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The alternating current propagation characteristics for carbon materials

H. SHIOYAMA
National Institute of Advanced Industrial Science and Technology, Midorigaoka 1-8-31, Ikeda, Osaka 563-8577, Japan

The alternating current propagation characteristics for various carbon materials were observed at room temperature. The results show that the alternating current propagation characteristics are dependent on the crystal structure and microtexture of carbon materials. The influence of oxidation and mechanical damage of carbon materials on the alternating current propagation characteristics is also discussed. The damage of each carbon materials is detectable observing the frequency dependence of the phase angle of the alternating current.

1. Introduction

Carbon materials are used extensively in a variety of applications. One reason for this is the heat-stability of carbon at the temperature range up to ca. 3000°C in an inert atmosphere. Basic properties of carbon materials both at room temperature and at high temperatures have been studied in detail. For example electrical conductivity at high temperatures was reported by many authors [1–5]. To measure the electrical conductivity, the four probe method is commonly used. This is a method in which a constant direct current is caused to flow through a sample, and the value of the electrical conductivity is determined from the voltage drop.

It is well known that each carbon materials has different crystal structure (i.e. the size, shape, and crystalline perfection of hexagonal carbon layers in the graphite crystallites) and microtexture (i.e. the formation of aggregation of the graphite crystallites) [6]. When an alternating current is used to study carbon materials, the current propagation characteristics would be expected to reflect the crystal structure and microtexture of the sample more than the value of direct current resistance. In an analogous manner, alternating current conductivity measurements revealed the role of bulk and grain boundary in the overall conduction process of semiconductors [7–9].

In this paper, we report the alternating current propagation characteristics for various carbon materials at room temperature. The influence of oxidation and mechanical damage of carbon materials on the alternating current propagation characteristics is also discussed, which might give a hint on how to detect damage of carbon materials during their use at high temperatures.

2. Experimental

We analyzed the propagation of an alternating current in samples by measuring the frequency dependence of the impedance and phase at room temperature within the frequency range of 1–2.2 MHz, using 5090 frequencies response analyzer from NF Electronic Instruments.

As samples, we used high-density isotropic graphite (HDIG) from Toyo Tanso Co., Ltd., (IG-11) and artificial carbon and graphite for electrode from SEC Corporation. Pieces of the analyzed materials were cut with to have dimensions of $10 \times 10 \times 120$ mm^3. Holes of 3 mmϕ were drilled 10 mm from either end of specimen. Contact terminals for measurement were fixed through these holes with metal screws. The alternating current propagation of these prepared samples, with an effective dimensions of $10 \times 10 \times 100$ mm^3, was measured. Further measurements were made for vitreous carbon available from Tokai Carbon Co., Ltd. (GC20, effective dimensions of $5\phi \times 100$ mm) and for highly oriented pyrolytic graphite (HOPG) available from Advanced Ceramics Corp. (ZYA grade, effective dimensions of $4 \times 0.5 \times 10$ mm^3).

3. Results and discussion

When an alternating current is applied to a measured system composed of a resistor, capacitor or coil, impedance and phase changes are observed depending on the sample and frequency. Fig. 1 shows the frequency dependence of the impedance $|z|$ and phase angle ϕ for a resistor, a capacitor and a coil of electronic devices. For a metal film resistor of 1 ohm, $|z|$ and ϕ are expected to be independent of frequency, with an impedance value of 1 Ω and phase angle of 0°. The result indicated, however, a slight change in both $|z|$ and ϕ at high frequencies (several hundred kHz). While coaxial cables were used for input/output of signals for the frequency response analyzer, ordinary leads were used around the measured sample. It is supposed that their coil component caused the change in impedance at high frequencies. In addition, the coil component in the metal film resistor device might have also contributed, although it is much smaller than the coil component of an ordinary wire-wound resistor. For the capacitor, the impedance was low and the phase angle was –90° at

