

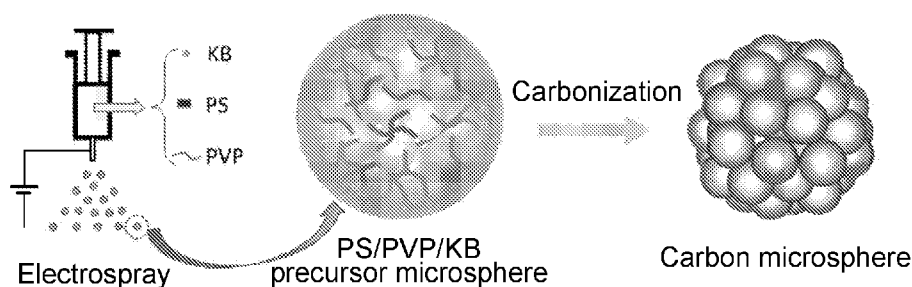
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62/498,766 06 January 2017 (06.01.2017) US(71) Applicant: **THE HONG KONG UNIVERSITY OF SCIENCE AND TECHNOLOGY** [CN/CN]; Clear Water Bay, Kowloon, Hong Kong (CN).(72) Inventors: **KIM, Jang-Kyo**; Office 2595, Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong (CN). **QIN, Xianying**; Lab 6148, Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong (CN). **XU, Zhenglong**; Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong (CN). **HUANG, Jianqiu**; Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong (CN). **CHONG, Woon Gie**; Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong (CN).nology, Clear Water Bay, Kowloon, Hong Kong (CN). **WANG, Xiangyu**; Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong (CN).(74) Agent: **TEE & HOWE INTELLECTUAL PROPERTY ATTORNEYS**; Yeping DING, 10th Floor, Tower D, Minsheng Financial Center, 28 Jianguomennei Avenue, Dongcheng District, Beijing 100005 (CN).(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: SYNTHESIS OF POROUS CARBON MICROSPHERES AND THEIR APPLICATION IN LITHIUM-SULFUR BATTERIES

**Fig. 1**

(57) Abstract: Lithium-sulfur batteries are formed with a high-capacity sulfur cathode, using porous carbon microspheres infused with sulfur, and lithium anode. A mixture of precursor solution is formed by dispersing superconductive carbon black particles in the dissolved polymer solution. The mixture is used to form carbon black/polymer precursor microspheres via electro spraying after solvent evaporation. The precursor microspheres are pyrolyzed to form a porous carbon microsphere substrate by removing the polymers, and then the porous carbon microspheres are infused with sulfur. The sulfur-infused carbon microspheres are employed as a cathode in the lithium sulfur battery.



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Synthesis of Porous Carbon Microspheres and Their Application in Lithium-Sulfur Batteries

RELATED APPLICATION

[0001] The present Patent Application claims priority to U.S. Provisional Patent Application No. 62/498,766 filed January 6, 2017, which is assigned to the assignee hereof and filed by the inventors hereof and which is incorporated by reference herein.

BACKGROUND

[0002] Technical Field

[0003] The present disclosure relates to synthesis of carbon microspheres (CMSs) with a hierarchical porous structure based on an electrospraying technique. The disclosure relates to the application of CMSs as sulfur host for high-performance lithium-sulfur batteries (LSBs).

[0004] Background Art

[0005] Portable electronic devices have been developed in the past couple of decades, these developments being attributed to the technology progress of lithium ion batteries (LIBs) as the main energy storage means. In order to extend the working hours of portable electronic devices and increase the driving distance of electric vehicles without extra charge, next generation energy storage devices need to be developed having higher energy densities, longer cycling life and lower cost. Lithium-sulfur batteries (LSBs) comprised of a high-capacity sulfur cathode and a lithium anode are considered one of the most promising alternatives to the current LIB system. Sulfur, an abundant element on the earth's crust, can offer a high theoretical capacity of 1672 mA h g^{-1} , which is an order of magnitude higher than those of the transition metal oxide cathodes. The high specific capacity arises from the conversion reaction of sulfur to form lithium sulfide (Li_2S) by reversible reaction of two electrons per sulfur atom as well as its relatively low molecular weight. Despite the overwhelming advantages, LSBs also have several technological limitations, such as poor cyclic stability, low Coulombic efficiency, loss of active materials on the cathode, dendrite formation on the anode, and inefficient electron/ Li^+ pathway through the thick electrode. These fundamental challenges facing

Li₂S systems originate from the inherent material characteristics of sulfur, including the insulating nature of elemental sulfur and lithium sulfides, large volume changes of sulfur during lithiation/delithiation, and dissolution of lithium polysulfides in electrolyte causing the so-called "shuttling effect".

[0006] The specific capacities and cycle life of LSBs have been greatly improved recently by developing new, multifunctional cathodes, interlayers and electrolytes. To overcome the aforementioned limitations of LSBs, the active sulfur or sulfides are usually combined with carbon, a conductive but electrochemically inert host material, to modify the characteristics of batteries. Existing technologies, using many different types of carbon materials (such as carbon black, carbon nanotubes, carbon nanofibers, carbon microsphere, graphite and graphene) with diverse structures (such as sphere, hollow, yolk-shell, honeycomb, pomegranate, sandwich, and scaffold), are implemented as conductive and confining hosts to entrap sulfur species and enhance sulfur utilization during the electrochemical cycles. Based on numerous previous studies, it can be concluded that, to obtain LSBs with superior performance, the carbon-based sulfur host should possess the following characteristics: (1) an excellent electrical conductivity to form an effective conductive network for high accessibility of active materials; (2) a hierarchical porous structure with a large pore volume to accommodate volume expansion of sulfur with high loading, and with large specific surface area to allow direct contacts between the conductive matrix and the active material, while facilitating permeation of electrolyte through the internal unimpeded pore channels; and (3) a micro-scale spherical architecture with an enclosed external surface and reduced exits to entrap polysulfides. The above understanding may offer better design and development of new carbon hosts toward achieving higher sulfur loading and uncompromised sulfur utilization.

[0007] In order to provide a suitable carbon host for LSBs, polymers are often used as the carbon precursor and oxide particles as the template to prepare porous carbon by chemical synthesis, followed by carbonization at an elevated temperature and an additional template etching process. Further activation is also often carried out to increase the porosity and surface area by creating micropores. The whole fabrication process is time-consuming and expensive, and environmentally harmful.

SUMMARY

[0008] Lithium sulfur batteries are produced by forming a carbon microsphere substrate and infusing the microsphere substrate with sulfur. This forms a sulfur-carbon microsphere composite. The sulfur-carbon microsphere composite is provided as a cathode in a lithium-sulfur battery.

