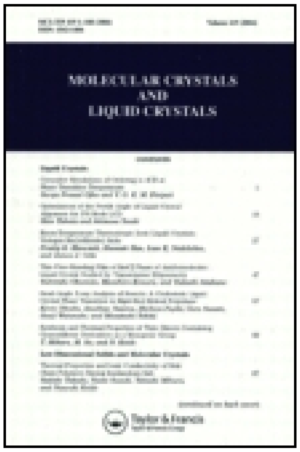

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Raman Study on Carbonaceous Materials Prepared by Mechanical Milling

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Raman study on carbonaceous materials prepared by mechanical milling

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Abstract
Through Raman spectroscopy studies, we show that mechanical grinding generates an increasing amount of unorganized carbon at a rate depending on the type of grinding mode used (Shear and Shock-type grinding). The first-order Raman spectrum for pure unground graphite has a well-known G sharp band at 1579 cm^{-1}, which corresponds to the E_{2g} vibration while the ground samples present a broadened G band accompanied by new components at about 1610 cm^{-1} (D'), 1510 cm^{-1} (D") and 1348 cm^{-1} (D), usually explained as arising from disorder and defects[1]. Shock-type grinding produces a faster disorder increase than shear-type grinding. The latter preserves part of the graphitic character. The general effect of mechanical milling remains however opposite to that of Thermal Treatment (Graphitization).

INTRODUCTION

Recently, various types of disordered carbons have received considerable attention, due to their interesting high electrochemical capacities, for anode in lithium-ion rechargeable battery[2]. Usually, these different types of carbonaceous materials are obtained by pyrolysis of organics[3]. We recently reported a new way to prepare tailor-made carbon materials by mechanical grinding[4,5]. By controlling the milling conditions (using shock or shear mechanical interactions), carbon powders with well-defined morphology, d-spacings, surface area and crystallite size can be made. In addition, this new technique allows to prepare carbon samples able to reversibly intercalate 2 lithiums per six carbon (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 to account for the reversible and irreversible capacities measured in these powders[3].

As an attempt to understand the surface modification induced by mechanical grinding, a Raman study has been performed. Such a technique has been used for quite a long time[6] to characterize carbonaceous materials. The width of the G band and the relative intensity ratio (I_D/I_G) where I_D is the area of the D band situated at about 1350 cm^{-1} and I_G the area of the G band, has successfully been used to determine the carbon nature and its degree of graphitization degrees[7,8].

In the present work, we show that the ratio of I_D/I_G in ground samples strongly depends upon the nature of the grinding interaction (shock or shear) and results in a strong increase in this ratio in the case of shock grinding. We also follow the evolution of disorder in different types of carbonaceous materials prepared by mechanical alloying and success in correlating our results with those of x-ray diffraction measurements (d-spacing d_{002})[3].

EXPERIMENTAL

A graphite with sheet-type morphology (commercial name F399), was mechanically ground 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[9]. Two different carbons (coke and SP black carbon) having a different ratio of disorder were ground only by shock interaction.

The Raman spectra were recorded at room temperature using a Omars 89 (Dilor) spectrometer equiped with a confocal microscope, a liquid nitrogen cooled CCD detector and the 514.5 nm line of an argon ion laser. The laser power was kept at about 1mW to avoid any thermal degradation of samples. With a 100x objective and a confocal hole of 500 μm, the analysed diameter was c.a. 5 μm. The spectral resolution was 3.6 cm^{-1}.

The 002 interlayer distance (d-spacing d_{002}) was obtained by x-ray diffraction using a Philips diffractometer PW 1710 with $Cu_{(k\alpha)}$ radiations (1.5418 Å).

Electrochemical measurements were carried out using Swagelok laboratory test cells by means of a "Mac-Pile" system[10].

RESULTS

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

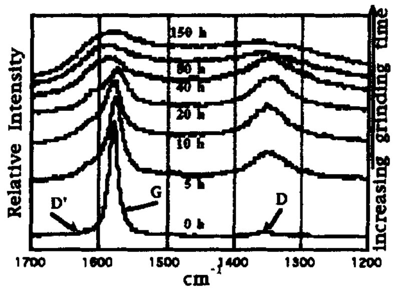

Fig.1 Raman spectra of graphite ground using a shock-type grinding and at different milling time.

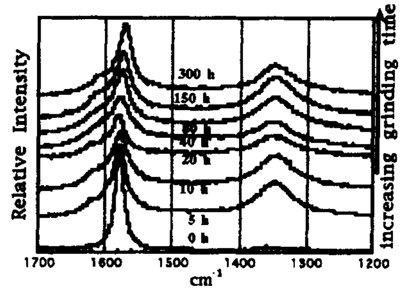

Fig.2 Raman spectra of graphite ground using a shear-type grinding and at different milling time.

In addition to a broadened G band which remains centered at about 1580 cm^{-1}, the ground samples present a D' band at 1610 cm^{-1} and a D band at about 1350 cm^{-1}. Fitting with lorentzian components reveals a fourth band at about 1510 cm^{-1} referred in the literature as D"[1]. So a minimum of four lorentzians components is needed to reproduce the experimental spectra of all ground samples. The spectral evolution as a function of shock or shear-type grinding time is however markedly different (figs 3,4) namely at high grinding times where shock-type grinding produces a strong and continuous increase of both I_D/I_G ratio and D bandwidth while both parameters remain constant for shear type grinding.

