

## ELECTRONIC CONDUCTIVITY OF BATTERY ACTIVE MASSES — A LIMITING FACTOR?\*

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### Summary

Powder mixtures, whose components possess very different conductivities, are used in battery technology, *e.g.*, in dry cells. A similar system arises during the discharge of lead accumulators. Using the well-known theories for calculating the conductivity of such mixtures, conclusions may be drawn on the usage of battery active masses. In the examples given for active substances in the lead accumulator and the  $\text{MnO}_2$ /carbon black electrode in dry-cell batteries, utilization limits arise, which depend on the number of electrical contacts per particle and the volumetric proportion of conductive components.

### Überblick

In der Batterie-Technik finden z. B. Trockenzellen-Pulvermischungen Verwendung, deren einzelne Komponenten sehr unterschiedliche Leitfähigkeiten besitzen. Beim Bleiakkumulator entsteht während der Entladung ebenfalls ein solches System. Wendet man die bekannten Theorien zur Berechnung der Leitfähigkeit solcher Mischungen an, so lassen sich hieraus Schlußfolgerungen für die Ausnutzung von Batteriemassen ziehen. Für die gewählten Beispiele der aktiven Massen im Bleiakkumulator und für die  $\text{MnO}_2$ /Russ-Elektrode in Trockenbatterien ergeben sich Ausnutzungs-Grenzen, welche durch die Anzahl der elektrischen Kontakte pro Partikel und durch den Volumenanteil der leitfähigen Komponente bestimmt sind.

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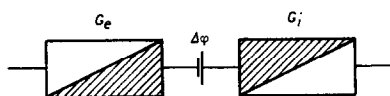


Fig. 1. Basic concept of the model electrode.  $G_e$ , electronic conductivity;  $G_i$ , ionic conductivity;  $\Delta\varphi$ , interface potential; shading, insulating component.

## 1. Introduction

Logarithmic equations [1], the Percolation Theory [2, 3], and the Effective Medium Theory [3 - 5] in particular, may be considered as rules for describing the conductivity of binary powder mixtures.

While the logarithmic equation is specific for cases in which the differences between the conductivity of the individual components are not particularly great, the latter two theories show the dependence of the electronic conductivity on the proportion of good conductive components when the conductivity differs strongly from that of the second component. In practice, the Effective Medium Theory corresponds, in the majority of cases, more closely to the experimental results [6].

With the Percolation Theory (PT) and the Effective Medium Theory (EMT), a mixture of particles with components of different conductivities is seen as a spatial resistance lattice. The PT uses the simplification that the conductivity of the components in a binary mixture differs strongly. In analysis, this reduces the number of contacts to be considered to the two alternatives: good/good and good/bad conductors.

With the EMT, one attempts to determine the conductivity of the network by means of a type of perturbation calculation. An equivalent network (effective medium) serves as the calculation medium; to the observer, its features correspond to those of the actual network. When the particle sizes of the two components are the same, an approximation formula is obtained, which describes the relationship of the conductivity of the mixture with the proportion of the good conducting components in the range 0 - 100%.

The PT, however, examines a minimum amount (percolation threshold) of components with good conductivity. From this threshold up to 100 vol.%, the PT approximation formula describes the relationship of the conductivity to the proportion of particles with good conductivity. In this paper, the PT and the EMT are applied to the heterogeneous systems of battery materials (lead accumulator and positive electrode of the dry-cell battery with  $\text{MnO}_2$  depolarizer).

The basic model for experiments is based on a simple electric series connection. Without at first paying attention to the spatial current distribution, the porous electrode in Fig. 1 is regarded as an electronic conductor,  $G_e$ , with an interfacial connection potential,  $\Delta\varphi$ , followed by the ionic conductor  $G_i$ . Only  $G_e$  is examined here. We must imagine that  $G_e$  represents a powder mixture of one or more conductive and one or more insulating ele-

ments. The same is true in principle for  $G_i$ . Since, in reality, the two conductors penetrate each other, the whole ionic conductor and its ion-conducting elements belong to the insulating elements in the electronic conductor and *vice versa*.