[0009] In one technique, the carbon microsphere substrate is formed by electrospraying a polymer solution comprising superconductive carbon black mixed with the polymer solution. The infusing of the microsphere substrate with sulfur may be performed by a molten sulfur infusion. In a particular technique, heat treating the mixture to form the carbon microspheres; and, after the heat treating, the carbon microspheres are constructed by stacking the branched superconductive carbon black compactly. In this technique; the carbon microspheres are adhered together by the amorphous carbon matrix derived from polystyrene (PS) and/or polyvinylpyrrolidone (PVP) polymers after evaporation of the heteroatoms.

[0010] In a further aspect, a battery is formed with a conductive substrate, a carbon microsphere layer infused coated on the substrate, as a sulfur-carbon microsphere composite adhered together with polymers. A lithium anode is provided in an adjacent relationship with the coated substrate, and an electrolyte is provided in communication with the coated substrate and the lithium anode. In particular configurations, the electrolyte comprises a material selected from the group consisting of lithium bis(trifluoromethanesulfonyl)imide ($\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ or LiTFSI), 1,3-dioxolane (DOL), dimethoxyethane (DME) and LiNO_3 , are used. In particular configurations, a Celgard[®] film separator is used.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Fig. 1 is a schematic diagram showing porous carbon microspheres (CMSs) and their synthesis procedure.

[0012] Fig. 2 is a scanning electron microscope (SEM) image of PS/PVP/KB precursor microspheres.

[0013] Figs. 3A and 3B are microphotographs of porous carbon microspheres (CMSs). Fig. 3A is a scanning electron microscope (SEM) image of the CMSs and Fig. 3B is a transmission electron microscope (TEM) image of the CMSs.

[0014] Figs. 4A-E are photomicrographs showing the morphology and structure of the sulfur-infiltrated carbon microspheres (S/CMSs). Fig. 4A is a SEM image. Fig. 4B is a TEM image. Fig. 4C is a scanning transmission electron microscope (STEM) image of S/CMSs. Figs. 4D and 4E are Energy Dispersive X-Ray Analysis (EDX) elemental maps corresponding to the STEM image of Fig 4C.

[0015] Figs. 5A-D are graphic depictions showing the pore properties of CMSs and S/CMSs. Figs. 5A and 5C depict nitrogen adsorption/desorption isotherm curves of CMSs and S/CMSs, respectively. Figs. 5B and 5D depict pore size distribution of the CMSs and S/CMSs of Figs. 5A and 5B, respectively.

[0016] Figs. 6A and 6B are graphic depictions showing the cyclic performance of S/CMS and S/KB cathodes. Fig. 6A shows the cyclic performance at 1 C ($1\text{ C} = 1672\text{ mA g}^{-1}$) and Fig. 6B shows the cyclic performance at 2 C ($2\text{ C} = 3344\text{ mA g}^{-1}$). The higher current density of 2 C results in a lower specific capacity than at 1 C because of the shorter time required for charge/discharge cycles at a higher current density.

DETAILED DESCRIPTION

[0017] Overview

[0018] According to the structural design principles for a carbon host mentioned above, carbon microspheres (CMSs) are prepared. The CMSs exhibited excellent electrical conductivity, a hierarchical porous structure, high porosity, a large specific surface area but with a low apparent surface area, based on a facile electrospray technique and subsequent heat treatment, without additional template removal and activation processes. After infusing molten sulfur, the sulfur/CMS (S/CMS) composites are used as the cathode for lithium sulfide batteries (LSBs). The S/CMS cell delivered excellent electrochemical performance with a high specific capacity, excellent rate capability and long cycle life. The simple fabrication method and commercially available precursors make the CMSs a promising sulfur host for the LSBs.

[0019] Carbon microspheres (CMSs) with a hierarchical porous structure and high electrical conductivity are prepared by electrospraying polystyrene/polyvinylpyrrolidone (PS/PVP) solution in dimethylformamide (DMF) containing Ketjen carbon black (Ketjenblack or KB), followed by subsequent heat treatment. Ketjenblack is a registered trademark of Akzo Nobel Chemicals B.V., Arnhem, The Netherlands, and describes a very pure carbon black used for antistatic and electroconductive applications. Ketjenblack EC-600JD is a trademark for a particular formulation of this type of carbon black. Ketjenblack EC-600JD is a non-limiting example of a superconducting carbon black. Ketjenblack EC-600JD presents approximately 6 times the surface area as ordinary carbon black. Ketjenblack EC-600JD presents a branched structure where the hollow carbon nanoparticles are interconnected to form conducting networks.

[0020] In the electrospraying polystyrene/polyvinylpyrrolidone (PS/PVP) solution in dimethylformamide (DMF), PS allows the formation of microspheres during electrospraying. PVP serves as a surfactant and facilitated uniform dispersion of KB nanoparticles in the solution. The branched and porous KB particles serve as conductive skeleton in the CMS products. The precursor microspheres are formed after evaporation of solvent under a high-voltage electrostatic force. In the precursor microspheres, branched KB particles are uniformly embedded in the polymer matrix, which also acted as pore template during the pyrolysis process. After the heat treatment, CMSs are constructed by stacking the branched KB compactly, in which the KB particles are tightly adhered together by the amorphous carbon matrix derived from the polymer. During the heat treatment, the PS/PVP polymers are converted into amorphous carbon after the evaporation of heteroatoms, such as nitrogen, oxygen and hydrogen. After the infusion of sulfur, the S/CMS composites are used as the cathode of LSBs, which deliver excellent electrochemical performance with a high specific capacity, excellent rate capability and long cycle life.

[0021] The present disclosure describes how the porous carbon microspheres (CMSs) are synthesized using an electrospray technique followed by a high temperature heat treatment. CMSs with a mean diameter ranging 1 - 5 μm , a large pore volume above 2 $\text{cm}^3 \text{g}^{-1}$, a large specific surface area above 750 $\text{m}^2 \text{g}^{-1}$, and a hierarchical pore distribution from micro- to macropores are successfully produced after direct carbonization. The CMSs are then used as the host to prepare sulfur/CMS (S/CMS) composites after infusion of molten sulfur via a traditional melt infusion technique.

After blending with binder and conductive additives, the S/CMS composite is used as the active material for cathode to assemble coin-type lithium-sulfur batteries (LSBs). The resulting LSBs deliver excellent electrochemical performance.

[0022] The present technique applies a facile electrospray method to prepare precursor microspheres (PMSs) derived from PS/PVP/KB solution, which are then directly carbonized to produce porous CMSs. In prior art applications, templates had to be removed and the carbon host was further treated chemically for activation to generate porous carbon materials with a large pore volume, a large specific surface area and a hierarchical pore structure. Here, the abovementioned extra processes including template removal and chemical activation are completely eliminated during the process of synthesizing porous CMSs. Branched KB nanoparticles serve as the structural skeleton to support CMSs that are assembled *in situ* due to strong adhesion by the amorphous carbon derived from the PS/PVP matrix during carbonization. The PS/PVP matrix forms massive pores after thermal pyrolysis in an inert atmosphere due to their low carbon yields at a high temperature. The carbon yield is a measure of the weight of remaining carbon after carbonization of polymers.

