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Physical characterization of carbonaceous materials prepared by mechanical grinding

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Abstract

By means of mechanical grinding, we recently reported the ability to prepare tailor-made carbon materials able to reversibly intercalate two lithiums per six carbons (e.g., Li_2C_6) while having irreversible capacities of 320 mA h/g. A schematic model involving two different types of surface area was previously proposed to account for the reversible and irreversible capacities measured vs. Li with these powders. We experimentally verified this model by means of differential scanning calorimetry (DSC) measurements. Transmission Electronic Microscopy (TEM), which is a powerful tool for the direct imaging of poorly organized materials at the atomic scale has been used, together with Raman Spectroscopy, to follow the disorganization generated by mechanical grinding.

Keywords: Lithium; Carbon; Mechanical-milling; TEM

1. Introduction

Recently, various types of disordered carbons have received considerable attention, due to their interesting high electrochemical capacities at low potential, allowing their use for anodes in lithium–ion rechargeable batteries [1]. Usually, these different types of carbonaceous materials are obtained by pyrolysis of organic precursors [2]. We recently reported a new way to prepare tailor-made carbon materials by mechanical grinding [3,4] (using two types of mechanical interactions: shock or shear). In addition, this new technique allows to prepare carbon samples able to reversibly intercalate two lithiums per six carbons (e.g., Li_2C_6) while having irreversible capacities of 320 mA h/g when the grinding is performed by shock mode. A schematic model involving two different types of surface area was proposed [3], and experimentally verified by differential scanning calorimetry (DSC) study [5] to account for the reversible and irreversible capacities measured in these powders.

As an attempt to understand the structural modifications induced by mechanical grinding, a Raman study has been performed. Herein, we show that the amount of disorder in ground samples strongly depends upon the nature of the interaction (shock or shear), and results in an increase in the I_D/I_G ratio in the case of shock grinding.

To really understand how the mechanical grinding locally affects our materials, they must be investigated at the quasiatomic scale, by means of Transmission Electronic Microscopy (TEM), which is a powerful tool for the direct imaging of poorly organized materials at the atomic scale. The evolution of the 002 lattice fringes displays different stages of disorganization depending upon the nature of interaction used (shock or shear interaction).

Moreover, we show that samples made by shock or shear interactions are of potential interest for battery and supercapacitors applications, respectively. Thus, the importance of selecting the right milling-mixer for tailor-made materials is highlighted.

2. Experimental

A classical lamellar graphite with sheet-type morphology (commercial name of F399) was mechanically ground

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in argon atmosphere by means of two types of mixer namely SPEX 8000 and FRITSCH P7 that generate normal mechanical strain (shock interaction) and tangential mechanical strain (shear interaction), respectively.

DSC scans were carried out on a Mettler apparatus at a hearing rate of 5°C/min from 30°C to 450°C under an argon flow. Multi-point BET surface area measurements are made using a Micromeritics Gemini II 2370 surface area analyser.

The Raman spectra of materials were recorded at room temperature using a computer driven triple monochromator Dilor Z24. An Ar-ion laser beam at the 514.5 nm line was used with a power of 50 mW in order to avoid any samples thermal degradation. The experiments were performed on powders using a microprobe device. The incident beam was focused into a spot size of 2 μm in diameter on a powder sample, and the laser power at the sample was about 2 mW.

High resolution imaging was made on a Philips CM20, with an excitation voltage of 120 kV, enabling a resolution of 0.144 nm.

All the electrochemical measurements were carried out using Swagelok laboratory test cells. A ''Mac Pile'' system operating in a galvanostatic mode was used to perform the measurements. Positive electrodes were prepared using Bellcore's dry plastic laminate technology, which consists in mixing milled samples with an organic binder PVDF (Aldrich), super P carbon black (SP) and dibutyl phtalate (DBP from Aldrich Chem.) dissolved in acetone (research grade). The cells were tested between 3 and 0 V at a constant current of C/10 vs. the nominal LiC_6 composition.

3. Results

3.1. Raman data

Figs. 1 and 2 show the evolution of Raman spectra vs. milling time for a graphite sample ground by shock interaction (Fig. 1) and by shear interaction (Fig. 2).

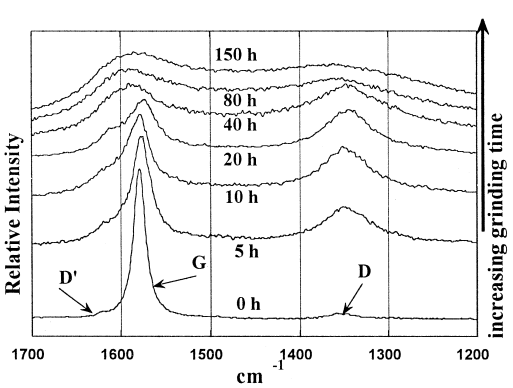

Fig. 1. Raman spectra of graphite ground using a shock-type grinding and at different milling times.

