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# Vacuum or flowing argon: What is the best synthesis atmosphere for nanodiamond-derived carbon onions for supercapacitor electrodes?



Carbon

Marco Zeiger<sup>a,b</sup>, Nicolas Jäckel<sup>a,b</sup>, Daniel Weingarth<sup>a</sup>, Volker Presser<sup>a,b,\*</sup>

<sup>a</sup> INM – Leibniz Institute for New Materials, Campus D2 2, 66123 Saarbrücken, Germany <sup>b</sup> Saarland University, Campus D2 2, 66123 Saarbrücken, Germany

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#### ABSTRACT

We present a comprehensive study on the influence of the synthesis atmosphere on the structure and properties of nanodiamond-derived carbon onions. Carbon onions were synthesized at 1300 and 1700 °C in high vacuum or argon flow, using rapid dynamic heating and cooling. High vacuum annealing yielded carbon onions with nearly perfect spherical shape. An increase in surface area was caused by a decrease in particle density when transitioning from sp<sup>3</sup> to sp<sup>2</sup> hybridization and negligible amounts of disordered carbon were produced. In contrast, carbon onions from annealing nanodiamonds in flowing argon are highly interconnected by few-layer graphene nanoribbons. The presence of the latter improves the electrical conductivity, which is reflected by an enhanced power handling ability of supercapacitor electrodes operated in an organic electrolyte (1 M tetraethylammonium tetrafluoroborate in acetonitrile). Carbon onions synthesized in argon flow at 1700 °C show a specific capacitance of 20 F/g at 20 A/g current density and 2.7 V cell voltage which is an improvement of more than 40% compared to vacuum annealing. The same effect was measured for a synthesis temperature of 1300 °C, with a 140% higher capacitance at 20 A/g for argon flow compared to vacuum annealing.

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#### 1. Introduction

Carbon has always been an element of central technological use, be it as primary energy source (coal), refractories (graphite), or abrasive medium (diamond). Especially the emergence of novel carbon nanoforms with intriguing properties has propelled carbon research over the last decades [1,2]. Carbon onions are a relatively new member of the vast carbon family, first discovered in 1980 by Iijima and described in 1992 by Ugarte [3,4]. They are spherical or polyhedral carbon nanoparticles and consist of several fullerene-like shells which are highly defective and disordered [5]. Typically, the size of carbon onions ranges between 2 and 50 nm, dependent on the synthesis method and parameters [6–8]. Several methods exist for their synthesis, like underwater arc discharge between graphite electrodes [9–11], electron beam irradiation of carbon containing materials [3,12], decomposition of carbon-containing precursors [13-16], mechanical milling [17], detonation reactions [18,19], or plasma spraying of nanodiamonds (ND) [20]. Thermal annealing of ND [7,21-26] has

E-mail address: volker.presser@leibniz-inm.de (V. Presser).

emerged as the most practical synthesis method, considering the very high yield of high purity carbon onions with a small size distribution between 5 and 10 nm and a large-scale material production with high reproducibility [2,7]. As precursor material, detonation NDs with a size of typically 5 nm are commonly used, which are engulfed by thin amorphous and disordered carbon layers [27–30]. The latter is also causing particle agglomeration forming entities of up to more than 100 nm [31]. Chemically, detonation ND consist out of 80–90 mass% of carbon, a few mass% of oxygen, hydrogen, nitrogen partially located in the core and coming from particle stabilizing functional groups, and possibly minor metal impurities [7,30,32].

Several experimental and theoretical studies have investigated the thermal transformation of ND to carbon onions. In a first stage, the decomposition of surface functionalities on NDs starts with the condensation of oxygen-containing surface functional groups, and their desorption together with water molecules [33,34] below temperatures of 200 °C. At higher temperatures, acidic groups like carboxyl, anhydride, and lactone groups decompose evolving CO and CO<sub>2</sub> gases [7,33]. Thus, functional groups decompose which initially had stabilized the ND surface. The thermal stability of ND surface functional groups has been investigated in several studies [7,34–37]. To minimize



<sup>\*</sup> Corresponding author at: INM – Leibniz Institute for New Materials, Campus D2 2, 66123 Saarbrücken, Germany.

the surface energy of newly formed dangling bonds, the surface reconstructs and this onsets a gradual transformation from ND to carbon onions. The reconstructive phase transformation from  $sp^3$ - to  $sp^2$ -hybridization has an onset between 700 and 1100 °C and we first see a phase transformation from diamond to disordered carbon from the outside of the particle to the inside [7,21,37,38]. At elevated temperatures, typically starting between 1100 and 1300 °C, the  $sp^2$ -carbon continuously graphitizes and builds highly graphitic carbon shells, resulting in a complete transformation from ND to carbon onion at temperatures between 1800 and 2000 °C [23,39]. More details on the mechanism of ND graphitization is described, for example, in Ref. [40].

The thermal transformation of ND to carbon onions has been investigated so far in vacuum [21–25,37,41], argon [7,42–47], nitrogen [48], and hydrogen [49]. The onset temperature for graphitization is typically in the range between 700 and 1100 °C, but varies as a function of used atmospheres, heating rates, and type of ND material. Different synthesis atmospheres may also differ in the amount of gases containing reactive oxygen from the atmosphere or desorbing from the precursor. The catalytic effect of oxygen decreases the onset of graphitization and increases the graphitization rate, which may lead to different carbon nanostructures [50–52].

