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Highly structured 3D pyrolytic carbon electrodes derived from additive manufacturing technology

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HIGHLIGHTS

• A new type of complex 3D carbon is developed by 3D printing of a resin precursor structure followed by a pyrolysis process.
• The influence of pyrolysis conditions on the microstructural and electrochemical properties of the carbons is assessed.
• The free-standing 3D carbon electrodes show outstanding electrochemical stability, reproducibility and storability.
• The scalability of the proposed approach to generate different electrodes dimensions is evaluated and verified.

ABSTRACT

With common manufacturing approaches it is impossible to fabricate complex free-standing 3D carbon electrodes with well-defined geometrical structures. Here, a novel and straightforward approach to generate free-standing 3D carbon structures is developed based on stereolithography printing followed by pyrolysis. By controlling the design, printing and pyrolysis parameters, complex 3D pyrolytic carbon electrodes with minimal features of less than 100 μm and excellent structural uniformity were fabricated. The effects of carbonization condition (kinetics of thermal degradation) and final pyrolysis temperature on the physicochemical properties of the derived carbons were examined. The results show that the microstructural and electrochemical properties of the electrodes are more dependent on the carbonization condition than the pyrolysis temperature. Approximately 20% higher cyclic voltammetry peak currents (I_p) and 31% lower charge transfer resistance (R_{ct}) were recorded for the kinetically-fast carbonized electrodes, compared to the gradually (kinetically-controlled) carbonized ones, which is ascribed to their relatively higher specific surface area measured by N₂ adsorption/desorption technique. Moreover, great flexibility to construct electrodes with different architectures, excellent electrochemical stability and repeatability was observed. Overall, we believe that the proposed approach opens up new possibilities for the simple preparation of free-standing 3D carbon electrodes for a broad spectrum of applications.

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1. Introduction

Carbon is one of the most abundant elements of the periodic table. It has a wide variety of allotropic forms that possess a diverse range of properties and is explored in a broad spectrum of applications in
many areas of science and technology [1,2]. As a consequence, large research efforts have been dedicated towards design and synthesis of new carbon materials from different carbon sources to achieve materials with particular mechanical, electrochemical, thermal, electrical and optical properties. The key factor resulting in the large variety of physicochemical properties of the carbon materials is the grade of the electronic carbon hybridization (sp², sp³ or sp bonds) [3]. sp² hybridization is typical for the amorphous structure of diamond; sp³ hybridization is a two-dimensional hexagonal network structure encountered in graphite; sp¹ hybridization is a one-dimensional structure which rarely exists in carbon materials. Almost all the carbon compounds are partially amorphous and consist both of sp² and sp³ hybridized carbon atoms, where the sp²/sp³ ratio dictates their physicochemical properties [3,4].

Among the various carbon materials, glass-like amorphous carbons obtained by pyrolysis of various polymeric precursors in an inert atmosphere have been used extensively in electrochemical applications [4,5]. The often-cited benefits of pyrolytic glass-like carbons include wide potential stability window, chemical inertness, low cost, low background currents and electrocatalytic activity for a variety of redox reactions [6,7]. By altering the chemical composition of the precursor and tuning pyrolysis conditions, the sp²/sp³ hybridization ratio and thereby physicochemical properties of the derived carbon can be tailored. For instance, Ranganathan et al. found that with increasing the pyrolysis temperature from 700 °C to 1100 °C, the electrical resistivity of the pyrolyzed carbon films derived from A24330 photoresist decreased from 84.6 MΩ cm to 5.1 MΩ cm, respectively, and more graphitic structures were obtained at higher carbonization temperatures [8].

Geometrical patterning of the precursors and subsequent fabrication of three dimensional (3D) pyrolytic carbon micro- and nanostructures provides substantial advantages for various electrochemical applications. The significantly higher specific surface area of the 3D carbon electrodes potentially provides a larger electrode/electrolyte interface and thereby improved electrochemical behaviour, lower resistivity and higher sensitivity. Various microfabrication methods such as multi-step UV lithography, X-ray and two-photon lithography have been proposed for micro- and nano-patterning of organic/polymeric precursors followed by pyrolysis [9–11]. Geometrically very well-defined 3D pyrolytic carbon microstructures with high resolution have been obtained by optimization of these manufacturing processes. However, fabrication of structures with a complex geometry and a height of more than a few 100 μm is very difficult or even impossible with these methods, thereby seriously limiting the expansion in the third dimension. Moreover, most of these manufacturing processes are complex and laborious, and require access to rather expensive equipment. Alternatively, during the last few years, origami and electrospinning techniques have also been proposed to fabricate 3D carbon structures [12–14]. However, those innovative approaches are typically not suitable for definition of highly precise geometrical features in a 3D volume. Additive manufacturing methods, such as direct-ink writing (DIW), fused deposition modeling (FDM), ink-jet printing and stereolithography (SLA), offer a flexible, efficient, and economical alternative to fabricate complex 3D patterned polymer microstructures [15–17]. During the last few years, simple 3D structures have been made from composites containing thermoplastic organic binders and conductive carbon fillers (e.g. graphite, graphene, carbon black and carbon nanotubes) by FDM 3D printing technology and applied as electrode in electrochemistry [18–22].

