

Synthesis and Structural Characterization of Carbon Powder by Electrolytic Reduction of Molten Li₂CO₃-Na₂CO₃-K₂CO₃

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A new method was proposed for the preparation of carbon powders based on the electrochemical reduction of a fused eutectic mixture of lithium-sodium-potassium carbonates at 450°C. Transmission electron microscopy observations have revealed the presence of three forms of carbon in the powder samples depending on the deposition potential values: amorphous carbon, graphite, and fibers. The presence of graphite and amorphous carbon was confirmed by X-ray diffraction measurements. The d_{002} values were rather constant whatever the sample and close to 0.34 nm. Moreover, surface analyses by X-ray photoelectron spectroscopy revealed the presence of nearly metallic and ionic lithium belonging to lithium oxides. The specific areas were measured by the Brunauer-Emmett-Teller (BET) method. Whatever the deposit potential values, the total BET specific surface area is much higher than that corresponding to external one because of the pore walls contribution. It has been shown that, for carbon powder dried at 400°C under vacuum, the specific surface area decreased as the deposition potential became more cathodic: from about 850 m² g⁻¹ at -2.4 V vs. CO₂-O₂ to about 500 m² g⁻¹ at -6.0 V vs. CO₂-O₂. With increasing negative values of the potential, the nucleation and the growth of carbon competes with the formation of nearly metallic lithium and/or lithium oxides. The presence of the latter induces the closure of some nanopores.

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Carbonaceous materials are extensively used in electrochemical processes.¹ For example, carbon is used as anodes during the electrolysis of molten KF-2HF for the preparation of fluorine,² in rechargeable lithium-ion batteries,³⁻⁶ and in supercapacitors.⁷

Several varieties of carbon, from highly crystalline graphite to strongly disordered carbons, are commercially available. The use of carbon materials depends on their structural characteristics; for example, graphite cannot be used as anode material for the electrolytic preparation of fluorine since exfoliation occurs. However, many types of carbon have been tested as alternative anodes for rechargeable lithium batteries: graphite,^{5,8-10} carbon nanotubes,¹¹ disordered soft (graphitizable),¹² hard carbons (ungraphitizable),¹³ etc. The use of such carbon anodes allows prevention of the well-known problem of dendritic shape of metallic lithium deposited during charge steps. In that specific example, graphite is still one of the most desirable candidates in lithium-ion batteries due to its excellent intercalation properties: good electric conductivity, low irreversible capacity, and low electrochemical voltage vs. Li/Li⁺. Its structure is formed by planar carbon layers stacked with a sequence of the type ABABAB... This particular lamellar structure is particularly well adapted to the intercalation of lithium occurs between the carbon sheets.

Except natural graphite, carbon can be obtained by pyrolysis of organic compounds. This reaction which takes place at temperatures up to 1000°C can be followed by a calcination at 1600°C for removing gases included into the crystalline structure. Carbon can also be obtained by chemical vapor deposition from the thermal decomposition of hydrocarbons. Carbon coatings or carbon with special electrochemical properties can also be obtained by an electrochemical route.¹⁴⁻¹⁸ Recently, Kawamura and Ito¹⁸ studied the electrodeposition of carbon films on aluminum in fused LiCl-KCl-K₂CO₃ at 500°C. These authors have shown that, depending on the electrolytic conditions, the morphology and the cohesiveness of the deposited carbon film are changed. The electrochemical reaction involved dur-

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ing the deposition of carbon is the reduction of the carbonate ions, and therefore, the amount of carbon obtained is strictly dependent on the carbonate ion content.

In the present work, a new approach is proposed based on the deposition of carbon powder by electrolytic reduction of the liquid ternary system Li_2CO_3 - Na_2CO_3 - K_2CO_3 at 450°C. This reduction process could give rise to substantial deposits of carbon powder.¹⁷ The reaction mechanism is briefly discussed based on the analysis of cyclic voltammograms (CVs) depending on the electrode substrate (carbon and nickel). Structural characteristics of the carbon powders, performed by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) are presented. Finally, the specific surface area and the pore texture of the carbon powder samples are determined by nitrogen gas adsorption using the Brunauer-Emmett-Teller (BET) method.

