



Nanostructure and agglomerate-of-spheres model

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Abstract

A nanostructure, consisting of particles with nanometer-sized linear dimensions, may be produced by electrocrystallization procedures at low concentrations and temperatures. The agglomeration-of-sphere model has been developed to describe the behaviour of an electrocrystalline network created by a formation process. The model is used to describe and understand observed phenomena during the sintering of metal powders and the properties of electrochemically produced electrodes. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Since a couple of years, the physicists have focused their attention on the behaviour of very small particles called ‘nanostructure’. These are particles with linear dimensions around nanometers only. Very often these structures are produced by electrocrystallization procedures at small concentrations and low temperatures, circumstances that do not allow the formation of large and well-ordered crystals. Such ‘nanoparticles’ exhibit lateral dimensions comparable with the wavelength of electrons in the conduction band of metals and semiconductors, (SIMIT-model by G. Nimtz and P. Marquardt [1]).

When being charged, the active materials in the electrodes of electrochemical accumulators are subjected to the mentioned conditions to form ‘nanostructures’. The negative as well as the positive electrodes consist of primary particles that agglomerate to secondary ones. Since all of these particles are electronically connected and exhibit—more or less—a spherical shape, we have developed the agglomerate-of-spheres (AOS-) model [2]. In German, we call it ‘Kugelhaufen-Modell’. The AOS model distinguishes between the sphere’s and the neck’s phase that are different from each other in a thermodynamic sense [3–5].

We have applied the AOS model on problems of powder metallurgy and electrochemistry.

2. The agglomerate-of-spheres model

The AOS model describes the behaviour of an electrocrystalline network created by a formation process. The material may be a metal like cadmium, lead, copper or silver or a metal oxide like Cu_2O , AgO or PbO_2 . It is important for our considerations that an evenly distributed compound is the source of ions that form the solid body by an electrochemical precipitation process. We assume that this compound exhibits a small solubility. Therefore, the ions that form the agglomerate-of-spheres body are present in the liquid phase in a low concentration. To shorten the path of the ions to their discharge and precipitation points, a part of the over-voltage must be spent to form nuclei for the precipitation process. The powdery salt guarantees the supply of the ions into the solution. This picture corresponds to the formation process of the lead electrode, the lead-dioxide electrode, the cadmium electrode and the nickel electrode but also to the electrochemical production of manganese dioxide. The same is true for the precipitation of Pt on carbon during the production of Pt catalysts, Figs. 2 and 3. Our model assumes a low formation temperature and, therefore, a highly disordered lattice of the solid body. This gives the lattice a high deformability. The surface tension acts on the precipitated clusters of atoms

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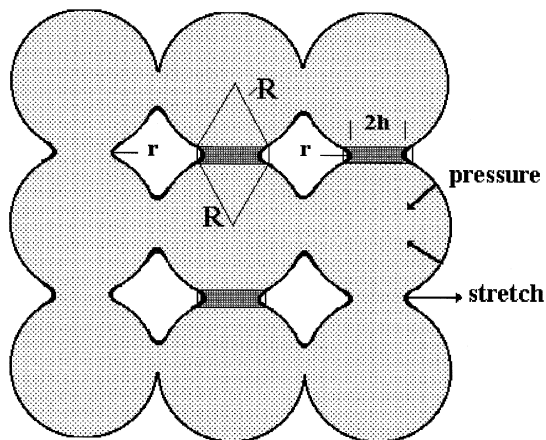


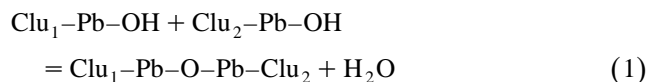
Fig. 1. Agglomerate of spheres of radius R , neck-radius h , throat-radius r .

and forms ball-like agglomerates as long as this force is strong enough to overcome the internal friction in favour of an internal material flow. This force decreases with increasing diameter of the particle. Finally, the surface tension is no longer strong enough to change the shape of the particle. To guarantee a further growth of the solid body, the process must form a planar nucleus on the surface of the sphere to start the growth of a new sphere. At this moment, the particle loses its spherical shape. The assumption of a sphere as shape of a particle is an idealisation. We could as well speak about a 'shaped particle' that exhibits a closed surface with a mean curvature directed to the interior of the particle. All of our considerations remain valid.

