Biomass-derived carbon materials for energy storage applications

Aurora Gómez Martín
BIOMASS-DERIVED CARBON MATERIALS FOR ENERGY STORAGE APPLICATIONS

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Aurora Gómez Martín

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Supervisors:
Julián Martínez Fernández
Joaquín Ramírez Rico

Department of Condensed Matter Physics
University of Seville

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“You look at science (or at least talk of it) as some sort of demoralizing invention of man, something apart from real life, and which must be cautiously guarded and kept separate from everyday existence. But science and everyday life cannot and should not be separated. Science, for me, gives a partial explanation for life.”

——— Rosalind Franklin
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Abstract

Energy storage systems are an essential link in the implementation of renewable energies and in the development of electric vehicles, which are needed to reduce our dependence on fossil fuels and the emission of greenhouse gases. Various technologies have been proposed for energy storage based on different working principles, including lithium-ion batteries, emerging sodium-ion batteries and electric-double layer capacitors. Besides the quest for improving key aspects such as energy and power densities, current research efforts are devoted to foster the manufacturing of more environmentally friendly devices using sustainable materials. Carbon-based electrodes hold considerable promise in such terms due to their low cost, tailorable morphology and microstructure, and the possibility of processing them by direct carbonization of eco-friendly and naturally-available biomass resources.

The main goal of this thesis is to develop carbon materials from biomass resources and study their applications as electrode for lithium-ion batteries, sodium-ion batteries and electric-double layer capacitors. En route towards that goal, it also aims at expanding our understanding of the microstructural changes of biomass-derived carbons with varying processing conditions and their effect on the electrochemical performance for each of these technologies.

The first part of this work reports on the synthesis of graphitized carbon materials from biomass resources by means of an Fe catalyst, and the study of their electrochemical performance as anode materials for lithium-ion batteries (LIBs). Peak carbonization temperatures between 850 °C and 2000 °C were covered to study the effect of crystallinity, surface and microstructural parameters on the anodic behavior, focusing on the first-cycle Coulombic efficiency, reversible specific capacity and rate performance. Reversible capacities of Fe-catalyzed biomass-derived carbons were compared to non-catalyzed hard carbon and soft carbons materials heated up to 2800 °C. Moreover, in-situ characterization experiments were carried out to advance our understanding of the mechanisms responsible for catalytic graphitization.

The second part of this work reports a comprehensive study on the structural evolution of hard carbons from biomass resources as a function of carbonization temperature (800 - 2000 °C), and its correlation with electrochemical properties as anode materials for sodium-ion batteries (SIBs). Synchrotron X-ray total scattering experiments were performed and the associated atomic pair distribution function (PDF) extracted from the data to access quantitative information on local atomic arrangement in these amorphous materials at the nanoscale, as well as its evolution with increasing processing temperature. Then, electrochemical properties and the storage mechanisms involved on Na ions insertion into hard carbon structures at each characteristic potential regions were elucidated and correlated with microstructural properties.
Finally, the third part of this work reports on the synthesis of nanostructured porous graphene-like materials from biomass resources using an explosion-assisted activation strategy by nitrate compounds and Ni as a graphitization catalyst. The thermal behavior during carbonization as well as the resulting microstructural and surface properties were evaluated at two different processing temperatures, 300 and 1000 ºC. Finally, their application as electrode materials for electric-double layer capacitors (EDLCs) and LIBs is investigated, with a view to their performance under high charge/discharge specific current densities experiments.
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<th>Description</th>
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<tr>
<td>AC</td>
<td>Activated Carbon</td>
</tr>
<tr>
<td>ASA</td>
<td>Active Surface Area</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated Total Teflection</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett And Teller</td>
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<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda</td>
</tr>
<tr>
<td>BMD</td>
<td>Bockris-Müller-Devanathan</td>
</tr>
<tr>
<td>CE</td>
<td>Counter Electrode</td>
</tr>
<tr>
<td>CMC</td>
<td>Carboxymethyl Cellulose</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
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<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
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<tr>
<td>DEC</td>
<td>Diethyl Carbonate</td>
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<tr>
<td>DF</td>
<td>Dark Field</td>
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<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
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<td>DGM</td>
<td>Dyglime</td>
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<td>DMC</td>
<td>Dimethyl Carbonate</td>
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<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
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<td>DTG</td>
<td>Differential Thermogravimetric</td>
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<tr>
<td>EC</td>
<td>Ethylene Carbonate</td>
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<tr>
<td>EDLC</td>
<td>Electric Double-Layer capacitor</td>
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<td>EDX</td>
<td>Energy Dispersive X-Ray</td>
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<td>EG</td>
<td>Expanded Graphite</td>
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<td>Ethyl Methyl Carbonate</td>
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<td>ICP-OES</td>
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<tr>
<td>LIB</td>
<td>Lithium Ion Battery</td>
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<td>Discharge time</td>
</tr>
<tr>
<td>$v/v$</td>
<td>Volume to Volume Ratio</td>
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<tr>
<td>wt.</td>
<td>Weight</td>
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Chapter 1
Introduction
1.1. Motivation

As a result of climate change and global economic growth, the topic of energy supply and storage has emerged as one of the main issues that humanity faces and, despite their impact in global warming, fossil fuels still remain our main source of energy (1). However, due to the global concerns regarding a future shortage of fossil fuels and raising levels of environmental pollution, there is an urgent need to develop new renewable and sustainable energy sources.

