Investigation of the life process of the electric double layer capacitor during float charging

Ryutaro Nozu *, Mami Iizuka, Motoi Nakanishi, Mitsugu Kotani

Nisshinbo Industries Incorporated, Research & Development Center, 1-2-3 Onodai, Midori-ku, Chiba 267-0056, Japan

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ABSTRACT

The electric double layer capacitor (EDLC) should have an almost indefinite life, because the EDLC is charged and discharged by the electrostatic adsorption and desorption of ions on electrodes whose processing involves mass transfers without a chemical reaction. However, the actual life of an EDLC is finite, such that its performance begins to slowly degrade and is significantly deteriorated at some point. We have investigated this phenomenon in detail by analyzing changes in the species of the EDLC during its life. We found that reactions on the positive and negative electrode occurred in phase with the consumption of oxygen, carbon in the electrode materials, and anions in the electrolyte during EDLC charging to change the electrode potentials and the abundance of ions on the electrodes. A product and/or disappearance by the side reactions deteriorated the performance of the active materials. Here we suggest a life process during the float charge of the EDLC and a directional concept for extending its life while comparing experimental data with theoretical models of EDLC charging.

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1. Introduction

The electric double layer capacitor (EDLC) containing activated carbon with an organic electrolyte has attracted much attention as an energy storage device for hybrid electric vehicles (HEVs) and fuel cell electric vehicles (FCVs) as well as lead–acid (Pb–acid) batteries, nickel–cadmium (Ni–Cd) batteries, nickel–metal hydrate (Ni–MH) batteries, and Li-ion batteries [1–3]. The principle of the EDLC is that an electric charge is accumulated at the interface of the electrode and electrolyte [4]. The EDLC storage capacity has been increased by using a carbon with a higher surface area or by using an organic electrolyte with a larger potential window than that of an aqueous solution, because the surface area ratio of the materials can increase the capacitance of the EDLC, and the storage energy of the EDLC is proportional to the square of the voltage [5].

The EDLC has a high power performance because it is charged and discharged by the electrostatic adsorption and desorption of ions in the electrolyte on the electrodes, and the electrostatic adsorption and desorption rates are much faster than the charge transfer rate (reaction velocity) [6–8]. Also, the device's life is believed to be almost permanent because the EDLC charge processes are only mass transfers without any chemical reactions [9]. However, the energy density of the EDLC is much lower than that of other secondary chemical batteries. Recent EDLC developments have focused on efforts to increase its storage energy density without reducing the high power performance [8,10,11]. Researchers have tried to develop an activated carbon that has a high surface area [12,13] by using a carbon fiber [14] and by controlling the functional groups on the activated carbon [15] to increase the EDLC capacitance. Many salts, for instance, tetraalkylammonium salts, pyridinium salts, and phosphonium salts [16–18], and solvents including esters and ethers [19,20] have been studied as potential electrolytes.

Although these studies of the EDLC are very important and have provided information that will help increase EDLC performance, they are all based on the major premise that the life of the EDLC is almost limitless, when in fact the life of the EDLC is limited and it is much shorter than expected. As part of research into extending the life of the EDLC, many new materials have been studied for use at high temperature or high voltage [21,22]. Investigations into the EDLC processes are done by analyzing materials that have changed in the electrodes by measuring the electrode potentials. In this study, we investigated changes in the materials and in the electrode potentials during the float charge of the EDLC.

A basic principle is that anions and cations, which have moved from the bulk electrolyte, adsorb on the surface of the positive and negative electrodes, respectively, when the EDLC is charged [6,7,11]. We might have been considered only the state that there are anions on the positive electrode and cations on the negative electrode over a long period of time. On the one hand, sealed Ni–Cd or Ni–MH

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* Corresponding author.
  E-mail address: nozu@nisshinbo.co.jp (R. Nozu).

batteries can change not only the capacities of the positive and/or negative electrodes, but also the state of the charges of the positive and/or negative electrodes. That is to say, in these sealed batteries with a negative electrode whose capacity is greater than that of the positive electrode and which have a reserve capacity for discharge and a reserve capacity for charge [23,24], the reserve capacities change during the cycle life [25]. The sum of the capacity that is proper for reactions to store energy and a capacity that is proper for side reactions during charge only has to be maintained between the positive electrode and negative electrodes because the number of electrons going to the negative electrode has to be equal to the number of electrons that have been taken from the positive electrode as the capacities consumed by both the positive and negative electrodes are equal. If the charge reaction on the positive electrode and the reaction on the negative electrode are different in quantity, the states of charge in the positive and negative electrodes are unable to remain in balance. However, the state of charge of the positive electrode could become different from that of the negative electrode in the EDLC.

We measured changes in the potentials of the positive and negative electrodes, inner pressure, and gas composition during the float charge of the EDLC for various types of gases that were substituted in the sealed EDLC before the charging to determine the states of charge of the positive and negative electrodes, which might have been oxidized or reduced. Changes in the size, shape, surface state, and composition of the elements of the positive and negative materials during the float charge of the EDLC were also carefully analyzed. Our results suggested that there was a reaction mechanism during the float charge of the EDLC.

We found that side reactions occurred with the adsorption of ions during the float charge and that the side reaction on the positive electrode utilized the carbon in the positive materials, the anion in the electrolyte, and oxygen. The particular anion may have formed an amorphous film on the positive materials to inhibit the desorption and diffusion of ions. Because the positive and negative potentials changed during the float charge by the side reactions, the states of charge of the electrodes may change, as is also seen in chemical secondary batteries. Here we propose a life process during the float charge of the EDLC and a directional concept for extending EDLC life by providing experimental data and theoretical models about the balance of the capacities and the changes in the electrode potentials.

2. Experimental procedures

2.1. Cell preparation for the investigation of the influence of atmosphere gas on EDLC performance

The float charge test at a constant voltage of 3.0 V and 70 °C was selected for the investigation of EDLC performance [26]. The EDLC samples were made according to the following procedure. Activated carbon (Kurarekohl YP, KURARAY Co., Ltd.), acetylene black (HS-100, DENKI KAGAKU KOGYO KABUSHIKI KAISHA), polyvinylidene fluoride, polyhexafluoropropylene copolymer P(VdF-HFP) $[-(CH_2-CF_2)_n-(CF_2-CFCF_3)_m-]$ (KF-P#9305, Kureha Co.), and poly(vinylidene)fluoride (PVdF) $[-(CH_2-CF_2)_n-]$ (KYNER#461, Atofina Japan K.K.) were mixed in N-methyl-2-pyrrolidone (NMP, Wako Pure Chemical Industries, Ltd.) at 100:11.1:7.1:1.8 by weight. The mixture was coated on both sides of etched Al (30CB, Japan Capacitor Ind. Co., Ltd.), and the sheets coated with the materials were dried, pressed, and used as the positive sheets. In the same way, sheets coated with activated carbon, acetylene black, polyvinylidene fluoride, polyhexafluoropropylene copolymer, and poly(vinylidene)fluoride at 100:8.2:7.5:1.9 by weight were prepared as the negative sheets.

The positive and negative sheets were cut into 130 mm × 70 mm rectangles with a tab whose size was 30 mm × 10 mm. A 1.47-g positive sheet and 1.86-g negative sheet were selected as the positive electrode and negative electrode, respectively. An element with 17 positive electrodes and 18 negative electrodes alternately stacked with polyethylene separators (NI040A, Nippon Sheet Glass Co., Ltd.) and with the tabs of the positive and negative electrodes welded to each other was constructed. The reference electrode was an etched Al foil with Al ribbon welded to it [27]. The potential of the reference electrode was kept constant because equilibrium existed between the metal Al used for the ribbon and oxidized Al used for the etched foil. The materials already used as the positive and negative substrates of the capacitor were chosen for the reference electrode. Though we understand that the reference electrode is not too common, the redox potential of Fc/Fc$^+$ vs. this reference was stable during the voltammetry of the platinum electrode in the electrolyte including ferrocene as an internal standard (Fig. 1). The voltammograms of the positive electrode in the electrolyte without the internal standard were plotted to compare the potentials.

