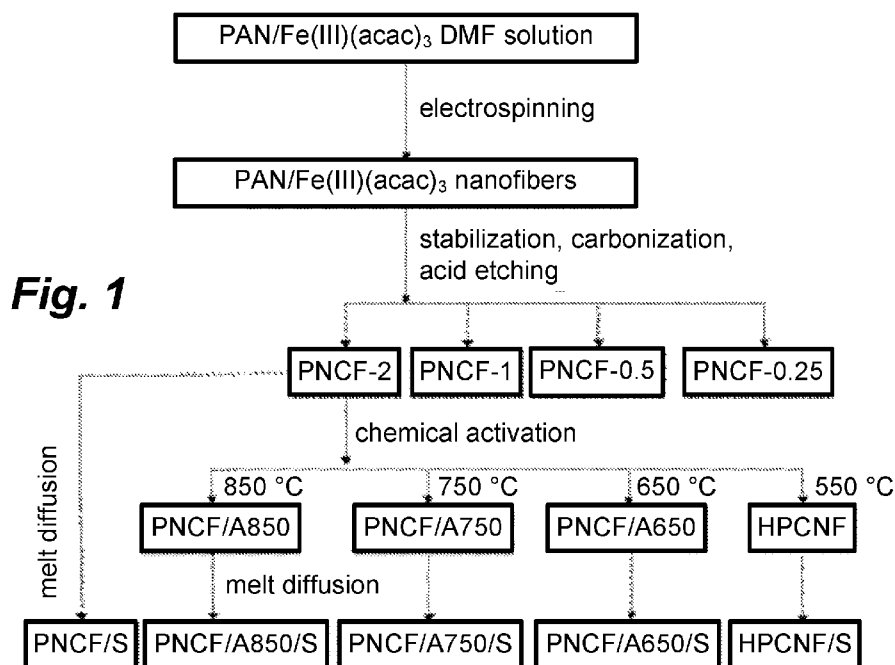


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ATTORNEYS; Yeping, Ding, 10th Floor, Tower D,(54) Title: TUNABLE AND SCALABLE SYNTHESIS OF HIERARCHICAL POROUS NANOCARBON/SULFUR COMPOSITE
CATHODES

(57) **Abstract:** Hierarchical porous carbon nanofiber/sulfur composites (HPCNF/S), useful in the manufacture of lithium sulfur batteries are formed of a cathode having a hierarchical porous carbon nanofiber/sulfur (HPCNF/S) composite, a conductive additive, polyvinylidene fluoride binder and a foil current collector. The HPCNF is formed by electrospinning polyacrylonitrile/iron (III) acetylacetonate fibers from polymer precursor, stabilizing, carbonizing and acid etching to form porous CNFs, effecting chemical activation of porous CNF to form hierarchical porous carbon nanofibers (HPCNFs) and effecting encapsulation of sulfur in pores of HPCNFs by melt-diffusion. When used as a battery, the HPCNF/S composite functions as a cathode.

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**Tunable and Scalable Synthesis of Hierarchical Porous Nanocarbon/Sulfur
Composite Cathodes**

RELATED APPLICATION(S)

[0001] The present Patent Application claims priority to Provisional Patent Application No. 62/493462 filed 6 July 2016, which is assigned to the assignee hereof and filed by the inventors hereof and which is incorporated by reference herein.

BACKGROUND

[0002] Field

[0003] The current disclosure relates to the synthesis of hierarchical porous carbon nanofibers (HPCNFs) and to the process of preparing HPCNF/sulfur (HPCNF/S) composites. In particular, the disclosure relates to the application of HPCNF/S composites as cathodes in rechargeable lithium sulfur batteries (LSBs).

[0004] Background

[0005] The ever-growing portable electronics markets demand energy storage systems with high energy/power densities, long cyclic performance, low costs and ecofriendly characteristics. Among many electrochemical energy storage devices, lithium ion batteries (LIBs) have dominated the market for over two decades benefiting from their long cyclic life, high energy densities and affordability. To satisfy the emerging application in electric vehicles (EVs) requiring higher energy densities of above 500 Wh kg⁻¹, the current LIBs using graphite as anode and lithium metal oxides as cathode are far from sufficient. Lithium sulfur batteries (LSBs) are considered one of the most promising alternatives to LIBs because sulfur can offer a high specific capacity, for example, 1675 mAh g⁻¹, a moderate working potential of about 2.1 V and a remarkable theoretical energy density of 2567 Wh kg⁻¹. Moreover, sulfur is abundant on earth and environmentally benign.

[0006] The wide application of LSBs has been hindered by the poor cyclic stability and low power densities of sulfur cathodes. Three major reasons are responsible:

1. The poor electrical conductivity of sulfur, $5 \times 10^{-30} \text{ S cm}^{-1}$, at room temperature.
2. The dissolution of long-chain lithium polysulfides formed during cycles in the electrolyte and the migration of polysulfides between the anode and cathode in the so-called "polysulfide shuttle" effect.
3. The large volume expansion 80% of sulfur particles during lithiation.

[0007] To mitigate the above issues, sulfur/carbon composites with different micro- and nanostructures have been synthesized to take advantage of the high capacity of sulfur and the excellent electrical conductivities of carbon materials. Among various carbon materials, porous carbon nanofibers (CNFs) seem to be one of the best choices because the highly porous CNFs can offer not only a large empty space to host sulfur particles and to accommodate the volume expansion, but also effectively immobilize polysulfides during cycles. Despite these advantages, currently available CNFs so far developed have many deficiencies:

1. The CNFs derived from direct carbonization of electrospun polymer precursors often result in poor electrical conductivities due to the low degree of graphitization.
2. In addition, the vast majority of the pores created in CNFs are either totally open or closed, making it difficult to control the lithium polysulfides diffusion or incorporate sulfur particles. This means that new design strategies need to be developed to enhance the degree of graphitization and to properly control the geometry and distribution of pores in CNFs.
3. The sulfur loading capacities of most sulfur/CNF composites were below 70 wt.%.
4. High rate capability and high power outputs measured at high current densities have rarely been achieved.

SUMMARY

[0008] Hierarchical porous carbon nanofiber/sulfur composites (HPCNF/S) are formed by electrospinning polyacrylonitrile/iron (III) acetylacetonate neat fibers from a polymer precursor. Stabilization is effected, and the neat fibers are carbonized and acid etched to form porous carbon nanofibers, followed by chemical activation of the porous carbon nanofibers to form hierarchical porous carbon nanofibers (HPCNFs). Encapsulation of sulfur in pores of the HPCNFs is performed by melt-diffusion to form the HPCNF/sulfur (HPCNF/S) composites.

[0009] In one configuration, hierarchical porous carbon nanofiber/sulfur (HPCNF/S) composites are synthesized. A mixture of polyacrylonitrile and iron is provided. The mixture is used to form polyacrylonitrile/iron (III) acetylacetonate neat fibers with different mass ratios of polyacrylonitrile: iron (III) acetylacetonate of 1 : 0.25 to 1 : 2.0, preferably at a range of 1 : 1.07 to 1 : 1.12, by electrospinning to form fibers. The fibers are stabilized and carbonized to obtain carbon nanofiber/Fe₃C composites. The carbon nanofiber/Fe₃C composites are etched with fuming nitric acid, to obtain porous carbon nanofibers, with the porous carbon nanofibers at different mass ratios ranging from 0.25 to 2.0 and preferably between 0.5 and 1.0. The porous carbon nanofibers are chemically activated at different temperatures, to obtain hierarchical porous carbon nanofibers (HPCNFs) having different structures in accordance with the temperatures of chemical activation. Subsequent to activation, a melt-diffusion process is performed on the porous carbon nanofibers to infiltrate molten sulfur to obtain porous carbon nanofiber/sulfur composites corresponding to the different structures, thereby forming hierarchical porous carbon nanofiber/sulfur (HPCNF/S) composites.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Fig. 1 is a flow diagram showing the synthesis processes of hierarchical porous carbon nanofiber/sulfur (HPCNF/S) composites.

[0011] Figs. 2A-C are graphical depictions, showing the porosity of various porous CNF samples. Fig. 2A shows nitrogen adsorption/desorption isotherms of porous CNF prepared with different sacrifice contents. Fig. 2B shows nitrogen

adsorption/desorption isotherms of porous CNFs prepared at different activation temperatures. Fig. 2C shows the pore size distribution of HPCNFs.

[0012] Figs. 3A-3D are photomicrographs of as-prepared HPCNF fibers using the disclosed synthesis method. Fig. 3A is a scanning electron microscope (SEM) image at a low magnification. Fig. 3B is a transmission electron microscope (TEM) image. Figs. 3C-D are high resolution transmission electron microscope (HRTEM) images of graphitic carbon spheres.

[0013] Figs. 4A-G are images of the microstructure of HPCNF/S fibers. Fig. 4A is a TEM image of an individual fiber. Figs. 4B-4D are energy dispersive spectrometer (EDS) mapping images of the fiber, presenting the elemental distributions of carbon, sulfur and nitrogen, respectively. Figs. 4E-G are the EDS elemental maps of graphitic carbon spheres containing sulfur.

