N/S-co-doped porous carbon nanoparticles serving the dual-function of sulfur host and separator coating in Lithium-Sulfur batteries

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Abstract

Porous carbon nanoparticles (PCN) co-doped with nitrogen and sulfur have been produced by applying a straightforward template-free method entailing a high-temperature reaction between polypyrrole nanoparticles and sodium thiosulfate. The activation process gives rise to porous carbon nanoparticles that combine several important properties: a) a uniform size of ~ 80 nm; b) a well-developed porosity with BET surface areas of up to ~ 1700 m² g⁻¹ and pore volumes of up to 2.20 cm³ g⁻¹; c) a sizeable N and S heteroatom content (of up to 2.7 % N and 7.7 % S); and d) a good electrical conductivity (up to 3 S cm⁻¹). The synthesis strategy offers a great versatility since two types of materials, PCN or S/PCN (nanocomposites comprising elemental sulfur infiltrated into the PCN), can be produced by introducing minor changes to the procedure. These materials have been tested on two components of a lithium-sulfur cell. The S/PCN nanocomposite is used as the cathode, whereas the PCN material is deposited onto the separator to form a thin packed layer in order to restrict the mobility of the polysulfides. Remarkably, the PCN coating layer notably enhances the utilization of sulfur (increase of 23 % during the first cycles) and it provides robustness during long-term cycling. The battery assembled with these two components exhibits a highly stable cycling performance from the very first charge-discharge cycles, and delivers a reversible capacity of 841 mAh g⁻¹ after 100 cycles at 0.2C with a coulombic efficiency of 99.3 %. Despite using a S/PCN composite with a high sulfur content (>70%), the cell was successfully

cycled at 2C over 500 charge-discharge cycles, and experienced a capacity decay of only 0.089% per cycle.

KEYWORDS: *carbon nanoparticles, porous carbon, nitrogen and sulfur doping, lithium-sulfur battery, sulfur/carbon nanocomposite, polysulfides barrier.*

1. Introduction

Lithium-sulfur (Li-S) batteries are one of the most promising rechargeable energy storage systems because of the low cost, environmentally-friendly nature and natural abundance of sulfur, as well as its high theoretical capacity (1675 mAh g^{-1}) that can provide a high specific energy of $\sim 2600 \text{ Wh kg}^{-1}$ ($\sim$ five times higher than that of conventional Li-ion batteries).¹⁻² However, the viability of Li-S batteries is limited by the rapid capacity decay of the sulfur cathode, mainly due to the *shuttle effect* caused by the migration of intermediate soluble lithium polysulfides (LiPS).³

In order to improve the electrochemical performance of Li-S batteries, mitigation of the shuttle effect represents a serious challenge and, in consequence, much effort has been devoted to this problem. Thus, in recent literature numerous strategies centred on hampering the mobility of LiPS in order to restrict their access to the lithium anode have been reported.⁴ A well-known procedure for restricting the mobility of LiPS consists in confining the sulfur inside the pores of conductive carbon hosts.⁵⁻⁶ In combination with this strategy, it has been verified that the doping of the porous carbon hosts with certain elements (N, O, S, B, etc.) serves to restrict the diffusion of LiPS because of the strong specific interactions between these heteroatoms and the soluble polysulfides.⁷ Furthermore, non-carbon inorganic sulfur hosts with polar

surfaces, such as metal oxides,⁸⁻⁹ sulfides⁹ or nitrides¹⁰ have also shown an ability to chemically block the shuttling of LiPS. Although the fabrication of sulfur cathodes according to the above strategies can reduce the mobility of LiPS, the capacity decay with cycling persists, highlighting the need for additional LiPS control schemes. A rational design of the sulfur cathode in combination with other measures to ensure a better control of the diffusion of LiPS appears to be the most appropriate strategy. To this end, much attention has been focused on the modification of other battery components (*i.e.* binder, separator or electrolyte).¹¹⁻¹³ More specifically, the objective is to transform these elements into bifunctional systems so that, besides their specific purpose, they include an additional feature that contributes to suppressing the mobility of LiPS.

The modification of pristine polypropylene (PP) separators is a simple and effective way to reduce the mobility of LiPS.¹³⁻¹⁵ Basically, it consists in coating the side of the separator facing the sulfur cathode with a layer of a functional material that impedes the diffusion of LiPS (obstruction) or, alternatively, exhibits a certain affinity towards soluble LiPS (adsorption). A variety of substances have been investigated with this purpose in mind: carbons, polymers (*i.e.* polypyrrole, polyaniline, Nafion, *etc.*),¹⁶⁻¹⁷ MOFs¹⁸ or inorganic materials (*i.e.* oxides, silicates, sulfides, *etc.*).¹⁹⁻²¹ In particular, carbon coated separators have received much attention due to the unique physicochemical properties of carbon materials which combine a good electrical conductivity and chemical stability with an easy-to-design pore structure, morphology and particle size. The carbon particles deposited onto the separator not only serve as a barrier to obstruct/adsorb the LiPS dissolved in the electrolyte, but also as a second current collector that enhances the electronic accessibility of the

active material.²² A plethora of carbon materials has been deposited onto the pristine PP separator, including graphene and graphene oxide sheets,²³ carbon black,²⁴ carbon nanofibers,²⁵ carbon nanotubes,²⁶ carbon capsules²⁷ and a variety of porous carbons. Manthiram *et al.* were the first to report in 2014 the fabrication of bifunctional separators made up of a layer of carbon nanotubes²⁸ or carbon black (super P)²⁹ deposited onto one side of a PP separator. Although these non-polar and non-porous carbon materials can obstruct the diffusion of LiPS, their ability to adsorb polar LiPS is limited. In contrast, the deposition of a layer of porous carbon particles, besides acting as a physical barrier, will serve to adsorb a certain amount of soluble LiPS into the porous structure. To this end, a few authors have investigated the fabrication of PP separators coated with porous carbons particles, such as microporous carbon nanofibers³⁰ or mesoporous carbons fabricated by means of nanocasting techniques based on the use of SiO₂³¹ or MgO³² as sacrificial templates. It is important to note, however, that these carbon coatings increase the mass/volume of the separator, which translates into lower values of cell energy density. For this reason, the carbon loading and layer thickness need to be limited to values of $\sim 0.3 \text{ mg cm}^{-2}$ and $< 30 \text{ }\mu\text{m}$, respectively. These limitations imply that the size of the porous carbon particles needs to be around or below $1 \text{ }\mu\text{m}$, which excludes the use of conventional porous carbons, what are usually made up of particles larger than $100 \text{ }\mu\text{m}$. However, the synthesis of porous carbon particles with a size $\leq 1 \text{ }\mu\text{m}$ is complex and usually requires the use of sacrificial templates.³³⁻³⁴

In the present paper, we report an easy template-free strategy for fabricating N,S-co-doped porous carbon nanoparticles smaller than 100 nm .

