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Chapter

Deterioration Factors of Electric Double-Layer Capacitors Obtained from Voltage Hold Test

Daisuke Tashima

Abstract

A chemical analysis was carried out before and after a constant voltage hold test (applied at 2.5, 2.8, 3.0, and 3.2 V individually for 1 week) that was an acceleration deterioration examination to clarify the deterioration factors of electric double-layer capacitors. The results showed that the stress test slightly raised the internal resistances and decreased the capacitances. It was also confirmed that a range of fluorochemicals was formed on the electrode surface for approximately 10–13 nm in depth using electron spectroscopy for chemical analysis. From a chemical analysis of the electrolyte using an inductively coupling plasma-optical emission spectrometer (ICP-OES), it was confirmed that the electrolyte included Si, which is an ingredient element of an electrode, and that the increase in the holding voltage during the stress test decreased the Si density in the electrolyte.

1. Introduction

In contrast to chemical batteries, electric double-layer capacitors (EDLCs) store and release electrical energy by utilizing the physical adsorption and desorption of an electric charge, but without utilizing any chemical reactions. Compared to chemical batteries, EDLCs have superior responsiveness, and since they allow for rapid high-voltage charging and discharging, they are high-performance device, last through a high number of charging/discharging cycles, and theoretically do not deteriorate. Owing to these advantages, EDLCs have recently been utilized as auxiliary power supplies in hybrid electric vehicles (HEVs), which combine an internal combustion engine and an electric motor with the aim of being maintenance free. However, performance degradation has recently been confirmed in commercially used EDLCs owing to overvoltage and high temperatures, including a decrease in capacitance and an increase in internal resistance. To confirm these phenomena and to predict degradation mechanism, chemical and electrochemical aging test were performed using original electrode under acetonitrile (AN)-based electrolyte, propylene carbonate (PC)-based electrolyte [1–7], and ionic liquid as electrolyte [8]. It was also reported that aging model was calculated and aging diagnosis was built up using manufactured EDLCs under overvoltage and high-temperature condition [9–20]. For this chapter, we performed a voltage hold test, which is a type of accelerated degradation test for EDLCs using the application of overvoltage, on

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cylindrical EDLCs, which are used in actual applications [21]. We confirmed the degradation behaviors caused by the application of overvoltage by measuring the capacitance and internal resistance before and after the tests. Moreover, we disassembled the EDLCs once testing was complete and ran a variety of analyses on the polarizable electrodes and the electrolytes that form its constituent parts. By comparing and studying the analytical results and the deterioration behaviors, we studied the deterioration mechanism of EDLCs.

2. Experimental method

As shown in **Table 1**, voltage hold tests were conducted by applying overvoltages of 2.8, 2.9, 3.0, 3.2, and 3.5 V continuously for 1 week to commercially used cylindrical EDLCs with a rated voltage of 2.5 V. Using a Sanyo Electric Co., Ltd., incubator (MIR-254) and a charging/discharging tester (PS-97010) by PowerSystem Co., Ltd., three accelerated deterioration samples were produced for each voltage at a constant temperature of 25°C.

Rated voltage [V]	2.5				
Rated capacitance [kF]	1.2				
Size	Height: 150 mm, Diameter: 40 mm				
Type	Cylindrical				
Holding voltage [V]	2.8	2.9	3.0	3.2	3.5
Number of samples	3	3	3	3	3

Table 1.
Experimental conditions and sample properties.

3. Measuring capacitance and internal resistance

3.1 Measuring method of capacitance and internal resistance

Before and after the voltage hold test, charging and discharging were performed at a constant current of 6 A and a voltage of 2.5 V using a stabilized DC power supply (PAN60-6A) and an electronic load device (PLZ603WH) by Kikusui Electronics Corp. Using the energy conversion method, the capacitance was calculated based on the obtained charge and discharge waveforms, and the internal resistance was calculated based on the voltage drop.

3.2 Measuring results of capacitance and internal resistance

Figure 1 shows the variance in the capacitance and internal resistance before and after the voltage hold test for each holding voltage. The internal resistance increased most for a holding voltage of 3.5 V, with a rise of approximately 30% compared to
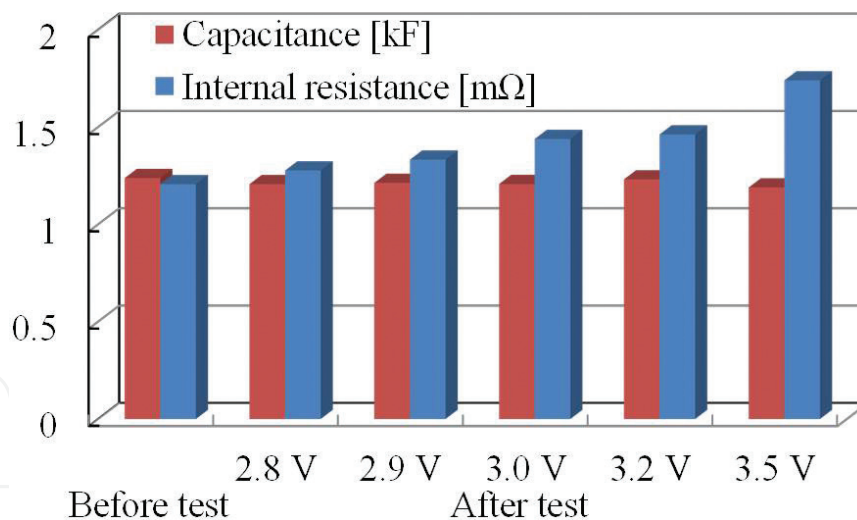
Figure 1.
Pre/postvoltage hold test properties for each applied voltage.

the value prior to the voltage hold test. Regardless of the holding voltage, the capacitance did not vary significantly from that before the test. Based on this, it was found that the rise in the holding voltage during the voltage hold test greatly affected the factors that cause an increase in the internal resistance.

4. Chemical analysis of polarizable electrodes

For qualitative and state analyses of the polarizable electrodes, we used an X-ray photoelectron spectroscopy (XPS) analysis device [electron spectroscopy for chemical analysis (ESCA-3300)] by Shimadzu Corporation. A scanning electron microscope (S-5500) by Hitachi Ltd. was used to observe the polarizable electrode surfaces.

