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Fabrication of high-energy hybrid capacitors by using carbon-sulfur composite as promising cathodes

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HIGHLIGHTS

- Hybrid capacitor is fabricated with porous carbon-sulfur as cathode materials.
- The hybrid device displays high energy density of 125.3 Wh kg^{-1} at 17350 W kg^{-1}.
- The application of sulfur is extended to a new field.

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ABSTRACT

The full realization of the high energy density concept in current hybrid capacitors is still a challenge due to the huge difference in specific capacity and reaction kinetics of the commonly used cathode and anode materials. Herein, for the first time, the carbon-sulfur composite is proposed as the high-capacity cathode for hybrid capacitors to achieve a high energy density. The as-prepared carbon-sulfur composite delivers a high specific capacity of 212.2 mAh g^{-1} (424.4 F g^{-1}) at 4 A g^{-1}, which is much higher than that of the pure carbon cathode. Additionally, the kinetics gap between cathode and anode is narrowed by using carbon-sulfur composite as the cathode. As a result, the carbon-sulfur composite based hybrid capacitor delivers a high energy density of 258.4 Wh kg^{-1} at 995 W kg^{-1}. Even at high power density of 17350 W kg^{-1}, the energy density can still remain 125.3 Wh kg^{-1}. This study provides an alternative approach for designing hybrid capacitors with both high energy and power density by using carbon-sulfur composite as the cathode, and also paves a way to extend the application of sulfur to a new field for taking its advantages of high-capacity, environmental friendliness, low-cost.

1. Introduction

The ever-increasing demand for energy storage systems with high energy and power density applied in the field of portable electronic devices and electric vehicles has sparked the intensive research in hybrid capacitors due to its combination of the merits of both high-energy lithium-ion batteries (LIBs) and high-power supercapacitors (SCs) to bridge the gap between them [1–5]. Up to now, activated carbon (AC) is still unbeatable cathode material for hybrid capacitors because it allows hybrid capacitors to be operated at a high voltage [6–8]. Nevertheless, the 100–300 F g^{-1} specific capacity of ACs cathode based on the physical adsorption/desorption of solvated ions at the electrolyte-electrode interface is much lower than that of anode via faradaic process, such a huge capacity difference between cathode and anode impedes the full realization of the high energy density concept [9,10]. Additionally, the energy densities of hybrid capacitors often degrade noticeably at high rates due to the differences in the charge storage kinetics between anode and cathode, because of the reaction kinetics of anode based on the faradaic reaction is far slower than that of the cathode [11,12].

The surface functional groups modification on ACs can be regarded as an alternative solution to improve the capacitance with the aid of pseudocapacitive effect. For instance, Leon L. Shaw functionalized AC powders with C=O groups, leading to the specific capacitance increasing 3 times, which lies in that Li^+ react with C=O groups reversibly to impart pseudocapacitance [13,14]. Unfortunately, the cycle stability of functionalized ACs cathode is always a concern due to the irreversible reactions between oxygen and electrolyte ions, giving rise to the decomposition of the electrolyte [15]. Moreover, the oxygen-modification can distinctly diminish the electrical conductivity of the electrode materials and consequently worsen their electrochemical performance. Recent studies have revealed that addition of lithiated

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intercalation materials into the ACs cathode of lithium-ion hybrid capacitors is another possible strategy to enhance energy density [16–18]. The energy density of hybrid capacitors by using $LiCoO_2$ combined with 5%–20% ACs as cathode and nanostructured $Li_4Ti_5O_{12}$ as anode can be up to 40 Wh kg^{-1}, which is higher than that of hybrid capacitors with ACs as cathode [19]. Due to the low theoretical specific capacity (150–250 mA h g^{-1}) of lithiated intercalation materials, a large amount of materials are needed to add into the ACs cathode to achieve high energy density, while, this will result in an unsatisfied power capability [20,21]. The above unsolved problems have motivated the investigations of alternative cathodes to improve the energy density of hybrid capacitors without compromising their cyclability and power capability. On the other hand, for anode, attempts mainly focus on enhancing rate performance by shortening the ion diffusion length or using pseudocapacitive anode that can reduce the gap of kinetic imbalances during electrochemical reactions in anode and cathode electrodes to realize a high rate performance for hybrid capacitors.

Sulfur(S), a light-weight element, possesses a high theoretical capacity of 1675 mAh g^{-1} based on a two-electron transfer reaction, which is an order of magnitude higher than that of the lithiated intercalation material [22–24]. In combination with the natural abundance and environmental friendliness, sulfur is considered as the next-generation cathode materials for lithium-sulfur (Li-S) battery. Nevertheless, its practical application is hindered currently by the insulating nature of sulfur and high solubility of the long-chain lithium polysulfides generated during the discharge/charge process [25,26]. To settle these shortcomings, sulfur is always incorporated into carbon materials that are capable of delivering electrons efficiently to the sulfur as well as trapping the soluble polysulfides [27,28]. In theory, the lower sulfur content in the carbon host, the higher the sulfur utilization and cycle stability. However, in principle, high sulfur content ($\geq 70\%$) is required in Li-S batteries for achieving a higher energy density [29,30].