The nanoparticles will serve two purposes: i) as a barrier against LiPS and ii) as the sulfur host in the cathode. Accordingly, on the one hand, the N,S-co-doped porous carbon nanoparticles (PCN) were used to coat a side of the PP separator and construct a barrier to repress the mobility of soluble polysulfides, and on the other hand, sulfur-carbon nanocomposites made up of PCN nanoparticles loaded with controlled amounts of sulfur ($\sim 40\text{-}80\%$) were used to fabricate the sulfur cathodes. The PCN, synthesized using polypyrrole nanoparticles as carbon precursor, combine several suitable properties: a) a uniform diameter of around 80 nm; b) a well-developed porosity (BET surface area $\sim 1600\text{ m}^2\text{ g}^{-1}$ and pore volume $\sim 1.5 - 2.2\text{ cm}^3\text{ g}^{-1}$) with a hierarchical pore structure made up of micropores and mesopores; c) a high electrical conductivity of $\sim 2 - 3\text{ S cm}^{-1}$; and d) a good packing density of $\sim 0.33 - 0.47\text{ g cm}^{-3}$. Furthermore, these carbon nanoparticles are co-doped with nitrogen and sulfur heteroatoms, which facilitates the retention of polar polysulfides.³⁵⁻³⁶ To fabricate the sulfur-PCN (S/PCN) hybrid nanoparticles, we used a procedure similar to that employed for PCN with a minor modification that includes the *in situ* generation and incorporation of elemental sulfur. This synthesis scheme allowed the production of PCN nanoparticles and the incorporation of the sulfur to be unified in a single process in accordance with our recently reported protocol.³⁷ The S/PCN-based cathode with a high sulfur content ($>70\%$) coupled with the PCN-coated PP separator exhibited a notably improved electrochemical performance compared to the cell with the pristine separator. The PCN coating layer shows its effectiveness at two different levels: first, the conductive coating enhances the redox availability of the sulfur by lowering the cell resistance and acting as a second current collector; and secondly, its ideally

suited pore structure and surface chemistry acts as an efficient barrier against polysulfides, thereby favouring a long-lasting battery cyclability.

2. Experimental

Synthesis of the porous carbon nanoparticles (PCN).

Polypyrrole nanoparticles (PPy) are the precursor of PCN and they were synthesized following the procedure reported by Lee et al.³⁸ Briefly, 1.32 g of polyvinyl alcohol (MW 31,000, Aldrich) was dissolved in distilled water (400 mL) under vigorous stirring for 30 min. Then, 29.9 g of FeCl_3 (Aldrich) was added and the resulting PVA/ FeCl_3 solution was stirred at a speed of 350 rpm for 1 h. Subsequently, 2.55 g of recently distilled pyrrole (Aldrich) was slowly added to the solution under continuous stirring. After 2 h of polymerization, the solid product was collected by centrifugation, washed several times with distilled water, re-dispersed in water and then, in order to avoid the agglomeration of polypyrrole nanoparticles, the water was removed by freeze-drying. The polypyrrole nanoparticles synthesised were thermally treated, under a N_2 atmosphere, up to 500 °C (1 h). This treatment resulted in a carbonization yield of around 70 %. The preparation of PCN samples was carried out by employing sodium thiosulfate as the activating agent.³⁹ In a typical synthesis procedure, 1 g of pre-carbonized polypyrrole nanoparticles (PCPy) was mixed by hand-grinding in a mortar with appropriate amounts of KCl (Aldrich) and $\text{Na}_2\text{S}_2\text{O}_3$ (Alfa-Aesar). The mass ratio of sodium thiosulfate to polypyrrole varied from 1.5 to 2.4, while the $\text{KCl}/\text{Na}_2\text{S}_2\text{O}_3$ ratio was kept at 3.3. The resulting powder was heated under N_2 up to 800 °C at a heating rate of 5 °C min^{-1} , and held at this temperature for 1 h. Finally, the carbonized solid was washed with distilled water for several hours and the PCN sample was collected by filtration and

dried at 120 °C. The carbon samples were denoted as PCN-*X*, where *X* is the sodium thiosulfate-to-PPy mass ratio (*X*=1.5, 2.0, 2.2, 2.3 or 2.4).

Synthesis of the sulfur-carbon nanocomposites (S/PCN).

The hybrid sulfur-carbon nanoparticles were synthesized following a procedure similar to that used for PCN except that, after the thermal treatment at 800 °C, the carbonized solid was immersed in HCl (5 M) for 15 h under continuous stirring. The resulting S/PCN nanocomposites were washed with deionized water for several hours, collected by filtration and dried at 100 °C. The amount of infiltrated sulfur was determined by heat treatment of a portion of the composites up to 600 °C in a N₂ atmosphere. The sulfur-carbon composites were labelled as S/PCN-*X*.

PCN-coated separator preparation.

For the preparation of the PCN-coated separator, a thin slurry containing 80 wt.% of PCN, 10 wt.% of Super C65 carbon black and 10 wt.% of PVDF in N-methyl-2-pyrrolidone (NMP) was cast onto one side of the pristine polypropylene separator (Celgard 2500) using the doctor blade technique. The coated separator was then vacuum-dried at 50 °C overnight under a certain mechanical tension to avoid twisting. The dried coated film was cut into discs with a diameter of 14 mm. The areal carbon loading of the coated separators was of 0.20 mg PCN cm⁻².

