X-ray photoelectron spectroscopy studies of sodium modified carbon films suitable for use in humidity sensors

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Carbon films obtained using the spray pyrolysis technique are used in the construction of humidity sensitive resistors and capacitors. Both the electronic and surface properties of these films are dependent on several factors such as the carbonization temperature and duration. An addition of sodium containing salts (sodium acetate) to the basic precursor i.e., furfuryl alcohol, produces carbon films that have very specific surface properties. X-ray photoelectron spectroscopy studies revealed that the sodium atoms are located in the mother carbon network. These sodium atoms are associated with oxygen forming structures corresponding to Na_2O. These spots act as centres of durable CO_2 adsorption. This results in an intensive oxidation of the surface leading to a state where the surface layer contains more than 45% oxygen. Such an intensively oxidized surface is highly hydrophilic which results in an intensive water vapour adsorption that follows an I-type adsorption isotherm. The electronic conduction in the sodium modified carbon films is extremely sensitive to water adsorption and it increases by thousands of times after an exposure to humid air.

1. Introduction

The spray pyrolysis technique has found application in the growth of thin carbon films on inert substrates such as glass, silica and silicon. The application of these films in the construction of humidity sensitive resistors has been reported in the literature [1, 2]. It has been noted that the modification of the standard precursor by the addition of sodium containing water soluble salts such as acetate or carbonate yielded carbon films with electrical properties that were highly sensitive to the humidity content in the surrounding atmosphere. As an example of such behaviour, one may highlight the dramatic decrease in the electrical resistance of some Na-modified carbon films from 100–500 MOhm to the level of several kohms on an increase in the relative humidity from 5 to 75% at room temperature [2]. This high sensitivity to the adsorption of water molecules may be achieved by carbonization of the films at the relatively low temperature of 873–923 K. Films of this type are generally denoted as low temperature (LT) carbons.

The enhanced sensing properties of LT carbons towards water vapour are in contrast to those of HT carbons, i.e., carbons that undergo carbonization at elevated temperatures in the range of 1073–1173 K. Generally, the electronic properties of HT carbons show little sensitivity to water adsorption or to catalysis induced alterations. Therefore such films have not been used in the construction of chemically sensitive resistors or diodes. However the HT carbons, because of their high electric conductivity, have been utilized in the manufacture of chemically sensitive electrodes [3].

Despite numerous papers in the literature that deal with the sensing properties of LT and HT carbons the surface state of pure and Na-modified carbon films has not been rigorously studied.

2. Experimental procedures

The carbon films were obtained using the spray pyrolysis technique that has been described in detail elsewhere [4]. Furfuryl alcohol is used as the main component of the liquid precursor sprayed onto a hot substrate (glass or silicon plate). The thus obtained polymer films are subjected to a vacuum carbonization at either 873–923 K or 1073–1123 K that lasts for 60–90 s. The LT and HT carbon films after cooling in vacuum, are stored in the open air.

The mixing of the furfuryl alcohol with a 2M aqueous solutions of sodium acetate in the ratio of 3:1 before the spray pyrolysis experiments results in Na-modified carbon films. The films obtained without sodium acetate are designated as "pure" carbon films.

All the films underwent surface examination by means of X-ray photoemission spectroscopy (XPS) using an ESCALAB 210, (VG Scientific). The thinness of the films and their moderate porosity makes vacuum outgasing easy to perform inside the spectrometer and one may begin measurements after a

20–30 min evacuation of the vacuum chamber (pressure *ca.* 5×10^{-8} Pa).

The XPS spectra were recorded using a K_α Al (34 mA, 15 kV) lamp and the data were analysed using both standard manufacturers software and a program written at the Institut Chemii Fizycznej PAN, Warsaw, Poland.

