



POLYVINYLIDENE FLUORIDE (PVDF) NANOFIBER MODIFIED CURRENT COLLECTOR IN ANODE-FREE LITHIUM BATTERY

Hendri Widiyandari ^{*1,2}, Adama Dina Panuntun¹, Hanaiyah Parasdila¹,
Iqbal Firdaus³, Agus Purwanto^{2,4}

¹ Department of Physics, Universitas Sebelas Maret, Jl. Ir. Sutami 36 A, Surakarta, Central Java 57126, Indonesia

² Centre of Excellence for Electrical Energy Storage Technology, Universitas Sebelas Maret, Jl. Slamet Riyadi 435, Surakarta, Central Java 57146, Indonesia.

³ Department of Physics, Universitas Lampung, Jln Prof. Dr. Soemantri Brodjonegoro No.1 Bandar Lampung 35145, Indonesia.

⁴ Department of Chemical Engineering, Universitas Sebelas Maret, Jl. Ir. Sutami 36 A, Surakarta, Central Java 57126, Indonesia

*hendriwidiyandari@staff.uns.ac.id

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ABSTRACT

The anode-free lithium-ion battery (AFLB) is one of the new model possibilities that gives significant energy density at the same battery size. However, AFLB has some drawbacks, such as low coulombic efficiency caused by uncontrolled dendritic growth. Therefore, PVDF nanofiber electrospun was used to coat the Cu current collector in an anode-free lithium-ion battery (AFLB) to prevent dendrite growth and improve battery performance. This study investigated two electrospinning process parameters: polymer molecular weight and electrospinning time. The PVDF nanofiber from polymer with Mw of 1.300.000 and 9 h spinning had the most considerable porosity and highest elongation of 47.031% and 39.7%, respectively. However, PVDF nanofiber from polymer with Mw of 534.000 and spinning time of 9 h had the highest tensile strength of 2.33 MPa. According to the results of the AFLB battery tests, the Cu-collector modification with PVDF nanofiber was able to increase the specific capacity of the battery by 10%, with a coulombic efficiency value in the first cycle that was nearly the same, around 86%.

Keywords: Anode-free; LIB; Nanofiber; Electrospinning; PVDF

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INTRODUCTION

Energy is one of the main needs in carrying out regular tasks. Portable gadgets can store and capitalize on energy, making it easier for them to support regular activities. One of the main approaches for storing energy, particularly electrical energy, is the application of batteries. The most promising type of battery is the Lithium-ion (Li-ion) battery, which is commonly used in portable devices like mobile phones, laptops, medical equipment, carpentry equipment, and other electronic devices. Lithium-ion batteries (LIB) are now being developed as an alternative energy source that supports cutting-edge technology for electric

vehicles (electric bikes, motorcycles, cars, and drones), as well as a large-scale energy storage system that offers significant power and energy ^[1-2].

High energy density, high capacity, outstanding thermal stability, exceptional power performance, high energy efficiency, and a lengthy battery life cycle are several advantages of lithium-ion batteries. The typical Li-ion battery configuration consists of the following elements: Cu and Al serve as current collectors, C₆ (graphite) serves as the anode material, separator, and LiXO (LCO, LMO, NCA, and LFP) serves as the cathode material^[3]. Graphite is a particularly popular anode material in the li-ion battery manufacturing sector. Graphite was chosen because it provides excellent safety amount, even though storage capacity is not sufficiently large ^[4-5]. Graphite use started to be replaced by other materials. One option for replacing graphite is lithium metal. A substantially larger capacity of 3860 mAh/gr is possible using lithium metal.

In comparison to other anode materials, this value is the greatest. However, because li metal is very reactive, using it as an anode carries a significant risk, particularly in terms of safety ^[6-8]. However, using ultra-thin Li metal (thickness 50 m, 20 m, or thinner) produces positive results, has excellent safety standards, and has a larger energy density^[9]. Additionally, silicon (Si), silicon dioxide (SiO₂), and zinc oxide (ZnO) can all be used as substitutes for graphite ^[10].

