

Monolithic Carbon Spherogels as Freestanding Electrodes for Supercapacitors

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(sliceable) carbon spherogels are explored. Following physical activation with carbon dioxide, only 277 nm templated samples, featuring one thin-walled (<20 nm) and one thick-walled (>60 nm) variant, retain a freestanding bulk constitution and hence are suitable for the application as binder-free electrodes. The electrochemical evaluation demonstrates the advantage of hollow carbon sphere aerogels in comparison to conventional carbon aerogels with respect to capacitance, particularly at high scan rates. The analysis of the electrolyte diffusion kinetics and the network morphology after 10,000 charge/discharge cycles reveals the necessity of wall thickness optimization. Thick-walled variants are favored due to a much higher rate capability of 30 kW kg⁻¹ compared to 10 kW kg⁻¹). Additionally, a post-mortem TEM analysis reveals the loss of a central cavity and sphere degradation in thin-walled samples.

KEYWORDS: carbon aerogels, carbon spherogels, hollow carbon spheres, microporous materials, supercapacitors, sol-gel chemistry

1. INTRODUCTION

Carbon aerogels are a fascinating and unique class of synthetic open porous materials. They combine typical properties of classical silica-based aerogels such as a very low bulk density $(0.01-0.1 \text{ g cm}^{-3})$, ultrahigh porosity (up to 99%), specific surface area $(500-2500 \text{ m}^2 \text{ g}^{-1})$, and chemical stability with electrical conductivity.¹ Carbon aerogels are commonly manufactured in straightforward and low-cost sol-gel production routes, which enable a distinct control over mechanical and chemical properties.² The commercialization of carbon aerogels is implemented in state-of-the-art high-performance applications such as energy storage, separation, insulation, and catalysis.³

Carbon aerogels are typically based on amorphous carbon yielded from organic polymer precursors, typically aromatics (e.g., phenols) and aldehydes (e.g., formaldehyde or furfural), or other carbon allotropes such as carbon nanotubes or graphene.⁴ Recently, carbon aerogels prepared from sustainable, biomass-based sources have also shown the potential of environmentally green chemistry approaches.^{5,6} The nanostructure of carbon aerogels consists of a random arrangement of irregularly shaped, microporous particle clusters, resembling pearl beads, interconnected in a three-dimensional network featuring pores in the meso- and macroporous range.^{7,8} The ability to tailor the carbon aerogels' microstructure and porosity is limited by sol–gel parameters, such as precursor concentration, catalyst amount, pH value, or postsynthesis, the selection of the gel drying method as well as carbonization or activation conditions.³

A much more powerful approach uses sacrificial sphere templating to yield nanoscaled, hollow carbon sphere (HCS) materials,⁹ which have been intensively investigated as electrode materials in lithium-ion batteries,¹⁰ sodium-ion batteries,¹¹ lithium–sulfur batteries,¹² and supercapacitors.¹³ The controllable and unique feature of HCS structures is the nano- to mesoporous carbon shell, which enables electrolyte accessibility into the interior macroporous void space and thereby enhances electrode to electrolyte contact. Therefore, HCS-based electrodes offer uniquely excellent capacities and

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rate capabilities in state-of-the-art energy storage devices.^{9,14,15} The void space can simultaneously facilitate reversible compressibility for extended cycling strain during electric charging and discharging processes and accommodate pore swelling effects¹⁶ as well as serve as a chemical nanoreactor or drug delivery host.^{17,18}

Previously, our group templated single-shell hollow carbon aerogels structures, *carbon spherogels*, by introducing polystyrene (PS) nanospheres into the sol–gel process of resorcinol–formaldehyde (RF) with the result of monolithic and reversibly compressible samples.¹⁹ PS was discovered to be a perfect polymer in the templated sol–gel process of RF due to its molecular similarity to resorcinol. This chemical resemblance results in attractive molecular interactions, such as $\pi-\pi$ stacking, between the aromatic rings and facilitates the coating of resorcinol onto PS. Subsequent pyrolysis enables the formation of hollow carbon spheres concomitantly with the benefit of a nonhazardous template removal by thermal PS decomposition, in contrast to etching protocols in the case of commonly used silica templates.¹⁵

