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Technical Note

Thermoelectric e.m.f. of Battery Grade Manganese Dioxide

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Summary

Measured Seebeck coefficients of 5 battery grade manganese dioxide powder samples against solid graphite are reported. Temperature: 10 and 50 °C, respectively. Pressure: 7.5 megapascal (1 MPa ≙ 10 bar). All samples exhibit *n*-type semiconductivity with very high carrier concentration and very low mobility. Apparently, close correlations exist between thermoelectric behaviour, powder conductivity, water content, and electrode potential.

Überblick

Über Messungen der Thermokraft von 5 pulverförmigen Batteriebraunsteinen gegen festen Graphit wird berichtet. Temperatur: 10 bzw. 50 °C, Druck: 7,5 Mega-Pascal (1 MPa ≙ 10 bar). All verhalten sich wie *n*-Halbleiter mit sehr hoher Trägerkonzentration und sehr niedriger Beweglichkeit. Zwischen Thermokraft, Pulverleitfähigkeit, Wassergehalt und Elektrodenpotential gibt es wahrscheinlich enge Korrelationen.

Résumé

Ci-dessous, on va rapporter sur la force thermoélectrique de 5 échantillons de bioxyde de manganèse pulvérulant, adaptés à l'application dans la fabrication des piles sèches, contre le graphite solide. Température: 10 et

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Dedicated to my very dear colleague, Prof. Dr. Josef Hoelzl, Kassel, on the occasion of his 60th birthday on August 20th, 1981.

50 °C, respectivement; pressure: 7,5 Mégapascal (1 MPa $\hat{=}$ 10 bar). Tous les échantillons montrent sémi-conductibilité du type *n*, avec très grande concentration des porteurs et mobilité très basse. Il existe, entre la force thermoélectrique, la conductibilité, la teneur en eau et le potentiel vraisemblablement des relations assez étroites.

1. Background, Introduction

The electric conductivity, κ, of battery grade manganese dioxide varies considerably, between 0.1 and 10^{-6} ohm^{-1} cm^{-1}, depending on the modification, manufacturing process, origin, etc. Its conduction mechanism is mainly unknown. The little information we have deals mainly with the pure, solid β-MnO$_2$. The dependence of the conductivity of β-MnO$_2$ *powder* upon temperature shows an activation energy of 0.25 eV between 10 and 90 °C. It has not yet been determined whether this can be interpreted as a band gap. Some speculative conceptions about the band arrangement have been developed by Brenet [1], comparing β-MnO$_2$ with other, better known oxidic semiconductors.

Above fully occupied π and σ valency bands, Brenet expects a multitude of acceptor and donor terms which, in general, are more or less fixed within the lattice. However, *above* the Fermi level, terms are arranged so closely that they overlap each other band-like. In the majority of cases, these terms can be attributed to the Mn partial lattice. The energy distance between the uppermost valency band, a π electron band, and the lowest conduction band, a σ electron band, is estimated to be about 0.25 eV. The donor terms, which are responsible for the electrical conductivity, are situated only 20 - 80 mV below the conduction band. Thus, high carrier concentrations can be expected.

The second, even more important battery grade manganese dioxide family, the γ-MnO$_2$ family, has also been considered by Brenet. In his opinion, γ-MnO$_2$ is an intrinsic semiconductor, having a band gap of 0.7 eV. A peculiar species belonging to this family, having a band gap of 0.4 eV, has been found.

Between 10 and 60 °C, Kirchof [2] measured the slope of the Schottky plot of 3 different γ-MnO$_2$ species pressed at 100 MPa from which he obtained a value of 0.47 - 0.49 eV. Again, it has not yet been decided whether this is to be regarded as the band gap, the donor or acceptor distance, or the energy threshold of a thermally induced carrier diffusion process. In spite of this, Tye *et al.* [3] assume that γ-MnO$_2$, as well as β-MnO$_2$, is an *n*-type semiconductor, doped by oxygen deficiency. These authors noted, however, that the conductivity, κ, of γ-MnO$_2$ *increases* with rising oxygen partial pressure. Furthermore, we have observed a steep decrease during the discharge of dry cells. Thus, γ-MnO$_2$ probably has a much more complicated band or term arrangement, responsible for its electric behaviour, than previously expected. In addition, the particles of the powder are covered with surface layers of varying composition.