3. Results and discussion
3.1. C1s spectra of LT and HT carbon films
Figs 1 and 2 present C1s spectra of pure-LT and Na-modified-LT carbon films, respectively. The C1s spectrum of the pure-LT carbon is closely related to the C1s spectra of active carbons described in the literature [5–7]. The spectrum of Fig. 1 and those published in the literature are characterized by a continuously decreasing intensity of the sub peaks that can be attributed to highly oxidized forms of carbon. The larger the energy shift of a peak representing an oxidized carbon atom, the lower is the height of that peak. This situation usually leads to the conclusion that the content of carbon atoms present as carbonate or carboxylic type surface functional groups is smaller than the number of carbon atoms bonded in the carbonyl groups. Thus, the number of carbon atoms in Figs 1 and 2 with the specified chemical state changes in the following order: carbon (graphite) > alcoholic carbon > carbonyl carbon > carboxylic carbon > carbonate carbon < carbon in CO_2.

The most intensively shifted sub peak, near 292 eV, can be attributed to chemically adsorbed CO_2. This sub peak's intensity is relatively larger than the one corresponding to a carbonate carbon.

Table I summarizes the data in numerical form. The distribution of oxidized carbon states shown on Fig. 1 is characteristic for non-modified carbons, i.e., carbons obtained from an organic precursor containing mainly carbon, oxygen and hydrogen without any subsequent chemical or physical treatment. The presence of significant amounts of other elements such as nitrogen or sulphur could complicate the direct attribution of the C1s peaks exclusively to carbon–oxygen structures. Therefore the elemental composition of each carbon film was also determined, see Table II. It can be seen that the carbon, oxygen (and sodium in the Na-modified films) exceeds 95 at%. The remaining
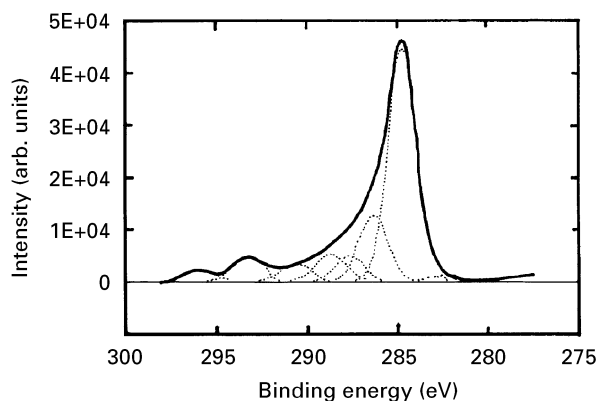

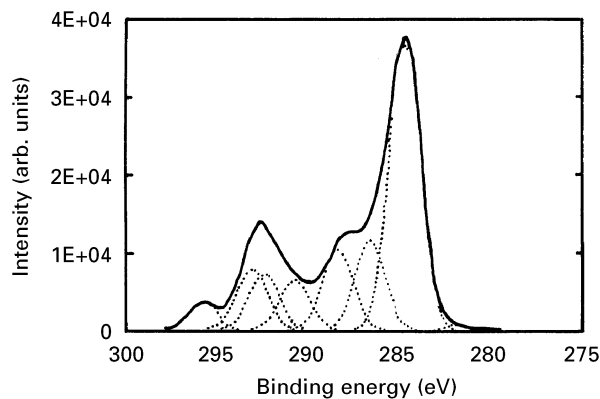*Figure 1* Typical C1s spectrum of pure LT carbon film.

Figure 2 Typical C1s spectrum of Na-modified LT carbon film.

TABLE II Elemental composition of the surface layer of pure and Na-modified carbon films of the LT and HT types determined by XPS

Carbon type	Element at%		
	C	O	Na
LT virgin	68.8	24.4	3.8
LT Na-modified	29.8	43.4	21.8
HT virgin	71.2	18.1	3.3
HT Na-modified	34.3	37.7	26.1

TABLE I Deconvolution of C1s peaks recorded for pure and Na-modified carbon films of the LT and HT types

