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Electronic conductivity of lead dioxide powder: separation of core and surface resistance of the particles

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The electronic conductivity of active battery materials has seldom been investigated in detail. The problem is to separate the resistance contributions located in the particle cores and in the particle surfaces. In this paper battery PbO_2, the best-known model substance, has been studied.

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1. Introduction

The power generating processes in primary and secondary batteries require the transport of current carriers. To effect the electrode processes, electrons as well as ions have to be transported. Porous or soluble metals offer satisfactory transport modes to both types of carriers. Positive plate active materials, however, exhibit in most cases only moderate electronic conductivity. MnO_2, HgO and $NiOOH/Ni(OH)_2$ therefore need the addition of conductive material. Bulk PbO_2 has a fairly high electronic conductivity, similar to metallic Hg, about $10^4\,\Omega^{-1}\,cm^{-1}$, at room temperature. In battery electrodes, however, its conductivity is fairly low, down to $50\,\Omega^{-1}\,cm^{-1}$.

In primary battery research, and later on in the patents relating to alkaline secondary batteries, the problem of insufficient electronic conductivity is well-known [1–6]. Lead–acid batteries, however, are often designed without any consideration of the electronic conductivity of the active mass. The design concentrates on the pore system [7].

The chemistry [8], electric conductivity, carrier density and Hall mobility of bulk PbO_2 are known [9]. A few measurements of the conductivity of positive plates have been published, also its electrochemistry and the question of modification have been investigated [10–13]. In general, the PbO_2 in a battery is well defined, thus allowing results of many groups to be valid for different types of electrode designs and formula. In our group, several experimental investigations of PbO_2 *powder* have been carried out [14–25]. Certainly, the PbO_2 is formed, in the battery plate, not simply as a compressed powder. It is rather a cake, cemented by other lead compounds, or even by genuine PbO_2 bridges. However, the easy shedding of active mass from positive plates shows that the individual particles have not bonded very strongly. Thus, we treat PbO_2 battery electrodes as a compressed powder sample.

2. Batteries as electrical networks

Neglecting the resistance of the metallic grid or of the spines in the ironclad plates, the charged PbO_2 electrode consists of an assembly of individual particles, which are in mutual electrical contact. We can presume from [20], that a large number of current conducting connections exists between the particles, at least ten connections per particle. Nevertheless, the PbO_2 particles fill only about 50% of the entire electrode volume. During the discharge, the mean density decreases from $9.4\,g\,cm^{-3}$, relating to pure PbO_2 down to $6.2\,g\,cm^{-3}$, relating to pure $PbSO_4$. During the discharge, the pores are partially filled with the

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expanding solid material. In this paper we report the study of the electronic conductivity of the charged PbO_2. The changes of the electronic conductivity during the charge/discharge cycles are under study, and will be published later [25].

The early measurements showed that the contact resistance is fairly large. Bulk PbO_2 exhibits a conductivity of $10^4\ \Omega^{-1}\,cm^{-1}$ at room temperature, both modifications behaving similarly. In the plates, the conductivity is about 20 to 300 times smaller. Therefore, the electronic part of the electrode has to be represented by a three-dimensional network of n small resistors, R_P, and m fairly large resistors, R_C. n represents the number of particles, m the number of current conducting intergranular contacts, R_P is the electronic resistance of a particle, R_C the contact resistance. R_P is not necessarily identical with the bulk resistivity. We suppose, that $R_P < R_C$ and $n < m$. m is not identical to the number of contacts between the particles, because some of the contacts occur at equipotential plains, not participating in the conduction processes. The problem to be investigated here relates to the problem of distinguishing between R_P and R_C and between n and m, respectively. The separation of R_P and R_C is a very important step for the better understanding of the physical processes in the PbO_2 plates. A network of a large number of finite elements can be replaced by an equivalent circuit, having only very few elements. To develop such equivalent circuits, one has to look for special properties of the four parameters of interest.

3. Equivalent circuits

To define the properties of the four equivalent circuit elements seems possible only for restricted types of substances. The battery depolarizers, in most cases, are non-stoichiometric oxides of unknown composition.

3.1. *Particle resistor R_P*

In general, R_P is ohmic. It changes with the temperature and depends in a complicated way on the pressure. With rising pressure, more current carrying contacts are formed, their area increases, and insulating surface layers are destroyed. Within the scope of the known geometric definition, R_P can be reduced to a specific resistivity ρ_P. The low ρ_P of good conducting PbO_2 will be charged with geometric inductance, L_P.

