Synthesis of carbon core–shell pore structures and their performance as supercapacitors

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A B S T R A C T

High-power supercapacitors require excellent electrolyte mobility within the pore network and high electrical conductivity for maximum capacitance and efficiency. Achieving high power typically requires sacrificing energy densities, as the latter demands a high specific surface area and narrow porosity that impedes ion transport. We present a novel solution for this optimization problem: a nanostructured core–shell carbonaceous material that exhibits a microporous carbon core surrounded by a mesoporous, graphitic shell. Our tunable synthesis parameters yielded a structure that features either a sharp or a gradual transition between the core and shell sections. Electrochemical supercapacitor testing using organic electrolyte revealed that these novel core–shell materials outperform carbons with homogeneous pore structures. The hybrid core–shell materials showed a combination of good capacitance retention, typical for the carbon present in the shell and high specific capacitance, typical for the core material. These materials achieved power densities in excess of 40 kW kg⁻¹ at energy densities reaching 27 Wh kg⁻¹.

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1. Introduction

Electrochemical capacitors, also called supercapacitors, are attracting wide attention as energy storage devices. Compared to batteries and conventional capacitors, they present a unique balance between high power densities [1–3]. Supercapacitors exhibit high power densities that give them a performance advantage in applications including hybrid electrical vehicles, pulsed laser systems, solar-powered streetlights, and power tools [1,4,5]. This rapid charge/discharge capability is influenced by rate of ion electrosorption and transport through pores, which is especially inhibited at low operation temperatures [6], as well as electrical conductivity of electrodes. Although mesoporous materials feature greater ion mobilities and capacitance retention than microporous carbons, they exhibit lower specific surface areas and, subsequently, limited energy densities [7]. Although ions achieve optimal desolvation and packing densities in systems with matching ion-pore diameters [8], microporous electrodes often inhibit ion transport and reduce rate handling abilities [9]. Recent research efforts have introduced external surface structures, e.g. onion-like carbons [10] or, carbon hollow spheres [11] approaches to enhance power densities. However, these alternatives still exhibit low specific surface areas and limited charge storage capabilities. Therefore, an optimal material for supercapacitor electrodes must provide an appropriate balance between the properties needed for high energy density and the ones necessary for rate handling capability and high electrical conductivity [12–14].

Hierarchically structured materials can fulfill these demands and require i) prevalence of micropores to maintain high capacitance, ii) network of mesopores to facilitate rapid ion transport, and iii) direct introduction of graphitic structures to improve electrical conductivity. In this work, we introduce a novel synthesis methodology that enables the production of innovative porous carbons that features a mesoporous/graphitic shell (allowing both fast ion transport and high electric conductivity) that envelops a microporous core that features a high specific surface area. The schematic of this core–shell electrode structure
2. Experimental

2.1. Preparation

Core-shell materials were synthesized by reactive extraction of Ti from non-porous commercial TiC (99.5%, typically 2 μm, Alfa Aesar) in a vertical quartz tubular reactor (d_i = 0.034 m, l = 1 m) by using chlorine (purity 2.8, Linde AG) as extraction agent diluted in helium (purity 4.6, Linde AG). For route 1, a CDC shell on a carbide core was produced by reactive extraction of 0.5 g of TiC powder at 1200 °C for 15 min (0.5 mol m\(^{-3}\) Cl\(_2\), superficial velocity of 0.015 m s\(^{-1}\)). The interim product in route 1 is denominated as CDC-1200-35%. After flushing with helium (argon or another inert gas can be used), the reactor was cooled down to 800 °C and the reactive extraction continued at this temperature for 150 min at the same Cl\(_2\) concentration and superficial velocity (final product: CDC-STEP). For route 2 (CDC-GRADUAL synthesis), a cooling ramp (1200 °C–800 °C) at 10 °C min\(^{-1}\) was started after heating to 1200 °C and while adding Cl\(_2\) (0.5 mol m\(^{-3}\) Cl\(_2\), flow velocity of 0.015 m s\(^{-1}\)). To ensure full conversion after reaching 800 °C, the material was further chlorinated for 150 min at constant temperature. The final product of route 2 is denominated as CDC-1200-35%. After extraction of metals from carbides using chlorine gas at high temperatures, with the precursor and synthesis temperature governing the resulting porosity and degree of graphitization [16–20], this process is characterized by the temperature influence on the structure of the resulting CDC and the shrinking core reaction mechanism (SCM), hence, the conversion of the material from the outside towards the center during selective extraction [21,22]. We took advantage of accessible pore diameters (0.6–1.5 nm) of TiC-CDC produced by Cl\(_2\) etching in the 400–1200 °C temperature range [23,24]. Furthermore, since conversion follows SCM, a partially chlorinated carbide particle is likely to feature a CDC shell covering a carbide core [25,26]. Based on this knowledge, we propose a novel CDC synthesis procedure that relies on two-stage Cl\(_2\) etching to produce core–shell particles with different pore sizes and carbon microstructures on the surface and in the core. Results of two different routes of this non-isothermal CDC synthesis, using non-porous, commercially available TiC precursors, are presented in this work. The first route is the partial conversion of the carbide at a constant temperature, which determines the pore size distribution and graphic character of the CDC shell. Following an inert gas flushing step, the remaining carbide core is converted at a different temperature and, subsequently, features a different average pore size. This approach yields a sharp microstructure transition between the core and shell architectures (materials will be labeled as “CDC-STEP”). The second route implements a constant temperature ramp between two distinct temperatures, resulting in a gradual change of the pore structure and graphic character (materials henceforth labeled as “CDC-GRADUAL”). Both approaches depend on careful control of synthesis temperature and time steps and generate distinct porosities and divergent pore architectures in the outer and inner parts of the carbon particles.