After drying at 120 °C for 20 h while a reduced pressure of ca. 60 Torr was maintained, the element with the reference electrode was inserted into a bag made of a thermoplastic film laminated to an aluminum sheet (D-EL40H, Dai Nippon Printing Co., Ltd.), and then the electrolyte, which was prepared as a 20 wt% N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium tetrafluoroborate (DEME-BF$_4$) propylene carbonate solution [28,29], was injected. Excess electrolyte was used to fill the space volume in the bag containing the element and the electrolyte. Next, the bag was maintained at a reduced pressure of ca. 60 Torr for 4 h, and the extra solution was removed from it. A 120-g portion of the solution was left in the element, and the element with a reference electrode and electrolyte, in the bag, was used as the EDLC cell for test measurement.

The cell was placed in a sealed aluminum container with valves for substituting another gas and for connecting to a pressure sensor (FP101A-D, Yokogawa Electric Corp.) for internal pressure measurement, and with a gas sampler (SS-4CS-TW, Swagelok Company), as shown in Fig. 2. After the EDLC sample was left at 70 °C for 6 h, it was charged at a constant current of 700 mA, which was equivalent to ca. 1.0 C and a constant voltage of 3.0 V as the float charge test. Charging was stopped at arbitrary times, and the cell was discharged at a constant current of 700 mA to 1.0 V to determine the discharge energy of the EDLC. The sampled gas was analyzed for its components using a gas chromatograph (GC-9G, Shimazu Corp.) with an activated carbon column [30].

Earlier EDLC cells made of the same materials as the above EDLC sample were constructed to measure the surface area and capacitance of the positive and negative materials before and after the float charge of the EDLC. The surface areas of the positive and negative materials obtained after 0 h and 1000 h of float charge of the cells were measured by a surface area and porosimetry analyzer (TriStar 3000, Micromeritics Instrument Corp.). The reconstructed cells with the positive and negative electrodes obtained after 0 h and 850 h of float charge of the cells and new negative and positive electrodes, respectively, were made. The influence of the float charge on each electrode was investigated by measuring this capacitance.

2.2. Cell preparation for the investigation of the changes in positive and negative materials during the float charge of EDLC

Another type of EDLC sample was made for investigation of the changes in the materials during the float charge. Activated carbon (MSP 20, Kansai Coke & Chemicals Company), acetylene
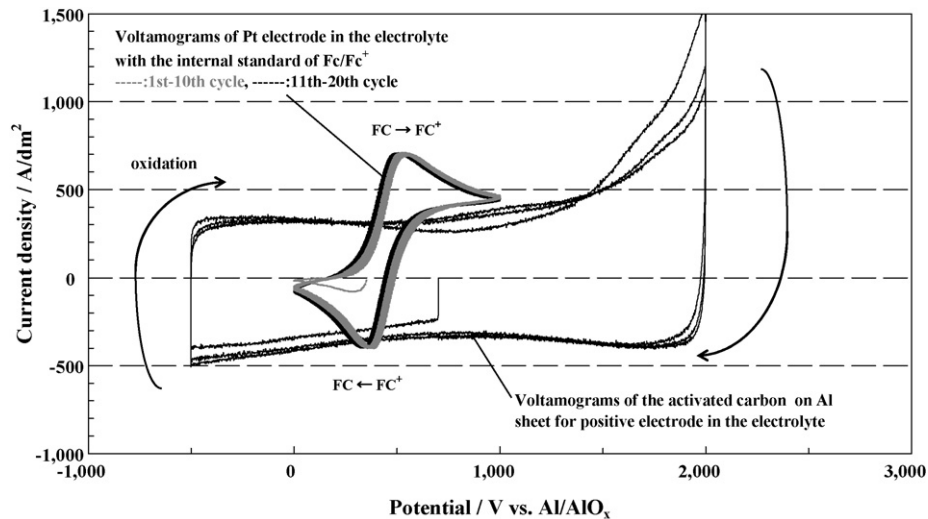
Fig. 1. Voltammograms of the platinum electrode in the electrolyte containing ferrocene as the internal standard. The plots of the positive electrode of the capacitor in the electrolyte without the internal standard are given for comparison.

black (HS-100), and styrene butadiene rubber (AZ-9001, ZEON Corp.) were mixed in a 0.8 wt% carboxymethylcellulose (DN-800H, Daicel Chemical Industries, Ltd.) aqueous solution at 100:10.0:4.0 by weight for a positive material. Activated carbon (Kurarekohl YP), acetylene black, and styrene butadiene rubber were mixed at 100:7.2:2.5 by weight for a negative material. A 2.0-g sample of carboxymethylcellulose was used with 100 g of activated carbon. The mixture was coated on one side of an etched Al (30CB, Japan Capacitor Ind. Co., Ltd.) and dried, and the pressed sheets were cut into 20 mm × 50 mm rectangles (a 20 mm × 10 mm area was left uncoated for tabbing). A 0.25-mg positive electrode and a 0.24-mg negative electrode were selected for use in the EDLC sample. An Al ribbon (width = 3.0 mm, thickness = 0.050 mm) was welded to the tab of each electrode. A positive electrode and a negative electrode were stacked face-to-face with a glass sheet (AGM separators, t = 0.200 mm, Nippon Sheet Glass Co., Ltd.) and a reference electrode. A 40 wt% N,N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium bis(trifluoromethanesulfonyl) imide (DEME-TFSI) propylene carbonate solution [31–33] was prepared as

an electrolyte. The EDLC samples for testing were made by drying the elements, injecting the electrolyte, and removing the extra electrolyte as already described, and the bags containing the element and electrolyte were sealed by hot pressing under reduced pressure. In this EDLC sample, fluorine and sulfur are given from only the THSI⁻ anions in the electrolyte.

After being left at 80 °C for 6 h, the EDLC samples were charged at a constant current of 6 mA (ca. 10 C) and a constant voltage of 3.0 V for the float charge test. After charging was halted at arbitrary times, the samples were discharged at a constant current of 6 mA or 2 mA to 0.0 V. An electrochemical measurement system (HZ-5000, Hokuto Denko Co., Ltd.) was used for measurement of the impedance through the electrolyte between the positive and reference electrodes and between the negative and reference electrodes after the float charge [34].

One cell was carefully opened for sampling of the positive electrode, the negative electrode, and the separator under a dew point of ca. −40 °C and under an Ar gas layer. The other EDLC samples were continuously charged. The sampled electrodes were dried at
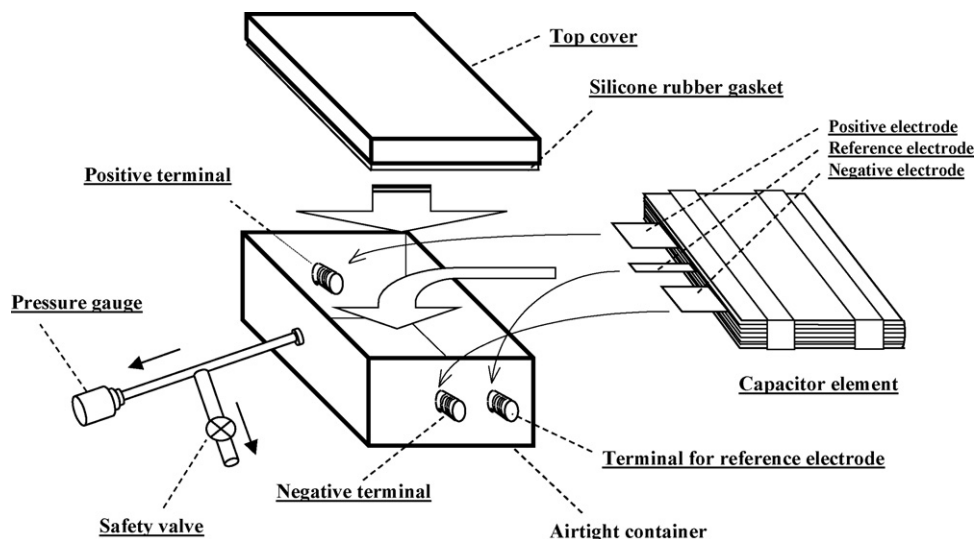

Fig. 2. Illustration of the EDLC cell and the experimental instrument with an airtight container and a pressure gauge for the investigation of its life process.