3.2. *Contact resistor R_C*

In general, R_C is *not* ohmic. Increasing electric field strength, E, or increasing measuring current, I, correspond to decreasing R_C, see [14, 22, 26]. The electric field effect develops slowly, over several seconds, and shows marked hysteresis. The temperature dependence of R_C is very complicated, because the elastic constants, e.g. the crushing strength, decrease with rising temperature. Consequently, the contact area increases. It follows exactly the well-known rule of Hertz, at least in the elastic (Hooke) regime. A defined specific contact resistance ρ_C can be expected in a metaphorical sense. It depends on the number of particles in the unit volume of the compressed sample. Thus, $\rho_C = K/r$ is inversely proportional to the grain size $2r$ with the ambiguous constant K. The very close neighbourhood of the particles forming the electric contacts causes R_C or ρ_C to be bridged by the contact capacity C_C. The capacity increases with increasing pressure and temperature. A specific capacitance c_C ($\mu F\,cm^{-1}$) can be defined, which again is inversely proportional to the grain radius r.

3.3. *Particle number n*

If $\Delta\tau$ is the mean volume of one particle, V the volume of the entire electrode and v the relative porosity, n is given simply by $n = V(1-v)/\Delta\tau$. If, as a first approximation, we put $\Delta\tau = (4\pi/3)r^3$ (particles are uniform spheres having the diameter $2r$), it can be written $n \approx V(1-v)(3/4\pi)/r^3$. The particle number can be split $n = s \cdot p$ into s series connected and p parallel contacted grains. Introducing the area A and the thickness h of the compressed sample gives $s \sim h/2r$ and $p \sim (A/2\pi)r^2$. The unwritten geometric constants contain the porosity v as well as the tortuosity factor a, and a few minor assumptions. In general, the integral sample resistor relating to the particles, becomes

$$R_I = \rho_P h/A \approx R_P s/p \approx R_P h\pi r/A.$$

3.4. *Contact number m*

From mixing experiments [17, 18, 20] and from the consequent application of the effective medium theory, the number of current carrying contacts in PbO_2 powder, taken from fully charged, new lead–acid automotive batteries, has been evaluated. m was found to rise fairly steeply with increasing pressure. Per particle, m/n was found to be approximately 8 at a pressure of 100 bar (10 MPa), and $m/n \approx 10$ and 12, at 200 and 500 bar, respectively. These figures relate to a powder. Similarly, slightly elevated figures of about $m/n \approx 12$ can be expected in the non-disintegrated positive plates.

It is possible to introduce the numbers s and p of series and parallel contacted particles, see Section 3.3. In general, the integral sample resistor relating to the intergranular contacts, can be given as

$$R_{II} = \rho_C h/A \approx (R_C s)/p = R_C h\pi r/A.$$

It is bridged by the contact capacitance

$$C_{II} = c_C A/h \approx C_C p/s = C_C A/(h\pi r).$$

At very low frequencies, the sum $R = R_I + R_{II}$, or $\rho = \rho_P + \rho_C$ is measured, at high frequencies the capacitance decreases R_{II}, and only R_I is measured. Possibly, at high frequencies, the inductance of the grains must be considered.

3.5. *Comparison of the equivalent circuit elements*

The particle resistance ρ_P follows the rules of solid state electronics, e.g. the Schottky rule $\log \rho_P \sim 1/T$ in the regime of intrinsic semiconductors, or it shows metallic behaviour. The contact resistance ρ_C depends simply on the contact area A, given in turn by Hertz as $A \sim p^{1/3} r$, thus giving $\rho_C \sim r/p^{1/3}$. We may also assume, that in the frequency range below 1 MHz, the capacity C_{II} does not depend on the frequency. This is correct in nearly all samples investigated. Thus, we can replace the three-dimensional multicomponent network by one of the four equivalent circuits, indicated in Fig. 1. It seems possible to separate the resistance contributions R_I and R_{II} by systematic variations of electric field strength E, temperature T, frequency f or pressure p.

In principle, R_I and R_{II} can be separated by two additional variations, i.e. (a) illumination: the active battery materials, however, are almost impermeable to light. No large effects are to be expected; (b) magnetic fields: we need, however, the magnetoresistance or the Hall voltage for the determination of carrier concentration and mobility, see [15, 19, 21, 23, 24].