The anode-free lithium battery (aflb) is another type of lithium battery in which the cu electrode is not coated with either graphite or li metal as an anode material. Cu/pp/lixo/al contribute to the aflb's structural components. By completely removing the anode material, the battery cells' overall weight is decreased, and their surface area is increased. Although the thickness will increase during the charging process due to the li-plating of cu-foil as a current collector, the energy density of anode-free libs can be higher than that of batteries in general ^[11].

Aflb has a low cycle stability during development. The phenomena of lithium dendrite growth is responsible for this, and it comes from an improper distribution of lithium ions. Lithium dendrit reduces the battery's coulombic efficiency and leads to separator destruction, which shortcircuits the battery by causing the separator to come crashing down ^[12]. Therefore, the objective of this research is to prevent the growth of dendrites using pvdf coating on cu current collectors to improve electrochemical performance in terms of capacity and cycle stability.

METHOD

Polyvinylidene fluoride (Mw 534.000 from Aldrich and Mw 1300.000 from Solvay) was used as the major component for nanofiber. Dimethylformamide (DMF) emsure and acetone (Mallinckrodt Chemicals) were used as a solvent.

The PVDF polymer solution was prepared by dissolving the pvdf powder into the solvents (a mixture of acetone and DMF with a volume ratio of 14:6). The PVDF solution was adjusted at 15% by weight ratio to the weight of the solvent. The solution was stirred for hours at room temperature.

The nanofiber was produced by electrospinning the PVDF solution on the Cu foil in different spinning times of 5, 7, and 9 hours. The conveyor speed was adjusted at 37 rpm, the voltage used was 15 kv, and the flow rate was 1.8 ml/hour. The distance between the syringe's tip and the conveyor was 10 cm. In an oven set to 80° c for 6 hours, the Nanofiber

was synthesized using the electrospinning method. With this method, the residual air vapor of nanofiber membranes' synthesis will be dried and wiped out.

The dried PVDF Nanofiber nanofiber membrane was cut into 3x3 cm parts and examined with SEM-EDX (Scanning Electron Microscopy Energy Dispersive X-Ray) to determine its morphology and composition, FTIR (Fourier-Transform Infrared Spectroscopy) to identify the functional groups on nanofiber membranes, and TG-DTA (Thermal Gravimetry-Differential Thermal Analysis) to identify mass changes and internal temperature changes.

By taking a sample with a size of 3x3 cm, measuring its mass using a digital scale, and soaking it in n-butanol for two hours, porosity testing was performed to see how effectively the PVDF Nanofiber maintained an electrolyte liquid that allowed ions to travel between the electrodes. To determine the mass difference between the sample's mass before and after immersion, the sample was immersed, dried for two hours, and then weighed.

The purpose of the shrinkage test is to determine how effectively the PVDF Nanofiber endures high temperatures. A sample was heated in an oven at 150°C for 30 minutes after being divided into 2 cm-diameter pieces. After reducing the sample to the standard size specified by ASTM D638-02A, the sample is placed under a tensile force until it is torn at the point where the strength value is determined. Additionally, the sample's difference in area is measured again after and before testing. Mechanical testing is then carried out to determine the PVDF Nanofiber's elasticity.

The synthesized PVDF Nanofiber and the Cu electrodes, which have been coated on the surface of Cu foil, are assembled into a full-cell cylinder-type 18650 battery during the battery assembly step. In order to remove any excess water from the battery, the produced battery cylinder is filled with LIPF₆ electrolyte in the glovebox and then locked in a hydraulic crimping machine. The performance of anode-free lithium ion batteries was then tested utilizing a battery analyzer device to ascertain their charge-discharge capacity, coulombic efficiency (CE), AND the durability of AFLB. The performances of AFLB were tested using tests that lasted 10 cycles at a current of C/20 of the battery's theoretical capacity.