This paper considers only two battery systems; lead accumulators and dry-cell batteries. Both cases are extremes; all others lie between these extremes. With the lead accumulators Pb and PbO<sub>2</sub> are good conductors in the charged plates. During discharge, practically insulating PbSO<sub>4</sub> appears, which has a far lower density. In the dry-cell battery the fresh, positive electrode comprises fairly well-conducting manganese dioxide (approx.  $10^{-3}$  ohm<sup>-1</sup> cm<sup>-1</sup>) with additional carbon black, which is a good conductor and, in certain cases, graphite. The MnO<sub>2</sub> is reduced during discharge. The conductivity then decreases by a factor of 100. Also, crusts of insulating zinc compounds appear in the electrode, e.g., of Zn(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> or Zn(OH)<sub>2</sub> or ZnO. In both cases, therefore, we are dealing with systems of good/bad conductor elements whose composition changes during discharge. In general, the conductivity is reduced during discharge. The negative electrode in dry-cell batteries is a simple zinc sheet and is not dealt with here.

When charged, porous electrodes have a pore volume of approx. 50%. The pores are at least partially filled with electrolyte and also contain gas. They form an ion-conducting network in the electrode. Here too, the conductivity  $G_i$  is reduced during discharge. On the one hand the fixed electronic components expand, causing the volume of pores to decrease. The sectional area shrinks and the alternative routes become longer. Also, the composition of the electrolytes changes. For the electron flow examined here, or for the electronic conductor  $G_e$ , the pore system is practically an insulator. It is taken as such in the model on which the PT and EMT are based. In simpler terms, the system of pores may be seen as a collection of rigid, insulating particles.

## 2. Results and discussion

For the electronic conductivity,  $\bar{x}$ , of a powder mixture of two components whose conductivities differ greatly, the following equations [6] apply to the relationship between the specific conductivity and the proportional volume of the component with the greatly superior conductivity:

(a) Percolation Theory (PT)

$$\bar{x} \approx x_a + (x_b - x_a)(A_b - c)^t \text{ valid only if } A_b > c. \quad (1)$$

(b) Effective Medium Theory (EMT)

$$\bar{x} = \frac{1}{z-2} (Q + \sqrt{Q^2 + 2(z-2)x_a \cdot x_b}) \quad (2)$$

with

$$Q = \left( \frac{z}{2} A_a - 1 \right) x_a + \left( \frac{z}{2} A_b - 1 \right) x_b.$$

$A_a$  = proportional volume of the component with bad conductivity;  $A_b$  = proportional volume of the component with good conductivity;  $x_a$  and  $x_b$  are the specific conductivity of the components;  $c$  = percolation threshold ( $c = f(z)$ ),  $t = 1.25$  (exponent);  $z$  = coordination number = number of contacts per particle.