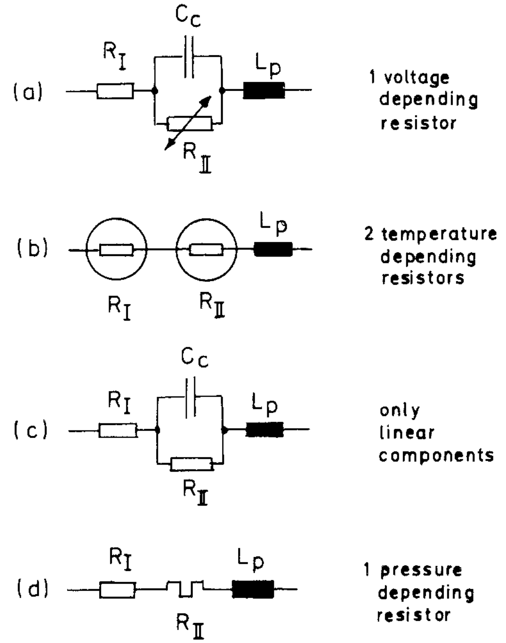

Fig. 1. Equivalent circuits for a compressed powder, representing only the influence of one parameter: (a) electric field strength E (and frequency f); (b) temperature T; (c) frequency f; (d) pressure p.

4. Experiments

Pressure, temperature, electric field strength and frequency variations were carried out.

4.1. *Pressure variation*

With rising pressure, the powder conductivity of a chemically prepared β-PbO_2 sample approaches slowly the bulk conductivity. However, it does not reach it completely, see Fig. 2. The remaining difference may be caused possibly by impurities or by residues of surface layers. Curve 2 in Fig. 2 relates to a PbO_2 powder sample from the positive plates of a charged lead–acid battery. Even at a pressure of 5000 bar, its conductivity remains by a factor of 500 below the conductivity of bulk PbO_2 pieces. Both results are reproducible to within ± 25%. As a result, it is clear that the

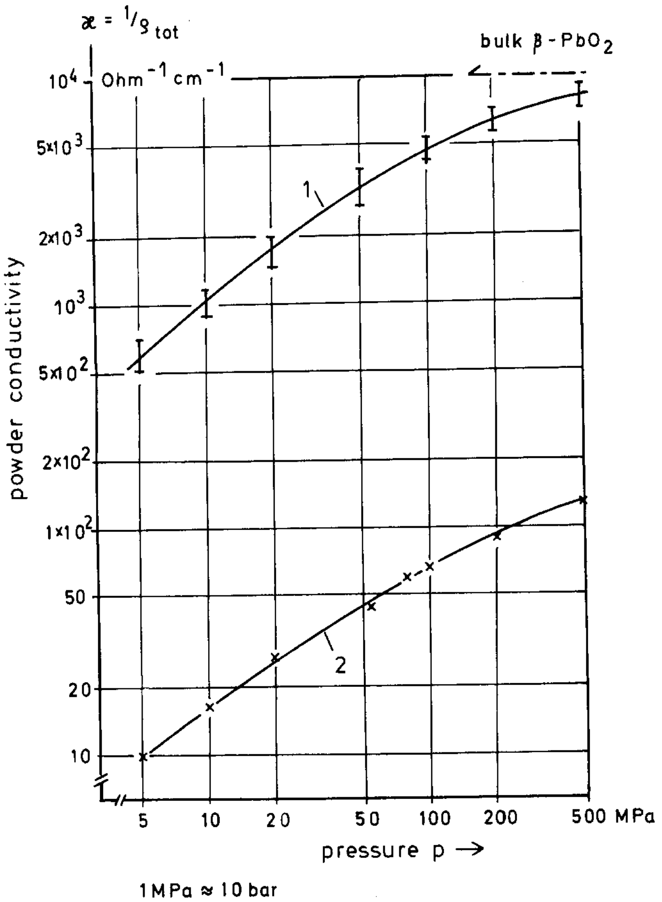

Fig. 2. Specific conductivity measured with low frequency and low field strength; dependence on pressure p. (1) PbO_2 powder no. 7407, from Merck, Darmstadt, chemically prepared. For comparison the conductivity of bulk PbO_2 is indicated. (2) PbO_2 powder taken from charged positive grid plates of a lead–acid secondary battery.

resistance contribution of the intergranular contacts is more important than the resistance of the grains itself. The battery PbO_2 consists mostly of β-PbO_2, containing a few per cent of the less-conducting α-PbO_2 and some insulating substances. We do not have any indication of more highly conducting battery PbO_2 even after having investigated more than ten different battery materials.

