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ORGANO-MODIFIED CARBON ELECTRODES. I. STUDIES OF MODIFIED LAYER VIA AMIDE BONDS BY CAPACITANCE MEASUREMENTS AND ESCA[1)]

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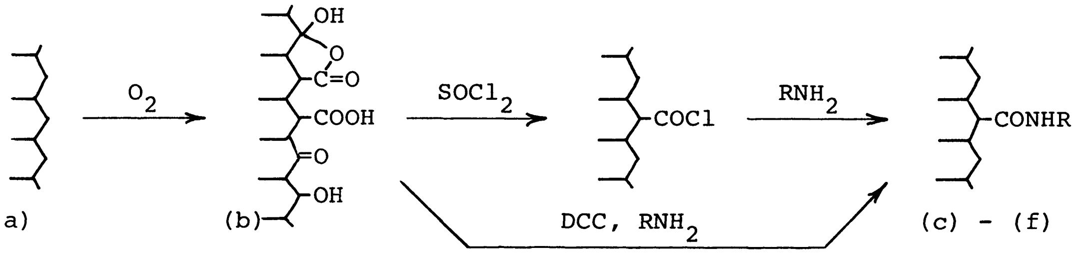
The electrochemical characteristics of chemically modified glassy carbon electrodes via amide bonds have been correlated with the results of surface analysis by X-ray photoelectron spectroscopy (ESCA). The double layer capacitance measurements were proved to be useful to determine the extent of surface modification as well as ESCA analysis.

Since the first report on a chiral electrode by Miller and co-workers,[2)] the chemical modification of surfaces as a means of making selective and catalytic electrodes has become of interest.[3-7)] These modified electrodes have been prepared through covalent attachment of chemical species containing functionally important groups, such as asymmetric carbons,[2)] ligands,[3,4)] and sensitizers[7)] to the surface of carbon[2,3)] and metal oxides[4-7)] via chemical reactions. Except the first modified carbon electrodes by Miller and co-workers,[2)] only organosilane chemistry has been employed thus far to prepare the chemically modified glassy carbon[3)] and metal oxide electrodes.[4-7)] These silanized surfaces have been investigated in detail by ESCA,[3-7)] Auger,[5)] and electrochemical techniques.[3-7)] However, to date there has been no report on the surface studies of modified carbon electrodes via amidation chemistry, though Miller and co-workers bound optically active amino acids via amide bonds and succeeded in their preparative work.[2)] Also, there has been no report of the effect of the chemical modification on the double layer capacitance except our previous paper of the modified SnO_2 electrodes,[6)] in spite of its importance as one of the electrochemical properties of the modified electrodes. In this paper, the change of the double layer capacitance of carbon electrodes caused by the modification will be described as well as ESCA spectra of the modified carbon surfaces.

EXPERIMENTAL

The glassy carbons (GC-30S) were obtained from Tokai Carbon Co. as a 17 mm × 17 mm × 2 mm plate for electrochemical use and as a 17 mm × 5.5 mm × 2 mm plate for ESCA. One end of each specimen was surfaced to a mirror finish by emery paper (successively finer one from No. 100 down to 2000) followed by polishing with alumina of 1 μ and 0.3 μ. After polishing, glassy carbon specimens were washed with water, ethanol, and benzene and baked in air at 160°C for 36 hr. The carboxylic acid on the carbon surface was introduced by this air oxidation, which was always accompanied by the formation of surface oxides in the forms of quinones, phenolic alcohols, and lactones.[8-10)] The surface synthetic procedure of the modified carbon electrodes was similar to that described by Miller and co-workers.[2)] However, not only the procedure via acid chloride,[2)] but also the direct dehydrative coupling between amine and the surface carboxyl group using dicyclohexylcarbodiimide (DCC)[11,12)] was employed to form the amide linkage.



R = n-C_4H_9- or n-C_8H_{17}-

The cell design and the electrochemical equipment used were similar to those previously described.[6] For ESCA analysis, an AEI Model ES 200 was used with Mg anode at vacua of 10^{-9} torr. Binding energies were referenced to the C 1s peak at 284.3 eV of the untreated glassy carbon electrode.[13,14] Solution was prepared by using doubly distilled water and G.R.-grade chemicals.