Tye *et al.* already suspected that the poorly conducting γ-MnO_2 species do not have throughpassing bands and that their conductivity is performed rather by hopping processes, with electrons jumping from one Mn ion to its neighbour. We can confirm that γ-MnO_2 powders behave like *n*-type semiconductors, having very low electron mobility, derived from the thermoelectric Seebeck coefficients we measured. Between 10 and 60 °C and at 100 MPa, Kirchhof [2] evaluated for a natural α-MnO_2 (Montana Trout Mine Ore) an activation energy of 0.69 eV from the Schottky slope of the powder conductivity, κ. Also, he investigated the Permanox used here, see no. (5) in Tables 1 and 2, evaluating an activation energy of about 1.0 eV.

2. The manganese dioxide samples

The five samples investigated here are given in Table 1. To define and explain the data compiled in the Table, the following remarks are made:

(a) BET is the inner surface of the dried (3 h at 105 °C) sample evaluated by nitrogen adsorption according to Brunauer, Emmett and Teller, measured with a simple volumetric installation.

(b) The grain diameter is obtained by visual observation of scanning electron microscope pictures.

(c) Gravimetric water content, evaluated as loss of weight after 3 h at 105 °C in ambient air.

TABLE 1

Some properties of the five manganese dioxide samples under study. Mean characteristic values taken from several samples of the same kind. (a) - (e): explanation in Section 2. AMD: activated natural manganese dioxide. CMD: chemically prepared artificial manganese dioxide. EMD: electrolytic manganese dioxide. NMD: natural manganese dioxide.

No.	Designation	Manufacturing process	Crystal modification	(a) B.E.T. (m^2/g)	(b) Characteristic grain size (μm)	(c) H_2O (%)	(d) pH	(e) Potential (mV)	Symbol in Figs. 2 and 3
(1)	Indian pyrolusite	NMD	β-MnO_2	5	40	1	5	470	#
(2)	Mitsui CSV	EMD	γ-MnO_2	40	20	2	4.5	650	●
(3)	Sedema MHV	AMD	γ-MnO_2	30	30	3	4.2	650	+
(4)	Knapsack LA	EMD	γ-MnO_2	40	25	2	4.5	630	×
(5)	Perstorp Permanox	CMD	amorph. (δ-MnO_2)	60	5	10	3.3	800	○

(d) The pH of 50 cm^3 of electrolyte solution after having shaken it with 1 g of manganese dioxide powder (as delivered) for 16 h at 20 °C overnight. Electrolyte composition: 400 g NH_4Cl and 260 g $ZnCl_2$ (dry) dissolved in 1400 cm^3 distilled water, density 1.18 g/cm^3, pH = 4.7.

(e) Potential in the same electrolyte as in (d) at 20 °C against saturated calomel electrode, 24 h after immersion.

The samples were investigated as delivered, *i.e.*, unwashed, only dried (3 h at 105 °C) and inspected under the low power microscope to exclude coarse impurities. A very few wood splinters, fibres, iron shavings, tiny pebbles, etc., were picked out. The samples were screened completely through a coarse 60 mesh DIN (about 150 mesh Tyler) sieve to assure disintegration of lumps and clusters. No pressing additives, no carbon black, graphite, solid salts, electrolyte solution, water, etc., were added.

3. Experimental

The MnO_2 powder, in about ten portions, is poured carefully into a glass tube having an inner diameter of 8 mm and is compacted 10 times under a pressure of 7.5 MPa. After pressing, it forms an almost homogeneous plug, 40 mm long, see Fig. 1. The pressure pistons are then replaced by new dry battery pencils as used in D-size dry cells, IEC standard no. R 20. The pencil consists of graphitized carbon, impregnated with mineral oil and furnished with the usual brass cap. The pencil has a diameter of 8 mm and a length of 56 mm. The electric contact between the MnO_2 sample and the carbon pencils is assured by a strong steel spring generating a force of about

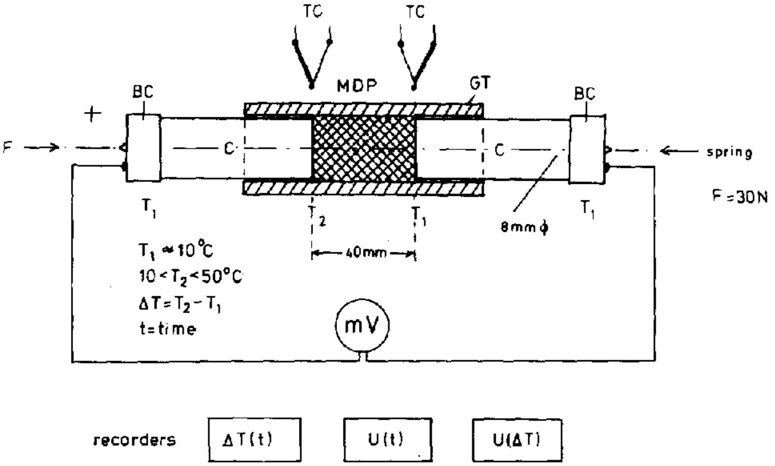

Fig. 1. Sample arrangement in the measuring equipment. MPD, manganese dioxide powder, pressed under 7.5 MPa; GT, glass tube; C, carbon pencil; BC, brass cap; F, spring force; TC, thermocouple.