4.2. *Temperature variation*

Dry α-PbO_2 can be heated up to about 200° C, β-PbO_2 up to 300° C without a significant loss of weight. The adhering water was driven out at 110° C. We investigated the dried powders in the temperature range from — 30° C (*in vacuo*) up to + 200° C. In our experiments over 2 years, we have not found temperature variation to be a useful method for separating grain and contact resistivities of PbO_2 powder samples. Other substances, e.g. copper oxides, can be investigated much better by temperature variation.

4.3. *Variation of the electric field strength*

With increasing electric field strength, the powder conductivity in general rises. Three different regimes must be distinguished.

(a) At very low electric field strength, the intergranular contact resistance behaves purely ohmically, the powder resistivity remains constant.

(b) In the intermediate range, for the battery PbO_2 powder investigated here between 1 and 10 V cm^{-1}, the conductivity rises reversibly with increasing field strength. There are three physical mechanisms, which can be responsible: (i) temperature increase as the consequence of the dissipated energy; (ii) thermionic Richardson emission between the grains; (iii) field emission

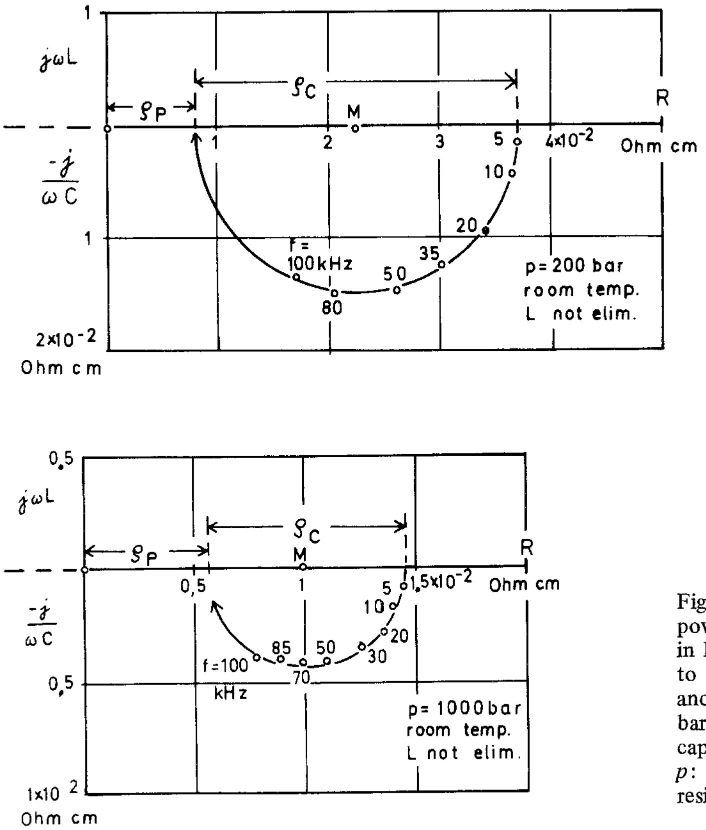

Fig. 3. Argand diagrams of the battery PbO_2 powder used for the measurements represented in Fig. 2. Room temperature, frequency range 5 to 100 kHz, low electric field strength, inductance not eliminated. Pressure $p = 200$ and 1000 bar. R: real (ohmic) component, C: equivalent capacity, L: inductance, ω: angular frequency, p: pressure, ρ_P: resistance of the grains, ρ_C: resistance of the contacts, $j^2 = -1$.

between the closely packed grains. Following the calculations of Herger [20], the latter seems to be the most probable mechanism.

(c) Above 100 V cm^{-1}, irreversible changes, similar to a heat breakthrough, are observed, which are caused by fritting or welding of the intergranular contacts. This is accompanied by changes of the dark brown colour into a light red, yellow or even grey.

Consequently, the variation of the electric field does not fit well to the problem under study here. The PbO_2 samples pass too high a current in the appropriate electric fields. Again it should be noted that the separation by field strength variation can be applied to less-conducting powders very successfully, e.g. to lower Pb oxides, Mn and Ni compounds etc.