Alternatively, HCS architectures are a very attractive scaffold for encapsulation as the inner void space can serve as a storage reservoir, chemical reactor, or even drug delivery host. Fabrication of so-called hybrid carbon nanomaterials included the incorporation of, for example, sulfur, germanium, copper, or titania.²⁰

In this study, we introduce freestanding monolithic carbon spherogels as direct, binder-free electrodes for supercapacitors. The use of CO₂-activated carbon spherogels as freestanding electrode materials and TEA-BF4 as the electrolyte eliminates the extra step of the binder/carbon slurry preparation. As a result, material and time are saved, and the use of potentially toxic and electrically inactive components is avoided. Being typically very brittle, carbon aerogels have been previously investigated as candidate materials for electrodes.^{21,22} Additionally, the fact that spherogel electrodes do not require any additives to be used as electrodes is highly favorable. With regard to the new concept "design for recycle", simple lowcomponent electrodes are required to facilitate recycling of the various components at the end of life of the device.²³ To the best of our knowledge, no report exists on HCS-based freestanding pure carbon aerogels directly applied as electrodes. The novel feature of carbon spherogels is the unique combination of nano- and macroscopic properties: the tailorable and monodispersed HCS nanomorphologies and a processable bulk, providing adequate material toughness for crack-free mechanical slicing. For realization, the synthesis of mechanically stable, sliceable, and homogeneous monolithic carbon spherogel samples is a prerequisite. Various parameter settings (R/W ratio, PS sphere templating concentration, and PS spheres size) to generate appropriate carbon spherogel samples were explored in this study. Following a postsynthesis, physical activation by carbon dioxide suitable candidates for electrode slicing were selected.

2. EXPERIMENTAL SECTION

2.1. Materials and Synthesis. Colloidal monodisperse polystyrene (PS) nanospheres in aqueous solutions (concentration higher 20 wt %) with diameter sizes of 277, 454, 736, and 907 nm and polydispersity index (PdI) values of 0.039, 0.063, 0.115, and 0.176, respectively (Figures S1–S3, Supporting Information), were prepared by emulsion polymerization of styrene with potassium persulfate (KPS) as the initiator agent and varying polyvinylpyrrolidone (PVP)

content as the stabilizing emulsifier.²⁴ Subsequently, dilution with distilled water yielded desired PS concentrations in the range between 0.075 and 20 wt %. For comparison, a nontemplated, pristine sample was also prepared by use of pure deionized water as solvent. The solgel precursors were added to the PS solutions in the following order: (1) 1.25 g of resorcinol (R; molar ratio of resorcinol to deionized water (R/W) = 0.008; (2) 1.85 g of formaldehyde (F; molar ratio R/ F = 0.5; (3) 0.024 g of sodium carbonate (Na₂CO₃; molar ratio R/C = 50) with a constant 5 min stirring time in between and a stirring speed of 100 rpm. The initial pH was measured as 7.6 and was lowered to 5.5 by the dropwise addition of 2 N nitric acid (HNO₃). Finally, the as-prepared sol was stirred for 1 h, filled into glass molds with a diameter of 12.5 mm, and sealed. After 7 days of gelation and aging at 80 °C, the wet gels were transferred into acetone baths which were renewed every day for 3 days. Subsequently, the alcogels were supercritically dried with CO2 at 110 bar and 60 °C in an autoclave (Parr Instruments) with a volume of 300 mL. Carbonization was performed at 800 °C with 10 °C h⁻¹ heating rate under a constant argon stream of 75 NL h⁻¹. For electrochemical investigations, the samples were physically activated in a tube furnace under a constant CO_2 flow of 60 NL h⁻¹ for 2 h at 900 °C.

2.2. Materials Characterization. The morphologies of carbon spherogels were analyzed with a ZEISS Ultra Plus scanning electron microscope (SEM) using an in-lens detector. The accelerating voltage was set at 4 kV. Transmission electron microscope (TEM) images were recorded on a TECNAI F200 field emission electron microscope using a Gatan Orius SC600 CCD camera. The accelerating voltage was set at 200 kV. Image analysis for the determination of the sphere diameters and wall thicknesses was performed with the software ImageJ. Nitrogen sorption isotherms were performed on a Micromeritics ASAP 2420 sorption system at -196 °C. The samples were previously degassed at 300 °C for 24 h. Specific surface areas and pore size distributions (cumulative and differential volume graphs) were calculated by applying an NLDFT model assuming nitrogen at -196 °C on carbon slit pores. Dynamic light scattering (DLS) measurements were conducted on a Malvern Zetasizer instrument. Data were recorded at a light-backscattering angle of 173°. Each measurement encompassed 30 separate DLS measurements with each DLS measurement with three subruns of 10 s duration. The bulk density of a carbon aerogel sample was defined by the ratio of the mass to the volume ($\rho = mV^{-1}$). The mass was recorded with an ALC microscale (ACCULAB). The monolith's dimensions were measured with a digital caliper (Alpha Tools) and approximated as perfectly cylindrical.