In a recent publication, we have shown a gradual volume increase during the transformation from nanodiamond to carbon onions in argon due to the lower density of graphitic carbon compared to nanodiamond [7]. Therefore, the specific surface area (SSA) increases with temperature and reaches a maximum at  $\sim$ 1300 °C dependent on the heating rate, holding temperature, and the precursor type [7]. In other studies, the maximum SSA was observed at 1500 °C [53] or 1800 °C [6], depending on the kind of ND. After reaching a maximum SSA, the increase in surface area saturates or the SSA may even decrease, especially for slow heating rates and long holding times [7]. Desorbing surface functional groups containing oxygen may partially etch the carbon onions and vield a redistribution process leading to large graphitic or polyhedral structures with high conductivity but low surface area [7,54]. Yet, no such structures were found after vacuum annealing, as described in other studies [21-25,37,41]. A decrease in surface area is disadvantageous for many electrochemical applications; ideally, a high surface area should be combined with a high electrical conductivity to enable a high energy and high power performance for supercapacitors [45,53]. Yet, it remains a challenge to find an optimum synthesis condition to maximize conductivity (1700-2000 °C) and surface area (typically at lower temperatures) [6,7,53].

Our study compares the benefits and limitations of carbon onion synthesis using either vacuum (minimum carbon redistribution) or argon (attractive for large scale synthesis). For this, we used rapid heating to and cooling from the annealing temperature (1300 or 1700 °C) within 2 min. This way, the ND powder is heated up to accomplish near-complete transformation to carbon onions without giving raise to extensive particle sintering. Local carbon redistribution may still facilitate nanocarbon formation between the carbon onions and impact on electrical conductivity (positively) and surface area (negatively). All synthesized materials were characterized comprehensively by 4-point probe, chemical analysis, transmission electron microscopy, Raman spectroscopy, nitrogen and carbon dioxide gas sorption, and X-ray diffraction (XRD) to determine the differences in carbon structure and ordering. The electrochemical properties were analyzed in organic electrolyte and 2-electrode configuration using cyclic voltammetry and galvanostatic cycling with potential limitation.

#### 2. Experimental section

#### 2.1. Synthesis of carbon onions

ND powders were thermally annealed in graphite crucibles  $(30 \times 20 \text{ mm}^2)$  using a custom-built dynamic furnace system (Xerion Advanced Heating Ofentechnik, Germany). To avoid structural changes during prolonged heating and cooling, we heated to and cooled from 1300 to 1700 °C within 2 min to have a nearly isothermal process. The holding time for all samples was 1 h and the temperature was measured directly at the sample. For each holding temperature, the ND powder was annealed either in argon flow (flow rate: 1 L/min) or in a high vacuum of  $10^{-2}$  Pa (during the annealing the vacuum changed to ca. 1 Pa for several seconds due to desorption of functional groups). The samples were named in reflectance of the treatment conditions; for example 1300-VAC for 1300 °C annealing temperature and the use of vacuum.

#### 2.2. Chemical and structural characterization

#### 2.2.1. Electron microscopy and chemical analysis

Transmission electron microscopy (TEM) was carried out with a 2100F microscope (JEOL, Japan) operating at 200 kV. Samples were dispersed in ethanol and drop casted on a copper grid with a lacey carbon film (Gatan, USA). The chemical composition of ND powder and carbon onion samples was analyzed using energy-dispersive X-ray spectroscopy (EDX), CHNS elemental analysis, and inductively-coupled optical emission spectroscopy (ICP-OES). EDX analysis was performed using a JSM-7500F (JEOL, Japan) scanning electron microscope equipped with an EDX system (Oxford Instruments, UK). The samples were fixed on a conductive carbon tape and 5 spectra were recorded at 5 different positions with 10 kV acceleration voltage. CHNS elemental analysis was conducted with a Vario Micro Cube system (Elementar Analysensysteme GmbH, Germany) after combustion of the sample under oxygen at 1150 °C in a tin holder. The CHNS analyzer was calibrated with sulphanilic acid using different masses (41.6 mass% C, 4.1 mass% H, 8.1 mass% N, 18.5 mass% S). For ICP-OES analysis, an Ultima 2 system (Horiba Jobin-Yvon, France) was used with a Czerny–Turner type monochromator with a focal length of 1 m and high frequency power of 1 kW was supplied by a regulated generator at 40.68 MHz. Prior to the analysis of each element, a screening was performed to survey all included elements. Calibration was performed using aqueous standard solutions of 0, 1.0, and 2.0 mg/L yielding a calibration coefficient of 0.999. For every sample analysis, ca. 50 mg of material was diluted to a total volume of 25 mL.

#### 2.2.2. Raman spectroscopy

Raman spectra were recorded using a Renishaw inVia Raman microscope equipped with an Nd-YAG laser with an excitation wavelength of 532 nm, a grating with 2400 lines/mm, a  $50 \times$  objective (numeric aperture: 0.9), and a spectral resolution of  $\sim$ 1.2 cm<sup>-1</sup>. The spot size on the sample in the focal plane was approximately 2 µm using an output power of 0.2 mW. The acquisition time was 30 s and 10 accumulations were used to eliminate cosmic rays and to improve the signal-to-noise ratio. Peak analysis and peak fitting were performed assuming several Voigt profiles dependent on the phase composition. Voigt profiles were used to fit broad Raman signals of amorphous carbon as well as sharp Raman modes for graphitic carbon. The background was subtracted using a linear baseline function. Only carbon onions were subject to Raman spectroscopy since NDs require UV laser radiation for a comprehensive characterization of sp<sup>3</sup>-hybridized carbon nanodomains.