[0014] Fig. 5 is a graphical depiction showing a thermogravimetric analysis (TGA) curve of HPCNF/S composite.

[0015] Figs. 6A-C are graphical depictions, showing representations of the electrochemical properties of HPCNF/S composite cathodes. Fig. 6A is the cyclic voltammetry (CV) curves at a scan rate of 0.1 mV s^{-1} between 2.8 and 1.7 V. Fig. 6B is the cyclic performance of HPCNF/S cathodes at 1.0 C in comparison with other porous CNF/S composites. The 1.0 C of 1675 mA g^{-1} is based on the theoretical capacity of sulfur. Fig. 6C is the charge/discharge capacities and Coulombic efficiencies of HPCNF/S cathodes at high current densities of 2.5 and 4.0 C for 100 cycles.

[0016] Figs. 7A-C are equivalent circuit and graphical depictions, showing Nyquist plots of batteries using the PCNF/S, PCNF/A750/S, and HPCNF/S cathodes. Fig. 7A is the equivalent circuit. Fig. 7B is a graph of the Nyquist plots before test and Fig. 7C is a graph of the Nyquist plots measured after 100 cycles at 1.0 C.

DETAILED DESCRIPTION

[0017] Overview

[0018] Hierarchical porous CNFs with ameliorating features are used to prepare advanced porous CNF/sulfur composite cathodes with high rate capabilities and long

cycle life. The CNF/sulfur composite cathodes are developed by controlling the contents of sacrificial agents/catalysis, the chemical activation conditions and optimizing the melt-diffusion process for infiltration of sulfur particles.

[0019] The current disclosure describes the synthesis of HPCNF/S composites using the electrospinning and melt-diffusion approaches. It is noted that there is a distinction between hierarchical porous carbon nanofibers (HPCNFs) and hierarchical porous carbon nanofibers/sulfur (HPCNF/S) and to the process of preparing HPCNF/sulfur (HPCNF/S) composites. Generally, hierarchical porous carbon nanofibers (HPCNFs) are processed by adding sulfur to form HPCNF/sulfur (HPCNF/S) composites.

[0020] HPCNFs with a high specific surface area of $893 \text{ m}^2 \text{ g}^{-1}$, a large pore volume of $0.81 \text{ cm}^3 \text{ g}^{-1}$ and hierarchical pores are successfully prepared by electrospinning. Both the pore size distribution and the pore volume are controllable by adjusting the content of sacrificial agents and activation parameters. Meanwhile, nanoscale hollow graphitic carbon spheres are created by etching the sacrificial agent/catalyzer particles, such as Fe_3C . A melt-diffusion technique is then used to infiltrate molten sulfur into the mesopores to form HPCNF/S composites. The HPCNF/S composites contain a high sulfur loading of 71 wt.%. When used as cathodes for LSBs, the HPCNF/S cathodes present a high capacity of 740 mAh g^{-1} after 200 cycles at 1.0 C. Even at high current densities of 2.5 and 4.0 C, corresponding to a full charge of the electrodes in 24 and 15 min, respectively, the HPCNF/S cathodes deliver exceptionally high capacities of 580 and 540 mAh g^{-1} after 100 cycles with remarkable capacity retention of above 90%. These properties are characterized by way of non-limiting example.

[0021] The present disclosure uses a simple electrospinning approach to produce gram scale HPCNF fibers in laboratory. The HPCNF fibers with desirable pores are produced in three steps: namely, (i) electrospinning of polymer precursors into neat nanofibers, (ii) stabilization, carbonization and etching off the sacrificial particles like Fe_3C , and (iii) activation of porous CNFs with potassium hydroxide (KOH). Graphitic carbon layers and Fe_3C nanoparticles are formed simultaneously in CNFs during the carbonization process, and hollow graphitic carbon spheres are created by subsequent

etching of Fe_3C particles. Micropores are further introduced in the graphitic carbon layers by moderate chemical activation. The porosity of HPCNFs can be easily controlled by adjusting the parameters of iron precursor content, carbonization temperature and chemical etching condition. Molten sulfur is infiltrated into the pores in the HPCNFs by melt-diffusion method. The infiltration of the HPCNFs by the sulfur produces the HPCNF/S composite. The cathodes prepared using the HPCNF/S composites with useful structural features exhibit exceptional cyclic capacities, especially at high current densities.

[0022] The current disclosure describes the synthesis of HPCNF/S composites using one-pot electrospinning and melt-diffusion approaches. Batteries made from the present cathodes can exhibit much improvements over prior art batteries in terms of sulfur loading, electrochemical cyclic stability and high rate capability.

[0023] Process

[0024] Fig. 1 is a flow diagram presenting the operation of a program for the synthesis of HPCNF/S composites. A mixture of polyacrylonitrile (PAN) and iron precursor is used to form PAN/iron (III) acetylacetonate neat fibers with different mass ratios of PAN : iron (III) acetylacetonate of ratios of 1 : 0.25 to 1 : 2.0, preferably at a range of 1 : 1.07 to 1 : 1.12, which are obtained by electrospinning (step 1). Example ratios are so example of 1 : 0.25, 1 : 0.5, 1 : 1.0 and 1 : 2.0. The neat fibers are stabilized in air at 220 °C for 3 h at a ramp rate of 5 °C min⁻¹ followed by carbonization to obtain CNF/ Fe_3C composites. The term "neat fibers" refers to as-obtained fresh fibers without any treatment. The CNF/ Fe_3C composites are etched with fuming nitric acid (step 2), to obtain porous CNFs (PCNFs), which are designated as PCNF-0.25, PCNF-0.5, PCNF-1 and PCNF-2 depending on their mass ratios. The porous fibers PCNF-2 are designated as PCNF therefrom and chemically activated at different temperatures between 550° C and 850° C, to obtain HPCNF(PCNF/A550), PCNF/A650, PCNF/A750 and PCNF/A850, depending on the activation temperature applied (step 3). After the activation, the porous CNFs underwent a melt-diffusion process to infiltrate molten sulfur (step 4), to obtain porous CNF/sulfur composites, including HPCNF/S (PCNF/A550/S), PCNF/A650/S, PCNF/A750/S,

PCNF/A850/S and PCNF/S. The different temperature designations, such as PCNF/A650, PCNF/A750, PCNF/A850 help to identify the activation temperature used to prepare these porous CNFs. The temperature ranges between 550° C and 850° C are given as non-limiting examples, and different ranges can be used within the scope of the disclosed technology.

[0025] Accordingly, HPCNF/S is made from HPCNF, and HPCNF is made by activating PCNF at 550 °C with KOH. PCNF/S is made from PCNF (PCNF-2).

[0026] The present disclosure technology provides a process for the preparation of HPCNF/S and their application as LSB cathodes. The process has distinct advantages of large scale production, a high degree of graphitic carbon, controllable porosity and excellent electrochemical properties of resultant cathodes. The technique uses the following process steps:

1. Electrospinning PAN/iron (III) acetylacetonate neat fibers using polymer precursor
2. Stabilization, carbonization and acid etching of neat fibers to form porous CNFs
3. Chemical activation of porous CNF to form HPCNFs
4. Encapsulation of molten sulfur in the pores of HPCNFs by melt-diffusion, thus forming the HPCNF/S composites

[0027] Preparation of cathodes comprising HPCNF/S composites

[0028] HPCNFs are prepared by electrospinning followed by stabilization, carbonization, acid etching and chemical activation, involving the formation of mesopores by etching Fe₃C particles and micropores by KOH activation. The amount of mesopores can be increased by increasing the content of iron precursor; however, the fibrous structure is difficult to obtain by electrospinning if the weight ratio of iron precursor to PAN is larger than 2. The activation is carried out at different temperatures, where the mass ratio of KOH to CNFs and the activation duration are already optimized in this disclosure.

[0029] The HPCNF/S are prepared by:

[0030] Step 1 - Electrospinning PAN/ iron (III) acetylacetonate neat nanofibers from polymer precursor: The electrospinning precursor is prepared by dissolving 0.5 g PAN ($M_w = 150,000$, supplied by Aldrich) in 10 ml N,N-dimethylformamide (DMF) solvent and magnetically stirring for 8 h at 80° C. Then, 1.0 g iron (III) acetylacetonate powder is added into the above solution, and keeps stirring for another 8 h. Other samples with 0.125, 0.25 and 0.5 g iron (III) acetylacetonate in 0.5 g PAN solution are also prepared. The polymer mixture solution is used for electrospinning on an electrospinner (KATO Tech. Co., Japan). A high voltage of 18 kV is applied between the stainless steel needle and aluminum foil collector, where a fixed distance of 15 cm between them is maintained during spinning. The flow rate of the polymer precursor is kept at 1.0 ml h⁻¹ and the rotation speed of the drum collector is 1.0 m min⁻¹. After electrospinning and drying in air at room temperature, the PAN/iron (III) acetylacetonate films are peeled off from the Al foil to obtain freestanding polymer fiber films.

