Highly-packed monodisperse porous carbon microspheres for energy storage in supercapacitors and Li-S batteries

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Abstract

Porous carbon microspheres and S/microspherical carbon composites with a highly-packed hexagonal arrangement have been synthesized by chemical activation of precarbonized resorcinol-formaldehyde spheres. Sodium thiosulphate is used as a harmless activating agent, S dopant and sulfur precursor. The porous microspheres exhibit large surface areas ($2060\text{--}2340\text{ m}^2\text{ g}^{-1}$) and adequate micro-mesoporosity. They also have a notable amount of sulfur heteroatoms (5-7 %) and high electronic conductivity ($2.3\text{--}3.1\text{ S cm}^{-1}$). The compact organization and suitable porosity of the microspheres allow competitive values of volumetric capacitance to be achieved when used in supercapacitors operating in aqueous and organic electrolytes (130 and 64 F cm^{-3} , respectively), while maintaining good rate capability. In addition, the sulphur/spherical carbon composites with a sulfur content above 80 % are tested as cathode material in lithium-sulfur batteries, demonstrating high sulfur utilization, large values of volumetric capacity (768 mAh cm^{-3}) and stable long-term cyclability (0.086 % capacity loss per cycle).

KEYWORDS: Sodium thiosulphate activation; porous carbon microspheres; Sulfur/carbon composite; Supercapacitor; Li-S battery.

1. Introduction

Electrochemical energy storage systems are essential components that allow energy to be supplied on-demand to mobile electronics and the efficient exploitation of renewable energy sources. Supercapacitors and rechargeable batteries are the preferred energy storage systems for power and energy supply, respectively.^[1–3] Supercapacitors store energy through the formation of an electrical double layer (EDL) in the electrode surface and so are able to store and deliver energy very quickly (in seconds) for thousands of cycles. In contrast, batteries are able to store much more energy than supercapacitors through intercalation or redox processes. However, the sluggish reaction kinetics associated with these processes limits the power these systems can deliver. Therefore, supercapacitors and batteries are complementary elements that can be combined to meet the ever-growing energy and power needs of emerging electronic devices.^[4]

The scientific community is making a huge effort to look for new materials that can store more energy and allow short charging times. In this regard, porous carbons are already considered a key component in emerging energy storage systems such as supercapacitors and lithium-sulfur batteries.^[3,5] Porous carbons incorporate a number of characteristics that mean they are suitable for use in these systems, such as their low cost, high electrical conductivity, large specific surface area, chemical inertness and easy-to-tune surface chemistry and pore structure. In particular, their highly porous texture provides a large active area for the sorption of electrolyte ions in supercapacitors, as well as confined spaces for the efficient trapping/retention of sulfur when used as the conductive host in Li-S battery cathodes. Many synthesis strategies have been developed with the aim of beating current commercial activated carbons in terms of energy storage capacity and rate performance. Besides KOH, other potassium-based salts such as potassium carbonate, potassium bicarbonate and potassium oxalate have also led to highly activated carbons with very large specific surface areas (up to $3000 \text{ m}^2 \text{ g}^{-1}$) and large energy storage capacities when used in SCs and Li-S batteries.^[6–11] Along these lines, we have recently introduced the use of a harmless chemical activating agent, sodium thiosulphate, for the synthesis of highly porous carbon materials with excellent performance in supercapacitive energy storage.^[12,13] This versatile strategy also allowed the *in situ* incorporation of elemental sulfur within the pores of synthesized carbons yielding sulfur/carbon composites that can be directly used for the fabrication of cathodes for Li-S batteries.^[14–16]

Due to the progressive miniaturization of portable and wearable devices, there is a growing consensus that the performance of electrode materials should be evaluated with a volumetric criterion. Many reported carbons with hierarchical porosities or 3D architectures based on the use of carbon fibres, nanotubes or graphene have shown improved ion transport properties and allow the use of high loadings of active mass,^[17–24] however, these carbons have considerable pore volumes that ruin the performance of these materials on a volumetric basis. Moreover, these empty electrode volumes need to be flooded with excess electrolyte, which increases the amount of inert mass in the device.^[25]

Several carbon-based materials with high packing densities have been proposed as electrode materials for SCs with high volumetric features. Non-porous functionalized carbons,^[26,27] strictly microporous carbons,^[28] compact graphene films and hydrogels,^[29,30] and graphene-based composites^[31,32] have shown impressive values of volumetric capacitance. However, the application of many of these materials is limited to low-medium current rates because their highly packed structures restrict the diffusion of the electrolyte ions. Thus, finding an optimized trade-off between particle density and adequate porosity with an optimized mesopore volume is the only way towards high performance compact ECs.^[33] Besides the porous structure, controlling the macroscopic arrangement of the carbon particles in the electrode seems to be an interesting strategy to reduce dead volume. The tap density of regularly shaped particles (e.g., spheres) is known to be higher than that of irregularly shaped particles.^[34] However, synthesizing carbons with controlled size and morphology is difficult as the materials are very sensitive to reaction conditions.

In the case of Li-S batteries, the tap density of the cathode is given by the pore volume of the carbon host and by the amount of sulfur infiltrated. While the sulfur content should be as high as possible in order to beat current Li-ion battery technology,^[23] the ideal sulfur host must provide enough space for the volume changes that occur during lithiation and delithiation while avoiding large unoccupied spaces. Several S/C cathodes with graphene-based architectures have shown ground-breaking values of volumetric capacity,^[35–37] but they are not compatible with the mature industry based on the roll-to-roll manufacture of electrodes composed of active material, conducting additive and binder.^[38]

In this paper we propose a novel synthesis approach for preparing porous carbon and sulfur-carbon composites made up of uniform spherical microparticles that are highly packed. Specifically, we report the production of porous carbon microspheres with a uniform diameter of around 0.5 μm by the activation of resorcinol-formaldehyde microspheres with $\text{Na}_2\text{S}_2\text{O}_3$. The resulting activated carbon achieves a specific surface area of above 2300 $\text{m}^2 \text{g}^{-1}$ and retains perfect spherical morphology, uniform size ($\sim 0.5 \mu\text{m}$) and a highly compact hexagonal arrangement. The activated particles combine a high micropore volume with a suitable number of small mesopores, and their ordered packing defines fully interconnected and regular voids. Such features are key to achieving a good electrochemical response at high rates when they are used as electrodes for supercapacitors, along with maintaining competitive volumetric performance in aqueous and organic electrolytes. By introducing minor changes to the synthesis procedure, the *in situ* infiltration of elemental sulfur in the porous structure of the carbon microspheres can be easily realized. In this way, sulfur/carbon microspheres with a high sulfur content (83 %) are synthesized. When tested as the cathode material in Li-S cells, they show good sulfur utilization and volumetric capacity, as well as excellent cycling stability.

2. Experimental

Synthesis of porous carbon microspheres (PCS)

The resorcinol-formaldehyde (RF) microspheres were synthesised according to Liu et al.^[39] Briefly, 0.4 g of ammonia was added to 100 g of a mixture of ethanol

and deionized water ($E/W = 0.4$, v/v) in a Teflon autoclave that was then closed and stirred at 900 rpm for 1 h at a constant temperature of 30 °C. Then, 0.705 g of resorcinol was added, the autoclave was closed and the solution was stirred for 30 more minutes at the same temperature. Finally, 1.15 g of a 37% formaldehyde solution (resorcinol/formaldehyde = 2, mol/mol) was added dropwise under continuous stirring. Following that, the Teflon autoclave was closed and stirred at 30 °C for 24 h. After this time, the autoclave was heated statically at 100 °C in an oven for 24 h. The RF microspheres obtained were recovered by centrifugation, washed with abundant water and ethanol, and dried at 100 °C for several hours. The polymerization yield was around 72 %.

