Proceedings of the 26th International Conference on Automation & Computing, University of Portsmouth, Portsmouth, UK, 2-4 September 2021

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

Mustehsan Beg, Dongyang Sun, Carmen-Mihaela Popescu, Keith M. Alcock, Amaka J. Onyianta, Dominic O'Rourke, Keng Goh and Hongnian Yu[1]

School of engineering and the built environment
Edinburgh Napier University
Edinburgh, UK
Email: mustehsan.beg@napier.ac.uk, h.yu@napier.ac.uk

***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 ($(C_6H_{10}O_5)_n$) 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 nanofibers 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 as 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.

[1] Correspondent Author: Hongnian Yu, h.yu@napier.ac.uk

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 ℃ 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.

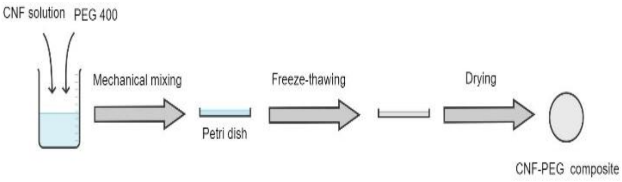

Figure 1. Schematic diagram of WHCNF/PEG 400 separators films.

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 ℃) 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].

$$\text{EU [\%]} = \frac{W1-W0}{W0} \text{ x } 100 \qquad (1)$$

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].

$$\text{Porosity [\%]} = \frac{Mw-Md}{Pb \; x \; V} \text{ x } 100 \qquad (2)$$

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 ℃ 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 compared to Figure 2 d) with 80 wt.% WHCNF. Table I shows the thickness, wettability, EU and porosity of separators. 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.

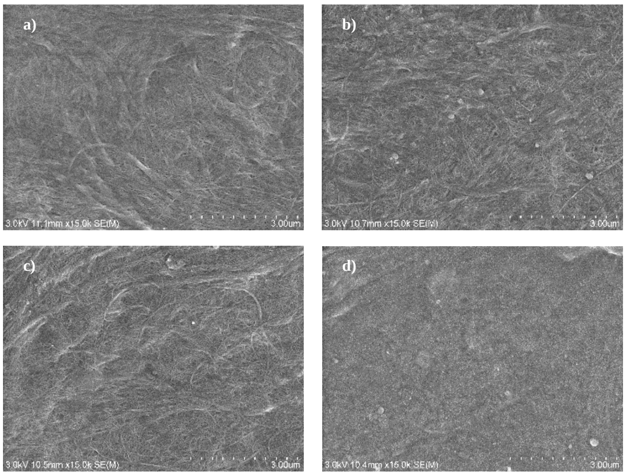

Figure 2. Shows the SEM images of a) 95 wt.% WHCNF b) 90 wt.% WHCNF c) 85 wt.% WHCNF d) 80 wt.% WHCNF at x15k magnification.

TABLE I. THICKNESS, WETTABILITY, EU AND POROSITY OF CELGARD AND WHCNF SEPARATORS.

Separators	**Characteristics**			
	Thickness (μm)	***Wettability (°)***	***EU (%)***	***Porosity (%)***
Celgard 2325	25	83.29	1129	32
95 wt.% WHCNF	25.4	51.84	1184	36.1
90 wt.% WHCNF	29.5	63.38	905	27
85 wt.% WHCNF	32.4	68.51	835	19
80 wt.% WHCNF	36.6	83.02	758	17.65

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.