Carbon type	C1s sub peaks					
	C (graphite)	C–O	C=O	COO–	CO_3^{2-}	ads. CO_2
	Maximum (eV)/contribution to the total C1s peak (at%)					
LT virgin	284.6/56	286.5/16	287.5/6	288.6/7	290.5/4	–
LT Na-modified	284.6/43	286.5/14	–	288.3/12	290.6/8	292.4/8 293.0/9
HT virgin	284.6/47	286.1/15	287.8/8	289.3/5	291.0/3	–
HT Na-modified	284.6/48	286.5/14	–	288.3/10	290.6/14	292.2/14

5% is shared by 4 to 5 other elements. Therefore, the small impurity content causes only minor side effects as compared to the very high oxygen content in the surface layer and its major influence on the C1s binding energy (BE). In addition, the BEs of C–N and C–S species are much closer to the basic C1s 284.6 eV maximum than are the BE maxima recorded for highly oxidized carbon atoms. As a matter of fact, the binding energies of 293 eV and higher are due to $\pi \to \pi^*$ electronic transitions resulting from the "aromatic nature" of the solid. However the heights of the corresponding peaks do not exceed 5–10% of the height of the basic ("graphite") C1s sub peak at 284.6 eV [5–10]. The intensity of the $\pi \to \pi^*$ sub peak is usually lower than the intensity of antecedent sub peaks ascribed to carbon–oxygen surface groups. Any departure from these two normal features may be treated as a superposition of a $\pi \to \pi^*$ sub peak and another sub peak resulting from the presence of a carbon derivative (probably carbon–oxygen groups). The exclusive attribution of the sub peaks on Figs 1–4 to carbon–oxygen structures is discussed in the next section of this paper that analyses the O1s spectra.

The C1s spectrum of a Na-modified LT carbon shown in Fig. 2 is dramatically different from the C1s spectrum of the pure carbon film. In this case two forms of carbon are dominating the spectrum; namely graphitic carbon (284.6 eV) and heavily oxidized carbon (290.7–292.5 eV). Moderately oxidized forms of carbon atoms entrapped in alcohol or carbonyl
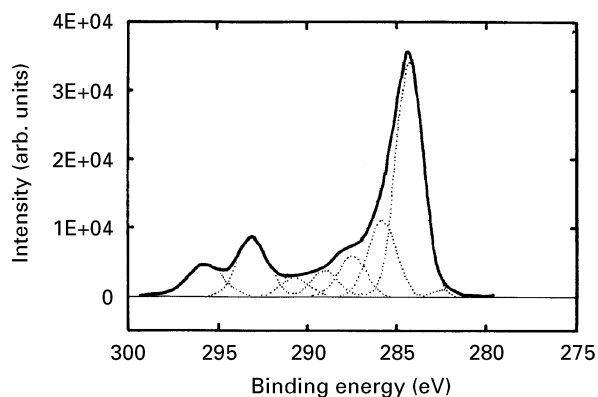

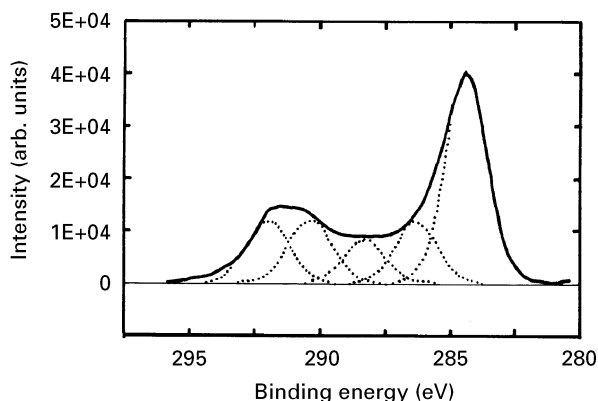*Figure 3* Typical C1s spectrum of pure HT carbon film.

Figure 4 Typical C1s spectrum of Na-modified HT carbon film.

functional groups contribute less intensively to the whole C1s peak. Such a carbon surface, after the Na-modification, is covered by a relatively high number of carbon atoms oxidized so intensively that their corresponding energy shift exceeds 290 eV. In some papers [8–10] this intensive shift in the binding energy is ascribed to carboxylic or carbonate structures. With regarding to the method of carbon film production and particularly the Na-modification process one has to discuss whether the 290.7–292.5 eV region corresponds to: (i) residual carboxylic groups from CH_3COONa introduced to the precursor, (ii) newly formed carbonate groups that may appear in the carbon after the thermal transformation of sodium acetate into sodium carbonate during carbonization, and (iii) carbon dioxide adsorbed onto the carbon surface during the storage of the samples in the open air.