For the synthesis of the porous carbon, the RF microspheres were first thermally treated at 500 °C (heating rate of 5 °C min⁻¹) under N₂ flow with a holding time of 1 h at this temperature (carbon yield: 60 %). Then, this pre-carbonized sample was physically mixed with the appropriate amount of sodium thiosulphate and KCl. The amount of Na₂S₂O₃ used was based on the mass of RF microspheres (Na₂S₂O₃/RF weight ratio in the 1.5-3.5 range). The KCl/Na₂S₂O₃ weight ratio was of 2.2. The three components were physically mixed by hand grinding and thermally treated at 800°C for 1 h under a nitrogen flow. The porous carbon was then recovered by washing with deionized water, filtration and drying at 120°C for 4 hours. The porous carbon samples were labelled as PCS-X, where X is the Na₂S₂O₃/RF weight ratio.

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

The sulfur/carbon composites were obtained following the same procedure as for the porous carbon, except that the carbonized product was washed with an HCl solution (concentration around 15 %) instead of water (see Figure 1). The S/C composite materials were denoted as SPCS-X, accordingly.

Physicochemical Characterization

The morphology of the carbon and carbon/sulfur microspheres was analysed by scanning electron microscopy (SEM) using a Quanta FEG650 (FEI) microscope. The same equipment was used to obtain the energy dispersive X-ray spectra (EDX). To calculate the sulfur fraction (elemental sulfur infiltrated in the porous structure) of the SPCS composites, 100-150 mg of each composite was thermally treated at 600 °C in nitrogen using a heating ramp of 5 °C min⁻¹. An ASAP 2020 apparatus from Micromeritics was used to record the nitrogen adsorption isotherms at 77 K. For this, around 0.1 g of each carbon or sulfur/carbon sample was degassed for 1 h at 200 °C or 70 °C, respectively. The BET method was applied to calculate the specific surface area of the materials. The amount of nitrogen adsorbed at a relative pressure (p/p_0) of 0.95 was used to calculate the total pore volume (V_p). The quenched-solid density functional theory method (QSDFT) was applied to the adsorption data to calculate the pore size distributions. A slit-like pore type was assumed in the model. The same method was used to calculate the micropore volume ($V_{<2nm}$). The X-ray diffraction (XRD) patterns were acquired by using a Siemens D5000 diffractometer. The patterns were obtained using a Cu-K α radiation source and operating at 40 kV and 20 mA. A Horiba (LabRam HR-800) spectrometer was used to record the Raman spectra. The laser radiation source operated at a power of 25 mW had a wavelength of 514 nm. The content of covalently bonded sulfur in the carbon microspheres was determined on a LECO CHN-932

microanalyzer. The X-ray photoelectron spectra (XPS) were acquired by a Specs apparatus which operated with a Mg KR radiation of 1253.6 eV at a power of 150 W. The tap density and the electronic conductivity of the carbon and sulfur/carbon materials was measured using an in-house piece of apparatus. 50-100 mg of each sample was pressed at 7.1 MPa between two stainless-steel plungers introduced inside a Nylon tube with an inner diameter of 0.8 cm. Displacement of the upper plunger due to the volume occupied by the sample was measured using a cathetometer. The tap density of the powdered samples was determined dividing the mass of the sample by this volume. The electronic conductivity of the sample was measured during the same experiment by applying an electrical current between the two plungers using a Promax DC-405 current source. The voltage difference between the two plungers was measured using a Fluke multimeter.

Supercapacitor assembly and electrochemical characterization of the PCS

Slurries containing 85 wt.% of the porous microspheres, 10 wt.% of polymeric binder (PTFE, 60 wt% aqueous suspension, Aldrich) and 5 wt.% of Super C65 carbon black were prepared by mixing the three ingredients using a few drops of ethanol. After thorough kneading, the doughs were rolled into thin films and cut into discs with a diameter of 1 cm. Two of these self-standing electrodes with similar mass ($\sim 10 \text{ mg cm}^{-2}$ of active material) were placed inside two-electrode Swagelok™ cells separated by a glassy fibrous separator. 1 M H_2SO_4 and 5 M LiNO_3 solutions were used as the aqueous electrolytes. These supercapacitors were assembled using gold or stainless steel current collectors for the 1 M H_2SO_4 and 5M LiNO_3 electrolytes, respectively. The mixture of the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIMTFSI) and acetonitrile (wt. ratio of 1:1) was used as the organic electrolyte. The cells using this electrolyte were assembled inside an Ar filled globe box using stainless-steel current collectors.

Electrochemical characterization of the electrodes was performed at room temperature using a Biologic VMP3 potentiostat. Electrochemical impedance spectroscopy (EIS) curves were obtained at frequencies between 1 mHz and 100 kHz. Cyclic voltammograms (CV) were recorded using cell voltages of up to 1 V, 1.7 V and 3 V in the 1 M H_2SO_4 , 5 M LiNO_3 and EMIMTFSI/AN electrolytes, respectively. The voltage was varied with a rate that ranged from 5 to 200 mV s^{-1} . The specific capacitance of the electrodes was calculated from the CV results as:

$$C_{\text{el}} = 4 \frac{I}{\nu \cdot m} \quad (\text{Eq. 1})$$

being I the current, in A, ν the scan rate, in V s^{-1} , and m the total mass of active material in the supercapacitor, in g. Galvanostatic charge/discharge (CD) plots were acquired within the same voltage windows at different current densities in the 0.2-80 A g^{-1} range. The current applied was calculated considering the mass of active material in one electrode. The specific capacitance of the electrodes, in F g^{-1} , was calculated from the discharge plots as:

$$C_{\text{g, el}} = 4 \frac{I}{(dV/dt) \cdot m} \quad (\text{Eq. 2})$$

where dV/dt is the slope of the discharge curve, in V s^{-1} . The upper half of the discharge plot was considered for the calculation of the capacitance, as

supercapacitors usually operate in the $V_{max} \sim \frac{1}{2} V_{max}$ voltage range.^[40] The volumetric capacitance, in $F\text{ cm}^{-3}$, was calculated according to Equation 3:

$$C_{v,el} = C_{g,el} \cdot 0.85 \cdot \rho_{el} \quad (\text{Eq. 3})$$

The packing density of the electrode (ρ_{el}) was calculated by dividing its total mass by its volume. The area of the electrodes was 0.785 cm^2 and their thicknesses were measured with a digital micrometer. The factor of 0.85 makes reference to the fraction of active material.^[41]

The cycling stability of the supercapacitors was studied by charging and discharging the cells over 10000 cycles at 5 A g^{-1} in the case of the aqueous electrolytes and at 10 A g^{-1} in the case of the EMIMTFSI/AN organic electrolyte. The gravimetric and volumetric energy densities (in Wh kg^{-1} and Wh L^{-1}) and power densities (in W kg^{-1} and W L^{-1}) were calculated according to Equations 4 to 7 to trace the gravimetric and volumetric Ragone plots.

$$E_g = \frac{1}{8} C_{g,el} \Delta V_d^2 \quad (\text{Eq. 4})$$

$$E_v = E_g \cdot 0.85 \cdot \rho_{el} \quad (\text{Eq. 5})$$

$$P_g = \frac{E_g}{\Delta t_d} \quad (\text{Eq. 6})$$

$$P_v = P_g \cdot 0.85 \cdot \rho_{el} \quad (\text{Eq. 7})$$

being ΔV_d the operation voltage after subtracting of the IR drop and Δt_d is the discharge time.

