Journal of Power Sources, 46 (1993) 211–217

The agglomerate-of-spheres model. Theoretical considerations

A. Winsel and E. Bashtavelova
Universität Gesamthochschule Kassel, Heinrich-Plett-Straße, 34132 Kassel (Germany)

Abstract

The 'agglomerate-of-spheres' (AOS) model associates the resistivity and the mechanical strength of PbO_2 with the narrow zones between the sphere-like agglomerates. Some fundamentals of the electric contact theory are reported. The apparent conductivity of the electrocrystalline network and its relaxation are effected by the mechanical stress in the 'neck' zones. To complement this hypothesis, we have considered the surface tension to be effective when a new particle is growing from a planar nucleus, thus forming the 'neck'. The surface tension acts to minimize the surface of the particle and casts it into a sphere as long as this force, which is proportional to the reciprocal of the diameter, is large enough to overcome the internal friction or strength of the solid body inside its surface. Therefore, during the formation of the PbO_2 active material a so-called electroformative force is observed. It represents the force, which is needed to create the new order of the agglomerate-of-spheres. The nature of this force is similar to that one, which in winter time cracks freezing water pipes. Our theoretical considerations do create the expectation, that at the beginning of discharge, the apparent specific resistance of the PbO_2 network should decrease, but sharply increase at the end of discharge. A further expectation states a shrinking during discharge and a re-expansion during recharge. This expectations are based on the existence of a coherent network with stable necks as long as the necks are not cracked by the discharge process itself or by deposition of too much of lead sulfate within the pores.

Definition of the agglomerate-of-spheres electrode

An 'agglomerate-of-spheres' (AOS) electrode (also known as the 'Kügelhaüfen-Elektrode') is a porous body that consists of interconnected spherical particles. In such a body, it is possible to move from one inner point of a sphere to any second point in another sphere on a path that does not intersect the surface of the solid-state electrode body. The spheres are welded together by so-called 'necks' in all places where the spheres are in contact. Such bodies are generated by pressing and sintering of pulverized materials or by electrochemical deposition. With respect to the electrons, their electrochemical potential (Fermi potential) is the same in all parts of the inner solid phase.

Short description of the AOS model for PbO_2

Like many other electrodes, the structure of the PbO_2 electrode exhibits an electrocrystalline network of agglomerated spheres. This becomes evident from electron

0378-7753/93/$6.00

micrographs. These show ball-like particles that are interconnected by electron-conducting bridges. In the AOS model, the conductance of the PbO_2 network is determined by the narrow neck zones. But why does this structure result from the formation process? It is one objective of the authors' research programme to answer this question. A second objective is to obtain more detailed information on the physical behaviour of this network.

Assumptions underlying the theoretical approach

The primary particles grow from an electron-conducting network of PbO_2 by 'fishing empty' the electrolyte in the neighbourhood. The very few Pb^{2+} ions in the solution, which are oxidized to Pb^{4+} ions, become highly condensed and form a solid body. Hence, the solution is very quickly impoverished, except near to the $PbSO_4$ crystals. This is the reason for the electrometasomatic growth of the electrode structure. Under the AOS model, the formation of a new sphere can only proceed if a planar nucleus has been created previously. From this planar nucleus, the growing new sphere can develop a new fishing area. By this way, chains of interconnected spheres are formed, which are linked in three dimensions by the same type of necks.

Indeed, the low solubility of the Pb^{2+} ions is the reason why the macroscopic habit of the PbO_2 network corresponds very much to that of the $PbSO_4$ from which it has been generated. This fundamental aspect of the 'transformation' model (which was developed at VARTA Batterie AG (Kelkheim am Taunus, Germany), under an ILZRO contract) will always remain true, despite any other models that may be constructed.

Parameters of the AOS model

Mechanical behaviour

An AOS is characterized by a set of parameters, that, to date, have not been considered to be important for the behaviour of a PbO_2 electrode. These parameters are: the mean radius of the spheres, R; the mean radius of the necks, h; the surface tension, σ; the strength, ϵ, of the solid phase material.

