

THE CONDUCTIVITY OF COMPRESSED POWDERS. A REVIEW*

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Summary

The electrical conductivity of battery materials, *e.g.* manganese dioxide, carbon black, graphite, black mix, etc. has been measured in battery laboratories since the 1930s. However, the electrical properties of powders are complicated. In particular the conductivity depends not only on pressure and particle size, but also on the field strength and frequency of the measuring current, on the method of compression, *e.g.* mechanical or hydraulic, slow or fast, etc. In addition the samples have to be carefully prepared by a standardized method. If, however, all these conditions are taken into consideration, interesting results are obtained. A few of these are presented in this paper: the exponential influence of pressure, the anomalous exponents for several materials, the absence of any correlation with density, unexpected effects of particle size, the influence of the rate of application of pressure and the laws predicting the behaviour of mixtures.

Résumé

Dans des laboratoires de l'industrie des piles primaires, on a mesuré la conductibilité électrique des matériaux déjà depuis plus de 40 ans. Il s'agissait du bioxide de manganèse, de la fumée, du graphite, des mélanges dépolarisants, etc. Mais les propriétés électriques des matériaux pulvérulants sont assez compliquées. La conductibilité dépend non seulement de la pression et du diamètre des particules, mais encore de l'intensité et de la fréquence du courant appliqué, et des circonstances de compression, par exemple, compression par des installations mécaniques ou hydrauliques, lenteur ou rapidité, etc. Aussi, la préparation correcte des poudres est d'importance. D'autre part, si on observe ces conditions suffisamment, on va obtenir des résultats très importants, dont quelques-uns seront présentés ici: l'influence exponentielle de la pression, les exponents géants de quelques matériaux, pas de corrélation avec la densité, des effets du diamètre des grains imprévus, l'influence de la vélocité de la compression et quelques règles de mélange.

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Überblick

Die elektrische Leitfähigkeit aktiver Batterie-Werkstoffe, z.B. Braunstein, Russ, Graphit und Depolarisations-Mischungen wird seit Beginn der dreissiger Jahre in den Laboratorien der Batterie-Industrie gemessen. Die elektrischen Eigenschaften pulverförmiger Stoffe sind aber ziemlich kompliziert. Die Leitfähigkeit der pulverförmigen Stoffe z.B. hängt nicht nur vom Druck und von der Korngrösse, sondern ausserdem von der Feldstärke und der Frequenz der zum Messen benutzten Spannung ab, sowie von der Kompressionsmethode, ob mechanisch oder hydraulisch, langsam oder schnell usw. Die Pulverproben müssen sorgfältig vorbereitet werden. Wenn man aber diese Bedingungen berücksichtigt, erhält man interessante Ergebnisse. Einige davon werden hier angesprochen: die exponentielle Druckabhängigkeit, die übersteilen Druckexponenten einiger Substanzen, die mangelnde Korrelation mit der Dichte, unerwartete Effekte der Korngrösse, Einflüsse der Pressgeschwindigkeit und Mischungsregeln.

Introduction

It had already been discovered more than a hundred years ago that carbon powder is sensitive to changes in environmental pressure, and in 1876 Bell used this effect in the design of his first telephone. The application of field strength effects in metal powders also took place before 1900 and Branly [1] in 1890 invented the fritter or coherer and used it to detect radio waves. In 1931 the work of Holm [2] on surface layers on electrical contacts and that of Skaupy and Kantorowicz [3] on metal powder conductivity were published. These works are the basis for the simple geometrical and elastic theories of powder conductivity of Holm and Holm [9] and Euler [12] respectively. An important advance was the work of Ballhausen [5] in 1951 on the distribution of pressure in compressed powders, and this work is both the real basis and the justification of the present work.

In battery electrodes the conductivity, both ionic and electronic, is secondary in importance only to potential and overvoltage. The investigation of the conductivity of battery materials started early in this century and the methods used have progressed from the simple "conductivity presses", designed for example by Arndt, to the sophisticated a.c. impedance methods used by Atlung and Jacobsen [18] and Braun [14] to eliminate contact resistance and to separate the resistance of the inner core from that of the surface layers of the particles respectively [4, 6, 7, 10 - 16, 18, 21 - 24].

The systematic study of the conductivity of battery materials started with graphite [4], manganese dioxide [6, 10] and carbon black [7], whilst sintered metals have also been investigated [8, 9]. However, many battery materials have not been investigated at all, whilst for others only a few roughly measured values for samples of unknown origin are available. Thus although

TABLE 1

Electronic conductivity of active battery constituents (pressure given in bar = 9.81×10^4 Pa)

		$\text{Ohm}^{-1} \text{cm}^{-1}$
Positive dry cell electrode, not discharged, dried, not disintegrated, original shape, without pressure $\text{MnO}_2/\text{carbon black} = 5.9:1$		0.12
$\text{MnO}_2/\text{graphite} = 3:1$		10
$\text{MnO}_2/\text{graphite} = 5:1$		5
Positive nickel mass NiOOH , without graphite or Ni flakes from electrodes disintegrated, washed, dried, screened pressure 60 bar		
	charged	10^{-3}
	50% 5 h discharged	5×10^{-4}
	completely discharged	10^{-4}
Ni sintered plate without active mass		10^4
PbO ₂ from washed and dried grid plates		
	charged	10 - 20
compact	10 h discharged	5 - 0.5
HgO mass from disintegrated plates, washed, dried, screened, pressure 60 bar, HgO/graphite 9:1		
	new	5
	discharged	5

the investigation of the conductivity of powders is a fairly old problem, up to 1970 the published papers indicate more accidental studies than systematic work. Table 1 shows some results which have been previously obtained by the author.

In general, the first aim is still to furnish the battery industry with reliable data, and to show what happens to the conductivity in a battery; or what is to be expected, what has to be envisaged, what can be changed and what has to be accepted as being unalterable. The second aim is to evaluate the physics of conduction, whether the material behaves like a metal or a semiconductor, intrinsic, *p* or *n* type, whether there are mobile ions, etc. In some cases, band gaps, carrier concentrations and mobilities can be evaluated. Later on it may be possible to measure surface states, but this will be difficult because of the large active surface area and the morphological changes which it undergoes in the battery [27].

