Characterization of carbon fibers using X-ray phase nanotomography

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ABSTRACT
X-ray ptychographic tomography has been recently developed for quantitative imaging of specimens on the nanometer scale. Here we present its application for the characterization of carbon fibers by mapping in three dimensions the mass density of entire fibers with diameters of several tens of micrometers with a resolution of about 100 nm. We characterized two fibers produced from two different precursors, revealing the spatial distribution of porosity and highly graphitized regions within the fibers. We further discuss the potential of ptychographic tomography as a new complementary technique for the characterization of carbon materials.

1. Introduction
Carbon fibers (CFs) are key components of a wide range of reinforced composite materials with multiple applications [1–4] due to their unique combination of properties such as low weight, high elastic modulus, and high tensile strength. They are typically produced from a polymer precursor, which is subject to several heat treatments at different temperatures and different environments while applying tension. The resulting fibers develop graphite sheets aligned to the fiber axis giving the fiber its strength. The mechanical properties of the final product are closely related to the degree of graphitization, porosity, density, and their distribution within the fiber [5,6].

Mapping the three-dimensional (3D) density on the nanoscale within an entire section of a CF would offer an overview of its porosity and graphitization, providing a complementary characterization tool to high-resolution but very localized imaging methods such as scanning [7,8] and transmission electron microscopy [9,10]. It can also complement small- and wide-angle X-ray scattering, where nanoscale and atomic structure is averaged over the entire illumination volume, which can cover several fibers [11,12] or be smaller than a single fiber [13,14]. X-ray absorption tomography can provide a 3D image of the structure inside carbon (C) materials with resolutions typically in the micron range [15]. Although X-ray absorption contrast does not yield a direct measurement of the mass density, careful calibrations can allow its determination with high accuracy [16]. In the last years, a few emergent X-ray microscopy techniques have been applied in materials science [17,18] but, to the best of our knowledge, individual CFs have not been investigated.

Ptychographic X-ray computed tomography (PXCT) is a recently developed technique to obtain 3D images of specimens of several tens of microns in size with a resolution currently in the 50–100 nm range [19,20]. As a coherent diffraction imaging technique [21], ptychography [22] does not need a lens, which usually limits the resolution in X-ray microscopes. A finite, coherent X-ray illumination is used to scan the sample field of view in such a way that the illumination overlaps at adjacent positions, and coherent diffraction...
patterns are recorded in the far field at each scanning position. Using phase retrieval algorithms [23,24], the two-dimensional complex-valued transmissivity function of the specimen is reconstructed with a resolution theoretically limited by the largest scattering angle which can be recorded. Although in practice limited by noise in the data acquisition and positioning accuracy, the achieved resolutions are still typically at least an order of magnitude better than the size of the illuminating beam. The phase contrast sensitivity of ptychography makes it especially useful in the hard X-ray regime [25,26], where absorption contrast is weak, allowing the imaging of thicker specimens than those typically investigated with soft X-ray microscopy. By combining the phase of ptychographic reconstructions at different incident angles of the beam onto the sample, a quantitative 3D map of the electron density inside the sample can be obtained [27].

Here we use PXCT to obtain 3D density maps of whole sections of individual CFs with a resolution of up to 100 nm. We have characterized two different CFs: a commercial fiber made from a polyacrylonitrile (PAN) precursor and a fiber under development made from a lignin-based precursor. In the PAN fiber we observed a core shell density structure, probably indicating a partial carbonization of the fiber, while the lignin fiber exhibits a complicated pore structure in a low-density matrix with a few high-density inclusions attributed to a high degree of graphitization. We further discuss the implications that such a unique insight into whole individual fibers may have in the investigation of CFs and C materials.

2. Samples investigated

The PAN-based fiber was a commercial high-strength, standard-modulus CF with 10 μm diameter. The second sample was a 24 μm diameter fiber made from a lignin-based precursor. PAN precursors are usually preferred for industrial applications because they provide fibers with optimal mechanical properties. However, the production of PAN fibers is expensive, and there is a need for the development of new precursors for CFs with improved performance and reduced cost [5]. Lignin is a polymer found in natural materials such as wood and is a good candidate as a replacement of PAN for fiber production due to its higher C yield. The lignin-based fiber which was the object of our study was produced after a first carbonization process at a temperature of 1100 °C in a nitrogen gas atmosphere followed by a graphitization process at 2200 °C in an argon atmosphere. Transmission electron microscopy (TEM) inspections of the specimen revealed a high degree of graphitization localized in some regions of the sample and graphitization was also confirmed by wide-angle X-ray scattering (WAXS) measurements, which revealed diffraction peaks corresponding to graphite lattice inter-plane distances with no preferred orientation. TEM and WAXS data are not shown here.