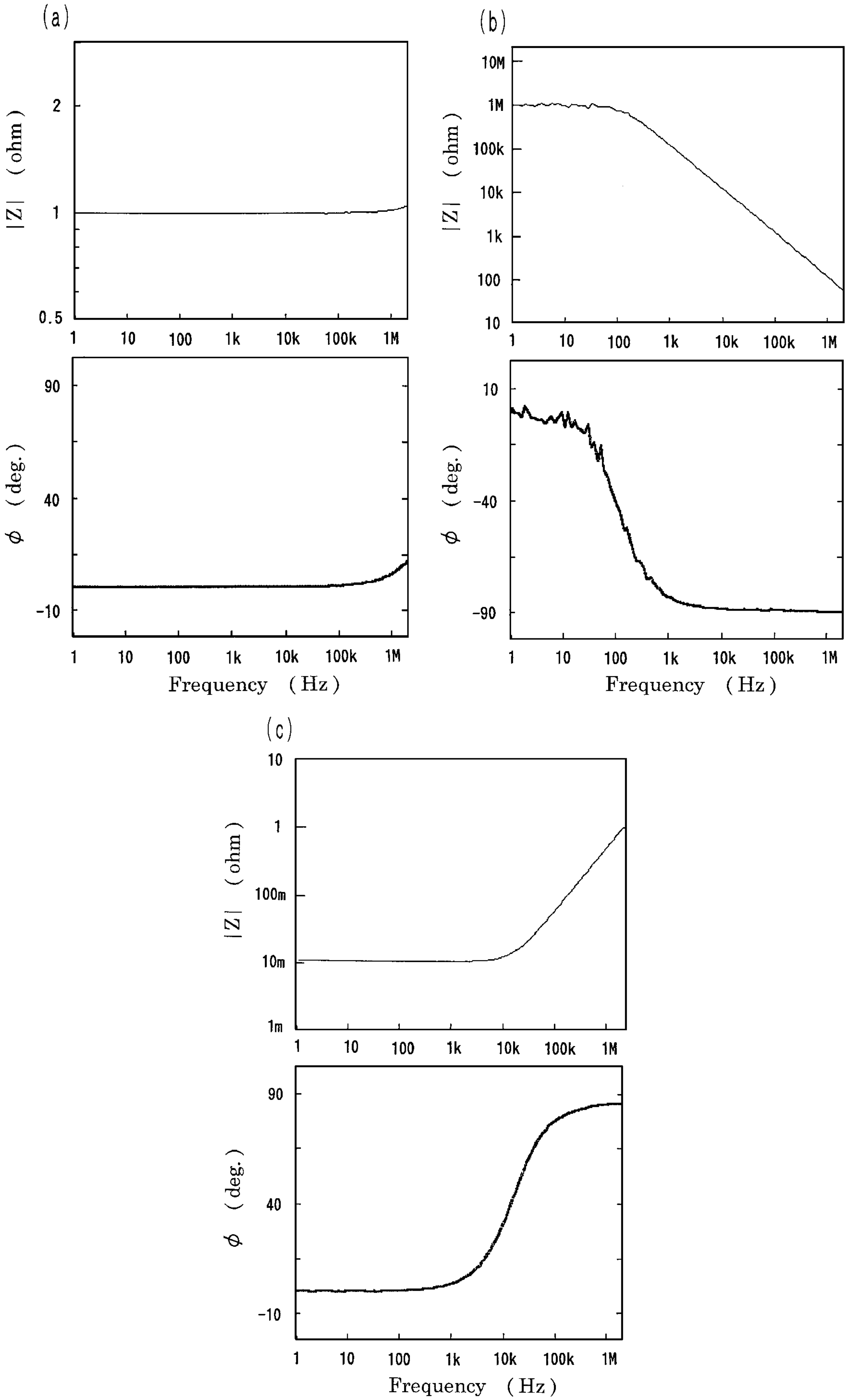

Figure 1 Frequency dependence of impedance |z| and phase angle ϕ of electronic devices; (a) metal film resistor (1 ohm), (b) capacitor (1000 pF) and (c) self-made coil.