120 °C for ca. 10 h while being maintained at the reduced pressure of ca. 60 Torr. The positive materials and negative materials on each electrode were opened, powdered in a mortar, and dispersed with acetone. The dispersion was dropped onto a 5.0 mm × 5.0 mm square nickel (Ni) substrate and dried by evaporation of the solvent.

The positive and negative materials on the Ni substrate were observed by a scanning electron microscope (SEM, S-4800, Hitachi High-Technologies Corp.), and analyzed for their elemental composition using an energy dispersive X-ray microanalyzer (EDX, EX-320 with S-4800, Horiba, Ltd.). The chemical shifts on the surface of the materials were analyzed using an X-ray photoelectron spectroscope (XPS, JPS-90MX, JEOL, Ltd.) [15,35–38].

3. Results

3.1. Influence of atmosphere gas on EDLC performance

We measured the changes in the storage energy, potentials of the positive and negative electrodes, and internal pressure of the EDLC sample during the float charge at 70 °C to study the performance of the EDLC. The lengths of time when the EDLC samples were charged to a constant voltage are shown on the horizontal axis as the elapsed charge time. The influence of the gas atmosphere on the performance of the EDLC was investigated by charging the EDLC using a vented (the element of the EDLC sample was being exposed to air all the time), sealed container whose inner gas was substituted with dry air or Ar.

Changes in the discharge energy of the EDLC samples are shown in Fig. 3a. The discharge energy was measured by discharging of the EDLC at a constant current of 700 mA to 1.0 V after the float charge was stopped at an arbitrary time. We found that the discharge energy of the EDLC sample with the vent drastically decreased, while the sealed sample with dry air or Ar was maintained for a relatively long period. The internal pressure of the sealed EDLC was influenced by the atmospheric gas during the float charge of the EDLC, as shown in Fig. 3b. The increase in the internal pressure of the EDLC with Ar occurred later than the increase with dry air, as the pressure of the former hardly changed for over ca. 1400 h from a period when the pressure had slightly increased, while the pressure of the latter kept increasing all the time. Two relatively large increases of internal pressure occurred, at an early stage and after the positive potential reached a plateau in the sealed EDLC samples with dry air or Ar. We observed some electrode reactions generating gas at these times. The positive and negative potential changes of the EDLC samples were measured at a constant voltage of 3.0 V during the float charge (Fig. 3c). The positive and negative potentials of the vented EDLC and the sealed EDLC with dry air became significantly more positive after shifting more in the negative direction during the initial 100 h. The discharge energy of the vented EDLC decreased severely after its positive potentials reached and stayed at about 3.0 V vs. Al/AlO$_x$. The positive potential of the sealed EDLC with dry air slowly became more positive after exceeding about 2.5 V vs. Al/AlO$_x$. It then became more negative after reaching about 3.0 V vs. Al/AlO$_x$ with a relatively significant decrease of discharge energy. The potentials of the sealed EDLC with Ar changed only slightly until ca. 600 h and then subsequently gradually became more positive. The gas in the EDLC influenced the rate of change in the potentials, and the potentials of the EDLC provided the oxygen or the gas like vapor water including oxygen atom changed fast. Our results indicate that the discharge energy decreases significantly if the positive potential reaches about 3.0 V vs. Al/AlO$_x$.

We sampled and analyzed the gas generated during the float charge of the EDLC to determine its composition. Hydrogen and carbon monoxide were detected in the sealed EDLC with dry air dur-
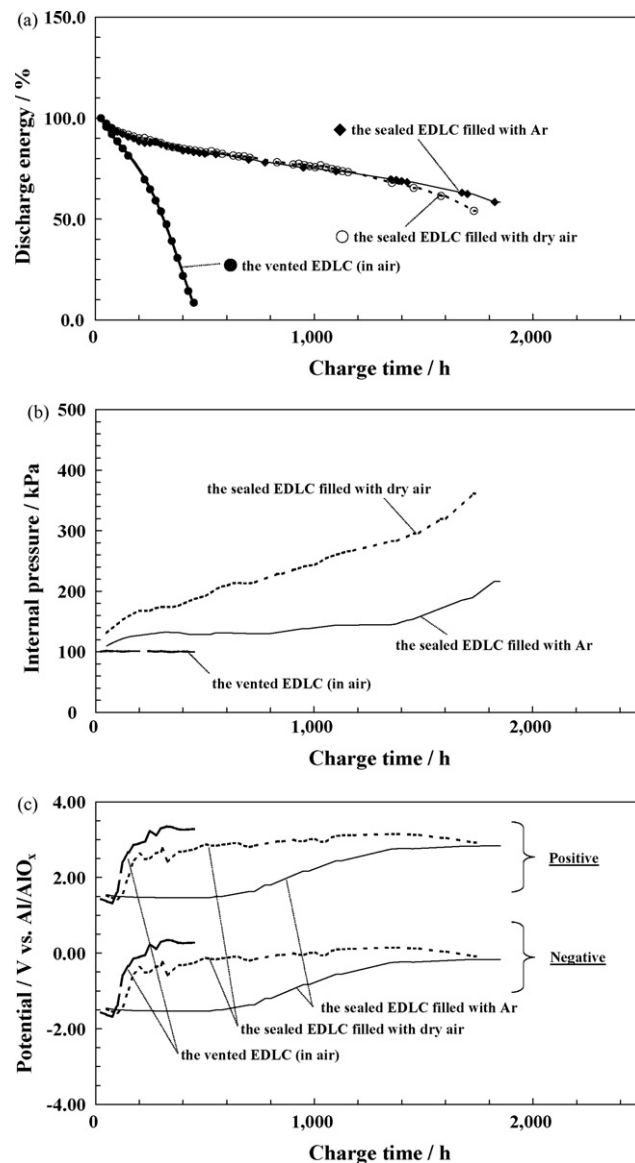

Fig. 3. (a) Discharge energy changes, (b) internal pressure changes, and (c) positive and negative potential changes of the EDLC samples under various atmospheric conditions during the float charge at a constant voltage of 3.0 V and 70 °C.

ing an early stage of the float charge, and the proportion of carbon monoxide increased while the oxygen content decreased during charging (Fig. 4a). In other words, the reaction proceeded while consuming oxygen. However, the proportion of carbon monoxide increased in the EDLC with Ar, and increase occurred much later than did that for the EDLC with dry air (Fig. 4b). While the life of the sealed EDLC with dry air had been expected to be much shorter than that with Ar, we also found that the performance of the EDLC with dry air was maintained as long as that of the EDLC with Ar. This means that almost all of the oxygen in the EDLC with dry air might be consumed in about 1000 h of a float charge to maintain its discharge energy, and thus the oxygen in the EDLC influences its life.