Renewable energy sources, such as solar or wind, have been steadily increasing in recent years (2), but still fall short on supplying energy in a stable and continuous manner due to their strong dependence on atmospheric conditions, which means that peak renewable production normally occurs during periods of low energy demand. Thus, one of the current topics of study is the implementation of large-scale energy storage systems next to power plants to offset the problem of continuity of supply and endow such technologies with future prospects (3). In addition, the growing market of electric vehicles with lower CO₂ emissions and portable electronic devices has also prompted the development of energy storage technologies (4, 5).

The development and improvement of energy storage systems constitutes one of the greatest challenges of present times and has become a primary focus in the scientific and industrial communities (6). Among the variety of systems based on either chemical or physical processes that are capable of storing electrical energy, two major technologies are nowadays in the front line: rechargeable batteries and supercapacitors (7). Lithium-ion rechargeable batteries represent the state-of-the-art technology for portable and electric vehicles applications due to their high gravimetric and volumetric energy densities, despite their poor power density (8). Alternatively, sodium-ion batteries have been proposed as alternative devices to lithium-ion batteries because of the wider availability of source materials and lower manufacturing costs. Meanwhile, supercapacitors deliver excellent cyclic stability and power density, but have rather low energy densities.

Besides the quest for higher energy and power densities, there is interest in developing more environmentally-friendly processes for the manufacturing of these devices, as currently state-of-the-art systems rely on scarce resources, the extraction of which has a tremendous environmental impact (9,
Despite intensive effort devoted to find alternative active materials for electrode formulation, carbon materials are still at the forefront of research due to their interesting intrinsic physicochemical properties such as good electrical conductivity, high chemical stability, tailorable surface properties and ease of processing. Carbon materials can be easily obtained from carbonization of naturally available biomass resources, making their synthesis eco-friendly and cost-effective in a circular economy framework (11). However, further efforts are needed to optimize the electrochemical performance of biomass-derived carbon electrodes. Our understanding of how the carbon microstructure and surface properties evolve with processing conditions and their effect on the electrochemical properties is still lacking.

1.2. Aim and objectives of the thesis

The main goal of this thesis is to develop sustainable carbon materials from biomass resources, for their use as electrodes in energy storage systems such as lithium-ion batteries, sodium-ion batteries and supercapacitors. To achieve this goal, we need to establish a correlation between electrochemical properties and structural aspects of the materials, and understand how they are influenced by processing conditions. Accordingly, the specific objectives addressed along the thesis are as follows:

- Explore routes to obtain highly crystalline graphitic materials from biomass resources, by using Fe as a catalyst to induce graphitization at low temperatures (850 - 2000 °C), as well as to contribute to our understanding of the mechanisms responsible for catalytic graphitization.
- Evaluate the electrochemical properties of Fe-graphitized carbons as anodes for lithium-ion batteries and investigate the influence of processing, microstructural and surface parameters on the anodic electrochemical properties.
- Study the effect of processing parameters on the microstructural and textural characteristics of biomass-derived hard carbon materials (800 - 2000 °C). Carry out a comprehensive study on their structural evolution and local range atomic order as a function of target processing temperature by alternative approaches.
- Evaluate the electrochemical properties of hard carbons from biomass resources as anodes for sodium-ion batteries. Obtain further insight into the storage mechanisms involved at characteristic potential regions and study the dependence of the structural evolution and microstructural features on the anodic electrochemical properties.
- Synthesis and microstructural characterization of nanostructured porous graphene-like carbon materials derived from biomass resources, using an explosion-assisted activation strategy by nitrate compounds and Ni as graphitization catalyst. Evaluation of their electrochemical properties as electrodes in supercapacitors as well as lithium-ion batteries.
1.3. Outline of the thesis

This thesis is structured in six chapters. This first chapter states the goals of this thesis, followed by an outline of each of the following chapters.

The second chapter reviews the classification of carbon materials in terms of their microstructure and the phenomena of catalytic graphitization process by transition metals. Then, the chapter gives an overview of current energy framework, energy storage devices technologies, and state-of-the-art carbonaceous electrode materials for lithium-ion batteries, sodium-ion batteries and electric double-layer capacitors.

The third chapter presents the main results of the graphitization of biomass resources by using Fe as a catalyst and the related microstructural and surface characterization as a function of treatment temperature. Then, the chapter focuses on the electrochemical study of these materials as anodes for lithium-ion batteries to discuss the correlation between microstructural features and anodic electrochemical properties.

The fourth chapter reports on the synthesis of hard carbons from biomass resources and their application as anode materials for sodium-ion batteries, in order to understand the relationship between microstructure and anodic electrochemical properties. This chapter gives significant insights into the sodium storage mechanisms at each characteristic potential regions, contributing to the current debate regarding storage mechanisms of sodium ions into hard carbon structures.

The fifth chapter presents the results of the thermal and microstructural characterization of porous graphene-like carbon materials synthetized by an explosion-assisted activation strategy using highly concentrated nickel nitrate solution as the activating agent. Then, the electrochemical performance of these materials as electrodes for supercapacitors and lithium-ion batteries is reported.

Third, fourth and fifth chapters include each a brief scientific background of previous works on specific topics to better understand the main motivation of performing such investigations.

Finally, the sixth chapter outlines the main contributions of this thesis to each of the topics covered and the main conclusions. In addition, some possible future research lines are presented.

1.4. List of publications

The following works are original and fully carried-out by the author and co-authors during the thesis period. The author has express authorization for using their content as parts of the thesis.

Papers in indexed journals directly related to this thesis:

“New insights into the correlation of structure and performance of hard carbons as anodes for sodium ion batteries” (under review).


Contributions to national and international conferences directly related to this thesis:


Papers in indexed journals not directly related to this thesis:


Contributions to national and international conferences not directly related to this thesis:


Awards in national and international conferences:


1.5. References