Key aspects for the development of hard carbon anode materials with advanced performance in sodium-ion batteries

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Hard carbon (HC) is the most promising and scalable anode material for sodium-ion batteries (SIBs). HC do not cost much and can be synthesized using carbon-based precursors such as saccharides, phenolic resins, and biomass [1-3]. HC demonstrate superior characteristics compared to all other carbonaceous materials for SIBs as sodium ions cannot be intercalated into graphite structure in a significant amount [4]. However, the initial Coulombic efficiency (ICE) and the discharge capacity is still lower compared with graphite anodes in lithium-ion batteries. Thus, it is of great importance to produce HCs with electrochemical characteristics. Moreover, the mechanism of sodium ion intercalation is still debatable and should be thoroughly investigated.

In this work, we consider many sources of hard carbons as carbohydrates, biopolymers and biomass. Pretreatment methodics of precursors as air pretreatment including caramelization of carbohydrates, hydrothermal carbonization and template synthesis were also consedered. Obtained intermediates and HCs were investigated using FTIR-spectroscopy, elemental analysis, small angle and wide angle X-Ray scattering (SAXS/WAXS), BET surface area measurements, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and scanning transmission electron microscopy (STEM) with integrated differential phase contrast (DPC). The electrochemical performance of half and full cells was tested by galvanostatic charge-discharge cycling.

We have demonstrated the importance of the accurate choice of conditions of the pretreatment stage for the synthesis of hard carbon anode material. Tuning the temperature and the regime of caramelization or hydrothermal carbonization as the first stage of synthesis could help to produce hard carbon with different morphological features, such as the “monolithic” carbon and microsperic morpholigy with close-to-zero surface. Obtained HCs demonstrated excellent ICE up to 91% with a capacity over 300 mAh g^{-1} in a sodium half-cell configuration. Furthermore, the correlation between the electrochemical performance, the morphology, the surface area, defectiveness, the surface atomic ratio of C:O was established.

Additionally, for the first time, hard carbons were obtained from Heracleum sosnowskyi, a highly invasive plant, which is dangerous for humans and can cause skin burns but produces a large amount of green biomass in a short time. We proposed a simple synthesis method that includes the pretreatment stage and further carbonization at 1300 °C. Obtained materials demonstrate >220 mAh g^{-1} of the discharge capacity, high values of the initial Coulombic efficiency reaching 87% and capacity retention of 95% after 100 charge-discharge cycles in sodium half-cells.

The sodium-ion storage mechanism was also studied. Based on *operando* Raman spectroscopy, *operando* X-Ray diffraction, *ex situ* STEM/DPC, *ex situ* SAXS/WAXS, we proposed the combination of adsorption process, intercalation and pores filling at different stages of the sodiation/desodiation.

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References

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