[0023] The present technique uses an energy-efficient and environment-friendly approach for the preparation of porous CMSs and S/CMSs. The coin-type LSBs made of the as-prepared S/CMSs are of high specific capacity, good current rate capability, large sulfur mass loading, ultra-long cycle life, which have great potential for application in the next generation energy storage devices.

[0024] **Process**

[0025] The precursor solution for electrospray is prepared by dissolving PS and PVP polymers in DMF solvent by stirring at an elevated temperature and dispersing KB nanoparticles in the solution by sonication.

[0026] Fig. 1 is a schematic diagram showing porous CMSs and their synthesis procedure. The synthesis procedure is used for the preparation of PS/PVP/KB PMSs and porous CMSs as the final product. After evaporation of the solvent, PMSs are obtained from the droplets by electrospraying the PS/PVP/KB solution at a high voltage, an optimized flow rate and distance between the nozzle and collector. Then, the as-sprayed PMSs are heat treated at a high temperature in an inert atmosphere. Upon

decomposition of polymers, porous CMSs consisting of branched KB skeleton and amorphous carbon matrix derived from polymers are formed.

[0027] The S/CMSs are prepared via mechanical grinding and subsequent melt infusion. Sulfur nanoparticles and CMSs are ground together at a large sulfur proportion. The mixture is heated in an Ar atmosphere to infiltrate sulfur into the pores of CMSs.

[0028] The morphologies and pore structures of PMSs, CMSs and S/CMSs are characterized by SEM, TEM and BET analysis. CR2032 coin cells are assembled in an Ar-filled chamber to measure the electrochemical properties of S/CMS composite cathode in LSBs using lithium foil as the anode. The use of an Ar-filled chamber is given by way of non-limiting example, as any suitable inert or non-reacting atmosphere or a vacuum can be used for the assembly. The specific capacities, rate capabilities and cycle life of the LSBs are measured on a Land 2001A test system.

[0029] The disclosed technology provides a process for the preparation of porous CMSs and S/CMS composite cathode in LSBs. The process has distinct advantages of low power consumption, high yields, environment-friendly and being easy to be scaled up for mass production. In a non-limiting example, the technique uses the following sequence:

- 1: Preparation of electrospray solution by dissolving PS/PVP and dispersing KB in DMF
- 2: Formation of PS/PVP/KB PMSs based on high-voltage electrospray
- 3: Formation of Porous CMSs by pyrolyzing PS and PVP at a high temperature
- 4: Fabrication of S/CMS composites by infusing sulfur to CMSs
- 5: Assembly of coin cells as cathode for LSBs

[0030] Step 1 – Preparation of electrospray solution by dissolving PS/PVP and dispersing KB in DMF: 0.3 - 0.8 g PS, 0.3 - 0.8 g PVP, 0.1 - 0.5 g KB and 11 ml DMF are placed in a sealed flask. The mixer is stirred at 60 - 80°C for over 3 h and dispersed for over 1 h under ultrasonic agitation using ultrasonic vibrational energy. After

dispersion by ultrasonic agitation, the precursor solution containing dissolved PS/PVP and KB is obtained.

[0031] Step 2 – Formation of PS/PVP/KB PMSs based on high-voltage electrospray: The precursor solution is poured into a syringe. The syringe pump feed rate is maintained at 0.5 - 5 ml/h to supply the solution for electrospray. A stainless steel nozzle with an AWG (American Wire Gauge) ranging 19 - 23 (with varying diameters of 1.06, 0.9, 0.81, 0.71 and 0.63 mm) is used to spray droplets and connect the high-voltage emitter clamp. A high voltage of 10 - 30 kV and a constant distance of 5 - 30 cm are maintained between the nozzle and aluminum foil collector. Upon evaporation of the solvent, PS/PVP/KB PMSs are obtained from the electrosprayed droplets. The PMS films are carefully peeled from the collector.

[0032] Step 3 – Formation of porous CMSs by pyrolyzing PS and PVP at a high temperature: The as-sprayed PMSs are heated in Ar at 500 - 1200°C for 0.1 - 6 h at a heating rate of 2 - 10°C min⁻¹ to form porous CMSs. After carbonization, the porous CMSs are obtained after the furnace is cooled to 25°C overnight.

[0033] Step 4 – Fabrication of S/CMS composites by infusing molten sulfur into CMSs: Sulfur nanoparticles and CMSs are ground together at a sulfur content of 50 - 70% in the mixture. The mixture is heated at 155°C in Ar for 12 h at a heating rate of 2°C min⁻¹ to allow the sulfur to infiltrate into the pores of CMSs. The S/CMP composites are collected after cooling to 25°C overnight.

[0034] Step 5 – Assembly of LSB cells using S/CMSs as cathode: CR2032 coin cells are assembled in an Ar-filled chamber to investigate the electrochemical properties of S/CMS cathodes in LSBs. The electrochemical performance including specific capacities, rate capabilities and cycle life for the LSBs are measured. To prepare the S/CMS cathodes, the slurry mixture of S/CMSs (active material), Super P™ (conductive additive) and PVDF (binder) at a weight ratio of 8:1:1 in NMP is prepared by stirring for 3 h, which is uniformly applied on a carbon-coated aluminum foil and dried at 60°C under vacuum for 12 h. Super P is a trademark of Alfa Aesar, to describe the product Alfa Aesar Carbon black, Super P™, and is usually used as conductive additive for electrodes of commercial Li-ion batteries. The mass loading of sulfur is controlled at 0.3 - 3 mg cm⁻² by adjusting the thickness of the slurry coating. Lithium foil is used as the counter electrode. Celgard® 2250 film is employed as the separator between the S/CMS cathode

and the lithium anode. Celgard® 2250 is a 25 μm microporous trilayer membrane (PP/PE/PP), manufactured by Celgard, LLC of Charlotte, North Carolina, USA, and is given by way of non-limiting example. Moderate liquid electrolyte is added into both the S/CMS cathode and lithium anode sides dropwisely using a pipette. The batteries are discharged from 2.8 to 1.7 V and charged from 1.7 to 2.8 V (vs Li/Li⁺) on a Land 2001A cell test system.

[0035] Materials:

[0036] Ketjenblack EC-600JD (KB), commercially available branched porous carbon, is used to construct the framework skeleton structure in the CMSs. Ketjenblack EC-600JD is a superconductive carbon black material with an electrical conductivity of about 10^6 S/m. Polystyrene (PS, $M_w = 192,000$, Aldrich) and polyvinylpyrrolidone (PVP, $M_w = 1,300,000$, Aldrich) are used to construct the PMSs via electrospray. N,N-dimethylformamide (DMF, Fisher) is used as a solvent for the electrospray process without further purification. Sulfur nanoparticles are provided by Aldrich. Poly(vinylidene fluoride) (PVDF, $M_w = 534,000$, Aldrich) is used as the binder for S/CMS cathodes. Commercial Super P is used as the conductive additive for S/CMS cathodes. The electrolyte consists of 1M bis (trifluoromethane) sulfonamide lithium salt (LiTFSI) dissolved in a mixture of 1,2-dioxolane (DOL) and dimethoxymethane (DME) (1:1 by volume) with 1 wt% LiNO_3 .

