Determination of the Electrical Resistivity of Particulate Carbons

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Factors affecting the determination of the electrical resistivity of a particulate, amorphous carbon have been investigated. Weight and particle size of sample charged into the resistance cell are found markedly to affect the resistivity. The moisture in the air is found to have a less pronounced, but detectable, effect on resistivity. The data for electrical resistance and pressure give a straight-line log–log plot over a considerable pressure range. In the light of the results, a recommended experimental procedure for the determination of electrical resistivities of particulate carbons is outlined.

PROBABLY no single property of a carbon is of more significance than its electrical conductivity. From a scientific standpoint it permits evaluation of the graphitic character of different carbons. S. MROZOWSKI[1] and others have shown that the electrical resistivity of graphitizable carbons decreases markedly with increasing temperature of heat treatment.

The technique frequently used to determine electrical conductivity is to pass a known current through a cylindrical specimen and to determine the voltage drop across a fixed length by a potentiometer. The value of the contact drop between the metal plungers and sample is not required. The result is readily reproducible with moulded or extruded carbon and is independent of pressure applied and weight of sample used. On the other hand, for particulate carbons the sample must be packed into a non-conducting container and the voltage drop across the entire sample plus some fraction of the metal plungers determined. This necessitates information on contact drop. Furthermore, the resistivity of the sample is markedly affected by pressure applied and weight of sample used, among other conditions. Failure to standardize the technique for determination of resistivity of particulate carbons has resulted in a lack of correlation of results on the same material between different laboratories.

Difficulty was encountered when assembling the apparatus because of the lack of information on factors that affect the determination of resistivity values for beds of particulate carbons. Determinations were therefore made of the effect of pressure change on three important factors:

(*1*) variation in the contact resistance between electrode and powder

(*2*) change of contact resistance between particle and particle

(*3*) alteration of bulk density and, therefore, the effective cross section of the carbon granules at any particular point.

EXPERIMENTAL

Resistivity apparatus—A circuit diagram of the resistivity apparatus is shown in *Figure 1*. The voltage drop across a known resistance R_1, and across the carbon sample resistance R_s, is measured and the sample resistance calculated.

The variable resistance R_2 permits convenient values of voltage drop to be obtained across the carbon samples as their resistance varies. The cell holding the particulate carbon samples consists of a steatite container ($\frac{1}{2}$ in. inside diameter, $1\frac{1}{2}$ in. outside diameter and 2 in. long) glazed* on the inside. Steel plungers with a hard copper tip on each face fit snugly into the steatite container and have connections at their top for current and voltage leads. The

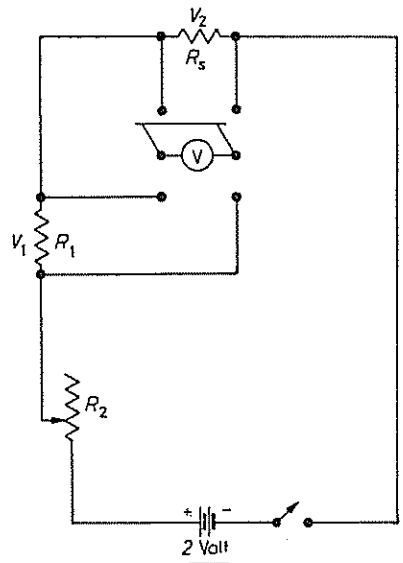

Figure 1. Circuit diagram of resistivity apparatus: R_S sample resistance, R_1 known resistance

top plunger is graduated to allow the height of carbon sample in the cell to be measured. Pressure is applied to the plungers by a standard laboratory hydraulic press.

Carbon used in the investigation—An amorphous carbon GBC *A*, consisting of crushed electrodes composed of 85 per cent petroleum coke (filler) and 15 per cent coal tar pitch (binder) heated to 950°C, was used.