4.4. *Frequency variation*

Fig. 3 shows experimental Argand diagrams in the impedance plane, for a slightly different battery PbO_2 powder, from Varta, 90% β-PbO_2 and 10% α-PbO_2, at 200 and 1000 bar pressure. The electric field strength was kept very small; no field effects were observed. Obviously, circuit (c) in Fig. 1 represents the powder behaviour quite well. As expected, semi-circles are observed in the capacitative direction cutting the ohmic coordinate into two parts. The figures are reproducible within ± 10% of the powder resistivity. It seems reasonable to interpret the two sections as the specific resistivity contributions ρ_P and ρ_C of the grains and the contacts.

If we accept this interpretation, the desired distinction between grain and contact resistivity can be effected by a frequency variation in the range 5 to 100 kHz. The battery PbO_2 powder sample investigated here, exhibits a reduced powder conductivity, which agrees reasonably with Fig. 2. In Table 1 the contact ρ_C and grain resistivities ρ_P are indicated together with the total powder resistivity ρ_{tot}, as a function of the pressure p. The two additional columns are

Table 1. Contribution of the specific contact resistivity ρ_C and the specific grain resistivity ρ_P to the total powder resistivity ρ_{tot}, found by extrapolation of the semi-circles in the Argand diagrams [16]. $(\rho_C)_{corr}$ and $(\rho_P)_{corr}$ are corrected by inductance elimination. PbO_2 powder from charged positive plates of a lead–acid battery

Pressure, p (bar)	*Specific resistivity* (Ω cm)					*Specific capacity,* c_C (μF cm^{-1})
	ρ_C	ρ_P	ρ_{tot}	$(\rho_C)_{corr}$	$(\rho_P)_{corr}$	
100	0.050	0.0084	0.0584	0.051	0.0074	
200	0.029	0.0077	0.0367	0.031	0.0057	56
600	0.013	0.0073	0.0203	0.016	0.0043	
800	0.0108	0.0065	0.0173	0.0117	0.0056	
1000	0.0090	0.0056	0.0146	0.0097	0.0049	180

corrected, following a method of Braun [16], to eliminate the inductance. Fig. 4 exhibits the corrected contact $(\rho_C)_{corr}$ and grain resistivities $(\rho_P)_{corr}$, as a function of pressure p.

The capacity c_C shunting the contact resistivity ρ_C can be calculated by the application of the Thales circle to the Argand diagrams. However, the interpretation of c_C is hardly possible in the sense of solid state electronics. Nevertheless, two figures are included in Table 1. c_C relates to a powder sample having the outer geometrical area of 1 cm^2 and the thickness of 1 cm. It is given in μF cm^{-1}.

5. Discussion

The most surprising result is certainly the high contribution of the grain resistivity $(\rho_P)_{corr}$, much above that of the bulk resistivity. Even at 1000 bar (100 MPa), $(\rho_P)_{corr}$ remains by a factor of almost 50 above the figures published [9, 10] for bulk pieces of PbO_2. These results, however, were con-

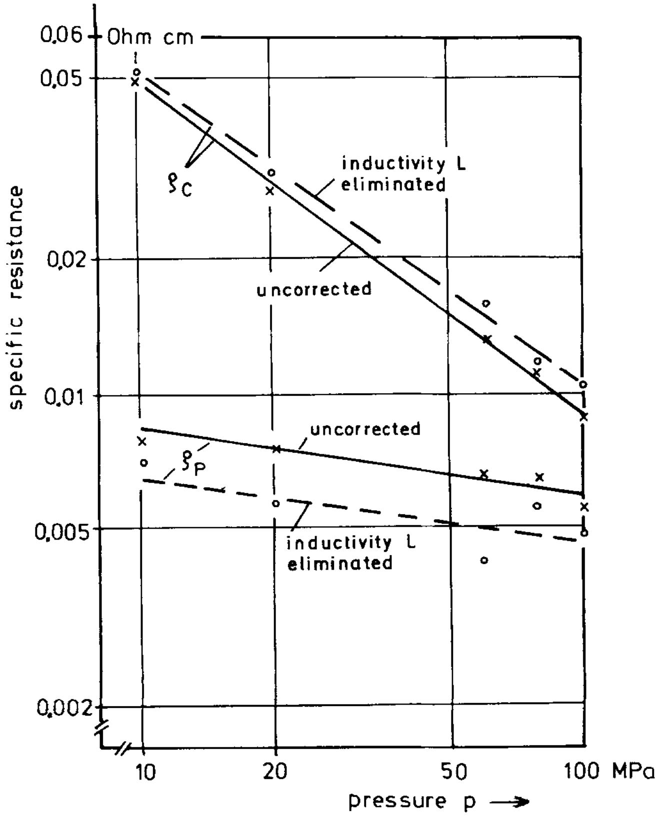

Fig. 4. Specific contact resistivity $(\rho_C)_{corr}$ and grain resistivity $(\rho_P)_{corr}$; dependance on the pressure p. PbO_2 powder from plates of a fully charged lead–acid battery, identical to Fig. 3.