#### 2.2.3. X-ray diffraction and helium gas pycnometry

X-ray diffractogramms (XRD) were measured using Cu-Ka radiation with a Bruker AXS D8 Advance diffractometer (Bruker AXS, Germany). The step size was 0.02° and the measurement time was 1 s/step. Prior to the measurements, the system was calibrated with a LaB<sub>6</sub> single crystal. Pycnometric densities were measured with an AccuPyc 1330 gas pycnometer (Micromeritics, Germany) using helium gas (purity grade: 5.0). Adsorbed water was removed by drying the samples in an oven at 120 °C and 1 kPa for 1 h prior to the measurement. The sample holder had a maximum volume of 1 cm<sup>3</sup> and the pycnometer was programmed to perform 10 purges, followed by an analysis of 20 separate measurements. Both purge and analysis fill pressures were set at 134 Pa and an equilibration rate of 34 Pa/min was used. The theoretical SSA of spherical carbon onions (SSA<sub>OLC</sub>; OLC: onion-like carbon) derived from NDs with a surface area of SSA<sub>ND</sub> was calculated using the pycnometric density assuming a volume expansion and constant mass according to Ref. [7] (Eq. 1):

$$SSA_{\rm OLC} = SSA_{\rm ND} \cdot \left(\frac{\rho_{\rm ND}}{\rho_{\rm OLC}}\right)^{\frac{2}{3}} \tag{1}$$

#### 2.2.4. Gas sorption analysis

Gas sorption analysis was carried out using an Autosorb iQ system (Quantachrome, USA). First, powder samples were outgassed at 300 °C for 10 h under vacuum conditions (10<sup>2</sup> Pa). Nitrogen gas sorption was performed at -196 °C in the relative pressure range from  $5 \times 10^{-7}$  to 1.0 in 68 steps. The pore size distribution (PSD) between 0.56 and 37.5 nm was derived using the guenched-solid density functional theory (QSDFT) [55,56] supplied by Quantachrome assuming a slit-shape pore geometry. The latter has recently been shown to be the most appropriate model for carbon onions [45]. The SSA using the BET equation after Brunauer-Emmett-Teller [57] was calculated in the linear regime of the measured isotherms at a partial pressure range between 0.1 and 0.3 P/P<sub>0</sub>. Carbon dioxide gas sorption measurements were carried out at 0 °C in the relative pressure range from  $1 \times 10^{-4}$  to  $1 \times 10^{-2}$  in 40 steps. SSA and PSD values were calculated from CO<sub>2</sub> sorption data for pore sizes between 0.3 and 1 nm with the ASiQwin software using non-local density functional theory (NLDFT) [56,58].

# 2.2.5. Dynamic light scattering and electrical conductivity measurements

Volumetric particle size distributions were measured using dynamic light scattering method with a Nanotrac Ultra (Microtrac Europe GmbH, Germany). For all samples a 0.1 mass% water dispersion was used and 3 independent measurements were performed with an acquisition time of 30 s.

The electrode conductivity was measured with a custom built 4-point probe (tip diameter: 1.5 mm; tip distance 1.75 mm). The areal resistance was measured 10-times on different positions of the electrode material  $(3 \times 3 \text{ cm}^2)$  and Eq. (2) was used to calculate the electrode conductivity normalized to the thickness.

$$\sigma = \frac{\ln(2)}{\pi} \frac{I}{U \cdot d} \tag{2}$$

In this equation, I is the current, U the voltage, and d the thickness of the electrode measured with a micrometer screw.

#### 2.2.6. Electrochemical characterization

To prepare polymer-bound carbon electrodes, carbon onion powder was dispersed in ethanol, sonicated for 10 min, and then heated to 90 °C to remove some solvent. The viscous slurry was put into a mortar and 10 mass% of polytetrafluoroethylene (PTFE, 60 mass% solution in water from Sigma Aldrich, USA) were added. The dough-like carbon paste was rolled with a rolling machine (MTI HR01, MTI Corp., USA) to 200  $\mu$ m thick free standing electrodes and dried at 120 °C at 2 kPa for at least 24 h.

For all measurements, 1 M tetraethylammonium tetrafluoroborate (TEA-BF<sub>4</sub>) in acetonitrile (ACN) from BASF (Germany) was used in a 2-electrode setup. The electrode discs (12 mm in diameter) were separated by a glass-fiber separator with a diameter of 13 mm (type GF/D, GE Healthcare, USA). The electrode/separator/electrode arrangement was placed between two carbon-coated aluminum foils (diameter 12 mm, type Zflo 2653, Coveris Advanced Coatings, USA) and compressed with spring-loaded titanium pistons. The cells were dried at 120 °C and a vacuum of 2 kPa for 12 h before they were put in an argon-filled glove box (MBraun, Germany; Labmaster 130;  $O_2$ ,  $H_2O < 1$  ppm), where they were vacuum filled with a syringe containing 1 M TEA-BF<sub>4</sub> in ACN.

All electrochemical measurements were carried out using a VSP300 or VMP300 potentiostat/galvanostat from Bio-Logic (France) in cyclic voltammetry (CV) and galvanostatic mode (GCPL). Cyclic voltammograms at different scan rates from 1 mV/s to 2 V/s from 0 to 2.7 V were conducted. Each voltage was applied for 3-times and the capacitance at 2.7 V for every scan rate was calculated using Eq. (3).

$$C = \frac{\int_{t_0}^{t_{end}} I(t) dt}{U}$$
(3)

with the capacitance *C*, the time  $t(t_0: \text{start of discharge}, t_{\text{end}}: \text{end of discharge})$ , and the electrical potential *U*. The specific capacitance was determined with Eq. (4):

$$C_{\rm sp} = 4 \cdot \frac{C}{m} \tag{4}$$

with the active mass m of both electrodes and the device capacitance C. Using GCPL mode the current was varied to apply different current densities from 0.1 to 20 A/g with 10 s resting time between charging/discharging and a potential limitation of 2.7 V. The specific current relates in this case to the active mass of both electrodes and the resulting capacitance was calculated from the current and the time for discharge with respect to the IR drop of the cell (Eq. 3).