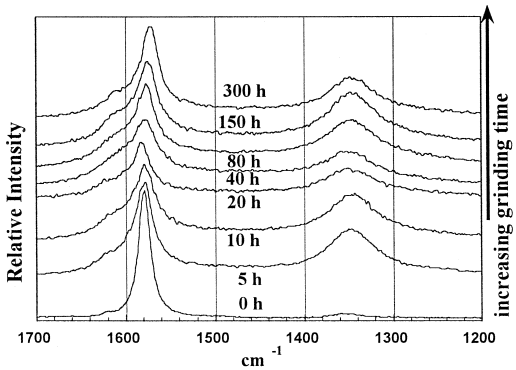

Fig. 2. Raman spectra of graphite ground using a shear-type grinding and at different milling time.

The unground graphite exhibits a single Raman band at 1580 cm^{-1} (namely G band), which corresponds to the E_{2g} vibration (C=C aromatic; C sp^2) while the ground samples present three bands at different intensity depending upon the type of interaction used, the first at about 1580 cm^{-1}, the second at 1620 cm^{-1} and another at ~1350 cm^{-1} (namely D band). These two last bands were previously ascribed to disorder and defects [6] and disappeared with the graphitization.

When a shock-type grinding is used (Fig. 1), the two bands at 1350 and 1620 cm^{-1} present at 5 h milling time, increase upon increasing milling time, while the 1580 cm^{-1} band vanishes in correlation with the onset of the disorder in our ground samples (as determined by X-ray diffraction). The band at 1620 cm^{-1} always changes in the same way as the defect band [7] at 1350 cm^{-1}.

When a shear-type grinding is used (Fig. 2), the 1580 cm^{-1} band decreases slowly in intensity, and is still present after 150 h milling time while the defect 1350 cm^{-1} band increases upon increasing milling times.

Fig. 3 compares the intensity ratio (I_D/I_G) for the shock and shear mixer-milled graphite as a function of the

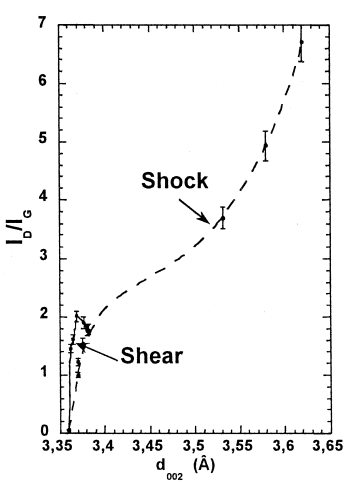

Fig. 3. Evolution of I_D/I_G in function of interaction used and d_{002}.

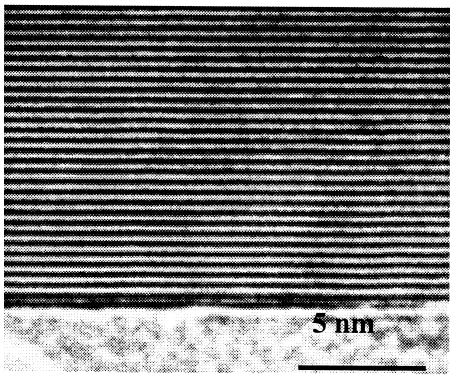

Fig. 4. 002 lattice fringe for the starting material.

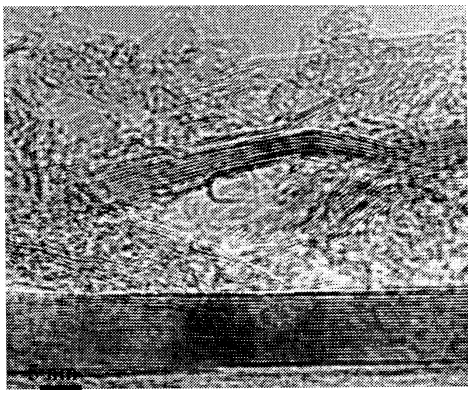

Fig. 6. 002 lattice fringe for graphite ground 80 h by shear-type grinding.

interlayer distance d_{002}. The relative intensity (I_D/I_G) where I_D is the area of the D band and I_G the area of the G band has been used to determine the carbon nature and its degree of graphitization degrees. The graphite samples ground by shock and having a large unorganized carbon amount, according to high value of d_{002}, exhibit a large intensity ratio (I_D/I_G). On the other hand, the graphite samples prepared by shear interaction exhibit a weak value of $d_{002} < 3.39$ Å for 300 h of milling time therefore a smaller value of intensity ratio (I_D/I_G). The materials are very disordered when shock-type grinding is used.

