Optimization of large scale produced hard carbon performance in Na-ion batteries: effect of precursor, temperature and processing conditions

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Abstract: Hard carbon materials were prepared from different precursors (phenolic resin and commercially available cellulose and lignin) under different pyrolysis and processing conditions using industrially adapted syntheses protocols. The study of their microstructural features enabled to assess that the nature of the precursor and the temperature of pyrolysis are the major factors determining the carbon yield and the surface area, the latter one having a major effect on the electrochemical capacity. Finally, the presence of surface groups and physisorbed water can also play a role both on the maximum reversible capacity achievable (by influencing the interaction of sodium ions with the hard carbon surface) and the irreversible capacity.

Phenolic resin combining high carbon yield (~50%), tap density (0.7 g·cm⁻³) and reversible capacity (249 mAh/g) was found to be the precursor producing the most suitable hard carbon for practical use in Na-ion batteries. Cellulose can be a good candidate as well, the lower carbon yield being counterbalanced by its lower price and higher capacity (280 mAh/g).

Introduction

Sodium-ion batteries (SIBs) are based on a concept analogy with the ubiquitous lithium-ion batteries (LIB) and have emerged in the last five years as a viable technical alternative holding promise for higher sustainability^{1,2,3} and lower cost. While graphite is the most widely used commercial negative electrode material in LIB, it is not able to insert sodium ions^{4,5} unless solvated to form ternary intercalation compounds,⁶ and thus hard carbon is today the only feasible negative electrode material. The mechanism for sodium insertion in hard carbon involves two distinct steps: a sloping potential region extending to ca. 0.2V and a low potential plateau.⁷ Although the attribution of each part of the curve is still controversial,⁸ the first part (above ca. 0.2 V) has often been related to the insertion of alkaline ions between the layers, while the second would be related to the adsorption of ions in the micropores. Recently, for high temperature annealed hard carbons (>2000°C) a single voltage plateau at ~ 0.1 V has been observed and related to the nanopores filling with Na⁺ ions⁹ which would be consistent with an opposite attribution.¹⁰

The earliest work on the evolution of carbon structure as a function of heat treatment followed by XRD was carried out by Franklin in the 1950's¹¹ and whilst her work has been refined since then, the general principles remain. She differentiated carbons into three groups on the basis of their response to heat treatment, which was associated with the way in which small domains were ordered at the lower temperatures and their ability to reorder as a result of heat treatment at higher temperature. Non graphitising (hard) carbons are extensively cross linked at low temperature and heat treatment at high temperature leads to very little structure development or loss in low angle scatter with, in some cases, the development of small isolated domains with well-developed crystallinity. Most hard carbons are prepared by pyrolysis of different precursors at T<1500°C and exhibit a structure in which most of the carbon atoms are arranged in an approximately planar hexagonal network but ordering in the c direction is lacking. This structure is characterized by amorphous areas embedding more graphitic structure segments consisting of aligned small-dimensionality sp² (graphene) layers. Since the degree of crosslinking depends on the state of aggregation of the intermediate phase

during pyrolysis, hard carbons are commonly products of solid-phase pyrolysis, with the composition of the precursor having an important influence on the reaction yield (related to the carbon content in the precursor) and the presence of heteroatoms, such as chemisorbed oxygen containing species which exhibit different thermal stabilities and are desorbed at different temperatures. A large number of studies have been devoted^{12,13,14,15,16} to preparation of hard carbon from very diverse precursors and using different protocols, with significant differences in electrochemical performance in sodium cells which, in some cases, may not be intrinsically related only to the materials but also to the testing protocols used.^{12,17} Indeed, a significant part of the electrochemical capacity delivered by hard carbon is achieved at very low potential, large cell polarizations related to a non-optimized electrolyte composition or cell configuration may result in the loss of a significant amount of capacity (note that the lower cut off potential for most tests reported in the literature is 0.02V vs. Na⁺/Na).¹⁸

In any case, if commercialization of SIB is to be foreseen, a compelling need emerges to carefully define scalable synthesis routes involving suitable but also available and affordable precursors. Herein we report on the synthesis of hard carbon at large scale (kg) using commercially available precursors with different carbon and heteroatom contents such as cellulose (C₆H₁₀O₅)_n, lignin (C₃₁H₃₄O₁₁)_n or phenolic resin (C₆H₆O)_n with adapted syntheses protocols and set ups, and the resulting electrochemical performance.

