On the correlation among surface chemistry, 3D structure, morphology, electrochemical and impedance behavior of various lithiated carbon electrodes

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Abstract

This work relates to a rigorous study of the correlation among surface chemistry (FTIR, XPS), 3D structure (X-ray and neutron scattering), morphology (SEM, AFM), and electrochemical and impedance behavior of lithiated carbon electrodes in commonly used liquid electrolyte solutions. Four different types of carbons were explored in a single study. These included, for comparison, two types of disordered carbons, single-wall carbon nanotubes (SWNT), and synthetic graphite powder as a reference system. All four types of carbons develop a similar surface chemistry in alkyl carbonate solutions which is dominated by solvent reduction. The differences in the 3D structure of these carbons leads to pronounced differences in the mechanisms of Li-insertion into them. The effect of the carbons' 3D structure on the solid-state diffusion of Li-ions is demonstrated and discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

An initial characterization of newly synthesized electrode materials designed for rechargeable Li batteries usually implies the following routines: (1) determination of the total and irreversible specific capacities of these materials; (2) analysis of the shape of the corresponding charging and discharging curves for purposes of separation between the different stages of Li-insertion/deinsertion process; (3) characterization of the above separate stages by a variety of electroanalytical techniques; (4) studies of the correlation between the 3D crystallographic structure, surface chemistry, and electrochemical behavior of these materials; (5) improvement of cyclability and the whole electrode performance on the basis of the detailed understanding of the Li-intercalation mechanisms. This paper briefly describes a comparative study of several types of carbonaceous anodes for Li-ion batteries with the emphasis on the correlation between structures and electroanalytical responses.

2. Experimental

Graphite powders from Timcal Inc., two disordered carbons denoted as NX-1 and NX-4 from Mitsubishi Inc., SWNT from Rice University, and ready to use, Li battery grade electrolyte solutions from Merck KGaA, have been used. The disordered carbons were produced by heat treatment of coal tar pitch (1100 and 700°C), and differ from each other by the H/C ratios of 0.04 and 0.13 for NX-1 and NX-4, respectively. The preparation of composite carbon electrodes and the performance of their FTIR, XPS, morphological, electrochemical, and impedance measurements were already described [1]. SWNT can be used as received ("bucky paper" [2,3]), or in composite electrodes. The performance of the 3D analysis by diffraction methods is described in [4]. Disordered carbon NX-1 exhibits a higher degree of order than NX-4. (R factors calculated from XRD are 9.1 and 6, respectively). The H/C

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ratios for these carbons were obtained from prompt gamma activation analysis.

3. Results and discussion

3.1. Specific capacities of the disordered carbon electrodes

NX-1 and NX-4 disordered carbons were cycled at a C/20 rate. The calculated specific capacities (first three cycles) are presented in Table 1.

From Table 1 it can be seen that the initial capacities of the disordered carbon materials are much higher than the theoretical capacity of graphite, 372 mAh/g. When moving from NX-1 to NX-4, the irreversible capacity increases from 12.7 to 34.5%, thus revealing a correlation with the decrease in temperature of synthesis of the disordered carbons from 1100 to 700°C. Eventually, the above increase in the capacity correlates well with the increase of the H/C ratio mentioned above. This emphasizes the role of C–H bonds in the lithium storage mechanisms in these carbons, as was postulated by Dahn et al. [5] and confirmed by computer modelling by Fischer et al. [6].

