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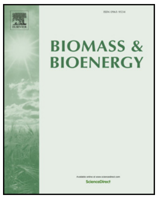

Research paper

Biochars from various biomass types as precursors for hard carbon anodes in sodium-ion batteries

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ABSTRACT

Last years have shown an explosion of interest about biochars. Until now, the applications targeted have mostly been in the fields of energy or agronomy. But high-added value applications in the field of electrochemistry, such as hard carbon precursor in anodes for sodium ion batteries, become more and more mentioned as promising uses to investigate. The present study aims at evaluating the feasibility of using biochars from various biomass types for this application and drawing links between biomass properties and the resulting hard carbon electrochemical performance. To achieve this goal, hard carbons were obtained by high-temperature slow pyrolysis of four woody and agricultural biomasses. These hard carbons were prepared as anodes, characterized regarding structural and textural properties and finally tested during successive cycles to assess electrode performances and correlate them with biomass composition. Whatever biomass, the hard carbon could be used in cells and thus biomass appears as a promising feedstock for this application. However, there are apparent differences between biomasses concerning coulombic efficiency and to some extent, cycle stability. Hence resinous wood appears to be the most suitable precursor, while wheat straw would be the least one, probably because of its too high surface area or inorganic element content. Based on these observations, hypotheses were suggested about the influence of lignin and hemicelluloses composition as well as of inorganic elements. To our knowledge, this study is pioneering in proposing a systematic study approach to understand the influence of different biomass properties in a hard carbon electrode for sodium-ion batteries.

1. Introduction

There is a high potential of available and cheap lignocellulosic biomass worldwide, including wood waste, agricultural waste and herbaceous crops [1]. Among the main processes to turn this feedstock into a valuable product is pyrolysis. This process consists on heating biomass at atmospheric pressure under an inert atmosphere, typically between 200 and 500 °C. Under these conditions, biomass releases volatile species and is converted into a carbon-rich solid called char or biochar. At the moment, after optional secondary thermal, chemical and/or mechanical treatments, this biochar is thought to be used mostly in the fields of energy, environment, and agronomy, *i.e.,* as combustion fuel, activated carbon in gas/water filters and soil amendment [2]. However, high-added value applications in the field of electrochemistry, as material in fuel cells, supercapacitors and batteries, are increasingly being investigated [3].

In the present energy context, one major topic in electrochemistry is the development of alternatives to lithium-ion batteries to solve the critical issue of lithium supply [4] [5]. Among the most developing options are sodium-ion batteries [4]. Indeed, sodium is a very abundant element on Earth, and the resulting batteries seem to exhibit excellent electrochemical performances concerning cycle stability and rate capability [6].

Contrary to the most common anodes in lithium-ion batteries, anodes in sodium-ion batteries cannot be made up of graphite since sodium insertion does not seem to be a thermodynamically favored process in this material, which finally leads significant loss of capacity [4] [7] [8]. A commonly used anode material in sodium-ion batteries is a carbonaceous material called hard carbon. This material presents highly disordered graphene sheets leaving larger interlayer space and microporosity for sodium insertion [9] [10]. The production of hard carbon usually uses compounds derived from fossil sources, i.e. phenolic resins [11]. It has consequently negative impact on process environmental balance and is moreover quite expensive. In fact,

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Table 1
Comparative values of commercial and biomass-based hard carbons.

Precursor	Pyrolysis temperature (°C)	Specific surface area BET ($m^2.g^{-1}$)	Electrolyte	Initial Coulombic Efficiency (%)	First cycle Reversible capacity ($mAh.g^{-1}$)	Reference
Carbotron (Commercial hard carbon from *Kureha Co.*)	Unknown	5	1 M $NaPF_6$ in PC with 2% FEC.	84	230	[14]
Argan shell	1300 °C	2.6	1 M $NaPF_6$ in EC and DEC 1:1 v/v	83.9	300	[15]
Apple waste	1100 °C + H_2SO_4 treatment	187.3	$NaClO_4$ 1 M in PC and EC 1:1 w/w	61	245	[16]
Peanut shell	1100 °C + H_2SO_4 treatment	29.8	$NaClO_4$ 1 M in PC and EC 1:1 w/w	68	298	[17]
Sorghum stalk	1300 °C	35.55	$NaClO_4$ 1 M in EC and DEC v/v 1:1 + 2 wt % FEC	62.2	255	[18]

commercial hard carbon is almost three times more expensive than the graphite used for Li-ion batteries [12], leading to higher overall costs. Thus, the use of biochar produced from unused biomass as a precursor for hard carbon anodes in sodium ion batteries would be highly beneficial for the process cost and environmental impact.

