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SYNTHESIS AND CHARACTERIZATION OF WATER HYCINTH POROUS CARBON FOR LITHIUM SULFUR BATTERY CATHODE COMPOSITES

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Abstract. Water hyacinth as a weed plant is a type of biomass with a fast growth rate. This condition causes problems in the environment and has a negative impact on life, including health and economic problems. To provide added value to the utilization of water hyacinth, a synthesis and characterization of porous carbon from water hyacinth has been carried out which is used as a sulfur cathode matrix in lithium sulfur batteries. From the results of the N_2 adsorption-desorption test, the surface area of porous carbon was 297.7 m^2/g and the total pore volume was 0.332 cm^3/g. The results of the composite test showed that the sulfur content in the composite for a ratio of 1:2.5 was 60.6 wt%. The cathode of a lithium sulfur battery has been made from a composite with a thickness 100 μm and a sulfur loading of 2.80 mg/cm^2. The initial discharge capacity of the battery was 264 mAh/g with a coulomb efficiency of up to 70%. Battery discharge capacity was 175.5 mAh/g at 50th cycle.

Keywords: lithium-sulfur battery, water hyacinth, porous carbon, capacity, composite

1. Introduction

Biomass has enormous potential as a source of porous carbon (PC) with properties including; renewable, easy to process, economical, and abundantly available in nature. Porous carbon has potential for practical applications in carbon electrodes, especially in energy storage systems [1]. As electrodes (supercapacitors and batteries), ideally porous carbon electrodes are able to work with fast charging rates, long cycles, and produce high power and energy density [2]. Various types of biomass have been made as porous carbon materials for carbon electrodes, among others; coconut shell [3], bamboo [4], tea leaves [5], banana peel [6], and corn [7]. These types of biomass are used because they are easy to obtain, renewable, low cost and environmentally friendly. Carbon electrode from biomass can show good performance. However, most of the biomass comes from agricultural products, such as coconut shells, bamboo, leaves, bananas and maize with limited availability for sustainable fabrication. On the other hand, there are sources of biomass that grow at an uncontrolled growth rate and generally have a negative impact on the environment as weeds.

Water hyacinth (Eichhornia crassipes) is a biomass that is considered the most problematic in the world. This is due to the uncontrolled growth of water hyacinth in open ponds, irrigation and other water containers. Water hyacinth (WH) can grow quickly to a very high density (more than 60 kg/m^2); this means that spreading across the surface of the water can occur, which has adverse effects on the environment, human health and economic development [8]. EG has a bio-chemical component consisting of 20.8%

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hemicellulose, 30.5% cellulose and 21.3% lignin [9]. EG naturally contains alkaline or alkaline earth elements such as Na^+, K^+, Ca^{2+}, Mg^{2+} and about 30% protein [10]. Water hyacinth porous carbon (WHPC) has been prepared and applied to lithium/sodium ion batteries and supercapacitors [10,11]. WHPC has the potential to be applied to Li-S batteries.

Since it was first discovered until now, Li-S batteries have continued to be researched and developed because they have a larger theoretical capacity than Li-ion batteries. Theoretically lithium has a specific capacity of 3861 mAh/g and sulfur of 1675 mAh/g and a theoretical specific energy density of 2600 Wh/kg [12]. Replacing the cathode with sulfur provides a low operating voltage (2.15 V), which has an impact on increasing battery safety [13]. A significant problem for Li-S batteries comes from the active ingredient sulfur, because sulfur is an insulator with an electrical conductivity of $5x10^{-30}$ S/cm at 25^oC. In addition, sulfur expands during the process of converting sulfur into polysulfides [14]. Another problem is the long-chain polysulfide dissolved in the electrolyte thereby inhibiting charge mobility during the electrochemical process [15]. The strategy used to solve Li-S battery problems in general is encapsulation and impregnation of sulfur in the PC matrix [16]. The high sulfur content in the cathode affects the energy density and discharge capacity of the battery. To obtain a high sulfur content (mg/cm^2), a composite with a high sulfur content (wt%) and a thick layer of cathode slurry on Al foil substrate is required. The sulfur content in the composite (wt%) depends on several factors; surface area and pore volume of porous carbon, weight ratio of porous carbon to sulfur (WHPC/S). While the sulfur loading at the cathode (mg/cm^2) depends on the thickness of the cathode slurry layer. High sulfur content and cathode electrical conductivity provide good battery performance [17]. In this research, a composite with a WHPC/S weight ratio of 1:2.5 and a cathode with a layer thickness of 100 μm will be made.