To avoid heterogeneous structures in the powder bed (particles’ properties are largely governed by their location in the reactor), we adjusted the reaction system to facilitate convection and minimize mass transfer limitations. We achieved this by replacing the standard horizontal powder-filled crucible configuration with a quartz glass frit in the middle of a vertical tube reactor and feeding the gaseous reactant from the top (see Fig. S1 in the Supporting Information (SI)).
A VMP-3 Potentiostat (Bio-Logic Inc., France) was used to carry out electrochemical testing in a two-electrode configuration. A 1.5 M tetraethylammonium tetra-fluoroborate (NEt4BF4, Sigma Aldrich) solution in acetonitrile (HPLC grade purity, Alfa-Aesar) was used as electrolyte. Cyclic voltammograms were collected between 0.0 and 2.5 V using voltage sweeps ranging from 5 to 5000 mV s\(^{-1}\). Galvanostatic cycling was carried out at current density of 1.0 A g\(^{-1}\) between 0.0 and 2.5 V. Electrochemical impedance spectroscopy was performed using a 10 mV dampening oscillation centered on 0.0 V (vs. OCP). The frequency range was from 200 kHz to 10 mHz.

3. Results and discussion

3.1. Materials characterization

For route 1 mass analysis showed a degree of conversion of approx. 35% for the interim product (CDC-1200-35%). This material, the final product CDC-STEP, as also the reference materials converted fully at 800 and 1200 °C were analyzed with N\(_2\) sorption analysis. Pore size distributions (PSD) were determined using the Quenched Solid Density Functional Theory (QSDFT) model and are compared in Fig. 2a for PSDs normalized by total pore volumes. Absolute values of textural properties are summarized in Table 1. CDC-800 showcases a specific surface area of 1540 m\(^2\) g\(^{-1}\) and a 0.61 cm\(^3\) g\(^{-1}\) pore volume; subnanometer pores contribute to 87 vol.% of the latter. CDC-1200 exhibits the lowest surface area and the highest mesopore volume, which agrees with prior results\[30\]. The normalized PSD of both reference materials differ clearly and CDC-800 shows pores mainly below 1 nm.

For the interim product, where a porous carbon shell produced at 1200 °C is expected to cover a non-porous carbide core, the normalized PSD is nearly identical to the 1200 °C reference material. We observed pores in the micropore and mesopore range.

Raman spectroscopy – derived comparison of the carbon ordering of the interim product was compared to the fully converted reference material (Fig. S3a in SI). In accordance to literature, CDC-1200 shows a more crystalline character compared to the reference material produced at 800 °C, as expressed by the full width at half maximum (FWHM) and the intensity ratio of the D and G bands [15,18]. The carbon shell of the interim product shows D and G bands that closely resemble the reference CDC material produced at 1200 °C, as highlighted by similarities in the full width at half maximum (FWHM) and the intensity ratio given in the inset (see Table S1 in SI). Thus the first step in route 1, which produces the carbon shell, resulted in the expected pore- and microstructure properties, which are adjusted by the synthesis temperature of this step.