Physicochemical Characterization.

Scanning electron microscopy (SEM) images were recorded by using a Quanta FEG650 (FEI) instrument, whereas transmission electron microscopy (TEM) images were obtained on a JEOL (JEM 2100-F) apparatus operating at 200 kV.

Both instruments are equipped with EDX (energy dispersive X-ray spectroscopy) devices. The packing density and electrical conductivity of the carbon powder and composite powders were determined on a homemade apparatus in which the powders are placed between two stainless steel plungers inside a hollow nylon cylinder (inner diameter of 8 mm). A pressure of 7.1 MPa was then applied. The N₂ sorption isotherms of the carbon and hybrid samples were measured at -196°C using a Micromeritics ASAP 2020 sorptometer. The apparent surface area was calculated by the BET method. The total pore volume was determined from the amount of nitrogen adsorbed at a relative pressure (p/p_0) of 0.95. The pore size distributions (PSD) were determined by means of the Quench Solid State Density Functional Theory (QSDFT) method for nitrogen. X-ray diffraction (XRD) patterns were obtained on a Siemens D5000 instrument operating at 40 kV and 20 mA, using a Cu-K α radiation source. X-ray photoelectron spectroscopy (XPS) was carried out on a Specs spectrometer, operating with Mg KR (1253.6 eV) radiation from a double anode at 150 W. The elemental analysis of the samples was carried out on a LECO CHN-932 microanalyzer. The Raman spectra were recorded on a Horiba (LabRam HR-800) spectrometer. The source of radiation was a laser operating at a wavelength of 514 nm and at a power of 25 mW. The amount of infiltrated sulfur in the S/PCN nanocomposites was determined by thermal treatment up to 600 °C (N₂, 5 °C/min) in nitrogen. For the polysulfide adsorption experiments, a 0.1 M solution of Li₂S₆ was prepared by stirring stoichiometric amounts of Li₂S and S₈ in a mixture of DME/DOL (v/v: 1/1). The mixture was stirred at room temperature overnight until no solid residues were observed. For the calibration, diluted solutions between 1 mM and 10 mM were prepared since the polysulfide

concentration in real cells generally falls within this range.⁴⁰ For the batch adsorption tests, 10 mg of PCN-2.3 porous carbon nanoparticles were introduced into a closed vial containing 5 ml of a 2 mM solution of polysulfides in DME/DOL (carbon-to-solution ratio of 2 mg ml⁻¹). After the addition of the carbon sample, the suspensions were shaken manually and allowed to decant. Aliquots of the solution were extracted after 0.5, 1.5 and 24 h, and the concentration of polysulfides was determined by UV-VIS adsorption.

Electrochemical measurements.

In a typical preparation procedure, 160 mg of each sulfur/carbon composite, 20 mg of Super C65 carbon black and 20 mg of PVDF binder were mixed together and dispersed in NMP by magnetic stirring to form thick slurries. The slurries were cast onto aluminium foil using the doctor blade technique and then dried at 50 °C under vacuum overnight. Once dried, the coated foil was cut into discs with a diameter of 10 mm. The areal sulfur loading of the cathodes was around ~2.0 mg cm⁻². CR2032 coin-type cells were assembled in an Ar filled glovebox, using a Li metal foil as the anode and a pristine or PCN-coated polypropylene membrane as the separator. 1 M lithium bis(tri-fluoromethane) sulfonimide (LiTFSI) in a mixed solvent of 1,3-dioxolane and 1,2-dimethoxyethane (DOL/DEM, vol/vol = 1: 1) with 1 wt.% LiNO₃ was used as the electrolyte. The electrochemical performance of the cells was tested at room temperature in a computer-controlled potentiostat (Biologic VMP3 multichannel generator). Galvanostatic charge/discharge (CD) experiments were carried out over a potential range of 1.7–2.7 V (vs. Li⁺/Li) at different C rates, ranging from 0.2 to 2C (1C = 1675 mA g⁻¹ S). Cyclic voltammetry (CV) experiments were performed within the same potential window at a sweep rate of 0.05 mV s⁻¹.

Electrochemical impedance spectroscopy (EIS) curves were obtained from fresh cells at open-circuit potential within a frequency range of 100 kHz to 1 MHz at an amplitude of 10 mV.

3. Results and discussion

3.1. The synthesis strategy

The porous carbon nanoparticles (PCN) and the sulfur-carbon nanocomposites (S/PCN) were produced by the chemical activation of polypyrrole-based carbon nanoparticles with sodium thiosulfate in the presence of an inert salt (KCl), according to a procedure recently reported by our group.^{39, 41} In the activation process we employed polypyrrole nanoparticles precarbonized at 500 °C, since the direct use of polypyrrole nanoparticles leads to the formation of large aggregates of fused carbon particles (Figure S1). The synthesis procedure is schematically illustrated in Figure 1. At a high activation temperature (800 °C) the reaction between sodium thiosulphate and the precarbonized polypyrrole nanoparticles gives rise to a solid product made up of a mixture of the inert salt (KCl), porous carbon nanoparticles and sodium polysulfides (Na_2S_x). Once this solid has been washed with water, the inorganic substances (*i.e.* KCl, Na_2S_x) are completely eliminated, leaving a solid formed exclusively by highly porous carbon nanoparticles (PCN sample). On the other hand, when the solid product is immersed in an acid medium (*i.e.* HCl), polysulfides undergo a disproportionation reaction, leading to the formation of elemental sulfur as follows:⁴²⁻⁴³

Such *in situ* generated elemental sulfur spontaneously diffuses into the porous network of the PCN due to capillary forces,⁴⁴ giving rise to hybrid sulfur-carbon nanoparticles. This versatile and easy synthesis strategy makes it possible to produce either highly porous carbon nanoparticles (PCN) or sulfur-porous carbon nanocomposites (S-PCN), simply by introducing minor changes into the synthesis methodology (see Figure 1). In this work, both types of materials are used to construct the Li-S batteries. The hybrid sulfur-carbon nanocomposites (S/PCN) are employed as the electroactive material in the cathode whilst the porous carbon nanoparticles (PCN) are coated onto the polypropylene separator to form a shield against the migration of soluble polysulfides.