The electrochemical stability was measured using long-time voltage floating tests between 0 and 2.7 V with a constant current of 0.5 A/g and a holding time of 10 h. After three full galvanostatic cycles, the voltage was held for 10 h at 2.7 V and the procedure was repeated to an overall holding time of 100 h.

#### 3. Results and discussion

#### 3.1. Chemical and structural characterization

#### 3.1.1. Chemical composition

Chemical analysis was carried out using EDX, CHNS analysis, and ICP-OES (Table 1). The ND precursor is composed of 89.92 ± 0.91 mass% carbon, 2.34 ± 0.64 mass% nitrogen, and 1.43 ± 0.73 mass% hydrogen, according to CHNS analysis. Spectral analysis with EDX reveals the presence of small amounts of chlorine (0.8 mass%). Additional ICP-OES analysis shows minor amounts of Ag, Al, B, Ca, Fe, and Na (cumulatively less than 2 mass%). In comparison to EDX, CHNS and ICP-OES analyses are more adequate for quantitative chemical analysis; therefore, an oxygen content of 4.77 mass% was determined using the total mass of materials minus the detected elements of the CHNS and ICP-OES analysis. These values are in good agreement with the recent literature [31,32,59-63]. It is expected that the detected oxygen and hydrogen atoms mostly belong to surface functionalities like

Table 1

Chemical composition derived from the diffe	n of the ND and the OL erence of the total amo	C samples measured ount and the other c	using EDX and CHNS detected elements usir	elemental analysis. All ng CHNS analysis and I	values are given in mass ICP-OES.	%. Oxygen contents from	n CHNS analysis are
						-	

	Method	Al	В	Ca	Ag	Fe	Na
ND	ICP-OES	0.212	0.054	0.013	0.083	0.154	1.024
	Method	С	0		Ν	Н	Cl
ND	CHNS EDX	89.92 ± 0.91 90.20 ± 2.90	4.77 3.4 ± 1.9		2.34 ± 0.64 5.6 ± 3.5	1.43 ± 0.73 -	- 0.8 ± 0.3
1300-AR	CHNS EDX	96.62 ± 1.66 98.91 ± 0.22	3.38 1.09 ± 0.22		-	-	-
1300-VAC	CHNS EDX	$97.18 \pm 0.69$ $98.44 \pm 0.38$	2.82 1.56 ± 0.38		-	-	-
1700-AR	CHNS EDX	98.94 ± 0.28 98.76 ± 0.10	1.06 1.24 ± 0.10		-	-	-
1700-VAC	CHNS EDX	98.73 ± 0.53 99.26 ± 0.21	1.27 0.74 ± 0.21		-	-	-

carboxylic, ketonic, or hydroxylic groups [40]. Nitrogen found for ND commonly stems from surface functional groups like amide [35] or nitro groups [64,65], but can also be structurally bound in the diamond core [37]. Carbon onions synthesized at 1300 °C show around 3 mass% of oxygen when using argon flow (3.4 mass%) or vacuum annealing (2.8 mass%). For comparison, thermal annealing at 1700 °C yields only 1.1 mass% (1700-AR) and 1.3 mass% (1700-VAC) oxygen. It has been shown that oxygen containing surface functional groups desorb when heating to 1000 °C [7,33], but may partially re-adsorb during cooling or when re-exposed to ambient atmosphere. A higher degree of carbon ordering after annealing at 1700 °C may result in a lower number of dangling bonds on the surface, causing a decreased affinity for surface functional groups. This correlation can explain the higher oxygen content found for carbon onions synthesized at 1300 °C. Applying a high vacuum during the synthesis leads to the removal of desorbing functional groups. The lower content of molecules in the atmosphere inhibits the adsorption during cooling and induces lower oxygen contents for 1300-VAC than for 1300-AR.

#### 3.1.2. Carbon onion structure

Transmission electron microscopy demonstrates the structure and the morphology of carbon onions (Fig. 1). The samples show a characteristic particle size of 5–10 nm, spherical shape, several defective fullerene-like shells, and localized particle sintering to form agglomerates of several hundreds of nanometers. The only visible difference between samples synthesized at 1300 or 1700 °C is a more pronounced tendency to express a polyhedral shape at higher annealing temperatures (Fig. 1F), as has been reported in the literature [40]. Samples obtained in vacuum at 1300 °C show locally fused spherical carbon onions (Fig. 1C, D). When using argon at the same temperature, additional defective few-layer graphene nanoribbons (2-5 layers) can be found (Fig. 1A, B). The same is seen when comparing samples synthesized at 1700 °C and almost perfect carbon onions without a distinct amount of few-layer graphene nanoribbons or other carbon phases are obtained by vacuum synthesis. In contrast, 1700-AR is composed of carbon onions interconnected by a multitude of few-layer graphene nanoribbons (Fig. 1E). These layers are highly defective, partially curved, directly connected to carbon onions, and consist of 2-5 graphene layers (Fig. 1F). Compared to 1300 °C, the few-layer graphene nanoribbons seen after annealing ND at 1700 °C are more ordered and locally polygonised. The used term few-layer graphene nanoribbons is in accordance with the proposed nomenclature in Ref. [66].

