Surface Modification of Carbon Electrode for Electric Double Layer Capacitor

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Keywords: electric double layer capacitor, ESCA/XPS, glow discharges, nitrogen doping, surface modification

Summary

In this research, spatio-temporal profiles of positive and negative charges in an Electric Double Layer Capacitor (EDLC) which consists of activated carbon, treated by plasma discharges were measured. The plasma type was a high frequency glow discharge and the sample of activated carbon is set in the center of glow discharge. Optimal conditions for plasma surface treatment of activated carbon was examined from 0 min to 60 mins at 150 ℃ in nitrogen gas. As a result, nitrogen atom was doped onto the surface layer of the activated carbon. In addition, Electron Spectroscopy for Chemical Analysis (ESCA) spectra of nitrogen in the activated carbon was examined. By etching the surface layer of carbon electrode exposed to the plasma, the doped nitrogen atom penetrated about 3 nm of the surface layer of carbon electrode after 60 mins of plasma surface treatment.

1. Introduction

Recently, characteristics of EDLC [1] have been improved in many studies [2-8]; however, some characteristics still need enhancement, such as the specific energy density and capacitance. EDLC utilizes the double layer formed at the interface between the nanoporous carbonaceous electrode and the nonaqueous electrolyte solution. Porous carbons have been used as the electrode material in EDLC because of their relatively low cost and very high ratio of surface area. In addition, this capacitor does not participate in redox reactions. Therefore, there is little deterioration in the electrode, which has good cycle characteristics, and maintenance is unnecessary. However, the problem is that the energy density is low, and to solve this problem, development of a new electrolyte and a new carbon electrode material's research is still underway. The methods of making a metallic oxide in a carbon electrode and using nanocarbon for activated carbon have been established for the development of the electrode material. In addition, it was reported that capacitance increases by doping nitrogen or boron into these materials [9]. Electric double layer consists of space charge layer, helmholtz layer and diffusion layer, as shown in Fig.1. Usually, the capacitance of the space charge layer is very small but, the inner electrode works like a semiconductor in the charge and discharge process of EDLC by doping it into nitrogen. As a result, the capacitance of space charge layer can be improved.

In this research, we aim to change the state of the surface of the polarized electrode by plasma surface treatment and to improve the characteristics of the polarized electrodes [10]. We have applied the pulsed electro acoustic (PEA) method [11-15] to observe space charge distributions in EDLC. The PEA method is an established technique used for directly measuring space charge distributions in solid dielectrics. The data is useful for quantitative analysis of charge accumulation and charge transport.

In this paper, the effect of nitrogen doping by plasma surface treatment was examined.

Furthermore, by etching the surface layer of carbon electrode, depth profiles of the ESCA spectra of nitrogen's 1s orbital was analyzed. Moreover, spatio-temporal profiles of positive and negative charges in EDLC were measured by the PEA method.

2. Experimental Method

2.1 Plasma surface treatment

Figure 2(a) shows the experimental setup for plasma surface treatment. The chamber for plasma surface treatment was made by stainless steel with an internal diameter of 308 mm. The chamber was pumped to a residual pressure of about 1.3 Pa prior to deposition. A single turn RF antenna, with a radius of 130 mm, insulated from the plasma by a 10 mm diameter quartz glass tube, was placed inside the chamber. One side of the antenna was connected to a 13.56 MHz RF power generator through an impedance matching box, while the other side was connected to the grounded chamber wall. The sample holder was heated to 150 ℃ by using thermo controller. The quartz glass tube was slotted on the surface of the thermo controller to prevent the Faraday shield effect. The peak value of the RF field strength was about 200 V/m when the input RF was 300 W powers with 13.56 MHz frequency.

The plasma type was a high-frequency glow discharge and the sample of activated carbon was set at the center of the glow discharge. Optimal conditions for plasma surface treatment of activated carbon have been examined from 10 mins to 60mins at 150 ℃ in nitrogen gas. The pressure of gas was 13.3 Pa. The electrode was set up to cover the EDLC sample with the glow discharge. The effect of nitrogen doping and depth profile of ESCA spectra of nitrogen's 1s orbital after plasma surface treatment was analyzed using ESCA-3300 which was produced by the Shimadzu Corporation.