2. Material and Methods

2.1 Synthesis of Porous Carbon

Water hyacinth (WH) has been collected from swamps in several cities in the Jawa Barat, Indonesia. Water hyacinth porous carbon (WHPC) was synthesized by simply carbonizing the water hyacinth as the precursor for carbon. After cleaning, the WH stems and leaves were taken and dried in the sun for 5–6 days, followed by an oven at 100^oC for 2 h. The dried WH was carbonized at 400^oC for 2 h at a heating rate of 10^oC/min in air and then cooled to room temperature naturally, resulting in a black powder. The carbon was then pulverized to a size of 200 mesh, then mixed with $ZnCl_2$ 30% (Sigma Aldrich, CAS Number: 7704-34-9) in the weight ratio of 1:3; then it was soaked for 24 h at room temperature and dried at 110^oC for 2 h and heated at 800 ^oC for 1 h with a heating rate of 10^oC/min under Ar flow.

2.2 Composite Preparation of Water Hyacinth Porous Carbon-Sulfur

WHPC and the Sulfur (Sigma Aldrich 99%, St. Louis, MO, USA) were mixed with the weight ratio of 1:2.5 in a quartz mortar. The mixture was heated at 155^oC for 12 h to achieve the lowest viscosity of sulfur so that sulfur could easily enter the pores of the WHPC matrix.

2.3 Characterization

Characterization of the WHPC and WHPC/S composites were carried out by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS, S-4800, Hitachi

Limited, Tokyo, Japan), Brunauer–Emmett–Teller (BET, Quantachrome Nova 4200e, Anton Paar, Graz, Austria), and Thermogravimetric analysis (TGA, Perkin Elmer TGA 4000, Waltham, MA, USA). XRD patterns were determined by using Cu Kα (wavelengths = 0.15418 nm) in the range of $10^o \leq 2\theta \leq 80^o$ (scan speed 5^o/min and scan step 0.02^o) at room temperature. Morphologies and microstructures of the samples were observed and analyzed by using the SEM operating at 10 kV. The sulfur content was detected using the TGA measurement under an air atmosphere, and the temperature range was from room temperature to 700^oC with a heating rate of 10^oC/min. Nitrogen adsorption isotherms at 77 K were measured using the BET method.

2.4 Electrochemical Measurement

The battery cathode was prepared by mixing WHPC/S composite materials, black acetylene (Super P, 10 wt%) and polyvinylidene fluoride (PVDF, 10 wt%) with a composition of 8:1:1 with N-methyl pyrrolidone (NMP) solvent. The mixture was then stirred for 3 hours with a magnetic stirrer. Furthermore, the cathode slurry was layered on aluminum foil with a doctor's blade with a thickness of 100 µm which was dried at 60^oC for 12 hours in a vacuum oven. Then the film was cut into circles with a diameter of 14-15 mm according to the diameter of the coin. Coin cell type 2025 was assembled by making a WHPC/S composite as cathode, Li as anode, Celgard 2400 as separator, and glued in a glove box under an Ar atmosphere. The electrolyte was prepared from a mixture of 1.0 M lithium bis(trifluoro-methanesulfonyl)imide (LiTFSi) dissolved in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (v/v, 1:1) containing 1 wt% LiNO3 as additive. Galvanostatic testing was carried out over a voltage range of 1.6 - 3.4 V to test battery capacity and battery cycles at the rate of variation (1C = 1675 mAh/g).

3. Results and Discussion

The specific surface area of the WHPC and the WHPC/S composite is shown in Figure 1.

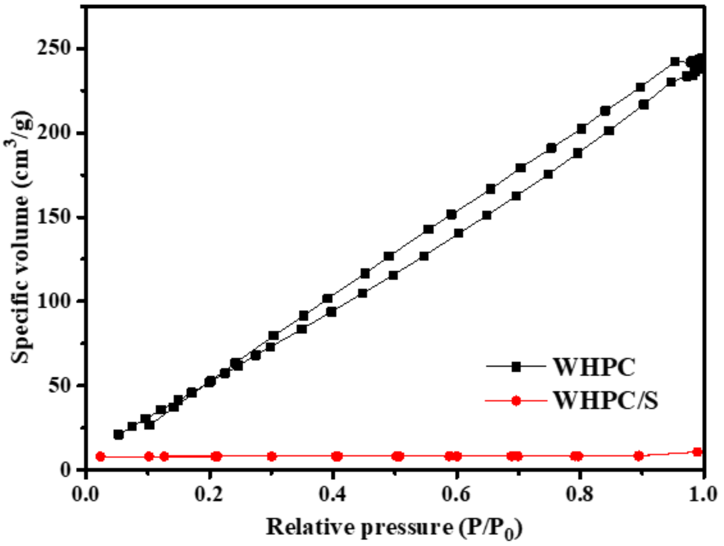

Figure 1. Isothermal N_2 77 K adsorption-desorption (a) WHPC and (b) WHPC/S

The results of the isothermal N_2 77 K adsorption-desorption test on WHPC obtained a surface area of porous carbon of 297.76 m^2/g and a total pore volume of 0.332 cm^3/g [18] with a mesoporous structure. Whereas for the WHPC/S composite with a ratio of 1:2.5, the specific surface area and total pore volume were 0.327 m^2/g and 0.0041 cm^3/g. This indicated that sulfur had entered the pores of the porous carbon.