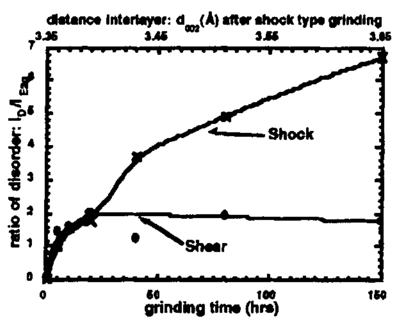

Fig.3 Evolution of the (I_D/I_G) ratio as a function of shock-type (crosses) and shear-type (circles) milling time. The d_{002} after shock-type grinding spacing is reported on top

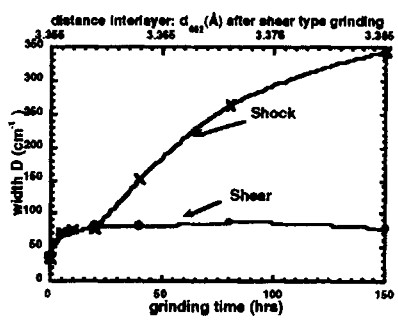

Fig4 Evolution of the D band width as a function of shock-type (crosses) and shear-type (circles) milling time. The d_{002} after shear-type grinding spacing is reported on top

This can be correlated to the measured increase of the d_{002} interlayer distance[3] and to the decrease of the microcristalline planar size L_a. The latter is usually evaluated according to the Tuinstra and Koenig's empirical relationship La=44*[I_G/I_D][11].

For short grinding time, shear-type grinding leads to the same changes as

shock type at short times (t<20h) but a steady state is then reached. The d_{002} value has indeed shown to remain smaller than 3.4 Å even after long milling times. On the other words, the major modifications of shear-type grinding take place during the first 10 or 20 hours and further grinding does not change any more the graphite character of the samples.

We have compared the evolution of Raman spectra as a function of milling time for carbons having a different ratio of initial disorder. The Raman spectra for unground and 80 hours ground carbons are shown in figures 5 and 6, respectively.

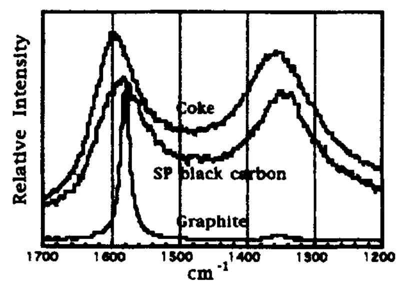

Fig.5 Raman spectra of different type of unground carbons: graphite, soft carbon (coke) and black carbon (SP).

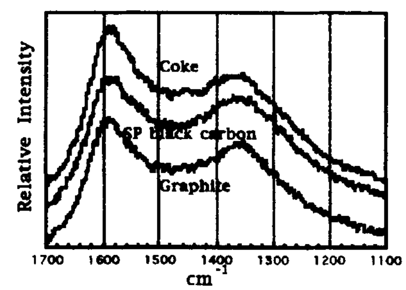

Fig.6 Raman spectra of different type of carbons: graphite, soft carbon (coke) and black carbon (SP) which have been ground by shock-type grinding at 80 hours of milling time.

Independently of the ratio of the disorder in the precursors, we note, as expected, that the degree of disorder of the carbonaceous materials increases upon grinding.

Electrochemical testing

The mechanical milling made disordered carbonaceous materials which were recently shown to exhibit high electrochemical capacities vs. lithium, so that they are presently considered as alternative anode in lithium-ion rechargeable batteries. Indeed, 2 Li per 6 C were reversibly intercalated in carbonaceous materials made by means of shock-type interaction, while graphite only intercalate 1 Li for 6 C.

Figure 7 shows the striking similarity between charge/discharge electrochemical curves of the three carbons (graphite, coke and SP) ground for 80 hours by shock-type interaction. Independently of the nature of the precursor, the mechanical milling allows to disorganize the carbons and to obtain materials which are good electrochemical properties

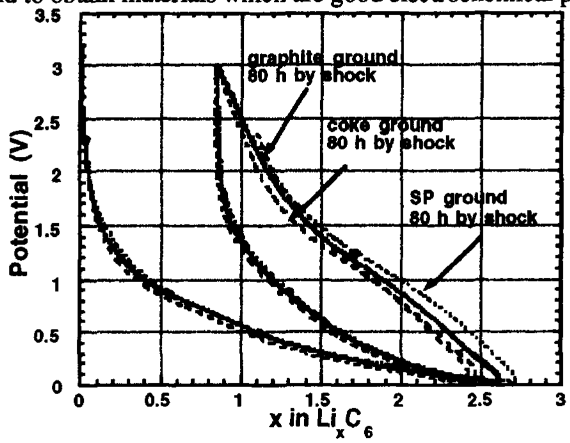

Fig. 7 The Voltage vs. composition profile is shown for carbon/Li cells between 0.005 and 3V using carbon milled powders from different carbon precursors. All the powders were ground for 80 hours by shock-type grinding.

Conclusion

Raman Spectroscopy was used as a powerful tool to investigate the effect of shock vs shear-type interactions on the degree of disorder in carbonaceous materials. During the 20 first hours, the two types of grinding produce very similar changes in the I_D/I_G ratio and in the D bandwidth taken as spectral probes of the degree of disorder. For longer times, the disorder keeps increasing by shock but does not seem to vary any more by shear. So, with the mechanical milling approach combined with a wise choice of ball-powder interaction, we are able to prepare different types of carbons with an amount of disorder on demand and thereby of well defined electrochemical properties vs lithium. Moreover, we show that the mechanical milling increases the degree of the disorder independently of the ratio of the disorder of the precursors.

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