2.2 PEA measurement

The experimental setup for measuring space charge distribution using a PEA system is shown in Fig.3. An EDLC sample made on an experimental basis was assembled using two sheets of collector made of Al 30 μm thick, a sheet of separator made of cellulose 20 μm thick , and two sheets of nonaqueous - electrolyte - immersed polarizing electrode made of activated carbon with the thickness of 150 μm. The EDLC was composed of five layers, and its total thickness was 380 μm. Each component had a sectional area of 30×30 mm^2. The nonaqueous electrolyte ($C_4H_5O_3$) was a mixed solution of propylene carbonate and tetraethylammonium tetrafluoroborate $(C_2H_5)_4NBF_4$ in a molar ratio of 1:0.8.

A dc voltage of 2.5 V, for electrical charge formation, was applied to the EDLC sample through an upper Al electrode with a diameter of 8 mm and a length of 5 mm. When the measurement of the space charge distribution was carried out, a high-voltage pulse for induction of elastic waves was applied to the EDLC sample through the upper Al electrode. The pulse had a maximum value of 600 V and a pulse width of 2.5 ms at a frequency of 400 Hz. It is noted that a semiconductor layer was formed between the upper Al electrode and the EDLC sample. The acoustic impedance was adjusted by the semiconductor layer on the interface between the EDLC sample and the upper Al electrode. A 10-μm-thick lithium niobate layer ($LiNbO_3$), arranged on a 10-mm-thick Al electrode 200 mm wide and 250 mm long, was used as a detector of elastic waves. The transformed voltage signal from the $LiNbO_3$ was amplified to 45 dB and recorded by a digital oscilloscope and a personal computer for further analysis.

The profile of space charge density for our PEA system was automatically calculated only by entering material properties such as density and the permittivity of the material properties. In addition, it must be noted that the reflection of elastic waves on interfaces influence the interpretation of results in the case where PEA measurements was carried out on a sample

constructed from layers differing in acoustic characteristics.

3. Experimental Results

3.1 Analysis of materials

ESCA spectra of nitrogen and activated carbon are shown in Fig. 4. The intensity of nitrogen's 1s of non-treatment located at 400 eV is low, but the intensity of the activated carbon exposed to high frequency glow discharge for over 5 mins are high. The intensity of the latter samples increased from 3 to 4 times because nitrogen was doped onto the surface layer of the activated carbon. It is understood that nitrogen is doped by treatment with high temperature treatment. It is also reported that the capacitance of EDLC increases with nitrogen doping because electrostatic capacity increases with the nitrogen doping [9]. Similar to an intrinsic semiconductor, the numbers of electrons and positive holes in carbon are almost equal. However, the career density increases with nitrogen doping in carbon. As a result, the capacitance in the space charge layer that was in one of the electric double layers increased, hence, increasing the total capacitance. The structure of the carbon consists of carbon atom layers piled on top of each other. There are strong linkages between the carbon atoms in each layer. The combinations between the adjacent layers show a large anisotropy because of the van der Waals forces. Moreover, the carbon has both electron-donating and electron-accepting characteristics. After the plasma treatment, the nitrogen atoms were pushed and their leads to expansion of the carbon atom layers. Thus, the chemical compound between the carbon layers was generated by the intercalation of nitrogen atoms. The left peak located on 407 eV is cadmium 3d orbital. This component was extrude from glass tube on plasma surface treatment and could not influence on characteristics of EDLC for measuring space charge.

Depth profiles ESCA spectra of nitrogen's 1s orbital on above results are shown in Fig.5(a)～(c). Each profile represents the depth of nitrogen's 1s orbital for various conditions of carbon electrodes after the plasma surface treatment. Argon ion laser was used on the treatment of etching on the surface layer of carbon electrode. The exposed time of argon laser was 15 seconds in one etching, and total measurement times were 225 seconds with 15 times of etching. In Figure 5(a)～(c), the left side shows the surface of the carbon electrode, and the right side shows the bulk part of the carbon electrode. It is understood that the peak value of nitrogen's 1s orbital decreases into the bulk. However, depth of nitrogen's 1s orbital seems to be various with the time of plasma surface treatment. Figure 6 shows depth of the surface layer where the nitrogen's 1s orbital detected for various exposure time of plasma surface treatment of carbon electrodes. The depth of nitrogen's 1s orbital of plasma surface treatment become deep and changes into undulation. Therefore, plasma surface treatment not only has effect of nitrogen doping for the surface of carbon electrode but also have the ability to cut down the surface layer of carbon electrode. It was clearly understood that nitrogen atom is doped onto about 3 nm of the surface layer of carbon electrode after 60mins of plasma surface treatment.