Figure 1. Illustration of the synthesis process for the preparation of porous carbon nanoparticles (PCN) and hybrid sulfur-carbon nanocomposites (S/PCN).

3.2. Morphology and physicochemical properties of the porous carbon and sulfur-carbon nanoparticles

An examination of the structure of the porous carbon and sulfur-carbon nanoparticles was carried out by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The synthesized polypyrrole consists of spherical nanoparticles with a size of around 90-130 nm (Figures

S2a, b and e). When the polymer is carbonized, the resulting carbon nanospheres exhibit a size of around 65-85 nm, which is considerably smaller than that of the polypyrrole (Figures S2c, d and f). It can be appreciated from Figures S3a and b that, unlike polypyrrole or carbonized polypyrrole nanoparticles, the activated nanoparticles do not have a perfect spherical morphology. What is more, they exhibit a size of 65 ± 10 nm, which is smaller than that of the carbonized polypyrrole, (Figure S3c). These results would seem to suggest a certain collapse of the internal structure, attributable to a weakening of the carbon framework as a consequence of the activation process. A PCN sample subjected to TEM inspection shows that the nanoparticles have a highly developed porosity (see Figure S4c). The porosity combines macropores (interparticle voids displayed in Figures S4a and S4b), mesopores (Figure S4d) and micropores corresponding to narrow voids between the disordered graphene-like carbon sheets, as can be seen in Figure S4e. This hierarchical pore organization is confirmed by the nitrogen physisorption experiments, as illustrated in Figure S4f.

Figures 2a and 2b show the SEM microphotographs obtained for the sulfur/carbon nanocomposite S/PCN-2.3 (70.4 %). A comparison with the PCN sample reveals that the S/PCN nanoparticles have a similar microstructural appearance, suggesting that the incorporated sulfur has integrated well inside the pore network. The size of the S/PCN nanocomposites is also similar to that of PCN, as illustrated in Figure 2c. Further examination of the structural characteristics of the S/PCN nanocomposites by TEM reveals an internal structure that is indistinguishable from that of the PCN material. Although none of the infiltrated sulfur is visible in Figures 2d-f, the elemental mapping obtained

by TEM-EDX shows that sulfur has been successfully infiltrated and is homogeneously distributed (Figures 2g-i). This result is corroborated by the SEM-EDX mapping of the sulfur for the S/PCN-2.2 sample (Figure S5).

Figure 2. Microstructure of the sulfur-carbon nano-composites: (a, b) SEM images, (c) particle size distributions, (d-f) TEM images and (g-i) TEM-EDX

elemental mappings of carbon (h) and sulfur (i) collected from the area shown in (g). Sample: S/PCN-2.3.

The textural properties of the PCN and S/PCN samples were investigated by nitrogen physisorption analysis. Figure 3a and b display the sorption isotherms and pore size distributions of the PCN samples, whilst the main textural characteristics (*i.e.*, BET surface area, pore volume and micropore volume) for both types of sample are listed in Table 1. The PCN samples have high BET surface areas, in the 1380-1690 m² g⁻¹ range, and large pore volumes (1.29-2.20 cm³ g⁻¹), the micropore volume (< 2 nm) being around 0.40 cm³ g⁻¹ and ~ 0.20 cm³ g⁻¹ in the case of the narrowest micropores (< 1 nm). Inspection of the sorption isotherms of the PCN samples shows that they have a hierarchical porosity made up of micropores, mesopores and macropores (Figure 3a and S4f). Hence, the large N₂ uptakes for $p/p_0 > 0.95$ can be attributed to the inter-nanoparticle voids (macropores) that are visible in Figures S4a-b. The pore size distributions in Figure 3b reveal that the PCN samples have a framework-confined porosity made up of two pore systems: one constituted by narrow micropores centred at ~ 0.8 nm and the other corresponding to micro-mesopores in the ~ 1.5-12 nm range. The incorporation of sulfur leads to a sharp drop in the textural properties in the S/PCN samples, as can be inferred from the sorption isotherms displayed in Figure S6a and from the textural properties shown in Table 1. An analysis of the pore volume values of the S/PCN composites reveals that, for the samples with sulfur contents of up to ~ 70 %, a fraction of the pore volume still remains unoccupied (see Table 1 for details). However, for sulfur contents > 80 % the pores are completely filled, as a result of which a certain amount of sulfur is present on the outer surface of the

carbon nanoparticles. The percentage of sulfur incorporated into the S/PCN nanocomposites can be modulated by simply modifying the amount of $\text{Na}_2\text{S}_2\text{O}_3$ used in the activation process, as illustrated in Figure S6b. Thus, the percentage of sulfur can be adjusted between $\sim 40\%$ and $\sim 80\%$ merely by increasing the $(\text{Na}_2\text{S}_2\text{O}_3/\text{PPy})$ weight ratio from 1.5 to 2.4. Concurrently with the increase in the amount of infiltrated sulfur, there is a dramatic drop in the carbon yield from 14% to 3.5% .

Table 1. Physico-chemical properties of the porous carbon nanoparticles and sulfur/carbon composites.

Material	Sample code	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_p ($\text{cm}^3 \text{g}^{-1}$) ^a	$V_{\text{micro} < 2 \text{ nm}}$ ($\text{cm}^3 \text{g}^{-1}$) ^b	$S_{\text{infiltrated}}$ (wt %) ^c	S_{doped} (wt %) ^d	N_{doped} (wt %) ^d	Electrical conductivity (S cm^{-1})	Packing density (g cm^{-3})
Porous carbon	PCN-1.5	1520	1.29	0.47 (0.22)	-	4.18	2.69	3	0.43
	PCN-2	1380	1.40	0.39 (0.20)	-	4.45	1.99	2.6	0.47
	PCN-2.2	1690	2.07	0.43 (0.22)	-	5.96	1.99	2.7	0.36
	PCN-2.3	1620	2.15	0.40 (0.20)	-	4.41	2.38	2.5	0.34
	PCN-2.4	1670	2.20	0.42 (0.19)	-	7.70	2.07	2.2	0.33
S/carbon	S/PCN-1.5	-	-	-	41.7	-	-	1.9	0.54
	S/PCN-2	140	0.28 (0.37)	-	54.8	-	-	1.9	0.98
	S/PCN-2.2	110	0.24 (0.51)	-	61.0	-	-	1.8	1.08
	S/PCN-2.3	60	0.18 (0.30)	-	70.4	-	-	0.9	1.79
	S/PCN-2.4	20	0.07 (~ 0)	-	81.9	-	-	0.7	1.90