firmed by several investigations in our group [14, 15, 16, 25]. Thomas [10] has found very low resistivity for bulk PbO_2, but he gave about 30 times larger values for (even heavily compressed) PbO_2 powder from lead–acid batteries. Thus, we have to try to explain the results.

5.1. *Geometrical factors*

The grains are fragments of different shape and size. The specific resistivities, however, are defined assuming similar cubic particles. The next approximation, spheres of non-uniform diameter, has been calculated by Braun [16], assuming spheres to have only two opposite, equal and circular contacts. The result does *not* depend on the radius r of the spheres, but only on the radius a of the circular current inlet,

$$R_s = \rho \frac{1}{(2-\sqrt{2})\pi a}.$$

R_s has to be compared with the resistor of the circum-cube $R = \rho(1/2r)$. The relation

$$R_s/R = \frac{2}{(2-\sqrt{2})\pi} \frac{r}{a} = 1087\, r/a$$

depends on the relation r/a of the radii r of the sphere and the inlet contact a. The relations easily reach $r/a \approx 10$ and do not depend on the grain size. With more than two contacts, but up to 12, as stated by Herger [20], R_s reduces considerably. In spite of this, we have to replace one cube by less than one, namely about 0.9, spheres, to consider the fairly high porosity. Also, a tortuosity factor of about 1.3 has to be considered. The latter two corrections may possibly balance the first. Thus, the geometrical narrowness of the current carrying contact may cause about one decade of the factor q between the grain resistivity $(\rho_P)_{corr}$ of the powder and the resistivity ρ_b of bulk pieces $q = (\rho_P)_{corr}/\rho_b$. Extrapolating the resistivity in Fig. 4 to a pressure of 10 000 bar, the grain resistivity reaches about 3×10^{-3} Ω cm, a factor $q \approx 30$ above the bulk resistivity $\rho_b \approx 10^{-4}$ Ω cm, and about a factor $q' \approx 25$ above the resistivity of pure, chemically prepared β-PbO_2 powder at 10 000 bar, see Fig. 3. Thus, there remains a discrepancy of a factor of about 3. It seems hardly possible to explain it by geometric considerations.

5.2. *Impurities*

Recent results [25] and the evaluation of mixing rules [17, 18, 23, 24] lead to the conjecture that even fully charged battery PbO_2 within the grains exhibit a lower conductivity than coarse pieces of bulk PbO_2. The samples we studied consist of grains. Several years ago, one of us (K. -J. E., unpublished) was able to show by radioactive tracer methods with sulphur 34, that carefully prepared small PbO_2 particles from fully charged, undamaged lead–acid batteries always contain a few percent lead sulphate, invisible in X-ray spectra. Probably, the grains contain thin, insulating layers, domains etc. of $PbSO_4$ or basic sulphates. It also cannot be excluded, that the grains contain small quantities of PbO_x which is a fairly good insulator [18]. However, the insulating layers or domains have not been verified, so far.

The range of existence of the phase β-PbO_2 and probably also of the phase α-PbO_2 is very small. Deviations from stoichiometric composition are to be expected during charge and discharge of the battery electrodes [27]. Its influence on the conductivity, however, remains small, the more so because PbO_2 behaves, to some extent, as a metal.

5.3. *Specific contact resistivity*

The specific contact resistance $(\rho_C)_{corr}$ pressure dependance p can be described by a uniform exponent k:

$$(\rho_C)_{corr} = \rho_0 p^k \text{ with } k = -0.7 \pm 0.03,$$

and ρ_0 a constant.

This behaviour confirms earlier results [22] and can be understood assuming that the grains are purely elastically deformed. The contact area grows with rising pressure, according to the rule of Hertz. In the case of spherical particles, the exponent should be exactly $k = -2/3$, the small deviation certainly is within the range of error.

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