3.2 Measurement of space charge distribution

Space charge distributions of EDLC using polarized electrodes exposed to plasma was measured by using the PEA method. Figure 7 shows the space charge distributions of EDLC. Each profile represents the spatial charge distribution in an EDLC for a charging time of 20 s with applied voltage of 2.5 V. The PEA measurement gives the curve of the space charge density versus the vertical distance from the electrode. The position, which is in the region between the two vertical dotted lines in Fig.7, is the depth of samples which is equal to the distance from anode to cathode. The dotted line on the left at 220 μm shows the negative side,

and the dotted line on the right at 600 μm shows the positive side. It is shown that the positive and negative charges appeared in the part of the electrode where a positive charge coexists with a negative charge. BF_4^- in the electrolyte and electrons in electrodes corresponding to negative charges and $(C_2H_5)_4^+$ in the electrolyte and a positive hole in the electrode corresponding to positive charge were observed. The accumulation of charges can be observed as an average space charge distribution of positive charges and negative charges in carbonaceous electrodes. The quantity of electricity was calculated when one dot shows a space charge density 4 μm wide. Space charge density is thought to be strongly affected by the charge in meso-pores of carbonaceous electrodes and the career density of nitrogen dope in space charge layer. The maximum value of the charge density of negative charge in the case of plasma surface treatment was high compared from the case of untreated electrodes. Hence, maximum charge density increased gradually. This results show that the enhancement of the surface area of EDLC and the depth of nitrogen's 1s of space charge layer can be achieved by the plasma surface treatment. The charge distribution in EDLC is also spatially uneven, i. e., hetero charge distribution, which is presumed to be caused by migration, polarization, and orientation of electrode materials [12].

4. Conclusions

In this study, we examined the effect of nitrogen doping and depth profile of ESCA spectra of nitrogen's 1s orbital on carbon electrodes of EDLC by plasma surface treatment. Measuring of the spatio-temporal profiles of positive and negative charges in EDLC with activated carbon which was exposed to high- frequency glow discharge, using the PEA method was also carried out. As a result, nitrogen is doped onto the surface layer of the activated carbon, and space charge of EDLC is a peak in the case of 10 mins of plasma surface treatment. Moreover, plasma surface treatment is shown to contribute to the increase

in the ratio of the surface area, and the improvement of electrostatic capacity can be expected.

Acknowledgements

We would like to acknowledge the technical assistance of Mr. Kazunori Nakata of Miyazaki Prefecture Industrial Technology Center on the ESCA analysis. This work is partly supported by a Grant-in-Aid for Core Research in Evolutional Science and Technology on priority areas of "Nanostructured material and system configuration turned to advanced use of energy'' from the Japan Science and Technology Agency, Japan.

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Figure captions.

Fig.1 Electric double layer model.

Fig.2 Experimental setup for plasma surface treatment.

Fig.3 Experimental setup for space charge measurement.

Fig.4 ESCA spectra of nitrogen's 1s orbital for various time of plasma surface treatment of carbon electrodes

Fig.5 Depth profiles of ESCA spectra of the nitrogen's 1s orbital for various conditions of carbon electrodes after the plasma surface treatment. (a) Non-treatment, (b) Plasma surface treatment after 10mins, (c) Plasma surface treatment after 30mins.

Fig.6 Depth of the surface layer where the nitrogen's 1s orbital detected for various exposure time of plasma surface treatment of carbon electrodes.

Fig.7 Space charge distribution of EDLC using polarized electrodes exposed to plasma.

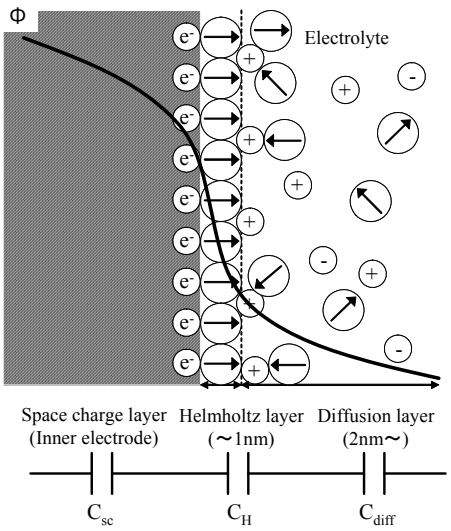


Fig.1 Electric double layer model.