3. Data acquisition and tomographic reconstruction

Ptychographic tomography experiments were performed at the cSAXS beamline at the Swiss Light Source in Villigen, Switzerland, using 6.2 keV X-ray radiation. We used a 3 μm diameter pinhole in order to define a finite, coherent illumination, as shown in Fig. 1. The sample was placed 3.1 mm downstream, mounted on a 3D piezo stage, which allowed positioning of the sample with nanometer precision. A rotation stage below the sample served to change the beam incidence angle over a range of 180°. Diffraction patterns were recorded with a Pilatus 2M detector [28] with 172 μm pixel size placed at a distance of 7.24 m from the sample.

In Fig. 2(a) we show a coherent diffraction pattern of the pinhole alone, without sample, acquired with the detector over a time of 0.1 s. The field of view corresponds to 192 × 192 pixels, spanning an angular range of about 0.2°, which corresponds to a spatial resolution of about 43 nm. We observe interference fringes arising from the shape of the pinhole aperture, which would be similar to those in the Fraunhofer pattern of a circular aperture if the pinhole was perfectly round. When we place the PAN fiber downstream the pinhole, the pattern does not visibly change, as shown in Fig. 2(b), which is an indication of a homogeneous structure within this sample. On the other hand, when mounting the lignin-based fiber instead, the diffraction pattern changes significantly (Fig. 2(c)). Due to the coherence of the illumination, the recorded speckle pattern encodes all necessary information in order to retrieve the exact position of all scatterers in the sample, which are the local changes in density projected along the beam direction. It is this information which is exploited in phase retrieval algorithms in order to retrieve the projection image of the specimen.

For the PAN fiber, a field of view of 22 × 22 μm² was covered by a scan consisting of a grid of concentric circles with 1.4 μm radial step, with a total of 180 points. At each scanning position, a diffraction pattern was acquired with an exposure time of 0.2 s. We repeated this scan for 180 different projections spanning an angular range of 180° in intervals of 1°. The total time employed for the measurement, including overhead due to sample positioning and detector readout, was 3 h and 40 min. A similar procedure was employed to measure the lignin fiber using a field of view of 40 × 25 μm² (horizontal × vertical), requiring 407 scanning points per projection with a 0.2 s exposure at each position. In this case, 360 projections were recorded with a step of 0.5° over a range of 180°, corresponding to a total measurement time of 20 h. Because the 3D resolution to be expected due to positioning accuracy and mechanical stability of the current instrument is 100 nm, the number of projections was chosen for each specimen in
such a way that the angular sampling, which depends on the sample diameter, was adequate for this resolution.

Ptychographic reconstructions were performed for each angular position using a difference map algorithm [26]. Post-processing of reconstructed phase projections included the removal of a constant and linear offset, which are inherent degrees of freedom in ptychographic phase retrieval reconstructions, and then projections were aligned [29]. Finally, tomographic reconstructions were performed using a modified filtered back projection algorithm as described in [29]. Using the air surrounding the sample as a reference, phase tomography yields directly the 3D electron density distribution within the specimen with no need of calibration [27]. The relation between electron density $n_e$ and mass density $\rho$ can be expressed as follows:

$$\rho = \frac{n_e A}{N_a Z},$$

where $A$ is the molar mass, $Z$ is the total number of electrons in a molecule, and $N_a$ is Avogadro’s number. The fact that $n_e$ depends on the atomic species prevents us, in general, from obtaining a map of the mass density directly from our measurement. However, in practice the ratio $A/Z \approx 2g$ for light atomic species except for hydrogen (H), and we can obtain accurate mass density maps especially for specimens consisting of a few well known atomic species, as is the case of CFs. In the following we will show results of the mass density maps measured for our samples assuming that they consist only of C, and we will discuss below the errors expected due to different components.