Battery assembly and electrochemical characterization of the SPCS

For the preparation of the sulfur/carbon cathodes, 160 mg of the composite, 20 mg of carbon black (Super C65) and 20 mg of PVDF binder were mixed together in NMP. The mixture was stirred magnetically for 2 h and then cast onto aluminium foil using a doctor blade. The coated foil was then dried at $50\text{ }^\circ\text{C}$ under vacuum for 12 h to remove the NMP. Once dried, discs with a diameter of 10 mm were cut out from the coated foil and used as the cathodes for Li-S batteries. These cathodes, which had an areal sulfur loading of $\sim 1.5\text{ mg cm}^{-2}$, were placed in the positive casing of a CR2032 coin cell, while a Li metal foil was used as the anode. A polypropylene membrane coated with a thin layer of C65 and PVP (70/30) was used as the separator (thickness of the coating layer: $\sim 0.5\text{ mg cm}^{-2}$). The electrolyte used was 1 M lithium bis(tri-fluoromethane) sulfonimide (LiTFSI) in DOL/DME (v/v = 1: 1) containing 1 wt.% LiNO_3 . The electrolyte/sulfur ratio was of $15\text{ }\mu\text{L/mg}$. All the battery assembly was performed inside a glovebox filled with Ar.

The batteries were charged and discharged galvanostatically within a potential range of 1.7–2.7 V (vs. Li^+/Li) at different current rates from 0.05 C to 1C (where 1C is $1675\text{ mA g}^{-1}\text{ S}$). The volumetric capacity of the cathode, in mAh cm^{-3} , was calculated according to Equation 8:

$$C_v = \frac{C_g \cdot A_s}{d_c} \quad (\text{Eq. 8})$$

being C_g the gravimetric capacity of the cathode per gram of sulfur, in mAh g^{-1} , A_s the sulfur loading in the cathode, in g cm^{-2} , and d_c the thickness of the cathode, in cm. Cyclic voltammograms were acquired within the same potential window at different sweep rates that ranged from 0.05 mV s^{-1} to 0.30 mV s^{-1} .

3. Results and discussion

The synthesis strategy

The synthesis procedure followed for the preparation of the porous carbon microspheres and carbon/sulfur spherical composites is shown schematically in Figure 1. In a preliminary stage, and in order to achieve consolidated carbonaceous matter, the monodisperse RF microspheres were thermally treated up to 500°C (under N₂). Then, the carbon microspheres were activated using Na₂S₂O₃ in the presence of KCl according to our recently reported protocol.^[12] In this step, the Na₂S₂O₃ first decomposes to Na₂SO₄, which, at higher temperatures, acts as a porogenic agent according to Reaction 1, giving rise to a carbonization product composed of the porous carbon microspheres (PCS) embedded in a mixture of KCl and sodium polysulfides.^[12,13] The porous carbon or the sulfur/carbon microspheres can be easily collected from this mixture. In fact, by rinsing the carbonized product with water, all of the inorganic by-products can be removed and the porous carbon microspheres are easily obtained. Alternatively, when the carbonized product is immersed in a dilute HCl solution, the formation of sulfur/carbon microspherical composites occurs. In this case, the sodium polysulfides suffer a disproportionation reaction that gives rise to hydrogen sulfide and elemental sulfur nanoparticles that spontaneously diffuse into the porous structure of the carbon microspheres (Reaction 2).^[15]

Figure 1. Scheme showing the synthesis procedure for the preparation of the porous carbon and sulfur/carbon microspheres.

The RF microspheres exhibit a uniform diameter of around 0.8 microns and they appear as highly packed clusters with a compact hexagonal ordering (see Figure S1). This highly ordered arrangement persists after their carbonization at 500 °C, as illustrated by the SEM images in Figures 2a and 2b.

These carbonized particles exhibit a perfect spherical morphology with a uniform diameter of ca. 0.7 μm . It should be highlighted that the uniformity in diameter is essential to achieve such highly ordered packing.^[42,43] Importantly, this spherical morphology is retained by the activated particles, as shown in Figures 2c and 2d. At this point, we want to indicate that, when the RF were directly subjected to activation with $\text{Na}_2\text{S}_2\text{O}_3$, large, bulky particles made up of fused spheres were obtained (see Figure S2), and the spherical morphology was completely lost. For this reason, the RF sample was subjected to a low temperature pre-carbonization prior to activation. Comparison of Figures 2b and 2d shows that the activation process gives rise to a reduction of the diameter of the microspheres from 700 nm to ca. 500 nm. It should be noted that, independently of the degree of activation, the diameter of PCS microspheres remains constant at ca. 500 nm. The extent of activation is mainly determined by the amount of $\text{Na}_2\text{S}_2\text{O}_3$ employed and, in consequence, the activation yield (mass of carbon per 100 g of RF) decreased significantly from 32 % to 5 % as the $\text{Na}_2\text{S}_2\text{O}_3/\text{RF}$ ratio changed from 1.5 to 3.5 (see Figure S3).

Figure 2. (a, b) SEM images of the carbon microspheres showing large domains with highly packed arrangements (The high magnification image in b) clearly illustrates the compact hexagonal packing). (c, d) SEM images of the porous carbon microspheres showing a similar packing.

The porous structure of the PCS was characterized by N₂ physisorption analysis. The main textural properties (*i.e.* BET surface area, total pore volume and micropore volume) are listed in Table 1, whereas the N₂ sorption isotherms and pore size distributions are illustrated in Figures 3a and 3b, respectively. The N₂ sorption isotherms are of type I+IV, with large nitrogen adsorption uptake at low relative pressures ($p/p_0 < 0.05$) and a quasi-linear slope that extends up to a relative pressure of 0.6 for the samples with the highest degrees of activation (PCS-3 and PCS-3.5). The first feature is indicative of the presence of a large number of micropores whereas the second reflects an increasing number of small mesopores as the Na₂S₂O₃/RF ratio increases. All of the PCS samples have high BET surface areas, in the 2060-2340 m² g⁻¹ range (Table 1). Their pore volumes rise with the amount of activating agent used from 1.20 to 1.74 cm³ g⁻¹ due to the increasing size of the mesopores. In contrast, the volume of micropores (< 2 nm) follows the opposite trend, decreasing from 0.84 cm³ g⁻¹ in CMS-1.5 to 0.59 cm³ g⁻¹ in CMS-3.5. This is better illustrated by the pore size distributions in Figure 3b. Thus, the pore size distribution of sample CMS-1.5 reveals the presence of two pore systems: the first one centred at ca. 0.8 nm and the second ranging from micropores wider than 1.1 nm to small mesopores of up to 4 nm. The maximum of this second pore system extends towards larger values of pore size as the Na₂S₂O₃/RF ratio increases. Concurrently, the volume of the first pore system decreases, which suggests that higher pore development brings with it the collapse of small micropores and the widening of already existing mesopores. Despite their high porosity, the PCS microspheres have good electronic conductivity (2.3-3.1 S cm⁻¹). This is supported by the fact that the spheres are very closely packed, which ensures a high number of contact points between neighbouring microspheres. The tap densities of the powdered samples vary from 0.56 to 0.44 g cm⁻³ as a function of their degree of activation (see Table 1).