SLA is a 3D printing process, which uses a laser beam to cure a photopolymer resin layer-by-layer constructing a 3D model [23,24]. At present, SLA still has some limitations in terms of surface roughness, printing resolution and precision. However, with the fast development of SLA printing technology and equipment, this issue will be addressed. In a few reports, the combination of SLA printing technology and pyrolysis was employed to generate polymer-derived ceramics [25]. However, to date no systematic study has been conducted to examine the possibility of generating 3D carbon microelectrodes through the pyrolysis of SLA printed samples. Herein, we propose and implement a novel, inexpensive, rapid and straightforward approach to generate 3D carbon electrodes with specified and controllable complex architectures using the SLA printing technology followed by pyrolysis. For this purpose, the pyrolyzability of a series of commercially available resins with different chemical compositions and physical properties was examined. Thereafter, different SLA-printed architectures and pyrolysis conditions were investigated and optimized to obtain geometrically defined and reproducible free-standing 3D carbon electrodes. The effects of carbonization condition and final pyrolysis temperatures on the physicochemical properties of the derived 3D carbon structures were examined using optical and scanning electron microscopy (SEM), X-ray micro-computed tomography (XR-μCT), thermogravimetric analysis (TGA), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and N₂ adsorption/desorption (BET) techniques. Moreover, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques were undertaken to evaluate the electrochemical behaviour of the prepared electrodes. Eventually, the scalability and flexibility of the proposed approach to generate complex 3D pyrolytic carbon electrodes with different dimensions were assessed, and performance was compared with electrochemical measurements. Due to their large surface area and the capability to design in different complex structures and scalability, these carbon electrodes have potential applications in batteries, electrochemical sensors, capacitors and electrochemical MEMS devices.

2. Experimental methods

2.1. Materials

All the commercial photopolymers, i.e. High Temp V1, Clear, Flexible, Dental LT Clear and Black resins, were procured from Formlabs Inc., USA. Phosphate buffered saline tablets (PBS), potassium ferrocyanide (K₄Fe(CN)₆), potassium ferricyanide (K₃Fe(CN)₆), and all other reagents used were of analytical grade and acquired from Sigma-Aldrich (USA). Deionized water (resistivity 18.2 MΩ cm) from a Milli-Q water purification system (Millipore Co., Billerica, USA) was used for electrochemical characterization.

2.2. Design and fabrication of 3D printed architectures

To evaluate the feasibility of using SLA-printed structures as precursors to generate 3D carbon electrodes, five commercial photopolymers, covering a broad range of physical properties and chemical compositions (Table S1, Supplementary Information), were assessed. The 3D architectures were designed with Fusion 360 (startup License, V. 2.0.5511, Autodesk, Inc.) software and exported as a stereolithography file (.stl) into the 3D printer software (PreForm Software V. 2.18.0 Formlabs Inc.). The models were printed with a Formlabs 2 SLA 3D printer (Formlabs Inc., USA) operating with a wavelength of 405 nm. The 3D printing was directly done on a 6-inch silicon wafer substrate mounted on the printer platform to enhance the uniformity and repeatability of the printed structures and subsequently improve the release from the substrate. A schematic illustration of the SLA printing technology and the 6-inch silicon wafer substrate mounted on the printer platform are shown in Fig. 1a. In preliminary experiments, it was found that a solid and bulky design hinders the complete degassing of the specimen during the pyrolysis process. The resulting high internal pressure of the trapped gaseous products leads to collapse and fracture of the structure. Therefore, an attempt has been made to design mesh structures with substantial high specific surface area respecting the SLA printing restrictions. A mesh structure with vertical and horizontal cylindrical connections (0.4 mm diameter and 0.7 mm mesh spacing) was chosen as the optimal design (Fig. S1, Supplementary Information). After printing, the specimens were released from the platform and gently washed with isopropanol for 10 min to remove any residual non-cross-linked
resin, and then post-cured under UV light at room temperature for 30 min.

2.3. Optimization of the pyrolysis process

The printed specimens were then carbonized using various pyrolysis conditions in a PEO-604 furnace (ATV Technology, Germany) in a nitrogen environment with a gas-flow rate of 20 SLM. To evaluate the impact of pyrolysis conditions on the physicochemical properties of the carbonized materials, two different pyrolysis processes, i.e. direct (10 °C/min ramping rate) and step-by-step ramping (10 °C/min to 375 °C, 1 °C/min to 425 °C, and 10 °C/min ramping rates) were examined to reach the final temperatures of 900, 1000 and 1100 °C with the same dwell time of 1 h. Dynamic and isothermal thermogravimetric analysis (TGA) were utilized to identify the critical degradation range and optimize the pre-pyrolysis conditions of the 3D printed structures, respectively. All TGAs were carried out on a TA Instrument (TGA-Q500, USA), operating under a nitrogen flow rate of 60 mL/min and 10 °C/min ramping rate using a platinum pan containing samples of approximately 400 mg.