Raman spectra were recorded on a Thermo Scientific DXR2 Raman microscope in the range of 500-3500 cm⁻¹ with a laser excitation wavelength of 532 nm and a laser power of 4 mW.

2.2.1. Electrochemical Characterization. The spherogel samples were tested as electrodes in symmetric supercapacitor (SC) cells. All measurements were performed in a two-electrode setup consisting of two similar carbon electrodes (mass: approximately 1-2 mg, the counter electrode being the heavier; dimensions: approximately 1 cm diameter and 0.5 mm thickness). The SCs were assembled in a coin cell (CR2032, MTI Corp.) in an MBraun glovebox ($H_2O < 0.5$ ppm, $O_2 < 0.5$ ppm) and connected to an SP300-potentiostat (Biologic, France). We used 1 M TEA-BF₄ in acetonitrile as the electrolyte and standard filter paper as the separator (Whatman, GE Healthcare Life Sciences, UK, grade GF/D). For the assembly of the coin cells, each of the electrodes and the separator were wetted with 150 μ L of the electrolyte which yields 450 μ L per cell. The coin cells were sealed with a gas-driven crimping machine (MSK-PN110-S, MTI Corp.). Before the actual measurements, the cells were galvanostatically charged and discharged for 500 cycles at 5 A g^{-1} to ensure good wetting of the electrodes with the electrolyte. Subsequently, cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements with a potential limitation of 2.5 V were performed at different rates. Impedance spectroscopy was conducted at an opencircuit voltage and with an amplitude of 10 mV in a frequency range of 10 mHz-1 MHz. Finally, capacitance retention was measured at a current density of 10 A g^{-1} for 10,000 cycles.

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Figure 1. Schematic of the sol-gel synthesis process of freestanding and monolithic carbon spherogels (sc = supercritical).

Table 1. Mechanical and Microstructural Properties According to the Applied R/W Molar Ratio

R/W	mechanical behavior	crack-free mechanical cutting	freestanding	spherogel structure	sphere wall thickness (nm)
0.001	fragile	no	no	no	10 ± 1
0.002	fragile	no	no	no	13 ± 1
0.004	fragile	no	no	no	31 ± 2
0.006	fragile	no	no	yes	32 ± 4
0.008	reversibly compressible	yes	yes	yes	70 ± 3
0.010	brittle, rigid	no	yes	yes	80 ± 8
0.016	brittle, rigid	no	yes	yes	144 ± 4
0.024	brittle, rigid	no	yes	yes	202 ± 5

3. RESULTS AND DISCUSSION

3.1. Parameter Sets for Carbon Spherogels. First, the required sol-gel parameters for the preparation of carbon spherogels were explored, targeting a perfect spherogel nanomorphology (adequate material toughness of the bulk material and a sufficient resistance against crack formation during mechanical cutting) for the direct preparation of binder and additive-free supercapacitor electrodes. Based on preliminary experiments, the precursor dilution (molar ratio of resorcinol to water), the PS concentration, and the PS sphere templating size were evaluated as crucial parameters, which directly influence the carbon micropore size, structure, and volume. Subsequently, following the state-of-the-art postsynthesis treatment for electrochemical applications, a set of carbon spherogels was physically activated with carbon dioxide to increase the specific surface area and carbon micropore accessibility for the electrolyte ions.²⁵

The sol-gel process is depicted in Figure 1 and can be described by three main steps: (1) gelation of a sol, containing resorcinol (R) and formaldehyde (F) with polystyrene (PS) nanospheres as a templating agent in deionized water (W); (2) solvent exchange to acetone and supercritical drying with CO_2 to minimize shrinkage effects and retain mechanically flexible bulk material behavior; (3) carbonization of the RF gel and decomposition of PS under an argon atmosphere to convert the cross-linked resin into an electrically conductive carbon spherogel, followed by physical activation with carbon dioxide.

