Contribution ID: **15** Type: **not specified**

A new model for the structure of hard carbons used as anodes in sodium-ion batteries

Tuesday 4 June 2024 14:00 (20 minutes)

Cotton is one of the main constituents of textile residues (> 33%) and can be used as raw material in the new value chain for sodium-ion battery (SIB) anodes, providing a double impact on the ecologic transition: a residual material is recovered for the circular economy and the further growth of renewable energies is promoted. Besides, SIBs will play a substantial role for the future electrochemical energy storage system as they are supposed to fill the gap left behind by the availability issues of lithium and other metals and it is the technology of choice for large-scale stationary application. However, SIBs still require a significant development boost for the electrodes, both anodes and cathodes as well as the complete cell configuration. Lithium technology involving a graphite support cannot be used due to different atom properties, mainly the atom size (as Na+ is larger than Li+). Hard carbon-based materials are promising materials to overcome this issue due to their safety, economic feasibility, high capacity, and good stability. One route to hard carbons involves hydrothermal carbonization (HTC) followed by a thermal post-treatment, although this valorisation route involves many knowledge gaps.

It is known that the crucial transformation of hydrochar into hard carbon proceeds in the range of 500 to 900 ℃, forming graphitic domains and a porous structure. Hard carbons (from other sources) have been studied for their application as electrodes, with the focus on the sodium storage mechanism as well as the structure-function correlation. Sodium storage may be related to: (1) adsorption/chemisorptions at defect sites/heteroatoms of graphitic planes; (2) intercalation between two graphitic planes with suitable interlayer distance; and (3) nanopore filling of small internal closed pores (up to 1 or 2 nm).

Herein, a new model for the structure of hard carbons derived from hydrochar is presented based on the transformation visualized in the van-Krevelen diagram. The transformation of cotton into carbon materials (elimination of the oxygen and hydrogen content) is governed by dehydration and condensation reactions. It is proposed that the intermediate is a linear polymer of aromatic nature that is enrolled like a wool ball, as inferred from FESEM images. With further thermal treatment graphene domains should grow; however, the tridimensional structure is already fixed and, therefore, the carbon material is not transformed into graphite which is the condition to be classified as hard carbon.

The new structure can be regarded as a fusion of the house of card model and the curved planes proposed for the structure of hard carbons before. It allows to identify different types of pores in the material: on one hand, flat interplanar spaces with distances superior of the one of graphite; on the other hand, conical ones with oxygen functionalities resembling to defect sites in graphene. The proposed structure is in accordance with XPS and Raman analysis; however, no clear proofs can be achieved with these techniques.

Stronger evidences for the characterization of the porous structure, especially for closed pores and graphitic domains should be obtained in scheduled experiments (ReMade program), namely by X-ray diffraction (structure) and small angle X-ray and neutron scattering (SAXS and SANS, pores). SANS can be carried out on as-prepared, empty samples (”dry” samples) and on samples with deuterated toluene adsorbed (”wet” samples). Measurements on “dry”samples will provide the total scattering from all porosity, including both open and closed pores. SANS on “wet”samples, when filling the open pores with the appropriated amount of deuterated toluene to match the scattering of the carbon matrix, will eliminate the contribution of the open porosity providing information about the remaining, inaccessible, closed pores. The full characterization of different sets of samples and further correlation with electrochemical measurements will allow the selection of the best preparation method for anode materials and will contribute to a better understanding of the basics for an

optimized electrochemical performance, especially for the sodium storage mechanism.
It is the aim of this contribution to devise and apply neutron scattering methods to further explore the structure of hydrochar-derived hard carbons and, thereby, to optimize their properties for sodium storage in rechargeable batteries.

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