Experimental

Hard carbon was prepared by pyrolysis of the three precursors at temperatures ranging from 500 to 1600°C. For final temperatures up to 800°C the pyrolysis was carried out in an unpurged multi-tube furnace. The typical conditions used were a slow heating rate (3°C/min to 300°C and 1°C/min to 400°C followed by 3°C/min to 700°C) and a powdered precursor load of 10kg (500g/per tube) with no gas purge. Where the treatment temperature is shown above 800°C the pyrolyzed carbons were subjected to a second heat treatment in a nitrogen purged furnace for 20 min. Thermogravimetric analysis of the precursors was carried out under inert gas flow using a NETZSCH -STA 449 F1 Jupiter with a heating ramp of 5°C/min. The polymer precursors used were high purity food grade commercial microcrystalline cellulose from JRS Pharma (identified as

MCC), a commercially supplied (Fibria) sample of unbleached pulped cellulose used in the production of tissue paper (identified as PC), a proprietary phenolic resin precursor prepared by MAST (identified as PR) and a powder high purity lignin supplied by Fibria. Pyrolysis was typically carried out using the as received precursors, in order to examine the possibility of improving the produced carbon properties further by reducing the surface area of the material at low carbonisation temperatures, compression of the precursor material before carbonisation was tested in some cases. Disk pellets (4mm in diameter and 4mm in thickness) were prepared by pressing 5g of cellulose material under 22kN pressure for 5 min. The details regarding the sample preparation conditions and denominations are gathered in Table 1.

The tapped density of the as prepared hard carbon samples was measured with a Quantachrome Autotap instrument. The tapping frequency provided by the equipment is 3.7Hz approximately. A known amount of sample (0.5-2g) was placed in a test tube and the volume measurements were taken between steps of 1000 taps until volume remained constant. The nitrogen adsorption/desorption isotherms were obtained with a Micromeritics ASAP 2420 instrument using N₂ adsorbate at -196 °C. The CO₂ adsorption was performed at 0°C using a Micromeritics ASAP 2020 set-up. Prior to the analysis, the samples were out-gassed in vacuum at 300°C for one night. The textural properties, i.e., specific surface area (SSA) was calculated using the Brunauer-Emmett-Teller method from the linear plot in the relative pressure range (P/P_0) of 0.05-0.25 for N₂ adsorption and 10^{-4} to 0.03 for CO₂ adsorption. The pore size distributions (PSD) were determined from the adsorption branch of nitrogen and CO₂ isotherms using the 2D-NLDFT heterogeneous surface model and the 2D-NLDFT het surface model for carbon materials, implemented in SAIEUS (Micromeritics)¹⁹.

X-Ray powder diffraction (XRD) patterns were obtained with a Philips X'Pert MPD diffractometer with Cu K $\alpha_{1,2}$ doublet and a flat-plate Bragg-Brentano theta-theta geometry. Particle morphologies and microstructure were studied by scanning (SEM) and transmission electron microscopy (TEM) with a FEI Quanta 200 FEG-ESEM and Jeol ARM-200F microscopes, respectively. Raman spectroscopy measurements were performed at room temperature in a backscattering geometry using a LabRAM BX40 (Horiba Jobin-Yvon) microspectrometer equipped with a HeNe excitation source ($\lambda = 532$ nm).