3.2. High resolution electron microscopy

Fig. 4 shows the 002 lattice fringes for an unground graphite. The layers are planar and perfect as normal graphite, which has been annealed at more than 2800°C, and without noticeable defect. What happens to carbon when it is energetically milled? For short milling times by shock grinding, the 002 lattice fringes visualization is not significant because the material is heterogeneous. At 80 h of milling time, the sample is homogeneous but has lost its graphitic nature (Fig. 5). The image shows small stacks of 2–3 parallel fringes less than 10 Å long forming small coherent domains namely BSU (Basal Structural Units). These latter are misoriented between them, and distributed at random to form mesopores. We do not observe any single layer. This material could compare to a saccharose coke prepared at 1000°C (non-graphitizing carbon) [8].

The shear-type grinding generates a weaker mechanical strain than the shock mode, and the samples are much less damaged with this grinding mode.

For example, at 80 h of milling time (Fig. 6), the structure and the texture are very different from those observed for a shock grinding (Fig. 5). The materials are very heterogeneous. The size of graphitic layers is five times larger than the number of stacked aromatic domains. The size of coherent domains is 2–3 stacked layers thick and 30 to 40 Å long while the BSUs for shock sample ground in the same condition (80 h) are formed of 2–3 parallel layers 10 Å long. The difference between these two materials (shock and shear treatments) is not a kinetics problem because the materials ground for 300 h by shear mode are always very heterogeneous constituted of large graphitic layers in disordered matrix.

3.3. DSC measurements

The DSC study [5] shows that it was possible to identify the reaction of the passivation layer products with electrolyte and Li_xC_6 by an exothermic peak at 140°C. Heat of

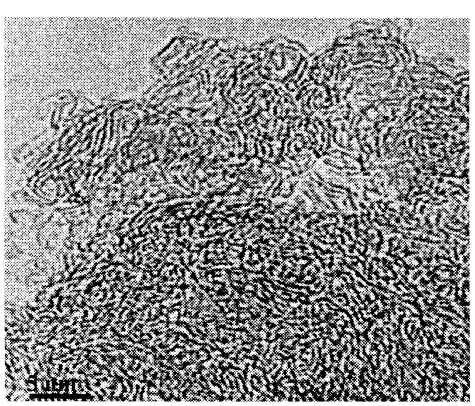

Fig. 5. 002 lattice fringe for graphite ground 80 h by shock-type grinding.

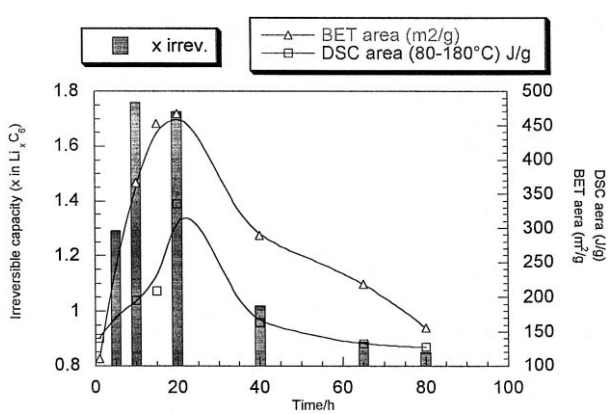

Fig. 7. Dependence of irreversible capacity, BET area and heat of interface reactions of delithiated milled carbons having various specific areas.

interface reactions was calculated from DSC traces in the 80°C–180°C range. These values were plotted together with the samples BET areas and the irreversible capacity vs. Li as a function of milling time for graphite ground by shock (cf. Fig. 7). The three curves were found to superimpose, within the accuracy of the measurements indicating the following correlation that is the higher the specific area, the higher the irreversible capacity (e.g., the higher amount of interface products) and thus a higher reaction heat per gram of electrode.

3.4. Electrochemical properties

Independently of the milling apparatus used (shock or shear), we observed upon increasing the milling time, a perfect correlation between irreversible capacity (x_{irrev}), BET area and specific capacitance (F/g) (Fig. 8). Different applications are possible for these ground materials. Samples ground by shock-type interaction are good candidates for batteries applications (Fig. 8a): the material ground for 80 h by shock interactions gives very good reversible capacities (1.76 Li for 6 C: twice the graphite reversible capacity). On the other hand, samples ground by shear-type interaction are good candidates for supercapacitors applications: high specific surface area of 680 m^2/g (300 h of shear milling (Fig. 8b), gives a high specific capacitance of 70 F/g.