Taking another look at the high capacity and shuttle effect of electroactive sulfur at high content, and considering the demands of hybrid capacitors for cathode materials, we propose a use of highly conductive porous carbon loaded a small amount of sulfur as a cathode to well match LIB-type anode. In this situation, the small amount of sulfur filled in the pores of the carbon materials can provide high specific capacity and restrict the dissolution of polysulfides, and the problem of huge capacity difference between cathode and anode of hybrid capacitors will be overcome. Additionally, the kinetics of sulfur based on the redox reaction is similar to that of most anode materials, which narrows the kinetics gap between two electrodes and makes the cathode kinetically match well with the anode.

Herein, we reported the use of carbon-sulfur composite as the cathode to improve the energy density of hybrid capacitors. The resultant composite cathode delivered a high specific capacity of 212.2 mAh g^{-1} (424.4 F g^{-1}) at 4 A g^{-1}, much better than that of the activated carbons without sulfur. Benefiting from the high capacity and moderate kinetics of the carbon-sulfur composite cathode, the fabricated hybrid capacitors delivered a high energy density of 258.4 Wh kg^{-1} at 995 W kg^{-1} and high cycle stability over 3000 running. This result clearly indicates that the carbon-sulfur composite is a promising candidate for high energy density hybrid capacitors, which will give further impetus to explore the fundamental science and applications of sulfur in the context of electrochemical energy storage.

2. Experimental section

2.1. Materials synthesis

At first, the commercially available porous carbon (Ketjenblack EC-600JD) denoted as C-01 and sulfur were ground together, heated to 155 °C in a sealed vacuum tube with a holding time of 12 h to facilitate sulfur diffusion into the carbon host. Then, the composite was maintained in an oven at 300 °C to volatilize sulfur residue on the outer surface of the carbon host. The content of sulfur in the carbon-sulfur composites was varied to be 23 wt% and 33 wt% by adjusting the heating time at 300 °C, which were named CS-02 and CS-03, respectively. The CS-02 with 23 wt% sulfur was obtained by maintaining the carbon-sulfur composite with 70 wt% sulfur in an oven at 300 °C for 160 min and the CS-03 with 33 wt% sulfur was obtained by maintaining the carbon-sulfur composite with 70 wt% sulfur in an oven at 300 °C for 90 min.

2.2. Characterization methods

Microstructural analysis was conducted with a field emission scanning electron microscope (SEM) by using a Hitachi S-4800 instrument at 10 kV, equipped with an energy dispersive X-ray spectrometer (EDX) for detecting the elemental signals and collecting the elemental mapping signals. Nitrogen adsorption-desorption isotherms were measured with a Tristar 3000 sorption analyzer (Micromeritics) at 77.4 K. Before the measurements, the carbon sample C-01 was degassed under vacuum at 200 °C for 12 h and CS-02 and CS-03 was degassed under vacuum at 50 °C for 16 h until the pressure was less than 5 Pa. Pore size distributions were determined from the adsorption branches of the isotherms using density functional theory. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas (S_{BET}). Total pore volumes were calculated from the amount adsorbed at a relative pressure, P/P_0, of 0.99. XRD patterns were obtained with a Rigaku D/MAX-2400 diffractometer using Cu Kα radiation (40 kV, 100 mA, $\lambda = 1.54056$ Å). TEM analyses were carried out with a Tecnai G220S-Twin instrument operating at 200 kV. Samples for TEM analysis were prepared by dropping an ethanol droplet of the products on carbon-coated copper grids and drying at room temperature. Thermogravimetric analysis (TGA) was measured from 40 to 800 °C with a heating rate of 10 °C min^{-1} under a nitrogen flow, using a STA449 F3 Jupiter thermogravimetric analyzer (NETZSCH). XPS data were obtained with an ESCALAB250 electron spectrometer. The conductivity of CS-02 and CS-03 were tested by four-tip probes method.

2.3. Electrochemical characterization

2.3.1. Preparation of electrodes

The cathodes were fabricated by mixing 75 wt% C-01, CS-02 or CS-03 with 15 wt% conductive carbon black and 10 wt% PVDF binder. The anode was prepared by using a mixture of 80 wt% commercial hard carbon, 10 wt% CNT conductive additives, and 10 wt% binder (LA133 and CMC). The mass loadings of the active materials in both cathode and anode are about 1–1.2 and 1.5–2 mg cm^{-2}, respectively.

2.3.2. Assembly of half-cells and LICs

Half cells were assembled to measure the electrochemical performances of C-01, CS-02, CS-03 and commercial hard carbon, in which lithium metal foil was used as the counter and reference electrode and 1 M LiTFSI in DME/DOL (1:1, v/v) was employed as the electrolyte. Celgard 2400 was used as a separator. Commercial hard carbon (HC) electrode was pre-activated for 3 cycles at 50 mA g^{-1} in a Li half-cell to obtain high efficiency and then lithiated to 0.05 V, and then the pre-activated HC anode was coupled with a CS-02 cathode to fabricate a hybrid capacitors, and the mass ratio of cathode/anode was 1:1.5.

2.3.3. Electrochemical tests

Galvanostatic charge/discharge tests of half cells were conducted in a voltage window of 1.7–3.5 V for C-01, CS-02 and CS-03 and 0.01–2.8 V for HC by using a LAND-CT2001 instrument at a room temperature. The specific capacity of the cathode was calculated based on the total mass of sulfur and carbon. Cyclic voltammetry (CV), galvanostatic charge/discharge cycling (GC) and electrochemical impedance spectroscopy (EIS) of hybrid capacitors were performed on a CHI660D electrochemical workstation (CH Instruments, China).