The final goal, the improvement of battery materials and design is far away. Simple, direct correlations between conductivity and electrochemical activity have sometimes been assumed, but certainly do not exist. Both con-

ductivity and electrochemical activity are caused by the interaction of bulk material properties and surface morphology, but the mode of interaction certainly differs in the two cases. The inner surface for example plays an important part in the electrochemical activity, but can be neglected when considering the electronic conductivity. However, we do not yet know much about these correlations and there is much work to be done on them.

Experimental

During the late 1920s simple conductivity presses were used. These were generally small lever arm presses with a sliding weight. The pressure range was very limited, 5 to 30 MPa (50 - 300 bar) and in most cases the sample thickness was in the range of 50 mm or more. This leads to erroneous results because the pressure distribution over such thicknesses is considerably disturbed.

In our laboratory the main instruments are precision screw and hydraulic presses. The screw press is a 100,000 N tensile testing machine, as normally used for materials testing. The rate of application of the force can be varied between 30 and 10,000 N/min. The machine is equipped with the necessary electronic equipment.

In screw, excentric and toggle presses the local position of the pressure piston is changed, the dimensions of the sample follow and the pressure change follows. In hydraulic installations the pressure is given and the dimensions of the sample change. In spite of this difference, both methods show comparable, but not identical results. In the future we plan to investigate the effects of impact compression, using either a fast moving excentric press or explosives. The pressure is always applied orthostatically from one or both sides. With isostatic installations it is more difficult to make electrical measurements and the installation is expensive. A preliminary investigation of the effects of additional transverse pressure has been started recently [25], but in most cases the direction of the force and of the conductivity measurements are parallel to each other. However, it must be kept in mind that in compressed powders, conductivity is a tensor with the better conducting direction perpendicular to the direction of the orthostatic pressure. (In compressed powders the galvanomagnetic and thermoelectric properties are also anisotropic.) The effect of transverse magnetic fields on the conductivity of compressed powders has also been investigated [19, 22].

It is also necessary to look very carefully at the pressure distribution. This can be improved by having two moving pistons, by the use of conical dies (Fig. 1) [5], and also by shaking, by "greasing" the inner surfaces of the die or by pressure additives [17]. In most cases pressure distribution can be kept sufficiently even, but there are materials, *e.g.* ZnO powder, which in pure dry form can hardly be measured. For such materials a special extrapolation method has been developed which is based on the use of more than two voltage probes (see Fig. 2).

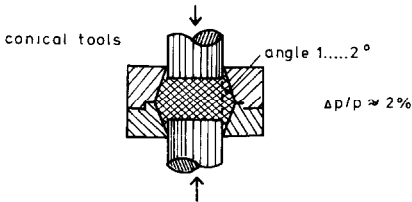
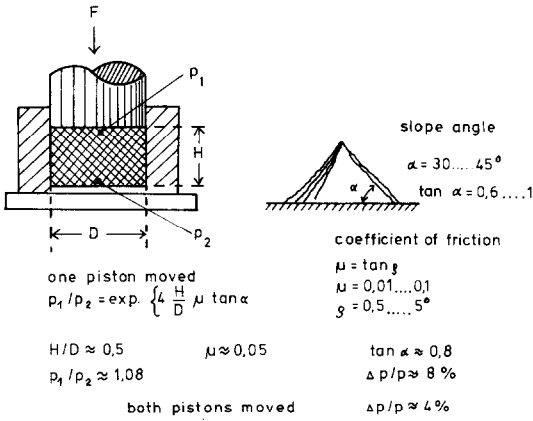


Fig. 1. Pressure distribution, after C. Ballhausen [5].

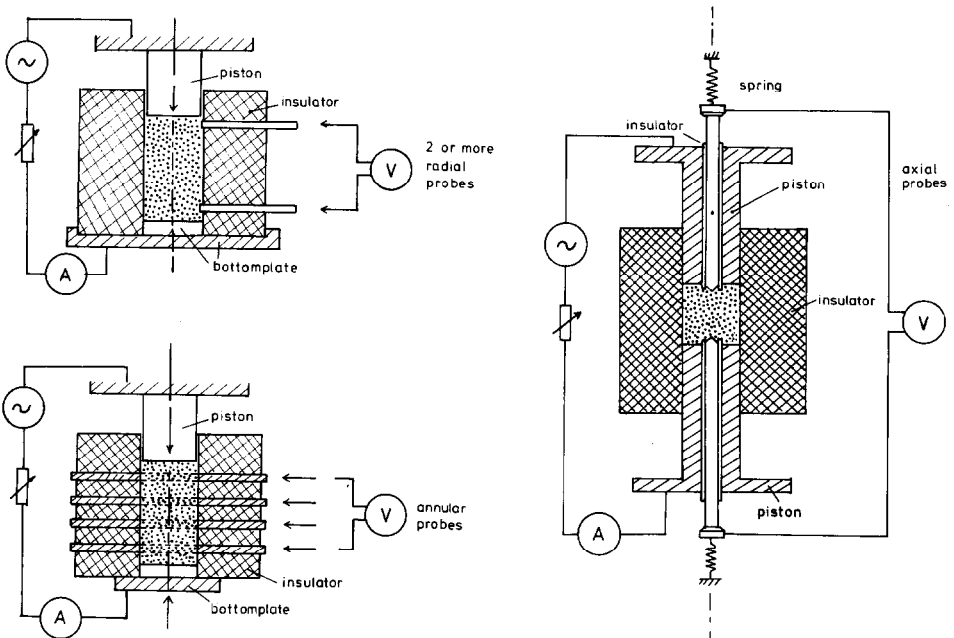


Fig. 2. Orthostatic press tools. Current parallel to the pressure.