^a The pore volume was calculated for $p/p_0=0.95$. The theoretically unoccupied pore volumes deduced by assuming that the sulfur is confined within the porosity of carbon are indicated in brackets. This parameter was calculated by using the formula: $[V_p \times (1 - a_s) - a_s / 2.07]$, where a_s is the fraction of sulfur and 2.07 its density; ^b The volume of micropores smaller than 1 nm are given in brackets, ^c S determined by thermal treatment up to 600 °C (N_2), ^d percentages of nitrogen and sulfur determined after the infiltrated sulfur has been removed by thermal treatment up to 600°C (N_2).

Figure 3. (a) Nitrogen sorption isotherms and (b) pore size distributions of the porous carbon nanoparticles. High-resolution XPS spectra of (c) N 1s and (d) S 2p, collected from the PCN-1.5 sample. In Figure (a), the isotherms of PCN-2, PCN-2.2, PCN-2.3 and PCN-2.4 are shifted up by 200, 400, 600 and 800 cm³ g⁻¹ respectively for the sake of clarity.

The microstructure of the S/PCN samples was analysed by X-ray diffraction and Raman spectroscopy. The XRD patterns in Figure S7a reveal that the composites with a S content of up to around 70 % do not exhibit any

sharp crystalline peak, but only a broad band at $2\theta \sim 15-30^\circ$, which is typical of carbons with a disordered structure. These results suggest that the infiltrated sulfur has integrated well within the pores of PCN as an amorphous S_8 phase. In contrast, the S/PCN-2.4 sample (with a sulfur content of 80 %) exhibits peaks that are characteristic of orthorhombic sulfur, indicating that a fraction of the sulfur is located outside of the pores in the form of a crystalline phase. This interpretation is confirmed by the Raman spectra in Figure S7b. Thus, whereas the composites with < 70 % of sulfur only exhibit two broad bands at $\sim 1350\text{ cm}^{-1}$ (D band) and $\sim 1600\text{ cm}^{-1}$ (G band) which are typical of carbon materials with a disordered structure, the spectrum of S/PCN-2.4 contains another three peaks at 154 cm^{-1} , 219 cm^{-1} and 473 cm^{-1} associated with S-S vibrational modes typical of crystalline sulfur.⁴⁵ These results show that for the S/PCN samples with sulfur contents lower than $\sim 80\%$, all of the sulfur is located inside the pore structure of the carbon host as an amorphous phase, which is in agreement with the data derived from the textural analysis.

The porous carbons used to accommodate the sulfur must have a good conductivity to allow the unimpeded transfer of electrons. The PCN samples satisfy this requirement, as can be inferred from the electrical conductivities of the pressed carbon samples that are in the $2.2-3\text{ S cm}^{-1}$ range (Table 1). Importantly, in the case of the S/PCN composites, the electrical conductivities are also high ($0.7-1.9\text{ S cm}^{-1}$); even the sample with 82 % S exhibits a conductivity of 0.7 S cm^{-1} (see Table 1). These results show that the electrical contact between the S/C particles is preserved, which in turn indicates that the sulfur is predominantly concentrated inside the pores of the PCN nanoparticles. Because of their high pore development, the PCN nanoparticles have relatively

low packing densities in the 0.33-0.47 g cm⁻³ range (Table 1). However, as the sulfur occupies more and more pores, the packing density rapidly rises to values close to the density of sulfur (2.07 g cm⁻³), as in the case of the fully infiltrated samples such as S/PCN-2.4 (82 % S, packing density: 1.90 g cm⁻³). This is an important point given that the higher the packing density, the smaller the amount of electrolyte needed to soak the battery.

An important feature of the porous carbons produced by our synthesis strategy is that they are co-doped with significant amounts of nitrogen (2-2.7 wt.%) and sulfur (4.18-7.7 wt.%) heteroatoms, as indicated in Table 1. These N and S groups have different origins. Whereas the nitrogen functionalities derive from the N-rich precursor (polypyrrole), the sulfur functional groups are generated during the activation process as a consequence of the high-temperature reactions between the carbonaceous matter and the oxidizing agent (sodium sulfate). The combination of both heteroatoms plays an important role in the electrochemical performance of the composites in a Li-S battery. Several authors have presented evidence to show that the dual doping of porous carbon hosts with N and S heteroatoms significantly increases the interaction with polysulfide species, which may help to suppress the shuttle phenomenon.^{35-36, 46-47} In particular, Zhou *et al.* demonstrated, by means of DFT calculations, that N/S co-doping has a synergistic effect that provides stronger binding energies for anchoring polysulfides than mono-doped (S or N) carbons.⁴⁷ The EDX mappings of sulfur and nitrogen in the PCN samples obtained by means of TEM (Figure S8) and SEM (Figure S9) analyses prove that these heteroatoms are uniformly distributed over the carbon particles. The nature of the N and S groups was determined by X-ray photoelectron

spectroscopy (XPS). The XPS survey spectra obtained for the porous carbons only contain four peaks associated to C 1s, O 1s, N 1s and S 2p, which rules out the presence of foreign elements (Figure S10a). The results of the deconvolution of the high-resolution C 1s, N 1s and S 2p XPS spectra corresponding to the PCN-1.5 sample are shown in Figures S10b, 3c and 3d, respectively. In the C 1s XPS spectrum, besides the peaks at 284.5 eV, 286.5 eV, 287.8 eV and 289.1 eV associated to C=C, C-O, C=O and O-C=O bonds, there is an additional peak at 285.4 eV that can be ascribed to carbon covalently attached to S or N atoms.⁴⁷ Regarding the N species, the peaks identified in the N 1s spectrum indicate the presence of pyridinic-N (398.2 eV), pyrrolic/pyridonic-N (400.1 eV), quaternary-N (400.9 eV) and oxidized nitrogen groups (402.6 eV). The S 2p spectrum exhibits two doublets, one at 164.1 and 165.3 eV, that is ascribed to thiophenic moieties (C-S-C), and another at 168.0 and 169.2 eV, that can be assigned to oxidized sulfur functionalities (C-SO_x-C).