The effective resorcinol coating on the PS sphere surface is favored due to noncovalent interactions of the aromatic rings of resorcinol and PS (π – π stacking) and general electrostatic interactions of the negative PS surface (presence of sulfate groups)²⁴ and partially positive resorcinol molecules (due to electron density distortion by hydroxyl groups). Subsequently, the addition of formaldehyde (cross-linking agent) and nitric acid (polymerization catalyst) initiates the gelation to a resorcinol–formaldehyde network. As previously reported,¹⁹ the pH value controls the pore geometry in the network, and a pH value in the range 5-6 yields reversibly compressible samples due to the presence of mechanically compressible macropores.

3.1.1. Effect of Resorcinol to Water (R/W) Dilution Ratio. The effects of various dilution ratios (R/W) in the range of 0.001-0.024 on carbon spherogels' morphology and physical properties are summarized in Table 1. Within this series, the PS diameter was kept constant at 277 nm, the PS concentration was 1.5 wt %, and a fixed resorcinol to formaldehyde molar ratio (R/F) of 0.5 was used. Below an R/W molar ratio of 0.008, only a very weak network after gelation was observed, which resulted in collapsed, fragile, and nonflexible gels after supercritical drying. Furthermore, these samples did not show a pure spherogel microstructure but separated hollow spheres embedded in a conventional carbon aerogel network (depicted by TEM micrographs in Figure S4A–D).²⁶ At the lower limit of R/W = 0.001 a thin wall thickness of around 10 nm was generated, leading to sphere collapse and the formation of bowl-shaped structures (Figure S4A). By increasing the R/W ratio of 0.002 to 0.006, the wall thickness increased from 13 ± 1 to 32 ± 4 nm. Thus, the minimum wall thickness for stable hollow spheres is 13 ± 1 nm, achieved with an R/W ratio of 0.002 (Figure S4B). At R/ W ratios higher than 0.008, brittle and rigid mechanical gel behavior was observed with a developed carbon spherogel nanostructure (Figure S4E,F). By increasing the R/W ratio up to 0.024, thus offering more precursor amounts for gelation, a wall thickness up to 202 ± 5 nm was obtained.

Finally, to prepare freestanding carbon spherogel samples suitable for mechanical cutting without material disintegration, the suitable molar ratio of R/W was confirmed to be 0.008. In this case, the morphology solely consists of hollow spheres and an adequate amount of macropores, which allows compressibility, as previously reported for RF²⁷ and carbon aerogels.^{19,28}

3.1.2. Low and High Limit of Suitable PS Concentrations. Subsequently, the window of suitable PS concentrations at a

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fixed R/W ratio of 0.008 was investigated for the synthesis of freestanding and mechanically stable carbon spherogel monoliths. A reference carbon aerogel sample was prepared without the addition of sphere templates in deionized water and compared to samples prepared within the range of 0.38-20 wt % PS in the aqueous solution. SEM and TEM micrographs show the resulting transition from an aerogel (0 wt % PS) over a mixed morphology (0.38 and 0.75 wt %) to a spherogel morphology (1.5 to 12 wt %) in Figure 2.



Figure 2. Low and high limit effect of PS concentrations (277 nm spheres) on the aerogel—spherogel morphology evolution and sphere collapse in an R/W system of 0.008. The left column displays SEM and the right column the corresponding TEM micrographs.

Pristine carbon aerogels are characterized by a network morphology resembling pearl beads (approximately 10-20 nm). The gradual addition of PS templating agents introduces hollow spheres into the carbon network (similar to the previous section for R/W ratios between 0.001 and 0.006), finally resulting in a network solely consisting of hollow spheres at PS concentrations higher than 1.50 wt %. The PS concentration can be increased up to 12 wt %; beyond, the sphere collapse into bowl-shaped structures due to weakened cross-linking between individual spheres resulting from thin walls (16 wt %). No gelation was observed at 20 wt % PS due to an excessive amount of templating agent preventing the dissolution of precursors. Mechanical and microstructural properties of samples depending on the applied PS concentration are summarized in Table S1. A direct correlation of wall thickness to the amount of PS templates is observed, and a suitable window between 1.5 and 12 wt % PS concentration emerges. To contribute to the rational design of the spherogels, the required synthesis conditions for the formation of reversibly compressible carbon spherogels were visualized by a ternary phase diagram of deionized water, resorcinol, and polystyrene (Figure 3).