RESULTS AND DISCUSSION

Contact resistance—The resistance of the steel plungers is negligible compared to the resistance of the carbon samples used, but the contact resistance between the plungers and carbon samples is a significant part of the total resistance and must be taken into account. The contact resistance between extruded and moulded $\frac{1}{2}$ in. diameter carbon and graphite rods is determined as a function of pressure, equal contact drop being assumed for compressed particulate carbons at the same pressure. The voltage drop over a segment of the rod is determined by touching two razor blade contacts, connected in turn to a potentiometer, against the sample. This voltage drop is multiplied by the length ratio (length of the rod to distance between razor blades) to give the voltage drop *A* across the rod. The voltage drop *B* is determined across the electrical contacts (similar to that described for the particulate carbons).The

* The glazed container was found to be a necessity in the case of 'hard' carbons. The material otherwise would have a tendency to stick to the container wall and resist compression.

contact voltage* between the rod and plungers is $B-A$. The contact voltage (or resistance) is found to decrease markedly up to a pressure of 2500 lb./in.^{2} and then to remain essentially constant. In addition the contact resistance is not significantly (considering the magnitude of the contact drop correction) affected by the graphitic character of the carbon rods or by the method of preparation.

In the pressure range 1000 to 2500 lb./in.^{2} the contact resistance decreased at about the same rate as the total resistance of GBC *A* and its contribution to the total resistance remained essentially constant. On the other hand, for pressures between 2500 and 15,000 lb./in.^{2}, the total resistance decreased more rapidly than contact resistance and, therefore, the proportion of contact

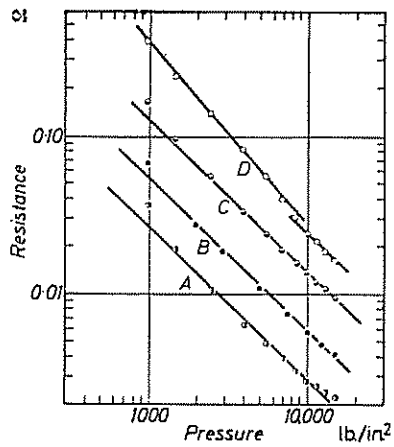

Figure 2. Effect of sample weight of 40 × 48 mesh GBC A on variation of resistance with pressure: A 0·5 g; B 1·0 g; C 2·0 g; D 3·0 g.

resistance to total resistance proceeded to increase. In either case, the contact resistance was a significant part of the total resistance and had to be taken into account in order to obtain an accurate value for resistance drop across the carbon charge. For example, for a 1 g sample of 40 × 48 mesh† GBC *A*, the contact resistance amounted to 6·4, 6·3 and 12·8 per cent of the total resistance drop at pressures of 1000, 2500, and 7500 lb./in.^{2}, respectively.

Effect of sample weight on electrical resistance and resistivity—Obviously, it is essential that electrical resistivity of particulate carbons should be unaffected by the weight of sample used; theoretically variations in sample weight will be removed by dividing the resistance by the sample length (it in turn being proportional to sample weight). *Figure 2* shows the effect of pressure on resistance of different weight charges of 40 × 48 mesh carbon. The data for the 0·5, 1·0 and 2·0 g samples give reasonably linear log–log plots over the pressure range 1500 to 11,000 lb./in.^{2}.‡

* It is well known that current does not pass through the entire macroscopic apparent contact area when carbon is in contact with a metal surface. Thus the contact voltage is composed of a voltage drop between the carbon and plungers and an additional voltage drop over a length of the carbon sample during which lines of equipotential flow are being developed.

† All mesh sizes are expressed as U.S. sieve series.

‡ It is to be emphasized, however, that the straight lines drawn through the points are largely arbitrary and the parallelism of the lines is not necessarily correct.