RESULTS AND DISCUSSION

Six types of carbon surfaces were examined by ESCA: (a) a washed but unbaked surface, (b) an oxidized surface at 160°C in air for 36 hr., (c) an amidated surface with n-butylamine via acid chloride, (d) an amidated surface with n-octylamine via acid chloride, (e) an amidated surface with n-butylamine using DCC, and (f) an amidated surface with n-octylamine using DCC.

An ESCA spectrum of glassy carbon baked at 160°C (type b) is shown in Fig. 1, together with the insets of spectra of O 1s, N 1s, and C 1s peaks in higher resolution. The spectrum in wide scan contains two strong peaks for O 1s at 532 eV and C 1s at 284.3 eV to which all binding energies were referenced.[13,14] In addition, there are several small peaks corresponding to plasmon (A,B) on the higher binding energy side of the main C 1s peak stimulated by Mg $K_{\alpha1\alpha2}$, the C 1s satellite (D) stimulated by Mg $K_{\alpha3\alpha4}$, the C 1s (Al K_α) stimulated by the radiation from the aluminum window, and the valence band (V_B) as reported in the literature.[14] However, it should be noted that no chemisorbed nitrogen is detectable on this surface.

The spectrum of C 1s peak in the narrow scan shows that the C 1s peak of the glassy carbon is asymmetrical as that of graphite, but bears no resemblance to the corresponding peak in diamond.[14] Thus, it can be concluded as having been done by Thomas and co-workers[15] for vitreous carbon that the bonding in the present glassy carbon is based on sp^2 rather than sp^3 bonded carbon. Since the photoelectron from carbon of the substratum within the escape depth is predominant, very little change in the shape of C 1s peak by the oxidation was observed between the spectra of type a and b. The appearance of small but broad peak on the higher binding energy side of the main C 1s peak by the oxidation may be attributed to the formation of the surface oxides. On the other hand, the O 1s peak showed a marked change in the profile by the oxidation. The appreciable increase in the half-width of the oxygen peak after oxidation indicates that several kinds of surface oxides were formed by heating in air. This agrees with the results previously obtained with other methods to characterize the surface functional groups such as titrations.[8] Further work is now in progress on the effect of the oxidation conditions, both in dry and wet methods, on the shift in binding energy and the change in the profile of C 1s and O 1s peaks. This will clarify the distribution of the variety of the surface oxides such as carboxylic acids, phenolic alcohols, and lactones and will be used to determine the optimal conditions for the surface oxidation as a pretreatment of the modifications of carbon electrodes. These results will be reported elsewhere.

The change in ESCA C 1s spectra with the modification of the surface carboxyl group on the oxidized carbon (type b) to n-butylamine derivative via acid chloride (type c) is shown in Fig. 2, where the spectra of other derivatives (type d, e, and f), which were almost identical to that of type c, are omitted. The introduction of linear aliphatic hydrocarbon chains onto the glassy carbon surface shifted the C 1s peak from 284.3 eV of graphitic carbon to the higher binding energy around 284.5 eV. Taking into accounts that the binding energy of C 1s of hydrocarbons is 285 eV,[13)] the C 1s peak of the modified surface (type c) is proved to consist of two peaks attributable to the overlaying hydrocarbons and the substratum of glassy carbon from the deconvolution analysis.

As a result of the amide bond formation on the derivatized surfaces, an appreciable ESCA N 1s peak around 399.6 eV was observed on every modified surface (type c to f) as shown in Fig. 3, while the N 1s peak is hardly discernible on the oxidized surface (type b) as a precursor of these modified surfaces. From the known binding energies of N 1s for the various kinds of nitrogen containing compounds,[16)] the nitrogen peak on the surface can be assigned to amide groups as we would expect. The profile of the ESCA O 1s peak of the oxidized surface was also affected by the introduction of the amide linkage, since the hydroxyl oxygen of the surface carboxylic acids was removed by the amidation with thionyl chloride or with DCC. The decrease of the width of the O 1s band of the modified surface (type d) compared with that of type b , as shown in Fig. 4, is attributable to such elimination from the known binding energies of O 1s for the