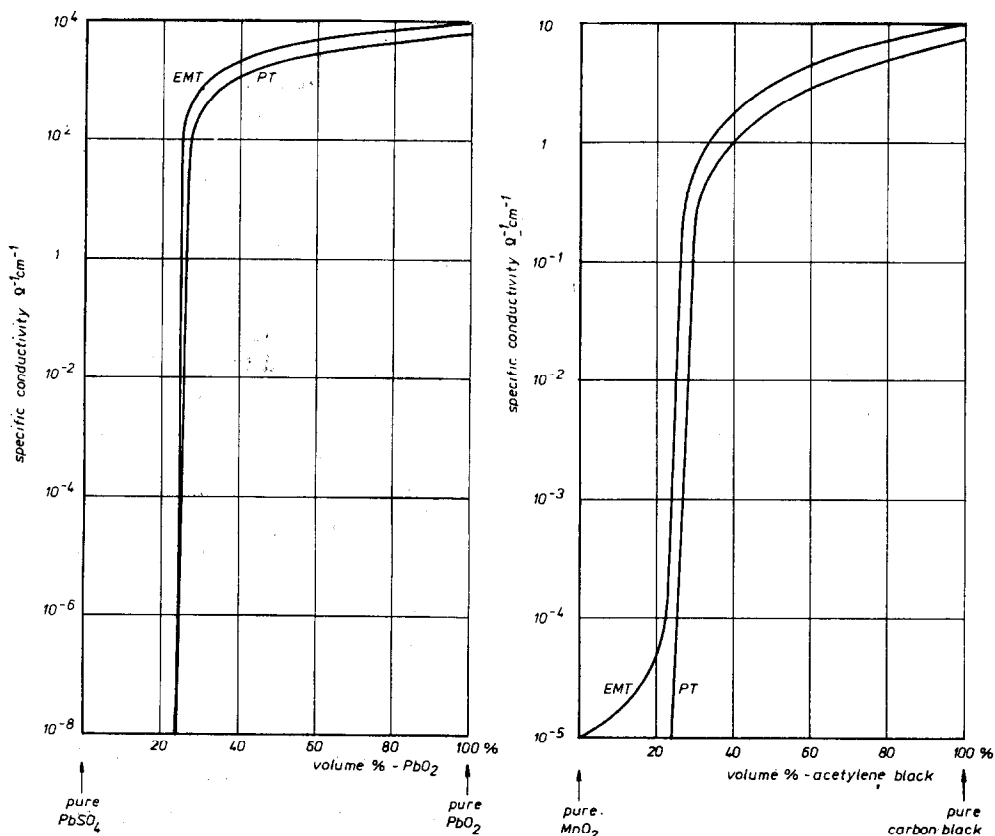


Fig. 2. The dependence between specific conductivity and percent. by volume of  $\text{PbO}_2$  in the system  $\text{PbSO}_4$ - $\text{PbO}_2$  ( $z = 8$ ;  $c = 24$ ;  $t = 1.25$ ).

Fig. 3. The dependence between specific conductivity and percent. by volume of carbon black in the system  $\text{MnO}_2$ -acetylene black ( $z = 8$ ;  $c = 24$ ;  $t = 1.25$ ).

Figure 2 shows the relationships calculated according to PT and EMT for the system  $\text{PbSO}_4$ - $\text{PbO}_2$  ( $x$  values per ref. 7), and Fig. 3 shows the relationships for the system  $\text{MnO}_2$ -carbon black (manganese dioxide: Japanese

EMD, type CSV + acetylene black,  $x$ -value per ref. 8). In Figs. 2 and 3 the volume of pores is not taken into account. If allowances were to be made for this, the percolation threshold, referring solely to the proportion of solid matter, would be doubled approximately.

The percolation threshold is indicated by the sharp rise in the specific conductivity when a certain volume percentage of the better conductor is reached. The percolation threshold is, in this case, a function of the coordination number  $z$ . If rigid particles of the same size are packed together, the coordination number may be defined as:  $z = 4$  for diamond packing,  $z = 6$  for simple cubic structures,  $z = 8$  for cubic body-centred, and  $z = 12$  for cubic face-centred structures, as well as for the hexagonal close-packed structure. In practice, the coordination number is very similar to the number of current-carrying contacts of each individual particle. The less spherical the shape of the particle and the less uniform its dimensions, the larger are the differences, *e.g.*, in comparison with the hexagonal closest-packed structure. Both very high (up to 50) and very low coordination numbers may occur. If, *e.g.*, in the interspaces of a very simple cubic structure ( $z = 6$ ) there is a large number of very small particles, the coordination number determined by the large and small particles can sink to  $z = 3$ . Taking into account that the small particles have no part in the electronic conductivity as they are only "one-sided connected", even smaller coordination numbers are feasible.

Based on EMT calculations for the system  $\text{PbSO}_4\text{-PbO}_2$ , Fig. 4 shows the relationship of the conductivity threshold to the coordination number  $z$  — here too, without taking the pore volume into account. If, on discharging the lead accumulator the proportion of good-conducting elements is reduced, the electronic conductivity drops abruptly below a certain critical volume level. This critical level of good-conducting material is determined by the mode of particle packing, *i.e.*, the coordination number.