RESULTS AND DISCUSSION

Figures 1 and 2 show the morphology of the PVDF nanofiber with different Mw 534.000 (Figure 1 a-d) and PVDF Mw 1.300.000 (Figure 2 a-d) in variations of spinning time of 5, 7, and 9 hours. The electrospinning process produces a nanofiber membrane with spots or beads because the flow rate is not constant, which causes the flow to freeze to form a gel when in contact with air and is pushed by the electrospinning flow, resulting in non-uniformity of nanofiber size. PVDF nanofiber with Mw 1.300.000 tends to have more beads than Mw 534.000. Table 1 shows the average fiber size; it is found that the molecular weight affected the fiber size.

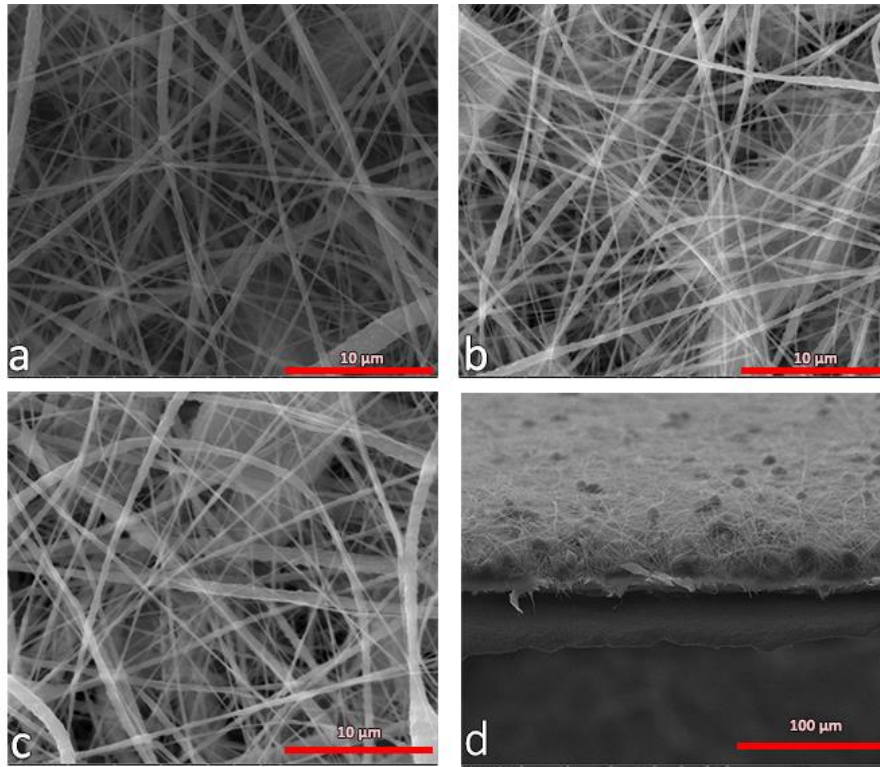


Figure 1. SEM images of the PVDF nanofiber from polymer with Mw 534.000, (a) A1 (5 hours), (b) A2 (7 hours), (c) A3 (9 hours), (d) cross-section of sample A1 (5 hours).