Figure 3. a) Nitrogen adsorption isotherms and b) pore size distributions of the PCS samples. The shaded area in b) indicates the micropore range. High resolution XPS spectra of c) C1s and d) S2p, collected from the PCS-2 microspheres.

All the inorganic reaction by-products are efficiently removed from the porous carbon microspheres by merely washing with water, as confirmed by SEM-EDX and XPS analysis (Figures S4a and S4b, respectively). In addition, the EDX analysis reveals the chemical fixation of sulfur heteroatoms during activation with sodium thiosulfate, which occurs as the result of secondary reactions taking place during the high temperature treatment. The sulfur contents in the carbon microspheres varies between 5 wt% and 7 wt%, as determined by elemental analysis (Table 1). As can be seen in the elemental S mappings shown in Figures S4c-d, the S heteroatoms are homogeneously distributed along the surface of the porous carbon microspheres. The surface chemistry of the PCS carbons was further examined by X-ray photoelectron spectroscopy (XPS). Deconvolution of the C1s XPS high resolution peak, shown in Figure 3c, reveals the typical signals corresponding to sp² carbon (284.5 eV), as well as C-O (286.2 eV), C=O (287.3 eV) and O-C=O (289.3 eV) functionalities. Another peak identified at 285.3 eV is ascribed to sulfur atoms

covalently attached to carbon.^[17] The nature of the S groups was studied by deconvolution of the S 2p high resolution peak (Figure 3d). This signal is the sum of two doublets corresponding to thiophenic sulfur (C-S-C, at 164.2 and 165.4 eV) and oxidised sulfur (C-SO_x-C, at 168.1 and 169.3 eV).^[17] The covalent fixation of sulfur is an important feature of PCS carbon microspheres since it has been proven to improve the electrochemical performance of the carbon electrodes in supercapacitors and Li-S batteries.^[44–46]

As indicated previously, the sulfur/carbon microspheres (SPCS) were obtained in the same way as the PCS, but washing the carbonized product with an HCl solution instead of water (see Figure 1). The sulfur content of these composites increased with the amount of Na₂S₂O₃ used, from 32 wt.% in SPCS-1.5 to 92 wt.% in SPCS-3.5 (Table 1 and Figure S3). These results were confirmed by the thermogravimetric analyses conducted for the S/C composites and shown in Figure S5. The S/C microspheres have a similar diameter (of ca. 500 nm) and external appearance to the porous carbon microspheres (Figure 4a), which clearly suggests that sulfur is occupying the pores of the carbon microspheres. Moreover, the S mapping in Figure S6 reveals that the infiltrated sulfur is homogeneously distributed. The more sulfur that is infiltrated in the pores of the PCS, the higher the packing densities of the composites. Thus, the SPCS-1.5 composite with a sulfur content of 32 wt% has a tap density of 0.57 g cm⁻³, a value which increased to 1.93 g cm⁻³ in the case of sample SPCS-3.5 with 92 wt.% of sulfur. The infiltration of sulfur during the HCl treatment led to a significant reduction of the textural properties (see Figure 4c and Table 1). In fact, as the sulfur fills the pores of the carbon, there is a drastic reduction in the pore volume and the specific surface area of the S/C composites. As Table 1 shows, the theoretically deduced unoccupied pore volumes in the composites are higher than those measured by the N₂ sorption experiments. From this, we can infer that the infiltrated sulfur is also blocking a certain amount of the unoccupied volume. When the amount of deposited sulfur is ≥ 80% the pores are completely filled and a certain fraction of sulfur is located outside the particles. This is supported by the drop in the values of electronic conductivity measured for the SPCS composites (Table 1). To monitor the location of the elemental sulfur in the carbon microspheres, XRD analysis of the S/C samples was carried out. Figure 4d shows the diffractograms of different CNS and SCNS samples. It can be seen that the XRD pattern of a S/C composite such as SPCS-2 is analogous to that of the porous carbon sample (PCS-2), with only two low intensity and broad bands typical of disordered carbons. The absence of XRD peaks corresponding to elemental sulfur strongly supports the idea that the *in situ* generated sulfur is within the pores of the carbon. On the contrary, in the case of the composites with a sulfur fraction above 80%, the pores are completely occupied and a fraction of sulfur needs to be accommodated outside the carbon particles, as suggested by the diffraction peaks present in the XRD pattern of the SCPS-3 sample. This result was further corroborated by the Raman spectra obtained for the SPCS composites (see Figure S7).

Figure 4. a and b) SEM images of the sulfur/spherical carbon composites SPCS-3 (sulfur content: 83%). c) nitrogen adsorption isotherms of the different SCPS materials. d) XRD patterns of elemental sulfur and representative PCS and SPCS samples.

Table 1. Physicochemical properties of the PCS and SPCS materials.

Material	Sample code	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_p ($\text{cm}^3 \text{g}^{-1}$) ^a	$V_{(< 2 \text{ nm})}$ ($\text{cm}^3 \text{g}^{-1}$)	$S_{\text{infiltrated}}$ (wt %) ^b	S_{doped} (wt %) ^c	Electrical conductivity (S cm^{-1})	Tap density (g cm^{-3}) ^d	Electrode packing density (g cm^{-3}) ^e
Porous Carbon Microspheres	PCS-1.5	2170	1.20	0.84	-	4.89	3.1	0.56	0.55
	PCS-2	2300	1.29	0.84	-	5.81	2.8	0.52	0.52
	PCS-2.5	2340	1.55	0.76	-	5.93	2.9	0.51	0.45
	PCS-3	2260	1.74	0.65	-	6.45	2.6	0.49	-
	PCS-3.5	2060	1.66	0.59	-	6.76	2.3	0.44	-
Sulfur/Carbon Microspheres	SPCS-1.5	830	0.45 (1.02)	-	32	-	2.2	0.57	-
	SPCS-2	450	0.31 (0.68)	-	47	-	2.0	0.91	-
	SPCS-2.5	20	0.02 (0.06)	-	63	-	1.7	1.21	-
	SPCS-3	<10	-	-	83	-	7.1×10^{-1}	1.34	0.91
	SPCS-3.5	<10	-	-	92	-	3.2×10^{-2}	1.93	-

^a The pore volume was calculated for $p/p_0=0.95$. In parentheses are indicated the theoretical unoccupied pore volumes in the sulfur/carbon microspheres deduced by assuming that the sulfur is confined within the porosity of the carbon. This parameter was calculated as $[V_p(1-a_s) - a_s/2.07]$, being V_p the pore volume of the porous carbon microspheres, a_s the sulfur fraction in the composite and 2.07 the density of sulfur in g cm^{-3} ; ^b sulfur content determined by thermal treatment at 600 °C (N_2); ^c content of covalently bonded sulfur determined after the infiltrated sulfur had been removed; ^d tap density of the powdered samples; ^e density of the electrodes used for the electrochemical characterization in supercapacitors and Li-S batteries.