The carbon surface functionality was analyzed by temperature programmed desorption coupled with mass spectrometry (TPD-MS). In a typical measurement, the sample is

placed in a furnace and heat-treated in vacuum with a linear heating rate of 10°C/min between of 25°C and 950°C. The gases evolved during the heating process were continuously detected by a mass spectrometer. Before experiments, the mass spectrometer was calibrated using N₂, H₂, CO, CO₂ and H₂O. The total amount of each gas released was computed by time integration of the TPD curves. The active surface area (ASA) was determined by TPD-MS as well. The carbon surface was first cleaned at 950°C for 30 min during the TPD experiment under high vacuum. In a second step, the carbon surface is exposed to oxygen atmosphere at 300°C during 10 h allowing surface oxygen complexes to be formed. After the removal of oxygen, the sample is heat-treated up to 950°C and the oxygenated complexes formed are decomposed into CO and CO₂ and their amount is further quantitatively determined by mass spectrometry. The surface area occupied by the chemisorbed oxygen (ASA) can be calculated taking into account the number of mole for each gas desorbed and considering the area of an edge carbon site that chemisorbs an oxygen atom as 0.083 nm².^{20,21,22}

Tape casted composite electrodes for electrochemical testing were prepared from slurries (85 wt. % hard carbon, 8 wt. % of Polyvinylidene fluoride binder (Arkema) and 7 wt. % of Super P carbon (Timcal) in N-Methylpyrrolidone (Aldrich))²³. Loading of electrodes was ca. 2 mg/cm². Electrochemical tests were performed using a Bio-Logic VMP3 potentiostat in two-electrode Swagelok cells in galvanostatic mode with potential limitation (GCPL) between 2 and 0.03V vs. Na⁺/Na at different rates, namely C/10, C/20, C/5, C and 2C (1C being one Na⁺ inserted in one hour), using sodium metal counterelectrodes. These enabled monitoring both the capacity evolution upon cycling and the rate capability, which is related to the power performances. The electrolyte used was 1M NaPF₆ (STREM Chemicals 99%) dissolved in a mixture (0.45:0.45:0.1 in weight) of ethylene carbonate (EC, Aldrich anhydrous 99.0%), propylene carbonate (PC, Aldrich anhydrous 99.7%) and dimethyl carbonate (DMC, Aldrich anhydrous 99.0%).^{24,25} The water content in all electrolytes was measured by Karl-fisher titration using a 899 Metrohm Karl-Fischer coulometer and found to be lower than 20 ppm in all cases.

Results and discussion

I. Synthesis and microstructure

Figure 1. Mass loss vs. T during the thermogravimetric analysis ($5^{\circ}\text{C}/\text{minute}$ under N_2) of phenolic resin (black line), lignin (red line) and MCC (blue line) precursors

Thermogravimetric analysis (Figure 1) under nitrogen indicated that most of the weight loss occurs around 400°C for phenolic resin ($\text{C}_6\text{H}_6\text{O}$)_n, MCC cellulose ($\text{C}_6\text{H}_{10}\text{O}_5$)_n and lignin ($\text{C}_{31}\text{H}_{34}\text{O}_{11}$)_n precursors. As expected the overall weight loss strongly depend on the chemical nature of the compound, despite not strictly following the expected trend relative to the amount of heteroatoms. Indeed, the overall C contents in phenolic resin, cellulose and lignin based precursors are, respectively 76, 44 and 64 wt.% and the mass remaining after heating up to 500°C (typical for polymer carbonization) were *ca.* 70, 8 and 50wt.%, respectively. Therefore, the yield of pyrolysis was never 100%, which indicates partial carbon burn off. While this occurs to a rather small extent for phenolic resin and lignin the value is much larger for cellulose precursor is used. This can be related to the different structures of the precursors which in the case of phenolic resin and lignin are mainly composed of aromatic rings while in the case of cellulose are D-glucose (α -D-glucopyranose) units. Thus, in terms of reaction yield, phenolic resin and lignin precursors may hold an important advantage over cellulose. Yet, this observation has to be taken with precaution as the yield is highly correlated to pyrolysis conditions such as gas flow, which cannot be modified in the available thermogravimetric setup. However, the trend observed for the different precursors is not expected to be influenced by the gas flow.