[0037] The LiNO_3 electrolyte is given as a non-limiting example, as other electrolytes suitable for the type of battery can be used. In the case of lithium-sulfur batteries, non-limiting examples of electrolytes can comprise a material selected from the group consisting of lithium bis(trifluoromethanesulfonyl)imide ($\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ or LiTFSI), 1,3-dioxolane (DOL), dimethoxyethane (DME) and LiNO_3 .

[0038] The Ketjenblack EC-600JD carbon black is used as a non-limiting example, and other sources for carbon black can be used. For example, the carbon black can be selected from Ketjenblack EC-600JD, Ketjenblack EC-330JMA, and combinations thereof, as well as from competitive products. By way of non-limiting example, the carbon black is chosen so that the resulting CMS and CMS/S composite have electrical conductivities of 3.5×10^4 and 1.1×10^3 Siemens per meter, respectively. The desired characteristics of the carbon black is that the carbon black have a high surface area, as

compared to conventional carbon blacks. For example Ketjenblack EC-600JD is claimed to have a surface area of approximately 1400 m²/g (BET), so that only one sixth the amount of Ketjenblack EC600-JD is needed compared to conventional electroconductive blacks in order to achieve the same conductivity.

[0039] Characterization:

[0040] The morphology and structure of as-sprayed PMSs and porous CMSs are characterized using a field emission scanning electron microscopy (FE-SEM, ZEISS Supra 55) and high-resolution transmission electron microscope (HR-TEM, FEI TECNAIG2 F30). Energy-dispersive X-ray spectroscopy (EDX) is carried out to obtain the elemental maps. The pore volumes, pore distribution and Brunauer–Emmett–Teller (BET) surface areas of CMSs and S/CMSs are measured on a Micrometrics ASAP 2020 analyzer. The electrochemical properties, including specific capacities, rate capabilities, cycle life and charge-discharge curves, of S/CMS composite cathodes in LSBs are charged and discharged between 1.7 V and 2.8 V (vs Li/Li⁺) on a Land 2001A cell test system.

[0041] Fabrication process:

[0042] Precursor solutions are prepared by heating and stirring the solution in a sealed flask on a heating stage, followed by dispersion by ultrasonic agitation using ultrasonic vibrational energy. PMSs are produced by electrospraying the precursor solution on an electrospinning apparatus. CMSs and S/CMSs are produced in an Ar-filled tube furnace at high temperatures and an optimized heating rate. The S/CMS composite electrodes are prepared using a slurry coating method. The S/CMS-based coin-type LSBs are assembled in a chamber and tested on a LAND cell test device.

[0043] Experiment 1 - Synthesis of porous CMSs:

[0044] 0.6 g PS, 0.6 g PVP, 0.3 g KB and 11 ml DMF were placed in a sealed flask. The mixture was stirred at 70°C for 5 h and then subjected to ultrasonic vibrational energy for 2 h. The precursor solution containing PS, PVP and KB was poured into a syringe. The feed rate of syringe pump was kept at 2 ml/h to supply the solution for

electrospray. A stainless steel nozzle sized at 21 AWG was used to spray droplets. A constant voltage of 18 kV and a constant distance of 150 mm were maintained between the nozzle and aluminum foil collector.

[0045] Fig. 2 is a scanning electron microscope (SEM) image of PS/PVP/KB precursor microspheres. Figs. 3A and 3B are microphotographs of porous carbon microspheres (CMSs). Fig. 3A is a scanning electron microscope (SEM) image of the CMSs and Fig. 3B is a transmission electron microscope (TEM) image of the CMSs. Referring to Fig. 2, the PS/PVP/KB PMSs were obtained after evaporation of solvent from the electrosprayed droplets. The PMSs were heated in Ar at 1000°C for 2 h at a heating rate of 5°C min⁻¹ to form porous CMSs. Referring to Fig. 3, after carbonization, the porous CMSs with diameters of 1 - 5 μm were obtained after the furnace was cooled to 25°C overnight.

[0046] Figs. 4A-E are photomicrographs showing the morphology and structure of the sulfur-infiltrated carbon microspheres (S/CMSs). Fig. 4A is a SEM image. Fig. 4B is a TEM image. Fig. 4C is a STEM image of S/CMS. Figs. 4D and 4E are Energy Dispersive X-Ray Analysis (EDX) elemental maps corresponding to the STEM image of Fig 4C.

[0047] Figs. 5A-D are graphic depictions showing the pore properties of CMSs and S/CMSs. Figs. 5A and 5C depict nitrogen adsorption/desorption isotherm curves. Fig. 5B depicts pore size distribution of the CMSs of Fig. 5A. Fig. 5D depicts pore size distribution of the S/CMSs of Fig. 5C. Based on the nitrogen adsorption/desorption isotherm curves (Fig. 5A) and the pore size distribution curves (Fig. 5B), the porous CMSs have a large pore volume of 2.08 cm³ g⁻¹, a large specific surface area of 75 m² g⁻¹ and a hierarchical pore distribution of 0.3 - 100 nm.

[0048] Experiment 2 - Synthesis of S/CMSs and assembly of LSB coin cells:

[0049] Sulfur and CMSs were mixed together at a weight ratio of 3:2 by mechanical grinding. Then the mixture was heated at 155°C in Ar for 12 h at a heating rate of 2°C min⁻¹ to obtain S/CMSs. Their pore characteristics are shown in Fig. 5C and 5D. For preparing the S/CMS cathodes, S/CMSs, Super P and PVDF at a weight ratio of

8:1:1 were mixed in NMP for 3 h to form a slurry. The slurry was uniformly applied to the surface of a carbon-coated aluminum foil and dried at 60°C under vacuum for 12 h to obtain the S/CMS electrode. The mass loading of sulfur was maintained at 0.5 mg cm⁻². CR2032 coin-type LSBs were assembled in an Ar-filled chamber using S/CMS as the cathode, lithium foil as the anode, Celgard™ 2250 film as the separator. A moderate amount of electrolyte consisting of LiTFSI, DOL, DME and LiNO₃ was applied to the cathode and anode.

[0050] Figs. 6A and 6B are graphic depictions showing the cyclic performance of S/CMS and S/KB cathodes. Fig. 6A shows the cyclic performance at 1 C (1 C = 1672 mA g⁻¹) and Fig. 6B shows the cyclic performance at 2 C (1 C = 1672 mA g⁻¹). The assembled LSBs were tested on a Land 2001A cell test system at a charge/discharge voltage ranging between 1.7 V and 2.8 V (vs Li/Li⁺) at different current densities. The S/CMS cells deliver a high reversible capacity of 1280 mAh g⁻¹ at 0.1 C (1 C = 1672 mA g⁻¹) and an initial capacity of 1006 mAh g⁻¹ at 1 C, maintaining 679 mAh g⁻¹ after 1000 cycles. The LSB cells exhibit an initial reversible capacity of 728 mAh g⁻¹ at 2 C and retain 499 mAh g⁻¹ after 2000 cycles.