Experimental

The electrochemical cell is described in Fig. 1. The electrolyte was composed of the eutectic mixture of 43.5 mol % of Li_2CO_3 , 31.5 mol % of Na_2CO_3 , and 25 mol % of K_2CO_3 (Prolabo R. P. Normapur). The constituent salts were previously dehydrated under



Figure 1. Electrochemical cell used for the deposition of carbon.

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Figure 2. (a) Voltammograms at a GC electrode at 450°C in Li₂CO₃-Na₂CO₃-K₂CO₃. Sweep rate: 0.1 V s⁻¹. $S \approx 5$ cm². Reference electrode: CO₂-O₂/CO₃²⁻. Marks on the voltammograms during the reduction step correspond to the limit of the potential window. (b) Voltammograms at a nickel electrode at 450°C in Li₂CO₃-Na₂CO₃-K₂CO₃. Sweep rate: 1 V s⁻¹. $S \approx 0.4$ cm². Reference electrode: CO₂-O₂/CO₃²⁻.

vacuum at 150°C and slowly heated to 450°C under a carbon dioxide atmosphere to prevent the rapid decomposition of the melt.¹⁹

The cell is made of an outer Pyrex envelope at the base of which was an alumina (Degussa) crucible as described in Ref. 20. During each experimental, run carbon dioxide was kept flowing through the cell. The mechanism of the carbon deposit on a rod of glassy carbon (GC, V25 Le Carbone Lorraine, France) and nickel (Weber Métaux, France) electrodes was studied by cyclic voltammetry (v = 0.1 V s⁻¹) using a Tacussel PRT 20-10X potentiostat.

The reference electrode was constituted of a gold wire placed in an alumina tube containing molten Li₂CO₃-Na₂CO₃-K₂CO₃.²¹ A



Figure 3. SEM micrograph of sample 3.

mixture of dry $CO_2:O_2$ (2/3:1/3) gases was maintained above the solution to have an atmosphere in equilibrium with the melt. A small hole in the bottom of the tube allows the ionic contact. This reference electrode is denoted CO_2-O_2/CO_3^{--} ; all potentials are referred to that reference, henceforth. The counter electrode was a sheet of gold.

The XRD patterns of carbon powders were obtained using a Shimadzu XD-610 X-ray diffractometer with Cu K α radiation ($\lambda=1.54178$ Å) and a nickel filter. XPS analysis using a Ulvac-Phi model 5500 spectrometer with a Mg K α excitation source was performed in order to determine the chemical interaction between carbon, lithium, and oxygen. The spectrometer was calibrated with copper at binding energies 75.1 and 932.6 eV for Cu $3p_{3/2}$ and Cu $2p_{3/2}$, respectively.

TEMs were obtained with a JEOL JEM 100 CX II transmission electron microscope equipped with a JEOL high resolution scanning attachment (STEM-SEM ASID 4D) and an energy dispersive X-ray detector (Li-doped Si with an ultrathin window).

SEM images were obtained with a Leica S 440 camera.

The specific area of carbon samples were deduced from nitrogen adsorption experiments (BET method) at boiling temperature (77 K).



Figure 4. XRD patterns of samples 2, 3, and 4.

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Table I. Values of the interlayer distance, d_{002} , between adjacent graphene sheets in graphite deduced from XRD patterns.

| Substrate | Samples | <i>d</i> ₀₀₂ (nm) |
|-----------|---------|------------------------------|
| Nickel | 2 | 0.337 |
| | 3 | 0.339 |
| Carbon | 4 | 0.335 |
| | 5 | 0.339 |

Results and Discussion

Mechanism of carbon deposit in fused alkali carbonates.—The mechanism of carbon deposition, partially reported elsewhere,¹⁷ is studied briefly hereafter from the analysis of CVs. A typical CV obtained with a GC electrode in carbonate melts is presented in Fig. 2a. The electroactivity range is about 2.7 V wide. The cathodic limit^{17,22} corresponds to the reduction of carbonate ions into carbon and oxide ions

$$CO_3^{2-} + 4e^- \rightarrow C + 3 O^{2-}$$
 [1]

The formation of lithium carbide compounds is also highly probably and is associated to that of lithium oxide anions according to the following reaction

$$Li_2CO_3 + (2x - 1)C + 6e^- \rightarrow 3 O^{2-} + 2LiC_x$$
 [2]

with $1 \le x \le 60$.