If the residual sodium acetate is present in large quantities in the Na-modified carbons then one should observe intensive sub peaks in the range 288–289 eV [10]. However, this region in Figs 2 and 4 contains only minor sub peaks suggesting a low contribution from sodium acetate. Therefore one may assume that carboxylic groups do not dominate the chemical map of the Na-modified carbon surface. Of particular interest to this discussion is that thermogravimetric examinations confirm that sodium acetate added to furfuryl alcohol decomposes to Na_2CO_3 during carbonization [11].

The problem of the origin of the 290.7–292.5 eV BE region has another aspect, i.e., the form of the remaining sodium carbonate in the Na-modified carbon films provided that such residuals really exist. Particularly, one has to consider the crystalline form of this compound and the size of the Na_2CO_3 crystallites. X-ray diffraction data presented elsewhere [11] suggest that during the carbonization of Na-modified LT and HT carbons, sodium acetate undergoes a transformation with the formation of Na_2CO_3 microcrystallites. This transformation only proceeds efficiently under the specific conditions created in bulk carbon samples. In the reported case the carbon powder had a grain size of 0.02–0.12 mm. The possible crystallization of Na_2CO_3 in thin carbon films is still not fully understood and it is under intensive examination. The possible presence of Na_2CO_3 microcrystallites in the carbon films cannot be fully excluded but their size should be comparable to the molecular scale (1–10 nm). It should be noted that any potential crystallization of Na_2CO_3 is a 3-dimensional process that requires a certain space to exist inside the films. Thus, any Na_2CO_3 microcrystallites formed in the films could influence the XPS detectable surface properties of the Na-modified carbon films provided some microcrystallites are placed just in the subsurface region and are partly exposed to the ambient atmosphere.

The analysis of the Na1s spectrum will be discussed at a later point of this paper.

C1s sub peaks that have a very large BE shift (above 290 eV) are observed in the spectra of Na-modified HT carbon films (Fig. 4) while there are only a minor

feature in the case of pure HT carbon films (Fig. 3). TPD temperature programmed desorption (TPD) and thermogravimetric measurements revealed that the Na_2CO_3 microcrystallites decompose at a temperature below 873 K [11, 12] due to a chemical reaction with the carbon matrix. Thus, the significantly shifted (above 290 eV) sub peaks in the C1s spectrum of HT carbon (Fig. 4) cannot be attributed to Na_2CO_3 microcrystallites since they should not exist in these samples. Therefore, it is probable that these peaks result from highly oxidized carbon atoms of the type of: CO_2 chemisorbed onto Na_2O (HT films) and CO_2 chemisorbed on Na_2O and/or Na_2CO_3 microcrystallites (LT).

The contribution of the significantly displaced C1s sub peaks to the total C1s peak is higher for LT carbons. This agrees with the concept that the intensively shifted sub peaks are the result of two forms of heavily oxidized carbon atoms in the LT films (CO_2 and Na_2CO_3) while in the case of HT carbon films the sub peak is solely the result of chemisorbed CO_2. Data in the literature suggests that the typical position of the C1s sub peak of the carbon atom in a CO_3^{2-} group is 290.7 eV [10] which does not explain the presence of the sub peaks above 292 eV (Fig. 4). In fact this value is characteristic for CO_2 [13] and it can be attributed to the chemisorbed CO_2 on the Na_2O centres.

The existence of a $Na_2O \cdot CO_2$ structure on the surface of Na-modified HT carbon films and the presence of CO_3^{2-} ions [2] in LT carbons was confirmed by Fourier transform afra-red spectroscopy [FTIR].

