ABSTRACT

Electrochemical energy storage devices, such as batteries, have been proven to be the most effective energy conversion and storage technologies for practical application. Among them, Li-ion batteries play a key role for portable devices and electrified vehicles, while a possible substitution is represented by the Na-ion batteries, with advantages in terms of resources availability and a drawback in terms of performances. Both kind of batteries commonly rely on carbonaceous anodes. Carbon-based materials used in batteries are usually derived from non-renewable sources as the fossil ones. Therefore, biomass is a natural green alternative carbon source with many desired properties, including the fundamental goal of the global energy sustainability.

In my thesis I report the results of a research work focused on the synthesis and characterization of biomass-derived Hard Carbons as anode materials for Li-ion and Na-ion batteries. The biomasses used as raw materials have been cherry stones, orange peel, olive leaves and olive pits. They have been chosen since they are common agricultural by-products in Italy.

The first part of the work has been focused on the synthesis of Hard Carbons (HCs), driven in order to compare different types of synthesis, which basically differ in the activation process applied before the carbonization of the raw material at high temperatures (around 900 °C). Three different procedures of activation have been developed for orange peels and olive pits (no activation, acid and alkali activation), one for olive leaves (acid activation) and one for cherry stones ($ZnCl_2$ activation), respectively.

The second part regards the structural and morphological characterization of the synthesized Hard Carbons. First of all, Thermogravimetric Analysis has been used to examine the physicochemical processes occurring in the HC's precursors, in order to understand the kinetics of the decomposition process of the samples, and exploit it to tailor the annealing of the sample precursors. Then, Raman Spectroscopy and X-Ray Diffraction have been used to examine and compare the structural characteristics of the HCs, since they produce typical spectral features and peaks. Finally, Scanning Electron Microscopy analysis has been performed in order to try to correlate the electrochemical behaviour with the different morphologies of the HCs.

In the third part, the electrochemical performances of the HCs have been tested. All of the HCs have been tested in Li-ion and Na-ion batteries, in different experimental conditions. Particular attention has been devoted to the choice of suitable binders (Na-CMC and PVdF) and to the definition of the optimal working potential range. Cyclic Voltammetry and Galvanostatic Cycling with Potential Limitation have been performed to evaluate and compare the electrochemical features of the HCs. Among them, olive stones, orange peel and olive leaves acid-activated hard carbons appear the most promising anode materials due to their relatively high specific capacity (at currents of the order of 300 mA/g) and electrochemical stability (in the range $0.02 < Ewe < 3.00$) both in Li-ion and Na-ion batteries. This probably reflects the ability of the acid to promote the hydrolysis of the carbon sources, such as lignocellulose, cellulose and sugars, which aids in obtaining optimal structure and morphology of the active materials.