3.2. Correlation between Li-solid-state diffusion kinetics and the extent of disorder in the synthetic carbons

Li-solid-state diffusion coefficients (D) were determined by the potentiostatic intermittent titration technique (PITT) (for details see [6]). Fig. 1 compares D versus E plots for graphite and NX-1 (a and b, respectively). It is obvious from this figure that the shape of D versus E plots for these two electrodes differs drastically. For graphite, sharp *minima* in D are observed in the vicinity of the corresponding differential capacity peaks, whereas the disordered carbon electrode reveals an unusually high *maximum* in D at ca. 0.4–0.5 V (versus Li/Li$^+$). A similar maximum was also found in the D versus E plot for the other disordered carbon, denoted as NX-4. Moreover, the ratio of the maxima in D versus E calculated for Li-intercalation and deintercalation was found to be strongly dependent on the extent of disorder in the carbons under study, namely, 4.5 for NX-1 and 13 for NX-4 (see the relevant ratio for NX-1 in Fig. 1b). Based on the lattice-gas approach [7–10], we show that these maxima may originate from the combination of two effects. The existence of repulsive interactions between Li-intercalation
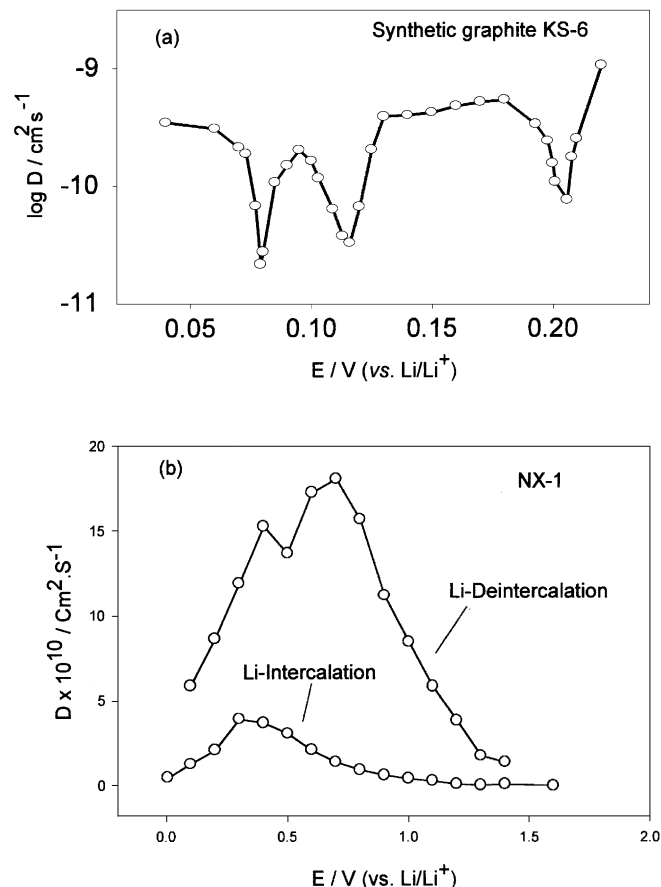

Fig. 1. Plots of the chemical diffusion coefficient D vs. potential E, obtained by PITT for graphite (a) and disordered carbon electrode, NX-1 (b). The minima on the D vs. E curves for graphite, marked by arrows, are close to the potentials of the corresponding peak currents on the voltammetric curves (SSCV).

sites and the fact that there are many possible types of different Li-insertion sites in these carbons, in terms of different electrical conductivity, energetics of interactions and redox potentials. The plots of specific Li-ion conductivity versus potential were obtained using a simple model of DC conductivity, first proposed for thin poly(Os(bpy)$_2$(v-py)$_2$)(ClO$_4$)$_x$ redox films [8]. The electroanalytical behavior of the disordered carbons may correlate to their peculiar structure described in terms of the "butterfly" model [11].