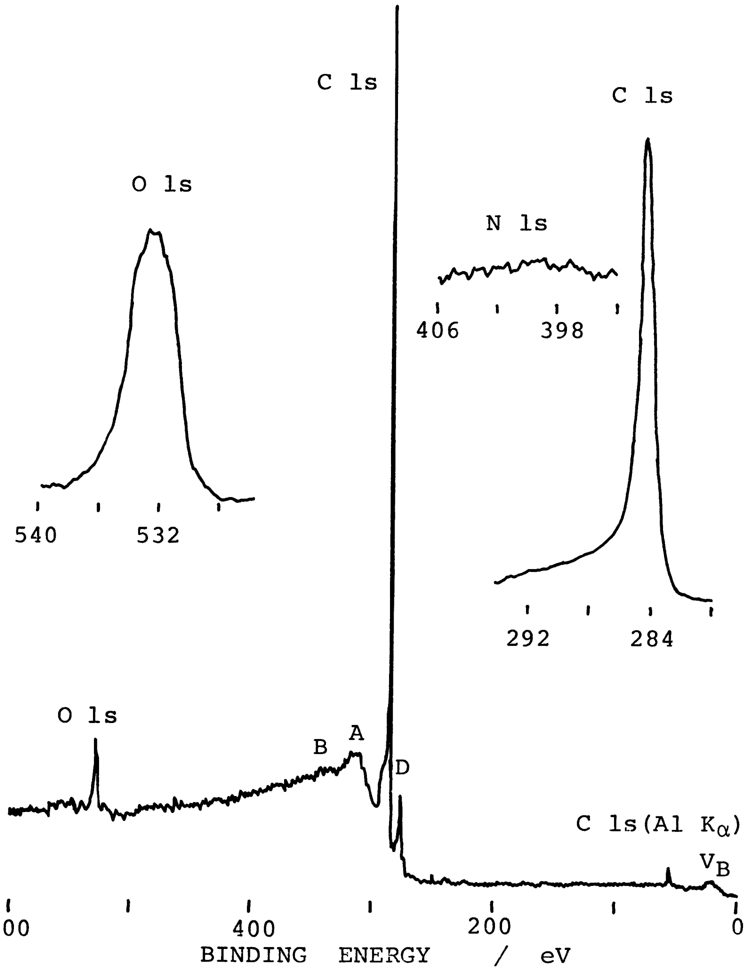


Fig. 1. ESCA spectra of oxidized glassy carbon.

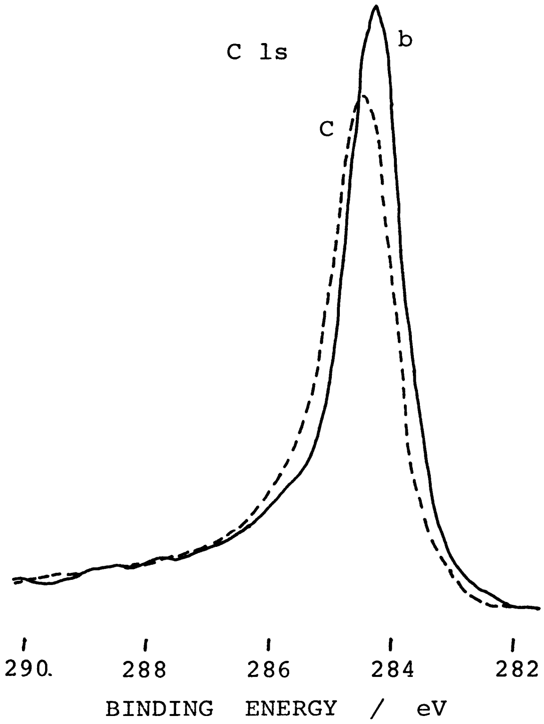


Fig. 2. The change in ESCA C 1s spectra caused by the modification of the oxidized surface (type b) to the alkyiamidated surface (type c).
——— oxidized surface
----- n-butylamidated surface

various forms of oxygen.17)

Miller and co-workers described in their paper2) that the modified electrodes were indistinguishable by eye or sweep voltammetry from the unmodified version. It was undoubtedly impossible also in the present study to distinguish the six types of electrodes (type a to f) from their appearance, but the cyclic voltammograms at the modified electrodes with linear saturated hydrocarbons (type c to f) showed apparently lower charging currents than those observed at the washed (type a) or the oxidized electrode (type b) against their observation as shown in Fig. 5. This lowering of the charging currents may be due to the decrease of the electrical double layer capacitance caused by binding the nonconducting hydrocarbons to the highly conductive glassy carbon surfaces as having been previously observed at the chemically modified SnO_2 electrodes.6) Such a lowering of the Helmholtz capacitance is observed in general when the surface active substances are added to the electrolyte and adsorbed physically at the electrode-solution interfaces.