Electrochemical performance of the porous carbon microspheres in supercapacitors

The porous carbon microspheres were tested as the electrode material in symmetric capacitors working in aqueous (1 M H_2SO_4 and 5 M LiNO_3) and organic (EMIMTFSI/acetonitrile (1:1) mixture) electrolytes, and using an electrode mass loading typical of commercial devices ($\sim 10 \text{ mg cm}^{-2}$). The morphology of the electrodes was analysed by SEM. In the top and cross-section views in Figure S8 it is clear that, despite mixing with carbon black and binder, the carbon spheres still appear closely packed (see inset in Figure S8a) and the electrode is free from cracks or large macroscopic voids. Electrodes made up of the PCS-1.5, PCS-2 and PCS-2.5 carbons have a thickness of ca. $200 \mu\text{m}$ (Figure S8b) and packing densities of 0.55 g cm^{-3} , 0.52 g cm^{-3} and 0.45 g cm^{-3} , respectively. As expected, the drop in the packing densities correlates with the pore volumes of the PCS carbons listed in Table 1. For comparison, we also fabricated electrodes out of the activated carbon YP-17D (Kuraray), typically used in commercial supercapacitors because of its good conductivity and high packing density (according to our measurements, the tap density of the carbon is of 0.74 g cm^{-3} , while the electrodes have a packing density of 0.68 g cm^{-3}). Such a high density is the result of a relatively low pore volume of $0.77 \text{ cm}^3 \text{ g}^{-1}$ (See Figure S9 and Table S1). The PCS samples have higher pore volumes ($1.20\text{-}1.74 \text{ cm}^3 \text{ g}^{-1}$) and, therefore, lower packing densities because of the presence of small mesopores. However, it needs to be stressed that the presence of narrow mesopores combined with high specific surface area is essential for achieving a good electrochemical performance at high current densities (*vide infra*).

Due to their higher packing density and large micropore volume, the PCS-1.5 porous microspheres were selected for electrochemical testing in 1 M H_2SO_4 . The Nyquist plot of the PCS-1.5 supercapacitor working in 1 M H_2SO_4 (as well as in 5 M LiNO_3 and EMIMTFSI/AN) is shown in Figure S10. The traces show the typical Warburg region (45° slope section) in the high-middle frequency range and an almost vertical line at low frequencies. In particular, the Warburg region for the H_2SO_4 electrolyte is very small, which is indicative of a very low restriction to ion diffusion (EDR of 0.62 Ohm). The electrochemical performance of PCS-1.5 in this electrolyte was analysed by means of cyclic voltammetry and galvanostatic charge-discharge experiments. The cyclic voltammograms have a quasi-rectangular shape that is maintained at a fast scan of 200 mV s^{-1} , indicating fast ion transport and good access to the surface area even at high charge-discharge rates (Figure 5a). The galvanostatic charge-discharge plot recorded at a low current density of 0.5 A g^{-1} is shown in Figure 5b. The plot is triangular and perfectly symmetrical, which indicates a pure EDLC mechanism. The ohmic drop at the beginning of the discharge is negligible, and still very small (28 mV) at a high discharge current of 20 A g^{-1} (Figure 5c). The ESR calculated from the discharge branches of PCS-1.5 has a value of 0.11 Ohm , which is in agreement with the very low resistance observed by impedance spectroscopy. In the case of YP-17D, the voltage drop is more than twice as high as in PCS-1.5 (65 mV) at the same current density. At 0.5 A g^{-1} , the PCS-1.5 electrode has a capacitance of 279 F g^{-1} (which corresponds to a surface area-normalized capacitance of ca. $13 \mu\text{F cm}^{-2}$), with a coulombic efficiency of 98 %. Remarkably, this value of capacitance is double that of the

activated carbon YP-17D (128 F g^{-1} at 0.5 A g^{-1}). The rate capability of both materials is shown in Figure 5d. Whilst the commercial active carbon is able to work up to a maximum current density of 40 A g^{-1} with a capacitance of 57 F g^{-1} , PCS-1.5 exhibits much better rate performance, retaining a specific capacitance above 200 F g^{-1} (72 % of capacitance retention) at 40 A g^{-1} , and still above 100 F g^{-1} at an ultrahigh rate of 80 A g^{-1} . Due to the high degree of packing of the porous carbon microspheres, they also achieve high volumetric capacitances of up to 130 F cm^{-3} , which is notably higher than that of the commercial activated carbon YP-17D (78 F cm^{-3}). It also compares favourably with other state-of-the-art porous carbons such as N-doped carbon spheres, hard-templated carbons, carbon nanocages and compact graphene-based films working in aqueous electrolytes (see Table S1).

Figure 5. Electrochemical performance in 1M H₂SO₄. a) Cyclic voltammograms of the PCS-1.5 supercapacitor at different sweep rates. Galvanostatic charge-discharge plots of PCS-1.5 and YP-17D at b) 0.5 A g^{-1} and c) 20 A g^{-1} . d) Gravimetric (filled dots) and volumetric (empty dots) rate performance of PCS-1.5 and YP-17D.

The capacitive behaviour of the porous microspheres was also tested in the aqueous 5 M LiNO₃ electrolyte. This neutral electrolyte was chosen on the basis that it does not require the use of noble metals as current collectors. Moreover, LiNO₃ has a high electrical conductivity (155 mS cm^{-1} at 25°C), withstands operating voltages of up to 1.8 V and surpasses the capacitance provided by other neutral aqueous electrolytes.^[47,48] For the PCS materials, a secure voltage window of 1.7 V was established, according to preliminary

characterizations by cyclic voltammetry, galvanostatic charge-discharge and floating tests (this is extensively described in Supporting Information: Supplementary Note 1 and Figure S11). The electrochemical performance of the PCS-1.5 microspheres was assessed first. As can be seen in Figure S12a, this material has a capacitance of 141 F g^{-1} at 0.2 A g^{-1} , but experiences a significant capacitance drop of 40 % at a current density of 30 A g^{-1} . This rate capability contrasts with the excellent capacitance retention that the same material showed in the $1 \text{ M H}_2\text{SO}_4$ electrolyte. This worse capacitance retention has also been observed for other neutral electrolytes, such as Li_2SO_4 , when compared to acid or alkaline electrolytes such as H_2SO_4 or KOH .^[19,49] Impedance spectroscopy allowed us to shed light on this behaviour. As shown in Figure S10, the Warburg region of PCS-1.5 in 5 M LiNO_3 is larger than that of the same material in $1 \text{ M H}_2\text{SO}_4$. In fact, the EDR value of PCS-1.5 in the neutral electrolyte is 1.56 Ohm , much higher than the 0.62 Ohm calculated for the H_2SO_4 electrolyte. The ESR value is also twice that recorded for the more conductive $1 \text{ M H}_2\text{SO}_4$ electrolyte (0.77 Ohm vs. 0.32 Ohm). In order to take more advantage of the neutral electrolyte, the PCS-2 microspheres (with a wider pore size distribution but still a high packing density) were also evaluated as supercapacitor electrodes. Their Nyquist impedance revealed a much lower resistance to ion diffusion compared to PCS-1.5 (EDR value of 0.91 Ohm). In fact, the PCS-2 microspheres exhibited much better capacitance retention compared to PCS-1.5, as confirmed by galvanostatic charge-discharge and cyclic voltammetry experiments (Figure S12a-c). These porous microspheres achieve 134 F g^{-1} at 0.2 A g^{-1} and are successfully cycled up to a current density of 50 A g^{-1} retaining 62 % of the maximum capacitance (83 F g^{-1}). Although both porous carbons have a similar maximum capacitance (see Figure S12a), the volumetric performance of the PCS-2 material is affected by its higher pore volume. Thus, PCS-1.5 achieves a volumetric capacitance of 66 F cm^{-3} versus 59 F cm^{-3} attained by PCS-2 (Figure 6a). However, as a consequence of its better rate performance, the volumetric capacitance of PCS-2 surpasses that of PCS-1.5 from a current density of 15 A g^{-1} . The Ragone plots in Figure 6b show that, compared to the results in the H_2SO_4 electrolyte, similar values of power density can be achieved in the LiNO_3 electrolyte with a notable increase in energy density. PCS-1.5 and PCS-2 achieve a maximum energy density of 14.2 and 13.6 Wh kg^{-1} (6.6 and 6.0 Wh L^{-1} , respectively), and PCS-2 still achieves 11.0 Wh kg^{-1} at a power density of 12.2 kW kg^{-1} (4.9 Wh L^{-1} @ 5.4 kW L^{-1}).