Hard carbon samples were prepared following a two step process with the first involving pyrolysis of the precursor at 500-800°C under the own off gases. Typical yields after this step are 18-20% for cellulose (both PC and MCC), 23% for pelletized cellulose, 38% for lignin and 55 % for phenolic resin. In the second step, samples are further treated under a nitrogen flow up to 800-1600°C. In this case 100 g batches can be prepared. It is clear from the results that whilst in the case of lignin and phenolic resin precursors there is good agreement between the large scale pyrolysis carbon yields in this study and the TGA results, this is not the case for cellulose. The TGA pyrolysis yield for cellulose in figure 1 (~8%) is in good agreement with other literature TGA studies,²⁶ but is clearly not representative of the yields in the larger scale furnaces used in this study which were typically around 20%. It seems likely that this is due to a combination of factors such as the volume of cellulose processed, gas flow and heating rate (most TGA experiments involve very fast heating rates combined with very small sample sizes). Indeed, Shen et al²⁷ demonstrated that the carbon yield does increase as the heating rate decreases. As observed in Figure 2, N₂ BET surface areas usually reach a maximum at temperature values around 700-800°C. Higher temperature pyrolysis results in hard carbons with lower values of BET specific surface area (Figure 2), which is in agreement with the expected closing of the microporosity at high temperature, but changes are much more significant in samples prepared from cellulose than in those prepared from the phenolic resin. For instance, at 1200°C, microcrystalline cellulose yields $\leq 10 \text{ m}^2/\text{g}$, Lignin $\sim 30 \text{ m}^2/\text{g}$ and pulp cellulose 70-100 m^2/g , while for the case of phenolic resin 30 m^2/g are achieved. The microcrystalline cellulose derived carbons showed the greatest decrease in BET surface area above 900°C falling to 7 m^2/g at 1200°C. This was in marked contrast to the pulp cellulose which had an area of 67 m^2/g at the same temperature. Nonetheless the much lower cost of the pulp cellulose, compared to the MCC, makes this worthy of further evaluation. The low surface area of the lignin derived carbon relative to the phenolic carbon associated with its lower cost makes this precursor also interesting for further evaluation. It is also worth mentioning that higher surface areas are obtained when samples are heat treated in the form of a pellet (such as MCC1200D and PC1200D, respectively 87 and 115 m^2/g) than as powder (MCC1200 and PC1200, respectively, 7 and 67 m^2/g), possibly due to the poorer own off gas evacuation with compact samples.

Table 1 Synthesis conditions used to prepare the hard carbons including pyrolysis temperature, precursor types and processing conditions along with their BET surface area determined by N_2 adsorption. Samples are denoted according to the final treatment temperature and the precursor (MCC stands for microcrystalline cellulose, PC for pulp cellulose, L for lignin and PR for phenolic resin, D indicates that the cellulose was pelletized into a disc prior to carbonization.).

Sample label	Precursor	BET (m^2/g)	T treatment ($^{\circ}C$)
MCC500	Cellulose	14	500
MCC600	Cellulose	221	600
MCC700	Cellulose	456	700
MCC800	Cellulose	487	800
MCC900	Cellulose	341	900
MCC1000	Cellulose	2.4	1000
MCC1100	Cellulose	0.8	1100
MCC1200	Cellulose	7	1200
PC1200	Cellulose	67	1200
PC1200D	Cellulose	115	1200
MCC1200D	Cellulose	87	1200
L1200	Lignin	33	1200
PR500	Resin	26	500
PR600	Resin	140	600
PR700	Resin	588	700
PR1100	Resin	131	1100
PR1200	Resin	30	1200
PR1300	Resin	81	1300
PR1400	Resin	56	1400
PR1500	Resin	58	1500
PR1600	Resin	72	1600

Figure 2. BET Surface Area as a function of Treatment temperature for phenolic resin, microcrystalline cellulose, pulp cellulose and lignin precursors

The particle size for the samples prepared from lignin and from phenolic resin was found to be radically different with those prepared from cellulose, the latter exhibiting in general larger particle size, in agreement with lower BET areas.