Fig. 2A presents the Raman spectra of the four types of carbon onions in the range between 500 and  $3500 \text{ cm}^{-1}$  and the fitting results can be found in Table 2. The spectra exhibit the characteristic G-mode between 1580 and 1590 cm<sup>-1</sup> indicative of sp<sup>2</sup>-hybridized carbon. More precisely, this mode represents the bond stretching of sp<sup>2</sup>-hybridized carbon atoms in rings and chains coming from the zone center  $E_{2g}$  mode [67]. Between 1330 and 1342 cm<sup>-1</sup>, the so-called D-mode can be seen. This peak represents the breathing mode of the sixfold rings, but is only Raman active because of the presence of "defects" in the widest possible meaning. Defects can be vacancies, additional atoms, curvature, and edges. Therefore, the D-mode is a double resonant Raman process, due to the scattering of the electron with the phonon as well as a defect [68]. Perfect graphite single crystals would be void of the D-mode [67].

1300-VAC samples show a Raman spectrum characteristic for carbon onions synthesized at rather lower temperatures with very broad D- and G-mode [7]. In comparison to the material after vacuum annealing at 1300 °C, the Raman spectrum of 1300-AR is significantly different although the annealing temperature and time were the same (Fig. 2A, B). The spectrum presents a much sharper D-mode, the G-mode shows a small shoulder at 1610  $\text{cm}^{-1}$ , and the transition between D- and G-mode is less distinct than for 1300-VAC. The Raman spectrum of 1300-AR is not characteristic for just *one* specific carbon material rather for the combination of *different* carbons. As seen from Fig. 2B, the D-mode shows a broad shape at the base, but a very sharp peak near the maximum. The same can be seen for the G-mode, where a doublet structure is caused by the emergence of a pronounced shoulder at higher frequencies. These features can be explained when assuming the presence of disordered nanocrystalline carbon onion similar to 1300-VAC with a broad D- and G-mode and additionally a second carbon phase with a higher degree of structural ordering responsible for the sharp part of the D-mode and the doublet structure of the G-mode. This assumption aligns very well with the TEM images shown in Fig. 1.

The same trend is seen for carbon onions synthesized at 1700 °C (Fig. 2A, B). 1700-VAC material shows very sharp D- and G-modes. The higher degree of carbon ordering at elevated synthesis temperatures comes from the rearrangement of carbon atoms, especially concerning the distortion of carbon rings, bond length variation, and interstitial atoms. For 1700-AR, the Raman spectrum is quite similar to 1700-VAC, but with the additional emergence of a shoulder at 1610 cm<sup>-1</sup> (similar to 1300-AR). For both synthesis temperatures, 1300 and 1700 °C, the second order Raman spectrum presents more pronounced peaks for carbon onions synthesized in Argon, reflecting the higher degree of carbon ordering.



Fig. 1. Transmission electron micrographs of 1300-AR (A, B), 1300-VAC (C, D), 1700-AR (E, F), and 1700-VAC (G, H).

To exemplify the impact of two separate carbon phases on the resulting Raman spectrum when using argon annealing, 1300-VAC carbon onions were mixed with graphite flakes and the resulting spectrum is shown in Fig. 2C. The graphite flakes

show a Raman spectrum resembling few-layer graphene nanoribbons. When admixing graphite flakes to 1300-VAC, we see the superimposition of two carbon phases with different degrees of structural ordering. The resulting spectrum shows the same



Fig. 2. Raman spectra of the carbon onion samples (A and B), Raman spectra of the combination of carbon onions and graphite flakes (C), and X-ray diffractogramms (D) of carbon onion samples.

## Table 2Properties of the deconvoluted Raman peaks.

		Pos. D (cm <sup>-1</sup> )	Pos. G	Area D	Area G	<i>I</i> <sub>D</sub> / <i>I</i> <sub>G</sub> ()	FWHM D (cm <sup>-1</sup> )	FWHM G
1300-AR	Carbon onion Few-layer graphene	1343 1331	1610 1585	44 40	29 21	1.52 1.90	135 47	96 64
1300-VAC 1700-AR	Carbon onion Carbon onion Few-layer graphene	1341 1345 1332	1592 1593 1584	106 62 20	63 42 11	1.68 1.40 2.10	139 69 45	87 69 33
1700-VAC	Carbon onion	1340	1588	90	56	1.61	74	71

characteristics than 1300-AR with an "unexpectedly" sharp D-mode, a less distinct transition between D- and G-mode, and a doublet structure of the G-mode. The existence of two different carbon species resulting in one Raman spectrum with doublet structure had also been shown for nanographite ribbons on HOPG [69].

To further understand the presence of different carbon phases, we performed peak deconvolution of the Raman spectra (Fig. 3). As both synthesis temperatures do not induce a complete transformation from diamond to graphite, especially for 1300 °C, a remaining nanodiamond core is expected. Given the use of visible light laser radiation (532 nm), this contribution will not show up in the Raman spectra. It was shown that nanodiamond first transforms into amorphous carbon before graphitization from the outside to the inside starts. Additionally, particle-particle connections are established and an amorphous carbon phase at the interface between graphitic shells and diamond core exists [70]. Therefore, besides a non-Raman visible diamond core and the actual carbon onion material, we have to consider amorphous carbon when fitting the spectra. Bogdanov et al. used one peak to describe amorphous carbon at  $\sim$ 1530 cm<sup>-1</sup> [39]. Yet, to adequately represent the Raman signal of amorphous carbon with very broad peaks, we fitted three peaks: one for transpolyacetylene (TPA) at ~1130 cm<sup>-1</sup> and two for the broad D- and G-mode of amorphous carbon coming from interstitial atoms with sp<sup>3</sup> connections in the planes of sixfold rings, or the presence of five- or sevenfold rings. The TPA-peak may also come from carbon chains in a transpolyacetylene-like ordering at the zigzag edges of the defective carbon shells on the particles [39]. The D-mode of amorphous carbon is seen as a small low-frequency shoulder of the G-peak [71]. Once accommodating for the presence of amorphous carbon, there are two more carbon phases to consider: The actual carbon onions and, in case of argon-annealed samples, few-layer graphene nanoribbons between the particles. For the latter two phases, each one pair of corresponding D- and G-modes were used to deconvolute the spectra (Table 2).