Additionally, the weight of the aluminum sheet as the negative substrate decreased about 1 wt% after ca. 2000 h of the float charge for the sealed EDLC with dry air, but the positive one hardly changed or had an uncertain increase. Many holes were observed in the negative electrodes after the float charge, because the negative substrates were particularly corroded, as shown in Fig. 5.
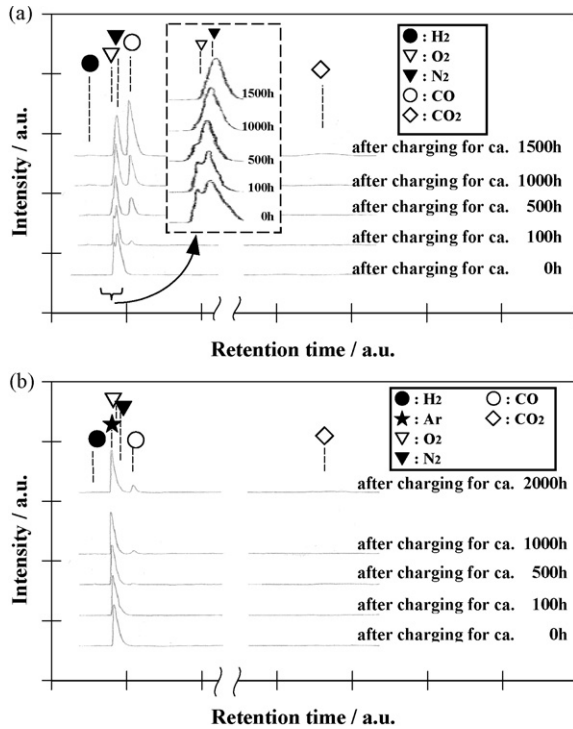
Fig. 4. Chromatograms of the gas collected from the sealed EDLC samples with (a) dry air and (b) Ar during the float charge at a constant voltage of 3.0 V and 70 °C.
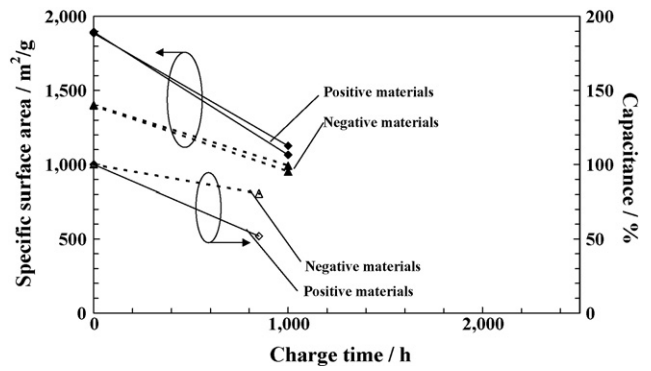

Fig. 6. Specific surface area changes of the positive and negative materials after 1000 h of the float charge of the EDLC, and capacitance change in the reconstructed cell with the positive or negative electrode after 850 h of the float charge of the EDLC.

In an equivalent investigation, the specific surface area of the positive material decreased more than did the negative material after 1000 h of the float charge. The capacitance of the cell using the positive electrode obtained after 850 h of the float charge decreased more than did that of the cell using the negative electrode (Fig. 6). The EDLC deteriorated during the float charge due to the performance decline of the positive electrode that occurred with the loss of its ability to adsorb ions.

3.2. Change in positive and negative materials during the float charge of EDLC

We charged some EDLC samples so we could investigate the changes in the positive and negative materials during the float charge. Styrene butadiene rubber (SBR), which does not include
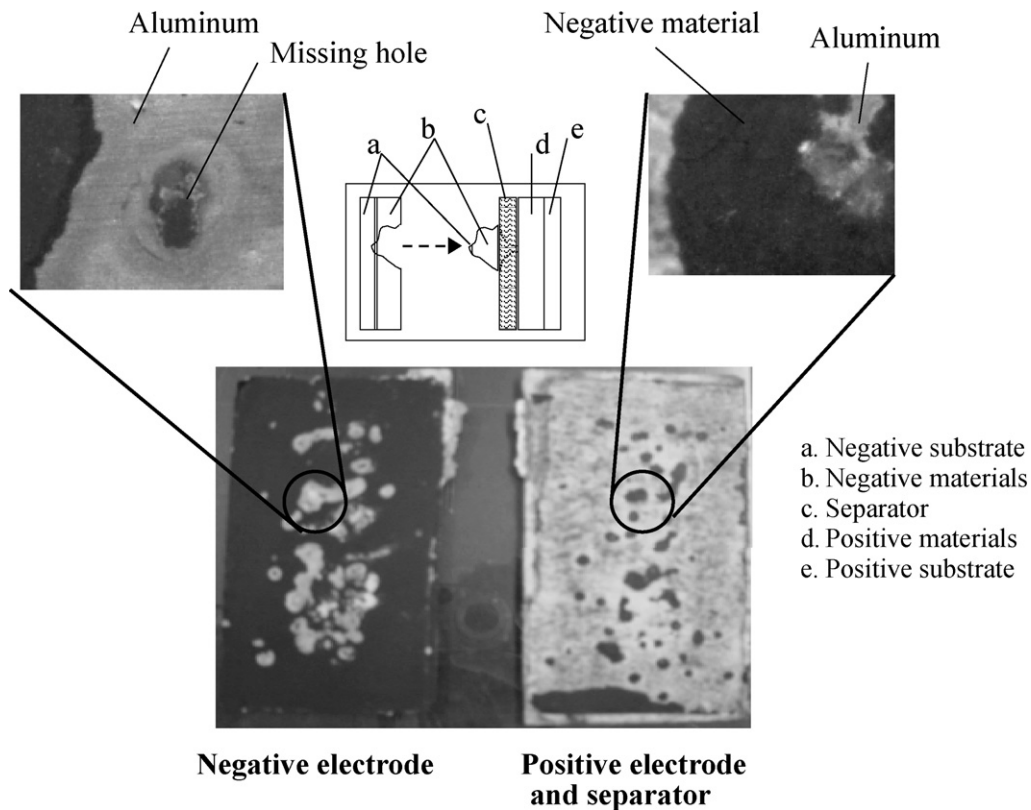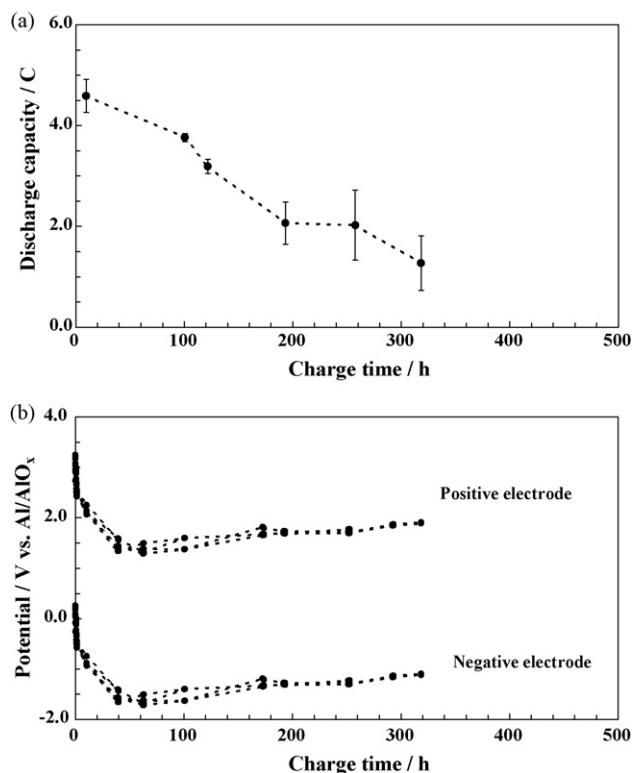

Fig. 5. Photographs of the positive and negative electrodes during the float charge of the EDLC with an illustration to show the movement of the negative material to the positive electrode.