In contrast with the CVs obtained from other metallic substrates,¹⁷ no reduction peaks were observed before the cathodic limit was reached. It means that, in the accessible potential range, GC remains an inert material which is not involved in the electrochemical reaction.

The anodic limit corresponds to the oxidation of carbonate ions into carbon dioxide and oxygen according to

$$2\text{CO}_3^{2^-} \rightarrow 2\text{CO}_2 + \text{O}_2 + 4\text{e}^-$$
 [3]

The oxidation peak observed at -0.4 and +0.2 V were attributed to the oxidation of the deposited carbon^{17,23}

$$2 \text{ O}^{2^-} + \text{C} \rightarrow \text{CO}_2 + 4\text{e}^- \qquad [4]$$

$$C + 2CO_3^{2-} \rightarrow 3CO_2 + 4e^-$$
 [5]

and to the oxidation of the LiC_x compounds formed during the reduction step (Reaction 2). When the cathodic limit of the potential sweep became more and more negative (Fig. 2), the intensities of the two oxidation peaks increased in the same manner. It confirms that these peaks are due to the oxidation of carbon and of LiC_x compounds.

In the case of nickel electrodes, the electroactive range is around 1.5 V wide (Fig. 2b). The two peaks related to the oxidation of the carbon deposit according to Reactions 4 and 5, and to the oxidation of the LiC_{x} compounds formed during the reduction step (Reaction

Table II. Results of XPS investigations on deposited carbon powder samples. The carbon, oxygen, and lithium contents were calculated from the intensity of the photoelectron peaks of Li 1s, O 1s, and C 1s peaks (surface area under each peak), respectively, displayed from the survey spectra.

| Samples | C 1s (%) | O 1s (%) | Li 1s (%) |
|---------|-------------|-------------|--------------|
| 1 | 85.3 | 7.5 | 7.2 |
| 2 | 83.1 | 6.2 | 10.7 |
| 3 | 73.0 | 15.8 | 11.2 |
| 4 | 88.5 | 7.7 | 3.8 |
| 5 | 76.2 | 11.0 | 12.8 |

2) were observed, as in the case of a deposit on a GC electrode. The anodic limit corresponds to the oxidation of nickel. Indeed, in oxidizing atmosphere, the oxidation of carbonate ions interferes with the nickel oxidation. As proposed by several authors,²⁴⁻²⁸ one can assume that NiO appears at the surface of the nickel electrode according to the reactions

$$Ni \rightarrow Ni^{2+} + 2e^{-}$$
 [6a]

and

$$Ni^{2+} + CO_3^{2-} \rightarrow NiO + CO_2$$
 [6b]

The overall reaction of nickel oxidation can be written

$$Ni + CO_3^{2-} \rightarrow NiO + CO_2 + 2e^{-}$$
 [6c]

It explains shoulders on the previous oxidation peaks (Reactions 2, 4, and 5) observed in Fig. 2b.

Pure stoichiometric NiO is an insulator. However, lithium ions present in the electrolyte can be incorporated into the NiO structure to form an electronic conductor Li-Ni-O.^{27,28} Therefore, during the reduction step, the peaks ascribed to the reduction of nickel oxide and/or Li-Ni-O compounds, and to the intercalation of lithium inside NiO were also observed.