2.4. 3D pyrolytic carbon electrode microstructure characterization

The 3D pyrolytic carbon electrode was subjected to XR-μCT investigations using a commercial Zeiss Xradia versa 410 system (Pleasanton, USA) to assess its microstructural characteristics and interior structure. The sample was mounted on a pin such that undisturbed 360° access to the sample was obtained. The pre-voltage was kept at 40 kV and the power at 10 W. All collected data were reconstructed by the commercial software connected to the system which relies on a Feldkamp, Davis, and Kress algorithm, based on filtered back-projection algorithm. Scanning electron microscopy (SEM) in low-vacuum mode, was employed to characterize the surface topography and porosity of the 3D electrodes pyrolyzed at different conditions. All SEM images were obtained using a Zeiss Supra VP 40 (Carl Zeiss NTS GmbH, Germany). The Image J software (National Institute of Health, Bethesda, USA) was used to measure the length, width, depth and diameter of the segments of 3D pyrolytic carbon from SEM and optical microscope images. In order to assess the influence of carbonization conditions on the physical properties of the 3D printed structures, cubic meshes with 5 mm edges and the aforementioned microstructural features were SLA printed and pyrolyzed at different heating rates and temperatures. For this purpose, a simulation of the pyrolysis process was conducted with a TGA instrument. The mass loss (%, derived from TGA results), linear shrinkage (S, %) and structural density (ρ, mg/mm³) parameters of the pyrolyzed cubic meshes were examined. The linear shrinkage and structural density parameters of the cubic meshes were calculated according to the Eqs. (1) and (2), respectively.

\[
S(\%) = \left( 1 - \frac{L_a}{L_b} \right) \times 100
\]

\[
\rho \text{ (mg/mm}^3\text{)} = \frac{m \text{ (mg)}}{V \text{ (mm}^3\text{)}}
\]

where \(m\) is the mass of the specimen after pyrolysis (mg), \(V\) is the volume of the specimen after pyrolysis (mm³), \(L_a\) and \(L_b\) are the length of
the edges of the cubic meshes before and after pyrolysis, respectively. The surface and depth profile composition of the SLA printed 3D structures before and after pyrolysis was determined using X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific Inc., K-alpha, USA) equipped with a monochromatic Al Kα X-ray source (pass energy: 200 eV for survey spectra). The atomic composition of surface elements was analyzed with the software package (Avantage Thermo VG) provided by Thermo Fisher Scientific. To analyze the impact of pyrolysis conditions on the graphitization of the 3D carbon electrodes, visible Raman spectroscopy (Model DXR, Thermo Fisher Scientific Inc., Denmark) with an excitation wavelength of 532 nm was acquired. The Raman spectra were obtained with a 10× objective and 10 mW laser power, and the data were processed by OMNIC software ( Nicolet Instruments, USA). The specific surface area and pore volume of the 3D pyrolytic carbon electrodes were determined by Brunauer–Emmett–Teller (BET) measurements: N2 adsorption/desorption were acquired at 77 K using a NOVATouch LX2 Analyzer (Quantachrome Instruments, USA). The samples were previously outgassed at 350 °C for 6 h.

2.5. Electrochemical measurements

Prior to electrochemical experiments, cleaning and activation of the electrode surfaces were performed with an oxygen plasma treatment (Zepto, Diener plasma surface technology, Germany) at a pressure of 0.6 mbar with a power of 120 W for 75 s. The electrochemical measurements were performed using an Autolab PGSTAT128N potentiostat/galvanostat in combination with NOVA program version 2.1.3 (Metrohm Autolab B-V, Netherlands). A micro-milled PMMA (poly methyl-methacrylate) electrochemical cell (approximately 3 mL volume) was employed with an Ag/AgCl (1 M KCl) electrode as reference electrode, a spiral platinum wire as counter electrode and the 3D pyrolytic carbon electrodes as working electrode. The electrochemical measurements included cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). To assess the reproducibility of results, each measurement was replicated three times and 3D electrodes from different printing batches were examined. The CV experiments were carried out in PBS solution (10 mM, pH 7.4) containing 0.01 M [Fe(CN)6]3-/4− in the potential range from −0.6 to 1 V with a potential scan rate of 50 mV s−1. EIS spectra were recorded within the frequency range from 0.1 Hz to 100 kHz at 100 mV AC signal amplitude.