[0031] Step 2 – Stabilization, carbonization and acid etching of neat fibers to form porous CNFs: The PAN/ iron (III) acetylacetonate films are stabilized in an oven (Memmert ULE500) in air at 220° C for 3 h. Then, the films are carbonized in a tube furnace at a temperature of 650° C under N₂ flow for 0.5 h at a ramp rate of 5° C min⁻¹. By way of non-limiting example, a temperature between 550° C and 950° C is applied to optimize the carbonization temperature for CNFs with the most balanced structure and properties. The established optimal temperature is 650° C which simultaneously gives a high degree of nitrogen doping and small-size Fe₃C particles. In sequence, the CNF films are soaked in 25 ml fuming nitric acid (HNO₃, 68 wt.%) for 12 h at 90° C to remove the Fe₃C nanoparticles. The porous CNFs are collected by vacuum filtration and washing with di-ionized (DI) water three times and the products are designated as PCNF-0.25, PCNF-0.5, PCNF-1 and PCNF-2 depending on their iron precursor contents.

[0032] Step 3 - Chemical activation of porous CNFs to form HPCNFs: Due to the largest pore volume and specific surface area, PCNF-2 is selected for the following processes and designated as PCNF. The PCNF films are mixed with KOH particles at

a mass ratio of 1:4, and then the mixture is transferred into a tube furnace and heated at 550° C for 0.5 h at a ramp rate of 2° C min⁻¹. The resultant materials are soaked in diluted hydrochloride acid (water : HCl, 9:1 by volume) and stirred for 8 h to remove the residual KOH particles. HPCNFs are obtained by vacuum filtration and washing with DI water, followed by drying in a vacuum oven (Thermcraft/Eurotherm) for 3 h at 80° C. The materials are also prepared at different activation temperatures, including 650° C, 750° C and 850° C, which are designated as PCNF/A650, PCNF/A750 and PCNF/A850.

[0033] Step 4 - Encapsulation of molten sulfur in the pores of HPCNFs by melt-diffusion to form the HPCNF/S composite: The HPCNFs and sulfur are mixed at a mass ratio of 1:4, and the mixture is soaked in carbon disulfide (CS₂) solution and stirred for 1 h to impregnate the dissolved sulfur molecular into the mesopores of HPCNFs. Then, the solvent is dried and the HPCNFs mixture is collected and placed in a tube furnace at 155° C for 12 h under N₂ flow to further infiltrate sulfur particles into HPCNFs to form the HPCNF/S composite. The HPCNF/S composite is heated at 250° C for 0.5 h to remove the sulfur particles attached on the fiber surface before cooling down to room temperature. Other porous CNF/sulfur composites are also prepared in the same way and designated as PCNF/A650/S, PCNF/A750/S, PCNF/A850/S and PCNF/S. The sulfur content encapsulated in the pores of HPCNFs has a range of about 50 wt.% to about 75 wt.%. In one non-limiting example, the sulfur content encapsulated in the pores of HPCNFs was 71 wt.%.

[0034] Step 5 - Preparation of cathodes comprising HPCNF/S composites: The HPCNF/S composites are mixed with carbon black (super P) and polyvinylidene fluoride (PVDF) binder at a mass ratio of 7:2:1 using N-methyl-2-pyrrolidone (NMP) solvent. The slurry is magnetically stirred overnight (about 8 h) and cast onto an aluminum foil to form a thin film. After drying at 80° C in an air-circulated oven, the cathode electrodes are cut into discs of 14 mm in diameter with a sulfur content of about 1.0 mg cm⁻².

[0035] By way of non-limiting example, a thickness of the cathode materials of about 5 μm to about 35 μm and a mass loading of sulfur of about 0.25 mg cm⁻² to about 2 mg cm⁻². The specific temperatures and flow rates are given as non-limiting

examples, and different ranges can be used within the scope of the disclosed technology.

[0036] Materials

[0037] The following reagents and solvent are used without further purification: polyacrylonitrile (PAN, Mw = 150, 000, Sigma-Aldrich), N,N-dimethylformamide (DMF, 99.8%, Sigma-Aldrich), iron(III) acetylacetonate (97%, Sigma-Aldrich), nitric acid (69-72%, Fisher), potassium hydroxide (KOH, $\geq 85\%$, Sigma-Aldrich), hydrochloric acid (HCl, 37 %, Sigma-Aldrich), carbon disulfide (CS₂, $\geq 99.9\%$, Sigma-Aldrich), sulfur powder (purum p.a., $\geq 99.5\%$, Sigma-Aldrich), carbon black (super P, Timcal Graphite & Carbon), polyvinylidene fluoride (PVDF, Mw = 180,000, Aldrich), N-methyl-2-pyrrolidone (NMP, 99.5%, Sigma-Aldrich), bis-trifluoromethane sulfonylimide (LiTFSI, 99.95%, Sigma-Aldrich), 1,3-dioxolane (DOL, 99%, Sigma-Aldrich) and 1,2-dimethoxyethane (DME, 99.5%, Sigma-Aldrich). Accordingly, HPCNF/S composites can be mixed with carbon black, the carbon black forming a conductive additive and the polyvinylidene fluoride as polymer binder into slurry using NMP solvent.

[0038] Characterization

[0039] The morphologies are characterized using a scanning electron microscope (SEM, 6700F) and a transmission electron microscope (TEM, JEOL2010). The elemental mapping of HPCNFs fibers is conducted on an energy dispersive spectrometer (EDS) within TEM JEOL2010. The N₂ adsorption/desorption isotherms are obtained at 77 K using an automated adsorption apparatus (Micromeritics, ASAP 2020). The surface area and pore size distribution are determined based on the Brunauer-Emmett-Teller (BET) equation and non-localized density functional theory (NLDFT), respectively. The composition of the HPCNF/S composite is evaluated by thermogravimetric analysis (TGA, Q5000) at a heating rate 5° C min⁻¹ in a nitrogen atmosphere.

[0040] Fabrication process

[0041] HPCNF/S composite electrodes are produced in the form of thin film using a single-nozzle electrospinning and a melt-diffusion method. The HPCNF is formed by etching Fe_3C nanoparticles with nitric acid and chemical activation with KOH. The encapsulation of sulfur in the pores of HPCNF is realized by simple melt-diffusion.

[0042] Experiment 1

[0043] Preparation of the HPCNF/S composites: The electrospinning precursor is prepared by dissolving 0.5 g PAN in 20 ml DMF solvent and magnetically stirring for 8 h at 80°C . Then, 1.0 g iron (III) acetylacetonate is added into the above solution and kept stirring for another 8 h. The polymer solution mixture is used for electrospinning on an electrospinner. A high voltage of 18 kV is applied between the stainless steel needle and aluminum foil collector, where a constant distance of 15 cm is maintained in between. The flow rate of electrospinning is kept at 1.0 ml h^{-1} and the rotation speed of the drum collector is 1.0 m min^{-1} . The PAN/iron (III) acetylacetonate films are then stabilized in an oven in air at 220°C for 3 h. Subsequently, the films are carbonized in tube furnace (Lindberg/Blue, 1700°C) at 650°C under N_2 flow for 0.5 h at a ramp rate of 5°C min^{-1} . The resultant CNF films are soaked in fuming HNO_3 at 90°C for 12 h to remove the Fe_3C nanoparticles. Different groups of porous CNFs are prepared by altering the mass ratios of iron (III) acetylacetonate to PAN when preparing the electrospinning precursor. The porous CNFs are collected by vacuum filtration and mixed with KOH at a mass ratio of 1:4. The porous CNF/KOH mixture is then transferred into a tube furnace and heated at 550°C for 0.5 h at a ramp rate of 2°C min^{-1} . The resulting materials are washed with diluted HCl acid and water to obtain HPCNF. The HPCNF is mixed with sulfur particles at a mass ratio of 1:4, and stirred in CS_2 solution for 0.5 h before drying. The HPCNFs mixture is placed in a tube furnace under N_2 flow and heated at 155°C for 12 h to impregnate molten sulfur into the HPCNFs to form the HPCNF/S composite.

The remnant sulfur particles on the surface of HPCNF/S are removed by heating at 250° C for another 0.5 h.

[0044] Experiment 2

[0045] Characterization of CNFs, HPCNFs and HPCNF/S composites: The morphologies of HPCNFs and HPCNF/S composite are characterized by SEM, TEM techniques, and the elemental distributions of HPCNF/S composite are evaluated by EDS mapping facilities equipped on TEM. The porosities of porous CNFs and HPCNFs are determined by N₂ adsorption/desorption isotherms, where the specific surface area and the pore size distribution are evaluated by BET and NLDFT methods, respectively. The chemical compositions of HPCNF/S composite are studied by TGA from RT to 400° C at a heating rate of 5° C min⁻¹ in a nitrogen atmosphere.