4.1 Polarizable electrode surface observation

Figure 2(a) and **(b)** shows scanning electron microscopy (SEM) images for the polarizable electrode surfaces during the pretest. Granular electrically conducting material can be confirmed through the images. Furthermore, it was found that the polarizable electrodes consist of activated carbon and electrically conducting material, and it was confirmed that there is no variance between the positive and negative electrodes. **Figure 2(c)–(l)** is SEM images for the posttest polarizable electrode surfaces for each holding voltage. It is clear from **Figure 2(a)** and **(d)** that when comparing the pretest polarizable electrode surfaces with those after testing at a holding voltage of 2.8 V, there is no variance in the activated carbon and electrically conducting materials. However, based on **Figure 2(e)–(l)**, for polarizable electrode surfaces after tests at holding voltages of 2.9, 3.0, 3.2, and 3.5 V, both an increase in the holding voltage and a deformation of the surfaces of the positive and negative electrodes can be confirmed. Surface irregularities can be confirmed for the positive electrodes, as well as the generation of a deposit layer on the surface. Moreover, the generation of granules smaller than the electrically conducting material can be confirmed on the negative electrodes. Accordingly, it is believed that deposits produced through a reaction of some sort inside the EDLC cell cause an increase in the internal resistance [5–7, 12].
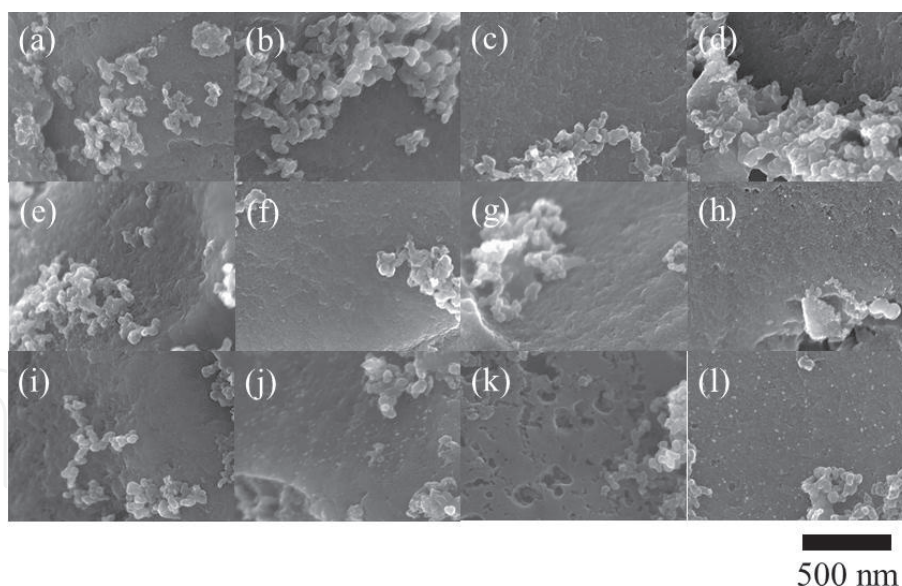
Figure 2.
Polarizable electrode surface (a) positive electrode (PE) before test, (b) negative electrode (NE) before test, (c) PE after test at holding voltage of 2.8 V, (d) NE after test at holding voltage of 2.8 V, (e) PE after test at holding voltage of 2.9 V, (f) NE after test at holding voltage of 2.9 V, (g) PE after test at holding voltage of 3.0 V, (h) NE after test at holding voltage of 3.0 V, (i) PE after test at holding voltage of 3.2 V, (j) NE after test at holding voltage of 3.2 V, (k) PE after test at holding voltage of 3.5 V, and (l) NE after test at holding voltage of 3.5 V.

4.2 Analysis of elements existing on polarizable electrodes

Qualitative analysis results show that no major spectral differences can be seen based on observations of the pretest polarizable electrodes and posttest polarizable electrodes for each holding voltage, and that the observations chiefly consist of three elements: carbon, fluorine, and oxygen. It follows that the deposits observed on the electrode surface are fluorine, oxygen, and carbon derived. To reveal how the deposits, which consist of the same elements as the polarizable electrodes, cause a reduction in performance of the EDLC, we conducted a more detailed state analysis of the electrode surfaces. It is believed that owing to the holding voltage in the voltage hold test (an accelerated deterioration test), a change of some sort is caused in the binding states of carbon, fluorine, and oxygen. We, therefore, applied an etching process to the electrode surface and measured the changes in spectral intensity in the depth direction for C1s, O1s, and F1s, thus studying to what depth the electrode surface deposits were produced.

Figures 3–**8** show the variance in the observed spectral intensity in the depth direction for (a) C1s, (b) F1s, and (c) O1s on positive electrode and (e) C1s, (f) F1s, and (g) O1s on negative electrode. Furthermore, (d) and (h) show the atomic composition ratios on positive electrode and negative electrode, respectively. It is clear from **Figure 3** that for the polarizable electrodes before the voltage hold test, the positive and negative electrodes consist of carbon, oxygen, and fluorine until a depth of 25 nm from the surface. Furthermore, since the composition ratio from approximately 2–3 nm below from the electrode surface is stable, it is thought that a 2–3 nm film exists on the polarizable electrodes. It is believed that since the cell interior was exposed to electrolytes prior to the polarizable electrodes being chosen, the polarizable electrodes reacted with the oxygen and the fluorine in the electrolyte at the solid-fluid interface.

No large difference is seen between the pre- and postvoltage hold-test polarizable electrodes at a holding voltage of 2.8 V. However, as shown in **Figure 5**, after the