[0051] Experiment 3 - Synthesis of S/KB and assembly of LSBs:

[0052] Sulfur and KB were mixed together at a weight ratio of 3:2 by mechanical grinding. Then the mixture was heated at 155°C in Ar for 12 h at a heating rate of 2°C min⁻¹ to obtain S/KB. For preparing the S/KB cathodes, S/KB, Super P and PVDF at a weight ratio of 8:1:1 were mixed in NMP for 4 h to form a slurry. The slurry was uniformly applied to the surface of a carbon-coated aluminum foil and dried at 60°C under vacuum for 12 h to obtain the S/KB electrode. The mass loading of sulfur was maintained at 0.5 mg cm⁻². CR2032 coin-type LSBs were assembled in an Ar-filled chamber using S/KB as the cathode, lithium foil as the anode, Celgard® 2250 film as the separator. A moderate amount of electrolyte consisting of LiTFSI, DOL, DME and LiNO₃ was applied to the cathode and anode. The assembled LSBs were tested on a Land 2001A cell test system at a charge/discharge voltage ranging between 1.7 V and 2.8 V (vs Li/Li⁺) at different current densities. The S/KB cells deliver a reversible capacity of 1143 mAh g⁻¹ at 0.1 C (1 C = 1672 mA g⁻¹) and an initial capacity of 793 mAh g⁻¹ at 1 C, retaining 449 mAh g⁻¹ after 1000 cycles.

[0053] Conclusion

[0054] It is understood that many changes in the details of materials parameters and processing conditions, such as precursor materials, solution concentrations, rate of flow, voltage and distance of electrospray, temperature and time of heat treatment, sulfur contents, which are described herein 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 invention as expressed in the appended claims.

CLAIMSWhat is claimed is:

1. Method of producing lithium-sulfur batteries, the method comprising:
forming a carbon microsphere substrate;
infusing the carbon microsphere substrate with sulfur, forming a sulfur-carbon microsphere composite; and
providing the sulfur-carbon microsphere composite as a cathode in a lithium-sulfur battery.
2. The method of claim 1, further comprising:
forming the carbon microsphere substrate by electrospraying a polymer solution containing superconductive carbon black particles to form a mixture of superconductive carbon black mixed with the polymer solution; and
heat treating the mixture to form the carbon microspheres.
3. The method of claim 1, wherein the carbon microsphere substrate comprises carbon microspheres with a mean diameter ranging 1 - 5 μm , and a pore volume $> 2 \text{ cm}^3 \text{ g}^{-1}$.
4. The method of claim 1, further comprising:
infusing the carbon microsphere substrate with sulfur by a molten sulfur infusion process.
5. The method of claim 1, further comprising:
forming the carbon microsphere substrate by electrospraying a polymer solution containing superconductive carbon black particles;
heat treating the mixture to form the carbon microspheres; and
after the heat treating, constructing the carbon microspheres by stacking the branched superconductive carbon black compactly; the amorphous carbon matrix derived from the polymers after evaporation of the heteroatoms cause the carbon microspheres to adhere together.

6. The method of claim 5, further comprising:
using, as the polymers, a material selected from the group consisting of polystyrene (PS)
and polyvinylpyrrolidone (PVP).
7. A method of fabricating porous carbon microspheres (CMSs), the method
comprising:
dissolving a soluble polymer and dispersing of superconductive carbon black
particles in solvent capable of carrying the polymers in solution to form a mixture of the
dissolved polymer and the superconductive carbon black particles to form a precursor
mixture;
applying the precursor mixture under electrostatic force and collecting of
polymer/superconductive carbon precursor microspheres (PMSs); and
pyrolyzing of the polymer/superconductive carbon PMSs to obtain porous
CMSs.
8. The method of claim 7 further characterized by:
using, as the soluble polymer, polystyrene (PS) and polyvinylpyrrolidone (PVP),
and dissolving the soluble polymers in N,N-dimethylformamide (DMF), thereby
providing the PS/PVP dissolved in the DMF as a precursor solvent capable of carrying
the polymers in solution, with the PS/PVP/DMF solution and superconductive carbon
forming the precursor mixture;
electrospraying the precursor mixture under electrostatic force to apply the
precursor mixture, and collecting of PS/PVP/superconductive carbon precursor
microspheres (PMSs); and
infusing the PMSs with sulfur to form sulfur-impregnated CMSs.
9. The method of claim 8 further characterized by:
subsequent to adding PS, PVP and superconductive carbon into DMF, heating
and stirring the solution to dissolve PS and PVP to form a polymer-superconductive
carbon mixture.

10. The method of claim 9, further comprising:
after dissolving PS and PVP in DMF, using ultrasonic vibrational energy to disperse the superconductive carbon uniformly in the PS/PVP solution.
11. The method of claim 8, further comprising:
in the preparation of the polymer-superconductive carbon mixture, changing the weight rates of components to control a structure and property of the PMSs and CMSs.
12. The method of claim 8 further characterized by:
subsequent to forming the polymer-superconductive carbon mixture, applying a high-voltage to form droplets of polymer/superconductive carbon to achieve evaporation of a solvent used to dissolve the polymers by applying a high-voltage electrostatic force; and
after applying an electrostatic force, adjusting electrospray distances and flow rates to effect the solvent volatilization of droplets and formation of PS/PVP/superconductive carbon PMSs.
13. The method of claim 8, further comprising:
changing temperatures, heating rates and holding times to control the structure and conductivity of porous CMSs.
14. The method of claim 7, further comprising:
changing temperatures, heating rates and holding times to control the structure and conductivity of porous CMSs.
15. The method of claim 7 further characterized by:
applying a high temperature to pyrolyze the polymer/superconductive carbon PMSs.
16. The method of claim 7 further characterized by:
applying a high temperature to pyrolyze the polymer/superconductive carbon PMSs, wherein the pyrolysis of PS/PVP/superconductive carbon PMSs comprises