3.2. Structure and polysulfide trapping ability of the PCN-coated separator

The PCN-coated separator was fabricated by coating a PCN-based slurry (80% PCN, 10% binder and 10% carbon black) onto one side of the pristine polypropylene separator using the doctor blade technique. As can be seen in Figure 4a, the thin layer of PCN is well-adhered to the pristine PP separator and it can be hardly flexed or twisted maintaining intact its mechanical integrity. The morphology of the PCN coating layer was investigated by SEM. The top view micrograph of the coating surface shows the absence of cracks or wrinkles (Figure 4b). Indeed, the thickness of the coating is very homogeneous and the PCN particles are densely packed. A compact PCN layer devoid of preferential

diffusion pathways is essential for an efficient trapping of lithium polysulfides. As can be seen in **Figure 4c**, the thickness of the carbon coating is as low as 10-15 μm . Remarkably, the mass loading of this coating is of only 0.25 mg cm^{-2} (0.20 mg cm^{-2} of PCN). It is important to note that a thin but effective porous coating is of special importance since high loads of coating would significantly increase the weight and thickness of the separator, as well as the amount of electrolyte required to soak the battery. The nanometric size of the PCN particles allows the effective and easy coating of the PP separator by means of a simple procedure that can be easily implemented in large scale production processes. Moreover, the PCN layer has a high surface conductivity of 3.95 S cm^{-1} , as determined by the Van der Pauw equation using the four-point probe technique. A good electric conductivity is a key characteristic for the carbon-coated separator since it can then act not only as a polysulfide barrier, but also as a peripheral current collector, boosting the redox accessibility of the sulfur species.

Figure 4. (a) Digital pictures of the PCN-coated PP separator showing the strong adhesion and mechanical stability of the coating layer. (b) Top and (c) cross-sectional SEM images of the PCN-coated separator. (d) Images of the H-shaped glass cells containing the polysulfide solution (left half-cell) and the DME/DOL mixture (right half-cell) connected by the pristine or PCN-modified separator. (e) Values of absorbance at 400 nm versus time for a 2 mM Li_2S_6 solution containing the PCN-2.3 porous carbon, and the corresponding digital pictures of the batch experiment.

The polysulfide trapping capacity of the PCN-coated separator was determined using an H-shaped glass cell. As shown in Figure 4d, the half-cell on the left was filled with a 50 mM solution of polysulfides (Li_2S_6) in DME/DOL, and the right half-cell was filled with the DME/DOL mixture. The two half-cells were separated by a disc cut out of the pristine PP separator (Figure 4d, left) or by the PCN-coated separator (Figure 4d, right). In the case of the pristine separator, the polysulfides rapidly diffuse towards the right half-cell, and quickly colour the DME/DOL mixture. However, with the PCN coating layer, the migration of polysulfides is impeded by virtue of the physical barrier effect and the polysulfide adsorption capacity of the porous nanoparticles. The capacity to adsorb polysulfides was further analyzed by means of a batch adsorption test. 10 mg of the PCN-2.3 porous carbon nanoparticles was added to a closed vial containing 5 mL of a 2 mM solution of polysulfides in DME/DOL. The adsorption capacity of the PCN was monitored by measuring the change in colour of the solution in contact with the porous sorbent. As shown in Figure 4e, the absorbance of the solution at 400 nm decreases sharply after only 30 min of contact without stirring, and reaches equilibrium after 1.5 h. The adsorption capacity of the PCN at this time is 0.69 mmol g^{-1} , and 0.62 mmol g^{-1} after only 0.5 h, as calculated by applying a mass balance to the adsorption results (see experimental section and Figure S11 for calibration details). On the basis of the porous structure of PCN-2.3, its maximum adsorption capacity concurs well with that calculated using the model proposed by Hippauf *et al.* for hydrophobic carbons, which assigns different polysulfide adsorption capacities for each type of pore (the theoretical adsorption capacity according to this model is 0.71 mmol

g^{-1}).⁴⁸ The high content in narrow micropores and surface N and S functionalities is the main factor responsible for the adsorption of LiPS (the micropores adsorb up to eight times more polysulfides than the mesopores),⁴⁸⁻⁴⁹ while the mesopores provide convenient diffusion channels that are responsible for the fast trapping ability of the PCN coating,⁴⁸ as can be deduced from the short equilibration time in the batch adsorption test.

3.3. Electrochemical performance of Li-S cells with a PCN-coated separator

As depicted in Figure 1, the S/PCN composites and the PCN nanoparticles were employed as the cathode active material and as the separator coating layer, respectively, in the Li-S batteries. The S/PCN-2.3 sample was selected for the formulation of the cathode because it combines a high sulfur content (70.4 wt%) with a good carbon yield (7 %) (see Figure S6b). Figure S12a shows the cyclic voltammograms corresponding to the S/PCN-2.3 cathode during the 1st, 5th and 10th charge-discharge cycles. The cathodic sweep reveals two peaks associated to the multi-step reduction of sulfur. Thus, at a cell voltage of 2.28 V the elemental sulfur is reduced to soluble long-chain lithium polysulfides (Li_2S_x , $4 \leq x \leq 8$), while the peak recorded at 2.05 V evidences the conversion of polysulfides to the solid discharge products Li_2S_2 and Li_2S . Analogously, the anodic sweep describes two overlapping signals centred at 2.33 and 2.38 V associated with the reversible oxidation of Li_2S and Li_2S_2 to S_8 .⁵⁰ As can be seen from the overlapping plots, there is little change in the redox peaks during the first charge-discharge cycles, which confirms the good reversibility of the process. The micro-mesoporous structure of PCN-2.3 seems to be the key to

this cycling stability, as it is able to accommodate well the volume changes taking place during the charge and discharge processes. The carbon scaffold does not contribute to lithium storage within the potential range studied, as deduced from the flat cyclic voltammogram of the battery using the PCN-2.3 cathode (without sulfur) shown in Figure S12b.