Positive electrode

(a) C1s

(b) F1s

(c) O1s

(d) Atomic composition ratio

Negative electrode

(e) C1s

(f) F1s
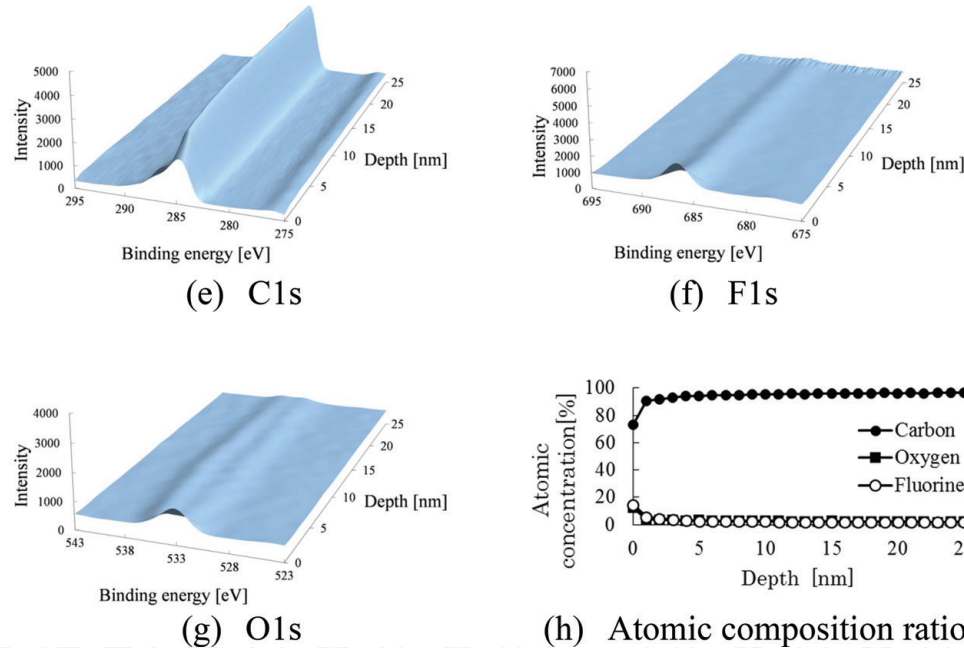
(g) O1s

(h) Atomic composition ratio
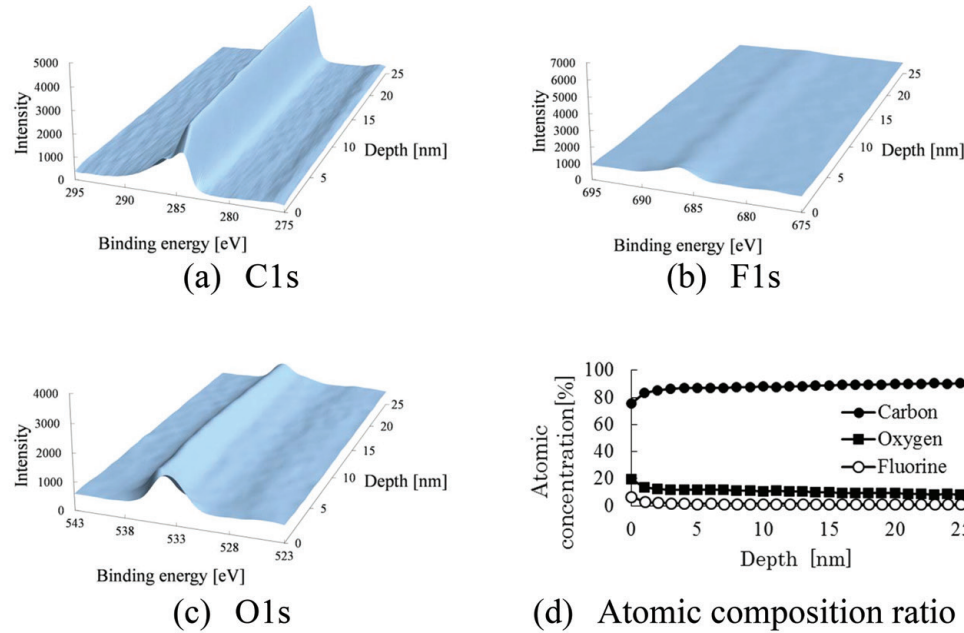
Figure 3.
Pretest polarizable electrode.

voltage hold test at a holding voltage of 2.9 V, the O1s spectral intensity decreased and the F1s spectral intensity increased. Graphs (d) in **Figure 5** show that they almost only consist of carbon and fluorine up to a depth of 15 nm. Accordingly, it is believed that through the application of voltages of 2.9 V and higher, the bond between carbon and oxygen in the polarizable electrodes is broken, and oxygen atoms are released. Moreover, since there is virtually no change in the composition ratio at a depth of approx. 10–13 nm from the surface, it is clear that the fluorine compound layer has increased in thickness compared to that before the test. Since this reactant consists of carbon and fluorine [5], it is believed to be graphite fluoride. It can be inferred from the fact that graphite fluoride is an insulator that the electrode resistance was caused to increase, thus causing the internal resistance

Positive electrode

(a) C1s

(b) F1s

(c) O1s

(d) Atomic composition ratio

Negative electrode

(e) C1s

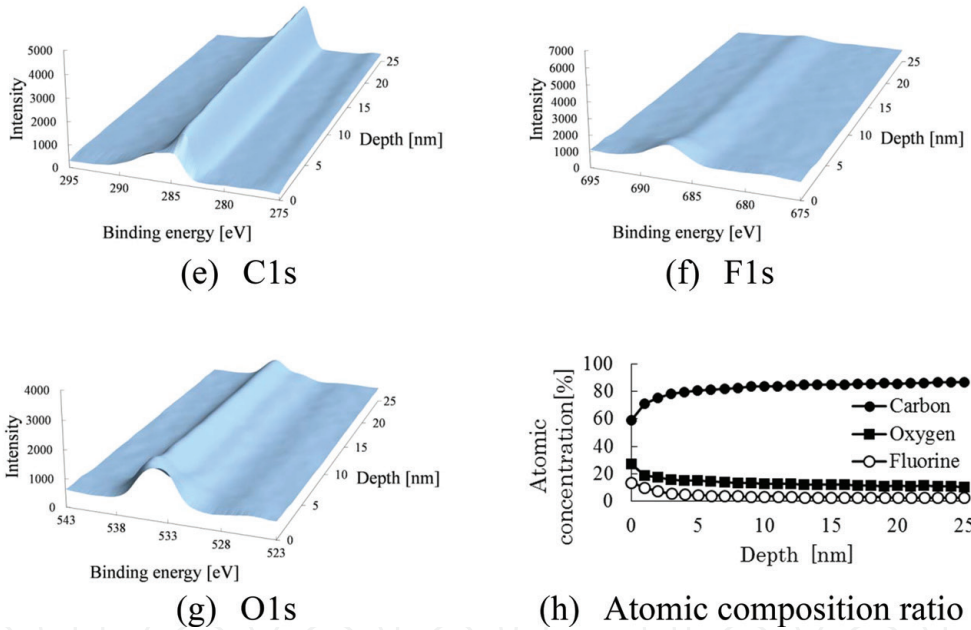(f) F1s

(g) O1s

(h) Atomic composition ratio
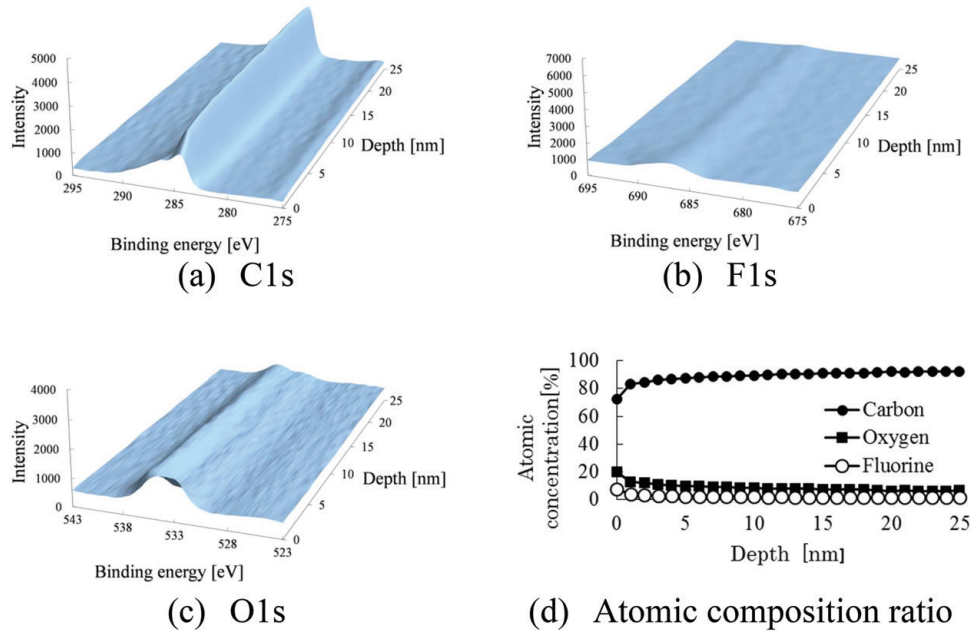
Figure 4.
Polarizable electrode after test with holding voltage of 2.8 V.

to increase. Furthermore, it was shown that no major difference was seen in the composition changes in the depth direction of the positive and negative electrodes.