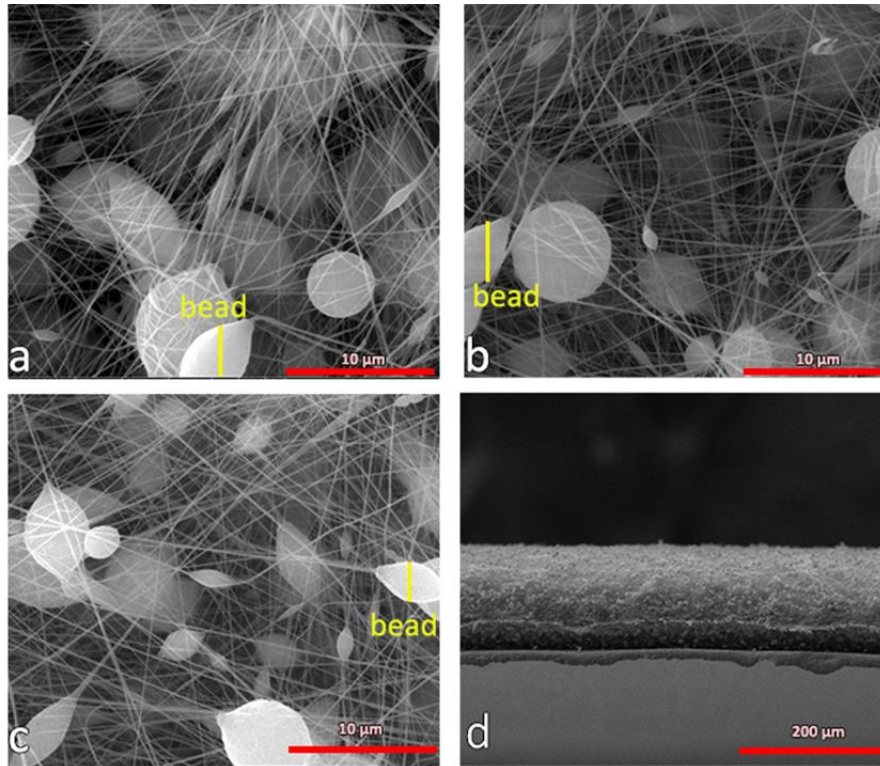


Figure 2. SEM images of the PVDF nanofiber from polymer with Mw 1.300.000, (a) A1 (5 hours) (b) A2 (7 hours) (c) A3 (9 hours) (d) cross-section of sample A1 (5 hours).

Table 1. The average fiber size of the PVDF nanofiber with different Mw and spinning time

PVDF Type	Sample	Average Particle Size
Mw 534.000	A1	274.4
	A2	262.2
	A3	255.8
Mw 1.300.000	S1	175.7
	S2	172.8
	S3	167.9

The porosity test results (Table 2) show that sample S3 has the highest porosity value, at 47.031%, and that the PVDF Mw 1,300,000 Nanofiber has a typically more excellent porosity value than the PVDF Mw 534.000 Nanofiber. According to Li et al.^[13], A higher porosity value will improve a battery's electrochemical performance by speeding up the transfer of Li⁺ ions. An Mw 1.300.000 S3 Nanofiber with a 9-hour fabrication time was selected as a sample for manufacturing an anode-free lithium-ion battery. The S3 nanofiber is substantially smaller, at 169.9 nm, and has good tensile strength and elongation values in addition to its high porosity value. 39.7% and 1.63 MPa, respectively. Figures 1(d) and 2(d) show cross sections of samples A3 and S3, which have nanofibers and beads with PVDF Mw 534.000 and PVDF Mw 1.300.000 compositions on their surfaces, respectively.

Table 2. Porosity Value of PVDF with different Mw and spinning time

PVDF Type	Sample	Porosity (%)
Mw 534.000	A1	24.005
	A2	38.409
	A3	45.725
Mw 1.300.000	S1	27.435
	S2	41.152
	S3	47.031

Table 3. Elemental Composition of PVDF Nanofiber with different Mw and spinning time

PVDF Type	Sample	Mass (%)		
		C	F	Cu
Mw 534.000	A1	68.2	29.5	2.3
	A2	66.0	32.2	0.8
	A3	68.5	30.5	1.0
Mw 1.300.000	S1	62.3	32.4	5.3
	S2	62.0	38.0	0
	S3	61.0	21.7	12.3

Table 3 shows the elemental composition of the PVDF nanofiber coated on the Cu Foil. PVDF nanofiber coated on Cu foil contains elements such as Carbon (C), flour (F), and copper (Cu). The PVDF polymer is composed primarily of carbon and flour, with copper appearing as an impurity on the PVDF membrane collecting plate during electrospinning.