[0046] Fig. 2 is a graphical display output showing the porosity of porous CNFs prepared with different sacrifice contents and activation temperatures. Fig. 2A shows the N₂ adsorption/desorption isotherms of PCNF-0.25, PCNF-0.5, PCNF-1 and PCNF-2. All samples are typical of type IV corresponding to a mesoporous structure. The pore volumes and specific surface areas are 0.39, 0.52, 0.58 and 0.79 cm³ g⁻¹ and 266, 299, 401 and 509 m² g⁻¹ for PCNF-0.25, PCNF-0.5, PCNF-1 and PCNF-2, respectively. These values imply the porosity of CNFs increases positively with increasing the amount of iron (III) acetylacetonate in PAN. PCNF-4 fibers or above containing excessive iron (III) acetylacetonate are difficult to prepare due to the too low viscosity of polymer precursor to form fibers by electrospinning. The PCNF-2 is selected for further investigation and designated as PCNF. Fig. 2B shows N₂ adsorption/desorption isotherms of porous CNFs prepared at different activation temperatures. It is noteworthy that the PCNF activated at 550° C designated as HPCNF has the best electrochemical properties after infiltration of sulfur, to be discussed later. The pore volumes and specific surface areas of the four samples are 0.81, 0.82, 0.86, 0.89 cm³ g⁻¹ and 893, 993, 1277 and 665 m² g⁻¹, respectively. These results suggest that the chemical activation significantly enhances the porosity of PCNFs and the porosity is dependent on activation temperature. The HPCNFs display typical of a type I/IV isotherm with a high adsorption volume at low relative

pressure, P/P_0 , below 0.1, and a hysteresis loop at P/P_0 between 0.4 and 1.0. The Type I/IV isotherm refers to a bimodal micro and mesopores. As depicted in Fig. 2C, the pore size distribution of HPCNFs, the peaks for mesopores are centered at 2.7, 25, 37 and 50 nm and the peaks for micropores are centered at 0.54, 0.86 and 1.26 nm. The mesopores can act as the sulfur container and the micropores are useful for charge transfer and entrapment of polysulfides.

[0047] Figs. 3A-3D are photomicrographs of as-prepared HPCNF fibers using the disclosed synthesis method. Fig. 3A is a scanning electron microscope (SEM) image at a low magnification. Fig. 3B is a transmission electron microscope (TEM) image. Figs. 3C-D are high resolution transmission electron microscope (HRTEM) images of graphitic carbon spheres. Figs. 4A-G are images of the microstructure of HPCNF/S fibers. Fig. 4A is a TEM image of an individual fiber. Figs. 4B-4D are energy dispersive spectrometer (EDS) mapping images of the fiber, presenting the elemental distributions of carbon, sulfur and nitrogen, respectively. Figs. 4E-G are the EDS elemental maps of graphitic carbon spheres containing sulfur. Fig. 5 is a graphical depiction showing a thermogravimetric analysis (TGA) curve of an HPCNF/S composite.

[0048] The low magnification SEM image of Fig. 3A shows HPCNFs, showing rough surface of HPCNFs and macropores between the fibers. Fig. 3B shows the mesoporous structure of HPCNFs. Fig. 3C is a HRTEM image of hollow graphitic carbon spheres. In Fig. 3D, micropores are observed within the graphitic carbon layers, which are beneficial to fast ion diffusion without compromising the lithium polysulfide immobilization.

[0049] Fig. 4A shows a TEM image of HPCNF/S composite with a solid structure, indicating successful encapsulation of sulfur. The presence of sulfur within the HPCNF/S composite is further demonstrated by the uniform distribution of C, N and S by EDS mapping in Figs. 4B-D. The N-doping is attributed to the highly intrinsic nitrogen content in the PAN precursor. The HRTEM image and corresponding EDS mapping of a hollow carbon sphere/sulfur are presented in Figs. 4E-G. The conductive HPCNF/S composite acts as a scaffold of sulfur particles and interconnected network to ensure the high electrical conductivity of the composite.

The sulfur content of the HPCNF/S composite determined by TGA is 71 wt.%, as shown in Fig. 5.

[0050] Experiment 3

[0051] Synthesis of LSBs comprising HPCNF/S composite cathodes: The HPCNF/S composite cathodes are prepared by mixing HPCNF/S composite, carbon black and PVDF binder at a mass ratio of 7:2:1 in NMP solvent. The uniformly mixed slurry is cast onto an aluminum foil to form a thin film. After drying at 80° C in an air-circulated oven, the cathode electrodes are cut into discs of 14 mm in diameter with an average sulfur loading of about 1.0 mg cm⁻². CR2032 coin cells are assembled in an argon-filled glovebox using HPCNF/S composite as the cathode and lithium foil as the anode. The 1.0 M lithium bis-trifluoromethane sulfonylimide (LiTFSI) dissolved in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1, v:v) with 1 wt.% LiNO₃ additive is used as electrolyte, and the polyethylene membrane (Celgard 2400) is employed as the separator.

[0052] Experiment 4

[0053] Electrochemical characterization of the HPCNF/S composite cathodes: The half cells prepared in Experiment 3 are cycled at different current densities between 1.7 and 2.8 V on a LAND 2001CT battery tester. Cyclic voltammetry (CV) curves are obtained on a CHI660c electrochemical workstation between 1.7 and 2.8 V at a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectra (EIS) are measured on the CHI660c electrochemical workstation at a constant perturbation amplitude of 5 mV in the frequency range from 10 mHz to 100 kHz.

[0054] Figs. 6A-C are graphical depictions, showing representations of the electrochemical properties of HPCNF/S composite cathodes. Fig. 6A is the cyclic voltammetry (CV) curves at a scan rate of 0.1 mV s⁻¹ between 2.8 and 1.7 V. Fig. 6B is the cyclic performance of HPCNF/S composite cathodes at 1.0 C in comparison with other porous CNF/S composites. The 1.0 C of 1675 mA g⁻¹ is based on the theoretical capacity of sulfur. Fig. 6C is the charge/discharge capacities and Coulombic

efficiencies of HPCNF/S composite cathodes at high current densities of 2.5 and 4.0 C for 100 cycles. 1.0 C refers to the current density that the battery needs to complete one discharge or charge in one hour. 1.0 C is equal to 1.0 C rate. For sulfur cathodes, the theoretical specific capacity is 1675 mAh g⁻¹, so 1.0 C = 1675 mA g⁻¹. The batteries can be tested at different C rates like 0.1 C, 0.2 C and 2 C, corresponding to 167.5, 335 and 3350 mA g⁻¹, respectively.

[0055] Fig. 6A shows the CV curves of a LSB in the first four cycles. During the lithiation sweeping, the HPCNF/S composite cathode presents two reduction peaks located at 1.94 and 2.22 V in the first cycle, which upshift to 2.0 and 2.3 V and remain stable in the following cycles. These observations are attributed to the formation of long-chain polysulfides and the conversion of polysulfide to lithium sulfides, Li₂S and Li₂S₂, respectively. The prominent peak located at 2.42 V in the delithiation sweeping is assigned to the conversion of lithium sulfides to sulfur. The perfectly overlapped CV curves in the 2nd-4th cycles indicate excellent reversibility of the electrochemical reactions in the HPCNF/S composite cathodes. To evaluate the cyclic stability of the HPCNF/S composite cathodes, especially at high current densities, the HPCNF/S composite cathode is cycled at 1.0 C for 200 cycles as shown in Fig. 6B. The initial reversible capacity of HPCNF/S composite cathode is 913 mAh g⁻¹ with a Coulombic efficiency of 97%. The HPCNF/S composite cathodes maintain a high capacity of 740 mAh g⁻¹ with capacity retention of 81% after 200 cycles. This value is much higher than 439, 552, 498 and 501 mAh g⁻¹ for the PCNF/A850/S, PCNF/A750/S, PCNF/A650/S and PCNF/S cathodes, respectively. In addition, the HPCNF/S composite cathodes also deliver excellent capacities of 581 and 540 mAh g⁻¹ after 100 cycles with exceptional capacity retention of above 90% at extremely high rates of 2.5 and 4.0 C. These remarkable electrochemical performances are attributed to the synergetic effects of ameliorating structural features, such as the hollow graphitic carbon spheres preventing polysulfide diffusion, the numerous internal micro/mesopores facilitating fast ion diffusion and the graphitic carbon layers with excellent electronic/ionic conductivities.

[0056] Nyquist plots and an equivalent circuit of the batteries containing PCNF/S, PCNF/A750/S and HPCNF/S composite cathodes are measured and simulated before and after 100 cycles at 1.0 C as shown in Figs. 7A-C and Table 1. Here, the R₀,

R_{ct1} and R_{ct2} in the equivalent circuit correspond to the system resistance, electrolyte-electrode interface resistance and charge transfer resistance, respectively. For fresh cells, R_{ct1} of the PCNF/A750/S is the smallest (89.5 ohms vs. 250.9 ohms for PCNF/S and 244.1 ohms for HPCNF/S composite), suggesting the lowest electrolyte-electrode contact resistance due to the largest surface area of $1277 \text{ m}^2 \text{ g}^{-1}$ for PCNF/A750. After 100 cycles, however, the HPCNF/S composite cathodes deliver the smallest R_{ct1} of 16.2 ohms, which is much lower than 244.1 ohms of the neat HPCNF/S composite cells measured before cycles. The significant decrease in electrolyte-electrode interface resistance may be associated with the structural rearrangement of sulfur particles and the effective electrolyte permeation during cycles. The charge transfer resistances of HPCNF/S composite before and after cycling are 1.33 and 1.66 ohms, confirming the effective polysulfides entrapment of micropores in HPCNF/S composite cathodes.