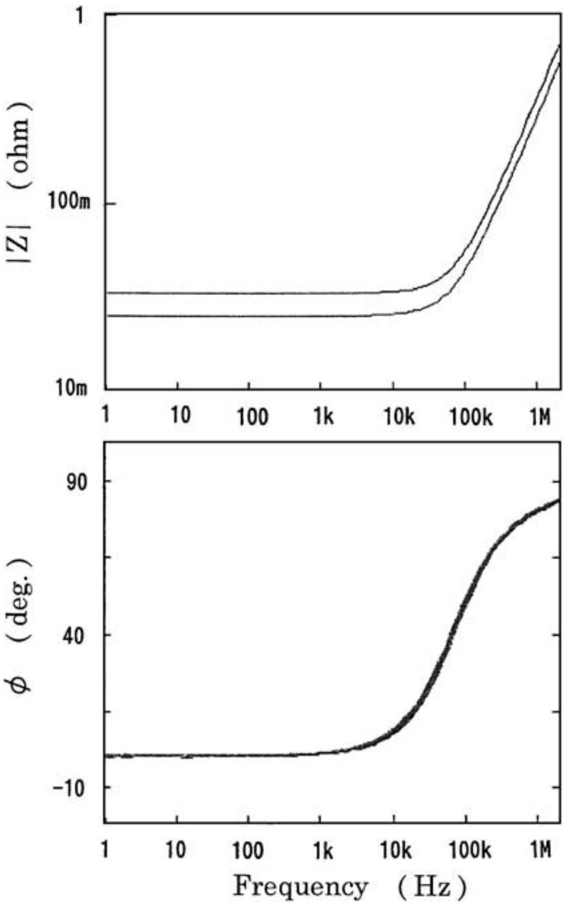

Figure 2 Frequency dependence of |z| and ϕ with HDIG.

high frequencies, whereas for the coil, the impedance was low and the phase angle was 0° at low frequencies. These results are as expected, and measurements were confirmed.

Fig. 2 shows results obtained from experiments conducted on high density isotropic graphite (HDIG). This figure shows two independent measurements demonstrating the frequency dependence of impedance and phase angle. For the impedance value, in particular, we can see a difference due to the preparation of the samples, including the wiring of the sample, from separate experiments. In the result obtained for HDIG, the impedance changes dramatically when frequency is increased above several tens of kHz; phase angle increases when frequency is increased above kHz. These alternating current propagation characteristics may be attributed to the structural properties of the sample. Particularly, the electric resistance of a graphite crystallite has anisotropy of an order of 10^4; thus a current flows much more easily in a direction parallel to the carbon hexagonal net plane. In the actual carbon materials the alternating current flows along a path dependent on the crystal structure and microtexture. For example, a detoured path would result in coil and capacitor components. Thus, It is expected that the dependence of alternating current flow on the crystal structure and microtexture of the HDIG sample lead to the propagation properties as shown in Fig. 2.

Fig. 3 shows the alternating current propagation characteristics for HOPG and vitreous carbon. In contrast