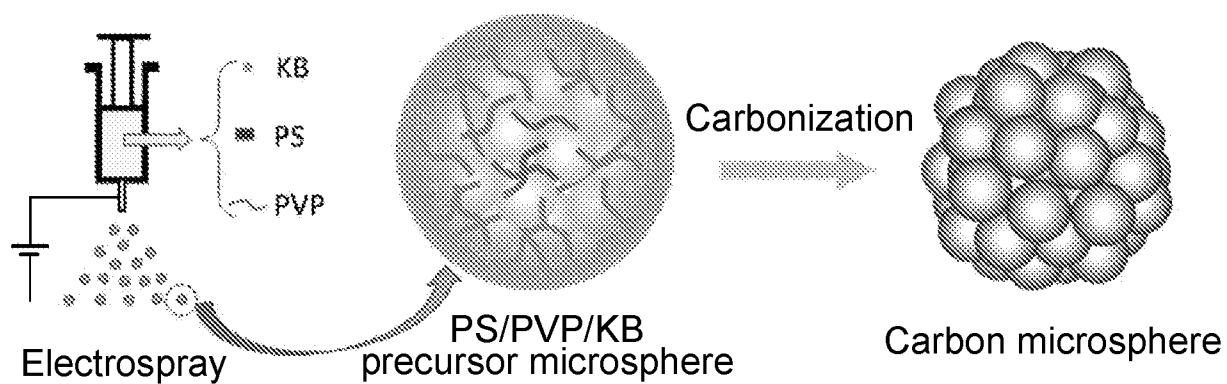
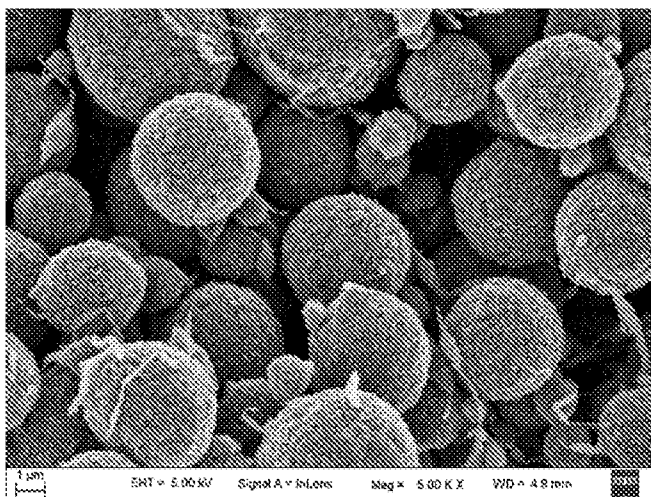
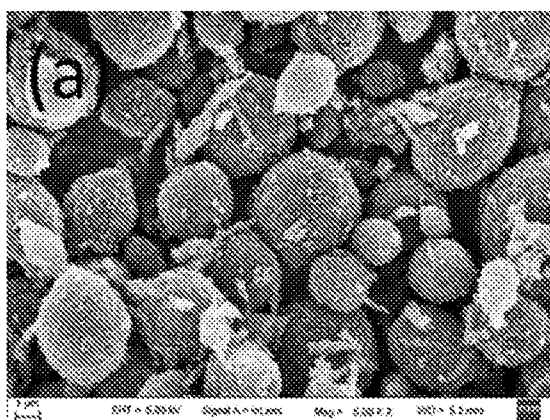
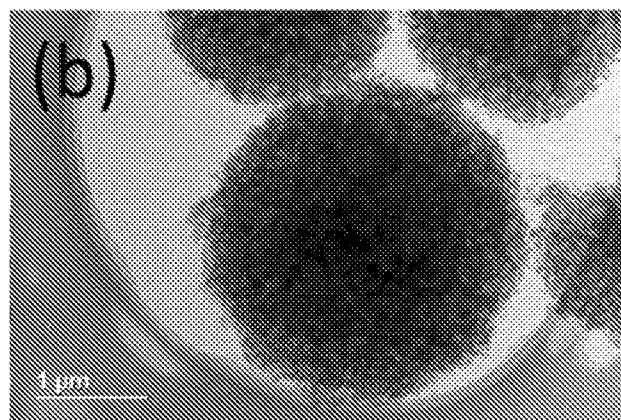
heating the samples in a tube furnace in an inert atmosphere, followed by cooling to room temperature to obtain porous CMSs.

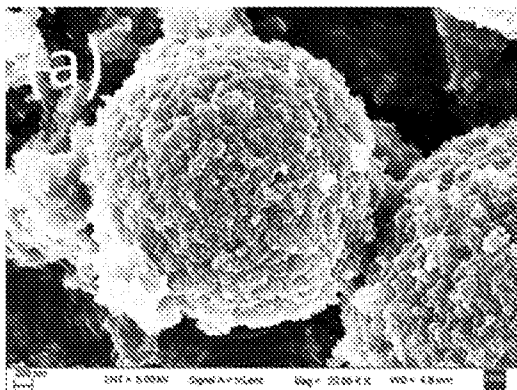
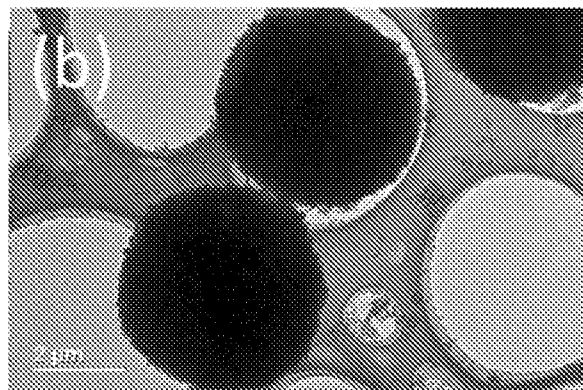
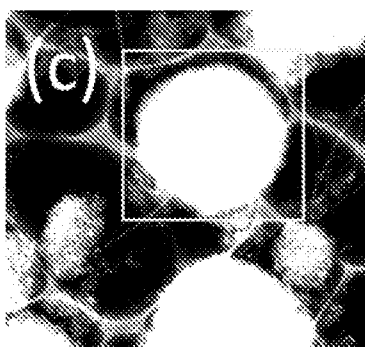
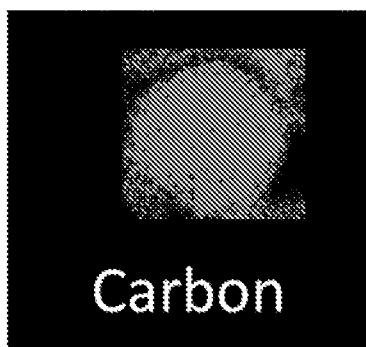
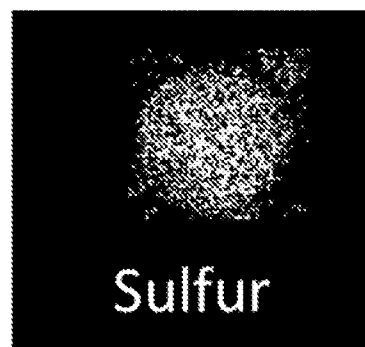
17. The method of claim 7 further characterized by:
subsequent to forming the polymer-superconductive carbon mixture, applying a high-voltage to form droplets of polymer/superconductive carbon to achieve evaporation of a solvent used to dissolve the polymers by applying a high-voltage electrostatic force.
18. A method for fabricating sulfur/carbon microsphere (S/CMS) composite, the method comprising:
preparing a bed of porous CMSs; and
infusing the CMSs with sulfur into the porous CMSs in an inert atmosphere to form the S/CMS composite.
19. The method of claim 18, further comprising:
adjusting a weight ratio of sulfur to CMSs to control the sulfur content in S/CMS composite.
20. The method of claim 18, further comprising:
adjusting an infusion temperature of the sulfur, time and heating rate to affect the distribution of sulfur in the porous CMSs.
21. A method for assembling lithium-sulfur batteries (LSBs) using S/CMSs as cathode material, the method comprising:
preparing of a slurry for cathode coating using a mixture comprising S/CMSs and a polymer in a solvent, with the polymer in solution with the solvent;
coating the slurry on a conductive substrate;
placing a lithium anode in an adjacent relationship with the coated substrate, and assembling an LSB in an inert or non-reactive atmosphere; and
providing an electrolyte in communication with the coated substrate and the lithium anode.