5. Chemical analysis of electrolyte

5.1 Measuring moisture content of electrolyte

It was shown that in samples subject to high voltage, the electrolyte reacts with the polarizable electrode at the solid-fluid interface, altering the atomic composition ratio of the polarizable electrode. Moreover, since the reaction at the solid-fluid interface accelerates with an increase in the applied voltage, it can be inferred that some sort of change is also occurring in the electrolyte. We, therefore, measured the
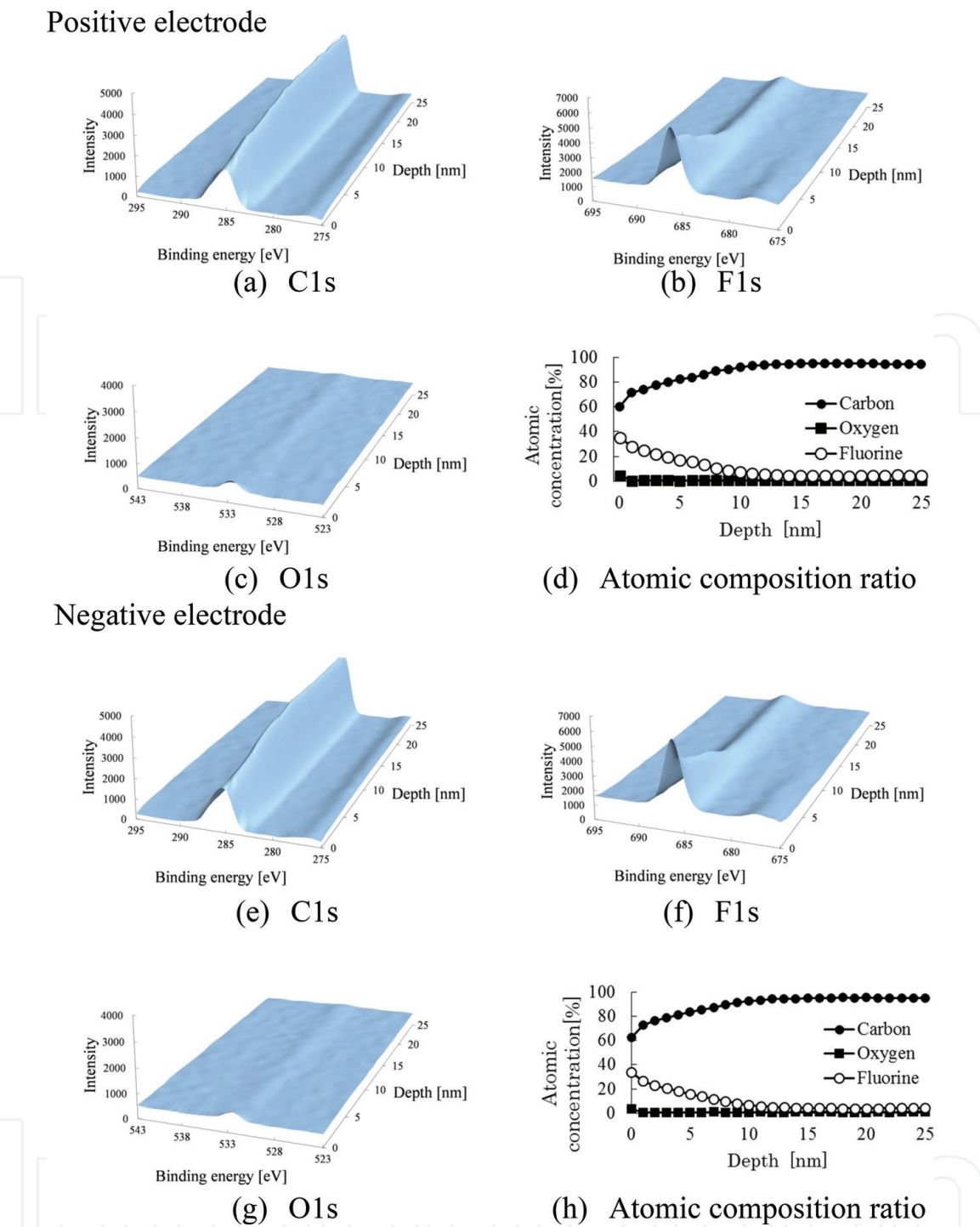
Positive electrode

(a) C1s

(b) F1s

(c) O1s

(d) Atomic composition ratio

Negative electrode

(e) C1s

(f) F1s

(g) O1s

(h) Atomic composition ratio

Figure 5.
Polarizable electrode after test with holding voltage of 2.9 V.

moisture content in the electrolyte taken from the EDLCs. A Karl Fischer Moisture Titrator (MKC-610) by Kyoto Electronics Manufacturing Co., Ltd., was used for these measurements.