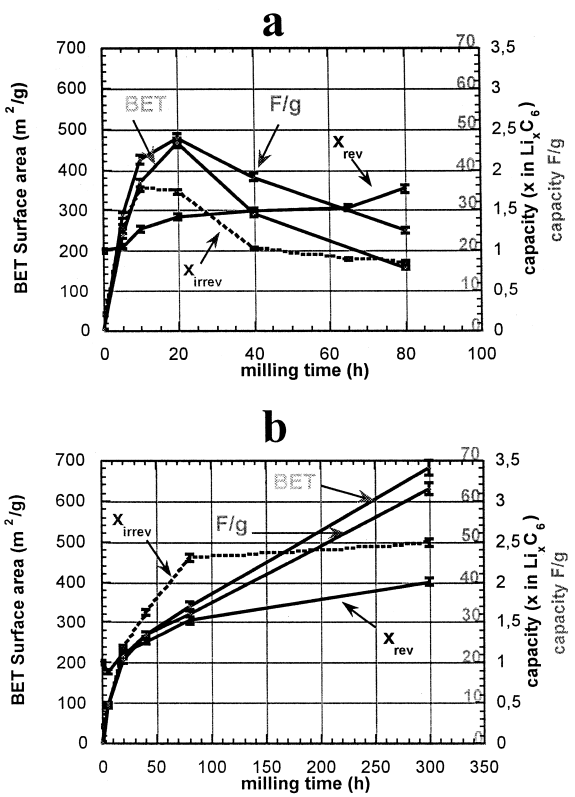

Fig. 8. Correlation between electrochemical capacities, specific capacitance and BET area for graphite ground by: (a) shock-type grinding, (b) shear-type grinding.

4. Discussion

Raman spectroscopy [9] and TEM [10] were used as powerful tools to investigate the effect of shock vs. shear type interactions on the degree of disorder, texture and structure in carbonaceous materials. The mechanical energy transferred depends on the interaction used, and is the largest for shock-type interactions.

For instance, on graphites, the shock-type grinding creates a large disorder as indicated by Raman studies (drastic increase in I_D/I_G ratio and broad lines at 1580 cm^{-1} as generally observed in non-graphitic or disordered carbon like glassy carbon, charcoal, etc.). On the contrary, with shear-type grinding, the graphitic nature of carbons is mainly preserved consistent with the linewidth of 1580 cm^{-1} that remains small.

Using TEM, our schematic model has been verified, and we have shown that the mechanical milling does not follow opposite stages to that of graphitization [8]. To confirm this point, the carbon ground 80 h by shock was annealed at 2800°C, and did not convert back to graphite. An explanation is to consider that the formation of the surface dangling bonds is possible during the milling by shock. These dangling bong will form a new bond between adjacent free bond to form a hard carbon-like structure.

By shock-type interaction, the heat amount released during the ball to powder interaction is small and an important part of the mechanical energy is transferred to the powder. In this case, three successive stages division–fracture–agglomeration can be deduced from the evolution of the BET surface area and the collected MEB micrographs [4]. In the first stage, e.g., at the beginning of milling time, the particles are reduced in size and the infinite number of graphene sheets, piled-up in a stack sequence ABABAB, decreases upon increasing milling time due to the weak interlayer bonding. In addition, the exfoliation of the graphene layer produces a slight increase in the d_{002} distance interlayer as shown by X-ray diffraction, and as confirmed by TEM [10]. The cumulated mechanical energy from the repeated shocks produces a high density of defects into the 002 planes, resulting in a decrease in the number of layers. The overall result being that the energy generated by mechanical milling is high enough to break the covalent bond within the graphene fringes. For long milling times, the ground powder having a large ratio of disorder and a large value of d_{002} is composed of BSU domains of 2–3 layers of 10 Å in diameter. This BSU domains are completely distributed at random as well as misoriented between them.

When a shear-type grinding is used, the carbonaceous materials obtained are much less disordered. The materials are very heterogeneous. The friction produces a lot of heat,

and only a small amount of mechanical energy is transferred into the powder. Upon increasing milling, the fringes number slightly decreases, and we observe a small exfoliation of the layers. The 80 h ground carbons present turbostatic disorder (observation of $hk0$ asymmetric peaks by X-ray diffraction), which is related by the 002 wrinkled layers. The mechanical energy transferred to this powder is not strong enough to generate a propagation fissure within the plane. The mechanism of disorganization generated by mechanical milling is different depending upon the interaction used as we have just seen.

Let us now discuss some of these results in conjunction with the electrochemical properties of these materials. Mechanical milling either shock generates a large ratio of disorder within the powder, which could permit to increase the number of lithium in the new disorder structure. Concerning the irreversible capacity, DSC measurements confirm that the formation of the passivation layer is linked to the carbon surface.

5. Conclusion

To conclude, we have reported the effect of mechanical milling on the structure and amount of disorder on carbonaceous materials. Depending upon the type of grinding used, energetic interactions of different intensity are generated allowing for a disorganization of the carbonaceous materials. TEM enables a direct visualisation of our schematic model which explained the physical and electrochemical properties of ground carbons. The powders ground by shock have high electrocapacitive performances, and are constituted of a disorder matrix with BSU domains. While the shear powders seem to be good candidates for supercapacitors.

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