This ternary diagram shows a limited window for the carbon spherogel synthesis: to form carbon spherogels with sufficient material toughness for crack-free mechanical cutting, the minimum concentration of polystyrene templates and resorcinol ranges from 1.5 wt % and respectively 4.7 wt %, yielding a hollow sphere with a wall thickness of 70 ± 3 nm (marked by green crosses in the ternary diagram). Increasing the resorcinol amount beyond 4.7 wt % at a fixed 1.5 wt % PS amount results in an increased wall thickness and increased bulk density, accompanied by a more brittle behavior. Below 4.7 wt % resorcinol and 1.5 wt % polystyrene, mixed aerogel/ spherogel structures are formed due to insufficient amount of templating agents to build the three-dimensional gel network. For the preparation of monoliths with different wall thicknesses (with a fixed R/W ratio of 0.008), a sphere templating range between 1.5 and 12 wt % can be applied.

3.1.3. Carbon Spherogels with Varying PS Template Diameters. Varying template diameters were investigated as a third tool to tailor pore arrangement on the nanoscale and to optimize possible mechanical properties and thus potentially the electrochemical performance of carbon spherogels. Colloidal polystyrene solutions were prepared in four diameter sizes-277, 455, 736, and 907 nm (see SEM micrographs in Figure S1, DLS analysis in Figure S2, and TGA analysis in Figure S3)—and applied separately as templating agents to the RF sol-gel process. For each size, a sample with a low polystyrene concentration (1.5 wt %) and high PS concentration (12 wt %) was prepared. In Figure 4, for each templating size, both variants' micromorphologies with thin and thick sphere walls are depicted by the corresponding TEM micrographs. Sphere templating with PS spheres of 277 and 454 nm resulted in perfect hollow sphere geometries for thin and thick walls with a varying wall thickness between 14 and 77 nm. Further increasing the PS templates to 736 and 906 nm caused partial collapsing of the thin wall variants. On the contrary, mechanically stable carbon spherogels were obtained with thicker walls in the range of 55-72 nm. Relevant physical and geometrical properties of carbon spherogels with different sphere templating sizes are summarized in Table S2. All carbon spherogel samples show specific surface areas in the range $600-700 \text{ m}^2 \text{ g}^{-1}$. Evaluation of isotherm and pore size distribution data indicates high porosity in the micropore range with the result of bulk densities lower than 0.066 g cm^{-3} (Table S2). N₂ sorption analysis is presented in Figure S5. Isotherms of thin-walled variants show isotherms with a distinct H4 hysteresis, which indicates sudden evaporation of nitrogen from the sphere interior.²⁹ This effect is hindered in thick-walled variants by longer diffusion pathways for nitrogen gas (Figure S5 1.A-1.D). A predominance of micropores in the range of 0.5-0.6 nm is present in every sample variation (Figure S5 2.A-2.D).

3.2. Physical Activation of Carbon Spherogels with Carbon Dioxide. The synthesis of spherogels from RF resins



Figure 3. Ternary diagram of the system deionized water/resorcinol/polystyrene at constant resorcinol to formaldehyde molar ratio of 0.5 and resorcinol to sodium carbonate molar ratio of 50. The green crosses mark the combinations which result in spherogel structures (at 277 nm sphere diameter). Orange crosses mark the combinations which result in spherogel structures without a reversibly compressible mechanical behavior.

onto PS templates is a convenient route to produce versatile monolithic carbon networks with tunable microstructures and porosities in the micro- to mesopore range (<50 nm). Physical activation does not affect the integrity of the hollow sphere network beyond a change in surface roughness (Figure S6). However, for applications such as supercapacitors, the relatively low microporosity of the spherogels (Table S2) limits their ion storage capacity. The microporosity of the sphere walls is not developed enough to maximize electrostatic interactions between the charging ions and the carbon network.

Thus, CO_2 activation was used as a route to increase the microporosity, while maintaining the structural integrity of the monoliths. Four samples with various sphere size (277, 455, 734, and 907 nm) and sphere wall thickness in a thin (respectively 14 ± 1 , 22 ± 2 , 25 ± 6 , and 34 ± 6 nm) and thick (respectively 69 ± 4 , 77 ± 8 , 55 ± 6 , and 72 ± 9 nm) variant were activated, and their sliceability was assessed after activation.