During the formation of a PbO_2 particle at the end of an electronic path by oxidation of Pb^{2+} ions to Pb^{4+} ions, its surface tension acts with a tendency to construct a sphere. The internal friction, e.g., the tensile strength, acts against this tendency and interrupts the growing of a sphere. Thus, an equilibrium is established between both these forces. Now, by continuation of the electrochemical oxidation, a planar nucleus as a precursor of the 'neck' occurs, from which a new sphere can grow. Under these circumstances, the AOS body consists of ball- and neck-regions with different states of mechanical strength and different Laplace pressures. Its total energy is assumed to be in equilibrium with the forming overpotential. From this reason, these forces are called 'electroformative'. After formation or after a recharge process, when the current is switched off and the stress of the oxidation potential is no longer effective, the AOS is left in a nonequilibrium state, which has the tendency to relax.

Due to the small solubility of $PbSO_4$, the growing of the PbO_2 particles can only occur in the neighbourhood of the $PbSO_4$ crystals, where sufficient lead ions are available. Therefore, changes in the geometric structure by diffusion are very slow. On the other hand, under the action of 'electroformative' forces, clusters and even

complete spheres may be moved inside the AOS electrode. This provides an explanation for the shape changes observed in this type of electrode.

A discharge process, which affects the spherical regions but conserves the necks, will in first instance increase the radius R (like in a rugby ball) and reduce the Laplace pressure, under the action of the surface tension, however, a reduction of the radius R is more convenient to the system. Thus, a shrinking of the entire structure is expected as long as the formed $PbSO_4$ crystals can be placed within the pore system. If this last condition fails, the coherence of the PbO_2 network will be interrupted and the electrode will lose its stability and conductivity. During recharge, the electroformative forces are acting and, consequently, a swelling of the free-standing active mass or an increase in the force on its boundaries is anticipated.

If the current is switched off, a relaxation of the structure will occur, because the active material is left in a nonequilibrated state. The phenomenologic parameters that have been used so far may depend on other properties. For example, if by loss of water the tensile strength increases, an increase of the pressure of the active material on its boundaries is to be expected. On the other hand, the fugacity, p^*, of the oxygen atoms is in equilibrium with the electrode potential and describes the deficiency δ in $PbO_{2-\delta}$. If p^*, is considered as an internal pressure, a swelling of the entire AOS structure should occur with increasing potential (i.e., decreasing δ). If the potential is reduced to the reversible potential, a shrinkage should take place. A mechanical action is also expected with changes in parameters or boundary tension. Thus, on the basis of the AOS model, predictions can be made. It is more important, however, that the model offers the possibility to quantify new facts, that may be experimentally observed in forthcoming experiments.

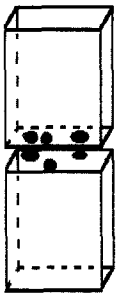
Electric behaviour

A second theoretical model has been considered that might provide an understanding of the spherical growing of the PbO_2 electrode. This model is based on the 'Size Induced Metal Isolator Transition' ('SIMIT') effect' [1]. This argues, that the conductance of very small particles is dependent on their size. If they are very small, they are isolators; if they are large enough, they behave like bulk material. Given this effect, a new sphere can only grow from an existing one if the size of the existing sphere is sufficient to provide adequate conductivity for the passing of electrons in the formation process. Therefore, the growing network consists of ball-like particles that are connected by necks; the conductance of the single ball is governed by its diameter. In summary, the conductance of the resulting PbO_2 network must be comparable with that of the electrolyte in order to generate a porous body that grows towards the counter electrode.

Calculations indicate that the SIMIT effect might have an influence at diameters of 10^{-8} m. This is a factor of 10 smaller than the neck diameter, which measures 10^{-7} m. By regarding PbO_2 as a 'fractal' structure, the SIMIT model may be true for the primary particles that can be seen in electron micrographs.

