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Author	水島, 三知(Mizushima, Sanchi)
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New Methods for Electrical Resistivity Measurement of Semi-conductive Powdered Materials*

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Sanchi MIZUSHIMA**

Abstract

Two methods have been devised to measure the electric resistivity of powdered conductive materials. The one utilizes the eddy current effect in a conductor placed in an alternating magnetic field and the other is based on the principle that the conductivity of an electrolytic solution depends upon that of the powders of the specimen suspended in it. It is shown that both methods are practical enough.

I. Introduction

In the course of investigation on the electric resistance of semi-conductors, especially of various kinds of carbons, it became necessary to devise some reliable methods which enable the measurement of the true resistance of powdered samples. Usually for such samples, only the apparent resistance is measured under determined pressure on a certain amount of the specimen: by extrapolating the resistance vs. pressure curve to infinite pressure the true resistance of the individual particles is determined. Since in this case the apparent resistance is composed of the bulk resistance and the contact resistance, between which the role of the latter exceeds that of the former always, this way of measurement is subject to some doubt, and moreover as there are many unknown or uncertain factors which seem to govern the measured values.

Raw materials for the production of carbon are frequently in the form of fine particles. Blocks of pitch or petroleum coke, the most important raw materials in the artificial graphite industry, are powdered into fine particles which are subsequently mixed with binding materials, and after being molded into desired forms are baked to the final products. The knowledge of the true resistance will be thus useful for the control of production as well as for the fundamental understanding of the changes of the electric and other physical properties during carbonization of organic materials and graphitization of amorphous carbons.

In the following sections are described two new methods for the measurement of the true electric resistance of powdered specimens. The one should not be said

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** 水島三知 Assistant Professor at Keio University

to be new in principle: it utilizes the eddy current loss phenomenon in individual particles in an alternating magnetic field. The other may be called substitution method: the sample is immersed in an electrolytic solution and the conductivity of the whole is measured, from the values of which the desired resistivity of the specimen is determined.

II. Eddy Current Loss Method

The principle of this method is as follows. In a conductive material which is placed in an alterating magnetic field eddy current arises converting some amount of the applied field energy into heat. Since the lower the specific resistance of the sample the bigger the effect, the resistivity can be determined by the measurement of the losses. Now, when a spherical conductor of radius α is in the field, the eddy current loss P is expressed by the equation, as long as the skin effect can be neglected,

$$P=(\pi/15)\omega^2(\alpha^5/\rho)Hm^2\times10^{-16}\text{watt.},$$

where ω is the circular frequency of the field, ρ is the specific resistance and Hm the peak value of the field. When the condition $\alpha\sqrt{4\pi\omega/\rho}\ll1$ is fulfilled, the skin effect is negligible.

Thus, the total loss of an assemblage of spherical particles is given by

$$P=(W/20D)\omega^2(\alpha^2/\rho)Hm^2\times10^{-16}\text{watt.},$$

where D is the density of the bulk, not the apparent density, and W is the total mass.

If the magnetic field is produced by a solenoid and the specimen is placed in its central position, the effective resistance of the coil increases owing to the eddy current loss by the amount

$$R_e=(W/10D)\omega^2(\alpha^2/\rho)(0.4\pi N)^2/(l^2+4\pi r^2)\times10^{-16}\Omega,$$

where N,l and r are the number of windings, the length and the radius of the coil respectively. This relation makes the determination of the true resistance of individual particles possible provided that other quantities are known.

In the present experiment the increase R_e of the coil resistance was measured by a Q-meter. The quality Q of a coil is given by $Q=\omega L/R$ at the series resonance with a variable condenser, where L is the inductance. R the resistance of the coil respectively. R_e is given then by

$$R_e=\omega L(Q'^{-1}-Q_0^{-1}),$$

where Q_0 and Q' are the values of Q for the cases without and with the specimen respectively.

Though the resonance frequency should vary more or less with the change of the coil inductance caused by the insertion of the specimen, the deresonance was found to be so small in this experiment that the additional adjustment was not needed throughout.

A number of coils were prepared, of which the construction data of a typical

one is as follows. The full length is 11cm, the number of windings 8, pitch of the coil 1.4cm, radius 1.10cm. The bobbin is of a glass tube and the inductance 0.588μH.

Because each particle has to be insulated from the other, the powdered samples were taken into a test-tube and filled with mineral oil. Moreover that the particles have sizes as equal as possible among them is desirable. They were separated into three stages by Tyler meshes No. 30~45, 45~55, and 55~80.

As for the shapes of these particles, it is natural that they are not perfectly spherical. But I contented myself in this experiment by the microscopic observation which revealed that they were rather block-like in form while needle-like or flake-like ones were lacking.

Now, preliminary tests were made on samples prepared by grinding and sieving from an artifical graphite electrode with the electric resistance of $1.2\times10^{-3}\Omega$cm in its original form. The following is the results obtained by the use of a 0.472μH coil.

Table 1. Specific resistance of artificial graphite

Particle size, mesh	Frequency MC	Specific resistance $10^{-3}\Omega$cm
No. 45~55	15	0.9
〃	25	1.1
No. 55~80	15	0.9
〃	25	1.1

Here the bulk density of the specimen was taken to be 2.0g/cm^3.