5.2 Moisture content of electrolyte: measurement results

Figure 9 shows the moisture content in the electrolyte taken from the EDLCs before the tests and after the tests at each applied voltage. A comparison of moisture content in the electrolyte before and after the test when 2.8 V is applied found an increase of approximately 14.4%. However, it was found that compared to the value before the test, the moisture content decreased after tests that applied 2.9, 3.0, 3.2, and 3.5 V. The lowest moisture content was seen in the electrolyte after the 2.9-V
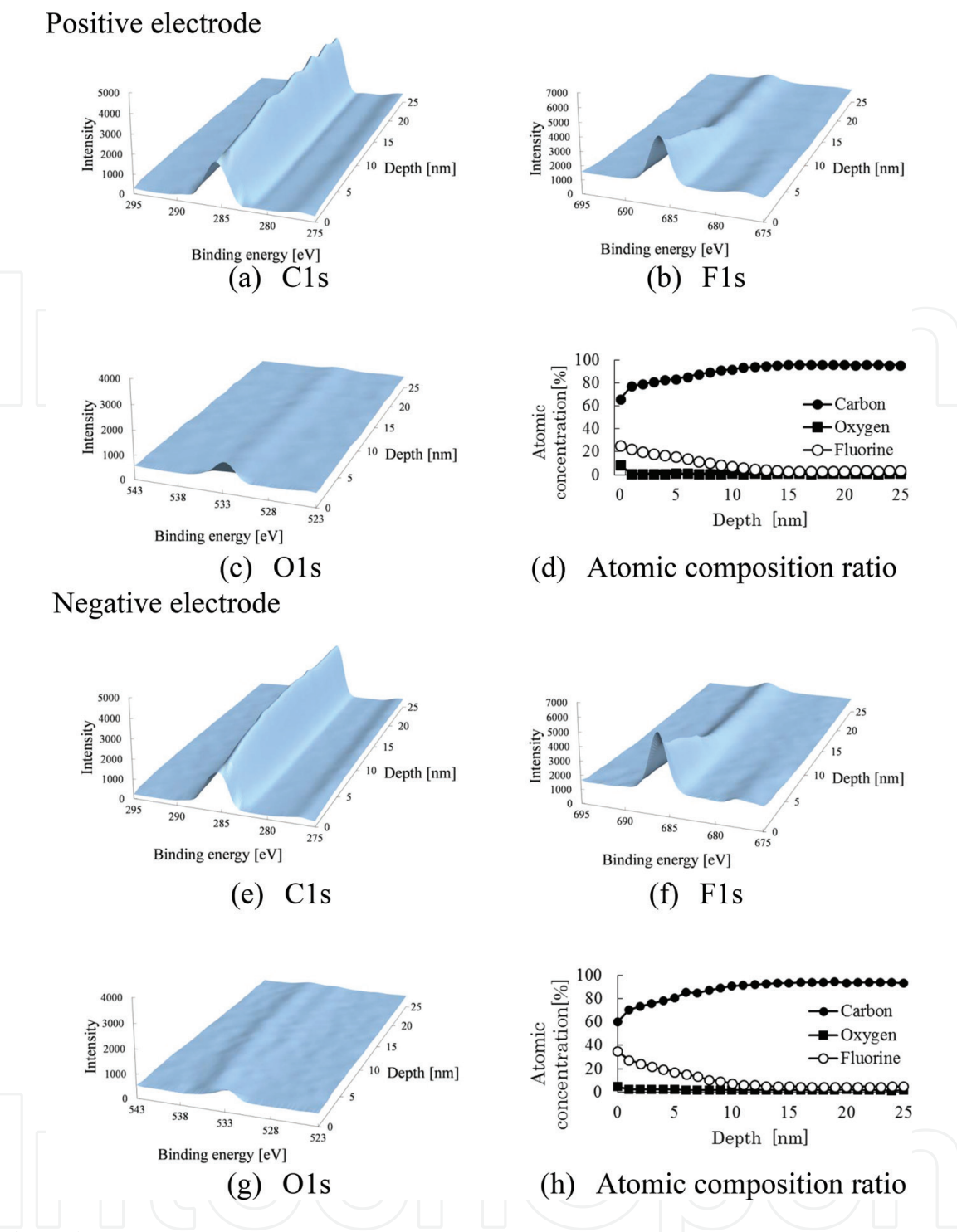
Positive electrode

(a) C1s

(b) F1s

(c) O1s

(d) Atomic composition ratio

Negative electrode

(e) C1s

(f) F1s

(g) O1s

(h) Atomic composition ratio

Figure 6.
Polarizable electrode after test with holding voltage of 3.0 V.

test, with a 16.9% decrease compared to that before the test. Based on these results, it is believed that there is no correlation between increasing the applied voltage and decreasing the moisture content, and that the moisture content included when the EDLCs were built is retained.

5.3 Measuring electrolyte element concentrations

It was revealed that there was no correlation between an increase in the holding voltage in the voltage hold test and an increase or decrease in the moisture content shown in **Figure 9**. Accordingly, any chemical changes in the electrolyte owing to an increased holding voltage can be considered to be other than moisture related. The elution of electrode material into the electrolyte sometimes occurs during
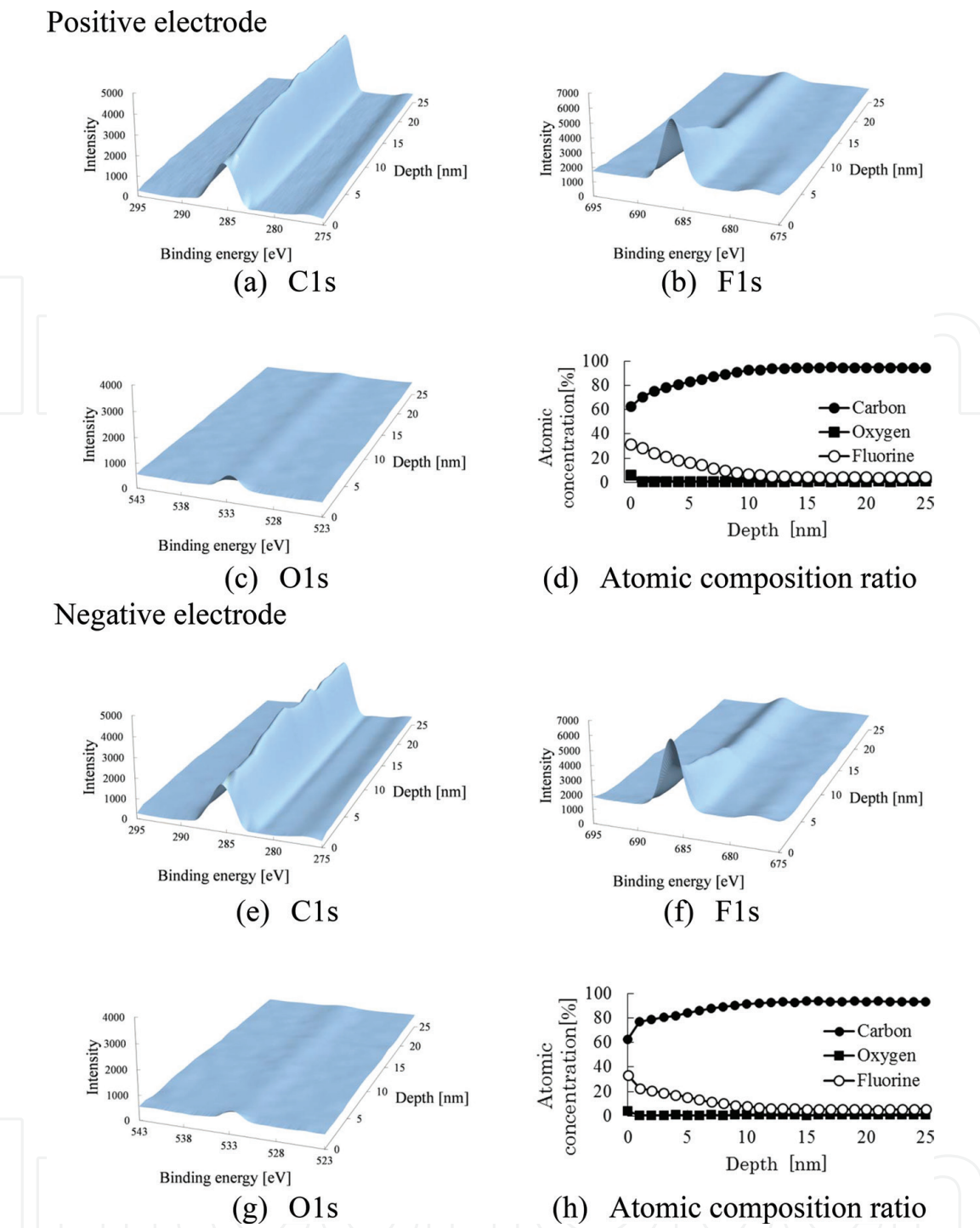
Figure 7.
Polarizable electrode after test with holding voltage of 3.2 V.

electrolysis and is also applied in electrolytic refining. Chemical reactions of the electrodes are not desirable in EDLCs, and a mere action through physical adsorption and desorption are considered ideal [14]. However, the behavior of components contained in ash that cannot be eliminated in the activated carbon generation process is worth noting.