The electronic properties of the AOS network have been described previously [2]. The electronic conductance of the network is governed by the constriction resistances of the neck regions [3]. The following two important facts of the contact theory should be recognized:

(i) The value of the resistance between two contact-forming pieces of the same material is inverse to the value of the force by which both pieces are pressed together. Like friction, the resistance does not depend on the contact area itself, because the real contact area is formed by material flow in those parts of the contact area that are bearing the force, Fig. 1. This material flow proceeds as long as the tension in



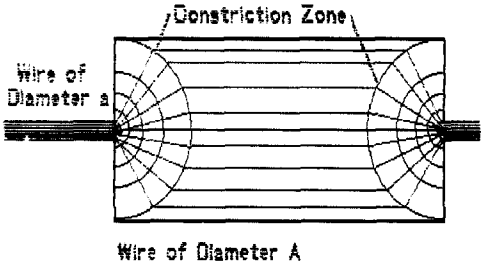


Fig. 1. Schematic of real contact area between two contact-forming pieces of the same material; the contact resistance is inversely proportional to the applied force.

Fig. 2. Schematic of constriction zone between wires of small and large diameter. Constriction resistance $= \delta^*/2a$.

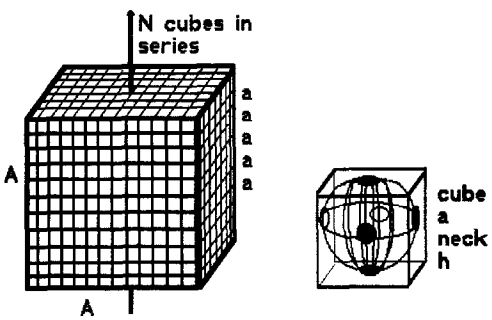


Fig. 3. Schematic showing influence of constriction resistance on specific resistance of a Kugelhaufen electrode.

these parts exceeds the stress yield. If there is no layer of another material between the contact pieces, cold-welding takes place in this real contact area. There is no reason to suppose that this should not also be true for PbO_2 material. There is, however, a problem with the stability of such 'cold-welded' necks. It has been shown that for thermodynamic reasons the quotient spheres–radius/neck–radius cannot exceed the critical value of 6, i.e., $R/h < 6$, otherwise the neck is not stable. Therefore, only those cold-welded necks that have necks exceeding this critical value of 6 are stable under a decreasing contact force.

(ii) If a very small wire of diameter $2h$ is welded, as shown in Fig. 2, into a very thick one, the ohmic resistance is equal to the sum of the resistances of both wires and of an additional term that is equal to $\delta^*/4h$; δ^* is the specific resistance of the thick wire's material. This additional resistance is created within the thick wire near to the entrance of the thin wire. It is called a 'constriction resistance' and takes into account that, in this contact zone, only a part of the thick wire's length $\pi h/4$ and of cross-sectional area πh^2 is available for the current lines, which must be constrained to the small wire's diameter. The influence of the constriction resistance on the specific resistance of a Kugelhaufen electrode may be demonstrated by the following experiment, Fig. 3. Take two cubes, of edge length A, of an electronic conductor of specific resistance δ^*. Cut one cube in 10^6 cubes of edge length $a = 0.1\,A$. Bring an isolating layer on each of the six planes of each of the small cubes, except for a circular area

of radius h in the central part of each plane of the small cubes. After this operation, put all the small cubes together again and press them in a hydrostatic manner so that all the free central planes are welded to their neighbourings. Measure the resistances W_0 and W_e of both of the cubes against a current, which flows uniformly from one plane to the opposite one. The following results will be observed. In the case of the original cube, the resistance is $W_0 = A\hat{o}^*/A^2 = \hat{o}^*/A$. In case of the manipulated one, $n^2 = (A/a)^2$ rows of cubes are connected in parallel. Each row consists of n cubes in series-connection with the constriction resistance $\hat{o}^*/4h$ at the entrance and at the exit. Therefore, each little cube contributes $\hat{o}^*/2h$ as constriction resistance to the resistance of the total row, which is $n\hat{o}^*/2h$. For the cube with n^2 rows in parallel the resistance is:

