Journal of Power Sources, 4 (1979) 171 - 175

Short Communication

The Magnetoresistance of Lead Dioxide Powder*

ERWIN KRESS

Working Group of Practical Physics of the University (Gesamthochschule) Kassel, D-3500 Kassel (F.R.G.)

(Received May 2, 1979; in revised form June 2, 1979)

Summary

The increase in the apparent specific resistivity of compressed PbO_2 powder in transverse magnetic fields — the magnetoresistance — has been measured. At a pressure of 100 bar (10 Megapascal), at room temperature and 2 Tesla, a positive magnetoresistance of +(0.75 ± 0.15)% has been observed. A related apparent carrier mobility of (435 ± 90) cm^2/V s can be derived. Significant differences exist between battery PbO_2 and chemically prepared, inactive β PbO_2.

Zusammenfassung

Die Erhöhung des scheinbaren spezifischen Widerstandes von komprimiertem PbO_2-Pulver ist gemessen worden. Bei einem Druck von 100 bar (10 MPa), bei Zimmertemperatur und 2 Tesla, ergibt sich eine Erhöhung von +(0.75 ±0.15)%. Daraus kann man eine scheinbare Trägerbeweglichkeit von (435 ± 90) cm^2/V s ableiten. Zwischen dem PbO_2 aus Batterien und chemisch hergestelltem, inaktivem β-PbO_2 bestehen erhebliche Unterschiede.

---

1. Introduction

Lead dioxide is one of the most important and most interesting substances used in battery technology. In general, its chemical behaviour [1], the appearance of the two allotropic modifications [2], its electrochemistry *in vitro* [3] and in the working battery [4] are fairly well-known. Also, the

---

*Part of the Diploma Thesis, Kassel, 1977.

electronic conductivity of PbO_2 has been examined by several authors [5 - 7], and finally the Hall constant has been measured [8]. The following short contribution relates to a further electric property, the change of the specific electric powder resistivity in transverse magnetic fields, the magnetoresistance.

2. Experimental

As shown in Fig. 1, the arrangement is similar to the one used by Braun [8] for the investigation of Hall voltage. The powder sample (X) is com-

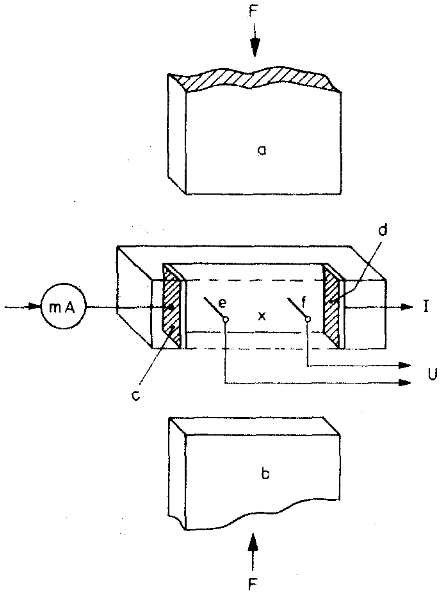

Fig. 1. Experimental arrangement, exploded, front wall of the die removed: X, powder sample; a, b, insulating pistons; c, d, current conducting electrodes; *F*, force; *I*, current; *U*, voltage drop between probes e, f.

pressed in an insulating die between insulating pistons (a, b) by the application of hydraulic force, *F*. The current conducting electrodes (c, d) are arranged on both sides of the die. The voltage drop, *U*, between gold-plated voltage probes is measured by an electronic voltmeter. The distance between the probes is Δz. If *A* is the geometric surface of the compressed sample perpendicular to the direction of current, the apparent specific resistivity, ρ_0, of the powder sample is simply $\rho_0 = AU/I\Delta z$. The press tool is arranged between the poles of a laboratory magnet, the magnetic field, *B*, being perpendicular to the pressure, *F*, as well as to the direction of the current, *I*. With increasing magnetic field strength, *B*, the resistivity changes from ρ_0 to $\rho_0 + \Delta\rho$. The relative change $\Delta\rho/\rho_0$ is the magnetoresistance given in percent. At constant pressure and constant current, the change in resistivity can be replaced by the change ΔU of the voltage drop, U:

$$\Delta\rho/\rho_o = \Delta U/U.$$

3. PbO_2 powder sample

The PbO_2 powder sample under study here had already been investigated by Braun [8]. It was taken from grid plates of fully charged lead–acid automotive batteries. The sample consisted of about 90% β-PbO_2. The remainder was composed of about 8% of α-PbO_2 and small amounts of lower oxides and basic sulfate. The powder sample had been stored at room temperature in a closed laboratory flask for about 4 years. Its pycnometric density was 9.22 g/cm^3, to be compared with the X-ray densities of pure β-PbO_2 (about 9.70 g/cm^3) and α-PbO_2 (about 9.87 g/cm^3).

The screened sample passed through a sieve of 40 μm width. From previous investigations we know that most of the samples have a grain size of less than 10 μm, but easily form aggregates. The powder had been dried for 2 h at 120 °C before being added to the die. To avoid complicated effects, *e.g.*, electrolytic decomposition, capacity, or inductive influences, or even heat effects, only a very small alternating current of moderate frequency was applied. The frequency remained between 1 and 10 kHz and the electric field below 1 mV/cm. The heat dissipated in the powder (volume several cm^3) remained, *e.g.*, at a pressure of 100 bar (10 MPa) below 10^{-4} Watt.