Figure 6. a) Volumetric rate capability of the PCS-1.5 and PCS-2 electrodes in 5M LiNO₃, and b) Ragone plots showing the gravimetric and volumetric energy and power densities of the PCS materials in the different aqueous electrolytes.

In order to further boost the energy density of the supercapacitors, the porous carbon microspheres were also tested electrochemically in an organic mixture of the ionic liquid EMIMTFSI and acetonitrile. Figure S13a shows the galvanostatic charge-discharge plot of the PCS-1.5 supercapacitor being cycled at 0.2 A g⁻¹ up to 3 V. The plot is triangular with hardly any distortion, which indicates the double layer formation mechanism. The quasi-rectangular cyclic voltammograms also confirm this behaviour (Figure S13b). The preservation of this shape at a high sweep rate of 200 mV s⁻¹ suggests the good charge propagation properties of the porous microspheres in this electrolyte. As shown in Figure 7a, the material achieves a maximum specific capacitance of 137 F g⁻¹ and retains 77 % of this value at a current density of 50 A g⁻¹. In volumetric terms, the material has a capacitance of 64 F cm⁻³ and is 49 F cm⁻³ at the highest current density studied. The stability of the supercapacitor was evaluated by galvanostatic cycling of the cell at 10 A g⁻¹ for 10 000 cycles. The retention of 87 % of its initial capacitance at the end of the test proves the robustness of the system (Figure S13c). Figure 7b shows the Ragone plot calculated for the PCS-1.5 supercapacitor in the organic electrolyte. By virtue of the extended voltage and the high degree of packing of the porous microspheres, the cell achieves a high volumetric energy density of 25.5 Wh L⁻¹ (42.7 Wh kg⁻¹) and still delivers 11.9 Wh L⁻¹ at a power density of 16.8 kW L⁻¹ (19.9 Wh kg⁻¹ @ 72.3 kW kg⁻¹). It should be noted that the use of microspheres with a larger mesopore content did not bring any improvement of the capacitance or rate capability in this electrolyte. In fact, due to their lower packing density, these materials exhibited a poorer response in volumetric terms over the entire range of current densities studied (Figure S13d).

Figure 7. Volumetric and gravimetric a) rate capability and b) Ragone plot of the PCS-1.5-based supercapacitor in EMIMTFSI/AN.

Electrochemical performance of the sulfur/carbon composites in Li-S batteries

As previously described, sulfur/carbon microspherical composites were synthesized by the *in situ* disproportionation of sodium polysulfides in the presence of porous carbon microspheres, both generated during the activation process with sodium thiosulfate. We tested the use of these S/C microsphere composites as cathode material in Li-S batteries. In particular, composite SPCS-3 was selected for testing because of its high sulfur content (83 wt.%). It is well known that minimization of carbon content is key to maximizing energy density at the cell level.^[38,50] This material was cast onto the Al foil and directly used as the cathode without any calendaring. As can be seen in Figure S14a, the cathodes were made up of a dense layer of sulfur/carbon microspheres that was well adhered to the Al current collector. The absence of cracks and the dense packing of the microspheres can be seen in the high magnification image of the cathode surface in Figure S14b.

Figure 8a shows the cyclic voltammograms corresponding to the SPCS-3 cathode at different voltage rates. The discharge sweeps describe two peaks associated with the multi-step reduction of sulfur. At the lowest scan rate, the signal at 2.30 V is ascribed to the reduction of elemental sulfur to soluble long-chain lithium polysulfides (Li_2S_x , $4 \leq x \leq 8$), and the peak recorded at 2.03 V corresponds to the conversion of these polysulfides to Li_2S_2 and Li_2S . The backward voltage sweep draws two overlapping intensity peaks with a maximum at 2.44 V associated with the oxidation of $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ back to S_8 .^[51] These redox signals are well retained with the increase in the scan rate from 0.05 to 0.30 mV s^{-1} . The effect of the scan rate on the intensity of the anodic peak was analysed by applying the Randles-Sevcik equation. The linear relationship found between this intensity and the square root of the scan rate (Figure S15) proves the reversibility of the electrochemical process, whose kinetics are governed by the diffusion of the electroactive species.

The rate performance of the cathode was investigated by galvanostatic charge-discharge experiments carried out at different current rates ranging from 0.05 C to 1 C (1C = 1675 mA g⁻¹). The galvanostatic plots recorded at those current rates are shown in Figure 8b. Regardless of the current rate, the plots retain their shape. The charge plots show an initial small overpotential of ca. 2.25 V followed by two overlapping plateaus that relate to the two merged intensity signals observed by cyclic voltammetry. The discharge profiles show the two characteristic plateaus at ca. 2.3 and 2.1 V corresponding to the two-step reduction of sulfur. At a low discharge rate of 0.05 C, the cathode achieves a high specific capacity of 1280 mAh g⁻¹, which corresponds to a sulphur utilization of ca. 80 %. It should be noted that, despite the composite having a high sulfur content of 83 %, the charge-discharge processes occur with a high coulombic efficiency of 98.5 %. When the battery was charged and discharged at higher rates of 0.1 C, 0.2 C, 0.5 C and 1C, it delivered capacities of 1102 mAh g⁻¹, 1035 mAh g⁻¹, 780 mAh g⁻¹ and 710 mAh g⁻¹, respectively. Figure 8c shows the retention of capacity over 100 charge-discharge cycles at different current rates. The composite retains the capacity well from the very first cycles, which is a likely consequence of the correct accommodation of the sulfur within the pores of the porous carbon microspheres and the effective trapping of the lithium polysulfides in the S-doped microporous surface.^[44] After 100 cycles at 0.1C, the battery still retains a capacity of 831 mAh g⁻¹ with a coulombic efficiency of 99.5 % that rules out any occurrence of the so-called shuttle effect. The impedance of the batteries remains almost unaltered upon cycling, as evidenced by the overlapping Nyquist plots acquired at different cycling states and shown in Figure S16.