At some higher pressures, depending upon the weight of sample and particle size, the rate of change of resistance with pressure is found to decrease continually. The data for the 3·0 g sample give essentially two straight line plots—one from 1000 to 6000 lb./in.², with a slope greater than those for the lighter weight charges, and one from 10,000 to 15,000 lb./in.² with a slope essentially the same as that for the lighter weight charges. According to

Table 1. Effect of weight and particle size of carbon on electrical resistivity

Mesh size	*Sample weight g*	*Resistivity, Ω cm²/cm at*			
		2500 lb./in.²	*7000 lb./in.²*	*10,000 lb./in.²*	*15,000 lb./in.²*
40 × 48	0·5009	0·0379	0·0169	0·0138	0·0127
	1·0015	0·0383	0·0174	0·0138	0·0112
	2·0003	0·0459	0·0194	0·0152	0·0117
	3·0010	0·0712	0·0262	0·0183	0·0128
60 × 100	0·5031	0·0432	0·0186	0·0138	0·0132
	1·0018	0·0456	0·0186	0·0150	0·0117
	2·0000	0·0538	0·0219	0·0175	0·0124
200 × 325	0·5002	0·0502	0·0229	0·0198	0·0150
	1·0029	0·0518	0·0237	0·0183	0·0132
	2·0015	0·0607	0·0254	0·0200	0·0146

S. MROZOWSKI[2], the slope of these plots for a given carbon is affected by the oxygen content on the surface—the higher the oxygen content the greater the slope.

Table 1 presents data for the calculated resistivity of different size fractions of GBC *A* at different degrees of compression as a function of sample weight. It is seen that, for pressures of 2500, 7000 and 10,000 lb./in.², the resistivity significantly increases with weight of sample. At a given pressure, the change in resistivity increases as change in weight of charge increases. (That is, dR/dW increases as W increases.) In going from the smallest to largest weight of carbon there is a decrease in the percentage change in resistivity as pressure increases. As the weight of carbon increases, the percentage change in resistivity at a given pressure decreases as particle size decreases. At 15,000 lb./in.² for each of the three particle sizes, the resistivity passes through a minimum when the charge is 1 g and then follows the previous pattern for further weight increases. With the 0·5 g sample of 40 × 48 mesh material, for example, the contact resistance at 15,000 lb./in.² was estimated at approximately 35 per cent of the sample resistance. If the value estimated for the contact resistance was too low it could make the calculated resistivity too high. As the weight of sample is increased, the effect of the error in contact drop on the calculated resistivity would be decreased and the prior trend of values again observed. Since the value of the contact resistance can only be estimated as previously discussed, the desirability of working at a pressure where its percentage contribution to the total resistance is at a minimum is obvious.

Data for the variation in bulk density with pressure for different weight charges of 40 × 48 mesh GBC *A*, as shown in *Figure 3*, clearly indicate, at

least qualitatively, that the increase in resistivity with increase in weight of charge is caused by an attendant decrease in bulk density. However, the variation in density with weight of charge does not appear to explain the resistivity results quantitatively. For example, density is seen to vary almost linearly with weight of charge, whereas the variation in resistivity is greater

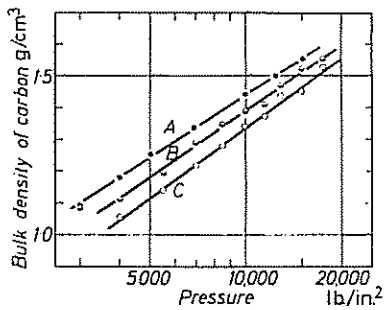

Figure 3. Effect of sample weight of 40 × 48 mesh GBC A *on its bulk density as a function of pressure applied:* A *1·0 g;* B *2·0 g;* C *3·0 g.*

when increasing the charge from 2 to 3 g than from 1 to 2 g. Furthermore, although the resistivities for the 0·5 and 1 g charges were in relatively good agreement, the density for the 0·5 g charge was, in general, higher than for the 1 g charge. The data for this charge were not plotted since there was invariably considerable scatter, probably caused by the inaccuracies in reading the small changes of length involved. *Figure 3* shows the slight convergence of the density data with increasing pressure. This perhaps explains the decrease in the spread of the resistivity data with increasing pressure.

