A methodology to optimize the quantification of sp²
carbon fraction from K edge EELS spectra

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ABSTRACT

A methodology is presented to select a consistent method, using electron energy loss spectroscopy (EELS), to extract the fraction of sp²-bonded carbon atoms in carbonaceous materials. According to this methodology, a reliable method has to conjointly fulfill two criteria. The first one consists in verifying, on a perfect graphite sample, that the experimental evolution of $R = I_{\pi^*}/(I_{\pi^*} + I_{\sigma^*})$-ratios is in good agreement with the one theoretically predicted as a function of experimental settings. The second criterion consists in measuring sp² fractions in amorphous carbon samples with a minimum of fluctuation. We test three commonly used R-extraction techniques, and we show that they exhibit some failures. We thus implement a more accurate R-extraction process that accounts for the predicted graphite R-evolution and exhibits a low intrinsic 4%-noise, as determined from the sp² fraction fluctuation. Moreover, we check the transferability of our method on a wide range of EELS spectra, acquired with different experimental resolutions on samples exhibiting various sp² contents.

1. Introduction

In present thermonuclear fusion devices, plasma-facing components are mainly constituted of carbon–carbon composites (usually named CFC for carbon fibre *reinforced* composite). The main issue is that interactions between hydrogen isotopes from the plasma and these carbon-based materials lead to a considerable fuel retention in the vessel. Two key mechanisms are mentioned to explain this significant retention: (i) hydrogen isotopes implantation in CFC with conjointly diffusion in the bulk [1]; (ii) erosion of carbon atoms by plasma–surface interactions processes leading to release of hydrocarbon species that deposit either in vicinity to their initial zone or in plasma-shaded regions (remote areas) [2]. Films deposited in remote areas can have very high hydrogen content. In order to continue using CFC in vessel, we need to better characterize these trapping mechanisms by an accurate post-mortem analysis of the deposited carbon layers in fusion devices [3,4], coupled with a comparison to samples produced by low-temperature laboratory plasmas. Indeed, properties and reactivity of these layers, similar to diamond-like synthesised carbon films [3,5–7], depend strongly

on three parameters [5]. The first one is the hydrogen content. The second is the clustering of the sp² phase. The third parameter, considered as the key one, is the fraction of sp²-bonded carbon atoms. Among all of methods employed to measure the sp² fraction, we focus in this work on the electron energy loss spectroscopy (EELS) technique [8]. EELS, performed in a transmission electron microscope (TEM), is currently the preferred method to quantitatively extract the sp² fraction of carbon-based materials at a high spatial resolution. The high-energy incident electrons can produce transitions from 1s core level electrons to unoccupied solid states, and the energy loss near-edge structure (ELNES) resulting modulations reflect features in these unoccupied electronic states, namely π^* and σ^* for carbon atoms. The carbon–K edge spectrum can thus be interpreted as a superposition of integrated intensities over a ΔE energy window, which are related to transitions from the 1s core level to states projected distinctly on p_z or (p_x, p_y) symmetry orbitals. These two intensities are, respectively named $I_{\pi^*(\Delta E)}$ and $I_{\sigma^*(\Delta E)}$, and their relative weight is described by the normalized $R = I_{\pi^*(\Delta E)}/(I_{\pi^*(\Delta E)} + I_{\sigma^*(\Delta E)})$ ratio. As $I_{\pi^*(\Delta E)}$ is exclusively provided by carbon atoms in sp² hybridization, the comparison of the normalized R-ratio of the unknown carbon material with that of a suitable 100% sp² standard gives a quantity directly proportional to the sp² fraction [9,10].

Precise sp² fraction quantification is therefore dependent on a reliable determination of the R-ratio from experimental ELNES

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spectra. To extract the R-ratio, *i.e.* in particular the π^* contribution, different methods exist in the literature which suggest for instance the use of windows [9,11], a given number of Gaussian or Lorentzian fitted functions [12,13], or functions issued from *ab initio* calculations [14]. Each method can be performed with many different sets of parameters, and the choice of these parameters is undoubtedly a critical point since extracted sp^2 fractions can dramatically vary as a function of this choice [11,14]. To our knowledge, the previous studies dealing with this issue were mainly dedicated to determine the best ranges of fit parameters leading to the smallest sp^2 fraction fluctuations. However, two main drawbacks can be noted concerning this criterion: on the one hand, the small sp^2 fraction fluctuation is not necessarily related to the parameter ranges most in agreement with physical considerations, and on the other hand, the smallest fluctuation does not guarantee that the experimentally extracted sp^2 fraction corresponds to the true one of the sample, which is all the same unknown. Therefore, it can be reasonably thought that the only criterion derived from the sp^2 fraction fluctuation is not sufficient to test the reliability of R-extraction methods. In order to account for the problems mentioned above, and more particularly the second one, we suggest testing the methods on graphite, since its electronic structure is perfectly known. However, it is worth recalling that the expected absolute value of the graphite R-ratio, which depends on experimental settings, can only be reached by simulations, and it is *a priori* affected by some uncertainties. Therefore, a test only involving a direct comparison between extracted and calculated R-ratios is expected to be unsuitable. Nevertheless, to still use graphite as a model material to check extraction methods, we suggest an alternative methodology. Indeed, the evolution of graphite R-ratios is predicted, for any experimental setting, by the knowledge of one unique R-value arbitrarily taken as a reference [15,16]. Therefore, the aptitude to reproduce the relative R-value has to be regarded as an improvement of the R-extraction method efficiency. In addition, this point is of great importance if graphite is used as a standard material in the sp^2 fraction quantification.