30 Newtons. The arrangement is clamped in four elastic, insulated copper clamps, three cooled by tap water to about $T_1 = 10$ °C, the other heated by thermostatic oil circulation up to $T_2 = 50$ °C. Temperatures T_1 and T_2, as well as the temperature difference $\Delta T = T_2 - T_1$ are measured by thermocouples. The thermoelectric voltage, U_C, is measured by sensitive electronic recorders, recording the dependence of ΔT and U_C on time t, or of U_C directly on ΔT, with increasing and decreasing T_2. The temperature T_2 rises at a rate of about 1.5 to 2 °C per min. In future experiments it is planned to use nickel rods instead of carbon pencils. The differences between the thermoelectric e.m.f., U_C and carbon, and U_{Ni} and nickel, can be evaluated easily: at the temperature difference $T = 40$ °C it is $U_{Ni} = U_C +$ 0.48 mV.

4. Results

Recently, we were able to show [4] that thermoelectric measurements of powder materials can be carried out, and that interesting results about the surface layers of the grains are to be expected. Thus, we decided to include manganese dioxide powder in our program. Figure 2 shows the measured thermoelectric voltage, U_C, against carbon, depending on the temperature, ΔT. With all five samples straight lines have been found. The zero point of the couple Permanox/carbon is not defined very well, being caused by instrumental error resulting from the very high internal resistance of about 5 megohms. The *hot* junction has always been found to form the positive

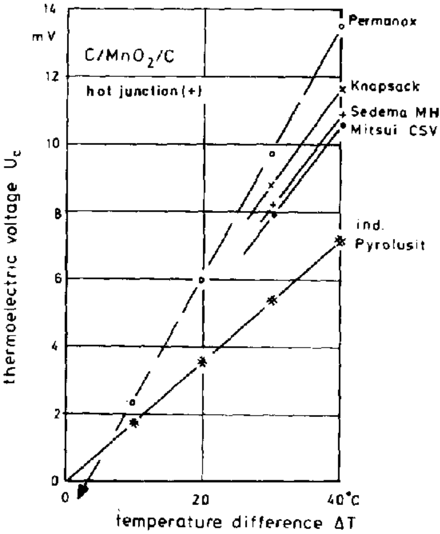

Fig. 2. Dependence of the thermoelectric e.m.f., U_C, on the temperature difference $T = T_2 - T_1$. Hot junction always positive. $T_1 \approx 10$ °C. The internal resistance of the Permanox couple is about 5 MΩ, resulting in a poor definition of the zero point.

pole, thus indicating n-type semiconduction of the MnO_2 powder. From U_C and T, the Seebeck coefficient, $\alpha = dU_C/d(\Delta T)$, can be derived. It is given in Table 2, column (f). The thermoelectric voltage in general can be reproduced within $\Delta U_C/U_C < 10\%$, the temperature difference better than ± 0.5 °C. The experimental results have been partly published in a short note [5].

TABLE 2

Seebeck coefficient, α, and electronic conductivity, κ, of the battery grade manganese dioxide powder samples under study

The identification numbers coincide with Table 1. (f) - (m) are explained in Section 5.

No.	(f) Seebeck coefficient, α α(μV/°C)	(g) Carrier concentration, c (cm^{-3})	(h) Electronic conductivity, κ (ohm^{-1} cm^{-1})	(i)	(k) Electron mobility, μ (cm^2/V s)	(m)
			10 MPa	1000 MPa	10 MPa	1000 MPa
(1)	180	1.1×10^{19}	2.4×10^{-2}	0.83	1.4×10^{-2}	0.47
(2)	265	0.75	1.9×10^{-3}	3.4×10^{-2}	1.6×10^{-3}	2.8×10^{-2}
(3)	270	0.74	1.2×10^{-2}	0.10	1.0×10^{-2}	8.4×10^{-2}
(4)	300	0.67	1.1×10^{-3}	2.5×10^{-2}	1.0×10^{-3}	2.3×10^{-2}
(5)	380	0.53	2.5×10^{-6}	3.5×10^{-5}	3.0×10^{-6}	4.1×10^{-5}