Table 4. Tensile strength and elongation of PVDF Nanofibers Mw 534.000 and Mw 1.300.000

PVDF Type	Sample	Tensile Strength (MPa)	Elongation (%)
Mw 534.000	A1	0.88	7.8
	A2	1.01	10.2
	A3	2.33	13.0
Mw 1.300.000	S1	0.62	23.3
	S2	0.65	27.0
	S3	1.63	39.7

The tensile strength of the PVDF Mw 534.000 Nanofiber was measured between 0.88 and 2.33 MPa, as shown in Table 4. The tensile strength of the Mw 1.300.000 PVDF Nanofiber is in the range of 0.62-1.63 MPa. The tensile strength value increases as the fabrication time of the two types of PVDF Nanofibers increases. These results were also observed in the elongation tests for the PVDF Mw 534.000 and PVDF Mw 1.300.000 Nanofibers; the magnitude of the elongation value is directly correlated with the amount of time the PVDF Nanofiber was manufactured; the results were obtained in the ranges of 7.8-13% and 23.3%-39.7%, respectively. Therefore, the PVDF Mw 534,000 and PVDF Mw 1.300.000 Nanofibers have the appropriate mechanical qualities and are strong enough to sustain pressure without causing a short to occur in the battery. In a battery, the charge-discharge process causes pressure on the Nanofiber either by expanding the cathode, anode, or both, according to Chen et al.^[14]. If the Nanofiber does not have sufficient mechanical qualities, this pressure might damage the battery.

A Memmert brand oven was used for the thermal shrinkage ratio test for 30-minute runtime and a temperature of 150 °C. Table 5 shows the test results and the extent of the thermal shrinkage (Figure 3). The PVDF nanofiber shrinkage changes over time and ranges from 19% to 36%. The nanofiber had the most significant thermal shrinkage in the time variation between 5 and 9 hours at Mw 1.300.000. The nanofiber observed the most minor shrinkage, with a time variation of between 5 and 7 hours at Mw 534.000. Several characteristics contribute, including colloids, porosity, and thermal conductivity. According to Czlonka et al.^[15], the thermal conductivity decreases with decreasing pore size and increasing porosity value. This claim is also consistent with Zivcova et al.^[16] research, which found an exponential relationship between pore size and thermal conductivity.

Table 5. Dimensional shrinkage value of PVDF nanofiber membrane and PP Nanofiber

Membrane Sample	Initial surface area (cm ²)	The final surface area (cm ²)	Difference in surface area (cm ²)	The percentage of shrinkage area (%)
S3	3.140	2.010	1.130	36.00
S2	3.140	2.269	0.871	27.75
S1	3.140	2.010	1.130	36.00
A3	3.140	2.269	0.871	27.75
A2	3.140	2.543	0.597	19.00
A1	3.140	2.543	0.597	19.00
PP	3.140	0.196	2.944	93.75