4. Results

We show in Fig. 3(a) and (b) two sections of the tomogram of the PAN fiber perpendicular and parallel to the rotation axis, respectively, where the gray scale indicates the mass density distribution within the fiber. We can clearly distinguish a high-density cylindrical core partially surrounded by a shell of lower density with a sharp density change at their interface. In the Supplementary material we provide a movie through all sections of the PAN fiber parallel to the rotation axis.

The tomogram of the lignin fiber shown in Fig. 3(c) and (d) shows a more complex internal structure. A section perpendicular to the rotation axis (Fig. 3(c)) reveals a complicated porous structure with pore sizes ranging from hundred to several hundred nanometers in diameter. Additionally, some sub-micron sized regions in the sample exhibit a relatively high density around $2 \text{ g/cm}^3$, while most of the sample has a lower density. A section parallel to the rotation axis (Fig. 3(d)) shows large pores elongated along the axis, as well as smaller, more isotropic pores. The high-density particles seem to accumulate inside the elongated pores, occupying only a small fraction of the pore volume. In the Supplementary material we provide a movie through all sections of the lignin fiber parallel to the rotation axis.

In Fig. 4 we show in blue the histogram corresponding to the full tomogram of the PAN fiber on a logarithmic scale. The peak at zero density corresponds to the air region surrounding the fiber, which is measured as a reference for the quantitative density values. We further find two clear peaks corresponding to the low- and high-density parts of the core–shell structure, respectively. By fitting Gaussian curves to these peaks, we obtain values for the average density, given by the position of the curve, and the spread of the density values, given by its width. For the high-density peak this results in a density of $(1.76 \pm 0.04) \text{ g/cm}^3$. The spread of 0.04 g/cm$^3$ is identical to that found for the air peak in the histogram, indicating a homogeneous density throughout the high-density region. The low-density peak of the histogram indicates a value of $(1.29 \pm 0.05) \text{ g/cm}^3$.

The histogram of the lignin fiber is shown in Fig. 4 with a red line. At zero density we observe a peak arising from the air around the sample, as for the other tomogram. The second pronounced peak in the histogram is centered at $\rho = 1.26 \text{ g/cm}^3$ and has a long tail towards the lower densities due to partial volume effects caused by the many pores in the sample. The higher-density particles contribute to a shoulder of the histogram at the higher density values, which is not visible in the histogram of the PAN fiber. The analysis of a similar histogram from the inner part of the lignin fiber shows that at the current imaging resolution the low density matrix occupies about 96% of the volume, while spatially resolved pores and high density particles occupy only 3% and 1%, respectively.
The spread values given by the width of the peaks in the full histogram are a measurement of the density spread within the entire sample. However, our measurement can be more sensitive to mass density variations within the sample. For example, within the dense core of the PAN fiber we identify a higher density region approximately shaped as a hollow cylinder of about $2.5 \times 10^{-4}$ m outer diameter and $600 \text{ nm}$ inner diameter. This is illustrated in Fig. 5, where we show in (a) and (b) details of cross-sections perpendicular and parallel, respectively, to the rotation axis, corresponding to the lower part of the PAN fiber shown in Fig. 3(b). In Fig. 5(a) and (b) we use a gray scale with increased contrast to show the density values within the core region of the fiber, and thereby the low-density part corresponding to the shell is not visible. We selected two cubic volumes of about $(430 \text{ nm})^3$ within the fiber core, one within the high-density hollow cylinder and the other one outside, as indicated by the colored squares in Fig. 5(a). Their corresponding density histograms are plotted on a linear scale in Fig. 5(c) with peaks at $(1.77 \pm 0.03) \text{ g/cm}^3$ and $(1.74 \pm 0.03) \text{ g/cm}^3$, respectively, clearly distinct from one another and with spreads slightly smaller than that of $0.04 \text{ g/cm}^3$ obtained from the width of the high-density peak of the full histogram shown in Fig. 4. Note that the spread on smaller regions of the sample is smaller than that obtained from the air peak of the full histogram. We have observed in simulations that sub-pixel errors in the alignment of the projections causes noise especially in regions outside the sample. We therefore attribute the larger spread of the air peak in the full histogram to a non-perfect alignment of the projections due to distortions caused by positioning errors during scans.

