Activated carbon with hierarchical porosity derived from biomass for lithium sulfur batteries

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Abstract

Highly porous activated carbon (RHAC) with micro/meso porosity has been synthesized through carbonizing rice husk and activating by K2CO3. Elemental sulfur has been loaded to the micropores through a solution infiltration method to form RHAC@S nanocomposite. The resulted RHAC@S nanocomposite with 0.25 and 0.38 mg.cm−1 of sulfur loading have been tested as novel cathodes for Li-S batteries. The 0.25 mg.cm−1 sulfur loading sample shows an initial discharge capacity of 1080 mA.h.g−1 at 167.5 mA g−1. After 50 cycles of charge/discharge test at the current density of 0.2C, the reversible capacity maintains at 312 mA.h.g−1. The material has delivered a capacity of more than 300 mA.h.g−1 at 284.75 mA g−1. These results suggest that the rice husk is a good candidate for large-scale production of activated carbon, which is a promising material for cathode of Li-S batteries.

Keywords. Rice husk, cathode material, carbonization process, activated carbon, lithium sulfur battery.

1. INTRODUCTION

The lithium-sulfur battery is one of promising energy storage device for electric power owing to their remarkably high theoretical energy density as high as 2500 Whkg−1 and high specific capacity which is 3-4 times higher than current lithium-ion battery system.[3-5] Sulfur is considered a promising cathode material due to its low cost, high theoretical capacity (1675 mAh.g−1), and nontoxicity.[6-8] Despite their beneficial features, the low electrical conductivities of sulfur and lithium sulfides and slow redox kinetics of the active materials hindered the practical use of Li-S batteries.[7-9] To overcome these problems, a variety of polar Lithium Polysulfides (LiPS) absorbents such as nano metal oxide[10-12], forming a composite of sulfur and carbon[13-15], coating with conductive polymer[16,17] to improve conductivity of cathode, prevent dissolution of lithium polysulfides to reduce the shuttle effect. Biomass is the most promising carbon precursor for preparing cost-effective porous carbon materials such as activated carbon materials.[18,19] Activated carbons are the porous materials with developed pore structure, large surface area and high adsorption capacity.[20,21] Various biomass-derived carbons (e.g. cherry stone, olive stone, mangrove charcoal, rice husk, peanut shell, cotton wool) have been investigated for high capacities and good electrochemical properties when apply in lithium batteries.[22-24] Agricultural by-products can be used as energy, chemicals, and materials that have shown prospects in electrochemical energy systems due to their abundance, low cost, easy regeneration and environmental friendly renewable resource.[25] The residual pore volume in the nanocomposite is designed to retain pathways for electrolyte/Li+ ingress and to accommodate the active mass volume expansion during cycling. It is believed that, for the porous carbon materials, specific surface area, pore diameter distribution, pore volume, and sulfur filling level are the key factors for battery performance.[26] Among these materials, the rice husk is one of the promising carbon precursors for producing of low-cost activated carbon.[27-29] The anticipated world rice production in 2012 was 489.1 million tons which means that approximately 122-163 million tons of rice husk bio-mass was generated globally in 2012. The major components of RH are SiO2, cellulose (38 %), hemicelluloses (18 %), and lignin (22 %), which yield carbon as pyrolysed product under inert atmosphere.[30]

Based on this principle, herein, we design a highly conductive hierarchically porous activated carbon with low cost and easy to scale up for Li-S batteries. The hierarchically structure with
micro/mesoporous activated carbon was obtained by carbonization from rice husk (RH) using chemical activation, namely activated carbon from rice husk (RHAC). The RHAC and RHAC@S composites were obtained by the method of melting diffusion. The synergetic effect of the meso/microporosity and the structure on the electrochemical performance of the RHAC@S cathode was investigated in detail.

2. MATERIALS AND METHODS

2.1. Activated carbon from rice husk (RHAC) preparation

The rice husk for the preparation of activated carbon was obtained from Thaibinh province, Vietnam. At first, RH was initially washed using hot deionized water (DI) several times to remove dust like impurities and dried at 120 °C in the oven for 24 h. The dried RH was pre-carbonized in tube furnace at 350 °C for 2 h with a heating rate of 5 °C.min⁻¹. For the chemical activation and removal of silica in RH, the sample was subjected to impregnation in K₂CO₃ solution (w/w = 1:2). The mixture was calcined at 800 °C (best carbonization temperature[31]) for 3 h with a heating rate of 3 °C.min⁻¹ under N₂ atmosphere in a tubular furnace. After cooling, the obtained sample was washed with DI water, treated with aqueous 1M HNO₃ three times and 1M HF solution to remove some inorganic and SiO₂ content in rice husk material, finally washed with deionized water and dried at 100 °C for 24 h in a vacuum oven.