Due to the large sulfur content in the composite and the high degree of packing of the porous carbon microspheres that harbour the active sulfur, the cathode has a high density of 0.91 g cm⁻³, with a corresponding sulfur density of 0.60 g cm⁻³. Based on this value, the cathode volumetric capacities were calculated for the different C rates (see Figure 8d). The high sulfur density in the cathode translates into high values of volumetric capacity of up to 768 mAh cm⁻³ (0.05 C). At 0.1 C, 0.2 C, 0.5 C and 1 C, the volumetric capacities achieved by the battery are 661 mAh cm⁻³, 621 mAh cm⁻³, 468 mAh cm⁻³ and 426 mAh cm⁻³, respectively. The capacity achieved by our battery compares well with other state-of-the-art cathodes despite having a higher sulfur content (see Table S2). The cycling stability of the battery was evaluated by galvanostatic charge-discharge at 0.2 C. Figure 8e shows the volumetric capacity retention of the battery run for 600 cycles (The plot for the gravimetric capacity is shown in Figure S17). At the 600th cycle the battery delivered 297 mAh cm⁻³ (495 mAh g⁻¹), which corresponds to a capacity decay of only 0.086 % per cycle. It can be seen that the capacity stabilizes with cycling and, from the 100th cycle onwards, the capacity fade is only of 0.015 %/cycle. Such capacity retention compares well with other high performance cathodes made of N-doped carbons, TiN or polar metal oxides/hydroxides with strong polysulfide adsorption abilities.^[52–57] The coulombic efficiency stays above 98 % at the 500th cycle, and decreases slightly to 96 % at the 600th cycle. Such a high faradaic yield indicates the effectiveness of the microspherical carbon scaffold preventing polysulfides from shuttling.

Figure 8. a) Cyclic voltammograms of the SPCS-3 battery at different sweep rates. b) Galvanostatic charge discharge plots and c) variation of the capacity over 100 charge/discharge cycles for the batteries run at different current rates. d) Volumetric capacities achieved in the 5th cycle at each discharge rate. e) Modification of capacity and coulombic efficiency over 600 charge/discharge cycles at 0.2C.

4. Conclusions

Porous carbon microspheres and sulfur/ carbon microspherical composites were successfully prepared by the chemical activation of pre-carbonized resorcinol-formaldehyde microspheres with sodium thiosulphate. This synthesis strategy allows the easy production of two types of materials: a) monodisperse S-doped porous carbon microspheres and b) monodisperse S/C microspheres made up of porous carbon filled by elemental sulfur generated and infiltrated *in situ*. Both materials are made up of monodisperse microspheres with a diameter of around 500 nm that are packed in a highly dense hexagonal arrangement. Because of this high packing density, these materials show a good electrical

conductivity and high electrode density. The porous carbon microspheres had high specific surface areas of up to $2340 \text{ m}^2 \text{ g}^{-1}$, pore volumes up to $1.74 \text{ cm}^3 \text{ g}^{-1}$ and a porosity made up of micropores and a small fraction of narrow mesopores ($< 6 \text{ nm}$). The porous microspheres and the sulfur/carbon microspherical composites were tested in supercapacitors and Li-S batteries, respectively. They exhibited remarkable performances in both systems, especially in volumetric terms, because of an advantageous combination of an extensive pore development and a relatively high electrode density provided by the dense packing of the microespherical particles. When used in supercapacitors, the porous microspheres achieved 130 F cm^{-3} , 66 F cm^{-3} and 64 F cm^{-3} in $1 \text{ M H}_2\text{SO}_4$, 5 M LiNO_3 and EMIMTFSI/AN, respectively (279 F g^{-1} , 141 F g^{-1} and 137 F g^{-1} , accordingly), values which were retained well at high current rates. In the case of Li-S batteries, it is notable that the electrodes consisting of sulfur/carbon microspherical composite containing a high percentage of sulfur of 83 % provide good volumetric capacities of up to 768 mAh cm^{-3} . They exhibit robust long-term stability with a capacity fade of only 0.085 %/cycle upon 600 charge-discharge cycles. Moreover, the charge-discharge processes occur in a high faradaic yield (coulombic efficiency $> 96\%$), which indicates the effectiveness of the rationally-designed carbon scaffold in preventing the shuttle effect.

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Conflict of Interest

The authors declare no conflicts of interest.

Bibliography

- [1]. J. R. Miller, P. Simon, *Science* **2008**, 321, 651.
- [2]. M. Armand, J. M. Tarascon, *Nature* **2008**, 541, 652.
- [3]. P. Simon, Y. Gogotsi, *Nat. Mater.* **2008**, 7, 845.
- [4]. P. Simon, Y. Gogotsi, B. Dunn, *Science* **2014**, 343, 1210.
- [5]. L. Borchardt, M. Oschatz, S. Kaskel, *Chem. Eur. J.* **2016**, 22, 7324.
- [6]. N. Diez, G.A. Ferrero, M. Sevilla, A.B. Fuertes, *J. Mater. Chem. A* **2019**, 7, 14280.
- [7]. M. Sevilla, G.A. Ferrero, A.B. Fuertes, *Carbon* **2017**, 114, 50.
- [8]. Y.T. Li, Y.T. Pi, L.M. Lu, S.H. Xu, T.Z. Ren, *J. Power Sources* **2015**, 299, 519.
- [9]. J. Guo, J. Zhang, F. Jiang, S. Zhao, Q. Su, G. Du, *Electrochim. Acta* **2015**, 176, 853.
- [10]. Z.H. Chen, X.L. Du, J.B. He, F. Li, Y. Wang, Y.L. Li, B. Li, S. Xin, *ACS*

Appl. Mater. Interfaces **2017**, 9, 33855.