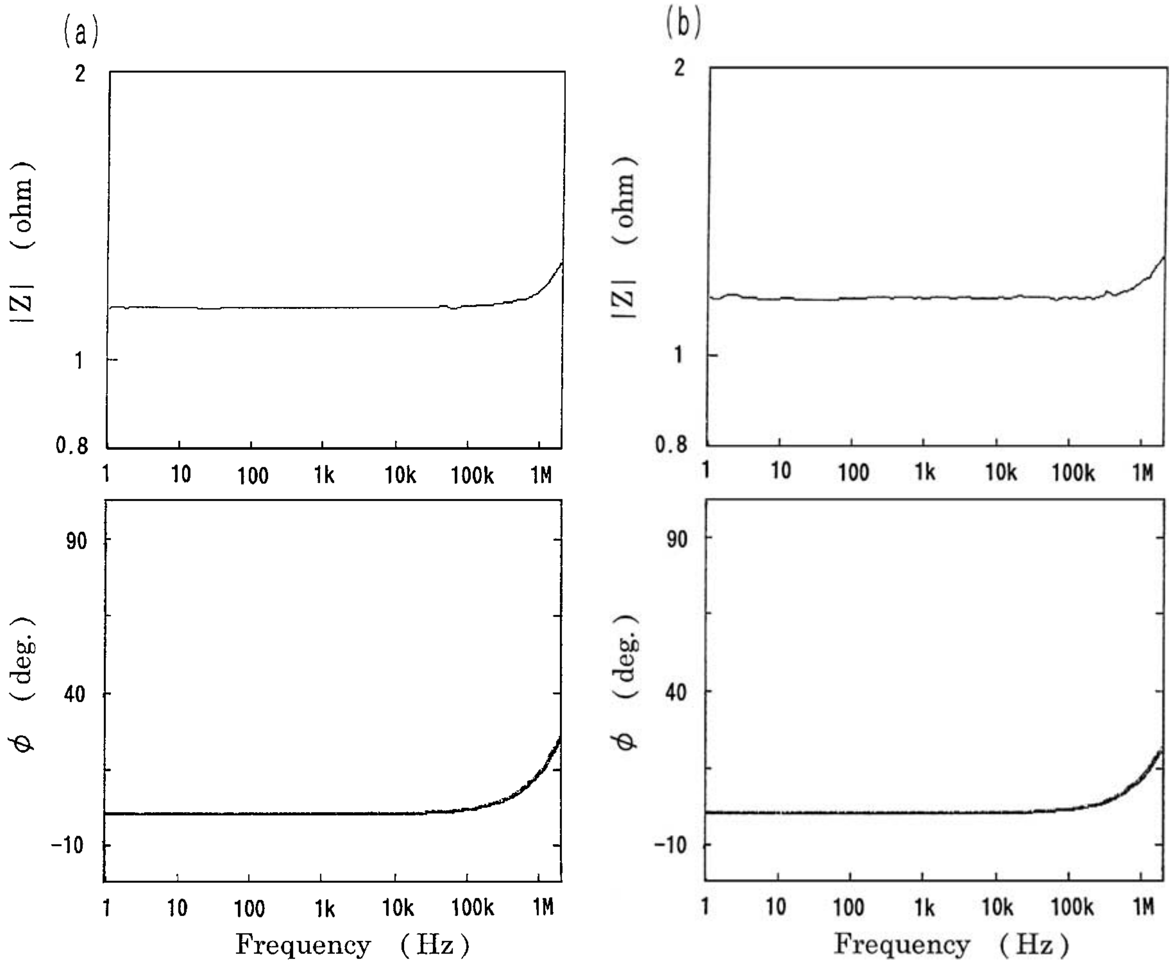

Figure 3 Frequency dependence of |z| and ϕ with (a) HOPG (Sample dimensions: $4 \times 0.5 \times 10$ mm^3, measured in parallel with carbon hexagonal net plane.) and (b) vitreous carbon (Sample dimensions: $5\phi \times 100$ mm).