4. Results

The electric powder conductivity, κ_o, at zero magnetic field, at a pressure of 100 bar (10 MPa), and at room temperature was found to be κ_o = 37 ± 3 ohm^{-1} cm^{-1}, corresponding to a resistivity ρ_o = (2.7 ± 0.2) × 10^{-2} ohm cm. It did not depend on frequency in the range between 1 and 10 kHz and did not depend on the electric field strength up to 10 mV/cm. Figure 2 shows the dependence of its magnetoresistance, $\Delta\rho/\rho_o$, on the magnetic field B. The parabolic $\Delta\rho/\rho_o \propto B^2$ rule seems to be fulfilled approximately. At B = 2 Tesla (≈20 000 Gauss), the magnetoresistance is about +(0.75 ± 0.15)%. The positive sign, as generally observed, indicates that the resistivity increases in transverse magnetic fields. (1 Tesla = 1 V s/m^2.)

From the magnetoresistance, an apparent carrier mobility, μ, can be calculated

$$\mu^2 = f(\tau, f_k)/B^2 \cdot \Delta\rho/\rho_o.$$

The dimensionless function, f, depending on the relaxation time, τ, and on the number, f_k, of freedom degrees has been put at approximately $f(\tau, f_k) \approx 1$. The result of μ = 435 ± 90 cm^2/V s coincides satisfactorily with the Hall

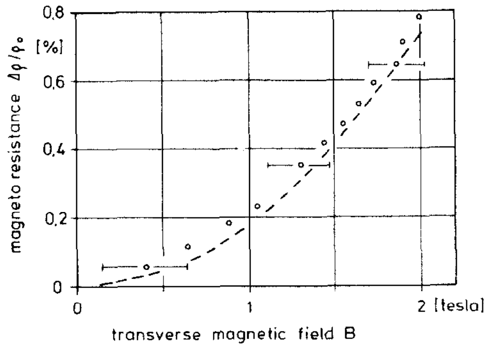

Fig. 2. Magnetoresistance of PbO_2 powder sample. Pressure, 100 bar (10 MPa); frequency, 2 000 Hz; current, 50 mA. The "limits" indicate the standard deviation. Dashed line: B^2.

mobility of the grain surface material evaluated by Braun [8] as 480 ± 50 cm^2/V s under similar conditions. It must be mentioned, however, that both carrier mobilities have a relevant meaning (relating to solid state physics) only in the case of univalent conduction types. For bulk PbO_2 it is generally assumed, that it shows nearly metallic behaviour. This has *not* been proved for PbO_2 powder, so far. Because the bulk PbO_2 has a very low resistivity, below 10^{-3} ohm cm, the intergranular contacts contribute, at low pressure, much more to the powder resistivity than do the grains themselves.

With rising pressure, the magnetoresistance, $\Delta\rho/\rho_0$, as well as the mobility, μ, decreases steeply. If we identify, *e.g.*, the bulk material with a powder under very high pressure, it cannot be excluded that the apparent mobility reaches the range of electron mobility in monovalent metals (*e.g.*, Cu exhibits 30 cm^2/V s). In the sense of this extrapolation, the results may be regarded as agreeing with previous predictions. However, it is planned to investigate the influence of pressure and temperature on the magnetoresistance of PbO_2 powder by further experiments.

The preparation of the powder has great influence on the resistivity and on the magnetoresistance. A few additional measurements have been made on another PbO_2 sample. It was prepared by treatment of Pb_3O_4 with nitric acid. Its pycnometric density was about 9.29 g/cm^3, and the grain size was similar to the battery sample. Under the same measuring conditions, its conductivity was found to be about twice that of the battery sample, see Table 1, at a pressure of 100 bar.

The data given here are reproducible for the sample under study but depend on its method of preparation. The results cannot be regarded as being completely understood in the sense of solid state physics. The difference between the lead dioxide from battery plates and the chemically prepared material is quite marked. These preliminary results suggest therefore that magnetoresistance and powder conductivity measurements may provide useful and rapid means of determining whether or not a particular sample of lead dioxide is electrochemically active.

TABLE 1

Electrical data of the PbO_2 sample from the lead–acid cell, and of chemically prepared, inactive β-PbO_2

	Battery PbO_2	Chemical β-PbO_2
Magnetoresistance at 2 Tesla	+(0.75 ± 0.15)	+(0.45 ± 0.09)%
Apparent carrier mobility	480 ± 50	340 ± 80 $cm^2/V\ s$
Powder conductivity	37 ± 3	79 ± 8 $ohm^{-1}\ cm^{-1}$

The director of the working group, Prof. Dr. Ing. Karl-Joachim Euler, is thanked for his steady encouragement, as are Mr. G. Kuhn, Mr. G. Leber, Mr. A. Malkomes, and Mr. K.-H. Otto for their valuable help in the laboratory. Last but not least, I am indebted to the editor, D.H. Collins, for an important remark on the discussion of the results.

References

1 Gmelin's Handbuch der anorganischen Chemie, Verlag Chemie, Weinheim, 8th edn., 1969, system No. 47: Lead, part C 1, p. 160.
2 H. Bode and E. Voss, Z. Elektrochem., Berichte Bunsenges., 60 (9/10), (1956) 1 053 - 1 056.
3 D. Spahrbier, Zum elektrochemischen Verhalten der Bleidioxid-Elektroden. Thesis, University (Technische Hochschule) of Stuttgart, 1960.
4 P. Rüetschi and B. D. Cahan, J. Electrochem. Soc., 105 (1958) 369.
5 A. Kittel, Beiträge zum Mechanismus der elektrischen Leitung in PbO_2 und Se, Thesis, University of Prague, 1944.
6 U. B. Thomas, J. Electrochem. Soc., 94 (1948) 42.
7 P. Herger, Die elektrische Leitfähigkeit von grobdispersen Werkstoffen unter Druck, Thesis, University (Gesamthochschule) Kassel, 1978.
8 H. Braun, Elektrischer Leitungsmechanismus in dispersen Festkörpern, Thesis, University (Gesamthochschule) of Kassel, 1975.