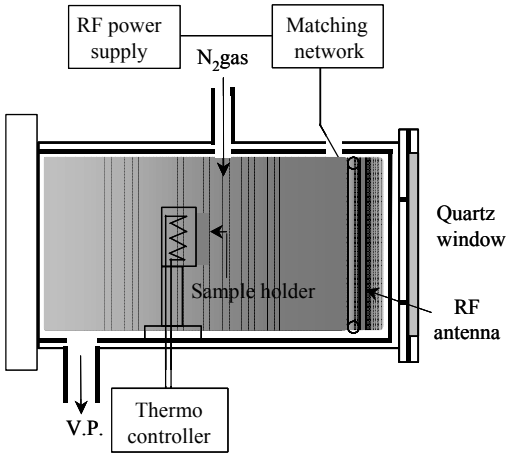


Fig.2 Experimental setup for plasma surface treatment.

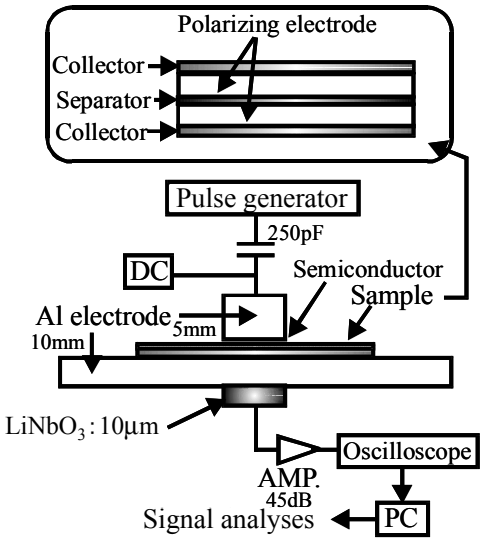


Fig.3 Experimental setup for space charge measurement.

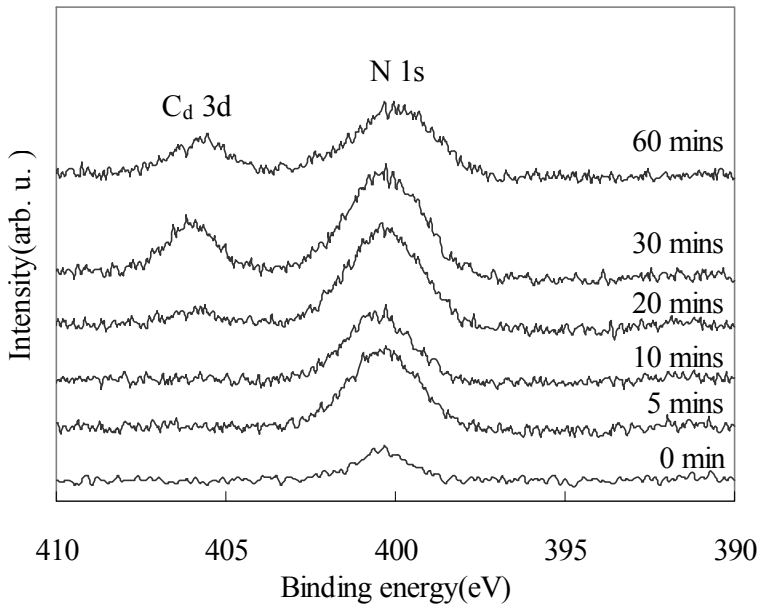
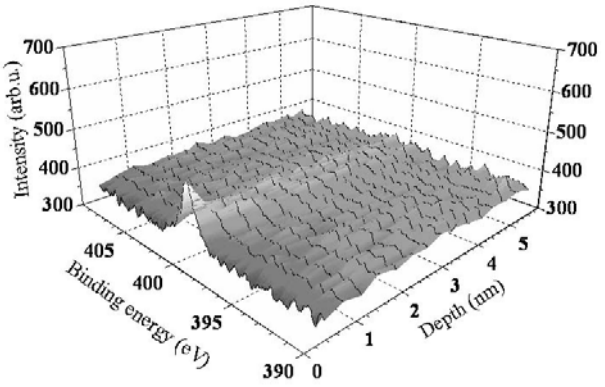
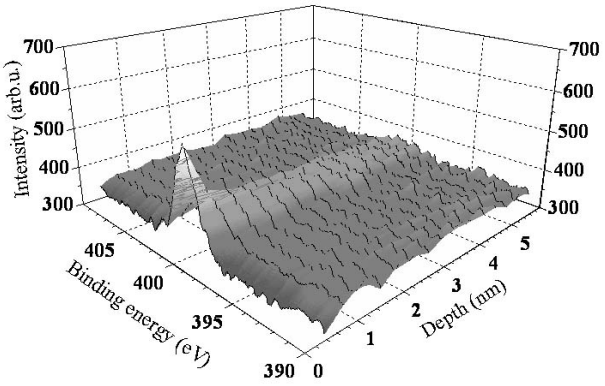