Electrical conductivity is measured by the simple, but versatile, current-voltage method which can be easily adapted to the particular test conditions. Direct and alternating current is used in the frequency range 10 Hz to 100 kHz. Both constant current and constant voltage generators are used. In most cases the two methods give similar results, but if the conductivity depends on field strength, constant voltage is to be preferred. With some powders unstable jumps of the conductivity occur which can be better observed if constant current is applied. As long as the compressed powder behaves like a combination of ohmic resistors, frequency and voltage independent capacitors and ironless inductances, impressed current and voltage give identical results. Often however, the boundary between the inner core and the surface layer of the grain acts as a $p-n$ junction or a Schottky diode. Because there are always two of these with opposite polarity connected in series, no rectification effects are observed, but the resistance or impedance depends on voltage or current. These non-linearities can always be excluded by the application of a small electric field strength.

In our laboratory we can vary the electric field strength from 1 mV/cm to 1 kV/cm. This can be applied for unlimited time but with limited power. Battery supplies are available to give more than 10,000 A at up to 24 V, or 250 A at up to 200 V d.c., whilst a 5 kVA alternator set is available for use in the frequency range 1000 to 2000 Hz.

Most of the results reported here were measured with low electric field strengths to avoid the complicated high field strength effects with different types of hysteresis (Fig. 3) [12, 13, 16]. Electrical conductivities of battery materials are normally measured at normal temperature in ambient air, but we are able to make measurements in the temperature range -30 to 300 °C and some tools can be evacuated or filled with various gases.

Figure 1 shows diagrammatically some of the tools used, with uniaxial pressure application by one or two pistons. The pistons act as current collectors or terminals. The direction of current flow and application of pressure are the same. Inserting more than two voltage probes Fig. 2 makes it possible to investigate the homogeneity or anisotropy of the conductivity. If the voltage drop dV/ds depends on the distance s from the piston which is moved, then one has to extrapolate dV/ds from the values measured at $s_1 \dots s_2 \dots s_3$ etc. back to s_0 . The extrapolated value, dV_0 , will then be used to calculate the conductivity, which is then correctly related to the pressure obtained by dividing the piston force by the tool area, the frontal pressure.

The most severe problem is to obtain satisfactory insulating material for the dies. Reinforced plastics, hard paper, plastic bonded paper, Bakelite or melamine bonded tissue, ceramics, sintered alumina, steatite, glass ceramics and combinations of these materials have been used, but nearly all fail after short periods of use. Our solution to this problem is to change the dies, completely or in part, as soon as the surface has become rough, impregnated with powder particles or cracked.

Figure 4 is a block diagram showing how the measurements are carried out. Some of the parameters are kept constant during a series of measure-

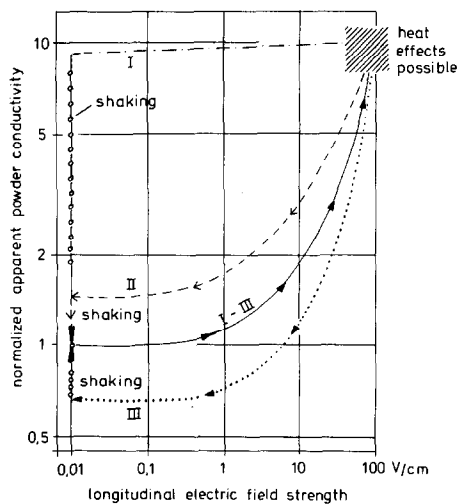


Fig. 3. The application of high electric field strength causes different types of hysteresis. 1, Sintering effect, Ag [1]; 2, expected effect, MnO₂ [13]; 3, anomalous effect, PbO₂ [16]. A, starting point at the given pressure.

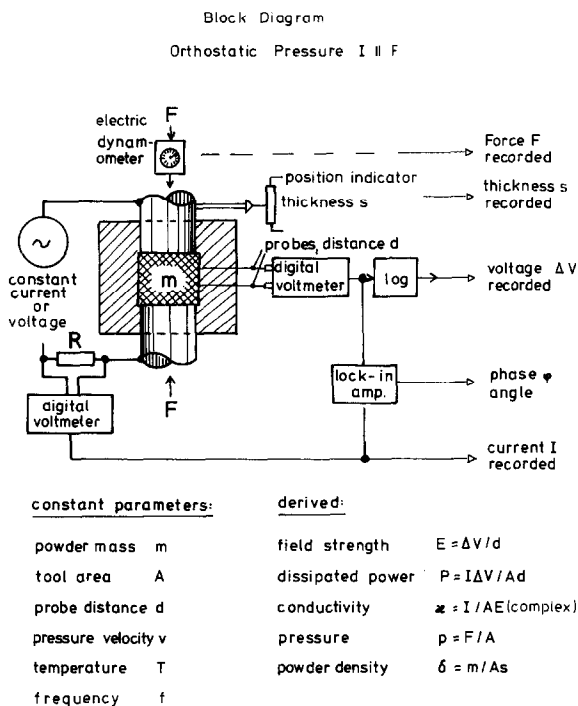


Fig. 4. Block diagram of method of measurement. Direction of current, I parallel to pressure p .

ments, e.g. the sample mass m , the tool area A , the distance d and arrangement of the voltage probes, the pressure velocity v or the pressure programme $v(t)$ in dependence on time, the temperature T , the atmospheric and electrical conditions, the method of preparing the sample, etc. The force F , sample thickness s , voltage ΔV , current I and phase angle φ are measured directly. The magnitude of the electric field strength $E = \Delta V/d$, dissipated power density $P = I\Delta V/Ad$, conductivity $\kappa = I/AE$ divided into the two complex components, frontal pressure $p = F/A$ and apparent mean powder density $\delta = m/As$ are then calculated.

Battery materials are a particularly interesting and fruitful subject of study. Figure 5 shows the changes which take place in battery materials on charge and discharge and the associated changes in electronic conductivity. The mechanical and thermal properties of the materials also change during charge and discharge, but whereas even in the most unfavourable case these properties change by a factor of about 10, the electrical changes are very large, as shown by the logarithmic scale of Fig. 5. Some typical values for a few bulk materials are given in Table 2.