$$W_e = n(\hat{o}^*/2h)/n^2 = (\hat{o}^* a/2h)/A \tag{1}$$

The term $\hat{o} = \hat{o}^* a/2h$ defines an apparent specific resistance. This resistance takes into account, that the current lines are always restricted to the h openings when entering or leaving a small cube. Due to this restriction and constriction, the material in the edges cannot contribute to the conduction of the current. If all of this ineffective material is removed and the small cubes are reduced to spheres of diameter $2R = a$ under the persistence of the small contact zones of diameter $2h$, the resulting Kugelhaufen or AOS electrode will exhibit the same apparent specific resistance, i.e.:

$$\hat{o} = \hat{o}^* \ (a/2h) = \hat{o}^*(R/h) \tag{2}$$

The accuracy of the apparent specific resistance is given by:

$$\hat{o}^*(R/h) < \hat{o} < \hat{o}^*[(R/h) + 1] \tag{3}$$

Changes in the microscopic structure and the stoichiometric composition will alter the apparent specific resistance in a manner that is predictable from this formula. The parameter, $\hat{o}$, like $\hat{o}^*$, is sensitive to all changes that effect the band structure, the number and mobility of the charge carriers in the PbO_2. The factor R/h, however, is equally important. This estimates the influence of changes in the microscopic structure on both the apparent conductivity and the current distribution of a PbO_2 electrode. Since, in this case, the sphere radius R represents the number of spheres per unit length in the formula for the apparent specific resistance, its value has to be considered as constant in this formula. Even if R is changed by the discharge of material, this will not effect $\hat{o}$. On the other hand, $\hat{o}$ is very sensitive to changes of h, which are expected to occur by deposition of lead, by strange metal ions or by expansion under the internal stress during relaxation. In a recent thesis, Geuer [4] has been able to explain all of his measurements on lead/acid batteries by application of the AOS model.

Optical investigations

The necks are too small to be measured by optical methods. Therefore, the most effective sensor of their behaviour is the apparent electronic conductivity, $\hat{o}$, of the PbO_2 network. This has been demonstrated experimentally [2, 5].

According to AOS model, the necks should also determine the strength of the PbO_2 network. If an AOS body is ruptured into two pieces, the resulting surface should be almost the weakest plane through the necks only. In order to measure simultaneously the electronic and the mechanical properties of the PbO_2 network, a new type of experiment and corresponding equipment have been developed. This equipment allows measurement of changes in the probe resistance, the probe tension and the probe dilatation during a rupture experiment.

Rupture experiment

In the rupture experiment, a negative force (pressure) is decreased until it changes sign and is converted into a stress. During this time, the probe is lengthened until the stress yield is passed and the probe is ruptured into two pieces. The two pieces are then pressed together and the changes in resistance and length are again registered while the force is changed. Although the theoretical model is not completed yet, an attempt has been made to describe the procedure of the calculations. For this reason, it is assumed that the probe of length l and cross section q is homogeneous in a statistical sense for all three directions. The resistance W_0 prior to rupture can be written as:

$$W_0 = l\hat{o}/q,\ \hat{o} = \hat{o}^* R/h_0 \tag{4}$$

Insertion of $l = n_l 2R$ and $q = (n_q 2R)^2$ leads to:

$$W_0 = n_l 2R(\hat{o}^* R/h_0)/(n_q 2R)^2 \tag{5}$$

According to eqn. (5), the distribution of the neck regions (specific number and neck radii) in the different directions of the probe determines the resistance. With the rupture of the probe, one plane of necks of radius h_0 is destroyed and replaced by a new one as determined by the force P with which the two ruptured pieces are pressed together again. Each neck contributes twice the narrow resistance to W_0. In order to calculate the new resistance W_1 of the probe, n_l is replaced by $n_l - 1$ and the term for the resistance of the new layer is added, i.e.:

$$2R(\hat{o}^* R/h_p)/(n_q 2R)^2 \tag{6}$$

This gives the new resistance W_1:

$$W_1 = W_0 + 2R\hat{o}^*(R/h_p - R/h_0)/q = W_0 + 2R\hat{o}(h_0/h_p - 1)/q = W_0 + W_0(2R/l)(h_0/h_p - 1) \tag{7}$$

