automotive, electric aircraft, renewable energy generation and wearable and portable electronic devices [2]. Key components inside a secondary battery are; current collectors, negative and positive electrode material, electrolyte and a separator [3]. A separator, which is a permeable membrane placed between a battery’s anode and cathode, is used to mechanically separate the electrodes while being permeable to the electrolyte, thereby maintaining the ionic conductivity. Hence battery energy, power-density, cycle-life and safety are strongly dependent on the separator [2].

Cellulose nanofibres (CNF) which a material composed of nanosized cellulose fibrils with a high aspect ratio and its composite have been investigated as an alternative to predominantly petroleum-based polymeric separators. Kuribayashi [4] uses CNF to reduce the possibility of separator meltdown, and show that Laboratory-scale cells that comprise LiCoO2/petroleum coke electrodes, 1.0 M LiBF4/PC:EC:BL (25:25:50 by volume, propylene carbonate: ethylene carbonate: γ-butyrolactone) electrolyte and the cellulosic separators exhibit acceptable initial discharge capacity and capacity retention over 41 charge/discharge cycles. Chun et al [5] fabricate a cellulose nanofiber paper from a CNF suspension and their separator manufactured with IPA–water = 95/5 (vol/vol%) exhibits CNF/IPA–water’s highly interconnected nano porous network channels. Kim et al [6] present an architectural strategy based on colloidal silica (SiO2) nanoparticle-assisted structural control in addressing the difficulty in forming controllable porous structure of pure cellulose nanofiber paper separators and their S-CNP separator shows high ionic conduction of CNF/silica nano particles. Kim et al [7] present heterolayered nanomat-based hierarchical/ asymmetric porous membrane which uses functionalised cellulose nanofibril to improve high-temperature cycling performance of the cell. Liu et al [8] propose an eco-friendly and relatively low-cost polyvinyl alcohol/CNF composite separator that could serve as a low cost and eco-friendly separator alternative. Liu et al [9] present polyformaldehyde/cellulose nanofibres blend separators which exhibit improved stable cycling and rate performance when compared with polyethylene separators. One of the features of their polyformaldehyde/cellulose blend separators is that the separators are thermally stable at high temperature as 180 °C. An ultra-light CNF separator created by Sheng et al shows an improved electrochemical performance compared to a commercial separator [10] and a hybrid CNF/Zeolitic imidazolate framework membrane illustrates an improved discharge retention stability when compared to the commercial polymer membrane [11].

Aluminium-ion (Al-ion) batteries are multivalent secondary batteries that are currently in the research stage.

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The main benefits of an Al-ion battery are; low cost as aluminium is one of the most abundant metals in the world with low flammability and a high volumetric capacity which is four times greater than lithium, and fast charging [12]. The main components of Al-ion cell are; aluminium as the negative electrode, carbon and its derivatives as a positive electrode, electrolytes with aluminium ions and a separator.

This research demonstrates the viability of using water hyacinth cellulose nanofibres (WHCNF) as an alternative cellulose separator for an Al-ion battery. WHCNF separators are prepared using a simple process utilising a freeze-thawing method and drying in the fume cupboard. Inexpensive and non-toxic PEG 400 is used to bind the WHCNF together providing flexibility in the separator papers. Therefore, WHCNF/PEG400 separators are prepared by using sustainable, low cost approach and eco-friendly materials.

II. EXPERIMENTAL SET-UP

A. Preparation of water hyacinth cellulose nanofibres and battery separator composites

Cellulose is extracted from water hyacinth and converted to cellulose nanofibres suspension using the method previously described by Sun et al [1]. Polyethylene glycol (PEG 400) is used as a binder for the separator composites due to its biodegradability, stability and ease of use with WHCNF. To prepare the separator film of 95 wt.% WHCNF and 5 wt.% PEG 400 with a dry mass of 0.25 gram (g) and a diameter of 10 cm; 0.2375 g WHCNF (dry mass) added with 0.0125 g of PEG 400; the beaker contained 0.55% WHCNF. Add 10 g of deionized water into PEG 400 in order to liquefy the solution, hence it is easier to mix. Mechanical mixing is achieved by T25 digital ULTRA TURRAX for 5 minutes at 7500 rpm and the mixed solution is poured in a petri dish. The crosslinking is achieved through freeze-thawing process, by freezing at -20 °C for 24 hours and thawing at room temperature for 24 hours, finally, the samples are put in the fume cupboard for drying. The steps are repeated for each wt.% of WHCNF. Figure 1 shows the process of preparing the WHCNF/PEG 400 film adopted in this paper.