[0057] Controlling impedance

[0058] Figs. 7A-C are equivalent circuit and graphical depictions, showing Nyquist plots of batteries using the PCNF/S, PCNF/A750/S and HPCNF/S composite cathodes. Fig. 7A is the equivalent circuit. Fig. 7B is a graph of the Nyquist plots before test and Fig. 7C is a graph of the Nyquist plots measured after 100 cycles at 1.0 C. Table 1 presents the fitted values for the equivalent circuit elements by simulating electrochemical impedance spectroscopy (EIS) data in Figs. 7B and C, where R_0 , R_{ct1} , R_{ct2} refer to the impedances caused by electrode components, electrolyte-electrode interface and charge transfer, respectively:

Sample	R_0 / ohm	R_{ct1} / ohm	R_{ct2} / ohm
Fresh			
PCNF/S	0.86	250.9	18.6
PCNF/A750/S	0.82	89.49	13.36
HPCNF/S	0.81	244.1	1.33
100 th cycle			
PCNF/S	2.45	17.54	5.19
PCNF/A750/S	2.34	30.08	3.81
HPCNF/S	0.98	16.22	1.66

(Table 1)

[0059] The charge transfer resistance of HPCNF/S composite cathodes may be about 244 ohms prior to cycling and stay below 16 ohms even after 100 cycles. The PCNF/S and PCNF/A750/S cathodes present charge transfer resistances of about 17 and 30 ohms, respectively, which are larger than that of HPCNF/S composite after 100 cycles, indicating that the latter electrode performed better than the former electrodes in immobilizing the lithium polysulfide and maintaining fast charge transfer. This observation is despite of the fact that the latter electrode has a large semicircle diameter before cycles.

[0060] Conclusion

[0061] Although only exemplary embodiments are described for the disclosure, it will be understood that many additional changes in the details, materials, steps and arrangement of parts, which have been herein described and illustrated to explain the nature of the subject matter, may be made by those skilled in the art. Additional changes in terms of electrospinning parameters, carbonization temperatures, sacrificial agent content, degree of chemical activation, sulfur content and arrangement of parts, which have been herein described and illustrated to explain the nature of the subject matter, may be made by those skilled in the art within the principle and scope of the disclosure as expressed in the appended claims.

CLAIMSWhat is claimed is:

1. A method for preparing hierarchical porous carbon nanofiber/sulfur composites (HPCNF/S), the method comprising:

electrospinning polyacrylonitrile/iron (III) acetylacetonate neat fibers from polymer precursor;

effecting stabilization, carbonization and acid etching of neat fibers to form porous carbon nanofibers;

effecting chemical activation of the porous carbon nanofibers to form hierarchical porous carbon nanofibers (HPCNFs);

effecting encapsulation of sulfur in pores of the HPCNFs by melt-diffusion to form the HPCNF/sulfur (HPCNF/S) composites.

2. Method of synthesizing hierarchical porous carbon nanofiber/sulfur composites (HPCNF/S) composites, the method comprising:

providing a mixture of polyacrylonitrile and iron and using the mixture of polyacrylonitrile and iron are used to form polyacrylonitrile/iron (III) acetylacetonate neat fibers with different mass ratios of polyacrylonitrile: iron (III) acetylacetonate of 1 : 0.25 to 1 : 2.0, preferably at a range of 1 : 1.07 to 1 : 1.12, by electrospinning to form fibers;

stabilizing the fibers;

carbonizing the fibers to obtain carbon nanofiber/ Fe_3C composites;

etching the carbon nanofiber/ Fe_3C composites with fuming nitric acid, to obtain porous carbon nanofibers, the porous carbon nanofibers at different mass ratios ranging from 0.25 to 2.0 and preferably between 0.5 and 1.0;

chemically activating the porous carbon nanofibers at different temperatures within a predetermined range, to obtain hierarchical porous carbon nanofibers (HPCNFs) having different structures in accordance with the temperatures of chemical activation;

subsequent to activation, execute a melt-diffusion process on the porous carbon nanofibers to infiltrate molten sulfur to obtain porous carbon nanofiber/sulfur composites corresponding to the different structures, thereby forming hierarchical porous carbon nanofiber/sulfur (HPCNF/S) composites.

3. The method of claim 1 or 2, further comprising:
preparing battery cathodes comprising HPCNF/S composite.
4. The method of claim 1 or 2, further comprising the application of one-pot electrospinning to prepare one-dimensional carbon nanofibers.
5. The method of claim 1 or 2, further comprising varying mass ratios of polyacrylonitrile : iron (III) acetylacetonate to alter the amount of mesopores in porous carbon nanofibers.
6. The method of claim 1 or 2, further comprising varying mass ratios of polyacrylonitrile : iron (III) acetylacetonate at a range of 1 : 0.25 to 1 : 2.0, preferably at a range of 1 : 1.07 to 1 : 1.12, to alter the amount of mesopores in porous carbon nanofibers.
7. The method of claim 1 or 2, further comprising the selecting temperatures of chemical activation to control the porosity of activated porous carbon nanofibers.

8. The method of claim 1 or 2, further comprising the employment of chemical activation at different temperatures including 550, 650, 750 and 850° C to control the porosity of activated porous carbon nanofibers.

9. The method of claim 1 or 2, further comprising the employment of chemical activation at different temperatures at a range of 550-850° C, preferably at a range of 550-650° C to control the porosity of activated porous carbon nanofibers.

10. The method of claim 1 or 2, further comprising:
encapsulating the sulfur into the hollow graphitic carbon spheres by melt-diffusion at approximately 155° C, following the electrospinning, stabilization, carbonization, acid etching and chemical activation.

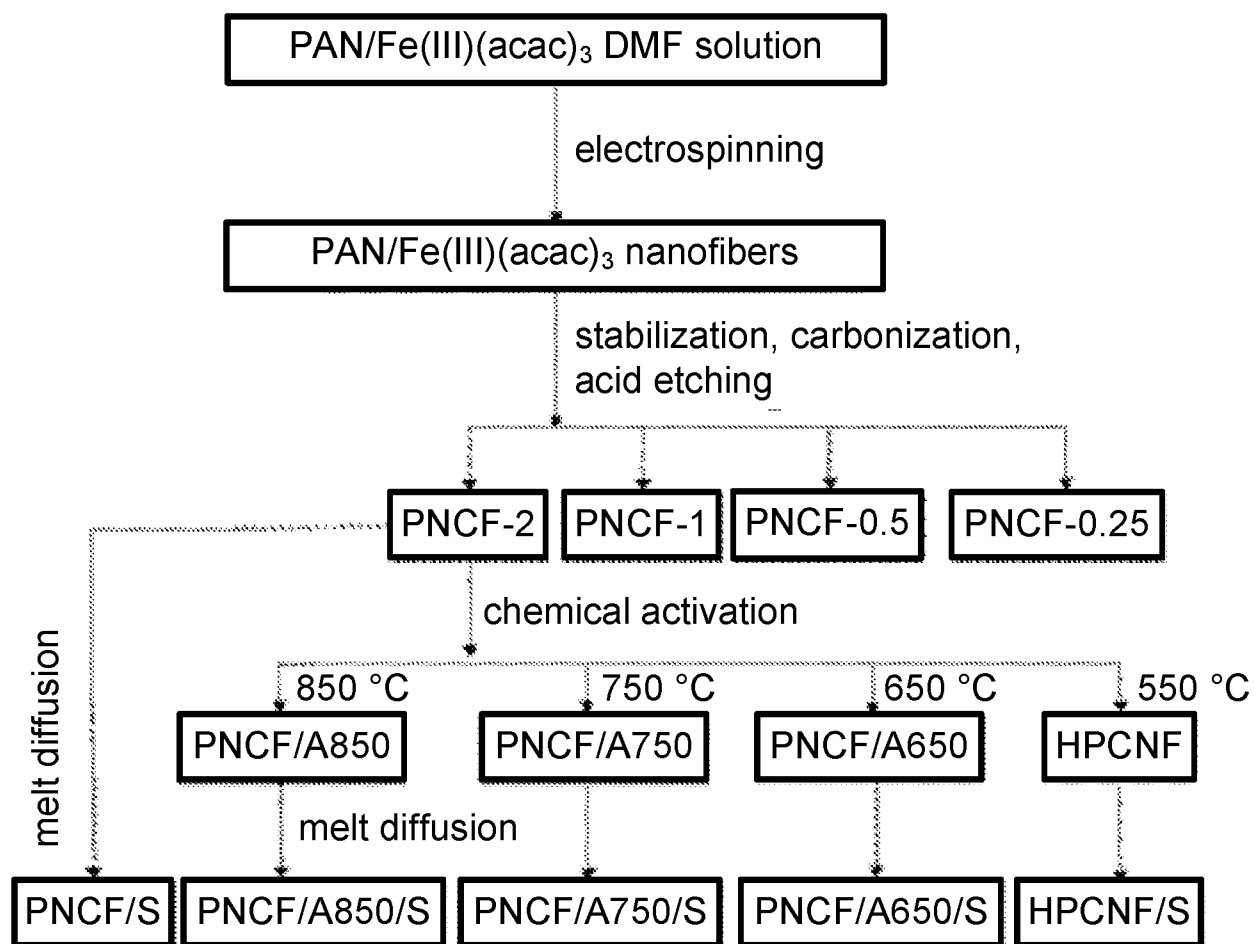
11. The method of claim 1 or 2, further comprising:
providing a mixture of polyacrylonitrile and iron precursor;
electrospinning the mixture, followed by stabilization and carbonization to form CNF containing Fe₃C particles;
acid etching Fe₃C particles to form mesopores and applying KOH activation to form micropores in CNF; and
controlling the amount of mesopores by increasing a content of iron precursor, while limiting a weight ratio of the iron precursor to polyacrylonitrile to less than approximately 2.