As can be seen from the table, reasonable values are obtained, which are slightly less than the original value $1.2\times10^{-3}\Omega$cm.

Nextly the measurements were done on specimens of pitch coke. Blocks were baked for an hour at different temperatures given in Table 2 and then were powdered. The results shown there are for the experiments on particles ranging from mesh number 30 to 45 in size.

Table 2. Specific resistance of pitch coke

Baking temp. °C	Frequency MC	Specific resistance $10^{-3}\Omega$cm
920	15	10
〃	25	9
1100	15	6
〃	15	6
industrial baking	15	4.5
〃	20	5

In the calculation of the above table the bulk densities of these three specimens were taken to be 1.8, 1.9, and 2.0g/cm^3 respectively.

Experiments were tried also on samples with baking temperatures below 800°, which gave no results owing to the too high values of the resistivity.

Comparison of these tabulated values with the apparent ones of the original

blocks was considered to be impractical since these blocks had numerous cracks and pores. The values in the table corresponding to different baking temperatures are, however, reasonable.

Table 3 shows the variation, if any, of the measured resistances with particle size. The specimens used therein are the same as the one given in the last columns in the above table.

Table 3. Measured resistivity vs. particle size

Particle size, mesh	Frequency MC	Specific resistance $10^{-3}\Omega$cm
No. 30~45	15	4.5
No. 45~55	〃	5
No. 55~80	〃	4
No. 80~110	〃	4

The speimen given in the last column of the above table is of particles with too small sizes that the loss is small and the result is less reliable.

It is not unexpected that the resistance varies with particle size because of the inherent porous nature of coke, but as is revealed by the table roughly equal values are obtained irrespective of particle size.

Thus, this method has been proved to be fairly practical for the measurement of the specific resistance of powdered carbons. If suitable selection of the frequency is made, the resistivity of many kinds of conductors will be able to be measured in this way.

III. Substitution Method

Another method for the measurement of the specific resistance of fine particles was devised which is based on a different principle from that given in the previous section. In this method, the specimen in powdered form is immersed in an aqueous solution of electrolytes with known concentration and comparison is made between the apparent electric resistance of the solution and that of the pure solution. Fig. 1 shows the measuring vessel, a part of the whole apparatus. As seen in the figure, the powdered specimen is dipped in a solution which fills the vessel and the conductance between the electrodes is measured by passing an alternating current. As long as the concentration of the solution and correspondingly its specific conductivity are high enough, the existence of the specimen lowers the apparent conductance by a certain amount. When the concentration

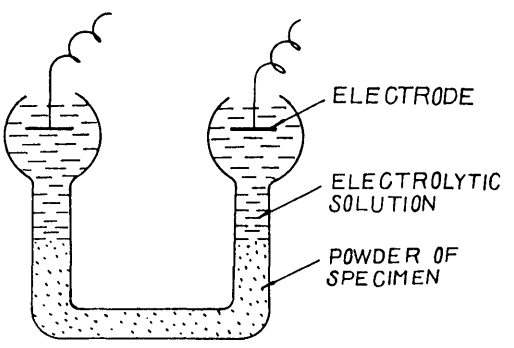

Fig. 1.

is subsequently decreased, since the conductivity of the solution itself decreases, there is one cross-point where the apparent conductivity coincides with that of the pure solution and the current passes as if there were no specimen in the solution.

Further lowering of the concentration results in the relative increase of the conductivity of the solution containing the specimen compared with that of the pure solution at the same concentration, as in this stage the conductivity of the specimen is higher than that of the solution. Thus, the measurement of the specific conductivity of the specimen is done by the determination of the point of coincidence of the conductance of the two solutions one of which contains the specimen while the other does not.

This method can be applied without recourse to the size, the form and the amount of particles of the specimen and moreover is not affected by the existence, if any, of insulating films on the particle surfaces. It should be noted, however, that the measurable range of specific resistance is limited because there are no suitable solutions which are applicable for specimens having specific resistance lower than about 1Ωcm.

For the purpose of studying the applicability of the above idea, tests were run on powders of several species of pitch coke baked at relatively low temperatures and of green carborundum. The particle size was so selected that they sink in the solution easily, and the specimen was poured into the vessel to occupy about 60~80% of the total current path by the apparent volume. As for the solution, aqueous solution of potassium chloride was used throughout while a conventional circuit composed of an A.C. bridge and a receiver was constructed to measure the conductance. The following is the results thus obtained.

Pitch coke 1; produced at the Wakamatsu factory of The Tokai Electrode Manufacturing Co. from coal pitch of the Kurosaki factory of The Mitsubishi Kasei Co. This was given laboratory-baking of 620°×30min. Results are given in Table 4.

Table 4. Pitch coke (baked at 620°)

Concentration, N	Conductance, $\mu\mho$	
	Pure solution	Solution and Specimen
0.0025	29	35
0.005	58	61
0.01	120	110
0.02	240	160
0.1	1159	550

Temperature 20°

Here the first row is for the concentration of the solution, the second for the conductance between electrodes in case of solution only and the third for that of solutions with specimens.