3. Results and discussion

3.1. Pyrolysability of 3D printed structures

An initial series of experiments was performed on pyrolysis of cubic meshes printed with five different photopolymers at a temperature of 900 °C for 1 h (the results are shown in Supplementary Information, Fig. S2). Although all the pyrolyzed samples showed very low electrical resistivity when it was assessed with a digital multimeter, isometric shrinkage and preservation of the shape and features of the 3D printed specimen was only observed for the HT resin precursor. Therefore, this photopolymer was chosen for further investigations. The acquired results are attributed to the different thermal properties, chemical composition and density of the employed precursors [26]. An illustrative scheme of the stepwise fabrication process of the 3D carbon electrodes is shown in Fig. 1(a) and (b). Fig. 1(c) shows a 3D reconstruction of an XR-μCT scan of the circular part of the pyrolytic carbon electrodes, which confirms preservation of the uniformity of the 3D structure during pyrolysis and clearly distinguishable layers. Higher magnification images and a cut plane of the scanned pyrolytic carbon electrode are shown in Fig. 1(d) and (e), respectively. The high roughness of the...
surface of the layers could be ascribed to the degassing of the specimen during the pyrolysis process.

Pyrolysis of a precursor material for converting it into carbon is encompassed by a mass loss corresponding to the dehydrogenation, polymer degradation and release of gaseous products, leading to a drastic shrinkage of the structure. During shrinkage, intrinsic stress can result in deformation and fracture of pyrolytic carbon structures, and the pyrolysis process of a given material should therefore be carefully optimized to mitigate these effects. Concurrent with mass loss, carbonization, cyclization, condensation, hydrogen transfer, and isomerization reactions also take place [27]. The electrical and electrochemical behaviour of carbon materials depends on their microstructure, and the structure is further related to pyrolysis conditions, including heating rates, final pyrolysis temperature, dwell time and atmosphere [1,28]. A typical dynamic TGA thermogram of the HT resin is shown in Fig. 2(a), which clearly identifies the onset temperature of decomposition ($T_{\text{onset}}$) and the maximum mass loss temperature ($T_{\text{max}}$; which is defined as the peak point of the derivation of the TGA curve) of 318 °C and 429 °C, respectively.

To precisely clarify the relationship between the operating temperature and the kinetics of thermal degradation, isothermal TGA measurements were carried out at different temperatures around $T_{\text{max}}$ (from 325 to 425 °C) for 180 min and mass loss over time was monitored. The isothermal TGA results are shown in Fig. 2(b). It can be inferred from the results that for temperatures below 375 °C, the degradation rate, which is proportional to the slope of the curves, is very low and more than 60% of the material is still left after 3 h heating. Compared to that, the degradation rates for higher temperatures are extremely fast. Overall, to systematically investigate the influence of degradation rate of the precursor on the physicochemical properties of the carbonized structures, two different pyrolysis conditions, i.e. fast and gradual carbonization processes, were chosen based on the TGA results and studied further. Hence, a carbonization process with three isothermal heating stages (3 steps ramping, 3SR) as shown in Fig. 2(c)-top was considered to allow for gradual mass loss and gas release before ramping to the final pyrolysis temperature. This thermal treatment was compared with the results obtained from a pyrolysis process with direct ramping (DR) to the final temperatures, as shown in Fig. 2(c)-bottom.

In order to assess the influence of carbonization conditions on the physical properties of the 3D structures printed with HT resin, the two pyrolysis processes were simulated using the TGA instrument. For this purpose, cubic meshes with 5 mm edges were prepared and utilized, as explained in Section 2.4. Due to the temperature limitations for the platinum TGA pans, only the final pyrolysis temperatures of 900 and 1000 °C were evaluated. The TGA results of the direct ramping (DR) and 3 steps ramping (3SR) to the final pyrolysis temperature of 900 °C are represented in Fig. 2(d) (results for 1000 °C are shown in Fig. S3, Supplementary Information). Moreover, the calculated values of linear shrinkage and structural density for the pyrolyzed cubic meshes are summarized in Table 1.

During pyrolysis, the precursor decomposition leads to aromatization of carbon atoms and microstructural densification, concurrent with mass loss (gas evolution) [15]. The obtained results demonstrate that mass loss and shrinkage of the structures are highly dependent on the pyrolysis conditions influencing the kinetics of thermal degradation (Fig. 2 and Table 1). For the gradual pyrolysis process (3SR, Fig. 2d, red curve), a slower decomposition rate and longer dwell times at intermediate temperatures allow more time for rearrangement of carbon atoms, which leads to less mass loss, less shrinkage and consequently a larger structural density. Whereas, in the case of fast pyrolysis process (DR, Fig. 2d, black curve), a higher decomposition rate leads to enhanced gas evolution, less time for formation of new carbon bonds and thereby more mass loss. Furthermore, higher pyrolysis temperature leads to increased shrinkage, slightly more mass loss and a higher structural density (Table 1). This could be ascribed to further evaporation of decomposition products and rearrangement of carbon atoms due to longer total duration of pyrolysis processes and higher temperatures [29].