During the potentiostatic deposition of carbon on GC and nickel electrodes, an increase of the current during the electrolysis was generally observed. This phenomenon was attributed to the increase in the electroactive surface of the electrode due to the formation of a carbon deposit. After electrolysis of molten Li₂CO₃-Na₂CO₃-K₂CO₃, the deposited carbon powders were immersed into hot water. After immersion, the hard gray carbon deposit is disintegrated. In fact, solidified salt constitutes about 90% of the total deposit, the remainder being the carbon. As described in Reaction 2, the formation of lithium carbide and lithium oxide competes with that of carbon. It is well known that lithium carbide strongly reacts with water to give lithium hydroxide and acetylene. Therefore, the gas evolution observed during the washing procedure of carbon powder deposited at potential values lower than -1.8 V is probably due to the decomposition of lithium carbide. The titration of the aqueous washing solution by hydrochloric acid coupled with atomic

Table III. Results of XPS investigations on deposited carbon powder samples. Fitting parameters of C 1s region: BE, FWHM peak height, and relative contributions of each group in the sample (I_i) .

| | | Sample 2 | | | Sample 3 | | | Sample 4 | | | Sample 5 | | |
|-----------------|------------|--------------|-------------|------------|--------------|-----------|------------|--------------|------------------------------|------------|--------------|------------------------------|--|
| Chemical States | BE (eV) | FWHM (eV) | I_{i} (%) | BE (eV) | FWHM (eV) | I_i (%) | BE (eV) | FWHM (eV) | <i>I</i> _i (%) | BE (eV) | FWHM (eV) | <i>I</i> _i (%) | |
| C—C | 284.3 | 1.4 | 49.8 | | | | 284.5 | 1.4 | 47.6 | - | - | - | |
| C=0 | 285.5 | 3.0 | 33.9 | 285.5 | 1.8 | 93.3 | 285.6 | 3.0 | 30.7 | 285.6 | 1.8 | 93.7 | |
| -COOH | - | - | - | 287.1 | 1.4 | 3.9 | - | - | - | 287.3 | 1.4 | 3.6 | |
| $-CO_{3}^{2-}$ | 288.8 | 3.1 | 13.3 | 288.9 | 1.5 | 2.8 | 288.5 | 3.1 | 16.6 | 288.9 | 1.5 | 2.7 | |
| Satellite | 291.7 | 2.2 | 3.1 | - | - | - | 291.7 | 2.2 | 5.1 | - | - | - | |

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absorption analysis of the solution have also shown that the solidified salt is not only composed of alkali carbonates but also of lithium oxide.¹⁷

Analysis of the carbon deposit.—The carbon deposits were analyzed using several techniques such as XRD, XPS, TEM, SEM, and BET. No significant difference was pointed out between the powder deposited on nickel and GC electrodes. Therefore, the results obtained for carbon deposited on nickel or GC will be presented alternatively henceforth.

The influence of the potential applied to the working electrode on the nature of the deposited carbon powders was studied. Hereafter, the different samples were numbered as follows

- 1: Carbon deposited on nickel at E = -1.6 V
- 2: Carbon deposited on nickel at E = -2.4 V
- 3: Carbon deposited on nickel at E = -6.0 V
- 4: Carbon deposited on GC at E = -2.4 V
- 5: Carbon deposited on GC at E = -6.0 V.

After deposition, the carbon powders were washed in hydrochloric acid in order to remove traces of electrolyte, and dried under vacuum at 400°C.

Structural characterization by SEM.—The morphology of the carbon deposits, studied by SEM, does not seem to depend on the values of the applied potential, because the size of the particles is roughly the same whatever the sample. As an example, Fig. 3 represents a typical SEM image of carbon deposit (sample 3). It is comprised of very fine and "quasi-spherical" particles which are aggregated on the image. The size of one particle is less than 100 nm.

Structural characterization by XRD.—The X-ray diffraction patterns of samples 2-4 are presented in Fig. 4. For samples 2 and 3, the bump observed at $2\theta \approx 20^{\circ}$ is characteristic of amorphous carbon. For sample 3, the XRD pattern was recorded between 15 and 100° to identify all the peaks. In spite of the presence of amorphous carbon, the well-defined peaks related to all the diffraction lines of graphitized samples were observed. For sample 4, the sharp shape of the (002) peak and the lower intensity of the bump at $2\theta \approx 20^{\circ}$ related to the presence of amorphous peak indicate that the carbon powder is much more crystallized on a carbon electrode (sample 4) than on a nickel electrode (samples 2 and 3).