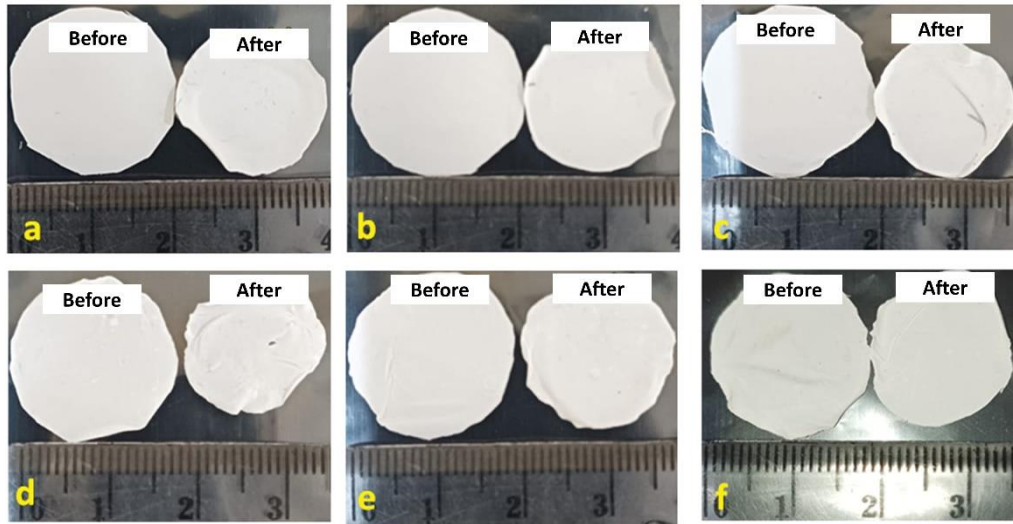


Figure 3. Thermal shrinkage ratio of PVDF nanofiber, before and after the shrinkage test. a) Sample A.1. b) Sample A2. c) Sample A3. d) Sample S1. e) Sample S2. f) Sample S3.

The thermal characteristics of the PVDF Mw 534.000 and PVDF Mw 1.300.000 samples are presented in Figures 4 and 5 based on the results of the TG-DTA test. The three samples share that an endothermic process happens between 150°C and 160°C. This is because the water content in the samples evaporates, but there is no observable mass loss. An exothermic reaction that caused the sample to lose up to 97-97.8% of its initial mass happened when the sample's decomposition reaction into carbon took place at a temperature of 450°C.

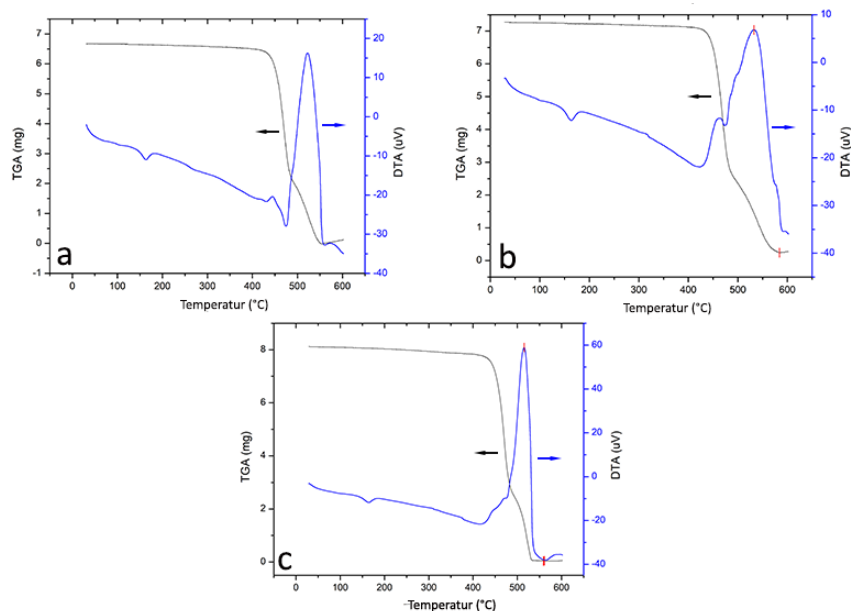


Figure 4. Graph of TG-DTA test results for PVDF sample Mw 534.000. a) Sample A1 (5 hours). b) sample A2 (7 hours). c) Sample A3 (9h).