2.2. Activated carbon from rice husk/sulfur composites (RHAC@S) preparation

The RHAC and S composites were prepared by following a conventional melting diffusion strategy. The RHAC and sulfur with different weight ratios (RHAC:S = 1:0.5, and 1:0.7) were hand ground together, transferred to a tubular furnace, and heated at 155 °C for 15 h with a heating rate of 3 °C.min⁻¹ under a N₂ atmosphere. After cooling down to room temperature, the RHAC@S composites were obtained with sulfur content of 0.25 mg.cm⁻² and 0.38 mg.cm⁻².

2.3. Physical measurement

Nitrogen adsorption–desorption isotherms were measured at 77 K on a nitrogen sorption apparatus (Micromeritics ASAP2020), and the surface areas were calculated using the Brunauer-Emmett-Teller (BET) method. The X-ray diffraction (XRD) diagrams were carried out with a D Max/2000 PC (Rigaku, Ltd). The surface morphologies of the composite were investigated with a scanning electron microscope (SEM, Hitachi, S4800) equipped with energy dispersive spectroscopy (EDS, OXFORD 7593-H) as an accessory of SEM.

2.4. Electrochemical measurement

2032-type coin cells were used to study the electrochemical performance of the RHAC@S cathodes. The cathodes for the battery test cells were fabricated with a mixture of the active material RHAC@S (60 wt%), super P carbon black (conducting agent, Timcal) (20 wt%), and a polyvinylidene fluoride (PVDF, KF 1300, Kureha) binder (20 wt%) by dispersion/dissolution in N-methyl-2-pyrrolidene (NMP). To prepare the electrodes, the cathode slurry was coated on aluminum foil and left it to dry at 45 °C for 24 h under nitrogen atmosphere and then roll-pressed prior to use. Lithium foil (Li) and Celgard 2400 sheets were used as the anode and separator, respectively. The cells were assembled in an argon-filled glove box, and 1.0 M LiNO₃ with 0.1M LiTFSI in DOL/DME (1:1 by volume) was used as the electrolyte.

The charge and discharge properties were performed on a cell life test system (PNE solution, Korea) at different current densities in the potential range of 1.8-2.8 V versus Li/Li. The cyclic voltammetry (CV) was conducted on the same instrument in the voltage range of 1.5-3.0 V at a scanning rate of 0.1 mV.s⁻¹ using electrochemical analyzer (America, Bio-logic, VSP). All the electrochemical tests were performed at room temperature. The specific capacity values were calculated according to the mass of sulfur.

3. RESULTS AND DISCUSSION

The morphology of RHAC and RHAC@S were investigated by SEM and shown in Fig. 1.

![Figure 1: SEM pictures and EDS mapping element of (a) RHAC and (b) RHAC@S samples](image)
As can be seen from figure 1a, the RHAC is filled with hollow tunnels which can be attributed to the gasification of volatiles upon activation. The pores are different in sizes and shapes. However, the particles display non-uniformity. It can be observed that the external surfaces of the activated carbons are full of cavities, quite irregular as a result of activation, large quantities of flake structure and slit-shape micro/mesoporous. It seems that the cavities resulted from the evaporation of K2CO3 during carbonization, leaving the space previously occupied by the K2CO3.[32] Results of EDS of the sample revealed that no trace of Si was observed. As a result, it is reasonable to suggest that the pores might be created due to the removal of SiO2. When sulfur impregnated into the pores, most pores disappear and some macropores change into mesopores in RHAC@S composite as shown in Fig 1b. EDS-element mapping was employed to detect the chemical composition and surface electronic states of the RHAC@S sample. EDS spectra clearly show the presence of carbon (C), oxygen (O) of RHAC sample and carbon (C), sulfur (S) of RHAC@S composite sample with high homogeneous distribution.

The powder X-ray diffraction (XRD) patterns of the pure sulfur and RHAC@S samples with various sulfur contents are shown in Figure 2. One can see that no diffraction peaks of graphic carbon was found for the case of RHAC sample, implying the amorphous nature of carbon material. The characteristic peaks of element sulfur at 26.4°, 29.17°, 30.76°, and 35.56° can be observed, clearly confirming the successful impregnate of sulfur into RHAC.[33] The intensity of crystalline sulfur peaks in the XRD pattern increases with the sulfur content.

Nitrogen adsorption-desorption curve provides qualitative information on the adsorption mechanism and porous structure of the carbonaceous materials.[34] The N2 adsorption-desorption isotherms of samples are shown in figure 3.