3.2. Structural characterization of 3D pyrolytic carbon

Fig. 3 shows the SEM images of SLA 3D printed cubic meshes before and after pyrolysis for the direct and 3 steps ramping up to 900 °C. From Fig. 3(a), it can be seen that a regular square pattern of the horizontal and vertical cylinders with an average diameter of 413.4 ± 5.8 μm was successfully produced during printing. The very close correlation between the experimental and designed values clearly verifies the accuracy and precision of the employed SLA 3D printing instrument. SEM images with higher magnifications (Fig. 3b & c) reveal that the micro-structure of the 3D printed specimen has a rough surface texture. From the low-magnification SEM images of the carbonized cubes obtained with different pyrolysis conditions, it is apparent that the fast pyrolysis (DR) leads to slightly non-isotropic shrinkage and formation of an inflated cube with mesh holes that are drastically squeezed and distorted (Fig. 3d). This observation suggests that a faster heating rate provides less time for degassing, causing high pressure of the gaseous products trapped within the specimen and thereby expansion and swelling of the pyrolyzed structure [26,29,30]. In the case of slow pyrolysis (3SR), the regular cubic shape of the 3D printed sample is approximately retained after the carbonization process (Fig. 3(g)), which is due to the more gradual degradation and degassing. The results with higher magnifications (Fig. 3(e), (f), (h) and (i)) also express that the pyrolysis conditions not only influence the macro-structure of the carbonized materials, but also play a significant role in the surface topography and shape of the micro-pores.

Raman and XPS spectra of the pyrolyzed 3D printed structures were examined to assess the influence of different pyrolysis conditions on the microstructure and chemical composition of the 3D carbon materials. The XPS spectra of the 3D printed materials before and after pyrolysis are shown in Fig. 4(a) and the results are summarized in Table 2. For the 3D printed sample before pyrolysis, the analysis showed silicon (Si2p), carbon (C1s), nitrogen (N1s) and oxygen (O1s) peaks at 104, 286, 401 and 533 eV, respectively, and an atomic O/C ratio of 43% was measured. The presence of silicone element could be ascribed to the silicone coupling agents of the photopolymer resin [31]. In comparison, no nitrogen and silicon signals can be observed for the pyrolyzed samples, suggesting that thermal degradation products and compounds containing Si and N are almost completely eliminated during the pyrolysis process. The atomic O/C ratios for the samples pyrolyzed at different conditions are approximately similar and above 4.5%, indicating that mostly carbon is remaining and that the pyrolysis process had no noticeably influence on the chemical surface composition.

In addition, XPS analysis can also be utilized to identify the sp² and sp³ structures of carbon-based materials [32,33]. Researchers have reported a binding energy difference of about 1 eV between the sp² and sp³ hybridized C1s peaks [33]. In Fig. 4b, high-resolution XPS spectra in the C1s region of the cross-linked HT resin and gradually pyrolyzed carbon are shown. The C1s spectrum of the cross-linked HT resin consists of peaks at the binding energies of 286 and 290 eV, corresponding to the sp² C—C bonds and carbon-oxygen bonds in their various bond states, respectively. In comparison, the C1s spectrum from the pyrolytic carbon material only showed a single asymmetrical peak at 284.4 eV with a small shoulder, and it could be concluded that the sp² and sp³ peaks are overlapping. The binding energy shift and narrowing of the C1s peak obviously confirm the graphitization of the 3D printed HT resin during pyrolysis. Moreover, the considerably large sp²/sp³ ratio observed through the C1s peak fitting is an evidence for the highly graphitic structure of the pyrolyzed samples. Fig. 4(c) shows the XPS sputter depth profile for oxygen for the fast pyrolyzed carbon electrode. The same results were also observed for the other pyrolysis conditions. Except for the outermost surface, which was directly exposed to air and hence more oxidized, the oxygen content remained almost constant at
approximately 3% throughout the depth of the pyrolytic carbon materials. The presence of oxygen within the interior structure of the 3D pyrolytic carbon could be ascribed to the existence of oxidized surfaces inside the material due to interconnected porous structures.