Figure depicts typical scanning electron microscopy (SEM) micrographs for MCC1200, MCC1200D and also PC1200 and PC1200D enabling to clearly asses the influence of pelletizing in the final carbon microstructure. For both cases, pelletizing results in a much homogeneous particle shape and smaller size (in agreement with BET values), which may be related to the fact that pelletizing may prevent efficient gas removal.

Figure 3. Typical SEM micrographs for hard carbon samples prepared from microcrystalline or pulp cellulose with (MCC1200D, PC1200D) (a, b) or without (MCC1200, PC1200) (c, d) pelletizing.

In order to better assess the relevance of the findings reported one needs to consider that pharmaceutical grade MCC is typically around \$4/kg in small volumes and could reduce to ~\$2.5/kg if purchased in bulk (tonne quantities). The use of amorphous pulp cellulose would reduce the precursor cost to ~50c/kg and lignin being a byproduct in the production of high purity cellulose would also have low cost. On the other hand phenolic resin is roughly around 3.5\$/kg but has the benefit of a significantly higher carbon yield, which may result in competitive costs for the final carbon.

II. Electrochemical performance

After the first treatment at 800°C all samples exhibit a high BET area and extremely low reversible capacity (see typical SEM micrograph and electrochemical curve in Figure 4). The electrochemical profile exhibits only a sloping region (no low potential plateau is observed).

Figure 4. Typical SEM image (a) and electrochemical behavior (b) of samples prepared from MCC cellulose after the first pyrolysis step at 800°C. Inset in graph depicts capacities on oxidation and reduction for the first two cycles.

The second synthesis step was therefore necessary in order to achieve good electrochemical performance and recover the capacity in the low potential plateau (see Figure 5). The reversible and irreversible electrochemical capacities after the second thermal treatment are significantly dependent on the BET surface area (see Figure 5 and table 1). For instance, both reversible capacities and first cycle coulombic efficiencies of the MCC and phenolic resin based hard carbons increase with the second thermal treatment temperature until optimum performance is reached, with decreasing capacity after treatments at higher temperatures. For instance, maximum reversible capacity for MCC precursor (*ca.* 280 mAh/g) is reached at 1100°C and at 1500°C for phenolic resin (*ca.* 250 mAh/g). It also appears that preparation of samples in form of pellets is

beneficial. Indeed, a reversible capacity of only *ca.* 150 mAh/g is recorded for MCC1200 (sample heated as a powder), while 280 mAh/g was achieved with MCC1200D (pellet) even though the latter present higher BET surface area (87 vs. 7 m²/g for MCC1200), which is most likely related to the differences in microstructure described above (Figure 3). Results for the MCC and Lignin derived carbons are very similar despite differences in the BET surface area, with the performance of the phenolic resin derived carbon (BET > 50 m²/g) is also surprisingly good. These are all indications that BET is not the only factor determining capacity and the microstructure or surface chemistry of the carbon may also have a significant effect. It is worth mentioning that reversible and irreversible capacity values obtained are comparable with the one of hard carbon produced from sucrose or phenolic resin pyrolysis in lab scale batches of few grams.^{12,16,28} Yet, comparison with values reported in the literature is tricky, as different IR drops resulting from slightly different experimental setups may limit the capacity achievable above a certain fixed potential limit. In addition to that, extrapolation of results is difficult coulombic efficiency in half and full cells may differ due to unstability of the SEI on the sodium counterelectrode.¹⁷ Overall, the crucial parameters for the synthesis of hard carbon exhibiting good electrochemical properties are the reaction temperature (the optimum temperature being precursor dependent) and the sample form before heat treatment (powder vs. pellet).

Figure 5. a) and b) First cycle voltage versus capacity profiles for electrodes containing hard carbons prepared between 1000 and 1600°C and using different precursors (MCC, PC, L and PR). c) and d) Capacity upon reduction versus cycle number for the corresponding electrodes and e) Bar diagram showing capacity upon reduction for the 1st, 2nd, 10th and 20th cycle for the electrodes containing hard carbons prepared from MCC between 600 and 1200°C and from L and PC at 1200°C.