The crystallinity of all these samples is also attested by the value of the interlayer distance, d_{002} , deduced from the Bragg relation; whatever the sample, these values (Table I) are close to the theoretical value obtained in the case of pure graphite, *i.e.*, 0.335 nm. However, the d_{002} values slightly increase with increasing negative potential values in fused alkali carbonates. That means that the crystallinity of the carbon particles formed at low negative potential values (samples 2 and 4) are slightly higher than that obtained at high negative potential values (samples 3 and 5).

Surface characterization by XPS.—XPS is a suitable technique for studying the elemental composition of surface layers through the analysis of electron core level peaks.

Analysis of the C, Li, and O contents.—The content of lithium, oxygen, and carbon in a sample was calculated from the intensity of the photoelectron peaks of Li 1s, O 1s, and C 1s peaks (surface area under each peak), respectively, displayed from the survey spectra. The values of the peak areas were calculated by including the sensitivity factor corresponding to each element: 0.25 (lithium), 0.711 (oxygen), and 0.296 (carbon). The results reported in Table II were obtained with samples 1-5. As shown above, the lithium content in the carbon deposit is dependent on the potential values applied to the electrode for the electrolysis of molten Li₂CO₃-Na₂CO₃-K₂CO₃: more negative deposition potentials resulted in an



Figure 5. XPS analysis. High resolution spectra of C 1s region of (a) sample 2 and (b) sample 3. High resolution spectra of (c) O 1s and (d) Li 1s regions of sample 2.

increasing lithium and oxygen content (formation of lithium oxide), and a decrease of carbon content of the deposit. Moreover, for a same deposit potential value, the nature of the substrate has a small influence on the carbon, the oxygen, and the lithium contents.

| | Sample 2 | | | Sample 3 | | | Sample 4 | | | Sample 5 | | |
|--|------------|--------------|------------------------------|------------|--------------|------------------------------|------------|--------------|------------------------------|------------|--------------|------------------------------|
| Chemical States | BE (eV) | FWHM (eV) | <i>I</i> _i (%) |
| Nearly metallic | 51.5 | 1.5 | 68.8 | - | - | - | 51.7 | 1.5 | 66.9 | - | - | - |
| Li ₂ O | 53.6 | 2.3 | 31.2 | 53.0 | 2.0 | 83.3 | 53.4 | 2.3 | 33.1 | 52.9 | 1.8 | 83.7 |
| Li ₂ CO ₃ and LiOH | - | - | - | 55.6 | 2.0 | 16.7 | - | - | - | 55.3 | 1.9 | 16.3 |

Table IV. Results of XPS investigations on deposited carbon powder samples, and fitting parameters of the Li 1s region. BE, FWHM peak height, and relative contributions of each group in the sample (I_i) .

Analysis of high resolution spectra of the C 1s region.—XPS individual curve fitting parameters of the C 1s region [binding energy (BE) full width at half maximum (FWHM) peak height, and relative contribution of each group in the same sample, I_i] for samples 2-5 are given in Table III. The detailed analysis of the high resolution spectra of C 1s regions for samples 2 and 3 are presented in Fig. 5a and b, respectively. The main peak observed in the C 1s region for sample 2 (Fig. 5a) at 284.3 eV (FWHM = 1.4 eV) is attributed to C—C bonds.²⁹ For samples 3 and 5, the C 1s peaks shift toward higher BE (Fig. 5b); in that case, the main peak located at 285.5 \pm 0.1 eV (FWHM = 1.8 eV) is resolved into one peak ascribed to carbon-oxygen double bonds.²⁹ The peak situated around 288.7 \pm 0.2 eV is related to -COOH surface groups. An additional peak is also observed at 288 \pm 0.2 eV due to the presence of C—O bonds into lithium carbonate.³⁰ In addition, a small plasmon satellite is also visible at 291.0 eV.