Interestingly, only the set of small, 277 nm-sized, carbon spherogel samples maintained a cylindrical, freestanding shape after exposure to a carbon dioxide stream of 60 NL h⁻¹ at 900 °C for 2 h. Severe damage occurs to 454, 736, and 906 nm template-sized monoliths, both to variants with thin and thick walls, whereas thin-walled samples were further damaged beyond the retention of a freestanding bulk. The properties of the spherogels (wall thickness and spheres sizes) influence the mass loss during activation and thus the stability of the monoliths. For 277 nm samples, a mass loss of ~60% was observed.

With larger sphere sizes, the mass loss increases. The observed sphere degradation suggests that the CO_2 gasifies the structure to a greater extent as the gas diffusion within the material is facilitated. As the bulk densities do not change from sample to sample due to the same amount of precursor, most likely this observed material damage is caused by larger spheres

offering higher accessibility for gas diffusion and therefore enhance activation effects.

Likewise, in thin-walled variants, CO_2 accessibility is further increased due to less material, resulting in a more collapsed structure than in the case of the thicker walls. Figure 5 shows carbon spherogel monoliths after activation and a visibly increasing damage at higher PS diameter and with thinner walls. TEM investigation of a spherogel sample (CS_907_thin, Figure S6) before and after activation reveals roughening of the sphere surface. However, individual spheres do not collapse or disintegrate and the damage occurs only to the bulk collective.

To assess the influence of the hollow sphere size and wall thickness on the electrolyte diffusion kinetics, the porosities of the 277 nm activated templated monoliths with thin and thick walls (14 and 69 nm wall thickness, Figure 4) are compared with the nontemplated conventional aerogel monolith. Nitrogen sorption isotherms at -196 °C were recorded to investigate the pore size distribution (Figure 6) as well as the specific surface areas and the micropore volume. All samples are mostly microporous with noticeable differences in the mesoporous region ($p/p_0 > 0.05$). Both 277 nm PS templated samples show a type IV isotherm shape with a type H4 hysteresis loop, revealing the microporous carbon shell.

Filling of the sphere interior is recorded by the sharp adsorbed volume increase at relative pressures close to $p/p_0 = 1$. Subsequently, both isotherms show the sudden evaporation of nitrogen in the desorption isotherm, also described as the tensile strength effect, at 0.5 p/p_0 .²⁹ This cavitation phenomenon of nitrogen takes place if the micropore diameter is below a critical limit of 6 nm.³⁰ In contrast to the aforementioned phenomenon, the reference sample, a non-templated aerogel sample, shows only a type IV isotherm behavior typical for a micro- and macroporous material. Herein, no enclosure of macropores, as estimated from electron microscopy (Figure 2, 0% PS), is verified. Macro-



Figure 4. TEM micrographs of carbon spherogels with thin (left, 1.5 wt % PS solution) and thick (right, 12 wt % PS solution) walls and different sphere templating sizes of 277, 454, 736, and 907 nm.

and micropore generation occurs concomitantly during the carbonization process (evaporation of H and O compounds in the RF shell and PS decomposition in the core). Applying the nonlocal density functional theory (NLDFT) and assuming slit-shaped pores, we obtain a specific surface area of 1822 \pm 100 m^2/g for the thin-walled and 1931 \pm 100 m^2/g for the thick-walled carbon spherogel samples compared to 1652 \pm 100 m^2/g for the pristine carbon aerogel sample. The



Figure 5. Freestanding and monolithic carbon spherogel samples (template diameter from left to right: 277, 455, 736, and 907 nm) after physical activation with CO₂ (2 h at 900 °C, 60 NL h⁻¹). Upper row: thin HCS wall (from left to right: 14 ± 1 , 22 ± 2 , 25 ± 6 , and 34 ± 6 nm); lower row: thick HCS wall variants (from left to right: 69 ± 4 , 77 ± 8 , 55 ± 6 , and 72 ± 9 nm).

corresponding cumulative pore size distributions show a similar nitrogen uptake for all samples up to 2 nm pore size. A difference can be determined for pore sizes from 2 to 32 nm: both spherogel samples show a higher pore volume compared to the aerogel sample, which can be considered as mesopore formation during carbon dioxide treatment.