Owing to the difference in viscosity between the harvested electrolyte and the oil-based 23 element standard solution by Seishin Trading Co., Ltd., used in the calibration curve method, the interference must be suppressed. Moreover, since the volume required for analysis (15 ml) was not reached, this needed to be adjusted. To that end, microwave-assisted decomposition was performed using a microwave digestion device (SpeedWave MS3) by Actac Project Services Corporation, adding 8 ml of nitric acid to 0.1 ml of electrolyte. Since this decomposition treatment was performed in a closed
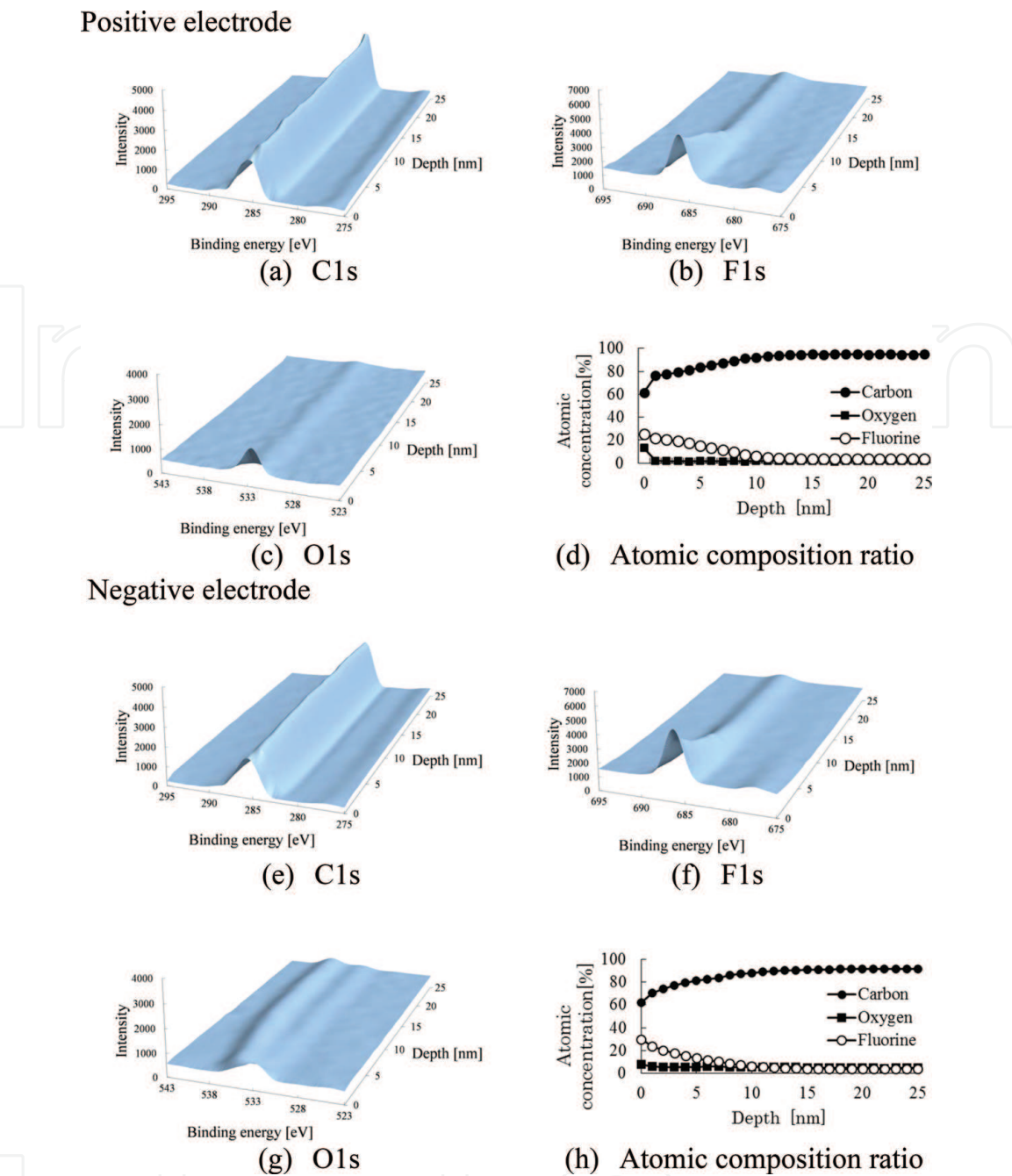
Positive electrode