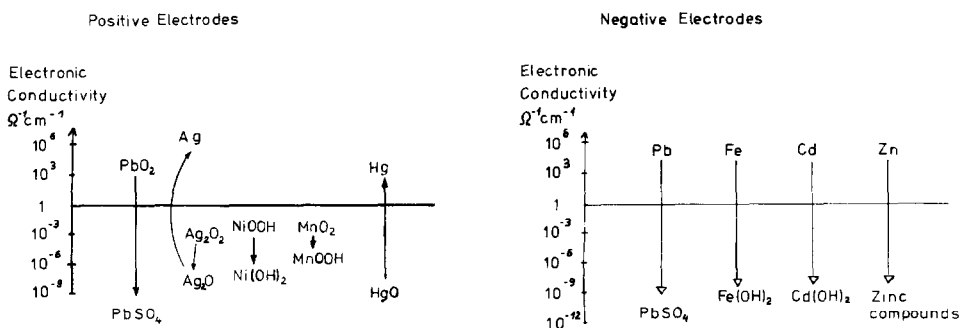


Fig. 5. Behaviour of battery electrodes. The arrow indicates discharge.

TABLE 2

Thermal conductivity λ and electrical conductivity κ of bulk Pb, PbO_2 and PbSO_4 at 300 K

$L = \lambda/\kappa T$, the Wiedemann-Franz-Lorentz number

Material	Thermal conductivity (W/cmK)	Electrical conductivity ($\text{ohm}^{-1} \text{cm}^{-1}$)	L (V^2/K^2)
Pb	0.33	5×10^4	2×10^{-8}
PbO_2	0.08	10^4	3×10^{-8}
PbSO_4	0.025	10^{-8}	8×10^3

It is certainly not to be expected that changes of this order of magnitude will be without influence on the electrical characteristics of the battery. It is, perhaps, necessary to add that in batteries the electrical contact between grains

or crystallites is due to residual pressure or to bridges formed by plastic deformation, recrystallization or cementing processes. Thus it is not possible to apply directly the conductivity measured in the pressure apparatus to the prediction of what happens in a battery. However, the general pattern of behaviour of a material can be recognised, the types of surface layers that exist can be seen and mutual comparisons can be made between materials.

Pressure dependence of powder conductivity

The general behaviour of the electrical conductivity of a compressed powder with respect to pressure is shown schematically in Fig. 6 [12, 13]. In branch A of the diagram, only dislocations take place. Nearly the same effect can be obtained by only shaking the powder, without application of external pressure, but just by the acceleration forces and by the impulses transferred by the mutual knocking together of the particles. In this range the powder is nearly reversible, it coheres weakly and disintegrates easily. The conductivity, however, is not reversible without disintegration of the powder bed. The measured values depend on many fortuitous circumstances.

In branch B elastic and plastic deformations take place. The powder coheres more strongly than in branch A, but can be disintegrated by small forces. The conductivity is partly reversible, removal of pressure means removal of elastic deformations. But plastic deformations remain, the grains remain as clearly visible individuals. Branch B is quite extensive and purely exponential with individual, but well defined, exponents. Branch B is more clearly defined than branches A and C, depending on the nature of the substance under study and its grain shape.

Branch C is characterized by the final deformation and closing of pores. A pseudo-bulk state is formed with nearly constant conductivity. It remains

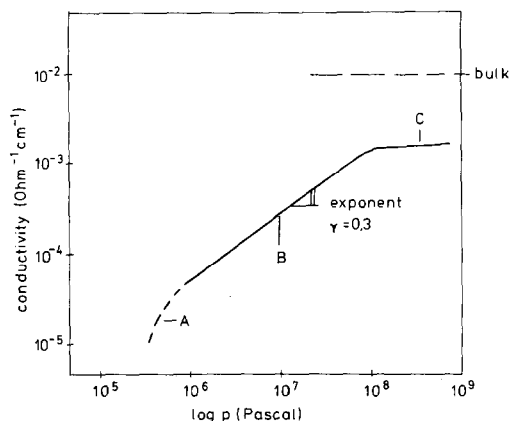


Fig. 6. Schematic representation of the dependence of electrical conductivity on pressure. A, Dislocation; B, deformation; C, final state.

below the bulk value because the surface layers remain as impurities within the compacted material. The compressed powder in this region coheres strongly and can be disintegrated only by the use of mills or crushing equipment. Moreover, original grain shape and dimensions are changed. There remain, however, large quantitative differences between the compressed and sintered powder. The application of heat brings the compressed material closer to the bulk state.

The powder in the die forms by dislocations either linear or closest arrangements, followed by elastic or plastic deformations. In ideal, fluid-like, substances, the grains form dodecahedrons having twelve pentagons as surfaces. These fit closely together. As well as dodecahedrons, tetradecahedrons are also observed, having fourteen faces, eight hexagons and six squares [23].

Figure 7 shows the apparent powder resistivity $\rho = 1/\kappa$ of 11 different varieties of manganese dioxide and of a chemically prepared, not well defined, γ -MnOOH. All the manganese dioxides are, or have been, used in batteries. The indicated pressure range is between 3 and 30 MPa. The samples can be characterized by the conductivity itself and by the pressure exponent, the slope of the logarithmic lines; the steepness. All the specimens exhibit well defined exponential behaviour but with different exponents. The most interesting are samples 1, 2 and 3 which show inverse behaviour; the resistivity increases with increasing pressure. This is due to the fact that the grains are covered with better conducting and mechanically soft layers.

The exponential behaviour follows from simple assumptions and from the theory of Hertz faces, as has been shown earlier [12]. The exponents indicate the properties of the surface layers. Spherical particles without surface layers have exponents of $\gamma \approx 2/3$ in the expression $\kappa = 1/\rho = ap^\gamma$, where a is a constant which can be calculated from the theory but is not of interest in the present work. It contains the elastic constants of the grain core and the surface layer, the two conductivities, the thickness of the surface layer and the grain diameter. Figure 8 shows the behaviour of technically important mixtures of an electrolytic manganese dioxide powder (EMD), a widely used Japanese variety produced in large quantities, with finely powdered graphite or acetylene black. The large exponents of the two upper curves indicate that 10 or more percent of graphite acts rather like pressure operated switches, possibly as a result of dislocations.