- [11]. J. Deng, T. Xiong, F. Xu, M. Li, Ch. Han, Y. Gong, H. Wang, Y. Wang, *Green Chem.* **2015**, 17, 4053.
- [12]. A.B. Fuertes, G.A. Ferrero, N. Diez, M. Sevilla, *ACS Sustain. Chem. Eng.* **2018**, 6, 16323.
- [13]. M. Sevilla, N. Diez, G.A. Ferrero, A.B. Fuertes, *Energy Storage Mater.* **2019**, 18, 356.
- [14]. M. Sevilla, J. Carro-Rodriguez, N. Diez, A.B. Fuertes, *Sci. Rep.* **2020**, 10, 1.
- [15]. N. Diez, G.A. Ferrero, M. Sevilla, A.B. Fuertes, *Sustain. Energy Fuels* **2019**, 3, 3498.
- [16]. N. Diez, M. Sevilla, A.B. Fuertes, *ACS Appl. Energy Mater.* **2020**, 3, 3397.
- [17]. G. Li, J. Sun, W. Hou, S. Jiang, Y. Huang, J. Geng, *Nat. Commun.* **2016**, 7, 1.
- [18]. Z. Li, Y. Jiang, L. Yuan, Z. Yi, Ch. Wu, Y. Liu, P. Strasser, Y. Huang, *ACS Nano* **2014**, 8, 9295.
- [19]. N. Diez, G.A. Ferrero, A.B. Fuertes, M. Sevilla, *Batter. Supercaps* **2019**, 2, 701.
- [20]. B. Yao, S. Chandrasekaran, H. Zhang, A. Ma, J. Kang, L. Zhang, X. Lu, F. Qian, Ch. Zhu, E.B. Duoss, Ch.M. Spadaccini, M.A. Worsley, Y. Li, *Adv. Mater.* **2020**, 32, 1.
- [21]. T. Tang, T. Zhang, W. Li, X. Huang, X. Wang, H. Qiu, Y. Hou, *Nanoscale* **2019**, 11, 7440.
- [22]. S.H. Chung, C.H. Chang, A. Manthiram, *ACS Nano* **2016**, 10, 10462.
- [23]. S.H. Chung, A. Manthiram, *Joule* **2018**, 2, 710.
- [24]. R. Fang, S. Zhao, P. Hou, M. Cheng, S. Wang, H.M. Cheng, C. Liu, F. Li, *Adv. Mater.* **2016**, 28, 3374.
- [25]. Y. Gogotsi, P. Simon, *Science* **2011**, 334, 917.
- [26]. J. Zhou, J. Lian, L. Hou, J. Zhang, H. Gou, M. Xia, Y. Zhao, T.A. Strobel, L. Tao, F. Gao, *Nat. Commun.* **2015**, 6, 8503.
- [27]. J. Yan, Q. Wang, T. Wei, L. Jiang, M. Zhang, X. Jing, Z. Fan, *ACS Nano* **2014**, 8, 4720.
- [28]. G.A. Ferrero, A.B. Fuertes, M. Sevilla, *Electrochim. Acta* **2015**, 168, 320.
- [29]. X. Yang, Ch. Cheng, Y. Wang, L. Qiu, D. Li, *Science* **2013**, 341, 534.
- [30]. Y. Tao, X. Xie, W. Lv, D.M. Tang, D. Kong, Z. Huang, H. Nishihara, T. Ishii, B. Li, D. Golberg, F. Kang, T. Kyotani, Q.H. Yang, *Sci. Rep.* **2013**, 3, 1.
- [31]. N. Diez, C. Botas, R. Mysyk, E. Goikole, T. Rojo, D. Carriazo, *J. Mater. Chem. A* **2018**, 6, 3667.
- [32]. N. Diez, M. Qiao, J.L. Gomez-Urbano, C. Botas, D. Carriazo, M.M. Titirici, *J. Mater. Chem. A* **2019**, 7, 6126.

- [33]. Y. Bu, T. Sun, Y. Cai, L. Du, O. Zhuo, L. Yang, Q. Wu, X. Wang, Z. Hu, *Adv. Mater.* **2017**, 29, 1.
- [34]. G.E. Amidon, P.J. Meyer, D.M. Mudie, in *Particle, powder, and compact characterization* ("Developing solid oral dosage forms: Pharmaceutical theory and practice", Eds.: Y. Qiu, Y. Chen, G.G.Z. Zhang, L. Yu, R.V. Mantri), Elsevier, **2017**, 271-293.
- [35]. R. Fang, S. Zhao, S. Pei, X. Qian, P.X. Hou, H.M. Cheng, C. Liu, F. Li, *ACS Nano* **2016**, 10, 8676.
- [36]. H. Shi, X. Zhao, Z.S. Wu, Y. Dong, P. Lu, J. Chen, W. Ren, H.M. Chen, X. Bao, *Nano Energy* **2019**, 60, 743.
- [37]. L. Bao, J. Yao, S. Zhao, Y. Lu, Y. Su, L. Chen, Ch. Zhao, F. Wu, *ACS Sustain. Chem. Eng.* **2020**, 8, 5648.
- [38]. W. Xue, L. Miao, L. Qie, Ch. Wang, S. Li, J. Wang, J. Li, *Curr. Opin. Electrochem.* **2017**, 6, 92.
- [39]. J. Liu, S.Z. Qiao, H. Liu, J. Chen, A. Orpe, D. Zhao, G.Q. Lu, *Angew. Chemie Int. Ed.* **2011**, 50, 5947.
- [40]. M.D. Stoller, R.S. Ruoff, *Energy Environ. Sci.* **2010**, 3, 1294.
- [41]. A.B. Fuertes, G.A. Ferrero, M. Sevilla, *Energy Storage Mater.* **2016**, 4, 154.
- [42]. C. Hu, C. Kirk, Q. Cai, C. Cuadrado-Collados, J. Silvestre-Albero, F. Rodríguez-Reinoso, M.J. Biggs, *Adv. Energy Mater.* **2017**, 7, 1.
- [43]. Z. Liang, H. Xia, L. Zhang, H. Liu, Y. Zhao, H. Li, W. Xie, *Results Phys.* **2020**, 16, 102912.
- [44]. L. Du, X. Cheng, F. Gao, Y. Li, Y. Bu, Z. Zhang, Q. Wu, L. Yang, X. Wang, Z. Hu, *Chem. Commun.* **2019**, 55, 6365.
- [45]. X. Ma, G. Ning, Y. Wang, X. Song, Z. Xiao, L. Hou, W. Yang, J. Gao, Y. Li, *Electrochim. Acta* **2018**, 269, 83.
- [46]. G. Hasegawa, in *Studies on porous monolithic materials prepared via sol-gel processes*, Springer, Tokyo, **2013**, pp. 79-89.
- [47]. J. Jiang, B. Liu, G. Liu, D. Qian, Ch. Yang, J. Li, *Electrochim. Acta* **2018**, 274, 121.
- [48]. K. Fic, M. He, E.J. Berg, P. Novák, E. Frackowiak, *Carbon* **2017**, 120, 281.
- [49]. A.B. Fuertes, M. Sevilla, *ChemSusChem* **2015**, 8, 1049.
- [50]. A. Bhargav, J. He, A. Gupta, A. Manthiram, *Joule* **2020**, 4, 285.
- [51]. A. Manthiram, Y. Fu, S.H. Chung, Ch. Zu, Y.S. Su, *Chem. Rev.* **2014**, 114, 11751.
- [52]. Y. Xia, R. Fang, Z. Xiao, H. Huang, Y. Gan, R. Yan, X. Lu, Ch. Liang, J. Zhang, X. Tao, W. Zhang, *ACS Appl. Mater. Interfaces* **2017**, 9, 23782.
- [53]. W. Zeng, M. M. C. Cheng, K. Y. S. Ng, *ChemElectroChem* **2019**, 6, 2796.
- [54]. Y. Xia, H. Zhong, R. Fang, C. Liang, Z. Xiao, H. Huang, Y. Gan, J. Zhang,

- X. Tao, W. Zhang, *J. Power Sources* **2018**, 378, 73.
- [55]. J. Zhang, Y. Shi, Y. Ding, W. Zhang, G. Yu, *Nano Lett.* **2016**, 16, 7276.
- [56]. Q. Xiao, G. Li, M. Li, R. Liu, H. Li, P. Ren, Y. Dong, M. Feng, C. Zhongwei, *J. Energy Chem.* **2020**, 44, 61.
- [57]. J. L. Shi, C. Tang, J. Q. Huang, W. Zhu, Q. Zhang, *J. Energy Chem.* **2018**, 27, 167.

Table of Contents

Densely-packed porous carbon microspheres were synthesized by $\text{Na}_2\text{S}_2\text{O}_3$ activation of RF spheres. Sulfur/carbon composites were also synthesized by the *in situ* reduction of activation by-products. The carbon exhibits high volumetric capacitance in aqueous and organic electrolytes, whilst the composite achieves a high volumetric capacity when used as Li-S battery cathode.