# Shining light on nitrogen heteroatoms in carbon fibers

Structural batteries could offer a solution to the current weight problem facing lithium-ion batteries (LIB) by using carbon fibers as structural components and as the cathode material. The promising combination of weight and capacity mean that they could be a solution for the current weight problem. A combination of atom probe tomography (APT) and hard X-ray photoelectron spectroscopy looked into the distribution and chemical state of nitrogen atoms.

## CHALLENGE

In electric vehicles, the weight of the battery itself can easily account for a quarter of the vehicle's total weight. This led to the idea of so-called structural batteries, in which carbon fibers act as the cathode but also as a structural component of the battery. An important factor that can enhance the electrochemical properties of carbon compounds is the incorporation of nitrogen (N) heteroatoms, which is already accomplished by using polyacrylonitrile (C3H3N) precursors. The three carbon fiber samples used for this research – M60J (Toray), T800 (Toray) and IMS65 (Teijin) display large differences in their capacity. While IMS65 has a capacity close to that of graphene, 358 mAh/g, M60J and T800 had much smaller capacities of 159 and 265 mAh/g respectively.

The distribution and chemical states of N heteroatoms are thought to be the one of the reasons behind the differences in capacity, and have been investigated in many studies before. However, these studies lacked sufficient spatial or depth resolution or were too insensitive to the low amount of nitrogen present. While the distribution problem is thought to be solved with lab-based APT, (in-depth) chemical state analysis calls for synchrotron HAXPES, with a tunable high X-ray flux and sufficient energy resolution capabilities. The capability to distinguish between the chemical states of nitrogen present is crucial and influences the electrochemical performance.

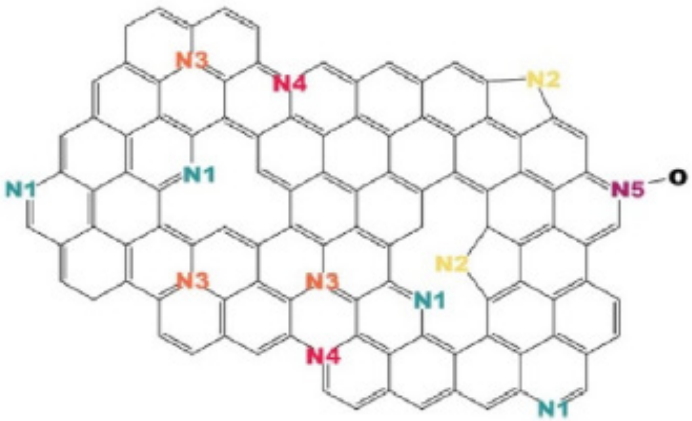


Figure 1 | Sketch of chemical states of nitrogen in carbon fibers. N1: pyridinic N, N2: pyrrolic N, N3: graphitic N, N4: edge-located graphitic N, N5: oxidic N. (Source: Source DOI: 10.1016/j.carbon.2021.03.061

## METHOD

Three commercially available carbon fiber samples – M60J (Toray), T800 (Toray) and IMS65 (Teijin) – with a thickness of 5 µm were studied using APT and HAXPES. In APT, a thin needle (<50 nm) is brought into the vicinity of the sample and a high electric field (~1010V/m) is applied between the needle and the sample. Atoms evaporate one after the other, driven by the voltage, and are detected by a position-sensitive time of flight detector. By evaluating flight time and hit position, a tomograph of the fiber samples can be recorded.

HAXPES was carried out on the P22 beamline at PETRA III at DESY, Hamburg. The samples were scanned in multiple sweeps with X-ray energies of 2.5, 4.6 and 7.2 keV. All samples were prepared before as spread-out tows of multiple fibers, as the incident X-ray beam is much broader (800 µm) than the fiber thickness (5 µm), and measurements were performed for three material depths, down to 40 nm.

## INSIGHTS & ANALYSIS

APT successfully gave insights into the distribution of N atoms at different depths. M60J contains almost no N heteroatoms and no further interesting results emerged. The other two fibers do contain nitrogen, roughly 2-3%, and the amount of N present rose slightly with increasing depth. The lack of nitrogen heteroatoms was believed to be responsible for the low capacity of the M60J fiber type, but the 25% capacity difference between the other two fibers could not be explained, as their nitrogen levels are too similar. Along comes HAXPES, which is able to resolve the chemical states of carbon, oxygen and nitrogen, the elements occurring in carbon fibers. In contrast to lab-based X-ray photoelectron spectroscopy, HAXPES was able to resolve N1s peaks, as well as carbon and oxygen peaks. The N1s peak recorded is the sum of different nitrogen species that occur in carbon fibers (cf. figure). The N1s peaks for T800 and IMS65 were analyzed in detail by deconvoluting the peaks with the respective photoelectron energies of each chemical state, to identify the distribution of the species. Despite acting as a N-type dopant and having a positive effect on electrochemical performance as a first approximation, less graphitic N was found in IMS65, which has better electrochemical properties than the T800 fiber. The difference could be explained by greater amounts of pyridinic and pyrrolic N in IMS65, which are thought to function as lithium ion absorption sites and therefore increase the performance of carbon fiber electrodes.

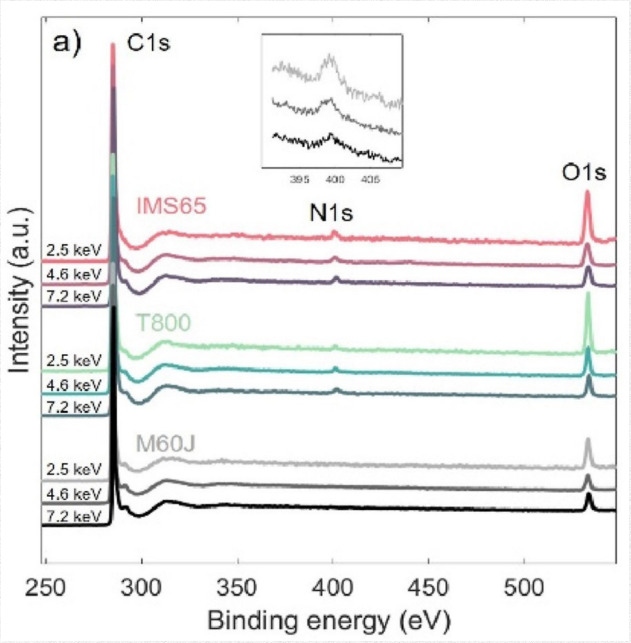


Figure 2 | HAXPES spectra of the three fiber samples IMS65, T800 and M60J, from top to bottom. Three incident X-ray energies were used for each sample, 2.5, 4.6 and 7.2 keV, penetrating the samples to different depths: 17, 28 and 40 nm respectively. Next to the prominent C1s and O1s peaks, HAXPES measurement on the P22 beamline at DESY resolved the N1s peak for the two fibers containing N, which are shown in the inset as well. (Source DOI: 10.1016/j.carbon.2021.03.061

## BENEFITS

The HAXPES measurement at PETRA III helped scientists to analyze the influence of nitrogen heteroatoms on the electrochemical performance of future carbon fiber electrodes. The synchrotron radiation allowed the amounts of different nitrogen species present to be identified, while lab-based X-ray photoelectron spectroscopy was hardly capable of detecting signals from nitrogen at all. Scientists now know which nitrogen species are favorable for performance, laying the groundwork for further studies regarding manufacturing processes to enhance the amount of pyridinic and pyrrolic nitrogen, and thus the performance of carbon fiber electrodes.

Reference DOI: 10.1016/j.carbon.2021.03.061

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