Batteries were assembled using the pristine and PCN-coated PP separators facing the S/PCN cathode. The PCN-2.3 sample (the carbon host for the S/PCN-2.3 composite employed as the cathode) was used for the separator coating layer. Due to the conductive nature of the thin PCN coating, the use of the modified separator reduced the internal resistance of the cell. This was revealed by electrochemical impedance spectroscopy experiments carried out on fresh batteries. Figure 5a shows the Nyquist plots of batteries with the pristine and the modified separators. Both plots display a semicircle in the high frequency region ascribable to the charge transfer resistance (R_{CT}), as well as a sloped line at low frequencies associated to mass transfer restrictions (R_{MT}). The R_{CT} values, given by the amplitude of the semicircle, are around 95 Ω and 69 Ω in the cells built with the pristine and modified separators, respectively, which represents a reduction of $\sim 30\%$ in cell resistance with the application of a thin PCN coating. The PCN layer is in contact with the outer surface of the cathode, where the electroactive sulfur is less accessible by electronic conduction. This coating acts as a supplementary current collector and facilitates charge transportation throughout the whole cathode.³¹ The cyclic voltammograms of the battery with the S/PCN-2.3 cathode and the PCN-2.3 coating layer at different scan rates are shown in Figure S13a. The redox signals were well retained as the scan rate increased. Moreover, following the

Randles-Sevcik equation, the intensity of the anodic peak bears a linear relationship with the square root of the scan rate (Figure S13b), which suggests that the electrochemical process is diffusion-limited.

Figure 5. (a) Nyquist plots of the batteries with the pristine and CPN-coated separator; (b) galvanostatic charge-discharge curves of the S/ PCN-2.3 batteries with the pristine separator and (c) with the coated separator at different cycling stages (current density: 0.2C); (d) cycling stability of the batteries with the pristine and modified separators; (e) cycling performance of

the batteries with the PCN-2.3-modified separator at different charge-discharge rates. The sulfur load in the cathodes is 2 mg S cm^{-2} .

Figures 5b and 5c show the galvanostatic charge-discharge profiles of the batteries with the pristine separator and PCN-modified separator, respectively, run at a current density of 0.2C. The profiles display two discharge plateaus associated with the sulfur reduction reactions, as well as two continuous charge plateaus related to the charge processes observed by cyclic voltammetry. The cell with the pristine PP separator experiences a significant decrease in the length of both discharge plateaus with cycling. The length of the upper plateau reflects the amount of polysulfides generated and the ability of both the carbon coating and the carbon scaffold in the cathode to retain polysulfides. As can be observed, this plateau gets notably shorter with cycling in the cell with the pristine separator. In contrast, the battery with the PCN-modified separator displays longer discharge plateaus that show little variation upon cycling. The initial capacity of the upper plateau (Q_H) is 318 mAh g^{-1} for the battery with the modified separator, and after 100 charge-discharge cycles 84% of this capacity is retained (see Figure S14). On the other hand, the high voltage plateau recorded for the battery with the pristine separator gets shorter much more quickly, and only 55 % of its capacity is retained in the 100th cycle. These results evidence that the PCN coating on the separator acts as a highly effective trap for polysulfides, favouring the reuse of sulfur/Li₂S and helping to sustain the reversibility of the charge-discharge process.

The cycling performance of the batteries with pristine and PCN-coated separators at a current rate of 0.2C is summarized in Figure 5d. Here it can be

seen that the capacity of the cell with the PCN-coated separator is fully retained from the very first cycles. This behaviour contrasts with the rapid decay in capacity observed in other reported Li-S systems, even when modified separators or self-standing barriers are used.^{31, 51-52} The battery with the PCN-2.3 coated separator exhibits an initial discharge capacity of 1020 mAh g⁻¹, and retains 841 mAh g⁻¹ after 100 charge-discharge cycles with a coulombic efficiency above 99.3%. After 200 cycles, the battery still capable of delivering 711 mAh g⁻¹. The capacity and cycling stability of this battery compares favourably with other reported battery systems with porous carbon interlayers⁵³ or graphene oxide- or CNT-coated separators.²³ The battery with the non-modified separator achieves a lower capacity of 828 mAh g⁻¹ in the first cycle, and experiences a worse capacity retention (only 466 mAh g⁻¹ at the 100th cycle). The significant increase in sulfur utilization with the introduction of a conductive membrane/coating layer between the cathode and the separator has also been mentioned in previous reports.^{31, 54-56} The effect of the thin carbon coating on the self-discharge of the batteries was also assessed. Thus, the batteries were charged and discharged at 0.2 C. During the 10th cycle, the discharge was stopped at 2.15 V and the batteries were allowed to rest for 3 days. As shown in Figure S15, the PCN coating layer is able to suppress the self-discharge phenomenon, diminishing the capacity drop experienced between the 10th and 9th cycles by ~50%. In this work we also explored the use of PCN-1.5 as a coating material for the separator. The porous nanoparticles in PCN-1.5 are richer in micropores (0.47 cm³ g⁻¹) than in PCN-2.3 (0.40 cm³ g⁻¹), while the latter has a notably higher pore volume (2.15 vs. 1.29 cm³ g⁻¹) including numerous mesopores larger than 4 nm (see PSD in Figure 3b). As

can be seen in Figure 5d, both the capacity and the cycling performance of the cell with the PCN-1.5 coating also exceed those of the battery with the unmodified separator. However, the highly porous network of PCN-2.3, which is rich in both micro- and mesopores, seems more beneficial. The superior electrochemical performance of the battery with the PCN-2.3-coated separator is attributed to two main factors. First, the conductive nature of the thin PCN coating allows electronic access to a larger fraction of the sulfur in the cathode, making it possible to achieve an initial capacity 23 % higher than that of the battery with the pristine separator. Secondly, as demonstrated in the polysulfide adsorption experiments, the porous structure of the compact PCN coating acts as a perfect trap for polysulfides, thereby preventing their migration to the anode side. At the same time, its micro-mesoporous network allows the accommodation and reutilization of the sulfur compounds, thus minimizing the loss of active material and providing the redox processes with a good reversibility. Comparable or higher values of capacity have been achieved by using barriers made up of nanocarbons (graphene, carbon nanotubes)^{28, 55} and/or metal oxides⁵⁴ or carbon coatings prepared by sophisticated fabrication procedures (e.g. using hard templates or multistep coatings).^{31-32, 57-58} However, the adoption of simple procedures with straightforward synthesis and processing stages such as the one proposed in this study, offers more promise from the point of view of applicability. The cycling performances of the batteries with the NPC-2.3 coating were studied at higher current rates of 0.5C, 1C and 2C. As shown in Figures 5e and S16, the capacity delivered by the batteries is well retained up to a current rate of 1C. It is important to note that, at this discharge rate, the battery is able to achieve a maximum discharge capacity of