Fig. 7. Change in (a) the discharge capacity and (b) the potential of the capacitor samples for the analysis of the electrode materials during the float charge at a constant voltage of 3.0 V and 80 °C.

Fig. 8. Evolution of the impedance diagrams of the ohmic drop through the electrolyte between (a) the positive and reference electrodes and (b) the negative and reference electrodes of the capacitor samples after the float charge at a constant voltage of 3.0 V and 80 °C.

fluorine, was used instead of PVdF as a binder material of the EDLC samples, and DEME-TFSI electrolyte was used instead of DEME-BF$_4$ for estimating the number of anions on the electrodes by analyzing the amount of fluorine and sulfur present. These samples were charged at a constant voltage of 3.0 V at 80 °C and were discharged at an arbitrary time. One of them was opened, and the positive and negative materials were analyzed.

The performance of the EDLC cells in this test depended on their internal resistance. We noted changes in the discharge capacity of the EDLC samples; the discharge capacity and potential changes are shown in Fig. 7a and b, respectively. The discharge capacity was significantly decreased at 100 h and 260 h. The positive and negative potentials of the EDLC samples during the float charge became more positive after shifting more in the negative direction at about 50 h. While the rate of change in the discharge energy and the potential did not reproduce the results obtained in the EDLC samples with the airtight container described in Section 1, the order of the staged potential changes proceeded in a similar manner. The discharge capacity seemed to decrease when the electrode potentials during the float charge became significantly more positive after ca. 100 h and ca. 250 h.

Diagrams of the evolution of the impedance between the positive and the reference electrodes and between the negative and the reference electrodes are shown in Fig. 8a and b, respectively. The changes in the internal resistance of the EDLC samples during the float charge depended on the positive electrode. The impedance corresponding to the charge transfer resistance of the positive electrode increased with the increase of the impedance in lower frequency during the float charge. The impedance increased significantly after ca. 100 h. The rate of ion adsorption and desorption on the positive electrode appeared to be slow. The impedance corresponding to the diffusion resistance of the negative electrode increased.
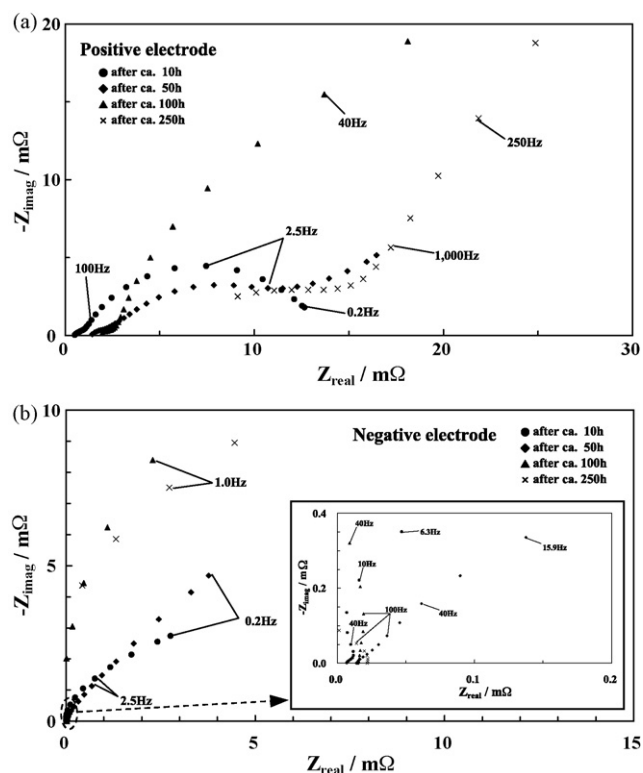
Fig. 9 displays the scanning electron micrographs of (a) the positive materials and (b) the negative materials with the surface of the substrate on which the electrode materials were pick away carefully after float charge of the EDLC samples. The activated carbon with a grain size of ~10 μm and the conductive carbon with a much smaller grain size can be seen in the positive and negative materials. As seen in Fig. 9a, although the positive substrate was covered with an amorphous film after 10 h, the film was not observed and the surface became rough from ca. 50 h to ca. 250 h. The positive materials were covered with an amorphous-like material after ca. 100 h. The amorphous material disappeared and the conductive carbon could hardly be distinguished after ca. 250 h. The conductive carbon may have been used to form the amorphous material while the positive and negative potentials became more negative during the float charge. Forming the amorphous coating on the positive materials may have increased the impedance between the positive and reference electrodes. As seen in Fig. 9b, the size and shape of the particles of the negative materials seem to hardly change until after ca. 100 h. An amorphous-like material, which may be different from the amorphous material coating the positive materials, was found to cover the negative material after ca. 250 h. The formation of the amorphous-like material on the negative electrode suggested that the float charge caused the potentials to become more positive when the impedance between the negative and reference electrodes was increased slightly from 100 h to ca.250 h.
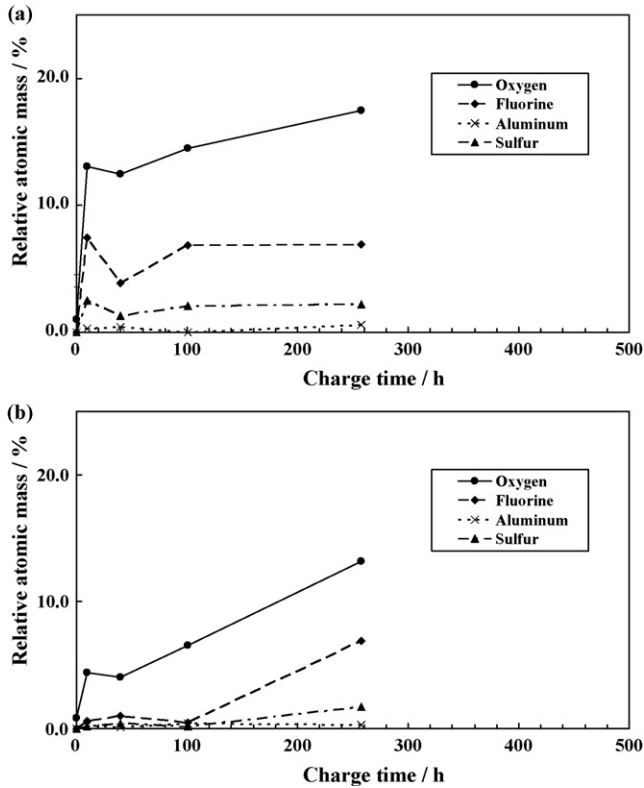
The amount of species included in the positive and negative materials after the float charge of an EDLC sample was measured by EDX. The relative abundance of oxygen, fluorine, aluminum, and sulfur as a ratio based on the abundance of the carbon element is shown in Fig. 10. Data for the positive and negative materials which did not include the electrolyte were plotted at 0 h as the basis for determining the relative abundance. As seen in Fig. 10a, the
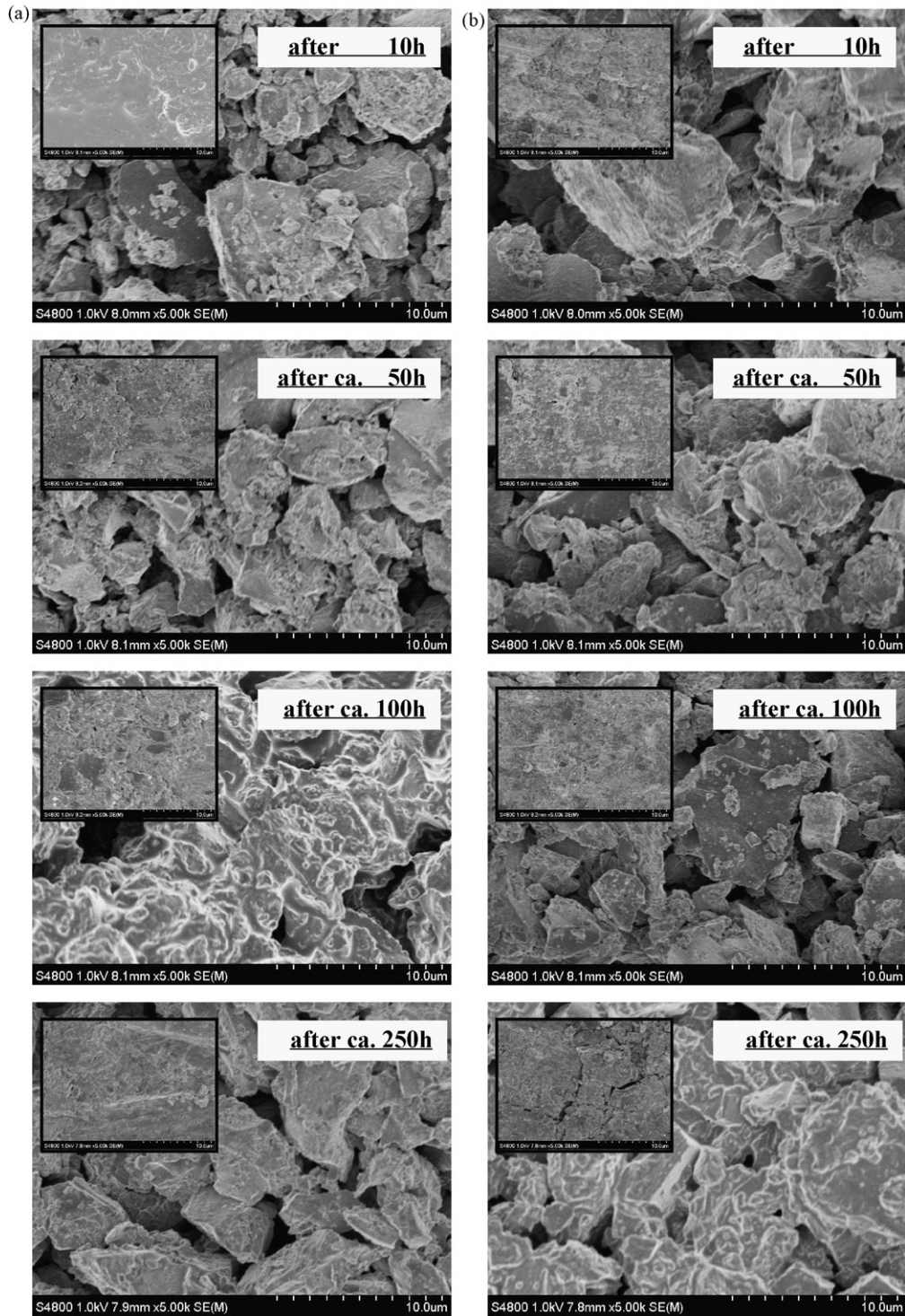
Fig. 9. Scanning electron micrographs of (a) the positive materials and (b) the negative materials of the capacitor samples with the surface of the substrate after the float charge at a constant voltage of 3.0 V and 80 °C.