Analysis of high resolution spectra of the O 1s region.—The detailed analysis of the high resolution spectra of O 1s regions of sample 2 is presented in Fig. 5c. The O 1s region consists of three contributions. The peaks indicating at 531.4, 533.0, and 535.3 eV are attributed to carbonyl groups²⁹ [denoted (C—O)_a in Fig. 5c] and/or Li-O bonds in LiOH,³⁰ to hydroxyl groups²⁹ [denoted (C—O)_b in Fig. 5c], and to H₂O adsorbed,³¹ respectively.

Analysis of high resolution spectra of the Li 1s region.-XPS individual curve fitting parameters of the Li 1s regions (BE and FWHM peak height, relative contribution of each group in the same sample, I_i) for samples 2-5 are given in Table IV. For example, Fig. 5d gives the high resolution spectrum of the Li 1s region for sample 2. The Li 1s region is composed of two contributions at BE = 51.5 and 53.6 eV. The first one is ascribed to nearly metallic lithium,³⁰ the second one to ionic lithium due to the presence of Li₂O.³⁰ From the analysis of the Li 1s region, the relative contribution of ionic lithium (Li2O) and nearly metallic lithium in each sample were also compared. It was found that the first one drastically changes from 31.2 to 83.3% with an increase of the negative potential values from -2.4 to -6.0 V. Indeed, the formation of lithium oxides (Reaction 1) competes with the formation of nearly metallic lithium and/or lithium carbide (Reaction 2). In the case of samples 3 and 5, the peak located at 55.3 eV is related to the presence of Li into LiOH and Li₂CO₃;³⁰ the latter is also detected in the C 1s region.

Structural characterization by TEM.—The TEM micrographs of sample 5 are presented in Fig. 6a-b. As observed by SEM (Fig. 3), the electrolysis of molten Li₂CO₃-Na₂CO₃-K₂CO₃ provides carbon bundles with particle size between 20 and 50 nm. Some of them were comprised of amorphous carbon (Fig. 6a). Others were surroundered by graphitized layers with a random orientation (Fig. 6b), as in the case of carbon black.³² The fringe spacing deduced from Fig. 6b is about 0.34 nm and is very similar to the theoretical distance between adjacent graphene sheets, d_{002} , in graphite and to that deduced from XRD analyses (Table I). In addition, in the case of carbon deposited on nickel electrodes, very well crystallized particles embedded in the carbon and surroundered by graphite, were also observed as illustrated in Fig. 6c for sample 3. The whole internal available space in the "holes" previously observed in Fig. 6b is now occupied by nickel particles. Such a phenomenon was already observed, for example, during the preparation of carbon from a gaseous phase (CO, CH4...) in presence of a nickel catalyst;³² in that example, depending on the temperature and the concentration of the gases, the metallic catalysts were surroundered by carbon shells instead of giving rise to carbon filaments. Another example is the crystallization, at moderate temperature, of carbon atoms during the thermal decomposition of metal carbide such as silicon or vanadium carbides.^{33-35^t} In our case, the chemical composition of these particles was determined from the X-ray spectrum presented in Fig. 6d. These particles were composed of nickel which could act as catalyst for the formation of graphite. However, one must notice that only few particles were detected by this technique. It explains why they were not detected by XPS or by XRD (<1 % wt).

TEM analyses have also revealed the presence of carbon fibers as presented in Fig. 6e for sample 1. The fibers have a diam of ~ 10 nm and a nearly uniform size, and were self-organized into long crystalline "ropes." The diameter of a rope is between 50 and 100 nm, which correspond to 5-10 tubes per rope.

Surface and pore texture analysis.—The method developed by Brunauer, Emmett, and Teller in the 1940s^{36,37} is a powerful and widely used tool to access to the surface characteristics and the porous texture of a powder material.³⁸ Thus, the total BET specific area and the external surface area, as well as the micropore area and volume, the average pore diameter of the deposited carbon powder were measured by nitrogen gas adsorption at boiling temperature (77 K). It is very important to understand the morphological parameters of carbon powders and their electrochemical behavior when they are used, for example, as anode material in lithium-ion batteries or in supercapacitors.