Material after vacuum annealing at 1300 °C shows a Raman spectrum related to carbon onions with a D-mode at 1341 cm<sup>-1</sup> and a G-mode at 1592 cm<sup>-1</sup> with relatively broad peaks indicated by a FWHM of 139 and 87 cm<sup>-1</sup>, respectively (Fig. 3A). According to the model by Ferrari and Robertson [72], a broad G-mode is indicative of a high degree of distortion of the sp<sup>2</sup>-hybridized carbon rings as well as their bond length variation leading to an incompletely graphitized material. This is supported by the G-mode position at 1592 cm<sup>-1</sup>, which is larger than for ideal graphite at 1580 cm<sup>-1</sup>. For comparison: the G-mode position of



Fig. 3. Raman spectra of (A) 1300-AR and 1300-VAC and (B) 1700-AR and 1700-VAC. Peak fitting was applied using Voigt line shapes.

#### Table 3

Surface area and pore volume values derived from gas sorption isotherms using nitrogen gas sorption (QSDFT) as well as carbon dioxide gas sorption (NLDFT), and the calculated SSA using the model from [7] derived from the pycnometric density.

N <sub>2</sub> sorption	BET SSA (m <sup>2</sup> /g)	QSDFT SSA (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Skeletal density (g/cm <sup>3</sup> )	Calculated SSA (m²/g)
1300-AR 1300- VAC 1700-AR 1700-	356 314 430 364	323 291 404 340	1.109 1.109 1.230 1.304	$2.42 \pm 0.03 \\ 2.36 \pm 0.01 \\ 1.91 \pm 0.01 \\ 1.97 \pm 0.01$	300 ± 14 305 ± 16 351 ± 18 344 ± 17
VAC CO <sub>2</sub> sorptio	on			Ultrami (cm³/g)	cropore volume
1300-AR 1300-VAC 1700-AR 1700-VAC				0.052 0.038 0.068 0.051	

nanocrystalline graphite should be at ca. 1600  $\text{cm}^{-1}$  [72]. This is larger than what we see for 1300-VAC due to the combination of different types of defects, a confinement due to the nanoscopic size, and defected sixfold rings. Considering the nanocrystalline (nc) and defective character of carbon onions, the Raman spectrum can be best discussed in view of the three stage model for carbon transition by Ferrari and Robertson [72]. This model assumes that ideal graphite is first transformed to nanocrystalline graphite due to a decrease in mean grain size and then the nanocrystalline graphite transforms to sp<sup>2</sup>-hybridized amorphous carbon with bond length variation and distorted carbon six-rings [72]. This means that the G-mode position is effectively a combination of the first two stages in the amorphization trajectory from Ferrari and Robertson leading to smaller G-mode position than for nc graphite but still larger than in ideal graphite. For 1300-AR, the FWHMs of D- and G-mode are similar to those of 1300-VAC indicating the same kind of incompletely graphitized material. This is supported by a similar  $I_D/I_G$  ratio and the similarity of the carbon onion phase from argon and vacuum annealing demonstrates that the carbon onions themselves are not directly affected by the synthesis atmosphere (Table 2).

When annealing in argon, the Raman spectrum can only be adequately deconvoluted when assuming besides some amounts of amorphous carbon and carbon onions also few-layer graphene nanoribbons as a third carbon phase. As exemplified for 1300-AR, this additional nanocarbon phase is composed of defective few-laver graphene nanoribbons, presenting very sharp peaks with a FWHM of 47 and 64  $\text{cm}^{-1}$  for the D- and the G-mode (Table 2). Such sharp Raman modes indicate a much more graphitic character compared to the carbon onions. The G-mode is located at 1585 cm<sup>-1</sup>, which is slightly larger than for perfect graphite and a large  $I_{\rm D}/I_{\rm G}$  demonstrates the nanocrystalline nature [72]. The same phase analysis was used for the samples synthesized at 1700 °C (Fig. 3B). Compared to 1300 °C, the Raman signal for amorphous carbon found in the material after annealing at 1700 °C is smaller and the signal for carbon onions is larger. Yet, an adequate fit can only be obtained when assuming the presence of some amounts of amorphous carbon. It is indicated that the remaining amorphous carbon at 1300 °C is transformed to a more graphitic material. This is supported by the decrease in FWHM of the Dand G-mode for both synthesis atmospheres. For 1700-AR, also a second phase consisting of graphitic nanoribbons is present similar to 1300-AR.

X-ray diffractogramms of the samples, including the ND material, are shown in Fig. 2D. With increasing synthesis temperature, the signal intensity of the (002)-graphite reflection (26°  $2\theta$  for 1300-VAC) increases, whereas the (111)-diamond signal (43.8°  $2\theta$  for 1300-VAC) decreases and vanishes at 1700 °C completely with the emergence of the (100)-graphite signal [23]. Yet, all samples obtained after annealing at 1300 °C show still the presence of a small amount of the diamond phase. This aligns with the literature, where it was shown that a small diamond core may remain at 1300 °C, especially for NDs with a larger diameter of up to 10 nm [7,23]. The diffraction pattern of 1300-VAC and 1300-AR are virtually indistinguishable. Finally, thermal annealing at 1700 °C yields a nearly complete transformation from ND to carbon onion with a large (002)-graphite reflection and a vanishing (111)-diamond reflection. 1700-AR shows an asymmetric (002)-graphite reflection with a sharp maximum at  $25.7^{\circ} 2\theta$ .