The final core–shell carbon structure (CDC-STEP) resulting for the first route shows a bimodal pore structure as a mixture of the 800 and 1200 °C pore size distribution (Fig. 2a). Furthermore, the share of pore volume below 1 nm, which was not present in the interim product and thus must stem from the porous carbon core produced at 800 °C, is in agreement with share of core and shell, adjusted by the degree of conversion of the interim product (35%). The absolute values of specific surface area of CDC-STEP are given in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>SSA/m(^2) g(^{-1})</th>
<th>(V^c/cm^3 g^{-1})</th>
<th>(V &lt; 1 nm^3/cm^3 g^{-1})</th>
<th>(d_v/\text{nm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDC-1200</td>
<td>970</td>
<td>0.73</td>
<td>0.18</td>
<td>1.51</td>
</tr>
<tr>
<td>CDC-STEP(^a)</td>
<td>1490</td>
<td>0.65</td>
<td>0.46</td>
<td>0.87</td>
</tr>
<tr>
<td>CDC-GRADUAL</td>
<td>1510</td>
<td>0.76</td>
<td>0.41</td>
<td>1.01</td>
</tr>
<tr>
<td>CDC-800</td>
<td>1540</td>
<td>0.61</td>
<td>0.53</td>
<td>0.79</td>
</tr>
</tbody>
</table>

\(^a\) Specific surface area (SSA) and pore volume (V) were determined using the QSDFT slit-pore model.

\(^b\) Subnanometer pore volume.

\(^c\) Average slit-pore diameter. \((d_v) = 2V/SSA.\)

![Fig. 2](image_url) a) Cumulative pore size distribution derived from N\(_2\)-sorption and QSDFT. b) Differential mass loss during temperature-programmed oxidation. c) TEM image of CDC shell on carbide core. d) SEM image of hollow core after burned amorphous part of CDC-STEP (color is used to highlight the shell and core) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).
To further characterize the stability of the core–shell material produced after route 1, temperature-programmed oxidation (TPO) was carried out and compared in Fig. 2b and S4 to the reference CDC produced by isothermal conversion. The reference materials showcased predominantly unimodal differential mass loss curves, confirming a homogeneous carbon structure. Materials with higher degree of graphitization become more thermally stable and are oxidized at higher temperatures than amorphous DCDS [31,32]. Hence, CDC-1200 demonstrated a higher oxidation onset temperature (595 °C) than CDC-800 (470 °C). The oxidation profiles for CDC-STEP material exhibited two oxidation peaks centered at 530 °C (Peak I) and 620 °C (Peak II), respectively, since they contain a mixture of carbons produced at 800 °C in the core and at 1200 °C in the shell. By integrating and comparing the peak area, the content of the low temperature core was estimated to be 74 wt.% of the entire particle and thus correlates with the achieved 85% degree of conversion for the second step.

We applied two approaches to confirm the core–shell structure of the material. We evaluated the CDC-STEP product using Transmission Electron Microscopy (TEM). A representative image of a single particle is shown in Fig. 2c. Due to the contrast difference of carbon and carbide, the electron-transparent carbon shell on the remaining carbide core can be observed clearly. Further investigation using HRTEM at the edge of CDC-STEP showcases a similar carbon structure compared to fully converted reference materials synthesized at 1200 °C (CDC-1200) presenting a multi-layer graphitic structure (see Fig. S5a and S5c). In a secondary approach, we oxidized the CDC-STEP material in air at 430 °C (burning away just the core) and analyzed the (mechanically crushed) hollow shell structures using SEM. Fig. 2d displays a cross-section of a 220 nm thick cracked shell with a hollow core. Furthermore, the shell thickness correlates to the adjusted 35% of degree of conversion for particle with 2 μm diameter. We are subsequently able to conclude that the stepwise temperature change in route 1 yielded hierarchically structured core–shell carbon materials, and that the carbon pore and microstructure can be controlled by the synthesis temperature.

Since the CDC-GRADUAL resulting from route 2 does not have a distinct border between its core and shell, the material is difficult to characterize using standard approaches. The results from N2-sorption and TPO are compared in Fig. 2a and b for the reference and CDC-STEP materials. Although a mixed pore structure and carbon microstructure is observed for this sample, the boundary between the core and shell of particles is less distinct, when compared to CDC-STEP. The pore size distribution most prominently shows this gradual transformation. In combination with the previous characterization results, this indicates that the pore size decreases from the outer surface towards the center of the particle and the microstructure from graphitic to amorphous.