12. A HPCNF/S composite formed by the method of claim 1 or 2, wherein the macropores, mesopores and micropores provide electrolyte infiltration channels, sulfur particle container and ion diffusion paths, respectively, and wherein micropores of less than 2 nm effectively prevent lithium polysulfide shuttling.

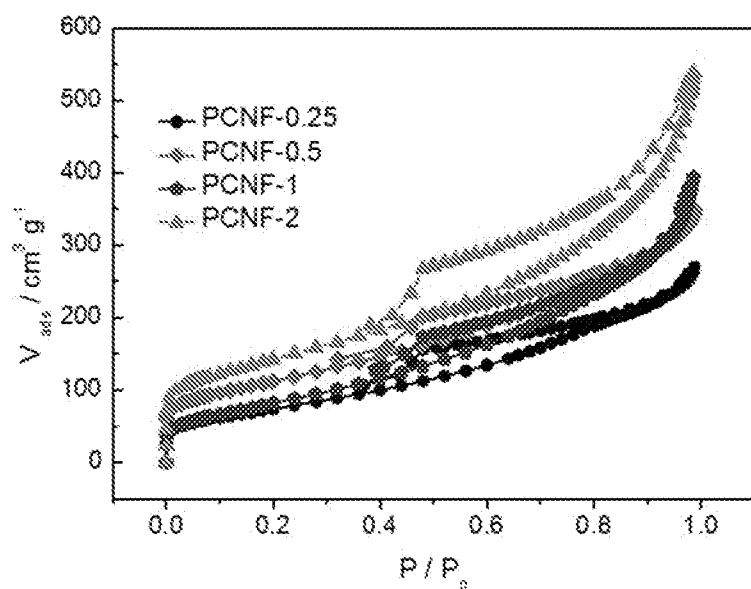
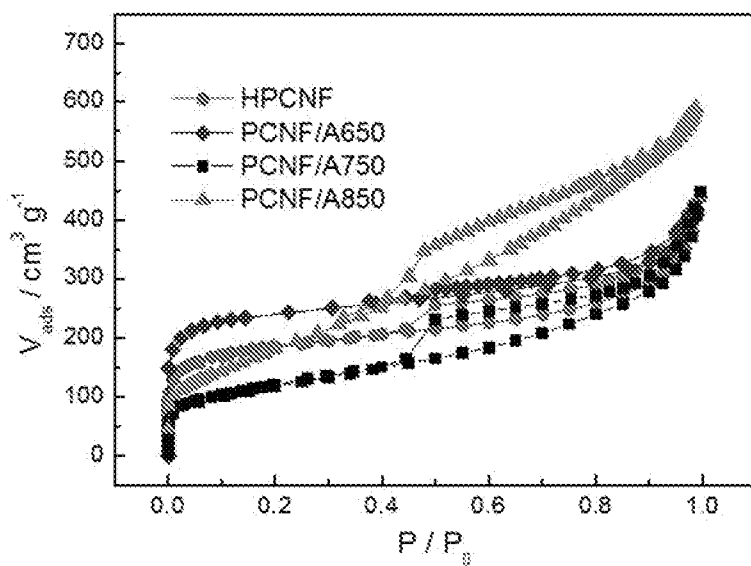
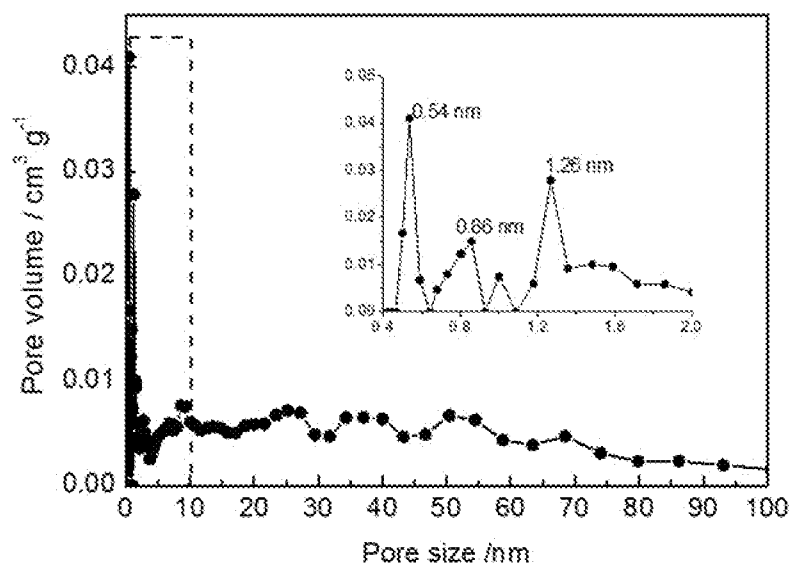
13. The HPCNF/S composite of claim 12, wherein the sulfur particles are encapsulated in the hollow graphitic carbon spheres.

14. The HPCNF/S composite of claim 12, wherein the sulfur content encapsulated in the pores of HPCNFs has a range of about 50 wt.% to about 75 wt.%.
15. A lithium sulfur battery comprising:
a cathode comprising hierarchical porous carbon nanofiber/sulfur (HPCNF/S) composite, conductive additive, polyvinylidene fluoride binder and Al foil current collector;
an electrolyte;
a separator; and
an anode.
16. The lithium sulfur battery of claim 15, wherein the anode comprises lithium metal foil.
17. The lithium sulfur battery of claim 15, further comprising:
HPCNF/S composites mixed with carbon black, the carbon black forming a conductive additive and the polyvinylidene fluoride as polymer binder into slurry using NMP solvent.
18. The lithium sulfur battery of claim 15, further comprising:
a thickness of the cathode materials of about 5 μm to about 35 μm and a mass loading of sulfur of about 0.25 mg cm^{-2} to about 2 mg cm^{-2} .
19. The lithium sulfur battery of claim 15, wherein the charge transfer resistance of HPCNF/S composite cathode significantly decreases after 100 cycles.