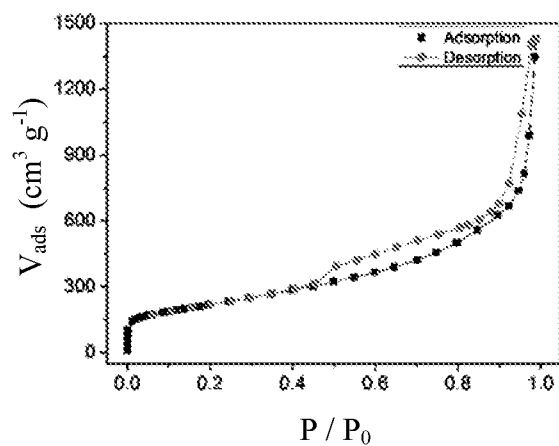
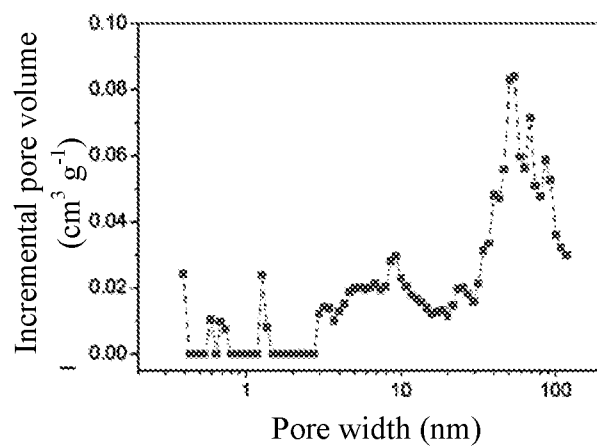
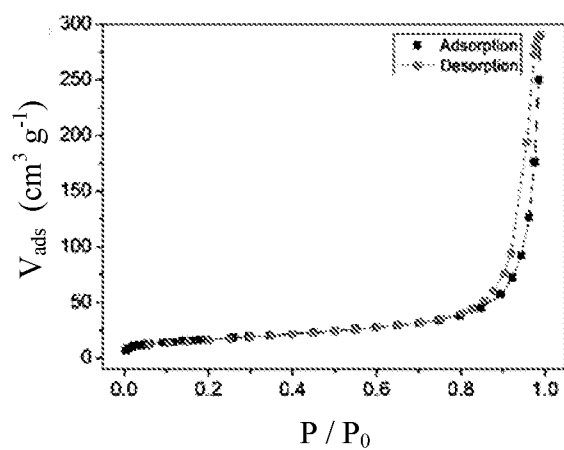
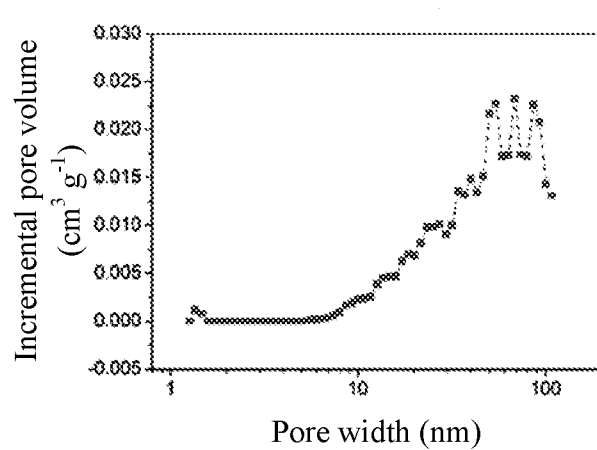
22. The method of claim 21, further comprising:
forming the S/CMSs by a process comprising:
forming a carbon microsphere substrate;
infusing the carbon microsphere substrate with sulfur, forming a sulfur-carbon microsphere composite; and
providing the sulfur-carbon microsphere composite as a cathode in a lithium-sulfur battery.
23. The method of claim 21, further comprising:
using, as the slurry, a mixture of S/CMSs, Super P and PVDF in NMP.
24. The method of claim 21, further comprising:
using, as the conductive substrate, a conductive substrate carbon-coated aluminum foil.
25. The method of claim 21, further comprising:
during the preparation of slurry, changing the weight rates of components to control a structure and property of the cathode.
26. The method of claim 25, further comprising:
controlling a thickness of coated slurry to affect mass loading of sulfur on the electrode.
27. The method of claim 25, further comprising:
subsequent to coating slurry comprising S/CMSs, Super P and PVDF on aluminum, drying the slurry in vacuum to remove solvent and obtain dried cathode.
28. The method of claim 21, further comprising:
using lithium foil the lithium anode, and solution comprising a material selected from the group consisting of LiTFSI, DOL, DME and LiNO₃ as the electrolyte.