### 3.2. Electrochemical characterization

To study the influence of the novel core–shell structure on the electrochemical performance of these materials, flexible, freestanding film electrodes of the core–shell and reference materials were fabricated as described in the experimental section. First insights are obtained by 4-Point probe measurements of these electrodes, which reveal an electrical conductivity 18 times higher for the more graphitic CDC-1200 (2.72 S cm⁻¹) when compared to using the amorphous CDC-800 (0.15 S cm⁻¹); the results are included in Table 2. Interestingly, the electrodes fabricated from both novel core–shell materials show a comparable high conductivity of 1.50 and 2.60 S cm⁻¹ for CDC-STEP and CDC-GRADUAL, respectively. Thus, the graphitic shell of the hybrid materials allows for a percolation pathway of the electrons and typically occurs in CDCs produced at 1200 °C [20].

The electrochemical measurements were conducted using a two-electrode configuration with 1.5 M solution of tetraethylammonium tetrafluoroborate (NEt4BF4) electrolyte dissolved in acetonitrile. The gravimetric capacitances obtained from cyclic voltamograms (CV) at scan rates of 10 and 500 mV s⁻¹ are shown in Fig. 3a and b. Charge/discharge profiles for all samples at 10 mV s⁻¹ yield rectangular CVs typical of ideal capacitors and show no mass transfer limitations. At this low scan rate, the highest capacitance of 115 F g⁻¹ is observed for the reference material CDC-800, due to its high specific surface area. In contrast, the low-SSA CDC-1200 reference material exhibits the lowest capacitance (40 F g⁻¹). Both core–shell pore structure materials show capacitances between those two extremes (95 F g⁻¹). At the high scan rate of 500 mV s⁻¹, distortion of the CV curve due to mass transfer limitations becomes obvious for CDC-800, and its capacitance decreases by 45%. Although some deviations from the ideal rectangular shape are observed for all samples, due to the bigger pores, the mass transport limitation is less pronounced and the drop in capacitance is only 15% for CDC-1200. Also importantly, the core–shell pore structured materials exhibited only minor mass transfer limitations: the drop in capacitance was around 20%.

Fig. 3c compares the surface area normalized capacitance in a broad range of scan rates. At low scan rates, the high surface area CDC-800 and both core–shell materials exhibit a similar surface specific capacitance. Hence, the observed minor drop in gravimetric capacitance results mainly from the slightly lower specific surface area of the core–shell materials. CDC-1200 showed a remarkably lower value, which can arise from the different wettability and influence of the pore size [8,33]. With increasing scan rate, the specific capacitance of CDC-800 continuously decreased above 20–50 mV s⁻¹ scan rates. This can be likely attributed to mass transfer limitation and only 70% of capacitance is retained at the scan rate of 200 mV s⁻¹. CDC-1200 shows the best capacitance retention with only a minor drop about 10% with increasing scan rates from 5 to 200 mV s⁻¹. Until reaching the 500 mV s⁻¹ scan rate, a plateau with a very low change in capacitance is observable. Both core–shell pore structures show similar charge/discharge profiles, despite the low amount of CDC-1200 in the shell.

The Randles-Sevcik (RS) coefficient (Table S3) was calculated based on CV measurements for the core–shell structure and the reference materials [1]. While CDC-800 shows significant diffusion limitations (RS = 0.836), both core–shell materials exhibit a near-ideal capacitive behaviors with RS coefficients approaching 0.920.

To further characterize the electrochemical behavior, the galvanostatic charge–discharge cycling was carried out with a current density of 1 A g⁻¹; results are shown in Fig. 4a. The voltage vs. time...
charge–discharge curves exhibit an ideal capacitive behavior and near-100% coulombic efficiencies. The specific capacitance values calculated from the discharge time are 42 (CDC-1200), 90 (CDC-STEP), 97 (CDC-GRADUAL), and 110 F g\(^{-1}\) (CDC-800). This applied current density is more or less comparable with the CV measurement with the scan rate of 20 mV s\(^{-1}\), thus the equal specific capacitance results. The electrode surface area resistances (R\(_{SA}\)) calculated from the ohmic drop occurring at vertex potentials and polarity shifts (see Fig. 4b) are summarized in Table 2. CDC-1200 and the novel core–shell structures show a low resistance.

**Fig. 3.** a) and b) CV measurement at 10 and 500 mV s\(^{-1}\). c) Capacitance normalized by specific surface area. d) Ragone plot of the core–shell and the reference materials.