The Na-modified HT carbons are characterized by the presence of the sub peaks in the range 290.7–292.5 eV, i.e., in the region associated with heavily oxidized forms of carbon atoms. Their summed contribution to the total C1s peak is slightly smaller than that for the Na-modified LT carbons despite the observed decomposition of the Na_2CO_3 microcrystallites. The Na_2CO_3 microcrystallites probably exist in the LT carbons but their presence is questionable in the HT carbons. These observations can be explained by assuming that the carbon atoms from the Na_2CO_3 microcrystallites, that were decomposed during the vacuum heat treatment, are replaced by the chemisorption of CO_2 molecules during storage in the atmosphere.

As mentioned, the summed contribution of the 290.7–292.5 sub peaks to the total C1s peak is almost equal for Na modified HT (28%) and LT (25%) carbons but the distribution between the sub peak near 290.7 eV (C atom in carbonate entity) and the sub peak near 292 eV (C atom in carbon dioxide) is different for these carbons (see Table I). The relative amount of adsorbed CO_2 increased with the change from LT to HT carbon. This behaviour supports the idea of the replacement of thermally removed carbonate CO_3^{2-} species by chemisorbed, CO_2.

3.2. O1s spectra of LT and HT carbon films

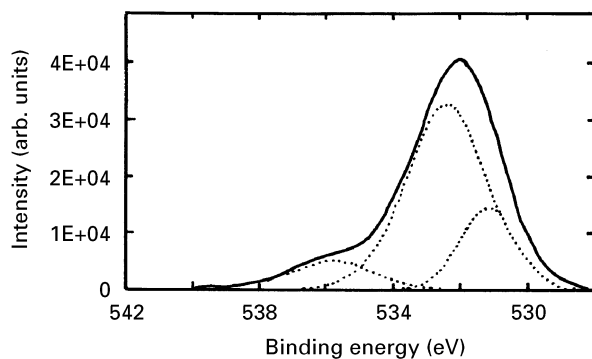The O1s spectra are usually used as complementary data to confirm the conclusions obtained by analysis

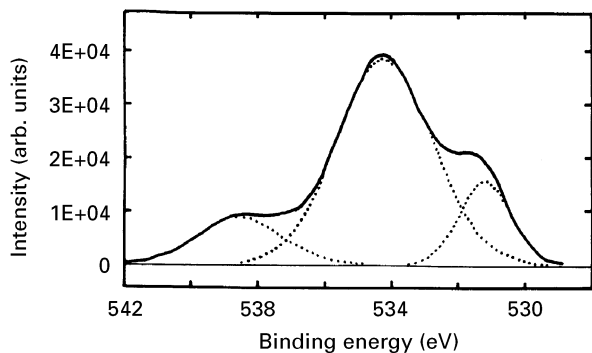*Figure 5* Typical O1s spectrum of pure LT carbon film.

Figure 6 Typical O1s spectrum of Na-modified LT carbon film.

TABLE III Deconvolution of the O1s peaks recorded for pure and Na-modified carbon films of the LT and HT types

Carbon type	O1s sub peaks		
	C–O	C=O	COO–
	Maximum (eV)/contribution to the total O1s peak (at%)		
LT virgin	531.1/21	532.3/69	535.0/10
LT Na-modified	531.1/15	534.1/71	538.4/14
HT virgin	531.6/51	533.2/41	535.3/5 537.0/2
HT Na-modified	532.4/31	533.8/48	538.0/21

of the C1s spectra. Figs 5 and 6 and Table III present typical O1s spectra of pure LT and Na-modified LT carbons. The spectra are characterized by the presence of three major sub peaks at: 531–532, 532.5–534 eV and 536–538 eV. The first two sub peaks are usually ascribed to C–O and C=O structures respectively [14]. The interpretation of the third sub peak is not clear but some authors attribute the peak to the single bonded oxygen atom in the carboxylic group or to carbonate entities [15]. No direct information on dealing with the O1s BE shift specific for chemisorbed CO_2 was found in the literature but it has been suggested [13] that these BE values will be close to the carbonate functional O1s BE region. Keeping in mind this assignment, one can state as follows (see Table III): (i) the number of O atoms (the first O1s sub peak) bonded to

C atoms by a single C–O bond decreases on the Na-modification but increases on the transition from LT carbon to HT carbon, (ii) the number of O atoms (the second O1s sub peak) oxidizing C atoms in a moderate way (C=O) increases on the Na-modification, and (iii) the number of O atoms (the third sub peak) included in the structures containing highly oxidized C atoms (carbonate and/or carbon dioxide) increases on the Na-modification.