The utilization of the active elements Pb and  $\text{PbO}_2$  in the lead accumulator is therefore limited by the fact that when their quantity falls below the critical volume for the good conductor, the electronic conductivity breaks down. The higher the porosity, the sooner this point will be reached (*cf.* Fig. 5). In Fig. 5 the coordination number is represented as a parameter. Its value cannot be easily determined. But on the supposition that in the plates of lead accumulators average coordination numbers prevail, we probably have a reasonable basis. By starting with a porosity of 50 vol.% and  $z = 8$ , the critical volume of the conductor will be reached upon utilization of half of the active masses. Because the densities of Pb and  $\text{PbO}_2$  are nearly the same, Pb behaves in a similar fashion to  $\text{PbO}_2$ . Figures 5 and 6 represent the dependencies for  $\text{PbO}_2$ . During discharge, the critical volume of the conductor will be reached a little sooner in the Pb system than in  $\text{PbO}_2$ .

Because carbon black forms chains in the manganese dioxide/carbon black mass of the positive electrode in dry-cell batteries, much higher average coordination numbers are to be found (up to  $z \approx 30$ ). Therefore, the critical volume of carbon black lies below 10 vol.%. Figure 7 demonstrates this effect for the system  $\text{MnO}_2/\text{acetylene black}$ . During discharge there is a

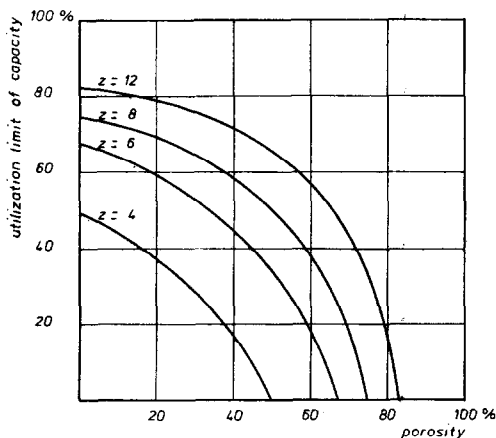
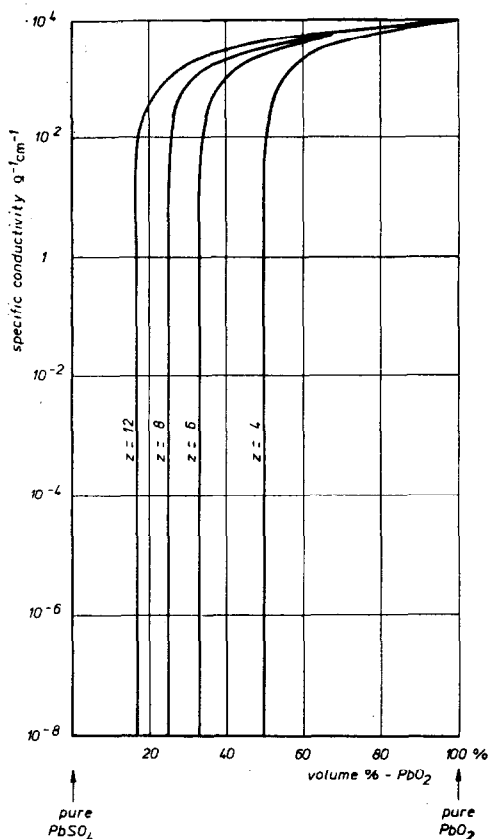


Fig. 4. The EMT computed dependence between specific conductivity and percent. by volume of  $\text{PbO}_2$ . The coordination number is represented as parameter.

Fig. 5. The dependence between utilization limit of capacity and porosity. The coordination number is represented as parameter.

change in the electronic conductivity only by reason of a (probable) decrease in the coordination number.

However, here too, the relationships are not uncritical. In fresh electrodes the mass has a composition similar to that given in Table 1. The apparent density amounts to approx.  $2.1 \text{ g/cm}^3$ . With these data and by using the pycnometric density of the elements, the pore volume and the percentage by volume of the different components can be determined.