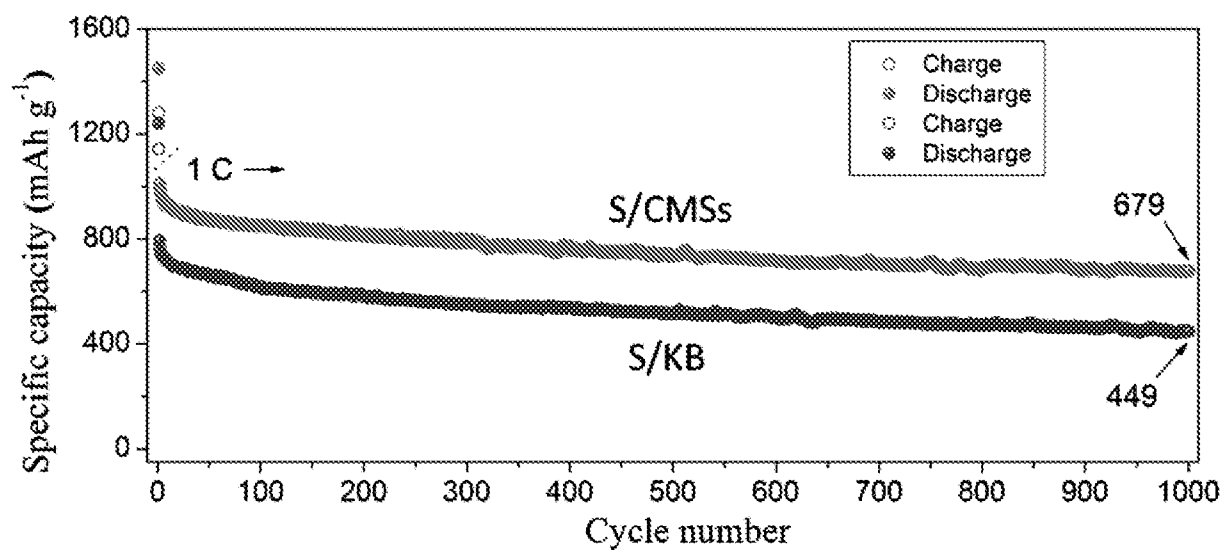
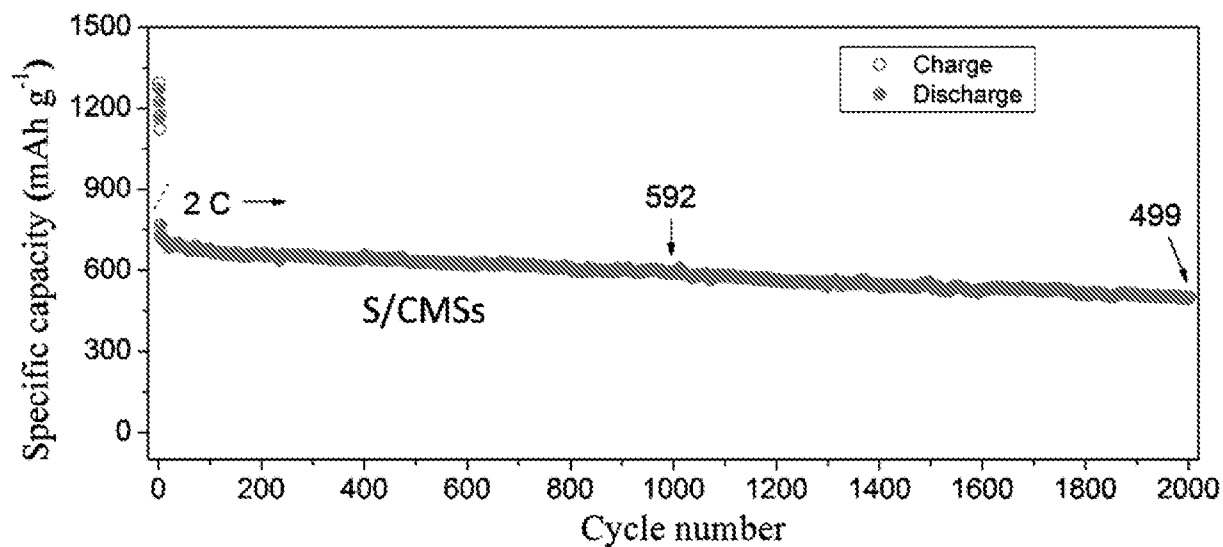
29. The method of claim 21, further comprising:
using lithium foil the lithium anode, Celgard[®] 2250 film as separator, and solution comprising LiTFSI, DOL, DME and LiNO₃ as the electrolyte.
30. A lithium sulfur battery comprising:
a conductive substrate;
a carbon microsphere layer coated on the conductive substrate, the carbon microsphere coating formed of carbon microspheres, and infused with sulfur to form a sulfur-carbon microsphere composite, the carbon microspheres adhered together by the amorphous carbon matrix derived from polymers after evaporation of the heteroatoms;
a lithium anode in an adjacent relationship with the coated substrate; and
an electrolyte in communication with the coated substrate and the lithium anode.
31. The lithium-sulfur battery of claim 30, further comprising:
the carbon microsphere substrate comprising carbon microspheres with a mean diameter ranging 1 - 5 μm , and a pore volume $> 2 \text{ cm}^3 \text{ g}^{-1}$; and
the amorphous carbon matrix polymers comprise polymers selected from the group consisting of polystyrene (PS) and polyvinylpyrrolidone (PVP).
32. The lithium-sulfur battery of claim 30, further comprising:
the conductive substrate comprising carbon-coated aluminum foil.
33. The lithium-sulfur battery of claim 30, further comprising:
a thickness of coated slurry selected to control mass loading of sulfur on the electrode.
34. The lithium-sulfur battery of claim 30, further comprising:
the lithium anode comprising lithium foil; and
the electrolyte comprising a material selected from the group consisting of LiTFSI, DOL, DME and LiNO₃.

35. The lithium-sulfur battery of claim 30, further comprising:
the lithium anode comprising lithium foil; and
the electrolyte comprising a material selected from the group consisting of
LiTFSI, DOL, DME and LiNO_3 ; and
a separator Celgard[®] 2250 film.

**Fig. 1****Fig. 2****Fig. 3A****Fig. 3B**

**Fig. 4A****Fig. 4B****Fig. 4C****Carbon****Fig. 4D****Sulfur****Fig. 4E**

**Fig. 5A****Fig. 5B****Fig. 5C****Fig. 5D**

**Fig. 6A****Fig. 6B**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2018/071546

A. CLASSIFICATION OF SUBJECT MATTER

H01M 4/08(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 4/-

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)

CNABS,CNTXT,CNKI,DWPLEPODOC,PATENTICS:carbon microsphere?,nanosphere?,Li-S batteries,lithium sulfur batterieselectrospray+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 102969487 A (NANKAI UNIVERSITY) 13 March 2013 (2013-03-13) abstract	1, 3-4, 18-20
A	CN 102969481 A (WUHAN UNIVERSITY) 13 March 2013 (2013-03-13) the whole document	1-35
A	CN 103441248 A (UNIV. HUOYINGDONG RES. INST. HONG KONG SCI.) 11 December 2013 (2013-12-11) the whole document	1-35
A	CN 1577926 A (SAMSUNG SDI CO. LTD.) 09 February 2005 (2005-02-09) the whole document	1-35
A	KR 10-2015-0131653 A (HYUNDAI MOTOR CO. LTD.) 25 November 2015 (2015-11-25) the whole document	1-35
A	Zhao, Cunyu et al. "Sulfur-infiltrated porous carbon microspheres with controllable multi-modal pore size distribution for high energy lithium-sulfur batteries" <i>Nanoscale</i> , Vol. 6, No. 2, 27 October 2013 (2013-10-27), ISSN: 2040-336, pages 882-888	1-35

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 "O" document referring to an oral disclosure, use, exhibition or other means
 "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

06 March 2018

Date of mailing of the international search report

28 March 2018

Name and mailing address of the ISA/CN

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2018/071546

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	102969487	A	13 March 2013	None			
CN	102969481	A	13 March 2013	None			
CN	103441248	A	11 December 2013	None			
CN	1577926	A	09 February 2005	KR	100497232	B1	23 June 2005
				JP	2005026230	A	27 January 2005
				KR	20050005352	A	09 February 2005
				US	2005003277	A1	06 January 2005
KR	10-2015-0131653	A	25 November 2015	None			