These statements are in good qualitative agreement with the interpretation of the C1s spectra but the deconvolution of the O1s spectrum does not yield as precise conclusions as does the C1s spectra. It is not possible to separate the sub peaks that correspond to carboxylic entities, carbonate entities and chemisorbed carbon dioxide. All these species are probably included in the third sub peak. It is again shown that the Na-modification leads to the formation of surface entities that contain highly oxidized carbon atoms.

3.3. Na1s spectra of Na-modified LT and HT carbon films

The Na1s spectrum of a Na-modified HT carbon film is presented in Fig. 7. The spectrum is unique because of the wide sub peaks located at 1072.8 and 1074.7 eV. These locations are quite unusual for sodium containing compounds. For example the Na1s BE values recorded for crystalline Na_2CO_3, $NaHCO_3$ and CH_3COONa have maxima in the range 1071.3–1071.7 eV [16,17]. Thus the currently measured values are shifted towards the Na1s peak of elemental sodium. Previously the 290–291 eV C1s sub peaks were interpreted as resulting from the presence of a CO_3^{2-} group probably in Na_2CO_3 microcrystallites however the Na1s data disagree with this conclusion if we neglect the presence of isolated Na_2CO_3 microcrystallites in the surface region. The 1072.8 eV maximum corresponds to the reported Na1s BE for Na_2O, i.e., 1072.5 eV [16]. It seems to be true that the sodium on the surface is present as Na_2O and is the centre of two forms of CO_2 adsorption: (i) "weak" adsorption with a low thermal stability providing an Na_2O adsorption centre and adsorbate CO_2 (292.5 eV C1s maximum) to the complex $Na_2O \cdot CO_2$, and (ii) "strong" chemisorption leading to the formation

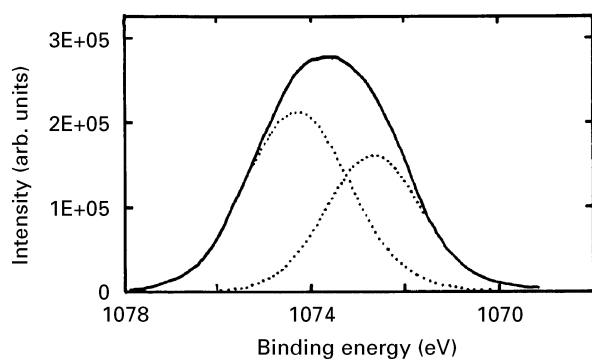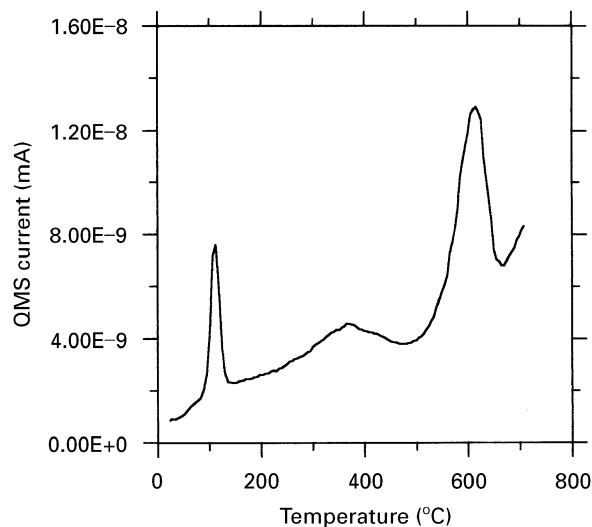Figure 8 TPD spectrum of the Na-modified HT carbon.

of *quasi* Na_2CO_3 molecules bonded to the surface (290.7 eV C1s maximum).