During the last years, some exploratory studies have appeared dealing with biochar-based sodium ion batteries [13]. All these studies followed the same approach. First, one or two biomass samples were collected and thermally treated. Then, the resulting hard carbon was characterized regarding structural and textural properties through several techniques, such as microscopy, N_2 adsorption and X-Ray Diffraction (XRD). Lastly, the hard carbon was prepared as an anode and its electrochemical performances were tested. These studies have shown promising results, with electrochemical performances comparable to existing commercial hard carbon [11], as shown in Table 1. However, these studies remained clearly focused only on the electrochemistry part and neglected the upstream parts of the process, namely pyrolysis and biomass feedstock. Therefore, relatively few studies dealt with the influence of pyrolysis conditions and their possible optimization [9]. Regarding biomass feedstock, the samples choice relied on criteria of local availability and low cost but not on criteria of quality, *i.e.,* of biomass properties diversity, in particular regarding composition. Characterization was neither made of composition in macromolecular organic constituents, *i.e.,* cellulose, hemicelluloses and lignin, nor of concentration in minor elements like nitrogen and inorganics such as calcium, potassium and silicon, although all these properties are known to have a major influence on the resulting char properties [2] and thus potentially on the electrochemical performances. Thus, the influence of biomass type on electrochemical performances could simply be observed without any explanation and no link could be drawn between biomass properties and electrochemical performances. The present study aims at characterizing this relationship. To achieve this goal, hard carbons were obtained from four different biomass types through the same pyrolysis procedure. These hard carbons were then characterized regarding structural and textural properties, prepared as anodes and finally tested during successive cycles to assess battery performance and suggest correlations with biomass composition.

2. Materials and methods

2.1. Feedstock

Four biomass types were selected according to criteria of availability and compositional diversity. The samples were constituted of one resinous wood (pine), one deciduous wood (ash wood), one agricultural cereal waste (wheat straw) and one herbaceous energy crop (miscanthus). Details about origin, collection and preparation of the samples can be found in Ref. [19]. Samples were grounded below 300 μm. The main properties in terms of composition are summarized in Table 2. For properties measurements, European standards on biofuels were followed when existing, as listed in Table 2. For the measurement of composition in macromolecular constituents, the methods used are detailed in Ref. [20].

2.2. Hard carbon preparation

To make comparison easier, and assess only the influence of biomass type, a unique thermal procedure was selected. It was adapted from the optimal procedure developed in a previous study performed with commercial cellulose by our group, in where the temperature treatment was carried out in a two-step pyrolysis process [9]. The first step consisted in heating the biomass sample until 450 °C at 1 $°C.min^{-1}$ under nitrogen atmosphere and immediately cooling it down to ambient temperature. The resulting char was then heated under argon atmosphere until 1400 °C at 3 $°C.min^{-1}$, maintained at this temperature during 1 h and finally also cooled down until ambient temperature under argon. Around 30 g of each biomass was used for the treatment. The resulting hard carbons were manually ground below 100 μm.

2.3. Hard carbons characterization

The surface area of the hard carbons was quantified using Brunauer, Emmett, and Teller (BET) theory. The single point measurements were made in a TriStar II of Micromeritics® analyzer between 0.01 and 0.3 partial pressures with N_2 at 77 K. The samples underwent preliminary degassing at 180 °C until 20 mbar to avoid any deviation of the results due to possible pollution on the sample surface. The uncertainty of the measured surface area is expressed as the standard deviation of three measurements. The detection limit of the system is given as 1 $m^2 g^{-1}$ of surface area.

X-ray diffraction (XRD) tests were performed on the hard carbon samples using a *D8 Advanc-AXS* diffractometer of *Bruker*® under air atmosphere. The X-ray beam wavelength of copper was used (1.5418 Å).

2.4. Electrochemical performance tests

2.4.1. Electrode preparation and cell construction

The electrodes were prepared from a slurry formulation consisting of 80 w% of the produced hard carbon. 10 w% of the conductor additive carbon black *super C65* from *Timcal*®, and 10 w% of polyvinilydene fluoride - PVDF in N-methylpyrrolidone - NMP as the binder. The slurry was coated over an aluminum foil for current collector and then dried at 55 °C during at least 24 h. Tablets of 14 mm-diameter where cut and then dried at 80 °C for 48 h under vacuum. Sodium-ion coin cells were assembled in an argon-filled glove box. Pure metallic sodium was used as the counter and the reference electrode (Sigma Aldrich 99.9%). A little piece of sodium was carefully placed over a support of stainless-steel and rolled using a plastic roller, a monolayer polypropylene CELGARD® 2400 membrane was used as the separator, and a VILEDON® membrane was used to ensure electrolyte's