The theory of elastically compressed powders [12] consisting of spherical particles coated with surface layers of different conductivities and strengths with respect to the interior predicts steepness exponents in the range between $-1/3$ and $5/3$. In fact such values are observed for many materials: MnO_2 [13, 15], PbO_2 [14, 16, 21], metal powders [8, 17, 21], (Fig. 9) and mixtures (Fig. 10). However, exceptions are carbonyl iron, the cadmium active mass used in the manufacture of nickel-cadmium batteries and graphite (Figs. 9, 11 and 12). The "oversteep" exponents for the carbonyl iron and cadmium active mass can be understood by assuming that smooth particles are covered by hard and brittle, badly conducting surface layers.

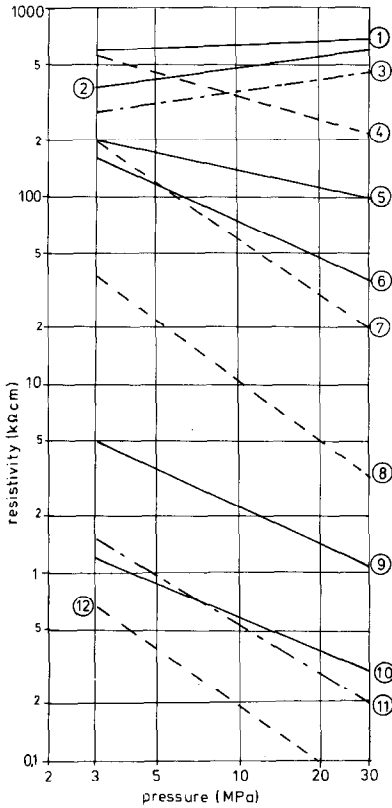


Fig. 7. Apparent resistivity of different types of manganese dioxide powder [12]. Pressure applied to one side only of 0.5 g samples between stainless-steel electrodes. Frequency, 5 kHz; electric field strength, 1 V/cm. 1, Manganese oxyhydrate from Riedel De Haen, a mixture of MnO_2 and MnOOH , ground; 2, highly hydrated, synthetic manganese dioxide, specific surface area $100 \text{ m}^2/\text{g}$, produced chemically; 3, highly hydrated manganese dioxide containing 5 wt.% ZnO; 4, highly hydrated manganese dioxide, by-product of saccharin manufacture; 5, highly hydrated synthetic manganese dioxide produced by the oxidation of a Mn(II) solution with chlorine; 6, synthetic manganese dioxide from the reduction of a permanganate solution; 7, natural cryptomelane, ground. Trout ore, Montana, U.S.A.; 8, natural $\gamma\text{-MnO}_2$, ground, Neo-granitis, Greece; 9, electrolytic manganese dioxide, finely ground, deposited on lead electrodes; 10, electrolytic manganese dioxide, anode sludge from zinc refining; 11, natural pyrolusite, Tschiaturi, Caucasia, Russia, ground; 12, natural cryptomelane, ground. Horseshoe mine, Australia.

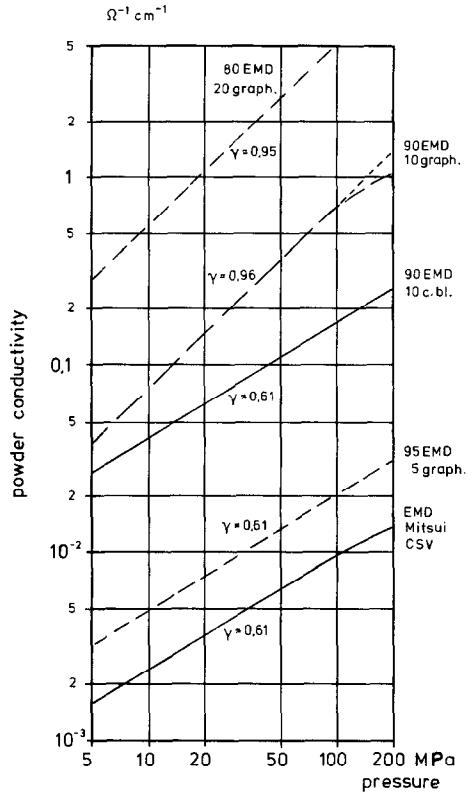


Fig. 8. Effect of pressure on the conductivity of mixtures of an electrolytic manganese dioxide, (EMD) from Japan, with graphite or acetylene black. After P. Herger [28], Screw press, conductivity correct to $\pm 5\%$.

This coating is destroyed in a narrow pressure range, and the cracks are penetrated by the plastic core metal. As a model one can imagine glass covered lead shot. The low value of the exponent in the case of flinz graphite probably results from the very flat grain shape. They are arranged nearly perpendicular to the pressure direction and easily undergo lateral dislocations thus

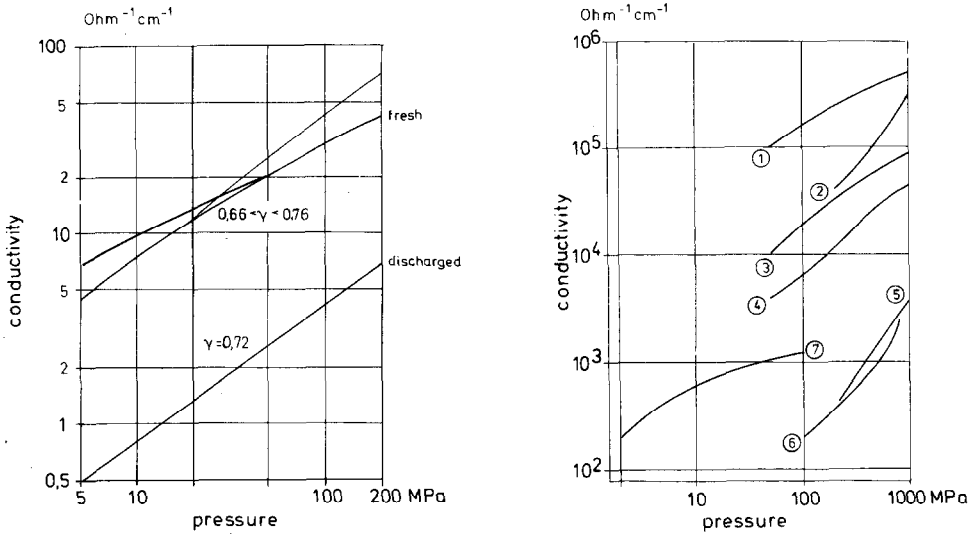


Fig. 9. Pressure dependence of the electrical conductivity of metal powders and natural graphite. Curves 1 - 6 after Schreiner [8], curve 7 after Caudle, Ring and Tye [11]. Pressure exponent = γ . 1, Electrolytically formed silver powder; 2, carbonyl iron formed from the gas phase; 3, electrolytically formed copper powder; 4, carbonyl nickel; 5, reduced molybdenum powder; 6, electrolytically formed iron powder; 7, natural graphite. Method of preparation of material 5 not known. Values have been recalculated [12].