Ptychographic tomography also enables addressing the density of individual high-density particles within the lignin fiber. As an example, the particle marked with a yellow box in Fig. 3(c) and (d) has a density of $1.91 \text{ g/cm}^3$. Since the spread in the latter case is $<0.15 \text{ g/cm}^3$, i.e., well beyond the noise level, we conclude that the measurement resolves density inhomogeneities within this particle.

5. Discussion

The mass density of PAN-based fibers has been measured in [30] as a function of the density of the original stabilized fibers, finding values for the final carbonized fibers ranging from approximately 1.7 to 1.9 $\text{g/cm}^3$. Our average density measurement in the high-density core of the PAN fiber lies between these two values, suggesting that it corresponds to the expected carbonized state of the fiber. The low density part of the fiber could be a region where carbonization has remained incomplete. The content variation of nitrogen (N) along the cross section of a fiber has been studied in [31].
finding a core–shell structure with an abrupt interface in which the core has 2% N content, as opposed to 7% content in the shell, with inner and outer diameters similar to those found in the PAN fiber described here. This is consistent with a higher degree of carbonization in the core of the fiber. As performed, our measurements are not element sensitive, and complementary measurements would be needed to confirm this relation.

At the molecular level, the carbonization process of lignin-based precursors is intrinsically different than that of PAN precursors [32], which causes lignin fibers to have a completely different internal structure compared to PAN fibers, characterized by a lack of orientation of the graphite and a notoriously heterogeneous structure. Indeed, the density map shown in Fig. 3(c) and (d) confirms a similar scenario on a larger scale which involves the whole fiber section. Pores are elongated along the fiber axis, and the higher-density particles could be highly graphitized regions in a similar way as described in TEM studies on an atomic resolution scale [33].

The absolute scale for the mass density shown in the tomograms in Fig. 3 has been obtained from the measured electron density distribution according to Eq. 1, assuming that the entire specimen is composed solely of C. It is known that, even after carbonization processes with temperatures above 1000 °C, PAN based fibers may have up to around 6% content of N and 6% content of H [34]. In some cases, up to 7% N content has been detected in the core part of the fibers [31]. In the case of the lignin-based sample, we measured a 93% content of C, 5% of H and 2% of oxygen by elemental analysis after carbonization. Taking this into account, we have calculated an error of 0.5% in the accuracy of our absolute mass density measurement for both fibers.

The 3D resolution of the tomograms has been estimated by Fourier shell correlation, which is a standard method in electron microscopy, using a threshold based on the half-bit criterion [35,36]. We found resolutions of 150 nm and 100 nm for the PAN and the lignin fibers, respectively. The reason for this difference lies in the very different structure found in each sample. As shown in Fig. 2, the porous nature of the lignin fiber provides a rich speckled scattering signal extending to high scattering angles, enabling ptychographic reconstructions with high spatial resolution in comparison with the PAN fiber.

6. Conclusions and outlook

We present X-ray tomograms of entire sections of CFs with resolutions of 100 and 150 nm yielding absolute mass density distributions within the fibers. As examples we employ a commercial high tensile strength PAN fiber and a fiber from a lignin precursor under development. Quantitative density maps show the porosity and degree of graphitization within the investigated samples, finding a core–shell structure of remarkably different densities in the PAN fiber, and a complex porous structure with very high density areas attributed to graphitized regions in the lignin-based fiber. Although two single measurements are not representative to conclude about the structure of PAN- and lignin-based fibers in general, with these examples we demonstrate the potential of X-ray phase nanotomography as a valuable characterization tool to investigate the mechanical properties of CFs.

Hard X-ray phase nanotomography has proven to provide unique insight within entire sections of fibers non-destructively at length scales bridging those achieved by electron microscopy and previously applied X-ray absorption

Fig. 5 – Inset of the PAN fiber cross section shown in Fig. 3(b) with a color scale enhancing density variations within the core of the fiber. We show cross sections perpendicular (a) and parallel (b) to the rotation axis. Scale bars are 2 μm. (c) Histograms within the regions indicated by colored rectangles shown in (a). (A colour version of this figure can be viewed online.)
tomography. We expect that the capability of providing absolute local density maps will prove helpful for the investigation of carbonization processes for the development of novel CFs and for elucidating graphitic structures at the atomic level.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2013.09.066.

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