Fig. 4(d) compares Raman spectra of the 3D pyrolytic carbon structures, and the derived results are given in Table 2. In principle, Raman scattering provides information about microcrystalline carbon structure, such as the degree of ordering and crystallinity of carbon materials [34]. In the analysis of pyrolytic carbon by Raman spectroscopy, the main focus is on the investigation of the G peak (E_{2g} vibrational mode at 1580 cm\(^{-1}\)), which represents crystalline graphite and the D peak (A\(_{1g}\) vibrational mode at 1360 cm\(^{-1}\)), that originates from amorphous carbon structure and various kinds of defects in the graphitic structure [34–36]. Raman results confirm the carbonaceous nature of the pyrolyzed 3D materials with the presence of signature graphitic D- and G-peaks. Here, it has been observed that for all the pyrolyzed materials, the G peak position is slightly shifted to larger wavenumbers, which probably could be ascribed to the relatively small size of the graphite phases and the presence of disordered graphite [37]. Moreover, the broad 2D peak at ~2700 cm\(^{-1}\) indicates the presence of highly disordered and randomly arranged graphene with more than few layers [38]. It is known that the ratio of the D and G peaks intensity (I\(_D/I_G\)) in carbon structure is inversely proportional to the in-plane crystallite size (i.e., I\(_D/I_G = 1/L_0\)). It means that a larger I\(_D/I_G\) ratio correlates with smaller L\(_0\) and graphitic fraction, which is associated with the presence of a higher disorder. The calculated L\(_0\) values for 3D carbon structures pyrolyzed at different conditions revealed that the gradually pyrolyzed samples (3SR) have slightly higher L\(_0\) values and thereby less microstructural disorder and smaller amorphous regions than the fast pyrolyzed samples (DR). In comparison to the temperature ramping during the pyrolysis process, it is observed that the final pyrolysis temperature within the examined temperature range, i.e. 900–1100 °C has no considerable influence on the microstructure and the graphitic content of the samples.

3.3. Electrochemical characterization of 3D carbon electrodes

The electrochemical behaviour of the carbonized materials is influenced by various parameters, such as their resistivity, microstructural properties and electroactive surface area, which are closely related to
the pyrolysis condition. Thus, to identify the relation between the pyrolysis process and electrochemical characteristics of the 3D carbon electrodes, a series of CV and EIS experiments with the redox probe \([\text{Fe(CN)}_6]^{3-}/4^-\) were carried out. CV provides information regarding the surface status of carbonized electrodes. Theoretically, the intensity of the anodic and cathodic peak currents of the CV curves are directly proportional to the electrons exchanged at the electrode-electrolyte interface [39]. Moreover, it is known that the peak-to-peak separation \((\Delta E_p)\) value is inversely correlated to the kinetics of electron transfer, and is minimal for an ideal reversible redox system [30,40,41]. On the other hand, the impedimetric response with EIS allows to understand the impact of different individual contributions on the overall impedance of the electrochemical set-up [29,42]. Generally, a typical shape of the impedance spectrum, also called Nyquist plot, includes a semicircle region and a straight line. The diameter of the corresponding semicircle part at high frequency range is ascribed to the charge transfer resistance \((R_{ct})\) at the electrode/electrolyte interface, which is inversely proportional to the charge transfer rate [43]. Overall, with respect to the above-given definitions, the electrodes with higher redox peak currents, less \(\Delta E_p\) and \(R_{ct}\) could be identified as the 3D pyrolytic carbon electrodes with the optimal electrochemical behaviour. The acquired CVs and EIS results are shown in Fig. 5 and the derived electrochemical values for the electrodes pyrolyzed at different conditions are summarized in Table 3.

As depicted in Fig. 5(a), quasi-reversible pairs of redox peaks were observed for all the electrodes pyrolyzed at different conditions. This is corresponding to the electron exchange between the \([\text{Fe(CN)}_6]^{3-}/4^-\) probe and the electrode surface and confirms the electrochemical activity of the electrodes surfaces. As shown in Fig. 5(b), the extracted absolute values of the anodic and cathodic peak currents for the fast pyrolyzed electrodes (DR) are considerably higher than those for the gradually pyrolyzed electrodes (3SR) regardless of the final pyrolysis temperature. Improvement in electrochemical behaviour is generally expected to result from enhanced graphitization [1]. However, the Raman spectroscopy results discussed above showed slightly higher graphitic fraction for the gradually pyrolyzed samples than for the fast pyrolyzed electrodes. Here, the observed higher oxidation and reduction peaks currents for the fast pyrolyzed samples are attributed to the high thermal degradation rate and fast weight loss during the pyrolysis process, which can lead to the formation of less condensed and thereby

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>C (Atomic ratio (%))</th>
<th>O (Atomic ratio (%))</th>
<th>O/C ratio</th>
<th>(L_a^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cured HT resin</td>
<td>62.4</td>
<td>28.1</td>
<td>45</td>
<td>-</td>
</tr>
<tr>
<td>DR to 900 °C</td>
<td>95</td>
<td>5</td>
<td>5.2</td>
<td>1.08</td>
</tr>
<tr>
<td>DR to 1000 °C</td>
<td>94.9</td>
<td>5.1</td>
<td>5.3</td>
<td>1.08</td>
</tr>
<tr>
<td>3 SR to 900 °C</td>
<td>94.9</td>
<td>5.1</td>
<td>5.4</td>
<td>1.08</td>
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<tr>
<td>3 SR to 1000 °C</td>
<td>95.4</td>
<td>4</td>
<td>4.8</td>
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<td>3 SR to 1100 °C</td>
<td>95.6</td>
<td>4.4</td>
<td>4.6</td>
<td>1.12</td>
</tr>
</tbody>
</table>