916 mAh g⁻¹, and as much as 757 mAh g⁻¹ in the 100th cycle. At a high current rate of 2C, the cell displays an initial capacity of 645 mAh g⁻¹, and is capable of running for 500 cycles with a capacity fade of only 0.089% per cycle (see Figure S17).

It should also be pointed out that the thickness of the separator coating layer is thin enough not to constitute an important volume/mass fraction in the overall cell configuration. This is of special importance since the energy density of the cell decreases with an increase in the coating layer thickness.⁵⁴ The structural and chemical characteristics of the PCN-2.3 porous carbon allow a good performance of the coating layer even with such a low thickness (only 10-15 μm). Other porous carbons used as polysulfide barriers usually need to be employed with much higher thicknesses or mass loadings to achieve a good performance or to build stable self-standing films.^{31, 51, 56, 59} In our batteries, the mass loading of the PCN coating accounts only for 6.6% of the mass of both the cathode and the PCN layer, which translates into a decrease in the sulfur fraction of only 3.7 wt.% if the two PCN-based components (the composite cathode and the PCN coating) are taken into account. This contrasts with notable decreases of as much as 30 % in the sulfur fraction reported for other modified separators.³¹ The mass fraction of the coating layer is significantly reduced when the batteries have cathodes with a higher areal loading. For example, we explored the use of S/PCN-2.3 cathodes with a sulfur loading above 6 mg cm⁻². These cathodes have a thickness of ca. 150 μm and a packing density of 1.01 g cm⁻³. In this case, the mass of the PCN-2.3 layer accounted for only 2.3 % of the mass of the cathode plus carbon coating, which represents a reduction in sulfur content of only 1.3 %. It is well known that the

performance of highly loaded cathodes is adversely affected by a poor electrical contact, and also that their integrity is severely damaged upon cycling.⁶⁰ However, the high loading S/PCN-2.3 cathode coupled with a PCN-modified separator displayed a good performance. Figures 6a and 6b show the galvanostatic charge-discharge profiles and the cycling stability of this battery, expressed in terms of areal capacity. As a consequence of its high sulfur loading, when it was first cycled at 0.1 C (1.04 mA cm^{-2}), the battery displayed an areal capacity as high as 6.4 mA h cm^{-2} (1025 mA h g^{-1} , see Figure S18). Furthermore, despite its high sulfur content and areal loading, the charge-discharge processes in this battery functioned to a high degree of efficiency, above 94 %, which evidences the absence of polysulfides shuttling. After a couple of cycles at 0.1C, the current density was doubled (2.08 mA cm^{-2}), reaching a capacity of 4.5 mA h cm^{-2} that was retained throughout the cycling. Moreover, the battery was still able to provide 2.7 mA h cm^{-2} even after 100 charge-discharge cycles.

Figure 6. Evolution of the areal capacity of the battery with the S/PCN-2.3 cathode and the PCN-2.3-coated separator, using a sulfur loading of 6.2 mg S cm^{-2} . (a) Representative galvanostatic plots and (b) cycling performance.

4. Conclusions

A new straightforward synthesis strategy for the production of porous carbon nanoparticles and sulfur/porous carbon composites is presented. The synthesis procedure relies on the use of polypyrrole nanoparticles as the carbon source and sodium thiosulfate as the porogenic agent and sulfur source. By introducing minor changes, this methodology allows the production of high surface area N-S-codoped carbon nanoparticles or sulfur-carbon composites made up of porous carbon nanoparticles filled with *in situ* infiltrated sulfur. The porous carbon nanoparticles possess a unique structure, combining a uniform particle size (~ 65 nm) with a high specific surface area (up to $1690 \text{ m}^2 \text{ g}^{-1}$), a high pore volume (up to $2.20 \text{ cm}^3 \text{ g}^{-1}$), a considerable amount of N and S heteroatom doping (up to 7.7 wt.% S and 2.1 wt.% N) and a high electronic conductivity ($2.2\text{-}3.0 \text{ S cm}^{-1}$). The *in situ* synthesized S/C composites were employed as cathodes in Li-S cells, while the porous carbon nanoparticles were used as a polysulfide barrier coating the separator. The nanosized porous carbon particles deposited on the separator gave rise to a thin yet effective barrier that improved the sulfur utilization and the cycling stability of the battery with only a negligible reduction in the sulfur content of the cell. The battery achieved $1020 \text{ mA h g}^{-1} \text{ S}$ at a discharge current density of 0.2C, and $645 \text{ mA h g}^{-1} \text{ S}$ with a tenfold increase in current, and these capacities were maintained from the very first cycles (capacity decay of 0.089% per cycle over 500 cycles). The applicability of these materials was further verified by the analysis of a battery with a S mass loading $> 6 \text{ mg cm}^{-2}$. The results confirm the suitability of our proposed versatile synthesis method for the unsophisticated preparation of carbon and

sulfur/carbon nanoparticles intended for implementation in different components of Li-S batteries.

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Conflict of Interest

The authors declare no conflict of interest.

Supporting Information

SEM and TEM images, SEM-EDX and TEM-EDX elemental mappings, Particle size distributions, N₂ adsorption isotherms, XRD patterns, Raman spectra, XPS general and high resolution C1s spectra, UV-Vis spectra and calibration line, cyclic voltammetries and galvanostatic charge-discharge results.

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