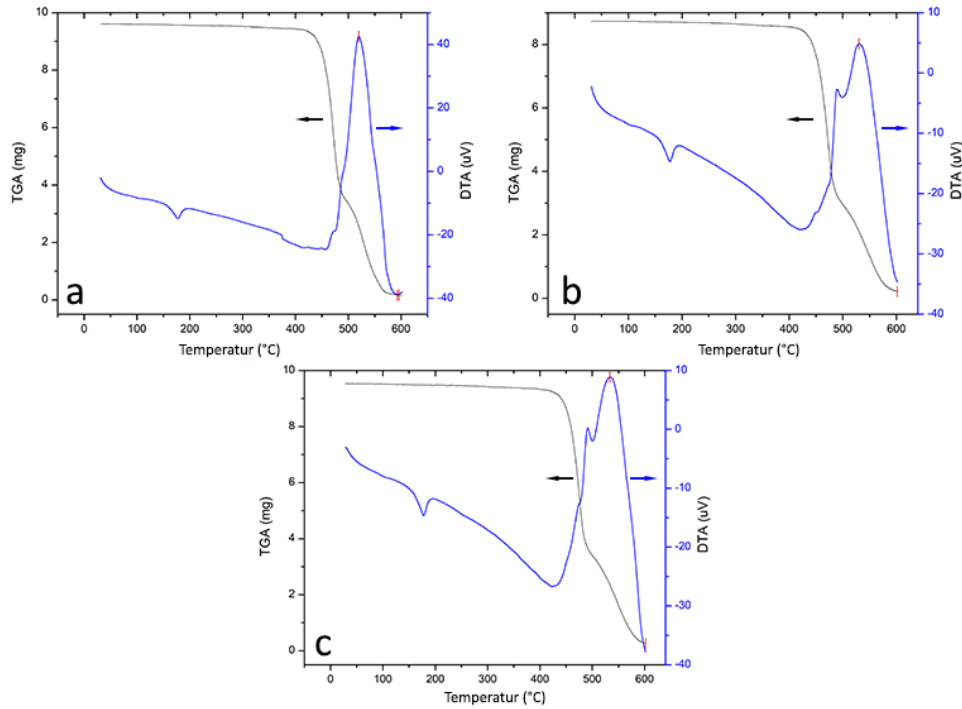


Figure 5. Graph of TG-DTA test results for PVDF sample Mw 1.300.000. a) Sample S1 (5 hours). b) sample S2 (7 h). c) Sample S3 (9 h).

The battery analyzer testing is in order to determine the value of the anode-free lithium battery's capacity, as well as the stability of the battery's capacity, for AFLB with PVDF nanofiber modified Cu current collector and compared to the AFLB with Cu current collector only. The battery assembly employs NMC 622, which has dimensions of 25.5 cm in length, 5.7 cm in breadth, and 4.4 grams in mass as a cathode. The battery analyzer test relies on a C/20 current and a ten-times cycle. Figure 6 illustrates the charge-discharge curve derived from the battery analyzer test results, with capacity on the x-axis and voltage on the y-axis.

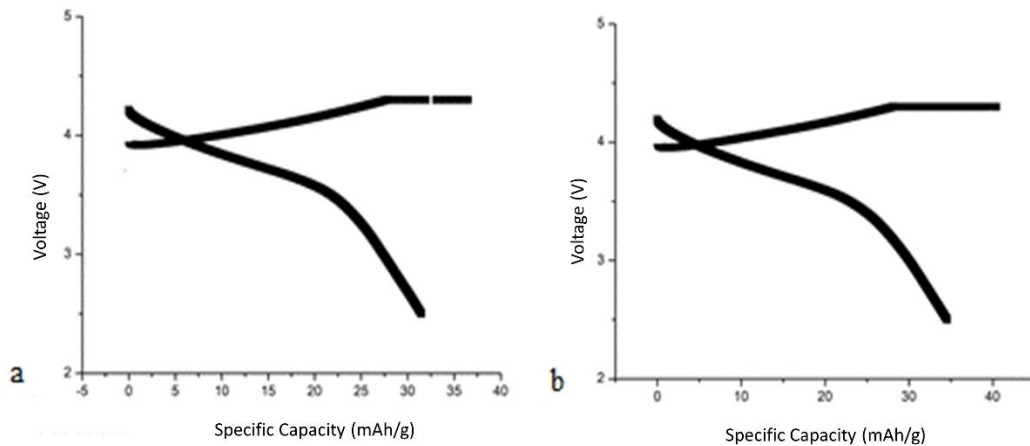


Figure 6. Graph of Charge-Discharge Test Results (a) AFLB Nanofiber PP. (b) AFLB Nanofiber PVDF S3.