![Figure 2: XRD pattern of pure S and RHAC@S composites with various sulfur contents](image)

![Figure 3: N2 adsorption-desorption isotherms of RHAC and RHAC@S samples](image)
sulfur to lithium polysulfide anions (Li$_2$S$_n$, n = 4~8). The second peak at 2.05 V involves the strong reduction of polysulfide ions to insoluble Li$_2$S$_2$ and Li$_2$S.$^{[36]}$ The oxidation process in the Li-S cell occurs in one stage. The narrow oxidation peak around 2.5 V is mainly attributed to the oxidation of Li$_2$S$_n$ (n > 2) into polysulfides.$^{[36-38]}$

The first charge and discharge profiles of the RHAC@S composite electrodes with different sulfur loadings given in Fig. 5 are in good agreement with the CV curves. All the discharge curves of the RHAC@S composite electrodes have two voltage plateau regions, corresponding to the multi-step reduction reaction of sulfur during the discharge process. The upper plateau at approximately 2.3 V is caused by the transformation of sulfur to higher-order lithium polysulfide (Li$_2$S$_n$, 4 ≤ n ≤ 8), while the lower plateau at approximately 2.1 V corresponds to the transformation of the higher-order lithium polysulfide to lower-order lithium polysulfide (Li$_2$S$_n$, n < 4), which can precipitate the solid products of Li$_2$S$_2$ and Li$_2$S owing to their low solubility in the electrolyte.$^{[9,33]}$ The cathodes with different sulfur loadings all exhibit capacities of about 1080 mA.h.g$^{-1}$ in the first cycle, indicating high utilization of active sulfur. It can be ascribed to the sufficient contact between the sulfur and the electrolyte because of the excellent electrolyte adsorption capability of high porous activated carbon materials. After the initial loss of capacity resulted from the decomposition of the electrolyte and the formation of solid electrolyte interphase (SEI) layer, the capacities at 0.1C current rate decrease to 900 and 819 mA.h.g$^{-1}$ for the cathodes with 0.25 and 0.38 mg.cm$^{-2}$ sulfur loading, respectively.

The cycling performance of the RHAC@S composites is presented in Fig. 6. The cycling performance of all samples is at a rate of 0.2C between 1.8 and 2.8 V of cut-off voltage. As shown in Fig. 6, it is clearly seen that the discharge capacity decays drastically upon cycling for all samples. For cells with 0.25 mg.cm$^{-2}$ sulfur loading, the capacity approaches 1080 mA.h.g$^{-1}$ in the first cycle. After the activating process at a low current rate, the capacity stabilizes at 750 mA.h.g$^{-1}$ and retains at 358 mA.h.g$^{-1}$ after 50 cycles with 47.73 % capacity retention. The capacity of cells with 0.35 mg.cm$^{-2}$ sulfur loading shows almost no degradation compared with that of 0.25 mg.cm$^{-2}$. The capacity stabilizes at 680 mA.h.g$^{-1}$ after activating the process and retains at 312 mA.h.g$^{-1}$ after 50 cycles with 45.88 % capacity retained. The rapid capacity decay in the first few cycles may be caused by the volumetric expansion and re-distribution of the active sulfur during the initial lithiation process.$^{[7]}$ An increase in the carbon content of the RHAC@S composite electrodes leads to higher discharge capacities in each cycle because of the high electron conductivities of the electrodes provided by the carbon, which may promote the electrochemical reactions of sulfur with lithium.$^{[39]}$

The rate properties of the RHAC@S samples at various current densities in the voltage range of 1.8 to 2.8 V (vs. Li$^+$/Li) at room temperature were tested and shown in Fig. 7. The cell with 0.25 mg.cm$^{-2}$ sulfur loading performs good rate performance with capacities of 1041, 650, 486, 395 and 305 mA.h.g$^{-1}$ at current densities of 0.1, 0.2, 0.5, 0.9 and 1.7 C, respectively. For the cells with 0.35 mgcm$^{-2}$ sulfur, the capacities are 992 mA.h.g$^{-1}$ at 0.1C, 570 mA.h.g$^{-1}$ at 0.2 C, 412 mA.h.g$^{-1}$ at 0.5 C, 317 mA.h.g$^{-1}$ at 0.9C, and 210 mA.h.g$^{-1}$ at 1.7 C. The
excellent rate performance indicates good stability of the RHAC@S during testing at different rates.

![Graph](image1)

**Figure 6:** Cycling performance of the RHAC@S samples at 335 mA g\(^{-1}\) in a voltage range of 1.8-2.8 V

![Graph](image2)

**Figure 7:** Rate capability performance of RHAC@S samples at different C-rates in a voltage range of 1.8-2.8 V

4. CONCLUSION

To further development of Li–S batteries for practical applications, we developed hierarchically micro/mesoporous structure of activated carbon from rice husk via a simple carbonization process in combination with K\(_2\)CO\(_3\) activation technique. The RHAC is amorphous with high surface area (S\(_{BET}\)) and pore volume of 1583 m\(^2\)g\(^{-1}\) and 0.93 cm\(^3\)g\(^{-1}\), respectively. As a result, when evaluated as a cathode material for lithium–sulfur batteries, the RHAC@S composites with the sulfur loading of 0.25 mg·cm\(^{-2}\) exhibit the high discharge capacity of 1080 mA·h·g\(^{-1}\), as well as the excellent cycle stability and high rate capability. We believe that our results will open new avenues for the development of Li-S batteries when using low-cost materials and adopting industry.

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