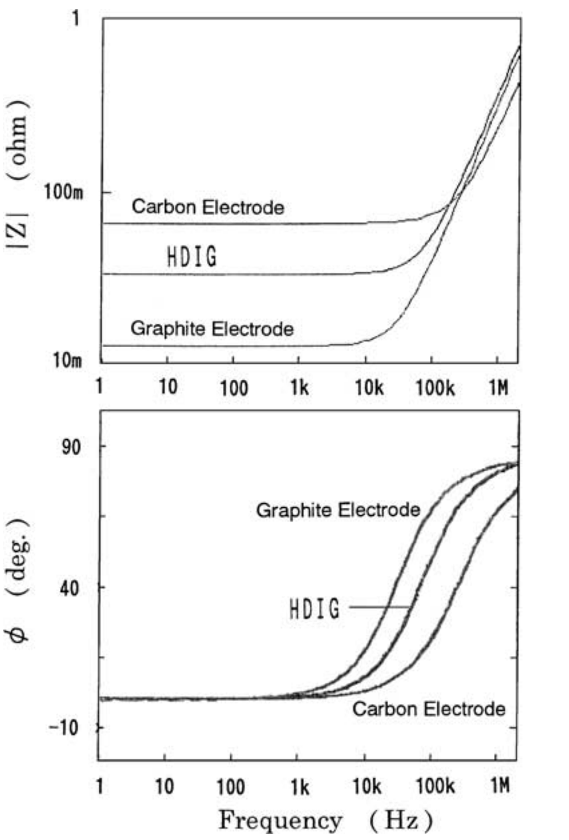

Figure 4 Frequency dependence of |z| and ϕ with artificial graphite and carbon for electrode and HDIG.

to HDIG, increases in impedance and phase angle at high frequencies were not found for HOPG and vitreous carbon. The alternate current propagation for these two samples is similar to that for the metal film resistor. By the alternating current within this frequency range, the crystal structure and microtexture in the HOPG and vitreous carbon is not detected.

The alternating current propagation characteristics for the artificial carbon and graphite for electrodes were measured. Fig. 4 shows the results in comparison with that of HDIG. It is seen from this figure that

(1) The impedance values in the low frequency range is:

Graphite Electrode < HDIG < Carbon Electrode.

(2) The impedance values in the high frequency range is:

Carbon Electrode < Graphite Electrode < HDIG.

(3) The change of phase angle in the high frequency range is:

Carbon Electrode < HDIG < Graphite Electrode.

Differences in the alternating current propagation characteristics presumably result from differences in the crystal structure and microtexture of the samples. In Fig. 5, schematic illustrations of the crystal structure and microtexture are shown for graphite electrode, carbon electrode and HDIG. A fine line in each illustration represents a carbon hexagonal net plane and a set of parallel lines means a graphite crystallite, and then its size and arrangement are considered to determine the microtexture. A bold line superimposed on each illustration means an example of current path in the material. The crystal structure and microtexture determines the degree of detour and the coil and capacitor components, which causes the difference shown in Fig. 4.

When carbon material is industrially used, its mechanical damage and oxidation should be considered. It is desirable to detect its degradation *in situ* during its use at high temperatures. One approach to this is to monitor the alternating current propagation characteristics to determine the limitation for the material being

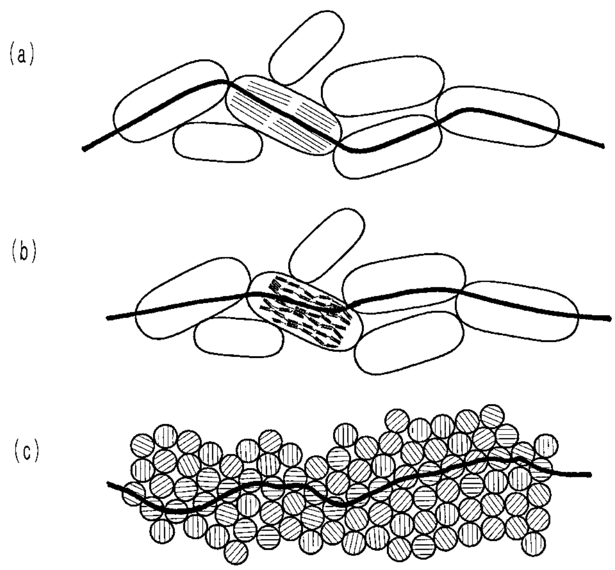

Figure 5 Schematic illustrations of the crystal structure and microtexture for (a) graphite electrode, (b) carbon electrode and (c) HDIG.