Fig. 10. Conductivity of the black mix of industrial dry cells [28]. Pressure applied by a screw press, values correct to $\pm 5\%$.

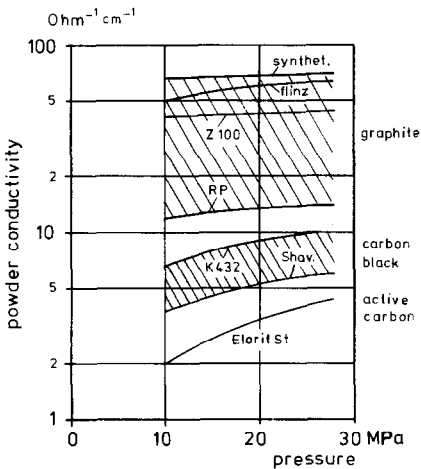


Fig. 11. Variation of the conductivity of various carbonaceous materials with pressure. After Drotschmann [30].

forming conducting stairs. The resistances of the surface layer and the core can be separated using the method developed by Braun [14] (see Fig. 13), in which impedance diagrams of PbO_2 powder are shown. The method is

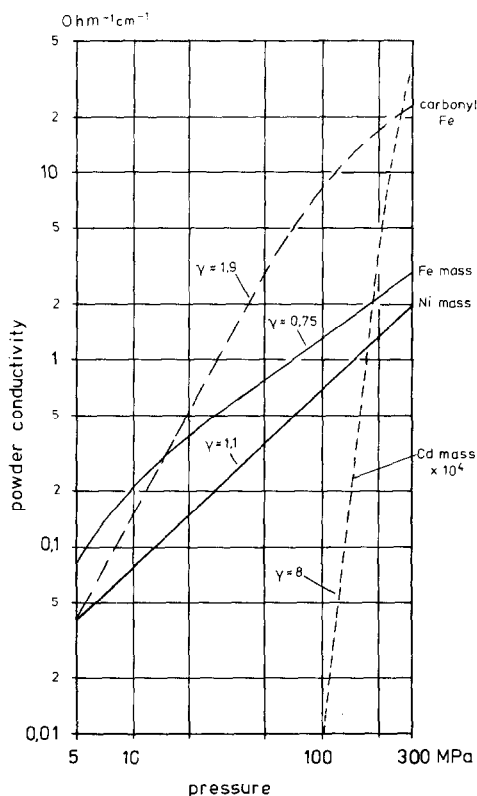


Fig. 12. Variation of the conductivity with pressure of various battery materials showing the abnormally high value of the pressure exponent obtained with some materials [29]. Hydraulic press, possible error $\pm 10\%$.

based on the extrapolation of impedance values measured between 0.5 and 100 kHz to complete the expected semicircle. Its base R_s is the resistance of the surface layer, which is bridged by a condenser. The resistance R_c of the core does not depend markedly on frequency and pressure.

A study of the effect of additional transverse pressure has only recently been started [25]. Figure 14 shows some of the preliminary results obtained. The most interesting feature is the hysteresis shown by PbO_2 , for which no explanation is at present available.

Apparent density

It has been proposed that the mean apparent powder density should be used as the variable instead of the pressure. Of course, if there is a marked, uneven pressure distribution in the powder bed, then the apparent powder density is a better approximation to the true state than the frontal piston pressure. However, it is only a rough, not self-evident, approximation which

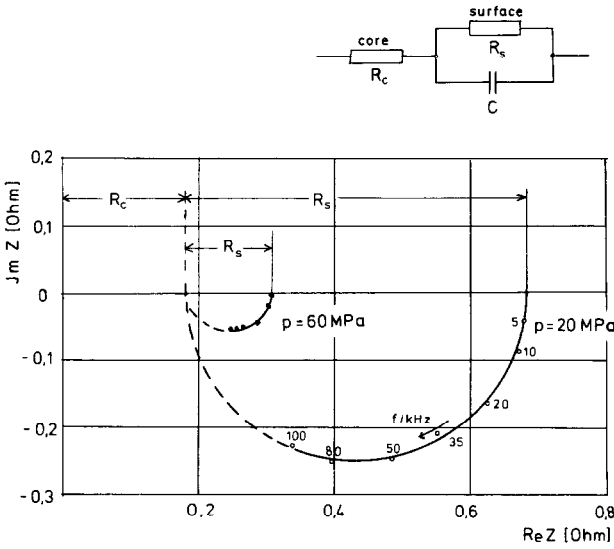


Fig. 13. Impedance of PbO_2 powder at 200 and 600 bar showing the possibility of separating the resistances R_s of the surface layer and the core R_c of the grain. After Braun [14]. Hydraulic press. R_s reproducible to within $\pm 15\%$.