In order to investigate the change in the double layer capacitance more quantitatively, the method of Gileadi and co-workers18) was employed to measure the capacitance as previously.6) Carbon electrodes are known to be oxidized and covered with the oxide film when they are anodized and to evolve CO and CO_2 at a high anodic potential. Therefore, the capacitance was measured in the moderate potential region from - 0.2 to 0.8 V vs. SCE in aq. 1M Na_2SO_4 in order to avoid such complexity arising from the oxides formation on the surface. On pyrolytic graphite electrodes in contact with 0.5M K_2SO_4, the double layer capacitance was estimated by Ateya and Austin19) to be 35 ± 3 $\mu F/cm^2$ for edge atom plane and 32 ± 3 $\mu F/cm^2$ for basal plane in the potential region between 0.1 and 0.5 V vs. SCE where residual current was minimal. On the untreated glassy carbon (type a) in the present work, the capacitance was determined to be 21 ± 2 $\mu F/cm^2$ in the potential region between 0.1 and 0.8 V vs. SCE. The error in the measured capacitance of about ten percent is probably due to the difference in the surface roughness. The

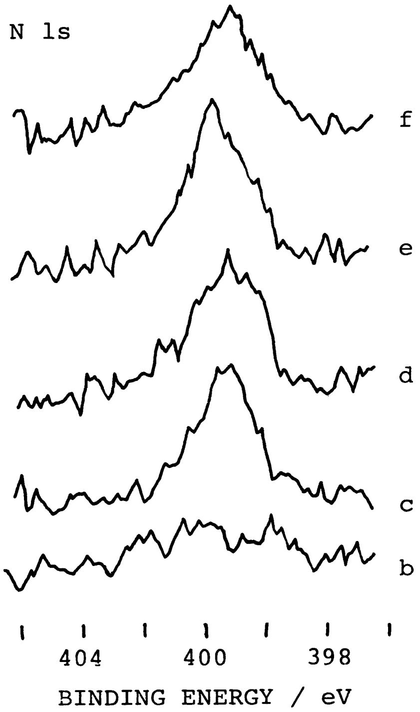


Fig. 3. ESCA N 1s spectra of oxidized (type b) and modified surfaces (type c - f).

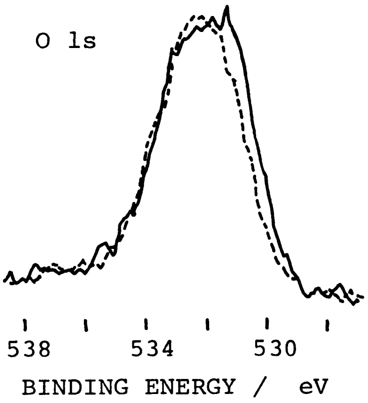


Fig. 4. The change in ESCA O 1s spectra caused by the modification of the oxidized surface (type b) to the alkylamidated surface (type d).
——— oxidized surface
----- n-octylamidated surface

capacitance was measured first from 0.8 to - 0.2 V vs. SCE at every 100 mV successively to cathodic potential (solid lines in Fig. 6) and then measured from - 0.2 to 0.8 V vs. SCE along the anodic direction (dashed lines in Fig. 6). However, little difference was observed between the capacitance results measured on different direction of the potential steps. The capacitance on the oxidized surface (type b) in 1M Na_2SO_4 was somewhat higher than that of type a and was 26 ± 4 $\mu F/cm^2$ in the potential region between 0.2 and 0.8 V vs. SCE. The increase of the capacitance must be due to the increase of the surface roughness caused by the oxidation, since the surface oxidized at the higher temperature showed the higher capacitance. The higher capacitance obtained by Ateya and Austin may be due to the increase of surface roughness during the pretreatment for cleaning by evolving oxygen and hydrogen.[19)]