\(L_a^*\) \(\propto\) 1/\(L_a\).
more porous structures with higher specific surface area [44]. Nitrogen adsorption isotherm was used to determine the specific surface area of the fast and gradually pyrolyzed electrodes at the final pyrolysis temperature of 1000 °C. The total BET surface area and pore volume values of the fast pyrolyzed electrode were found to be 19.56 m²·g⁻¹ and 0.021 cm³·g⁻¹, respectively. These values are approximately two times higher than the ones for the gradually pyrolyzed electrode (10.89 m²·g⁻¹ and 0.012 cm³·g⁻¹, respectively). The specific surface area and porous microstructure are key factors influencing the electrochemical performance of electrode materials [45,46] and unambiguously explain the observed electrochemical behaviour. The ΔE_p values measured in this research are higher than those of composite electrodes generated by FDM 3D printing technology, which might be ascribed to the porous structure of the fabricated electrodes [19,21]. For both series of pyrolyzed samples, the absolute values of the peak currents increased and the ΔE_p decreased proportionally with increasing the final pyrolysis temperature from 900 °C to 1000 °C, while further increasing the final pyrolysis temperature reversed this trend. In earlier studies, improvement of the electrochemical behaviour was reported for increasing pyrolysis temperatures [29], which typically was attributed to a more graphitic carbon. Here, the Raman results showed a similar graphitic fraction for the electrodes pyrolyzed with the same process, but at different final temperatures. Therefore, the measured increase of peak current from 900 °C to 1000 °C might be due to increased surface area. Similarly, observed increase in ΔE_p and decrease in the peak currents for 1100 °C might be attributed to the partial closure or collapse of micropores and consequently a decrease in the electroactive surface area. Similar observations have been reported for pyrolysis of other polymer precursors [7,47].

EIS was employed for further electrochemical characterization of the 3D pyrolytic carbon electrodes. The Nyquist plots for the fast and gradually carbonized electrodes at different final pyrolysis temperatures are shown in Fig. 5(c) and (d), respectively. The EIS results were interpreted by fitting the obtained Nyquist plots with an equivalent circuit (inset of Fig. 5(c)), derived from a modified Randles’ model [48], and excellent fitting was demonstrated throughout the entire frequency range (Fig. S4, Supplementary Information). This equivalent circuit consists of charge transfer resistance Rct, solution (electrolyte) resistance Rs, and
Warburg impedance $Z_w$, constant phase element CPE, and resistance $R_B$ and capacitance $C_B$ of the bulk carbon electrode material. The extracted values for different components from the fitting of the experimental data with the equivalent circuit are summarized in Table 3. The $R_{ct}$ values of the 3D carbon electrodes for different pyrolysis conditions showed similar trends as the corresponding CV results and the minimum charge transfer resistance was measured for pyrolysis at 1000 °C. Due to the improved electrochemical behaviour, 1000 °C was selected as the optimal final pyrolysis temperature for further experiments. For both pyrolysis processes, the $R_B$ values decreased with increasing the final pyrolysis temperature. The lower values of $R_B$ for higher pyrolysis temperatures might be caused by the higher sp²/sp³ hybridization ratio, resulting in a more graphitic and conductive material. This is similar to results reported by others, where resistivity of pyrolytic carbon decreased with increasing the final pyrolysis temperature [27,47]. In order to assess the suitability and performance of the electrodes serving as a platform in electrochemical applications, an important parameter to be considered is the relation between peak current intensity ($I_p$) and the electrochemical cell parameters. According to the Randles-Sevcik equation describing diffusion-controlled reversible electron transfer at an electrode (Eq. (3)), $I_p$ is proportional to the electrode surface area ($A$, cm²), bulk concentration ($C$, mol cm⁻³) and diffusion coefficient ($D$, cm² s⁻¹) of the redox probe and voltage scan rate ($ν$, mV s⁻¹).

$$
I_p = 2.69 \times 10^5 AD^{1/2}ν^{1/2}C
$$

The reversibility of the electron transfer process for the 3D pyrolytic carbon electrodes was investigated with CV at various potential scan rates ranging from 20 to 200 mV s⁻¹ with 10 mV increments. As it is shown in Fig. 6(a) and (b), the linear relationship observed between the redox peak currents and the square root of the scan rate is in agreement with Eq. (3), indicating that the electrochemical reactions on the surface of electrodes were predominantly diffusion-controlled processes.