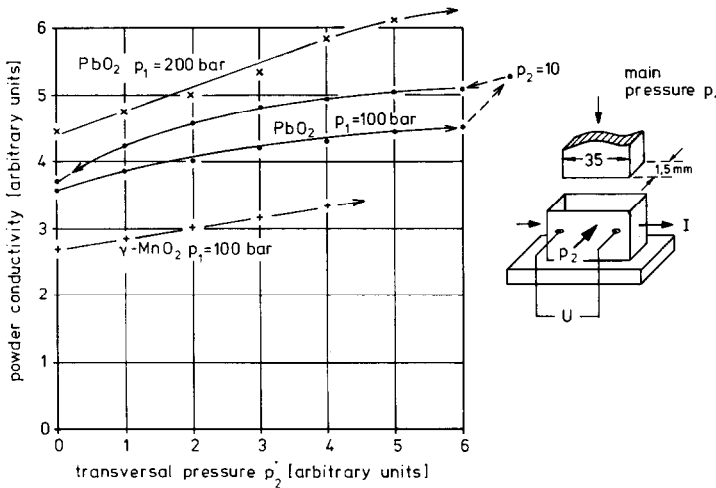


Fig. 14. Influence of transverse pressure at constant perpendicular pressure p_1 on the powder conductivity. After Kress [25]. p_1 hydraulic pressure, p_2 screw press.

always needs further explanation. We therefore continue to use pressure itself, and try to reduce the pressure drop in the powders. In general, correlations between conductivity and powder density within a class of similar materials do not exist. Figure 15 shows conductivity and powder density for 19 varieties of manganese dioxide used in batteries and two samples of $MnOOH$. Nothing more than a few rules of thumb, which have been known

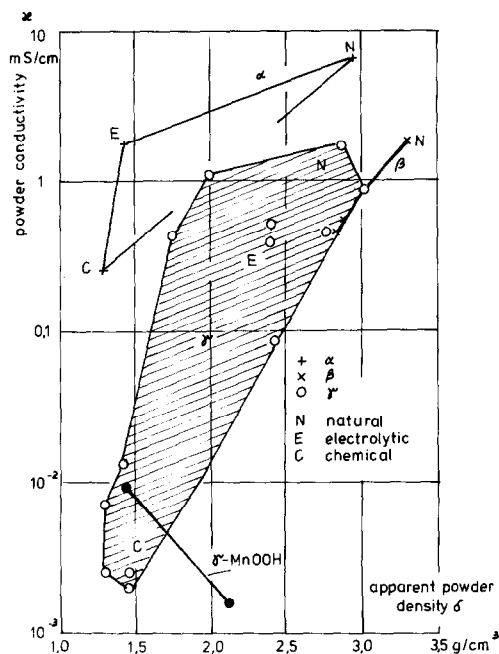


Fig. 15. Conductivity vs. density plot for various varieties of manganese dioxide [13]. $T = 18\text{ }^{\circ}\text{C}$, $p = 100\text{ bar}$, $m = 1\text{ g}$. Low electric field strength. Slow pressure velocity. Measured at 50 Hz with various types of presses. Results repeatable to $\pm 10\%$.

for a long time in battery laboratories, can be formulated: (a) proceeding from natural through electrochemical to chemical manganese dioxides leads to lower conductivity and lower powder density. The difference between natural and electrochemical materials is small, but the chemically prepared ones differ considerably; (b) the conductivity of α - and β -MnO₂ is better than the γ modification; (c) the density of β -MnO₂ samples is higher than that of the others; (d) discharged manganese dioxides show lower conductivity but unchanged powder density.

Effect of grain size

From the simple elastic theory of spherical grains [12] it follows that the influence of grain size should be given by the straight line in Fig. 16. The conductivity at a given pressure is proportional to the grain size. This can be observed sometimes, see the "steps" (2) in Fig. 16 which have been measured on spheroidal bronze powder, patinised by repeated immersion in acetic acid. Dendritic copper powder reduced in hydrogen (Fig. 16 (1)) shows no influence of grain size at all. This can be understood because these particles deviate considerably from the assumption of spherical shape. The third type of behaviour (Fig. 16 (3)) has been obtained with well sieved fractions of electro-

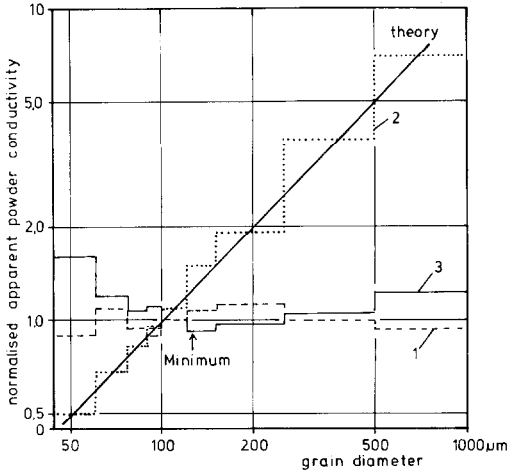


Fig. 16. Grain size effect, partly from ref. 13. Results reproducible to $\pm 8\%$. Sieved fractions, a small quantity of adhering fine particles may be present. 1, Reduced copper powder; 2, spheroidal bronze with patina; 3, EMD Perozono manganese dioxide.

lytic manganese dioxide. It shows a minimum conductivity near $120 \mu\text{m}$. The author first observed this effect 15 years ago and it has recently been repeated in his laboratories but it is as yet unexplained.

Effect of speed of application of pressure

The velocity of the application of the pressure has some effect on conductivity, as shown by the results of tests carried out in our laboratory (Fig. 17). The material used was an electrolytic manganese dioxide manufac-

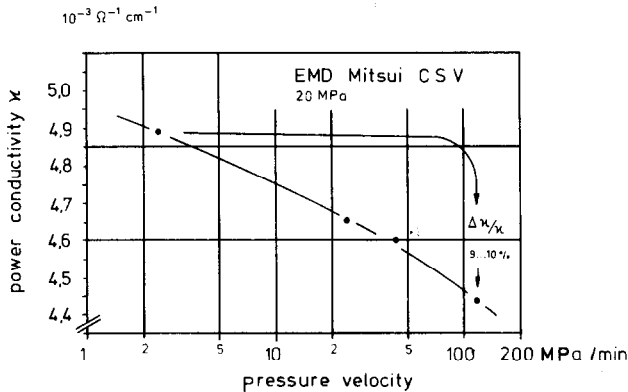


Fig. 17. Influence of pressure velocity. Electrolytic manganese dioxide. Low, 50 Hz, electric field strength. Tool area 0.8 cm^2 . Ambient air, normal temperature. Screw press, error less than $\pm 3\%$.

tured on a large scale in Japan. Low 50 Hz electric field strength was applied. For each point a new and equal sample was used, the press was started and allowed to raise the force at a given velocity. Current was kept constant and the voltage drop between two annular probes was recorded. The influence of the velocity of the pressure showed its greatest effect at 20 MPa, the value shown in Fig. 17. It is probable that the effect will be most marked with lumpy materials like ZnO and less apparent with free flowing ones like bronze powder. It is probable that the effect will be greater at higher velocities than those used here and also with the use of impact pressure.