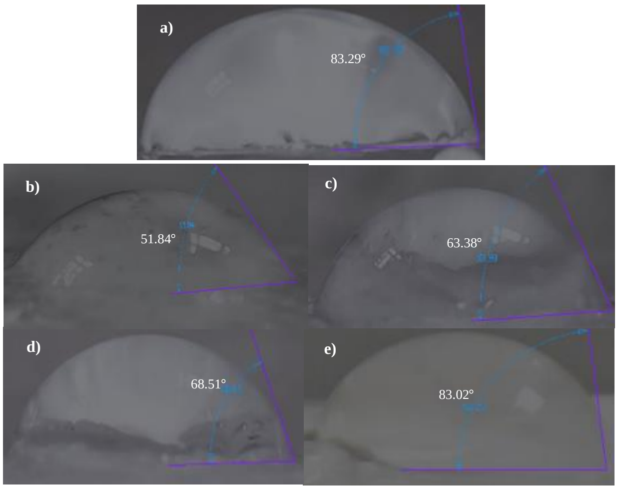

Figure 3. Wettability measurement of separators: a) Celgard with 83.29° of contact angle, b) 95 wt.% WHCNF-51.84°, c) 90 wt.% WHCNF-63.38°, d) 85 wt.% WHCNF-68.51° and e) 80 wt.% WHCNF-83.02°.

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 II. THERMAL STABILITY OF CELGARD AND WHCNF SEPARATORS AT 50 TO 150 °C.

Separators	**Thermal stability**		
	50 **°C**	***100*** **°C**	***150*** **°C**
Celgard 2325			
95 wt.% WHCNF			
90 wt.% WHCNF			
85 wt.% WHCNF			
80 wt.% WHCNF			

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 $25\mu m$ 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.

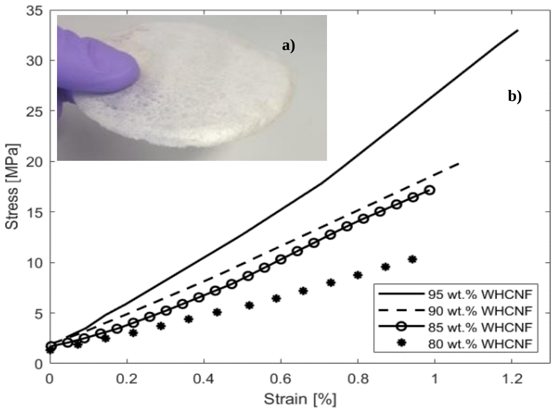

Figure 4. a) Photograph of WHCNF separator. b) A stress and strain graph of the WHCNF separators.

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 (R_{ct}) [9]. The magnitude of the R_{ct} 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.

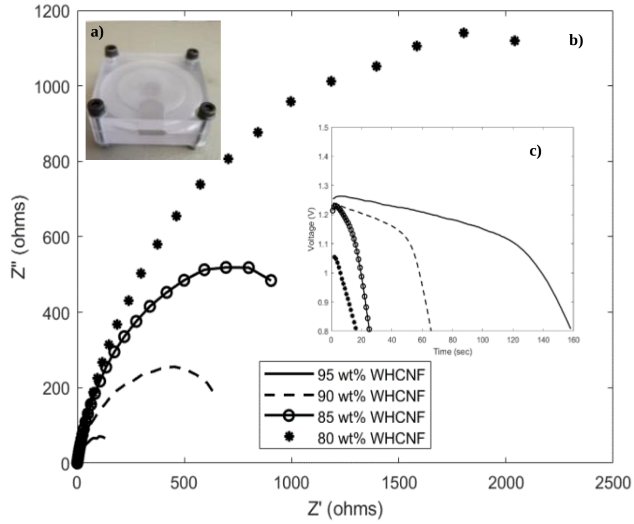

Figure 5. a) The PMMA case to test the WHCNF separators in an Al-ion button battery of the size of 9.5 mm radius, b) Nyquist plot of the Al-ion battery with WHCNF separators and c) the discharge curves of Al-ion cell with the WHCNF separators.

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 ℃ 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.

ACKNOWLEDGMENT

This work was supported by the SFC project, Investigation of a sustainable and environmental-friendly solution of battery manufacturing for electric-bicycles/scooters.