By reason of the high coordination number the electronic conductivity is sufficiently high although the volume of carbon black amounts to only 7.5%. During discharge large amounts of  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  needles or crusts of  $\text{Zn}(\text{OH})_2$  or  $\text{ZnO}$  are formed. This shows that the coordination number can

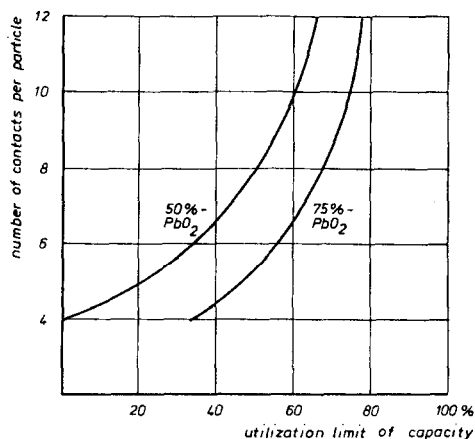
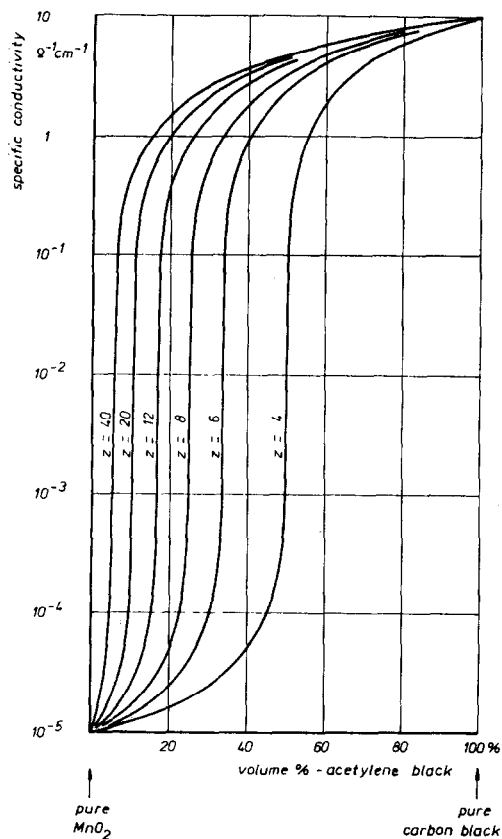


Fig. 6. The dependence between number of contacts per particle and utilization limit of capacity. The percent. by volume of  $\text{PbO}_2$  is represented as parameter.

Fig. 7. The EMT computed dependence between specific conductivity and percent. by volume of acetylene black. The coordination number is represented as parameter.



decrease strongly. Therefore it can be expected that in these electrodes also the electronic conductivity of the active masses limits the discharge capacity.

### 3. Conclusion

For binary mixtures of powders with good and bad conductivity the electronic conductivity of the mixture can be computed in relation to the composition of the mixture and the value of the conductivity of each powder by Percolation Theory and Effective Medium Theory. By using these concepts for the electronic current or electronic resistance in battery electrodes, an explanation can be found for the limits to the utilization of active masses.

TABLE 1

Gravimetric and volumetric composition of the active mass in dry battery cores, slightly simplified, cell not discharged

Component	Conductor or insulator for electrons	Pycnometric density (g/cm <sup>3</sup> )	% by weight	Vol.%
Carbon black	Conductor	2.3	8.0	7.5
Manganese dioxide	Nearly insulator	4.4	60	29
Solid NH <sub>4</sub> Cl	Insulator	1.54	12.0	16.5
Electrolyte	Insulator	1.2	20	35
Free pores	Insulator	0	0	12.0
Sum			100	100
Mean density		2.1		

For the negative and positive electrodes in lead accumulators and for the MnO<sub>2</sub>/carbon black electrodes in dry cells, a limitation of the electrochemical yield can be predicted. Its quantitative value depends on the number of electric contacts per particle, *i.e.*, nearly the coordination number,  $z$ . It is suggested that for Pb and PbO<sub>2</sub> electrodes  $z \approx 8$  and for MnO<sub>2</sub>/carbon black electrodes  $z \approx 30$ .

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