From the table the concentration at the cross-point is interpolated to be 0.007N which means that the specific resistance of the specimen is 1.1$K\Omega$cm.

Pitch coke 2; this is obtained by baking at 700° for 45min. the same raw coke as the above. Results are given below.

Table 5. Pitch coke (baked at 700°)

Concentration, N	Conductance, mʊ	
	Pure solution	Solution and specimen
0.1	0.09	1.75
0.3	2.8	3.5
1.0	8.3	8.3
3.3	20.0	16.0

Temperature 20°

From the table the concentration at the cross-point was found to be 1*N* and consequently the specific resistance of the specimen is 10Ωcm.

The above values of specific resistance of baked cokes are seen to be reasonable.

Nextly similar measurements were done on the powders of "Erema" produced by The Tokai Konetsu Co., heating element composed mainly of silicon carbide, and also of the green carborundum which is used for the production of the former. Experimental results on Erema powders are given in Table 6.

Table 6. Powders of "Erema"

Concentration, N	Conductance, μʊ	
	Pure solution	Solution and specimen
0.001	14	20
0.003	40	40
0.01	140	110
0.03	410	290

Temperature 23°

From the table the cross-point was determined to be 0.003N and the specific resistance of the specimen was found to be 2.5*K*Ωcm.

For the powders of silicon carbide, a certain type of the measuring vessel was used in which the powder of the specimen was filled completely between the electrodes. In this case it was noticed that because of the high specific resistivity of the specimen the experiment had to be done in the small concentration range and consequently the conductivity of the distilled water which was used for the preparation of the solution came into play. But this does not result to any experimental errors. Results are shown in Table 7, where not the values of the conductance but those of the specific conductance are given.

Table 7. Powders of silicon carbide

Concentration, N	Specific conductance, $\mu\text{ʊcm}^{-1}$	
	Pure solution	Solution and specimen
0.00000	3.18	—
0.00010	15.7	24.8
0.00015	33.3	28.8
0.0005	66.3	33.7
0.0010	127.1	51.0

Temperature 22°

In the table the specific conductance of the solution at zero concentration is just

that of the distilled water. From the position of coincidence the specific resistance of the specimen was determined to be $35K\Omega$cm.

Now, there seems to be no theoretical formula which expresses exactly the relations among the apparent specific conductivity σ_{app} of the solution containing the specimen, that of the pure solution σ_{sol} and that of the specimen itself σ_{sp}.

Making use of the formula for the apparent dielectric constant of a mixture of different dielectrics, we wish to approximate the actual dependency by

$$\sigma_{app}=\frac{2\sigma_{sol}+\sigma_{sp}-2P(\sigma_{sol}-\sigma_{sp})}{2\sigma_{sol}+\sigma_{sp}+P(\sigma_{sol}-\sigma_{sp})}\times\sigma_{sol}\ ,$$

where P is the volume ratio of the powder of specimen against the whole volume.

Since this holds for the case of spherical particles and under the condition $P\ll 1$, the agreement between the theory and experiment is not to be expected to be good. When P is taken to be 0.71 the above equation agrees fairly well with experimental results as seen in Fig. 2, while the measured value of P is 0.46. The curves in this figure corresponds to the data given in Table 6. But the agreement of this order of accuracy can be obtained simply by the equation

$$\sigma_{app}=(1-P)\sigma_{sol}+P\sigma_{sp}\ .$$

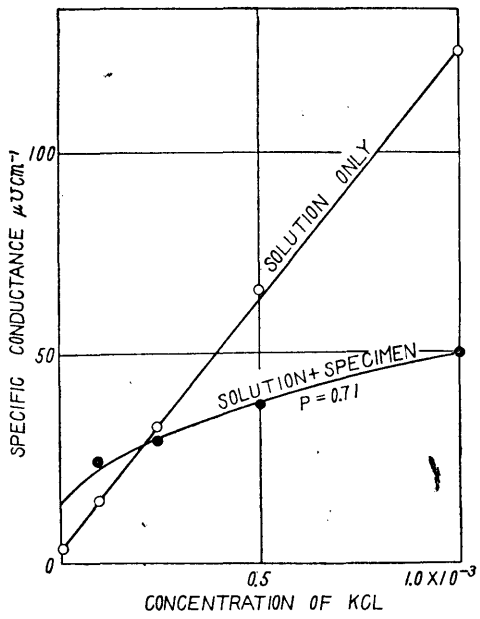

Fig. 2

In this case too, P has to be taken to be 0.46 to fit the data, showing the apparent conductivity of the whole is governed by that of the particles more strongly than expected from the volume ratio.

Thus the above processes enable the measurement of the specific resistance of powdered specimens in the range of $1\sim10^5\Omega$cm, where the following should be noted in the practical application.

1) Particles of the specimen should not react with the solution.

2) To cancel the capacitive reactance of the solution containing the specimen in the measurement, compensation by the use of condensers must be made in the corresponding arm in the A. C. bridge.

In conclusion, the author wishes to express his thanks to Mr. J. Okada of The Tokai Electrode Co. for kind collaborations.