3.3. Electrochemical Performance of Monolithic Carbon Spherogels. To understand the impact of the microporosity and structure on the storage performance and microstructure in supercapacitors, electrochemical testing was performed in the commercial electrolyte 1 M TEA-BF₄ in acetonitrile up to a potential of 2.5 V. The electrodes were produced by slicing the physically activated, untemplated, and templated (277 nm with thin walls and thick walls) monoliths into freestanding electrodes of ~1 cm diameter and 500 μ m thickness (Figure S7). The absence of conductive additives and binders in the electrode allows studying the influence of the sphere size and wall thickness on the capacitive performances without interfering effects arising from binders clogging the microporosity and hindering electrolyte penetration through the walls.

Because of the similar microporous surface areas of the activated samples (Figure 6), the presence of spheres does not

significantly affect the maximum capacitance which ranges between 100 and 125 F g⁻¹ at 5 mV s⁻¹ for all three activated samples (Figure 7a). The trend, however, shows that a higher volume of narrow micropores (<1 nm) provides a higher capacitance at low scan rates (<10 mV s⁻¹). Given the sizes of the TEA⁺ (bare: 0.67 nm; solvated: 1.35 nm) and BF₄⁻ (bare: 0.48 nm; solvated: 1.40 nm), a larger amount of pores below 1 nm accommodates more charges and results in a higher capacitance.³¹

However, the presence of hollow spheres and the thickness of their walls largely influence the electrolyte diffusion kinetics. The effect of sphere templating has a significant impact on the capacitance retention of the materials at scan rates above 10 mV s⁻¹. The templated structures built from hollow microspheres display much higher capacitances than the pristine sample at high discharging rates (beyond 10 A g⁻¹). The presence of hollow spheres allows the formation of an electrolyte reservoir which reduces the ionic diffusion length. The electrolyte buffer inside the hollow spheres, as already shown in various electrochemical systems.³² This contrasts with the pristine sample in which the carbon particles are solely microporous and the electrolyte penetration is hindered toward the center of the particle.

The capacitance retention is also largely affected by the thickness of the microsphere walls. The presence of walls of 70 nm provides twice as much capacitance as walls of 15 nm at a high current density of 60 A g^{-1} (Figure 7b). This correlates with the number of pores above 1 nm increasing by 25% with the wall thickness (Figure 7b). Thus, thicker walls provide a much higher power capability of 30 kW kg⁻¹ than thinner ones (10 kW kg⁻¹) as observed on the Ragone plot (Figure 7c).

The cyclic voltammograms at 5 mV s⁻¹ show that both the pristine and the thick-walled sample induce more degradation of the electrolyte than the thin walls as evidenced by the current peak at high overpotentials (Figure 7d). The cyclic voltammogram shows the stability window of the neat electrolyte is provided in Figure S8. This could be explained by the presence of unstable functional groups present on the carbon surface after CO₂ activation. The presence of thick



Figure 6. Nitrogen sorption isotherms (a) and cumulative and integral pore size distributions (b) of CO_2 -activated carbon spherogels with thin walls (15 nm, blue curves), thick walls (70 nm, green curves), and a nontemplated carbon aerogel sample for comparison (red curves).



Figure 7. Electrochemical results obtained in a two-electrode coin cell using 1 M TEA-BF₄ in acetonitrile: (a) capability from cyclic voltammetry measurements; (b) capability from galvanostatic measurements; (c) gravimetric Ragone plot; cyclic voltammetry at (d) 5 mV s⁻¹ and (e) 500 mV s⁻¹; (f) cyclability at 10 A g⁻¹.

walls also influenced the capacitance retention in the nonactivated analogues, which however exhibited capacitances below 10 F g^{-1} as expected from their relatively low microporosity (Figures S9 and S10).

After 10,000 charge/discharge cycles, the coin cells were opened and the electrodes were analyzed with TEM to understand the low stability of the thin wall sample upon charge and discharge. This post-mortem analysis reveals that hollow spheres with thin walls are mechanically too weak to maintain their central cavity (Figure S11). The continuous charge and discharge characterized by strong variations in osmotic pressure decenters the cavity within the spheres on more than 50% of the sample. This effect is, however, not observed on the spheres with more robust thicker walls. The electrolyte degradation observed in the presence of thicker walls (Figure 7d) tends to form solid aggregates (<20 nm in diameter) on the sphere surface, which do not affect the cyclic performances.