![Figure 1. Schematic diagram of WHCNF/PEG 400 separators films.](image)

B. Separator characterisation

The thickness of the WHCNF/PEG 400 separators is measured using Scanning Electron Microscopy (SEM, S-4800, Hitachi Company) with acceleration voltage of 3 kV. High wettability is required for the separator to be able to transport ions more efficiently, the wettability test is conducted at room temperature (25 °C) by measuring the contact angle of a drop of liquid using AutoCAD inventor. The contact angle of greater than 90° means hydrophobic and less than 90° means hydrophilic. The electrolyte uptake (EU) is measured using equation (1) at room temperature by soaking the separator for 4 hours in a 1 mole of KOH [9, 13].

\[ EU\ [%] = \frac{W_1-W_0}{W_0} \times 100 \]  

(1)

where, \( W_0 \) = mass of the separator before soaking and \( W_1 \) = mass of the separator after soaking. The porosity of the separator is obtained using equation (2) at room temperature by soaking the separator for 4 hours in a mineral oil [14, 9].

\[ \text{Porosity} \ [%] = \frac{M_{wb}-M_d}{P_b \times V} \times 100 \]  

(2)

where, \( M_w \) = mass of wet separator, \( M_d \) = mass of dry separator, \( P_b \) = density of the mineral oil and \( V \) = volume of the dry separator. The WHCNF/PEG 400 separators are cut to 10mm x 80 mm strips, tensile machine (Lloyd LS 5) is used to measure the tensile strength to produce the stress and strain curves at room temperature. The thermal stability of the separators is evaluated for two hours by setting the temperature of the chamber (Binder drying oven) at 50 to 150 °C for the separator strips (10mm x 20mm).

The materials required to make the Al-ion cell are all sourced from Fisher scientific. Aluminium with the thickness of 0.1 mm and purity of 99.997% is employed as a negative electrode, the aqueous electrolyte is created by mixing deionised water with aluminium chloride hexahydrate (Acros Organics, 99%) at the weight ratio of 5:1, graphite powder (Alfa Aesar, 99.95%) with acetylene black (Alfa Aesar, 99.9%) and polyvinylidene fluoride (dissolved in ethanol) with a weight ratio of 8:1:1 is used to create ink and dripped on the carbon paper (Toray Carbon Paper, TGP-H-60) to create the positive electrode. The cell case is made from Poly(methyl methacrylate) (PMMA). The performance of the 95 wt.%, 90 wt.%, 85 wt.% and 80 wt.% WHCNF separators in Al-ion cell are tested using an Ametek Modulab electrochemical system.

III. RESULTS AND DISCUSSION

The WHCNF/PEG 400 separators are prepared as shown in Figure 1. Separators are named 95 wt.% WHCNF for 95 wt.% WHCNF and 5% PEG 400; 90 wt.% WHCNF for 90 wt.% WHCNF and 10 wt.% PEG 400 and so on. Figure 2 shows the morphology of the WHCNF composites. As can be seen in Figure 2 a) the 95 wt.% WHCNF shows many more water hyacinth fibres
The thickness of the WHCNF separators increases with higher ratio of PEG 400, all the WHCNF separators are more hydrophilic than the Celgard showing higher ions transport efficiency of WHCNF. High porosity helps to increase the electrolyte uptake hence, increasing the ionic conductivity and reducing the interfacial resistance [15], as illustrated in Table I. It can be seen that the porosity and EU increases when the WHCNF ratio increases.

Figure 2. Shows the SEM images of a) 95 wt.% WHCNF b) 90 wt.% WHCNF c) 85 wt.% WHCNF d) 80 wt.% WHCNF at x15k magnification.

A. Wettability and electrolyte uptake

Contact angles are used to measure the wettability of the separators [9]. The Celgard separator exhibits a contact angle of 83.29° as shown in Figure 3 a), while the WHCNF-based separators show higher wettability with higher amount of WHCNF indicating the hydrophilic nature of the WHCNF material. This is in sharp contrast to low wettability of Celgard tri-layer separator containing polypropylene-polyethylene-polypropylene. The EU has a direct relationship with porosity independent of the material, as illustrated in Table I. The highest porosity (36.1 %) separator is 95 wt.% WHCNF with the highest EU (1184 %) and Celgard with the second highest porosity (32 %) and with second highest EU (1129 %). Therefore, it can be seen that increasing the amount of PEG in the composites leads to a reduced wettability, EU and porosity.

B. Thermal stability

The thermal effect on a separator can trigger a reaction as the temperature rises which can cause a short circuit in the battery resulting in thermal runaway [9]. Table II illustrates the Celgard reacting as the temperature increases while the integrity of the WHCNF, although showing some thermal changes, is kept to a minimum as the temperature increases to 150 °C.