As we would expect, the alkylamidated surfaces (type c to f) gave much lower capacitance than those of the untreated and oxidized surfaces (type a and b). Therefore, the capacitance measurements can be used to judge the extent of the surface modifications. As in the case of the intensity of ESCA N 1s peak and the binding energy of C 1s peak of the modified surfaces, the reproducibility of the capacitance measured at the alkylamidated surfaces was, however, not so good as that of the capacitance at the untreated or oxidized surfaces. For example, the capacitance ranged from 5 to 17 $\mu F/cm^2$ on the amidated surface with n-butylamine via acid chloride (type c). The variation in the surface density of the carboxylic acid introduced by the air oxidation from specimen to specimen may be responsible for the scattering of the capacitance and ESCA results of the modified surfaces, since the acidic surface oxides are bound at the edges of carbon layers, while basal surfaces are essentially free from of chemisorbed oxygen,[8,14)] and the glassy carbon surfaces consist of both edge and basal planes. This can be supported by the results that the fluctuation depended on origin of glassy carbon (probably how to cut out the plates from carbon block) rather than the reaction conditions of the chemical modifications, though the fluctuation is somewhat attributed to the change in

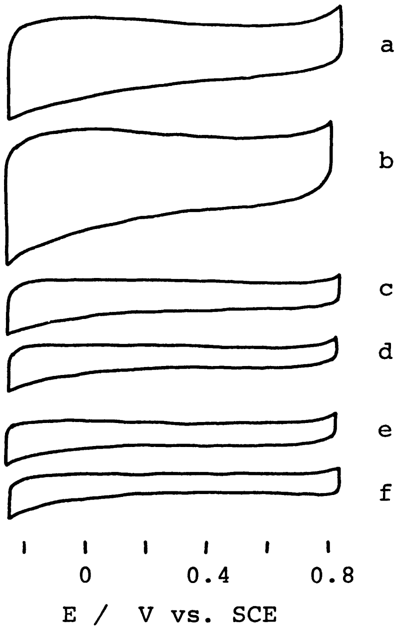


Fig. 5. Cyclic voltammograms on unmodified (type a and b) and modified electrodes (type c to f) in 1M Na_2SO_4. Scan rate: 220 mV s^{-1}.

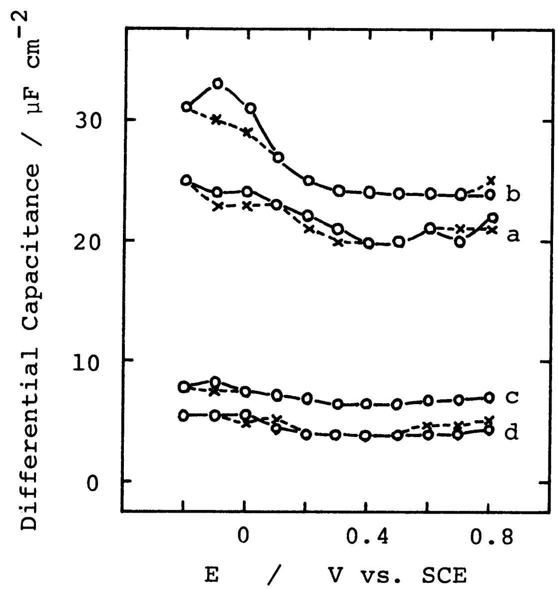


Fig. 6. Differential capacitance of the unmodified (type a and b) and modified electrodes (type c and d). Superimposed triangular wave: 50 mV p-p, 500 Hz.

the yield of the amidation. If the extent of the modification is the same between n-butyl and n-octylamidation, the capacitance of the n-octylamide derivative should be lower than that of the n-butylamide derivative because of the thicker Helmholtz layer of n-octylamide surface than that of n-butylamide one. Though the order was reversed often by the fluctuation, the results were in accord with the expectation on the average. On the other hand, the difference by the different preparation routes between acid chloride and DCC methods was not found appreciably. Accordingly, not only ESCA analysis but also the capacitance results showed that the chemical modification using DCC was successful as well as the modification via acid chloride. Typical capacitance results are shown in Fig. 6, where data on the alkylamide surfaces directly derived by DCC are omitted to avoid complication. These lower capacitances at the alkylamidated surfaces gradually increased probably due to the removal of the alkyl group from the surfaces when the high anodic potential was applied on the modified surfaces. Unless the potential exceeded beyond the potential range between - 0.2 and 0.8 V vs. SCE, little change in the capacitance at the alkylamidated electrodes was observed during the experiment.

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