We thus choose to impose that a reliable R-extraction method has to conjointly fulfill two criteria: (i) a good agreement with the theoretical graphite R-evolution and (ii) extracted sp^2 fractions of a-C films exhibiting the smallest possible fluctuation. In this work, we show that most commonly used R-extraction methods fail to fulfill both criteria. Therefore, we suggest another R-extraction method, which turns out to be in agreement with our requirements. We verify the transferability of our method on a wide range of different EELS spectra (see Fig. 1), either acquired in our laboratory (labelled from (a) to (d)) or directly taken from literature (labelled from (e) to (h)).

As a part of this work is performed on our data (spectra from (a) to (d) shown in Fig. 1), experimental details are given in Section 2. In Section 3, the tested methods are described: the most commonly used in literature (Section 3.1) as well as our suggested one (Section 3.2). In Section 4, according to our methodology, these methods are compared and it is shown that our alternative one exhibits more robustness and efficiency. In Section 5, a discussion is presented with an emphasis on the transferability of our method to other kinds of materials. In Section 6, a short conclusion is drawn.

2. Experimental details

2.1. Studied samples

We studied two classes of samples: highly ordered pyrolytic graphite (HOPG) and amorphous carbon. HOPG samples are ZYA
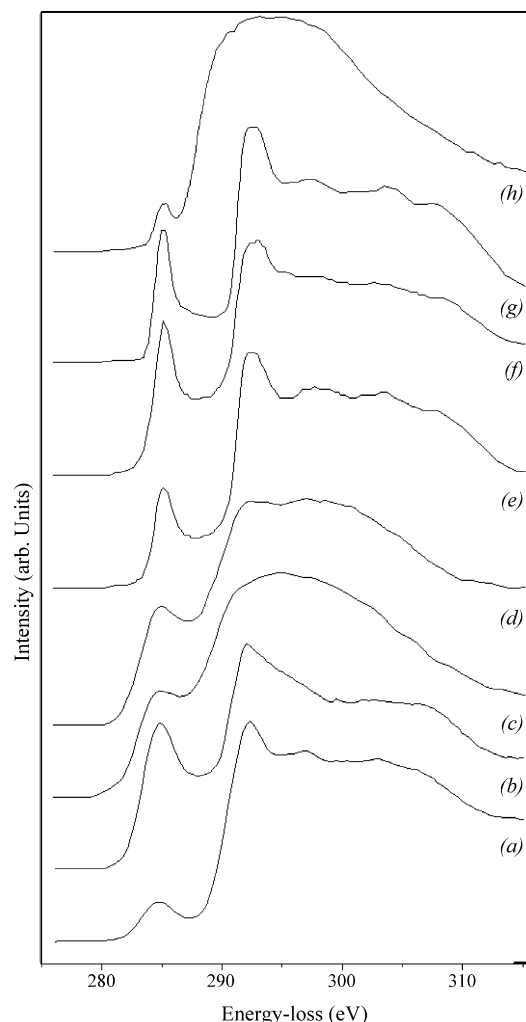
Fig. 1. Experimental C–K edge EELS spectra of (a) and (b) HOPG acquired with incident beam along [0 0 1] (respectively [1 1 0]) zone axis (see Section 2.1); (c) and (d) evaporated amorphous sample and plasma-deposited sample (see Section 2.1); (e) and (f) HOPG from Ref. [29] (see Section 4.1); (g) and (h) graphitized carbon and a-C films from Ref. [11] (see Section 4.2.2). Spectra are shifted vertically for better visualization.

grade and were bought from MikroMash^{TM}. This HOPG quality sample exhibits the lowest mosaic spread, *i.e.* $0.4 \pm 0.1°$.

Two kinds of amorphous carbon samples were used. The first one was fabricated at Max-Planck-Institut für Plasmaphysik, Garching, Germany. This sample was prepared by capacitively coupled r.f. plasma deposition with a CD_4 gas. The a-C:D films were deposited onto silicon substrates with deposition parameters as follows: CD_4 gas flow rate of 20 sccm, deposition pressure of 2 Pa, r.f. power of 25 W (electrode diameter of 200 mm), and bias of 300 V. The a-C:D films were then annealed such that the sample does not contain any more deuterium atoms. A part of this annealed sample was analysed by elastic recoil detection analysis to verify the total absence of deuterium atoms. HREM images and diffraction patterns of this sample show an entirely amorphous structure.

The second kind of amorphous carbon samples was deposited in the Med 010, Balzers apparatus in our laboratory. The sample was evaporated by a Joule effect heating of a carbon filament at a pressure of about 10^{-5} Pa. We know that our process is not completely under control (especially from the contamination point of view), but we assume that the structures are rather different from the plasma-deposited ones. This point is of importance since we