abundance of oxygen in the positive materials kept increasing after it slightly decreased from ca. 10 h to ca. 50 h. Fluorine and sulfur increased from ca. 50 h to ca. 100 h, and their levels were maintained until after 250 h. The increase of fluorine and sulfur seemed to form the amorphous-like material on the positive materials or to increase the amount of TFSI⁻ anions in the positive electrode. Aluminum slightly increased after ca. 250 h. As seen in Fig. 10b, the abundance of oxygen in the negative materials increased from

ca. 50 h to ca. 250 h at a faster rate than in the positive materials. Fluorine and sulfur increased from ca. 100 h to ca. 250 h and their increase seemed to correspond to formation of the amorphous-like material on the negative materials or the increasing of TFSI⁻ anions in the negative electrode. Because a small amount of aluminum in the negative materials was found constantly from ca. 10 h to ca. 250 h, aluminum of the negative substrate may dissolve and deposit during the float charge.

Fig. 10. Change in the relative abundance of oxygen, fluorine, aluminum, and sulfur in (a) the positive materials and (b) the negative materials of the capacitor samples after the float charge at a constant voltage of 3.0 V and 80 °C. Relative abundance is the ratio to the carbon amount.

We used XPS analysis to investigate the chemical shifts in the surface of the carbon in the positive and negative materials after the float charge of the EDLC samples. The XPS spectra of the carbon 1 s binding energy on the surface of the positive and negative materials are shown in Fig. 11. Peaks or shoulders can be seen at ca. 284 eV, ca. 286 eV, and ca. 288 eV. The spectra at 284 eV and 286 eV were identified as a C—C bond and C—O bond, respectively [15,36,37]. The spectrum at 288 eV was identified as a C=C bond [38]. The peaks at 290 eV and 292 eV show the presence of the CF$_2$ and CF$_3$ species, respectively [39]. As seen in Fig. 11a, a shoulder at ca. 286 eV corresponding to the C—O bond in the positive materials decreased until 100 h of the float charge and then held steady until 250 h. A peak at ca. 288 eV, which was considered to be the C=O bond, seemed to increase after 250 h. The CF$_2$ species were detected after 100 h when an amorphous-like material was formed on the positive materials, and decreased after 250 h. As seen in Fig. 11b, the C—O bond in the negative materials kept decreasing until after 250 h. The incorporation of the CF$_2$ and CF$_3$ species seems to have slightly increased from 100 h to 250 h. Increasing and decreasing of the CF$_2$ and CF$_3$ species seemed to correlate with forming the amorphous coating on the negative materials and changing the electrode potentials during the float charge of the capacitor.

3.3. Potential change models in charging and discharging of the capacitor with and without side reactions

If there are two types of reactions that consume electrons on the positive and negative electrodes when a capacitor is charged, then in principle one is a type of electrochemical ion adsorption and the other is a type of electroxidation for the positive electrode and electroreduction of the negative electrode. The amount of electric charge for charging the EDLC is the sum of the amount of charge for the electrostatic charge by the adsorption of ions and the amount of charge for the electrode reactions on the positive and negative electrodes, respectively.

When the capacitor is charged at current I, the following equations might occur on the positive electrode and on the negative electrode:
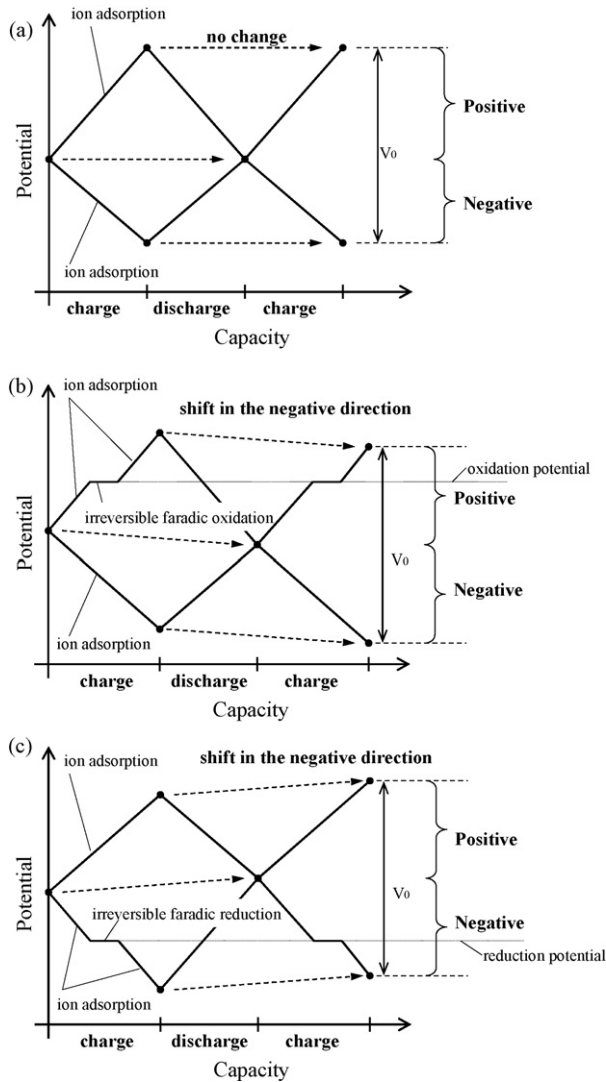
Positive electrode:

$$\int I\,dt = \int C_p dp + Q_{ox} \qquad (1)$$
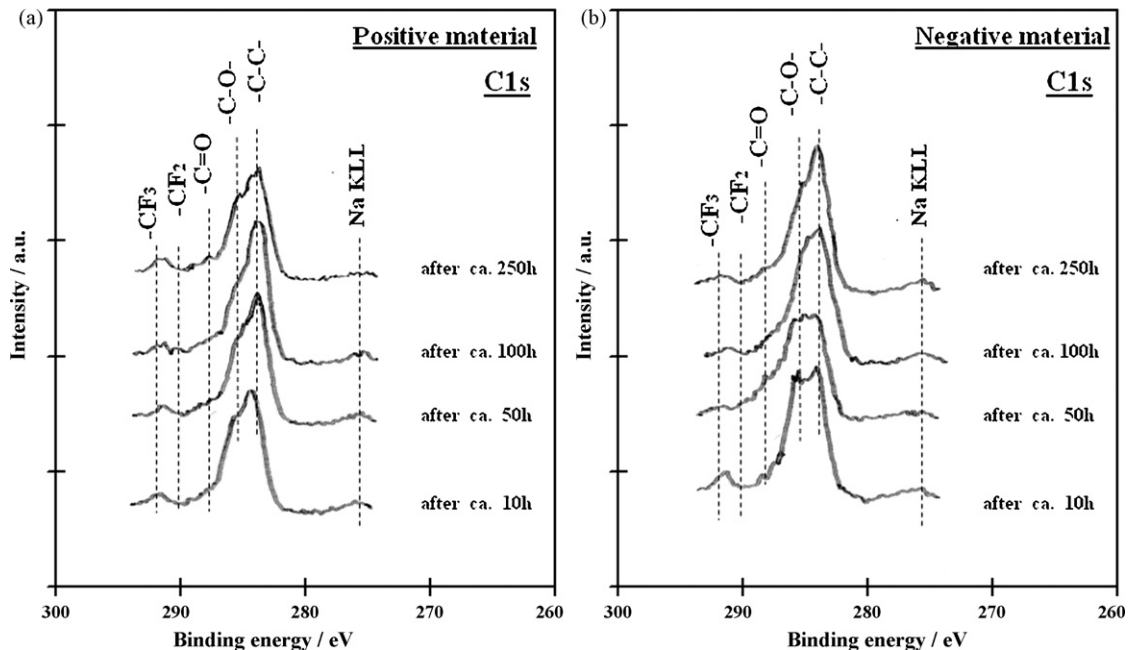
Fig. 11. X-ray photoelectron spectra of (a) the positive materials and (b) the negative materials of the capacitor samples after the float charge at a constant voltage of 3.0 V and 80 °C.

Fig. 12. Models of the changes in the positive and negative potentials during charging and discharging of the EDLC (a) without the faradic reaction, (b) with the irreversible faradic oxidation on the positive electrode, and (c) with the irreversible faradic reduction on the negative electrode.

Negative electrode:

$$\int I\,dt = \int C_n dp + Q_{red} \tag{2}$$

where t is the charge time, C_p and C_n are the electrostatic capacitances of the positive active material and the negative active material, respectively, p is the potential of the electrode, and Q_{ox} and Q_{red} are the capacities for the electroxidation and electroreduction, which might occur on the positive electrode and the negative electrode, respectively.

In the case of a system without any electrode reaction on the positive and negative electrodes ($Q_{ox} = 0$ and $Q_{red} = 0$), the variation in the electrode potentials for charging and discharging the EDLC does not change, because the electrons (from/to the power supply) are used only by the adsorption of ions to the positive and negative electrodes (Fig. 12a). This condition is idealized for the capacitor, and we believe that the state of the positive and negative electrodes will not be semipermanently changed. In the case of a system with a certain irreversible electrode oxidation on the positive electrode or when Q_{ox} is greater than Q_{red} ($\int C_p dp$ is less than $\int C_n dp$), the pos-
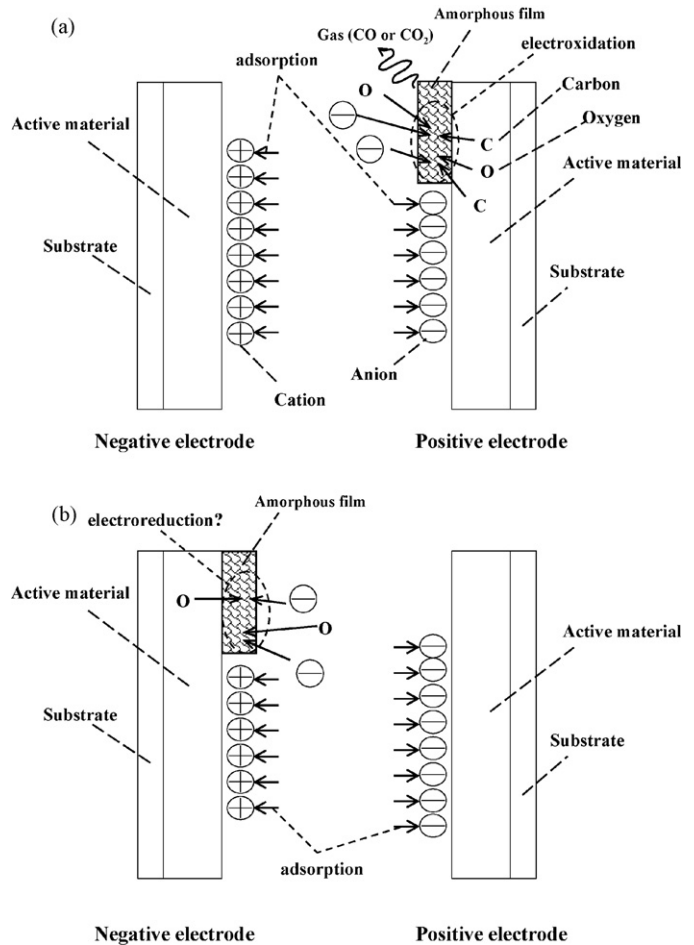
Fig. 13. Suggested scheme for the phenomena during the charge with (a) the electroxidation on the positive electrode and (b) the electroreduction on the negative electrode in the life process of the EDLC.

itive and negative potentials are considered to shift more toward the negative direction if the EDLC is repeatedly charged and discharged (Fig. 12b). In the case of a system with a certain irreversible electrode reduction on the negative electrode or when Q_{ox} is less than Q_{red} ($\int C_p dp$ is greater than $\int C_n dp$), the negative potential is maintained during the electroreduction on the negative electrode during the charge of the EDLC (Fig. 12c). The positive and negative potentials become more positive if the EDLC is repeatedly charged and discharged. In this case, there may be thermal oxidation on the negative electrode without electron transfer, because the species that is able to be electroxidized must be present.