Fig. 4. Particle- and agglomerate size distributions measured using DLS (A) and electrical conductivity of film electrodes (10 mass% PTFE) using 4-point probe (B).



Fig. 5. Pore size distributions derived from the gas sorption isotherms using carbon dioxide with NLDFT deconvolution (A) and nitrogen gas sorption with QSDFT deconvolution (B).

These characteristics align again well with the presence of two different carbon structures (i.e., carbon onions and graphitic nanoribbons).

XRD measurements are in good agreement with the skeletal densities measured by pycnometry (Table 3). Carbon onion samples synthesized using the same annealing temperature show an almost identical density:  $2.42 \pm 0.03$  and  $2.36 \pm 0.01$  g/cm<sup>3</sup> for 1300-AR and 1300-VAC, respectively, and  $1.91 \pm 0.01$  and  $1.98 \pm 0.01$  g/cm<sup>3</sup> for 1700-AR and 1700-VAC, respectively (Table 3). Using a reducing-sphere-model [21], this computes to a diamond mass fraction in the range of ~50% for 1300 °C and less than 10% for 1700 °C in agreement with the literature [73,74].

#### 3.1.3. Particle agglomeration and electrode conductivity

The pronounced tendency of ND powders to form agglomerates of several hundreds of nanometers is well known from earlier studies [7,30,31]. The ND powder used in our study showed as a dispersion in water a bimodal size distribution with a large peak at  $\sim$ 200 nm and a second much smaller maximum at 1.5 µm (Fig. 4A). After thermal annealing, we see an increase in the primary particle size due to a volume expansion from pycnometric measurements and TEM micrographs; this is accompanied by an increase in agglomerate size due to additional sintering and redistribution of carbon [7,21]. This effect is much more pronounced after annealing at 1700 °C than for 1300 °C, in agreement with Ref. [7].

Carbon onions synthesized in flowing argon show consistently larger agglomerate sizes compared to vacuum annealing for both studied synthesis temperatures (Fig. 4A). While this difference is expressed rather in a general shift of the monomodal particle size distribution for samples annealed at 1300 °C, we see a multimodal particle size distribution for 1700-AR. This strong agglomeration behavior is not the result of additional surface functional groups because no significant change in chemical composition was detected (Table 1). In agreement with Raman spectroscopy, XRD, and TEM, 1300-AR and 1700-AR built larger few-layer graphene nanoribbons which interconnect the carbon onions to form larger agglomerates.

The nanoscopic formation of graphitic ribbons and particle–par ticle-sintering also impacts on the electrical conductivity. Film electrodes with  $\sim$ 200 µm thickness (10 mass% of PTFE) were used to more accurately reflect the effectively usable conductivity and measurement inconsistencies when investigating non-compacted powders. As shown in Fig. 4B, the presence of graphitic ribbons between carbon onions lead to a higher electrode conductivity when comparing 1300-AR and 1700-AR with 1300-VAC and 1700-VAC. As a result, the electrical conductivity of 1300-AR (0.43 S/cm) is as high as 1700-AR (0.42 S/cm) although the annealing temperature has been much lower. When comparing only carbon onions annealed either in flowing argon or vacuum, we see an increase in electrical conductivity with higher synthesis temperature, in agreement with the literature [6,53].

#### 3.1.4. Porosity analysis

The pore size distribution pattern derived from  $CO_2$  and  $N_2$  gas sorption are shown in Fig. 5A and B, respectively. Correspondingly, the calculated pore characteristics are provided in Table 3. Using  $CO_2$  sorption for micropores smaller than ca. 1 nm, no significant difference between carbon onions synthesized in different atmospheres can be seen. The distribution patterns are characterized by pores between 0.4 and 0.9 nm and belong to interparticle pores because carbon onions must be considered as intrinsically non-porous carbon nanoparticles [7]. At higher synthesis temperature, the total pore volume increases and higher distribution peaks



**Fig. 6.** Cyclic voltammograms (A), capacitance dependent on the scan rate and capacitance retention for different scan rates (B), galvanostatic cycling using different current densities (C), and long-time voltage floating test with the charge efficiency (charge/discharge capacitance) at a rate of 0.5 A/g (D). All measurements were performed in 1 M TEA-BF<sub>4</sub> in ACN using a 2-electrode configuration and a cell voltage of 2.7 V. The color-coding for all panels is the same (as provided in panel A). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

can be seen for carbon dioxide and nitrogen sorption data. This pore volume increase stems from the volume expansion of the particles and the decrease in density. In ND powder, the individual particles stick strongly together. During annealing the particles expand and free volume is generated between the particles.

The PSDs derived from nitrogen gas sorption can be differentiated into pores related to particles in direct contact (for pores <1 nm), particles separated by spacer particles (at 1 nm pore size and between 2 and 20 nm), and pores between particle agglomerates [7,75]. We see an enhanced porosity for carbon onions annealed in flowing argon particularly in the range between 0.6 and 1.5 nm and a shift of the PSDs to smaller pore sizes (Fig. 5B). The increased pore volume for 1300-AR and 1700-AR can be explained by a smaller particle size and few-layer graphene nanoribbons between the particles. Additionally, there is necking of carbon onion particles and we also have to consider partially amorphous carbon between the particles. By etching the outer shells and the removal of amorphous carbon, the particle-particle connections are primarily removed and additional pore volume is created. This is supported by the redistribution of carbon to few-layer graphene nanoribbons between the particles leading to additional surface area. The smaller size of the particles alone cannot explain the shift to smaller pores because local particle sintering prevents the dynamic response of the carbon onions by a particle rearrangement when the size is reduced. Therefore, the removal of particle-particle connections is the main reason for the increase in pore volume. In addition, the formation of few-layer graphene nanoribbons between the particles effectively decreases the pore size between the particles.