A further indication of the importance of the effect of bulk density on resistivity can be obtained by comparing the resistivities determined at different pressures but at the same bulk density. The 1 g sample at a pressure of 7000 lb./in.^{2} has a bulk density of 1·34 g/cm^3 and a resistivity of 0·0174 ohmcm^2/cm (see *Figure 3*). The 3 g sample has a density of 1·34 g/cm^3 at a pressure of 10,250 lb./in.^{2} Its resistivity at this pressure is estimated at 0·0180 ohmcm^2/cm, in reasonably good agreement with the value for the 1 g sample.

The decrease in bulk density of sample with increase in weight of charge is probably caused by the increased resistance to compression at the container wall. It has been found that the more graphitic the sample compressed, and hence the greater its lubricating properties, the smaller the effect of sample weight on bulk density during compression.

Effect of sample particle size on electrical resistance and resistivity—The variation of resistance with pressure for different size fractions of a 2 g charge of GBC *A* is shown in *Figure 4*. The spread in resistance for the three sizes over the entire pressure range is essentially constant at approximately 22 per cent. The resistance of the 40 × 48 mesh fraction is the lowest at all pressures. At pressures between 3000 and 10,000 lb./in.^{2} the resistances for the two smaller size fractions are within the range of experimental accuracy. At higher pressures, the smallest size fraction shows some tapering away from the straight line, as previously discussed.

Data on the resistivities of the different size fractions are given in *Table 1*. At all pressures tabulated resistivity increases as particle size decreases. The difference in resistivity from the smallest to largest size fraction amounts to about 30 per cent at all pressures. The reason for the greater spread of the resistivity data than of the resistance data lies in the marked increase in bulk

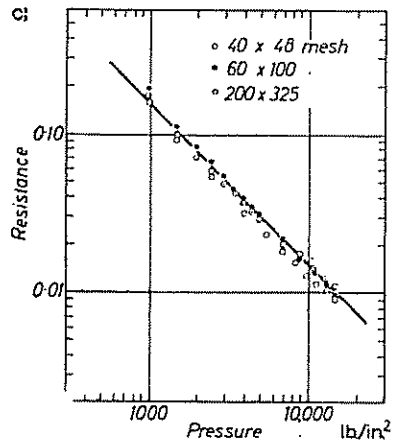

Figure 4. Effect of particle size on resistance of a 2 g charge of GBC A

density with decrease in particle size, that is, the spread in resistance results is further accentuated when converted into resistivities since the greater the particle size of the carbon the greater the length it occupies in the holder. It is seen that the differences in resistivities are less at the higher pressures. This agrees with the fact that the bulk density curves for different size fractions were found to converge as pressure was increased.

Effect of moisture on electrical resistance and resistivity—R. McINTOSH, R. S. HAINES and G. C. BENSON[3], and later W. W. SMELTZER and R. McINTOSH[4], showed that the physical adsorption of different vapours noticeably affects the resistance of active carbon rods. The effect of moisture

Table 2. Effect of pre-treatment on electrical resistance and resistivity of carbon

Pressure lb./in.²	Resistance Ω			Resistivity Ω cm²/cm		
	Dried sample	As received sample	Saturated sample	Dried sample	As received sample	Saturated sample
2,500	0·0200	0·0185	0·0170	0·0184	0·0169	0·0154
5,000	0·0106	0·0099	0·0095	0·0094	0·0087	0·0083
10,000	0·0066	0·0063	0·0061	0·0054	0·0051	0·0049
15,000	0·0055	0·0051	0·0051	0·0043	0·0039	0·0039

on resistance and resistivity was, therefore, qualitatively investigated to enable the desirable operating procedures to be further clarified.