III. Study of surface chemistry and correlation with electrochemical performance

The four samples exhibiting better electrochemical performance in terms of total reversible capacity are MCC1200D, PR1200, PC1200 and PR1500, despite the later exhibiting larger capacity fading upon cycling. These were selected for further investigation together with MCC900 with comparative purposes, the aim being to get

further insights in the factors determining reversible capacity, besides the above mentioned BET specific surface area. Tap density was measured for those five samples (see table 2). The highest values (0.7 g/cm^3) were obtained for phenolic resin based hard carbons PR1200 and PR1500 and the smaller ($> 0.3 \text{ g/cm}^3$) for cellulose based ones (PC1200 and MCC900) which could be somehow related to the very high carbon burn off observed for this precursor upon heat treatment (Figure 1). While this is not relevant when one considers gravimetric capacity, it is very important for volumetric capacity. Moreover, fabrication of highly loaded electrodes will only be possible for the samples with higher tapping density. For sake of comparison tap density of MCMB graphite powder (MCMB 25-28, Osaka Gas Co.), constituted of spherical particles, is ca. 1.3 g/cm^3 . The lower tap density of hard carbon when compared with graphite is a major issue that will need to be tackled for the practical development of high energy density Na-ion batteries and hence, the high values achieved for the phenolic resin derived carbons are most interesting. While there have been efforts to try to correlate tapping density of hard carbons with a large variety of parameters such as pyrolysis temperature, heating ramp, gas flow or powder pretreatments (acid washing or pelletizing), this did not lead to the establishment of conclusive trends with typical values oscillating between 0.6 and 0.9 g/cm^3 .²⁹

Table 2 Surface area, surface chemistry and tap densities for selected hard carbon samples (see text).

Sample	BET N ₂ (m ² ·g ⁻¹)	BET CO ₂ (m ² ·g ⁻¹)	ID/IG	d ₀₀₂ - space (Å)	CO+CO ₂ (mmol/g)	ASA (m ² ·g ⁻¹)	Tap Density (g/cm ³)	Reversible capacity at first cycle and C/10 (mAh/g)	Reversible capacity at C/5 (mAh/g)
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PC1200	67	301	1.42	3.478	0.67	31	0.2	223	188
MCC1200D	87	309	1.58	3.764	1.2	43	0.6	280	227
MCC900	341	377	1.78	3.759	1.2	63	0.3	137	113
PR1200	30	394	1.61	3.881	0.86	24	0.7	244	172
PR1500	58	139	1.52	3.721	0.64	17	0.7	249	111

Figure 6a presents the nitrogen adsorption/desorption isotherms corresponding to the whole series of investigated samples. As one can see, these typically exhibit I-type isotherm characteristic to microporous solids. The BET specific surface area determined from such data ranges from $\sim 30 \text{ m}^2/\text{g}$ to $\sim 80 \text{ m}^2/\text{g}$ for all of them, except for MCC900 which exhibits much higher values ($> 300 \text{ m}^2/\text{g}$) which can be related to the lower annealing temperature (900°C compared to 1200°C or 1500°C). Complementary measurements were carried out with CO_2 , as probe molecule to evaluate the presence of ultramicropores ($< 1 \text{ nm}$), with the corresponding isotherms being depicted in Figure 6b. All samples exhibit high and comparable CO_2 adsorbed volumes except for PR1500 which is characterized by significant lower amount of CO_2 adsorption. The determined BET surface areas are comprised between 300 and $400 \text{ m}^2/\text{g}$ for all samples except for PR1500 ($< 150 \text{ m}^2/\text{g}$). These values, which are much higher than those determined from nitrogen indicate the presence of ultramicropores, in agreement by the pore size distribution determined by 2D NLDFT model for N_2 and CO_2 adsorption isotherms (Figure 6d). The N_2 pore size distribution (Figure 6c) exhibits one important peak with the maximum placed at around 0.65-0.85 nm, with the specific value depending on the sample. The CO_2 pore size distribution (Figure 6d) exhibits only one peak around 0.48 nm for all materials, in agreement with the existence of very small pores, which are in larger amount compared to larger pores determined by N_2 adsorption. It is worth to highlight that PR1500 and PR1200 present similar N_2 BET ($30\text{-}60 \text{ m}^2/\text{g}$) but different CO_2 BET ($400\text{-}150 \text{ m}^2/\text{g}$, see table 2) indicating that PR1200 exhibits a much higher volume of ultramicropores. They both have reversible capacity of about 250 mAh/g during the first 10 cycles at C/10 (figures 5b and 5d) but after 40 cycles PR1500 drop to 150 mAh/g , while PR1200 presents very good cycleability and better rate capability (Table 2). These results suggest at a first glance that a high volume of ultramicropores is beneficial to the capacity retention and power performances of hard carbon electrodes,