In general we are working at a velocity of less than 400 N/min and a tool area of $A = 0.8 \text{ cm}^2$, equivalent to 5 MPa/min. The use of hydraulic installations instead of screw presses makes another similar effect apparent. The conductivity creeps after each elevation of pressure and takes several minutes to reach its final value. This behaviour is, presumably, due to slowly proceeding dislocations in combination with plastic deformations.

Despite all these difficulties, conductivities are reproducible. The range of errors depends to some extent on the nature of the sample and on the method of measurement. In general a limit of 10% can be attained, in the most favourable circumstances this will be reduced to between 3 and 5% for the conductivity and 1 to 3% for the steepness exponents. However, in many cases only 30% is attainable.

Behaviour of mixtures

From the theory of multicomponent conductors [20] straight logarithmic lines for the relationship between conductivity and pressure are predicted. This has been confirmed by Ernst [15] for mixtures of similar chemical substances with similar grain sizes and shapes (Figs. 18 and 19). These tests were carried out with two different samples of manganese dioxide, a natural ore from Manchuria and an electrolytic material (EMD) of Japanese origin. Both samples were ground and sieved and dried. The particles were fairly round with dimensions of approximately $60 \mu\text{m}$.

With acicular powder mixtures the situation is more complicated. In Fig. 19 curves are shown for dry mixtures of an electrolytic manganese dioxide with flint graphite and acetylene black. The mixture of EMD with zinc oxide powder has recently been investigated in our laboratory [26]. This mixture is characterized by two distinct logarithmic regions. It behaves like a system with an intermediate phase *P*, although such a phase does not really exist since chemical interaction can surely be excluded. Instead what is observed are well defined agglomerates having ZnO rich cores coated with a dense layer of pure manganese dioxide. No measurements were made above 90% ZnO because the conductivity of such mixtures was very low, less than $10^{-7} \Omega^{-1} \text{ cm}^{-1}$.

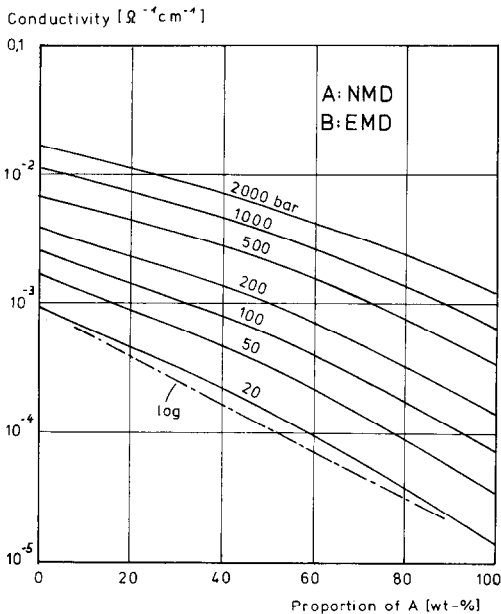


Fig. 18. Behaviour of mixtures [15]. Mixture of two samples of manganese dioxide, NMD ground, natural ore from Manchuria, EMD ground Japanese electrochemical ore. Screw press, results reproducible to within $\pm 10\%$.

Conclusions

The electrical properties of powders are an interesting field of research of great practical importance. In the case of batteries this work is of increased importance because of the changes which take place in the materials on charge and discharge. The effects observed are complex but can be understood in most cases by means of simple assumptions which can be readily accepted. A rough, but effective theory exists. Some interesting, often unexpected, results have been obtained. Not all of these have yet been explained, *e.g.* the influence of grain size. Many problems remain to be solved before the second step, the investigation of conduction physics, can be undertaken.

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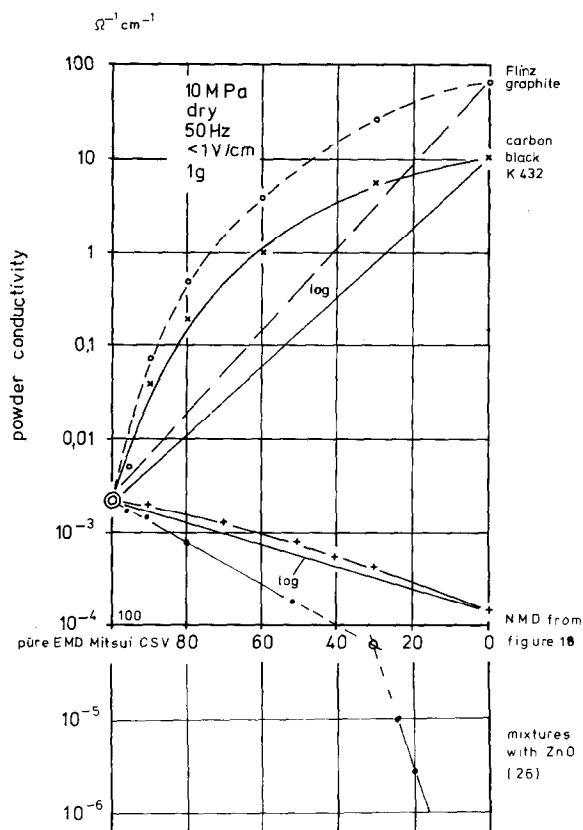


Fig. 19. Behaviour of mixtures [15, 26, 28]. Two component mixtures. ○, Flinz graphite + EMD; ×, Carbon black + EMD; +, NMD + EMD; ●, ZnO + NMD. NMD ground natural Manchurian ore, EMD ground Japanese electrochemical manganese dioxide. Measured on 1 g samples in dry air at 100 bar. 50 Hz, electric field strength less than 1 V/cm. Results reproducible to $\pm 10\%$.

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