<table>
<thead>
<tr>
<th>Separators</th>
<th>Characteristics</th>
<th>50 °C</th>
<th>100 °C</th>
<th>150 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Celgard 2325</td>
<td>Thickness (µm)</td>
<td>Wettability (°)</td>
<td>EU (%)</td>
<td>Porosity (%)</td>
</tr>
<tr>
<td>Celgard 2325</td>
<td>25</td>
<td>83.29</td>
<td>1129</td>
<td>32</td>
</tr>
<tr>
<td>95 wt.% WHCNF</td>
<td>25.4</td>
<td>51.84</td>
<td>1184</td>
<td>36.1</td>
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<td>90 wt.% WHCNF</td>
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<td>63.38</td>
<td>905</td>
<td>27</td>
</tr>
<tr>
<td>85 wt.% WHCNF</td>
<td>32.4</td>
<td>68.51</td>
<td>835</td>
<td>19</td>
</tr>
<tr>
<td>80 wt.% WHCNF</td>
<td>36.6</td>
<td>83.02</td>
<td>758</td>
<td>17.65</td>
</tr>
</tbody>
</table>

Figure 3. Wettability measurement of separators: a) Celgard with 83.29° of contact angle, b) 95 wt.% WHCNF-51.84°, c) 90 wt.% WHCNF-63.38°, d) 85 wt.% WHCNF-68.51° and e) 80 wt.% WHCNF-83.02°.
C. Mechanical and electrochemical testing

High mechanical strength is important for separators to withstand high voltages during battery operation, a typical lithium-ion battery with high voltages of between 3.5 to 5 volts require a 25μm thick separator with a minimum of 98 MPa [2]. Figure 4 a) shows the photograph of 80 wt.% WHCNF separator. A typical stress and strain graph is presented in Figure. 4 b) of the WHCNF separators, where 95 wt.% WHCNF shows the highest tensile strength of around 34 MPa, an Al-ion battery has lower voltages ~1.2-1.8 volts which will require a lower tensile strength. Figure. 4 b) also shows that the more ratio of WHCNF used in a separator film increases its tensile strength.

![Figure 4. a) Photograph of WHCNF separator. b) A stress and strain graph of the WHCNF separators.](image)

A 9.5 mm radius Al-ion button cell is made to test the WHCNF separators in a PMMA case shown in Figure. 5 a). The electrolyte used for the cell is a 5:1 weight ratio of deionised water to aluminium chloride hexahydrate. The WHCNF separators are soaked in the above electrolyte for two hours. The Nyquist plot (100 mV, 0.1 Hz to 10 kHz) in Figure. 5 b), where the Z’ decrease at the last data point indicating that after the frequency has peaked the range reduces corresponding to the interfacial resistance between the separator and electrodes, this is also known as charge transfer resistance (Rct) [9]. The magnitude of the Rct is; 95 wt.% WHCNF (146.2 Ω), 90 wt.% WHCNF (666.4 Ω), 85 wt.% WHCNF (1025.6 Ω), 80 wt.% WHCNF (2329.2 Ω). The result indicates 95 wt.% WHCNF separator with the best interfacial compatibility with the Al-ion cell. Figure. 5 c) shows the discharge curves at 0.15 mA of the Al-ion cell with WHCNF separators. It can be observed that the 95 wt.% WHCNF separator perform better than other separators maintaining the discharge duration to ~158 seconds.

![Figure 5. a) The PMMA case to test the WHCNF separators in an Al-ion button battery of the size of 9.5 mm radius, b) Nyquist plot of the Al-ion battery with WHCNF separators and c) the discharge curves of Al-ion cell with the WHCNF separators.](image)

IV. CONCLUSIONS AND FUTURE WORK

WHCNF separators are presented using a freeze-thawing method and drying in the fume cupboard. Full investigation including thickness, wettability, electrolyte uptake, porosity, thermal stability, mechanical strength and Al-ion cell performance are carried out. WHCNF separators exhibit high thermal stability as the temperature increases to 150°C thus increasing the safety of a cell. All the WHCNF separators have enhanced wettability showing the hydrophilic nature of the WHCNF with 95 wt.% WHCNF getting the highest wettability of 51.84° clearly indicating higher weight ratio of WHCNF in a separator increasing the separator wettability thus, transporting ions more efficiently. The early results are verified when the WHCNF separators are used in an Al-ion cell, 95 wt.% WHCNF showed the lowest charge transfer resistance of 146.2 Ω and maintained the highest discharge duration of ~158 seconds. The future work for the WHCNF separators will include increasing the porosity and strength of the composites utilising thermally induced phase separation process for increased microporous structure of the WHCNF separators, modelling and simulating the whole Al-ion cell and testing the cycle stability of the separator over the lifetime of the battery. The long-term goal for the project is to utilise machine learning methods to predict the performance of the cell when using new battery materials.

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