It can be seen from the data in Table 3 that the surface area for carbon onions synthesized in argon is always larger, with a BET SSA of 356 and  $430 \text{ m}^2/\text{g}$  for 1300-AR and 1700-AR, respectively,

compared to 314 and 364 m<sup>2</sup>/g for 1300-VAC and 1700-VAC, respectively. Using the geometric pore model from Ref. [7], it is possible to calculate the SSA based on the measured particle density and assuming a spherical shape. As seen from Table 3, the calculated values agree very well with the measured SSA data for vacuum annealed samples. The values for carbon onions obtained from annealing in argon are always slightly larger indicating the existence of additional surface area not coming from the particles themselves. This additional surface area is related to the redistribution of carbon atoms and the formation of few-layer graphene nanoribbons between the particles, in agreement with XRD, Raman spectroscopy, and TEM measurements.

#### 3.2. Electrochemical performance

Electrochemical characterization in organic electrolyte was performed on PTFE-bound carbon onion electrodes using cyclic voltammetry and galvanostatic cycling. Cyclic voltammograms were measured from 0 to 2.7 V which is the maximum electrochemical voltage window for acetonitrile based electrolytes (Fig. 5A) [76]. The cyclic voltammograms were normalized to the capacitance at 2.7 V. The CVs present a fast response with rectangular shapes indicative of near-ideal capacitive behavior. Carbon onions synthesized at 1300 °C show a rapid increase in current at 2.5 V. indicating the onset of electrolyte degradation due to high oxygen contents. In contrast, the more graphitic and less oxygen rich carbon onions after annealing at 1700 °C show no electrolyte degradation. This is in line with a recent study that showed improved electrochemical stability and enhanced Coulombic efficiency of carbide-derived carbons after post-synthesis treatment via high temperature vacuum annealing [77]. Electrolyte degradation will be further discussed using long-time voltage floating test in Fig. 5D. Carbon onions obtained by annealing at  $1700 \,^{\circ}$ C also show a very distinct capacitance increase in the CV with increased cell voltage. The resulting CV shape is commonly referred to as butterfly-shape and is characteristic of a material with a high degree of carbon ordering [45].

To investigate in more detail the power handling, we plotted in Fig. 5B the capacitance versus the applied scan rate (derived from cyclic voltammograms) and in Fig. 5C versus the current density in a potential window from 0 to 2.7 V (derived from galvanostatic cycling). The measured capacitance from GCPL testing at 1 A/g varies between 24 and 20 F/g for 1700-AR and 1700-VAC, respectively, and 22 and 21 F/g for 1300-AR and 1300-VAC, respectively. Such values are typical for carbon onion supercapacitors with a surface area between 300 and  $450 \text{ m}^2/\text{g}$ [45,53]. The capacitance values differ only slightly from sample to sample because of the minor differences in SSA: still. 1700-AR shows the highest capacitance value as it has the largest SSA. Fig. 5B, C demonstrates the rate handling behavior using cycling voltammetry and galvanostatic cycling and show the same trend. 1700-AR demonstrates a superior rate handling capability with still more than 50% of the initial capacitance at 10 V/s scan rate and more than 90% at 10 A/g current density. Using the same synthesis temperature but applying vacuum (1700-VAC), the rate handling is severely lowered with only 36% of the initial capacitance at 10 V/s and 84% at 10 A/g. Carbon onions synthesized at 1300 °C demonstrate a lower rate handling due to the lower degree of carbon ordering and the lower conductivity, in agreement with literature [6,45,53].

Due to the electrolyte decomposition above 2.5 V (Fig. 5A), we see an enhanced degradation for samples synthesized at 1300 °C during long-time voltage floating at 2.7 V (Fig. 5D) with 85% and 90% initial capacitance for 1300-AR and 1300-VAC. It can be expected that higher contents of oxygen might lead to electrolyte degradation for the low temperature carbon onions (see Table 1). This is supported by the charge efficiency (relative change of charge/discharge) shown in Fig. 6A. For the carbon onions obtained at 1700 °C. no significant change in charge efficiency is observed demonstrating the high electrochemical stability. In comparison, the low temperature carbon onions present a lower charge efficiency of ~92% until 50 h floating time. This indicates a chemical reaction of the functional groups with the electrolyte leading to the mentioned degradation. After 50 h floating time, (practically) all functional groups have reacted and the charge efficiency approaches 100%. The degradation of the electrolyte leads to the blocking of pores and accordingly to the decrease in capacitance (Fig. 5D).

#### 4. Conclusions

This study presents the influence of the synthesis atmosphere on nanodiamond-derived carbon onions. We used high vacuum and flowing argon atmosphere with ultrafast heating/cooling and two synthesis temperatures, 1300 and 1700 °C. It was shown that high-dynamic synthesis in vacuum leads to nearly perfect carbon onions with spherical shape and low amounts of interparticle carbon. In comparison, when only using flowing argon as synthesis atmosphere, oxygen containing desorbing gases were not removed and start partially etching the carbon, leading in the formation of few-layer graphene nanoribbons between the particles. This composition leads to higher surface area, higher conductivity, and better rate handling behavior as a supercapacitor electrode material in organic electrolyte for both synthesis atmospheres. Higher synthesis temperatures also yielded carbons lower in carbon heteroatom concentration and a higher electrochemical stability.

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