The morphology of the WHPC and WHPC/S composites was investigated by SEM-EDS. The surface structure of the WHPC and the WHPC/S composite is shown in Figure 2. Figure 2(a) shows the surface of the WHPC with the presence of scattered pores of different sizes. Only a small number of pores formed on the WHPC surface. Based on EDS point data, the content of elemental carbon (C) in the sample is only 66.3% and the remaining 33.7% are elements derived from raw materials and activators. This situation indicates that the chemical and physical activation process has not run optimally. Figure 2(b) shows the surface structure of WHPC/S. The presence of sulfur in the composite is scattered at several points and most of it has entered the WHPC pores. The results of the EDS point test showed that the sulfur (S) content in the composite was 66.8 wt%.

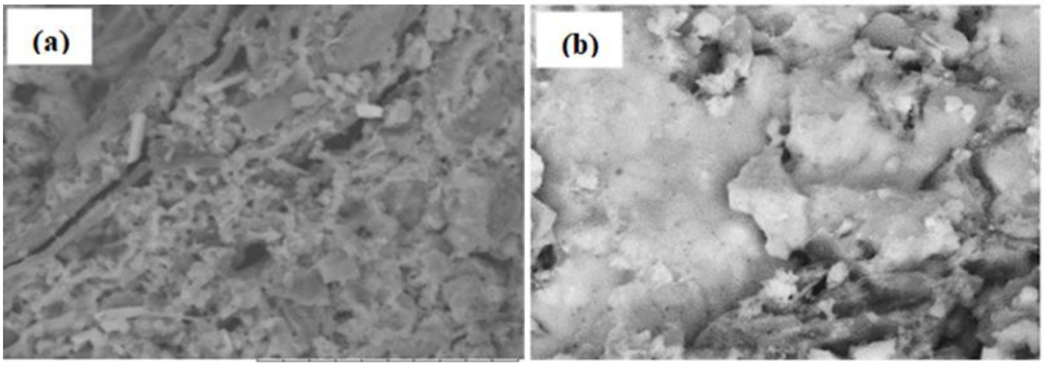

Figure 2. Morphological structure of (a) WHPC and (b) WHPC/S

The thermogravimetric (TG) testing of WHPC and sulfur (S) composites is shown in Figure 3(a). Figure 3(a) shows the weight loss of the WHPC/S composite (1:2.5) from 200^{o}C to 300^{o}C. The temperature begins to stabilize when the composite is heated to temperatures above 300^{o}C which is due to the fact that sulfur has evaporated from the WHPC mesoporous [19]. The sulfur content in the WHPC/S composite with a weight ratio of 1:2.5 was 60.6 wt%. Weight loss above 450^{o}C is carbon oxidation [19].

Conductivity testing with a four line probe (FLP) obtained an electrical conductivity of 3.93 x 10^{-2} S/cm for porous carbon and 5.4 x 10^{-4} S/cm for composites.

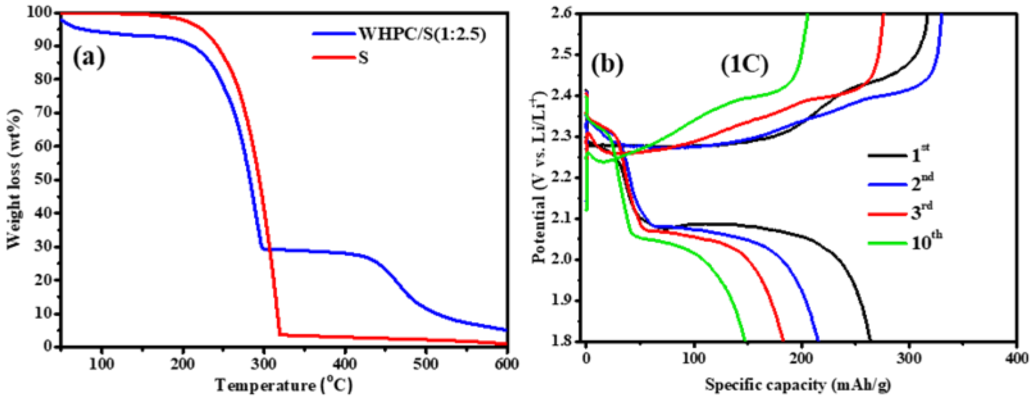

Figure 3. (a) The thermogravimetric curves of sulfur (S) and the WHPC/S composite. (b) Curves of charge and discharge capacity at a charge rate of 1C with a sulfur content of 2.80 mg/cm^2