Fig. 8 presents a thermal desorption spectrum of species with a mass of 44 a.m.u from the surface of the Na-modified HT carbon. The spectrum contains three major desorption peaks near the temperatures of 383, 653 and 883 K. As predicted, based on the analysis of the Na1s XPS line, CO_2 is adsorbed in two forms (the first and second peaks) that are very different with regard to their thermal stability. One has to remember that the Na-modified HT carbon underwent carbonization at 1073 K and thus a major amount of the Na_2CO_3 microcrystallites had already decayed. The third peak at 883 K is probably due to the decomposition of the residual Na_2CO_3 microcrystallites.

The Na1s 1074.7 eV maximum cannot be assigned to any common sodium containing species. This value is relatively close to the 1078 eV Na1s BE characteristic for elemental sodium. This maximum could be due to the Na atoms that are built into the mother carbon matrix and therefore possess a specific intermediate oxidation level below +1 and above 0.

The assignment of the C1s 290.7 maximum to the CO_3^{2-} group of pure Na_2CO_3 microcrystallites is rather questionable because the analysis of the Na1s spectra does not confirm the presence of sodium atoms contained in isolated microcrystallites of pure Na_2CO_3 in the surface region. Such microcrystallites, if they exist, are perhaps situated inside the carbon films with a limited access to the surface region.

3.4. Elemental composition of the surface layer of the carbon films

Table II lists the elemental compositions of all the investigated carbon films. It is interesting to note that the Na-modification produces carbon films with a highly oxidized surface. The degree of oxidation is high for both the LT and HT carbon films with a slight decrease in this tendency with an increasing
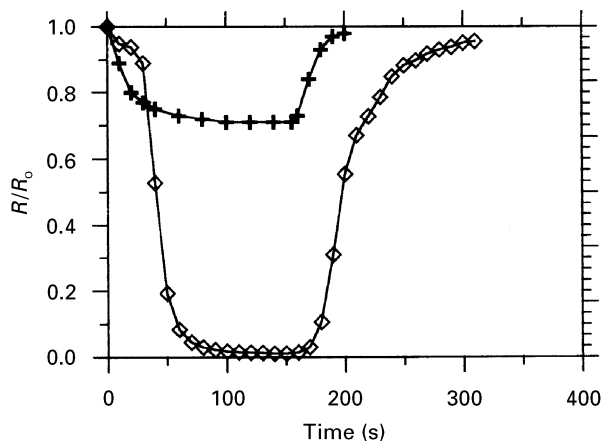

Figure 7 Typical Na1s spectrum of Na-modified carbon films of LT and HT type.

Figure 9 Relative resistance changes of (◇) Na-modified LT carbon film on a relative humidity change of 0 to 75% and (+) the data for the pure LT carbon film under the same conditions.

in the carbonization temperature from 923 to 1073 K. In some cases, the number of carbon atoms is smaller than 1/3 of all the atoms in the surface region. Almost 50% of all the surface atoms in Na-modified carbon films are oxygen atoms whereas the oxygen atom content for the pure HT and LT carbons is below 25% of all the surface atoms while the carbon atom content is close to 70%. It is possible to reach the paradoxical state when the carbon is a minority element in the surface region despite the point that the bulk of the film mainly consists of carbon.

The Na-modification technique used in this study is quite gentle in comparison to the standard nitric acid treatment which is a traditional way to obtain intensively oxidized carbon surfaces. The Na-modified carbon films produced in this study are hydrophilic [18] and their electrical resistance is very sensitive to the adsorption of water vapour. Fig. 9 shows a dramatic decrease of the resistance of such films on the adsorption of water vapour. This behaviour is typical for alkali metal modified carbons that find application as humidity sensitive resistors and capacitors [4]. The required properties of the films may be optimized by a judicious choice of the Na concentration in the precursor and the carbonization conditions (temperature and duration).

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