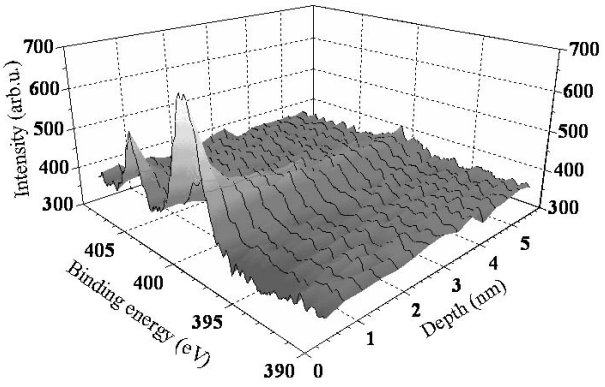
Fig.4 ESCA spectra of nitrogen's 1s orbital for various time of plasma surface treatment of carbon electrodes



(a) Non-treatment



(b) Plasma surface treatment after 10mins



(c) Plasma surface treatment after 30mins

Fig.5 Depth profiles of ESCA spectra of the nitrogen's 1s orbital for various conditions of carbon electrodes after the plasma surface treatment. (a) Non-treatment, (b) Plasma surface treatment after 10mins, (c) Plasma surface treatment after 30mins.

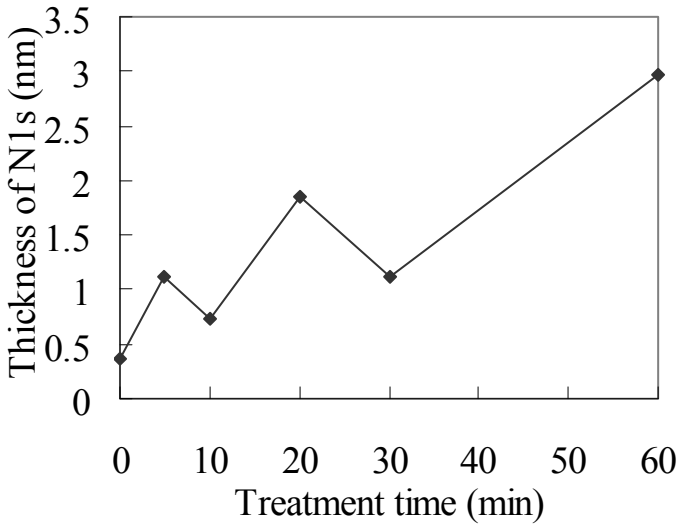


Fig.6 Depth of the surface layer where the nitrogen's 1s orbital detected for various exposure time of plasma surface treatment of carbon electrodes.

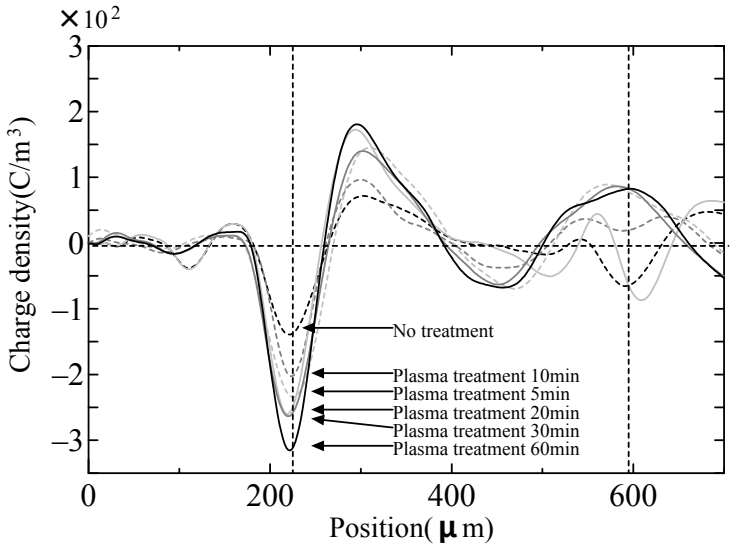


Fig.7 Space charge distribution of EDLC using polarized electrodes exposed to plasma.