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Hard carbon derived from cellulose as anode for sodium ion batteries: Dependence of electrochemical properties on structure[☆]

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ABSTRACT

Cellulose, the most abundant organic polymer on Earth, is a sustainable source of carbon to use as a negative electrode for sodium ion batteries. Here, hard carbons (HC) prepared by cellulose pyrolysis were investigated with varying pyrolysis temperature from 700 °C to 1600 °C. Characterisation methods such as Small Angle X-ray Scattering (SAXS) measurements and N_2 adsorption were performed to analyse porosity differences between the samples. The graphene sheet arrangements were observed by transmission electron microscopy (TEM): an ordering of the graphene sheets is observed at temperatures above 1150 °C and small crystalline domains appear over 1400 °C. As the graphene sheets start to align, the BET surface area decreases and the micropore size increases. To correlate hard carbon structures and electrochemical performances, different tests in Na//HC cells with 1 M $NaPF_6$ ethylene carbonate/dimethyl carbonate (EC/DMC) were performed. Samples pyrolysed from 1300 °C to 1600 °C showed a 300 mAh/g reversible capacity at $C/10$ rate (where $C = 372$ mA/g) with an excellent stability in cycling and a very good initial Coulombic efficiency of up to 84%. Furthermore, hard carbons showed an excellent rate capability where sodium extraction rate varies from $C/10$ to $5C$. At $5C$ more than 80% of reversible capacity remains stable for hard carbons synthesized from 1000 °C to 1600 °C.

1. Introduction

Nowadays, lithium ion (Li-ion) batteries are present in many applications such as mobile phones, computers, hybrid electric (HEV) and electric (EV) vehicles [1,2]. However, abundance, cost and especially accessibility of lithium may bring some issues for Li-ion development in the future [3]. These issues have led the scientific community to go back to sodium ion battery research [2,4,5], which had declined in the 1990s as a result of the development of Li battery technologies. Sodium seems to be an interesting alternative to lithium because of its abundance and availability. However, to be competitive to other technologies in the stationary domain, for instance, electrochemical properties such as capacity, rate capability and battery cycle life should be improved [6].

In the literature [7,8], carbon used as anode material for sodium-ion battery has been extensively studied such as hard carbon, carbon black, carbon nanospheres or nanotubes, carbon fibres and graphene. Main objective of these works was to increase sodium-ion reversible capacity of carbon material. Particularly, hard carbon has been firstly used in lithium ion batteries by Sony because this material can deliver a high capacity. However, the quite important irreversible capacity and the limited rate capability were detrimental to the development of these materials. These reasons led the scientific community to use a material exhibiting good reversible capacity and low initial irreversible capacity, such as graphite. Graphite intercalation compounds (GIC) with heavy alkali metals, i.e. potassium, rubidium and caesium, are well known [9]. GIC with lithium have been extensively studied for lithium-ion battery applications. Sodium intercalation in graphite has been studied [10,11]. It was stated that the richest sodium GIC is stage $n = 6$ in NaC8.n (i.e. NaC48). Regarding the low amount of inserted sodium ions into the graphitic structure, disordered structures were preferred. Hard carbon, a non-graphitic carbon, can deliver a reversible capacity between 100 and 300 mAh/g with important capacity fading and low initial Coulombic efficiency [12]. Also, safety issues could arise because of the low potential plateau where sodium dendrites can be formed [13].

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Cellulose is present as the main constituent of dried biostocks like wood, nut shells, fruit peel, etc. It is also known that using biomass as a source of hard carbon could be a very good alternative in order to reduce the cost and enhance the sustainability of this material. Furthermore, many groups are studying this possibility [14–20].

In the article written by Thomas and Billaud [19] in 2002, different hard carbon types have been evaluated electrochemically for sodium ion batteries. The best performances are reported for cellulose sample pyrolysed at 1000 °C with a reversible capacity reaching 279 mAh/g.

Ding et al. [20] tested carbon made from peat (organic matter) pyrolysis and obtained a reversible capacity of 255 mAh/g after 200 cycles with a current density equal to 50 mA/g. The initial Coulombic efficiency reaches around 60%. A good rate capability was also obtained: at a high current density of 500 mA/g, and a stable capacity around 200 mAh/g remains.

Recently Sun et al. [14] have synthesised hard carbon from shaddock peel pyrolysis with pyrolysis temperature varying from 800 to 1400 °C and the best performances were obtained for 1200 °C. The material exhibited a very high reversible capacity of around 400 mAh/g with a good stability over 200 cycles but a first Coulombic efficiency of 68% only.