REFERENCES

[1] D. Sun, A. J. Onyianta, D. O'Rourke, G. Perrin, C.-M. Popescu, L. H. Saw, Z. Cai and M. Dorris, "A process for deriving high quality cellulose nanofibrils from water hyacinth invasive species," *Springer,* 2020.

[2] E. Lizundia, C. M. Costa, R. Alves and S. Lanceros-Méndez, "Cellulose and its derivatives for lithium ion battery separators: A review on the processing methods and properties," *ELSEVIRE: Carbohydrate Polymer Technologies and Applications,* 2020.

[3] K. W. Beard and T. B. Reddy, LINDEN'S HANDBOOK OF BATTERIES 5th edition, The McGraw-Hill Companies, Inc, 2019.

[4] Kuribayashi and Isao, "Characterization of composite cellulosic separators for rechargeable lithium-ion batteries," *Journal of Power Sources,* pp. 87-91, 1996.

[5] S.-J. Chun, E.-S. Choi, E.-H. Lee, J. H. Kim, S.-Y. Lee and S.-Y. Lee, "Eco-friendly cellulose nanofiber paper-derived separator membranes featuring tunable nanoporous network channels for lithium-ion batteries," *Journal of Materials Chemistry,* 2012.

[6] J.-H. Kim, J.-H. Kim, E.-S. Choi, H. K. Yu, J. H. Kim, Q. Wu, S.-J. Chun, S.-Y. Lee and S.-Y. Lee, "Colloidal silica nanoparticle-assisted structural control of cellulosenanofiber paper separators for lithium-ion batteries," *Journal of Power Sources,* 2013.

[7] J.-H. Kim, M. Gu, D. H. Lee, J.-H. Kim, Y.-S. Oh, S. H. Min, B.-S. Kim and S.-Y. Lee, "Functionalized Nanocellulose-Integrated Heterolayered Nanomats toward Smart Battery Separators," *American Chemical Society,* 2016.

[8] C. Liu, Z. Shao, J. Wang, C. Lu and Z. Wang, "Eco-friendly polyvinyl alcohol/cellulose nanofiber–Li+ composite separator for high-performance lithium-ion batteries," *RSC Advances,* 2016.

[9] J. Liu, K. Yang, Y. Mo, S. Wang, D. Han, M. Xiao and Y. Meng, "Highly safe lithium-ion batteries: High strength separator from polyformaldehyde/cellulose nanofibers blend," *Journal of Power Sources,* pp. 502-510, 2018.

[10] J. Sheng, T. Chen, R. Wang, Z. Zhang, F. Hua and R. Yang, "Ultra-light cellulose nanofibril membrane for lithium-ion batteries," *Journal of Membrane Science,* 2019.

[11] X. Sun, M. Li, S. Ren, T. Lei, S.-Y. Lee, S. Lee and Q. Wu, "Zeolitic imidazolate framework-cellulose nanofiber hybrid membrane as Li-Ion battery separator: Basic membrane property and battery," *Journal of Power Sources,* 2020.

[12] D. Yuan, J. Zhao, W. M. Jr, S. Kumar and M. Srinivasan, "Emerging rechargeable aqueous aluminum ion battery: Status, challenges,and outlooks," *Nano Materials Science,* 2019.

[13] D. Endah, R. Purwanto, Agus, Widiasa, I. Nyoman and S. Heru, "Ionic Conductivity and Cycling Stability Improvement of PVDF/Nano-Clay Using PVP as Polymer Electrolyte Membranes for LiFePO4 Batteries," *MDPI,* 2018.

[14] J.-J. Woo, Z. Zhang, N. L. D. Rago, W. Lu and K. Amine, "A high performance separator with improved thermal stability for Li-ion batteries," *Journal of Materials Chemistry A,* 2013.

[15] D. Luo, M. Chen, J. Xu, X. Yin, J. Wu, S. Chen, L. Wang and H. Wang, "Polyphenylene sulfide nonwoven-based composite separator with superior heat-resistance and flame retardancy for high power lithium ion battery," *Composites Science and Technology,* 2018.