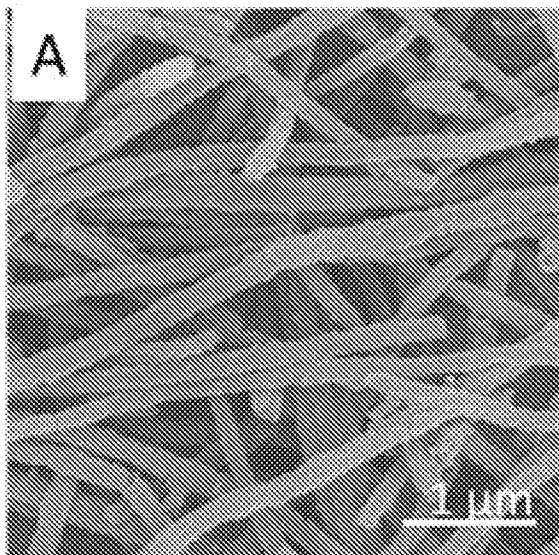
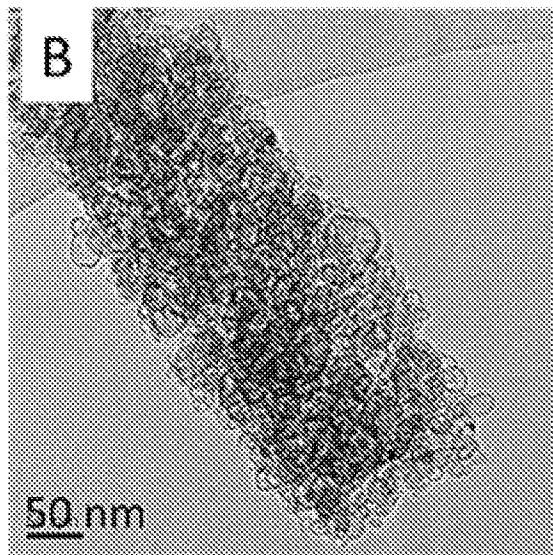
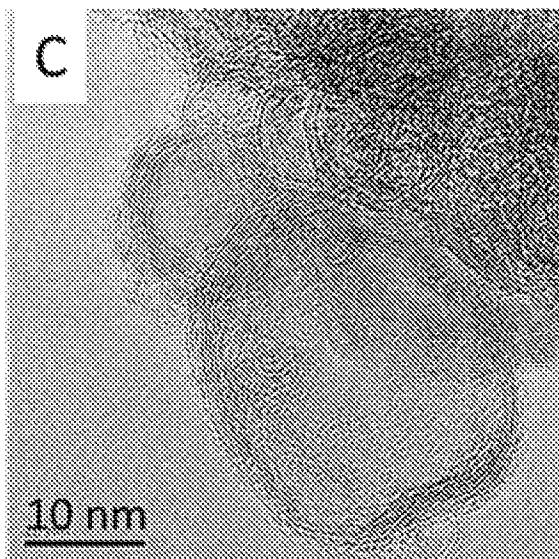
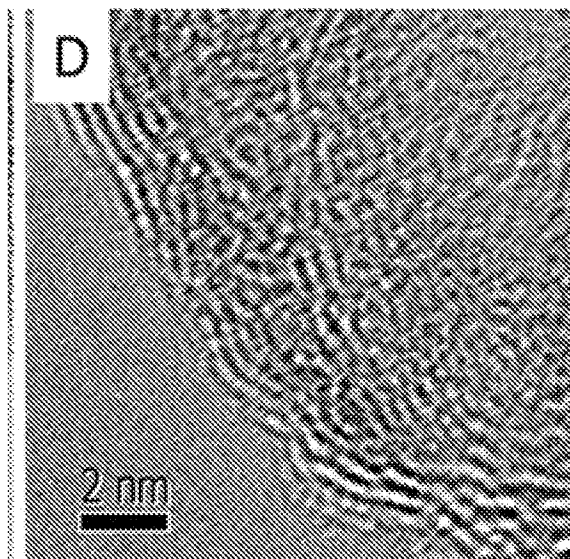
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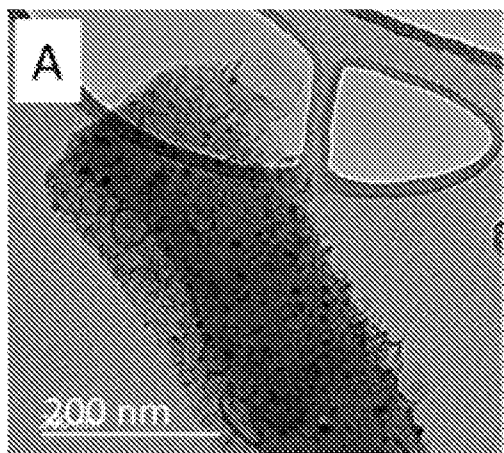
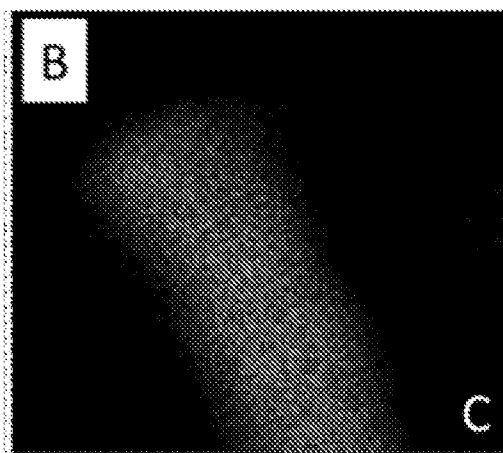
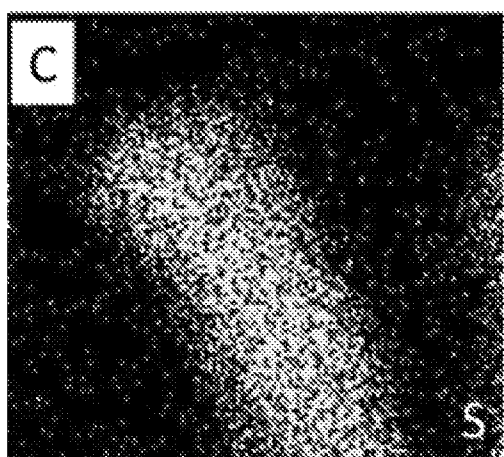
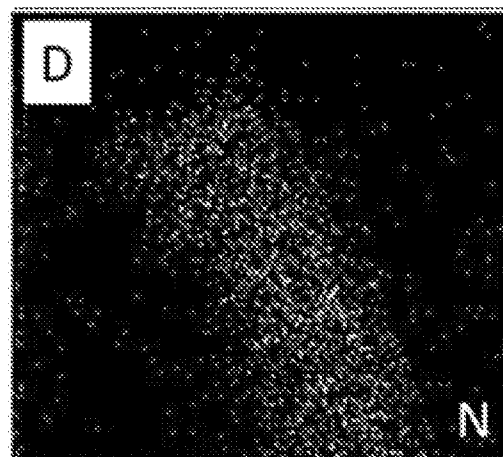
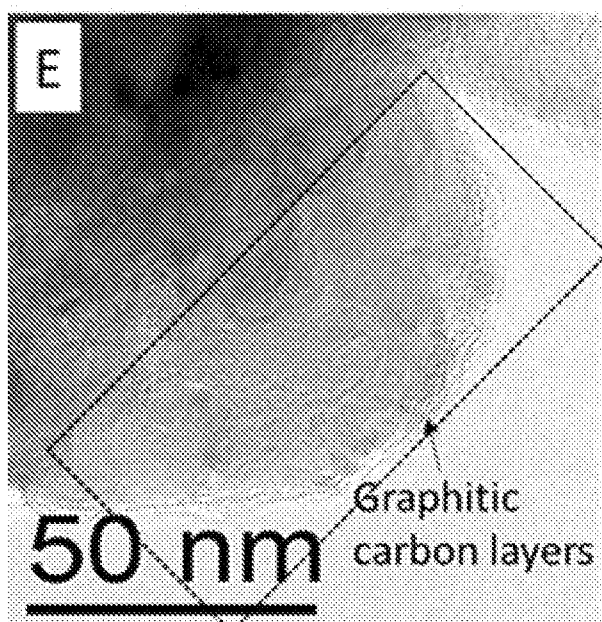
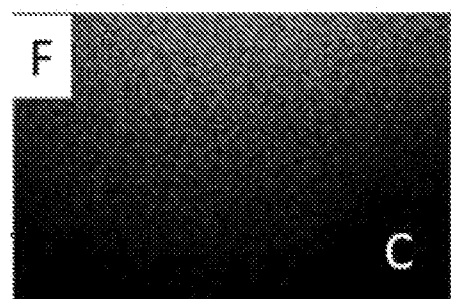
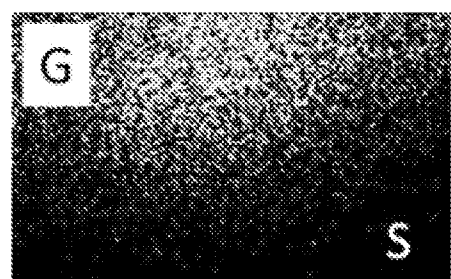
**Fig. 1**