PVDF S3 nanofiber was chosen out of all the samples in the battery assembly because S3 nanofiber has high porosity and small fiber size. Figure 6 shows the results of the charge-discharge test. The specific charge-discharge capacity of the unmodified-Cu current collector AFLB is 36.506 mAh/gr and 31.477 mAh/gr, respectively, with Coloumbic efficiency of 86.223%. Meanwhile, modified-Cu current collector AFLB (using sample S3) has a specific charge-discharge capacity of 41,352 mAh/gr and 34,579 mAh/gr, respectively, with Columbia efficiency of 83.626% efficiency. These results are consistent with Francisco et al.^[17] research, which was based on data showing the maximum charge-discharge capacity value when applying a PVDF S3 nanofiber-modified Cu current collector. It offers better ion transport capabilities because PVDF nanofibethey are manufactured using nonwoven methods.

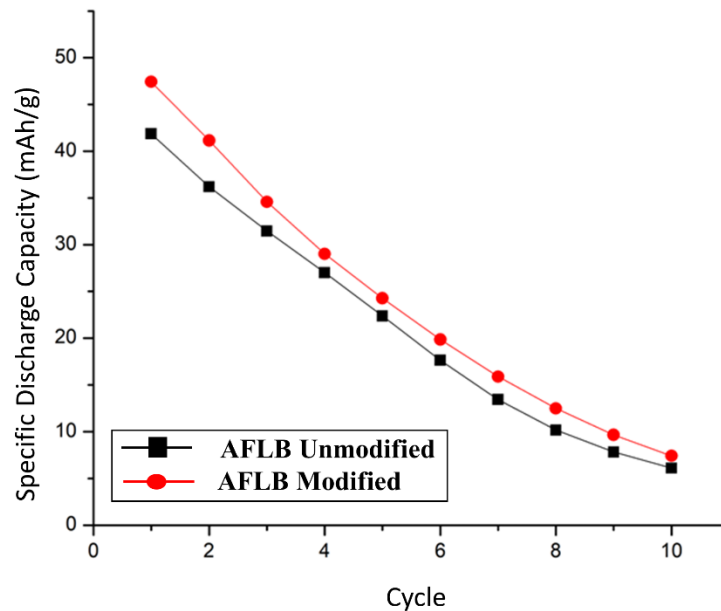


Figure 7. Graph of AFLB Battery Performance in 10 cycles.

Figure 7 shows the test results for the first ten cycles. The unmodified-Cu current collector AFLB shows the battery's capacity decreased by 41.877 mAh/gr in the first cycle and 6.104 mAh/gr in the final cycle, with a capacity retention of 85.421% on the tenth cycle. The capacity loss of the modified-Cu current collector (using sample S3) was 7.425 mAh/gr in the final cycle and 47.425 mAh/gr in the first cycle, with a capacity retention of 84.343%.

CONCLUSION

PVDF nanofiber has successfully electrospun the Cu foil as a current collector in an anode-free lithium-ion battery (AFLB). Two electrospinning process parameters were investigated: polymer molecular weight and electrospinning time. The PVDF nanofiber from polymer with Mw of 1.300.000 and spinning time of 9 hours had the highest porosity and elongation of 47.031% and 39.7%, respectively. PVDF nanofiber from polymer with Mw of 534.000 and spinning time of 9 h, on the other hand, had the highest tensile strength of 2.33 MPa. The Cu-collector modification with PVDF nanofiber increased the specific capacity of the AFLB battery by 10%, with a coulombic efficiency value in the first cycle that was nearly the same, around 86%.

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