Figure 3(b) shows the charge and discharge capacities of the battery for a sulfur content at the cathode of 2.80 mg/cm^2. The amount of sulfur content is obtained by weighing the cathode of a coin cell with a diameter of about 15 mm and a layer thickness of 100 µm minus the weight of clean, uncoated aluminum foil. The sulfur content results in a battery area capacity of 4.69 mAh/cm^2. This result is greater than the commercial cathode which is 2.5-3.5 mAh/cm^2 [14]. The initial discharging capacity is 264 mAh/g. The low initial capacity value indicates that the amount of sulfur involved in the electrochemical process is still limited. This is probably caused by a non-standard battery manufacturer. The discharge capacity continued to decrease to 198 mAh/g at the 10th cycle. This decrease was due to the formation of Li_2S_8 polysulfide during the electrochemical process of the battery [17]. The low charging and discharging can also be caused by the conductivity of porous carbon which is only on the order of 10^{-2} S/m. This will result in low sulfur electrical contact even though the amount of sulfur at the cathode is adequate [19].

The cyclic performance, coulomb efficiency for 1C charge rate and charge discharge with variations in load scan-rate are shown in Figure 4. Figure 4(a) shows the instability of the decrease in the value of discharging capacity that occurs from cycles 1 to 15. Furthermore, the discharging capacity is stable and even increases up to 50 cycles. This is due to the initial electrochemical activity not going well, then gradually the electrochemical activity improves until the cycle 50 [17]. The coulomb efficiency value varies from 70-90% for cycles 1 to 20, then the coulombic efficiency is stable at a value of 70% after cycles above 20 to 50. In the 20th cycle the discharge capacity is 140 mAh/g and in the 50th cycle the discharge capacity is 175 .5 mAh/g. Figure 4(b), shows the discharge stability for various charge rates from 0.5C to 0.1C. For each charge rate, five cycles of charge and discharge are carried out. Discharging capacities for variations in charge rates of 0.5C, 0.2C, 0.1C and 1C were 307.14, 335.71, 389.28 and 228.57 mAh/g, respectively. The smaller the charge rate given, the value of the emptying capacity increases.

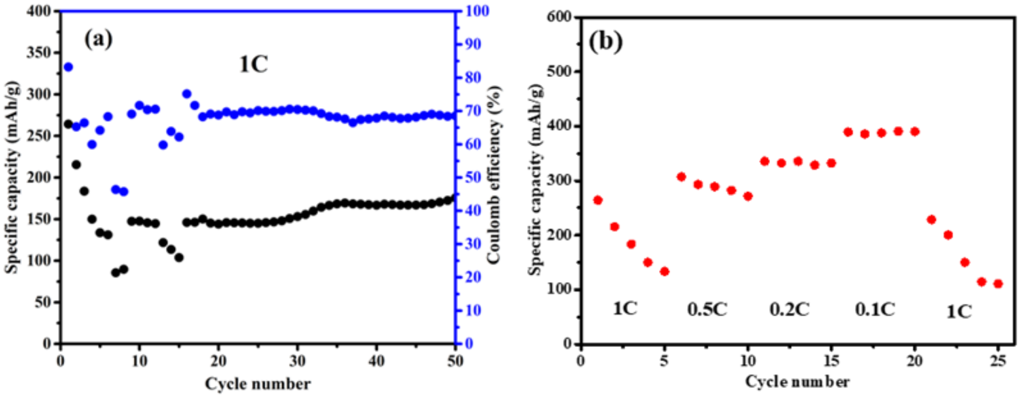

Figure 4. (a) Cycle stability and coulomb efficiency curves of a battery with a sulfur content of 2.80 mg/cm^2, (b) Discharging capacity for varying charge rates of 1C, 0.5C, 0.2C, and 0.1C.

4. Conclusions

Porous carbon from water hyacinth biomass (WHPC) has been successfully prepared with a surface area of 297.76 m^2/g and a total pore volume of 0.332 cm^3/g and has a mesoporous structure. Porous carbon from water hyacinth biomass was prepared as a composite with sulfur (WHPC/S) with a sulfur content of 60.2 wt% for a WHPC/S ratio of 1:2.5. The composite was prepared as cathode for Li-S battery with a sulfur content of 2.80 mg/cm^2 and a thickness of 100 µm. The battery cells made have an initial discharge capacity of 264 mAh/g and an average coulombic efficiency of 70%. From the results of battery manufacturing and testing, it is shown that the potential of water hyacinth waste can be utilized as a lithium sulfur battery cathode matrix, although the initial discharge capacity is still not optimal.

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