The most striking feature of the XRD peaks of these carbons is that the related reflections are very close to that of the crystalline graphite particles. In Fig. 2 we compare ex situ XRD patterns of pristine and fully intercalated NX-1

Table 1
Charge and discharge capacities of disordered carbons denoted as NX-1 and NX-4, obtained galvanostatically at a C/20h rate (discharge refers to insertion of Li into carbon)

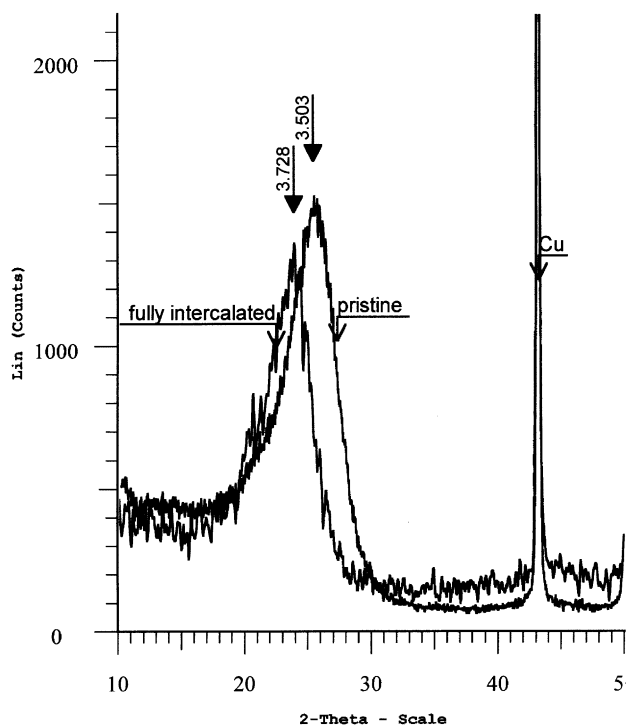| Carbon material	First three discharge capacities (mAh/g)			Irreversible capacity (%)	Capacity related to 0.3–0 V (%)	First three charge capacities (mAh/g)		
NX-1	557	383	368	12.7	49	486	381	357
NX-4	878	521	487	34.5	19	575	473	463

Fig. 2. XRD patterns for a pristine and a fully Li-intercalated NX-1 disordered carbon electrode.

electrodes (the Cu peak serves as a reference). As is seen in Fig. 2, the shift in the position of the XRD peak (and hence the change in the interlayer spacing) is also very similar to that of graphite. We believe that the (0 0 2)-like reflection in disordered carbons does not originate from a uniform $d_{0\,0\,2}$ spacing, but rather relates to the misalignment between layers, with the average interlayer spacing as in crystalline graphite.

3.3. The correlation between 3D crystallographic structure, surface chemistry and electrochemical behavior of the disordered carbons

FTIR spectra and XPS analysis of the pristine electrodes provide clear evidence for the presence of functional surface groups. These surface groups include OH, C=O and, probably, COOH. The concentration of the surface groups is the highest in NX-1 and NX-4 and less in graphite.

Fig. 3 presents FTIR spectra obtained for cycled NX-1 electrodes in three different solutions: (i) EC + DMC (1:3)+1 M LiAsF$_6$, (ii) EC + DMC (1:3)+1 M LiPF$_6$, and (iii) EC + DMC (1:1)+0.75 M LiC(SO$_2$CF$_3$)$_3$. These spectra are different, and reflect the formation of surface films comprised of ROCO$_2$Li, Li$_2$CO$_3$, ROLi and salt reduction products. We believe that the difference in the FTIR spectra of Fig. 3 is due to different combinations of the above Li salts, attenuated by the involvement of parallel salt reduction processes. In fact, all three salts used, contribute to the formation of surface species, as is evident from pronounced As, P and S peaks in XPS spectra of electrodes cycled in solutions (i)–(iii), respectively.

In general, the disordered carbons, the graphite and the SWNT electrodes that we studied develop similar surface chemistry, which is dominated by solvent reduction processes, which form surface organic and inorganic carbonates. The organic carbonates (ROCO$_2$Li species) may be further reduced to Li$_2$CO$_3$ or react with trace water to produce the same species: lithium carbonate (together with CO$_2$ and ROH).