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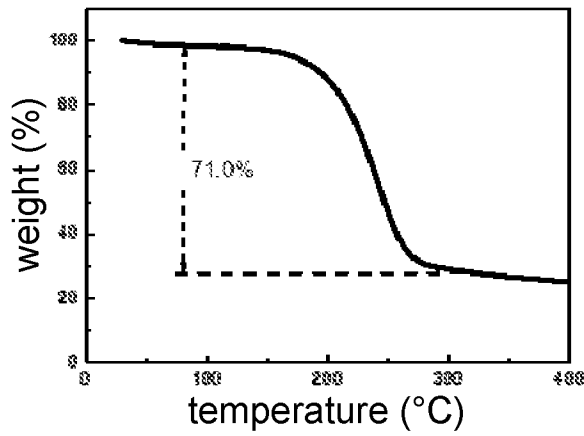
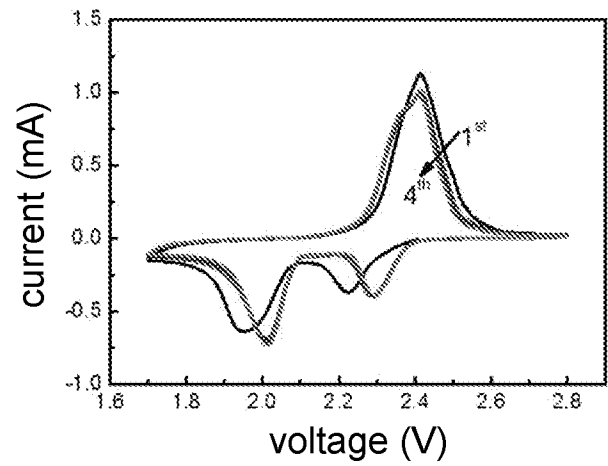
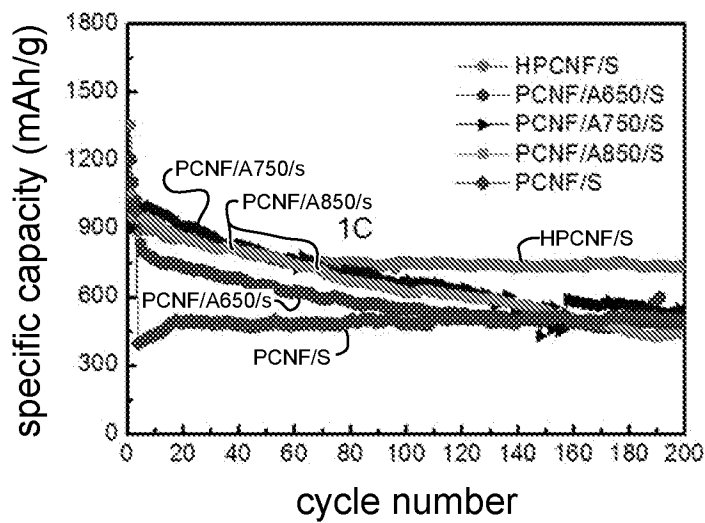
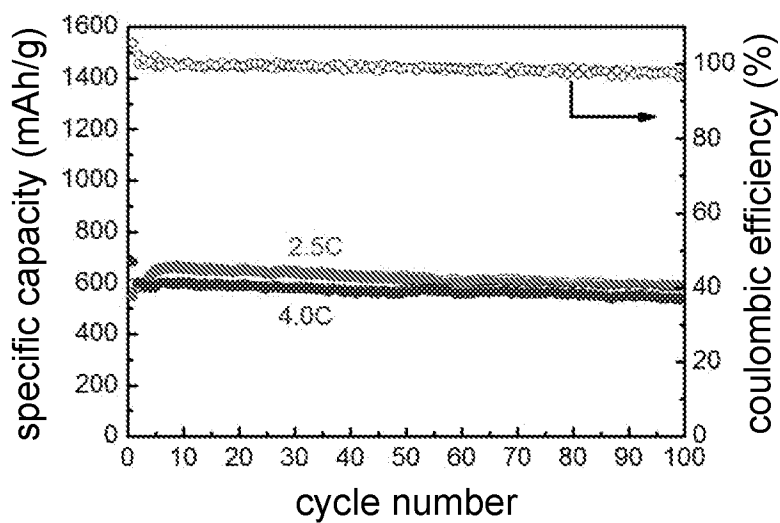
**Fig. 2A****Fig. 2B****Fig. 2C**

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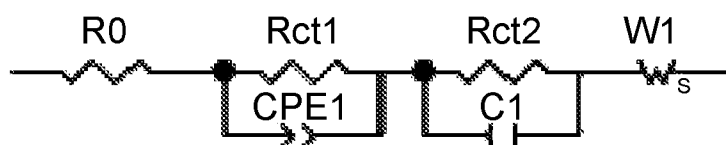
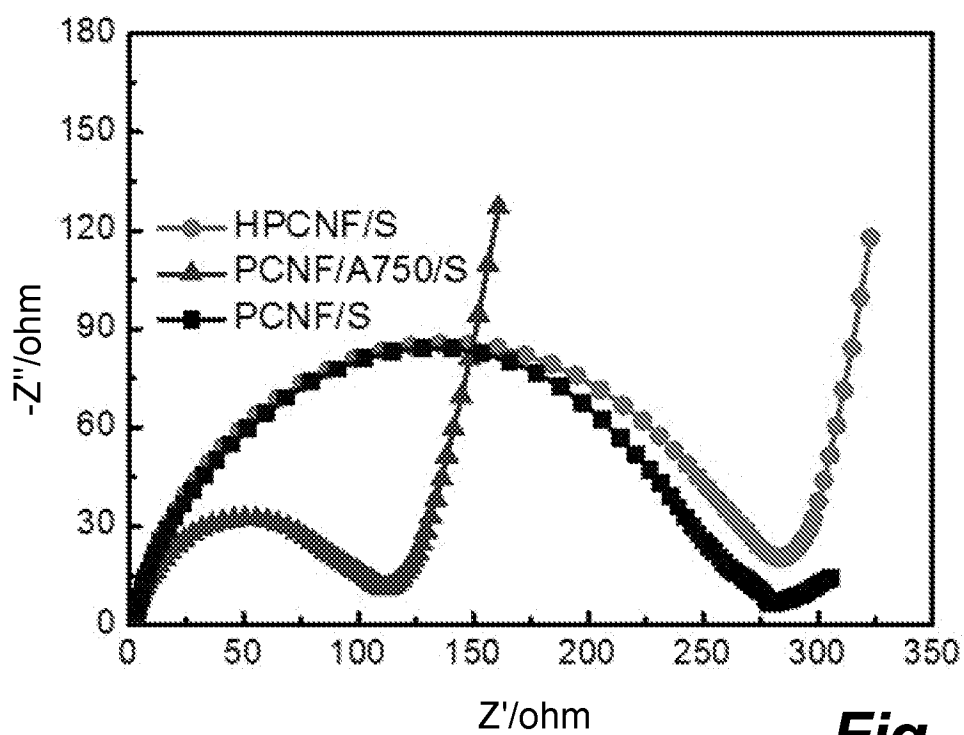
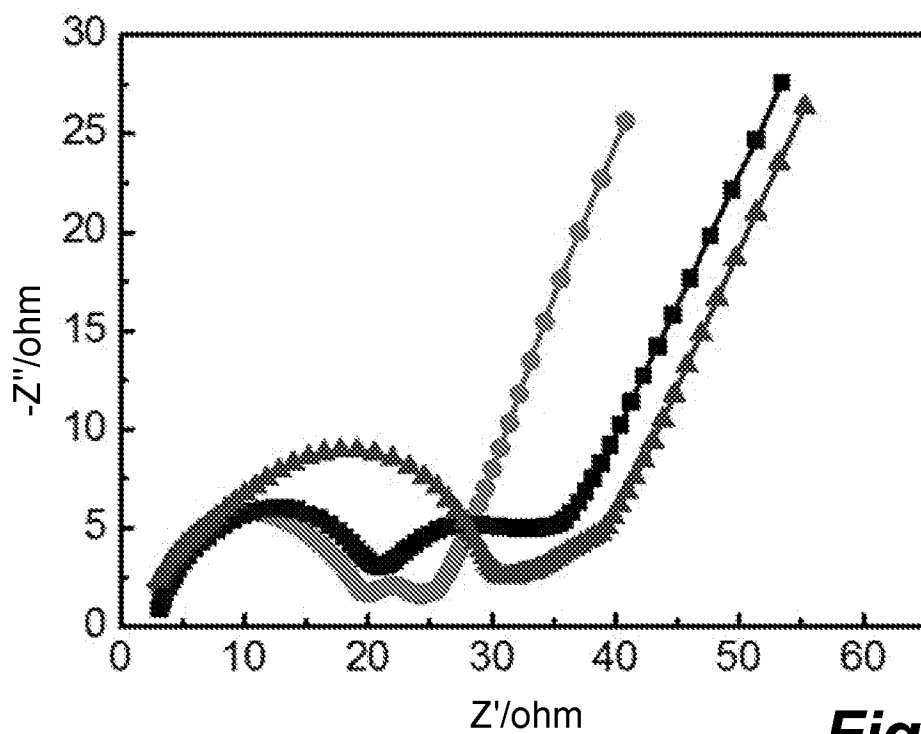
**Fig. 3A****Fig. 3B****Fig. 3C****Fig. 3D**

**Fig. 4A****Fig. 4B****Fig. 4C****Fig. 4D****Fig. 4E****Fig. 4F****Fig. 4G**

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**Fig. 5****Fig. 6A****Fig. 6B****Fig. 6C**

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**Fig. 7A****Fig. 7B****Fig. 7C**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2016/111487

A. CLASSIFICATION OF SUBJECT MATTER		
H01M 4/62(2006.01)i		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
H01M-		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
USTXT;CNABS;SIPOABS;DWPI;EPODOC;melt-diffusion, nanofiber, hierarchical, sulfur, porous, electrospin+, carbon;iron; etch+; pore		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	CN 104900880 A (UNIV. CHINA GEOSCIENCES WUHAN) 09 September 2015 (2015-09-09) description, paragraphs 0004-0021	1-14
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A	CN 104701507 A (ZHANGJIAGANG SHANMU NEW MATERIAL TECHNOLOGY DEV. CO. LTD.) 10 June 2015 (2015-06-10) abstract	1-19
A	CN 102969487 A (UNIV. NANKAI) 13 March 2013 (2013-03-13) abstract	1-19
A	US 2015180021 A1 (UCHICAGO ARGONNE LLC.) 25 June 2015 (2015-06-25) abstract	1-19
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
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Date of the actual completion of the international search		Date of mailing of the international search report
23 March 2017		07 April 2017
Name and mailing address of the ISA/CN		Authorized officer
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2016/111487

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