however, the different annealing temperature may induce different microstructural features as well.

Figure 6 Nitrogen adsorption/desorption isotherms (a) and CO_2 adsorption isotherms (b) and their corresponding 2D-NLDFT pore size distribution (c, d) for selected samples.

The microstructure of the materials was investigated by a combination of Raman spectroscopy and HRTEM. The Raman spectra (Figure 7a) of all samples exhibit the typical D (1307 cm^{-1}) and G (1552 cm^{-1}) bands. The D band is related to the breathing mode of carbon ring (defects) while the G band is assigned to the sp^2 carbon atoms motion and therefore related to ordered graphite domains and thus the ratio I_D/I_G is typically used to estimate the degree of ordering. This value ranges between 1.42 and 1.79 for the samples studied (see Table 2), indicating different degrees of organization. The smallest I_D/I_G value (1.42) is recorded for PC1200, which is very similar to that of MCC1200D and PR1200, also prepared at 1200°C and PR1500 pyrolyzed at 1500°C . The lower I_D/I_G are in agreement with the observation of well pronounced second order 2D (2648 cm^{-1}) and D+G (2888 cm^{-1}) bands corresponding to graphitic structures. The HRTEM pictures indicate coexistence of dense carbon with short graphene stacked

layers and ribbon-like spherical graphitic domains in all these samples (see Figure 7). In contrast, the value achieved for MCC900 is somewhat higher indicating with lower ordering at lower temperatures. XRD patterns (not shown) exhibit only two wide low intensity bands at ca. 23° and 42° in 2θ , corresponding to 002 and 100. The d_{002} spacing is expected to decrease with the graphitization degree, and calculated values (Table 2) are in full agreement with Raman spectroscopy results.

Figure 7 Raman spectra (a) and HRTEM pictures of PC1200 (b) and PR1500 (c) carbons.

The carbon surface functionality was analyzed by TPD-MS and the desorption rates of each gas evolved (H_2 , H_2O , CO and CO_2) during the thermal heating are plotted vs. temperature (see for instance Figure 8 for the case of MCC1200D). The decomposition of the functional oxygenated groups leads to the formation of gases such as CO and CO_2 . The type of CO_x groups released and their temperature give an indication of their nature. Typically, the CO_2 derives from carboxyl or anhydride groups while CO from carbonyl, ether and quinone groups.²² The type and amount of functional groups present in the carbon are important, as the surface chemistry can severely influence the interaction with the electrolyte, which is not only specific to hard carbon but a much more general trend affecting also positive electrode materials.³⁰ The water release is mainly due to the physisorbed water ($\sim 100^\circ C$) from the carbon porosity or water formed by in-situ reactions during the TPD-MS experiment between two neighbouring functional groups ($> 200^\circ C$). In this case, carboxyl groups ($-COOH$) may interact to form anhydride groups ($-COO-COR$) and H_2O . Anhydrides further decompose as observed by concomitant release of CO_2 and CO groups. Hydrogen evolution is usually observed at high temperatures ($> 800^\circ C$) and associated to the cleavage of the C-H bonds. For all materials similar amounts of water and hydrogen were released, only in case of MCC900 higher H_2 amounts were detected due to its lower annealing temperature ($900^\circ C$). The most prominent peaks in all samples investigated come from CO in the temperatures above $400^\circ C$ suggesting the presence of various oxygen functional groups such as anhydrides, phenols, ethers and quinone groups. All samples exhibit similar desorption profiles, the slight differences observed can be related to different relative amounts of certain groups in the diverse samples investigated. CO_2 peaks specific to acidic groups (carboxyl and anhydrides) are as well observed between 200 and $800^\circ C$. The integration of the desorption peaks allow to determine the amount of CO and CO_2 groups. The MCC900 and MCC1200D exhibit the highest quantities of oxygenated groups (Figure 9c) in line with their higher specific surface area and also with the preparation protocol, as for MCC900 the temperature is probably too low to remove all heteroatoms and for MCC1200D, the fact that the precursor is pelletized may prevent efficient gas removal. Oxygen adsorption on the materials at $300^\circ C$ allows the determination of the active surface area (Figure 9d). The active surface area represents the surface occupied by the edge planes defects (stacking faults, dislocations, vacancies,) and their amount depends on the carbon crystallite size/orientation, vacancy/impurity concentration, structural order.^{31,32} The values of ASA obtained seem