Impedance spectroscopic measurements carried out with the disordered carbons and the graphite electrodes, correlate well with the FTIR results. Fig. 4 shows the evolution of
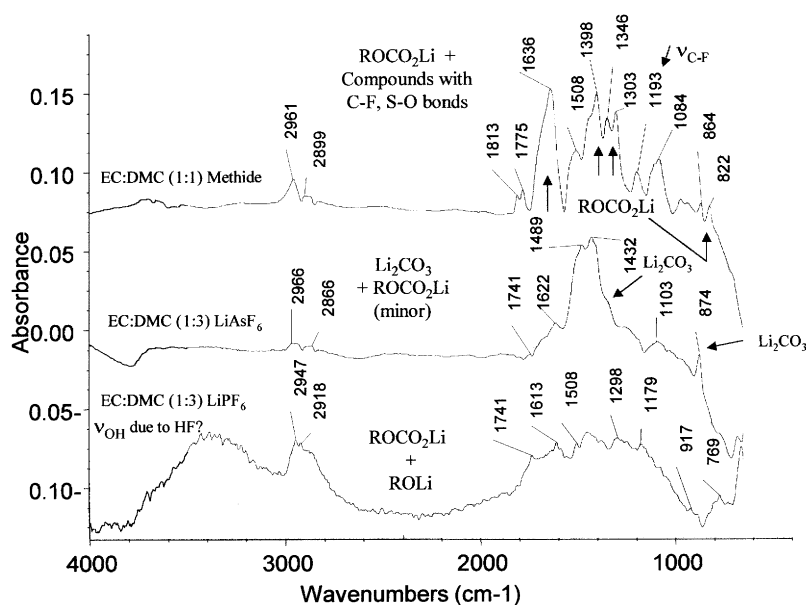

Fig. 3. FTIR spectra measured ex situ from a cycled NX-1 disordered carbon electrode in three different solutions: (i) EC + DMC (1:3)+1 M LiAsF$_6$, (ii) EC + DMC (1:3)+1 M LiPF$_6$, and (iii) EC + DMC (1:1)+0.75 M LiC(SO$_2$CF$_3$)$_3$.
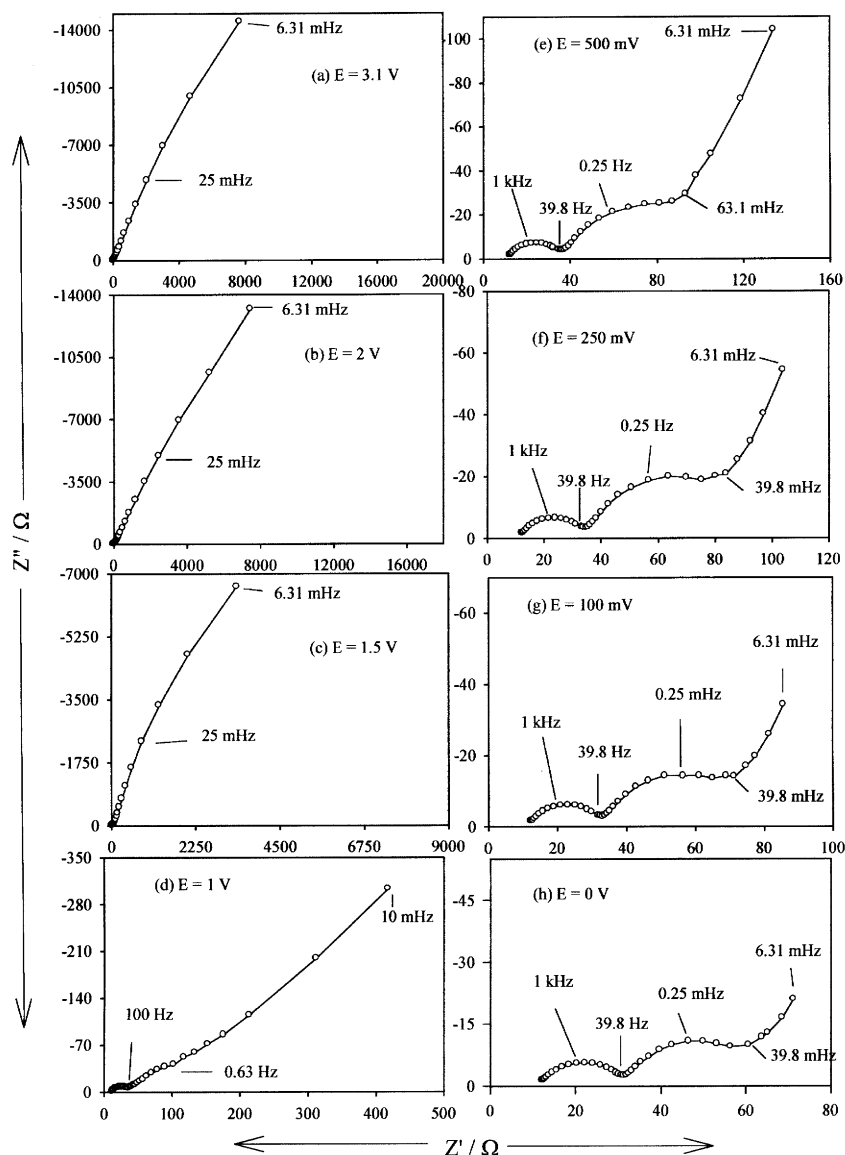
Fig. 4. A family of Nyquist plots measured from a composite NX-1 disordered carbon electrode at different potentials, as indicated.