(a) C1s

(b) F1s

(c) O1s

(d) Atomic composition ratio

Negative electrode

(e) C1s

(f) F1s

(g) O1s

(h) Atomic composition ratio

Figure 8.
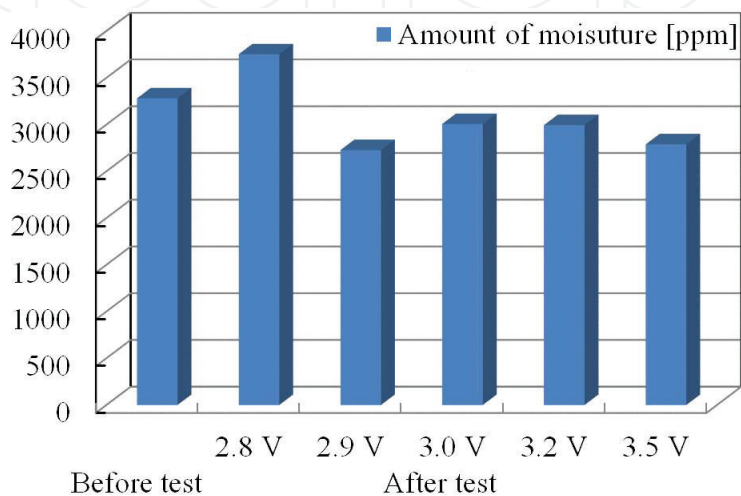*Polarizable electrode after test with holding voltage of 3.5 V.*
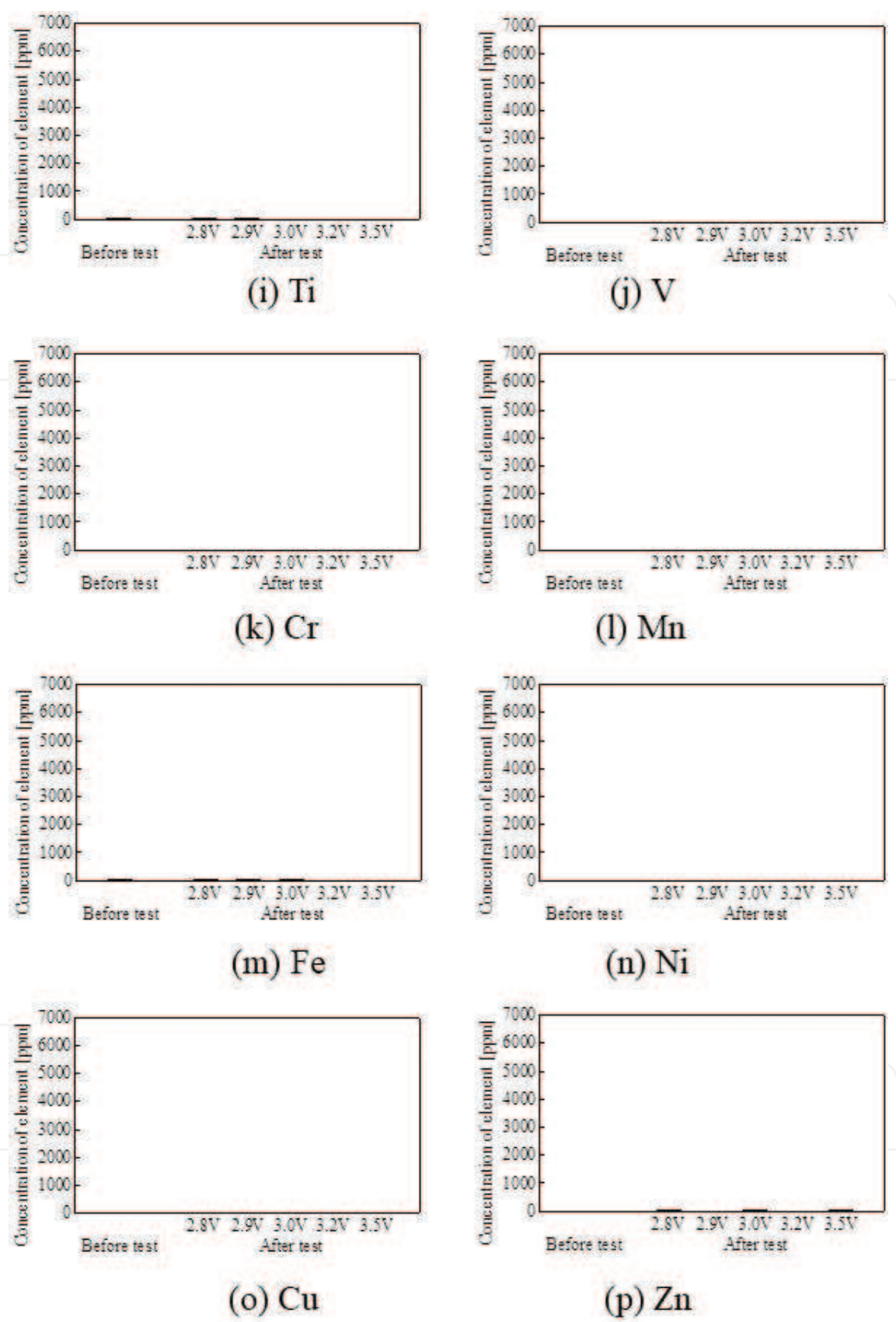

Figure 9.
Moisture content in electrolyte before and after test for each applied voltage.

system, we considered external element contamination to be almost nil. Subsequently, the solution was adjusted to 15 ml by diluting it with ultrapure water. After adjusting the volume as described above, the element concentration in the electrolyte was measured by introducing it into the inductively coupled plasma emission spectrometer (ICPS-8100) by Shimadzu Corporation.

5.4 Element concentrations in electrolyte: measurement results

Figure 10 shows the element concentrations in the electrolyte taken from the EDLCs before and after the tests for each applied voltage. An analysis showed that the electrolyte contained boron, sodium, aluminum, silicon, potassium, calcium,
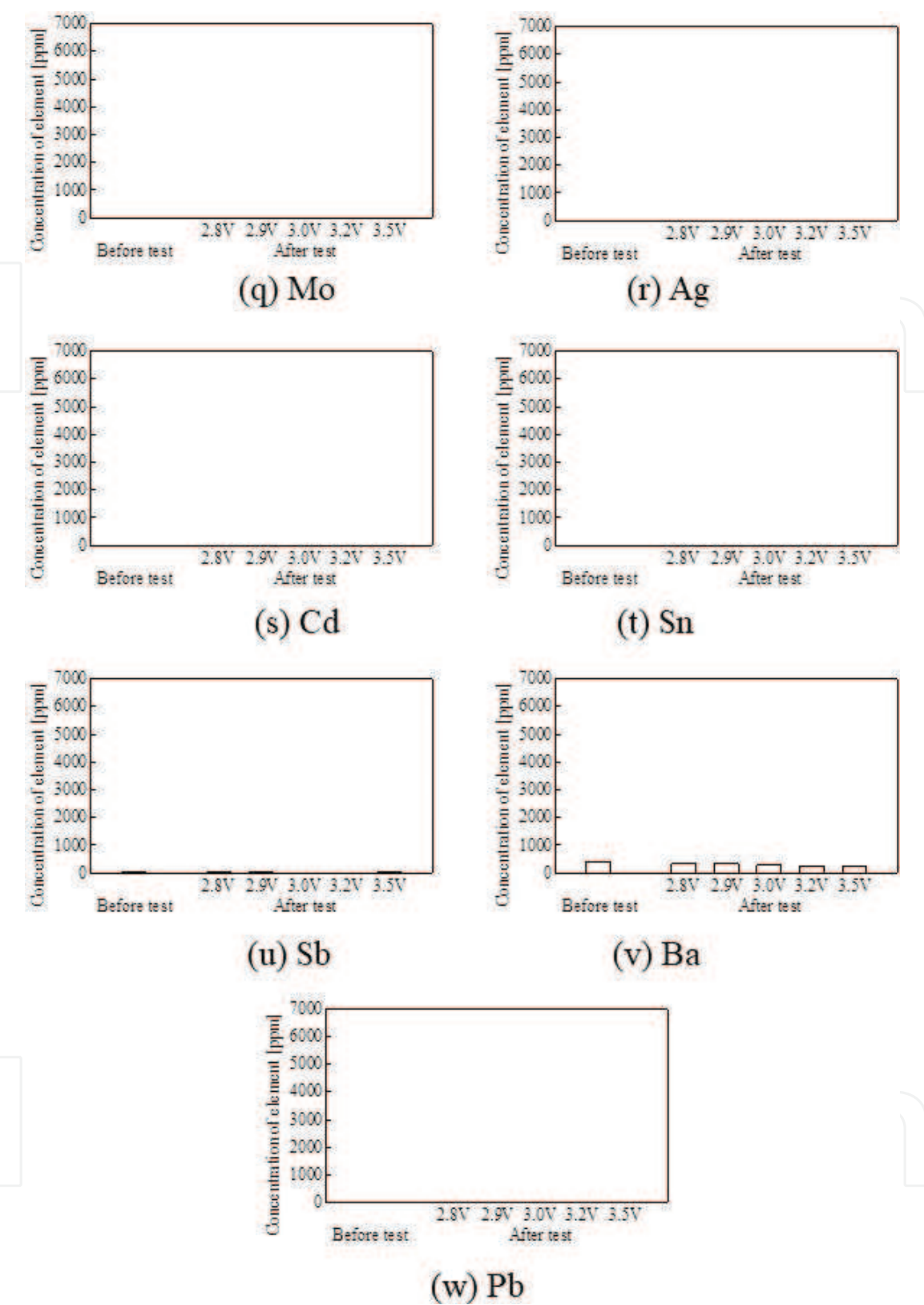
(i) Ti