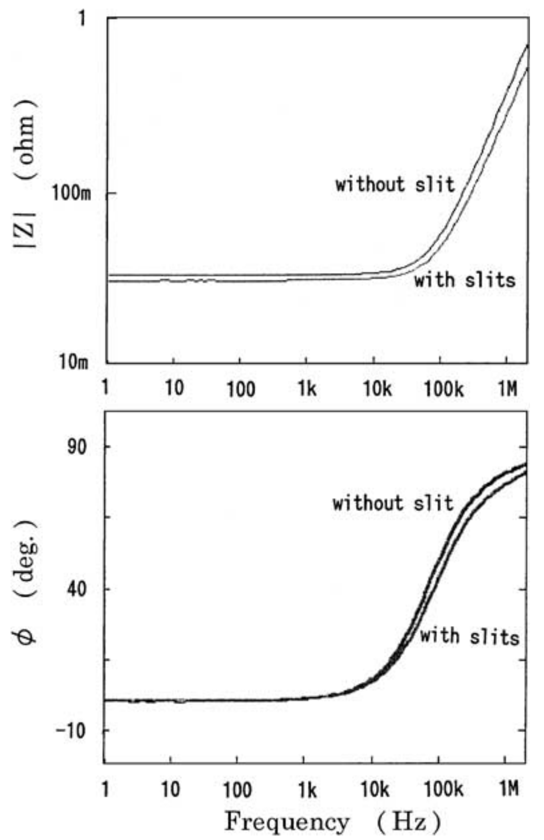

Figure 6 Differences in the frequency dependence of |z| and ϕ with HDIG, with and without artificially introduced slits in the specimen.

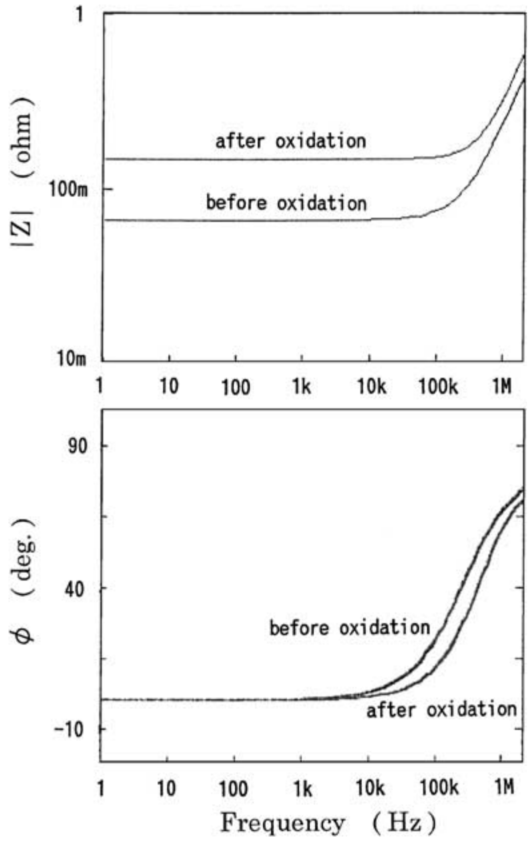

Figure 7 Differences in the frequency dependence of |z| and ϕ with the carbon for electrode, before and after oxidation in the air at 600°C for 1 hour.

used. We have found that measurements of alternating current propagation characteristics at room temperature can be used to detect mechanical damage and oxidation of samples. Fig. 6 shows the results for an HDIG specimen into which 9 slits are artificially introduced to simulate cracks due to a mechanical damage. The slit has 1 mm width and 5 mm depth, lining at intervals of 10 mm between two holes for terminals. The difference observed in the phase angle at high frequencies is regarded as significant. In a similar manner, the damage due to oxidation is detectable observing the alternating current propagation characteristics (Fig. 7).

4. Conclusion

The alternating current propagation characteristics of carbon materials have proved to be useful parameters in evaluating the crystal structure and microtexture and damage of the material. We plan to develop a method of detecting the degree of mechanical damage and oxidation, as well as a method to measure these properties at high temperatures.

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