impedance spectra, presented as Nyquist plots, measured from NX-1 carbon electrodes at different potentials. The high-frequency semicircle, characterized by a representative capacitance in the order of a few $\mu F/cm^2$, and a resistance around 20–70 Ω cm^2, is typical for surface films that are comprised of Li salts and are Li-ion conductors. A similar semicircle is also present in the impedance spectra, usually measured with graphite electrodes, thus revealing the common surface features of these carbonaceous materials.

The medium-frequency semicircle (see Fig. 4) is assigned to a slow Li-ion transfer through the interface between the surface films and the active mass. The diameter of this semicircle is much larger for the disordered carbons NX-1 and NX-4 than for the graphite. This is in line with the shape of the related chronovoltammetric curves; graphite demonstrates much more reversible behavior than the disordered carbons.

3.4. On the structural and electrochemical characterization of Li-insertion into SWNT

The single-wall, carbon nanotube is a new exotic material, which can be envisioned as a single graphene sheet rolled into a cylinder, with diameters in the range of 1–2 nm, several microns in length. The X-ray profile measured from purified SWNT (see Fig. 5a) shows well-defined reflections at 6.3, 10.5, 16.5, and 22°, which can be indexed on a two-dimensional triangular lattice with a lattice parameter of 16.8 Å [3] (see the insert in Fig. 5a). Large interstitial channels between the tubes with a diameter of ca. 6 Å may contain suitable sites for the accommodation of Li-ions. Fig. 5b shows the first cyclic voltammogram measured from a fresh composite SWNT electrode at a relatively high scan rate of 0.5 mV/s. The high cathodic peak at 1.15 V (versus Li/Li$^+$) is characteristic of this electrode, as well as
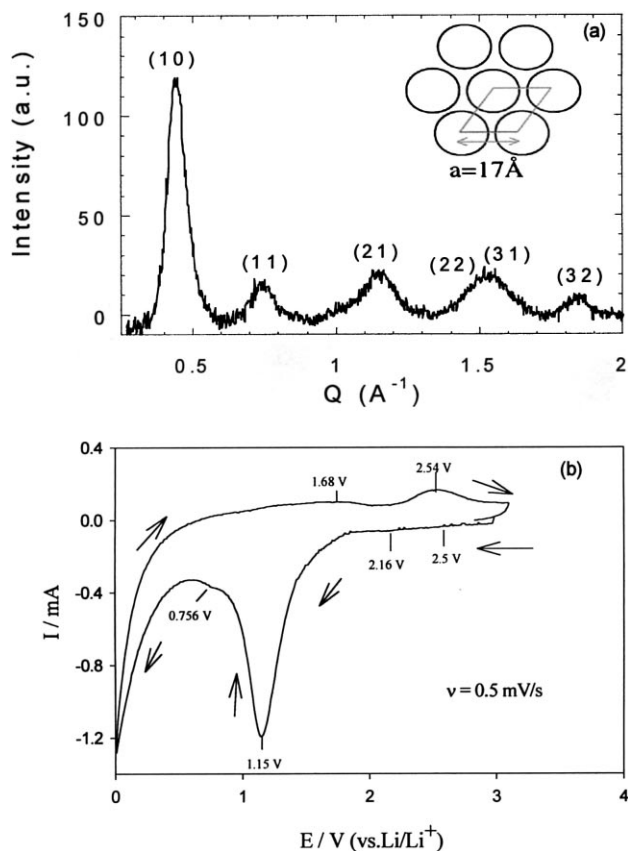
Fig. 5. (a) An X-ray profile for purified and annealed SWNT. Reflections are indexed in terms of a 2D triangular lattice represented in the insert. The interstitial channels between individual tubes are 6 Å in diameter; (b) a first cyclic voltammogram measured from a fresh composite SWNT electrode at a relatively high scan rate, 0.5 mV/s. The most prominent cathodic peak at 1.15 V (vs. Li/Li$^+$) appears only during the first discharge, and can be assigned to reduction processes of solutions which form surface films.