Dahn et al. worked on hard carbons made by sucrose pyrolysis in the case of lithium insertion [21]. Synthesis parameters such as final pyrolysis temperature, heating rate and argon flow rate were optimized. In the case of hard carbons made from sucrose pyrolysis for Li-ion batteries, a reversible capacity of around 650 mAh/g and a first Coulombic efficiency of 77% were obtained. Their synthesis protocol is used by other research groups, using different organic precursors. In 1999, extensive characterisation including X-ray diffraction and SAXS were performed by Dahn's group [22]. XRD measurements indicate no internal structure change with final temperature, but SAXS results evidence that micropore size increases with temperature. Concerning the opened structure, final temperature is a major parameter from 900 °C to 1100 °C where BET surface area decreases dramatically. Above 1100 °C, the BET surface area is relatively constant. In 2000, Stevens and Dahn [23] studied hard carbons synthesized from glucose pyrolysis for Na-ion and Li-ion batteries. Even though gravimetric capacity is lower for sodium ion batteries than for lithium ion batteries, their hard carbon samples can lead to a reversible capacity around 300 mAh/g in the case of sodium batteries. In this case, a very good Coulombic efficiency of around 84% is observed; however, the irreversible capacity remains quite important with 20 mAh/g at each cycle after stabilization.

The sodium insertion mechanism in hard carbon structure is relatively well described in the literature but some minor controversy persists. In the galvanostatic curve, the slopping part corresponds to sodium intercalation between graphene sheets and the low voltage plateau is related to the sodium insertion into "nanocavities" [3,23,24]. This is the basis of the card house model proposed by Dahn and co-workers. More precisely, both sodium insertions-between graphene sheets and into the nanopores were found to be reversible during cycling using XRD and SAXS [3]. In addition, Gotoh et al. [24] showed that, contrary to lithium insertion, sodium insertion into the "nanocavities" does not lead to the formation of quasi-metallic clusters in closed nanopores of hard carbon. Lately Bommier et al. [25] have proposed another point of view concerning the card-house model. A detailed study on sodium insertion mechanisms has shown the sloping region which can be better explained by sodium ion surface storage via defect sites and the low voltage plateau corresponds to both insertion in the micropores and intercalation between graphene sheets. Recent *ab initio* calculations also involve defects in the carbon surface—for the sloping region—that lead to Na ion adsorption and promote intercalation into disordered carbon [26]. According to these calculations, the low voltage plateau is due to sodium intercalation into sites around the defective carbon surface.

Table 1. Final temperatures of the two successive heat treatments and sample names.

Sample	Heat treatment 1	Heat treatment 2
HC450	450 °C	–
HC700	450 °C	700 °C
HC1000	450 °C	1000 °C
HC1150	450 °C	1150 °C
HC1300	450 °C	1300 °C
HC1400	450 °C	1400 °C
HC1600	450 °C	1600 °C

Another point to notice is the critical choice of the precursor. The same synthesis parameters can lead to different structures according to the precursor used. Heteroatoms in the precursor are an important parameter to consider because their chemical nature, their number and their location will have a strong impact on the material porosity. Consequently the electrochemical performances of the material will be modified by the presence of heteroatoms [16,17,27,28].

Even though many articles deal with hard carbon characterisation for Li and Na batteries, no complete study of hard carbons made from cellulose, a sustainable carbon source, has been reported to our knowledge and for the first time, in this paper, we propose a complete study from structural characterisations to electrochemical performances. This work combines many different characterisations such as microscopy (TEM and SEM), SAXS measurements, Raman spectroscopy, particle size measurements and N_2 adsorption. In parallel electrochemical tests were carried out to investigate cycling performances and rate capability of our samples. This work should contribute to better understand sodium ion insertion into carbon structure.

2. Experimental

2.1. Hard carbon synthesis

Six hard carbon samples (HC) were prepared from cellulose pyrolysis (Aldrich, microcrystalline powder) in two steps. Both heat treatments were performed under argon atmosphere in a horizontal tube furnace. In the first step, the temperature was increased at 20 °C/min to 200 °C and then at 1 °C/min to 450 °C before cooling down to room temperature. In the second step, the furnace temperature was raised at 3.33 °C/min to the final pyrolysis temperature, *Tfinal*. The temperature *Tfinal* was maintained for 1 h. Finally, the sample was cooled down to room temperature. Between both heat treatments, the sample is exposed to ambient atmosphere. The six different samples were synthesised using a *Tfinal* between 700 °C and 1600 °C (Table 1). This synthesis was inspired by the procedure reported by Dahn et al. [21–23].

2.2. Characterisation methods

X-ray diffraction (XRD) was performed with a D8 Advance Bruker AXS diffractometer equipped with Cu$K\alpha$. The 2θ angle was varied from 5° to 80° with a step size of 0.05° and a counting time of 1 s.

Small-angle X-ray scattering data were measured in transmission geometry using a home-made SAXS camera utilising a point source (size $\sim$200 µm $\times$ 200 µm) Bruker–Nonius (FR591) rotating anode generator with Cu-$K\alpha$ radiation ($\lambda = 1.5418$ Å) at 45 kV and 66 mA. The hard carbon samples were dried at 250 °C for at least