to be consistent with the relative amount of surface groups and in line with other hard carbons (add references 9 and 10).

Figure 8: TPD-MS of MCC1200D sample showing the water (a), H_2 (b), CO (c) and CO_2 (d) gas profiles

Figure 9 TPD-MS gas desorption profiles for CO (a), CO_2 (b), quantity of desorbed CO and CO_2 groups (c) and active surface area (d) of selected hard carbon materials.

The above described findings allow confirming the very different performance level observed in the hard carbons studied during this work. As observed in Figure 2, N₂ BET surface area values stabilize for pyrolysis temperatures above 800°C but optimum electrochemical performances are achieved above 1000°C, the exact temperature being precursor dependent. While a direct link between N₂ BET surface area values and electrochemical performances cannot be made, the best sample prepared in this work (MCC1200D) provided some insight on the basic features needed in order to achieve high reversible capacity and high rate capability hard carbon material. Indeed, the MCC1200D was the only sample presenting all the following characteristics: 1) N₂ BET surface area below 100 m²/g, 2) ID/IG below 1.6, 3) tap density ≥ 0.6 and 4) CO₂ BET surface area above 300 m²/g. Also, for samples with relatively low BET values, structural disorder seems to worsen performance while a richer surface chemistry seems to be related to higher reversible capacity values although the fundamental nature of the interactions behind this observation are not clearly elucidated at the moment. We tentatively attribute it to the nature of the pores and electrolyte wettability of the electrode.

Conclusion

Hard carbon materials outperforming “battery grade” commercial available samples have been successfully prepared from lignin, cellulose (very cheap and abundant raw materials) and phenolic resin through tuning the pyrolysis conditions so as to achieve low surface areas. However, two important issues for Na-ion technology were identified when dealing with material production cost and volumetric energy density: the reaction yield during the pyrolysis step for hard C synthesis and the density of the latter. The nature of the carbon precursor was found to play a crucial role and the use of phenolic resins led to the highest reaction yield (almost 50% and less than 10wt.% C loss) and to the highest tap density (0.7 g·cm⁻³), which has an obvious practical added value. Pelletizing the precursor prior to pyrolysis was found to have a significant influence in the particle size of the resulting hard carbon. The presence of surface groups and physisorbed water can also play a role on the maximum reversible capacity (by influencing the interaction of sodium ions with the hard carbon surface) and also the irreversible capacity.

Acknowledgements

Authors acknowledge Ministerio de Economía y Competitividad (Spain) for Severo Ochoa Programme for Centres of Excellence in R&D (SEV-2015-0496) and EC for funding through H2020 NAIADES project (LCE10-2014, Contract number 646433) and ALISTORE-ERI members for fruitful discussions. The authors thank Dr. Loïc Vidal for performing TEM analysis through the IS2M technical platform.

This work has been done in the frame of the Doctoral Degree Program in Chemistry by the Universitat Autònoma de Barcelona.

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