**Fig. 4.** a) Galvanostatic charge–discharge at 1 A g\(^{-1}\) at whole voltage window and b) at around the vertex potential (current density of 1 A g\(^{-1}\)). c) Nyquist plots (the inset: magnification in high frequency). d) Real part of capacitance normalized by capacitance at 10 mHz.
of about 2 Ω cm², while CDC-800 exhibits a high resistance of ~4 Ω cm². These values corroborate previously measured intrinsic conductivities of the electrodes. Therefore, we can conclude that both, the high conductivity of the outer shell and favorable pore structures, contribute to the exceptional power densities of the core−shell materials.

Electrochemical Impedance Spectroscopy (EIS) measurements were carried out to obtain the dynamic responses, and the corresponding Nyquist plots are shown in Fig. 4c. All the materials show vertical straight lines in the low-frequency region, characteristic of purely capacitive behavior with a minimal ionic resistance. Notably, the CDC-GRADUAL features a more vertical curve than the other electrodes, reflecting that it behaves more like an ideal capacitor. In the high frequency region, the plots of CDC-STEP, CDC-GRADUAL and CDC-1200 do not exhibit the semi-circular region that is characteristic of interfacial charge-transfer resistance (Rct), highlighting divergent porosities as predominantly responsible for observed electrochemistry differences [34]. In contrast, the Nyquist plot of CDC-800 exhibits a significant semicircle over the high-frequency region, indicative for a high Rct between the electrode and current collector. As listed in Table 2, the Rct value of CDC-800 is ca. 3 to 10 times higher than those of the other materials, probably arising from its degree of graphitization and the consequent lower electrical conductivity (0.15 S cm⁻¹). The equivalent series resistance (ESR) can be obtained from the intercept of the Nyquist plot. All materials show comparable ESR of about 0.7 Ω. The Bode impedance plots show the normalized capacitance response to frequency in Fig. 4d. The relative capacitance order is: CDC-1200 > CDC-GRADUAL = CDC-STEP > CDC-800, which corroborates the previously discussed scan-rate handling abilities of these materials. The small relaxation time constant (2 s) of the core−shell materials clearly shows their fast charge−discharge response.

A Ragone plot (given in Fig. 3d) was used to correlate energy and power densities. Among the materials, CDC-800 shows the highest energy density of 53 Wh kg⁻¹ at power density of 0.4 kW kg⁻¹. Due to the poor rate performance, the energy density decreases quickly with increasing power density. When CDC-800’s power density reaches 20 kW kg⁻¹, the energy density drops by 45%. CDC-1200 shows a much lower energy density of 19 Wh kg⁻¹ due to a lower SSA, but it decreases only slightly with increasing power density up to its maximum 30 kW kg⁻¹ value, which matched the maximum value achieved for CDC-800. Importantly, for the novel core−shell materials the drop in energy density with increasing power density is less steep (from the lowest power density till 20 kW kg⁻¹ for CDC-GRADUAL 18%, for CDC-STEP 25%) compared to CDC-800 (45%) and more comparable to CDC-1200. CDC-GRADUAL proves to be the best material at the energy density of 39 Wh kg⁻¹ or below, combining excellent power and energy densities. The maximum power density of both core−shell materials is a factor of 1.7 higher than for both reference materials.

4. Conclusion

Carbon core−shell materials were successfully synthesized by two routes that employed Cl₂ etching of TiC and precisely controlled by the temperature and time conversion steps. Characterization data (N₂ sorption, Raman spectroscopy, temperature-programmed oxidation, SEM and TEM) highlights the stepwise or gradual transition between the graphitic, mesoporous shells and microporous cores of these materials. We demonstrate a high degree of tunability of the shell thickness of these CDCs using temperature control. The temperature applied during shell or core synthesis also tunes the graphitic structure of the different phases of this nanostructure. As a supercapacitor electrode, this novel carbon nanostructure showcases an optimal combination of specific surface area, electric conductivity, and mesopore architecture that provides a critical performance advantage. The core−shell structures yield higher capacitance retention (only 6% capacitance drop associated with a tenfold sweep rate increase). The core−shell supercapacitor electrodes showcase 27 Wh kg⁻¹ energy densities and 40 kW kg⁻¹ power densities. In addition to energy storage systems, the beneficial pore and graphitic structure of these materials is highly applicable in electrocatalysis, thermal catalysis and gas or liquid phase sorption.

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Appendix A. Supplementary data

Supplementary information related to this article can be found at http://dx.doi.org/10.1016/j.micromeso.2015.07.007.

References