Data were obtained on 1 g charges of 40 × 48 mesh GBC *A* for samples 'as received', dried in a vacuum oven at 105°C for 12 h, and saturated with water at 20°C for 48 h (*Table 2*). As expected, the resistance and resistivity decrease as the moisture content of the samples increases. The percentage

difference in the values falls with increasing pressure, or the drier the sample the greater the fall in resistance with increase in pressure. This indicates that water is most needed at low pressures, where good particle–particle contact area is at a minimum, for the particulate carbons to conduct electricity. As pressure is increased, the particle–particle contact area increases and the need for the water is minimized.

Other 1 g samples of GBC *A* were dried in a vacuum oven at 105°C for 12 h and then exposed to the atmosphere (a day of high humidity being selected) for varying periods of time before their resistivities were determined.

Table 3. Effect of length of time of exposure of pre-dried carbon samples to room atmosphere on resistivity

Pressure lb./in.²	*Resistivity Ω cm²/cm*					
	0 *min*	9 *min*	17 *min*	80 *min*	720 *min*	*Average*
2,500	0·0367	0·0365	0·0371	0·0367	0·0373	0·0369 ± 0·0002
5,000	0·0224	0·0226	0·0233	0·0219	0·0223	0·0223 ± 0·0002
15,000	0·0137	0·0149	0·0144	0·0139	0·0132	0·0140 ± 0·0003

The time required to complete the measurements on any sample was approximately 6 min. The results are given in *Table 3*. They exhibit no trend and the agreement for the five individual samples is excellent. Apparently the rate of moisture uptake at room temperature in this case is relatively slow.

Reproducibility of results—The variation of resistance with pressure for three different 1 g samples of 40 × 48 mesh GBC *A* is illustrated in *Figure 5*.

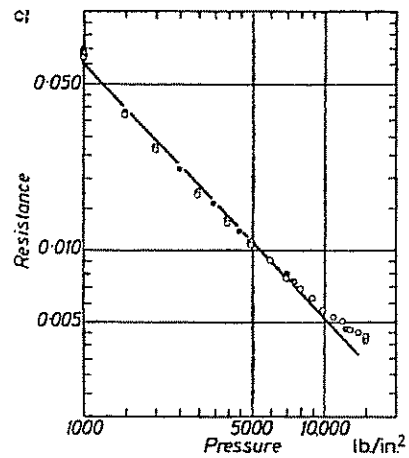

Figure 5. Effect of pressure on resistance of 40 × 48 mesh GBC A: three symbols represent the independent determinations

The samples were used on the 'as received' basis. Maximum deviation of the data from a smooth curve drawn through the points is ± 2·5 per cent if the values at 1000 lb./in.² are disregarded. Reproducibility of results to within at least this limit has been found possible for all samples of carbon and graphite investigated if a consistent experimental procedure is employed.

RECOMMENDED EXPERIMENTAL PROCEDURE

The following experimental procedure is recommended for the determination of resistivities of beds of particulate carbons. Use a hard material glazed on the inside for a sample holder so that the carbon will neither dig into the wall nor produce undue frictional resistance during compression. Dry the carbons in a vacuum oven at 105°C overnight prior to measuring their resistivities. To decrease contact resistance attach a thin layer of hard copper to each metal plunger and each day before operating gently polish the copper faces with a light weight emery cloth. Use a weight of carbon charge such that the sample height at a relatively low pressure (*ca.* 1000 lb./in.^{2}) is approximately equal to the container diameter. This will decrease the effect of wall friction on the resistivity results of carbons with different lubricating properties and at the same time ensure that the contact resistance does not become a significant part of the total measured resistance. In the apparatus used, a sample weight of one gram was convenient. Report resistivity data at a pressure where the contact resistance contributes a minimum amount to the total resistance and where the value of contact resistance for different carbons is best duplicated. In the present work, this pressure was approximately 2500 lb./in.^{2}

It would be desirable, when reporting resistivity data on a particulate carbon, to include a screen analysis (or electron microscopic sizing if the material is very fine). A B.E.T. surface area on the particulate carbon would also be helpful. Since resistivity is a function of particle size and permeability, the above data would complement the result and assist in comparing materials from different laboratories.

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