All the powder samples were degassed prior to the BET measurements to remove traces of moisture. Figure 7 gives the influence of the applied potential on the above parameters. Whatever the potential values, the total BET specific surface area is higher than that corresponding to the external one because of the pore walls contribution. Pores can have a regular or, more commonly, an irregular shape. Usually, three geometric forms are used to represent pore shape: cylinders (in some oxides like alumina and magnesia), slits (in active carbon and clays), and voids between connected solid spheres (in silica and many solids obtained from gels).³⁸ According to the results obtained from TEM and XRD analyses showing the presence of graphite, the pore shape of the carbon powder can be represented by slits, i.e., lamellar structure. This representation explains the high values of the micropore area compared to the external one. For example, in the case of sample 4, the micropore and the external areas are about 649 and 169 m² g⁻¹, respectively.

The surface area decreases dramatically with decreasing potential values; for sample 4, the BET specific surface area is about 850 m² g⁻¹ and reaches a value of around 500 m² g⁻¹ when the deposition potentials are made more negative (sample 5). As discussed above, for very negative values of the deposit potential, the formation of lithium and/or lithium oxides competes with the formation of graphite. Therefore, the nucleation and the growth of graphite should be affected greatly by very negative potential values, as



Figure 6. TEM images of (a,b) sample 5, (c) sample 3, and (e) sample 1. (d) X-ray emission spectrum of the particles observed in Fig. 6c.



Figure 7. Results of the nitrogen gas adsorption at boiling temperature (77 K) using the BET method for samples 4 and 5.

proved by the increase of the d_{002} values observed for samples 3 and 5. The evolution of the BET surface area can result from: (*i*) a decrease of the amount of graphite phases; and (*ii*) an increase of the lithium content as revealed by XPS (Table II) that results in the closure of some nanopores. Finally, a small decrease of the average pore diameter is observed when the potential applied to the electrode for the deposition of carbon is more negative: from 3.25 nm for sample 4 to 3.06 nm for sample 5.

Conclusion

An original electrochemical route for the preparation of carbon powders has been proposed based on the deposit of carbon powder by electrolytic reduction of the liquid ternary system lithiumsodium-potassium carbonates at 450°C. This reduction process could give rise to substantial deposits of carbon powder.¹⁷ Carbon powder has been deposited on nickel and GC electrodes from the electrochemical reduction of carbonate ions in a fused eutectic mixture of lithium, sodium, and potassium carbonates. The analysis of the reaction mechanism has been obtained from CVs. The reduction of carbonate ions gives rise not only to a carbon deposit but also to oxide ions and lithium carbide. Moreover, in the case of carbon deposited on nickel electrodes, the formation of nickel oxide containing small traces of lithium was also taken into account to get a better interpretation of the CVs.

After washing in HCl solutions and drying at 400°C to remove traces of water, the structural characterization of the carbon powders was performed. TEM analyses have revealed the presence of three forms of carbon depending on deposit potential values: amorphous, graphite, and fibers. The fibers have a nearly uniform size with a diam of ~10 nm, and are self-organized into long crystalline ropes. For increasing negative potential values, graphite was formed preferentially to amorphous carbon. XRD analyses give rise to the distance between adjacent graphene sheets, d_{002} , using the Bragg relation. Whatever the sample, this value is very close to the theoretical value of about 0.34 nm.

Surface analysis by XPS measurements have also revealed the presence of nearly metallic and ionic lithium in the carbon lattice. The latter is due to Li_2O , LiOH and/or Li_2CO_3 .

Finally, the carbon powders prepared in our experimental conditions exhibit large BET specific surface areas due to the presence of graphite. This surface area decreases with increasing negative deposit potential values. Finally, the total BET specific surface area is mainly due to the micropore area because of the pore walls contribution.

This work is a prelude to the study of the kinetics of the lithium cations insertion/deinsertion reaction into the carbon powders as prepared depending on the potential values for the deposit of the carbon powders into fused carbonates and on the temperature of the heat-treatment after washing in HCl.

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