The $ΔE_p$ values increased continuously with increasing the scan rate. This is comparable to the behaviour at a glassy carbon electrode (GCE), which is a well-known stable working electrode, and indicates that the 3D pyrolytic carbon electrodes behave similarly to the GCE [49]. Moreover, Fig. 6(c) and (d) illustrate representative CVs of the gradually and fast pyrolyzed 3D carbon electrodes, respectively, with different concentrations of [Fe(CN)₆]³⁻/⁴⁻ redox probes. The linear relation of the peak current values with the redox probe concentrations for both carbon electrodes also confirms good electrochemical reversibility. It must be noted that although for both fast and gradually pyrolyzed electrodes a remarkable linear correlation between the $I_p$ vs. $ν^{1/2}$ as well as $C$ were observed, the higher coefficient of determination ($R^2$) value recorded for the gradually pyrolyzed electrode reflects the fact that a slow carbonization process could result in more stable and reliable electrochemical behaviour.

With respect to the $I_p$ vs. $C$ graphs, the sensitivity of the 3D carbon electrodes was determined as the slope of the fitted linear function [50]. The values of 267.1 μA mM⁻¹ and 286.2 μA mM⁻¹ were derived as the sensitivity of the gradually and fast pyrolyzed carbon electrodes, respectively. The higher sensitivity value derived for fast pyrolyzed electrode could relate to its larger surface area as discussed above based on BET analysis. The low relative standard deviation (RSD) values recorded through 25 consecutive cycles of CVs (Fig. S5, Supplementary Information) implies excellent electrochemical stability and repeatability of the 3D pyrolyzed carbon electrodes. Moreover, the results showed that even after prolonged exposure to ambient conditions (2 months), the electrochemical results of the electrodes are very reproducible.
3.4. Scalability of 3D carbon electrodes

Finally, in order to prove the scalability and flexibility of the proposed fabrication method, three polymer precursor structures with different circular diameters D (10, 15 and 20 mm) were designed, 3D printed and pyrolyzed. From a structural point of view, very uniform and isotropic shrinkage and excellent preservation of shape was observed for the 3D printed structures with different dimensions, as shown in Fig. 7(a), top. The calculated linear shrinkage values of the circular diameter, electrical contact length, contact lead length and width are presented in Fig. 7(a) (bottom).

It can be deduced from the graph that regardless of the dimensions of the 3D printed structures, similar shrinkage values were measured for the different electrodes pyrolyzed at the same conditions, which demonstrates that the proportion of electrode dimensions are almost entirely preserved during the pyrolysis process [51]. Furthermore, the electrochemical behaviour of the electrodes with different surface area was evaluated through CV experiments and the results are summarized in Fig. 7(b) (see Supplementary Information, Fig. S6 for the CV curves). Improvement of the electrochemical behaviour with increasing the circular electrode diameter is correlated to an increase of the electrode surface area and strongly supports the scalability of the designed pyrolyzed 3D carbon electrodes. Moreover, considering the slope of variation of the oxidation and reduction peak currents against circular diameter, it could be deduced that the gradually pyrolyzed carbon electrodes have a higher sensitivity to the variations of the electrode surface area.

4. Conclusion

This study provides a simple and straightforward approach for fabrication of free-standing complex 3D pyrolytic carbon electrodes with different dimensions using the SLA printing technology followed by pyrolysis. Three steps of optimization, i.e. type of carbon precursor, 3D printing architecture and pyrolysis conditions, were carried out to obtain geometrically defined and reproducible free-standing 3D carbon electrodes. To precisely clarify the influence of degradation rate of the precursor on the physicochemical properties of the carbonized structures, two different pyrolysis conditions, i.e. fast and gradual carbonization processes, were designed and implemented. Although, based on the Raman and XPS characterizations, no significant differences in chemical composition were detected between the fast and gradually pyrolyzed 3D carbon electrodes, the CV and EIS experiments showed dominantly higher oxidation and reduction peak currents and lower charge transfer resistances for the fast pyrolyzed carbon electrodes. The superior electrochemical properties of the fast pyrolyzed carbon electrodes were explained by approximately two times higher surface area measured through BET experiments. Overall, our results showed that the specific surface area and porous microstructure are key factors influencing the electrochemical performance of pyrolytic carbon electrodes. Moreover, from the results, it could be stated that the impact and importance of the pyrolysis process on the electrochemical properties of the carbonized samples is higher than the one of the final pyrolysis temperature in the investigated temperature range. Altogether, due to their reliable, stable and reproducible electrochemical behaviour, specific macro- and micro-structural properties, and scalability, we believe that the proposed 3D pyrolytic carbon electrodes are really promising for a broad area of research and applications.

CRediT authorship contribution statement

Babak Rezaei: Conceptualization, Investigation, Methodology, Validation, Writing - original draft. Jesper Yue Pan: Investigation, Formal analysis. Carsten Gundlach: Formal analysis. Stephan Sylvester Keller: Supervision, Conceptualization, Investigation, Validation, Writing - review & editing, Resources, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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