For experimental evaluation, the more practical equations are:

$$W_1 - W_0 = W_0(2R/l)(h_0/h_p - 1) \tag{8}$$

and

$$W_1/W_0 = 1 + (2R/l)(h_0/h_p - 1) \tag{9}$$

Equation (9) shows that W_1 is equal to W_0 if the new necks exhibit the same radius, h_p, as the old ones, h_0. The factor $l/2R$ represents the very large number of spheres that must be put together in order to bridge over the length l. Therefore, a remarkable increase in resistance W_1 compared with resistance W_0 indicates that a larger part of the structure has been effected by the rupture process. On the other hand, an AOS structure, which has been formed by the formation process, may exhibit neck radii, that are larger than those produced by a simple 'pressing together' of two pieces of a PbO_2 electrode.

Summary of results of theoretical considerations

The 'Kugelhaufen' model has a phenomenological nature. It is applicable to pressed powder samples and electrochemical deposited bodies. The AOS model has the consequences as stated in the following logic chains.

Logic chain of consequences and results derived from the thermodynamics of the AOS model

(i) The AOS model states the existence of two different phases, e.g., the 'neck' phase and the 'sphere' phase. This is caused by different Laplace pressures of the surface curvatures.

(ii) The protection of the neck zones against corrosion and discharge is caused by the thermodynamic potential difference between the neck and sphere phases.

(iii) The preferred underpotential deposition in the neck zones is effected by the thermodynamic potential difference.

(iv) The growth of a new sphere from an existing one requires a two-dimensional nucleation in the neck region at recharge.

(v) A limited stoichiometric deviation, δ, limits the radii of the necks. Beyond a minimum radius, the necks are unstable.

(vii) Any overvoltage strangles the necks and causes shedding by sucking off lead ions from the neck zones. High overvoltage destabilizes the structure.

(vii) The geometry of the AOS body causes a decreased apparent conductivity compared with that of the bulk material. This is determined by the constriction resistance of the necks.

(viii) For kinetic reasons, the ratio of the necks' and spheres' radii depend upon the cycling regime. Consequently, 'good' and 'bad' regimes exist, the apparent conductivity changes.

(ix) Changes in the apparent conductivity alter the current distribution in the PbO_2 electrode. A change in the mass utilization to an 'insufficient mass utilization' is the consequence.

(x) The insufficient mass utilization of the PbO_2 electrode during cycling is caused by a decreased apparent conductivity due to smaller necks.

(xi) The increase in the apparent conductivity with increasing temperature is caused by softening of the material and by broadening of the neck zones under the stress of the neck's curvature. This effects a relaxation of the insufficient mass utilization.

(xii) The increase in the apparent conductivity after dipping the sample into an electrolyte solution is effected by material deposition and broadening of the neck zones as a result of local element action. This is the effect of doping with lead and tin.

(xiii) The relaxation of the insufficient mass utilization with time, or by heating, is effected by broadening of the necks.

(xiv) The maximum and the minimum apparent conductivity should differ by a factor of six due to the limited composition range of $PbO_{2-\delta}$.

Conclusions

The AOS model is based on nonspeculative physical laws. It provides a sensor for evaluating processes in electrode systems by measuring, simultaneously the strength and resistance of the network and evaluating these measurements with respect to quantitative scanning electron microscopic data. The model is applicable to most electrodes that exhibit shaped particles that are welded together by necks.

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