We studied the phenomena on the positive and negative electrodes during the float charge of the EDLC in terms of the side reactions and the positive and negative potential changes. Our results suggested that there are two types of EDLC charge process, as illustrated in Fig. 13. On the one hand, the positive electrode is charged with the electroxidation, as shown in Fig. 13a. The electric charges are used by the adsorption of ions to the positive electrode and the electroxidation on the positive electrode. Oxygen, carbon, which may be the conductive carbon in the positive materials, and the elements in anions of the electrolyte appeared to cause the electroxidation, and the products cover the positive materials while generating CO and/or CO_2 gas. Then, that the rate of the ion desorption and the diffusion on the positive electrode becomes slow. The potentials of the positive and negative electrodes shift in the negative direction during the float charge, because the state of charge

of the positive electrode decreases. On the other hand, the negative electrode is charged with the electroreduction, as shown in Fig. 13b. The electric charges are used by the adsorption of ions to the negative electrode and the electroreduction on the negative electrode. The products, which include oxygen and the elements in anions of the electrolyte by the electroreduction, may cover the negative materials. The potentials of the positive and negative electrodes become more positive during the float charge, because the state of charge of the negative electrode decreases. The performance of the EDLC appears to deteriorate in response to the two types of charge process, though the side reaction may be different at various stages. The deterioration of the positive electrode appeared to influence the performance of the EDLC during the float charge.

4. Conclusion

We studied the adsorption of ions to the positive and the negative electrodes and the side reactions, which were the electroxidation on the positive electrode and the electroreduction on the negative electrode, during the charge of the EDLC. The materials produced and/or diminished by the side reaction appeared to deteriorate the performance of the electrode for the adsorption and desorption of ions. And, the existence of the side reaction during the float charge of the EDLC changed the potential and the state of charge of the positive or/and negative electrode. The other side reaction may be caused by the electrode potential is changed. The two types of charge process may alternate during the life of the EDLC, thus influencing its performance.

In this work, the product of electroxidation on the positive electrode covered the positive materials to resist the desorption and diffusion of ions on the positive electrode. The product included oxygen, carbon, which may be the conductive carbon in the positive materials, and the elements in the anions of the electrolyte.

It is important for extending the life of the EDLC to control the side reactions that cause a loss of ability of adsorbing ions on the electrodes and that change the electrode potentials to cause the another side reaction.

References

[1] M. Okamura, H. Hasuike, M. Yamagishi, S. Shuuichi, Electrochemistry 69 (2001) 414.
[2] D.Y. Jung, Y.H. Kim, S.W. Kim, S.-H. Lee, J. Power Sources 114 (2003) 366.
[3] A.D. Pasquier, I. Plitz, S. Menocal, G. Amatucci, J. Power Sources 115 (2003) 171.
[4] H.I. Becker, V. Ferry, US Patent 2,800,616 (1957).
[5] D.L. Boos, J.E. Metcalfe, US Patent 3,634,736 (1972).
[6] B.S. Trasatti, P. Kurzweil, Platinum Met. Rev. 38 (1994) 46.
[7] B.E. Conway, J. Power Sources 15 (1995) 65.
[8] J.H. Jang, S. Han, T. Hyeon, S.M. Oh, J. Power Sources 123 (2003) 79.
[9] P.L. Taberna, P. Simon, J.F. Fauvarque, J. Electrochem. Soc. 150 (2003) A292.
[10] J.P. Zheng, J. Huang, T.R. Jow, J. Electrochem. Soc. 144 (1997) 2026.
[11] D. Que, J. Power Sources 109 (2002) 403.
[12] J. Gamby, P.L. Taberna, P. Simon, J.F. Fauvarque, M. Chesneau, J. Power Sources 101 (2001) 109.
[13] Y.-Z. Wei, B. Fang, S. Iwasa, M. Kumagai, J. Power Sources 141 (2005) 386.
[14] Y.O. Choi, K.S. Yang, J.H. Kim, Electrochemistry 69 (2001) 837.
[15] A. Yoshida, I. Tanahashi, A. Nishino, Carbon 28 (1990) 611.
[16] M. Ue, M. Takehara, Y. Oura, A. Toriumi, M. Takeda, Electrochemistry 69 (2001) 458.
[17] M. Ue, M. Takeda, A. Toriumi, A. Kominato, R. Hagiwara, Y. Ito, J. Electrochem. Soc. 150 (2003) A499.
[18] K. Xu, M.S. Ding, T.R. Jow, J. Electrochem. Soc. 148 (2001) A267.
[19] J.M. Vollmer, L.A. Curtiss, D.R. Vissers, K. Amine, J. Electrochem. Soc. 151 (2004) A178.
[20] M. Arulepp, L. Permann, J. Leis, A. Perkson, K. Rumma, A. Jänes, E. Lust, J. Power Sources 133 (2004) 320.
[21] M. Nakumura, R. Nozu, US Patent Publication Application 2006/0007637 (2006).
[22] K. Matsukawa, K. Kato, Y. Nakahara, K. Nishimura, M. Kimoto, JP Patent Publication Application 2005-268316 (2005).
[23] G. Neumann, U. Gottesmann, US Patent, 2,571,927 (1990).
[24] R.F. Nelson, J. Power Sources 31 (1990) 3.
[25] H. Kaiya, T. Ookawa, J. Alloys Compd. 231 (1995) 598.
[26] M. Okamura, Electric Double Layer Capacitors and Electricity Storage Systems, Nikkan Kogyo Shinbunsha, Japan, 1999, pp.107–112 (in Japanese).
[27] R. Nozu, M. Nakamura, K. Banno, T. Maruo, T. Sato, J. Electrochem. Soc. 153 (2006) A1031.
[28] T. Sato, G. Masuda, K. Takagi, Electrochimica. Acta 49 (2004) 3603.
[29] T. Sato, T. Maruo, S. Marukane, K. Takagi, J. Power Sources 138 (2004) 253.
[30] S.A. Greene, E.M.L. Moberg, E.M. Wilson, Anal. Chem. 28 (1956) 1370.
[31] S. Seki, Y. Kobayashi, H. Miyashiro, Y. Ohno, Y. Mita, A. Usami, N. Terada, M. Watanabe, Electrochem. Solid-State Lett. 8 (2005) A577.
[32] Y.-J. Kim, Y. Matsuzawa, S. Ozaki, K.C. Park, C. Kim, M. Endo, H. Yoshida, G. Masuda, T. Sato, M.S. Dresselhaus, J. Electrochem. Soc. 152 (2005) A710.
[33] K. Yuyama, G. Masuda, H. Yoshida, T. Sato, J. Power Sources 162 (2006) 1401.
[34] M. Dolle, F. Orsini, A.S. Gozdz, J.-M. Tarascon, J. Electrochem. Soc. 148 (2001) A851.
[35] A.D. Jannakoudakis, P.D. Jannakoudakis, E. Theodridou, J.O. Besenhard, J. Appl. Electrochem. 20 (1990) 619.
[36] E. Riedo, F. Comin, J. Chevrier, A.M. Bonnot, J. Appl. Phys. 88 (2000) 4369.
[37] Z. Jiang, W. Zhou, D. Tan, R. Zhai, X. Bao, Surf. Sci. 565 (2004) 269.
[38] M. Rjeb, A. Labzour, A. Rjeb, S. Sayouri, M. Chafik El Idrissi, S. Massey, A. Adnot, D. Roy, M. J. Condens. Matter. 5 (2004) 168.
[39] D.A. Brevnov, M.J. Barela, M.J. Brooks, G.P. López, P.B. Atanassov, J. Electrochem. Soc. 151 (2004) B484.