(j) V

(k) Cr

(l) Mn

(m) Fe

(n) Ni

(o) Cu

(p) Zn
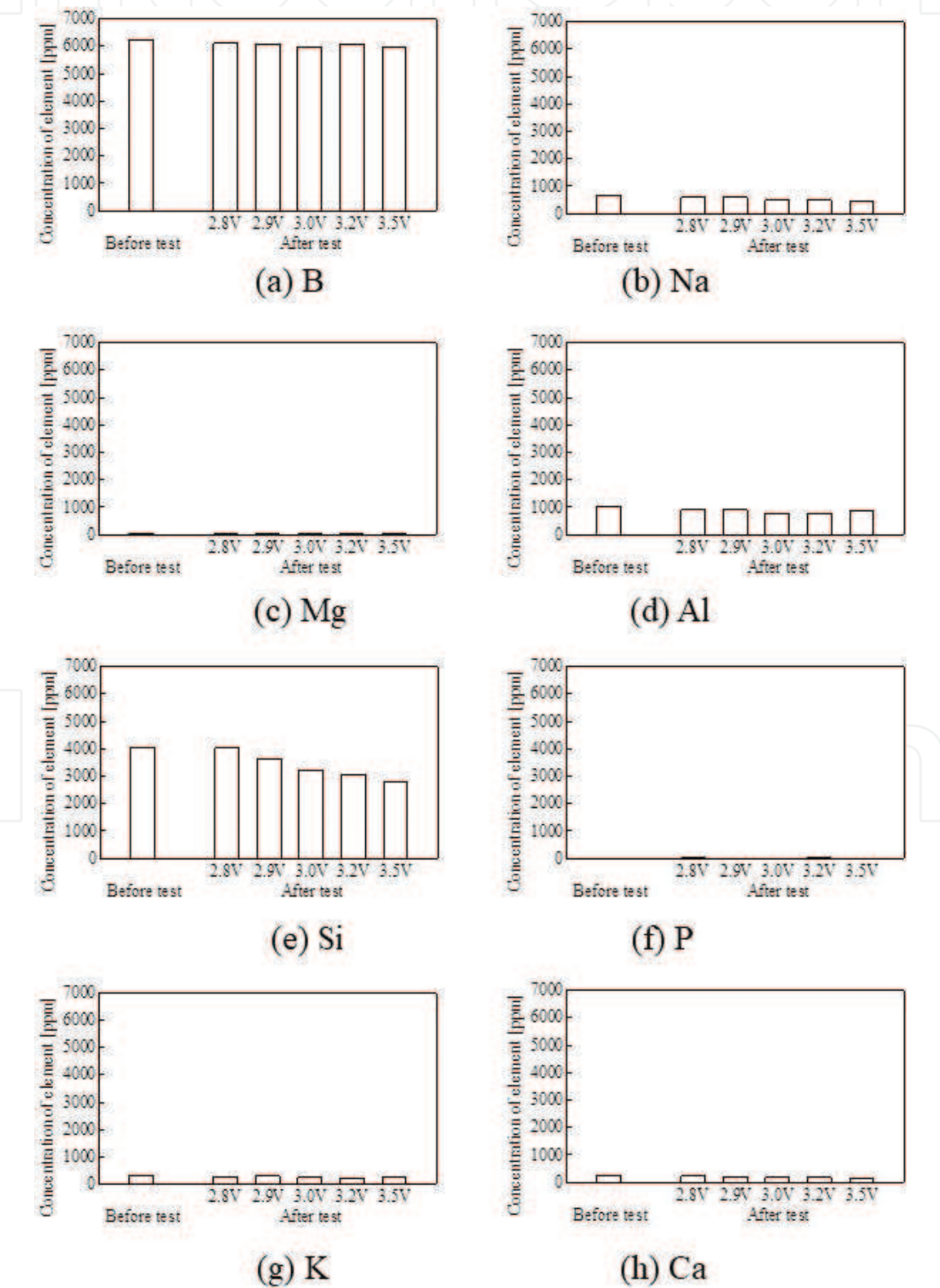
Figure 10.
Element concentrations in electrolyte before and after test for each applied voltage.

and barium. The electrolyte commonly used for EDLCs is tetraethylammonium tetrafluoroborate $[(C_2H_5)_4NBF_4/C_4H_6O_3]$, which does not contain the elements above. However, activated carbon, which is the polarizable electrode material, is over 90% carbon, and part of carbon consists of oxygen and hydrogen compounds. Carbon also contains, as components characteristic to the raw material, sodium, silicon, potassium, calcium, iron, etc., as ash content. Therefore, it is possible that these dissolved into the electrolyte.

Furthermore, the possibility that these components are included as additives to improve the EDLC performance can also be considered. It is clear from the analytical results that whereas almost none of the dissolved element concentrations showed any variance between before and after the test at any holding voltage, only the silicon concentration decreased in relation to an increase in the holding voltage. A decreased concentration in the electrolyte signifies deposits onto the electrode surface. It is surmised that tetravalent silicon, similar to carbon (which is the main component of activated carbon), deposits onto the electrode surface and is a primary factor in the deterioration that increases the internal resistance of the EDLC.

6. Conclusion

For this chapter, we performed a voltage hold test, which is an accelerated deterioration test, on a commercial cylindrical electric double-layer capacitor (EDLC) by applying overvoltage. We confirmed behaviors of deterioration induced by the application of overvoltage. Furthermore, we disassembled the EDLCs after testing and conducted chemical analyses on the polarizable electrodes and the electrolyte, which are the main components of the EDLCs. This resulted in the three findings:

1. It was found that the internal resistance tended to increase with a rise in the holding voltage applied in the voltage hold test. On the other hand, the capacitance was not affected by the holding voltage and did not change significantly. This also revealed that some factors leading to an increase in internal resistance also increase with a rise in the holding voltage.

2. It was found for polarizable electrodes that as the holding voltage rises, the polarizable electrodes react at the solid-fluid interface with the fluorine in the electrolyte, and fluorine compounds are generated up to a depth of 10–13 nm from the electrode surface in the depth direction. It is surmised that this fluorine compound layer closes the micropores, reduces the surface area, reduces the EDLC capacitance, and is a deteriorating factor that increases the internal resistance.

3. It was found that as the holding voltage increases, the silicon concentration in the electrolyte decreases. It is believed that as the electrochemical reaction progresses, deposited silicon becomes a deteriorating factor and, by hampering the charge transfer, leads to an increase in the internal resistance of the EDLC.

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Author details

Daisuke Tashima
Fukuoka Institute of Technology, Fukuoka, Japan

*Address all correspondence to: tashima@fit.ac.jp

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