The influence of the microstructure on the capability was further investigated by electrochemical impedance spectroscopy which reveals a more capacitive behavior of the spherogels compared to the pristine sample in the low-frequency region (<50 mHz). The presence of spheres lowers the real impedance Z' by half for a given imaginary impedance Z'', as displayed on the Nyquist plot (Figure 7a). At higher frequencies, a semicircle followed by a diffusion-controlled region is observed for all three samples. The semicircle

commonly observed in freestanding electrode systems indicates the presence of an electrolyte layer between the current collectors and the carbon material inducing a charge transfer resistance at the collector/carbon interface.^{33,34} The diffusion-controlled region (depicted by ovals on the Nyquist plot in Figure 8b) is characterized by a transition from a resistive (phase angle $\sim 0^{\circ}$) to a capacitive behavior (phase angle $\sim -90^{\circ}$) as the frequency of the excitation signal increases (inset of Figure 8a). The relaxation time for each sample can be extracted from the Bode plot (Figure 8c) by looking at the maximum imaginary capacitance on the frequency range tested. As expected from the rate capability measurements (Figure 7a,b), the presence of electrolytes within the hollow spheres shortens the ionic diffusion path and accelerates the surface adsorption during charge/discharge. This decreases the relaxation time from 9.5 s for pristine to 6.5 s for the thin walls and 1.9 s for the thick walls.

The relationship among microporosity, microstructure, and performances is summarized by the schemes in Figure 8d–f. The pristine aerogel composed of microporous beads of 30 nm diameter displays high diffusion length due to its mostly microporous structure. The presence of spheres allows faster adsorption of the ions into the micropores. The sample with thicker walls exhibits more mesopores and displays faster kinetics than the thinner walls which have fewer mesopores.

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Figure 8. Electrochemical results obtained in a two-electrode coin cell by using 1 M TEA-BF₄ in acetonitrile. (a, b) Nyquist plots; (inset a) phase angle diagram. (c) Bode plot showing the real capacitance C' and imaginary capacitance C'' and the relaxation times of the cells. (d-f) Schemes showing the influence of the spherogel structure and the micromesoporous structure on the capacitive performances of the materials.

4. CONCLUSIONS

This proof-of-concept study investigated the synthesis parameters for the preparation of freestanding and monolithic carbon spherogels which were directly applied as electrode materials in electrochemical investigations of supercapacitor setups. First, various parameters, such as R/W dilution ratio, PS templating sphere concentration, and PS sphere size, were examined to generate a homogeneous network built of hollow spheres (carbon spherogels). Concomitantly, samples were targeted which allowed mechanical processing into suitable dimensions for electrodes without crack formation. The desired physical properties were realized at an R/W molar ratio of 0.008 by use of a PS template concentration in the range of 1.5-12 wt % with possible template sizes between 277 and 907 nm. After physical activation with carbon dioxide only 277 nm templated carbon spherogel samples retained their original cylindrical shape, and thus a set of samples could be directly applied as electrode materials in a coin cell setup. Cyclic voltammetry measurements revealed the benefit of hollow sphere structures compared to a conventional aerogel sample with respect to capacitance, in particular at high scan rates. The analysis of the electrolyte diffusion kinetics and morphological changes after 10,000 charge/discharge cycles by transmission electron microscopy reveals that the thick-walled (>60 nm) sample is favored due to a much higher rate capability of 30 kW kg⁻¹ than the thin-walled analogues (<20 nm, 10 kW kg⁻¹), without damage of its micromorphology. To summarize, carbon spherogels are novel variants of carbon

aerogels and can be directly applied as binder-free electrode materials. As a prerequisite, a careful adjustment of sol-gel and templating agent parameters, and the knowledge of their correlation, is of paramount importance to prepare these unique materials and optimize their electrochemical performance.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.1c02055.

SEM, DLS, and TGA analysis of PS templating nanospheres, SEM/TEM images, N₂ sorption analysis of carbon spherogels prepared with different R/W dilution ratios and PS concentrations, TEM images of CO_2 activated carbon spherogels after 10,000 charge/ discharge cycles (PDF)

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Notes

The authors declare no competing financial interest.

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