of graphite and the disordered carbons. However, with SWNT electrodes this peak is the most pronounced. The discharge capacity at the above scan rate was very large, 914 mAh/g, whereas the value of the charging capacity was only 171 mAh/g. The highest irreversible capacity of SWCN (among all the studied carbonaceous materials) correlates with its high specific surface area of 350 m^2/g (obtained by BET). The decrease in the scan rate results in the increase of the reversible capacity. For instance, at $v = 0.01$ mV/s, the maximum charge capacity obtained was as high as 471 mAh/g, i.e. considerably larger than that obtained for graphite. This material has many interesting features, such as the irreversible loss of crystallinity upon cycling, as evident from in situ XRD [3], which probably means that Li-ions intercalate in the channels between nanotubes and disrupt the inter-tube binding.

4. Conclusion

We have applied a variety of electrochemical, surface and structural analysis techniques in order to conduct a com-

parative study of Li-intercalation into three different types of carbonaceous materials; graphite, disordered carbons and single-wall carbon nanotubes (SWNT). A common feature, that strongly affects their electrochemical behavior, is the formation of surface films due to the reduction of solution species at potentials above 1 V (versus Li/Li$^+$). The surface films formed on the various carbons in the same solutions have a similar chemical structure, related to the solution composition. This phenomenon is clearly reflected by the impedance spectra of these electrodes, i.e. a high-frequency semicircle with typical parameters (R, C) of surface layers, which are Li-ion conducting, is always present in the Nyquist plots of these electrodes. In contrast, the pronounced difference in the 3D structure of the above carbonaceous materials results in completely different mechanisms of Li-ion intercalation into the various carbons. Within the framework of a simple lattice-gas model with short-range interactions (adsorption-type behavior which can be represented by a Frumkin-type intercalation isotherm), we were able to quantify the difference in the Li-solid-state diffusion into the graphite and the disordered carbons [10]. Due to the very specific structure of the SWNT, we note that the nature of the Li-intercalation sites in the interstitial channels between the tubes is quite different from the well-ordered, doped superlattices observed in lithiated graphite. This, of course, leads to the pronounced difference in the electrochemical behavior of these carbonaceous materials.

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