5. Discussion

The Seebeck coefficient, α, given in column (f) of Table 2, decreases with rising powder conductivity, κ, related to the low pressure of 10 MPa (see Fig. 3). We have not shown the corresponding diagram for $p = 1000$ MPa, because its shape is similar. Combining columns (c) and (e) in Table 1 with the Seebeck coefficient, α, indicates clearly that close correlations exist not only between powder conductivity, κ, and thermoelectric e.m.f., but also between water content, electrode potential, and Seebeck coefficient*. Since the five samples have been selected fortuitously from about 30 samples of battery grade manganese dioxide which we have in our laboratory, we can expect that these correlations apply to more than just the samples now studied. From earlier experiences [5], however, we know that exceptions always exist. So it may be useful to measure thermoelectric e.m.f. to identify manganese dioxide samples in the laboratory or in the factory**.

The most important result we expected (and obtained) was a deeper insight into the conduction mechanism. Firstly, we have to state that without exception the five samples behave like n-type semiconductors.

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*The close correlation between water content and conductivity has been shown earlier [6].

**It should be mentioned that in 1864 Bunsen had already discovered the thermoelectric e.m.f. of natural pyrolusite against Pt.

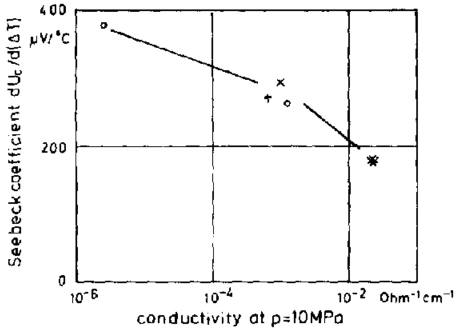

Fig. 3. Dependence of the Seebeck coefficient, $\alpha = dU_C/d(\Delta T)$, on the electronic powder conductivity, κ, at a pressure of $p = 10$ MPa.

Provided that the effective carrier mass does not differ too much from the mass of a free electron, the carrier concentration, c, can be taken as the inverse of the Seebeck coefficient, α, as a rough approximation, following the rule of thumb $c \approx 200 \times 10^{-19}/\alpha$ cm^{-3}, where α has to be inserted in µV/°C. Carrier concentration estimated in this way is given in column (g) of Table 2.

Combining c and the powder conductivity κ results in an approximation of the carrier mobility $\mu \approx \kappa/(e\,c)$, with the elementary charge $e = 1.60 \times 10^{-19}$ A s. Since κ of the powder depends strongly on the pressure p, the conductivity κ in columns (h) and (i) and the carrier mobility μ in columns (k) and (m) of Table 2 are given for $p = 10$ and 1000 MPa. Since the Seebeck coefficient, α, has been measured at very low pressure, we consider the mobility calculated for $p = 10$ MPa to be more significant. We know that the Seebeck coefficient of oxidized copper depends strongly on pressure [3] and we expect the same for manganese dioxide. At $p = 1000$ MPa, however, the conductivity approaches more closely to that of the solid material, but still remains one decade or more below the solid conductivity. Carrier concentration, c, and mobility, μ, of a piece of a particular species of natural β-MnO$_2$ have been evaluated previously [7] : $c = 3 \times 10^{15}$ cm^{-3} and $\mu = 200$ cm^2/V s. These data deviate considerably from the results obtained here with powders. The deviation may find its explanation in the fact that here the interparticular contacts play the overwhelming role, and that the inner core of the particles is not involved at the low pressure applied. The resistivity of a powder under low pressure consists mainly of the contact resistance between the particles. Thus, carrier concentration and mobility evaluated here relate to the heavily disturbed, less dense, water-rich surface layer of the particles. Its mobility is severely hindered, and its carrier density severely enlarged, into the degenerated regime. Even under the high pressure of $p = 1000$ MPa the data for the solid pyrolusite are not reached.

The loose surface layer of the particles is not only responsible for the thermoelectric e.m.f. and the powder conductivity, but also for the water adsorption and the (zero current) potential of the manganese dioxide powder. It is also responsible for the electron penetration into the particle. Thus, the measurement of thermoelectric e.m.f. is a promising tool for an investigation of the potential-forming process and the electron-conductivity-limited MnO_2 discharge yield in the dry cell. Further investigations are necessary to clarify the pressure dependent thermoelectric behaviour as well as its development during storage and discharge of the cells.

Acknowledgements

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