The agglomerate-of-spheres electrode consists of sphere-shaped particles that are agglomerated to larger ones. These are connected by 'necks' that are providing the agglomerate-of-spheres body with electronic conductivity and mechanical strength. A closed common surface separates the agglomerate from the surrounding electrolyte. It is possible to travel from the interior of one sphere to the interior of any other sphere without penetrating the common surface of the body. The surface acts by a local tension (pressure) on the inner phase of the agglomerate-of-spheres body, that is determined—at each point of the surface—by the mean radii of curvature. In the neck region, one of the mean radii changes its direction and stretches the solid instead of pressing it. Therefore, the agglomerate-of-spheres body possesses a mechanical state of tension, Fig. 1, that cannot relax, due to the large 'viscosity' of the material represented by the tensile strength. This state of tension has accumulated mechanical energy supplied during the formation process [6]. When heated, the solid material softens (lose its hardness) and flows under the influence of the mechanical tension. In a molecular picture, we regard this flow as a cooperative diffusion of voids and molecules.

3. The agglomerate-of-spheres electrode as a condensed nanostructure

SEM pictures of PbO_2 show clusters with lateral dimensions of nanometers that 'condense' to larger particles during the electrochemical formation process. The term 'condensation' may be understood as the condensation of water during the formation of droplets. We may also interpret it in a chemical sense as the formation of water during the agglomeration of the clusters. We want to describe this situation by Eq. (1):



This process is of importance for all of the electrochemical electrodes considered here. It controls the energy of the frozen non-equilibrium of the AOS body as long as the body has not relaxed into the equilibrium. The non-equilibrium state comprises all deviations from the state of the lowest energy of the ideal lattice. The term 'condensation' underlines the importance of the surface tension during the formation of the particles. Our question is: How large are the spheres and how thick are the necks of the AOS body, if the energy involved in the over-voltage during the formation of the electrode is in equilibrium with the mechanical energy based on the geometry of the body?

A few examples in Figs. 2–5 may show the relevance of this question. In Figs. 2 and 3, small spheres of Pt on active carbon granules are displayed.

Fig. 4 shows a pressed and sintered sample of Co powder. Fig. 5 shows PbO_2 particles of a ruptured electrode.

Since lead dioxide is the main subject of our considerations, we have listed its properties in Table 1. Some of these data are collected from the literature, as many as possible rely on our own experiments.

From the mechanics we know: A force that is acting on a deformable body results in deformations that are charac-

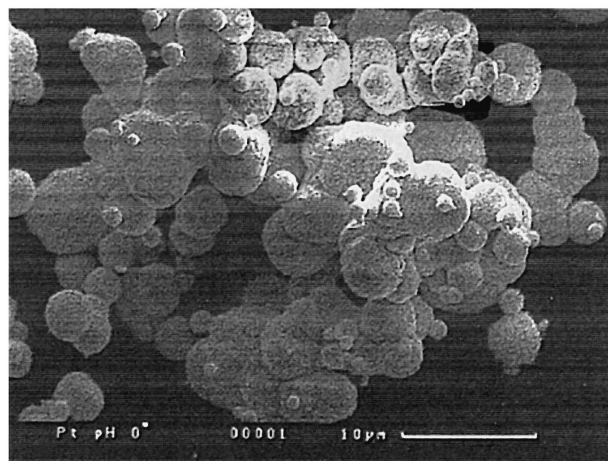


Fig. 2. SEM picture of small Pt-spheres precipitated at $\text{pH} = 0$ on an active carbon/PTFE-layer.

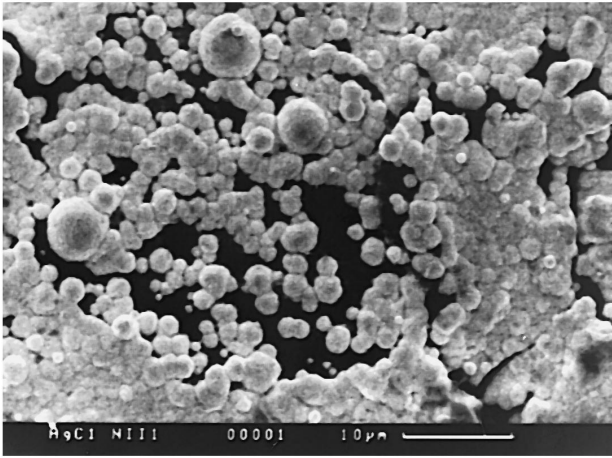


Fig. 3. SEM picture of a Pt catalyst. PtCl_4 was precipitated into a gas electrode made from a mixture of active carbon and PTFE. Then, the catalyst was formed by inserting the electrode into a solution of pH 7 under hydrogen pressure. 1.6 mg Pt/cm^2 [7].

terised by pushing and shearing tensions [10]. A tensor relationship exists between these tensions and deformations. We simplify the situation as if it would happen in a soap bubble or in a mercury sphere by the definition: In a regular polycrystal at constant temperature, T , a deformation, $(\partial V/\partial p)_T$, takes place when exposed to a homogeneously acting pressure, p . This deformation is described by the cubic compressibility, κ . Its definition is [11]:

$$\kappa = -(\partial V/\partial p)_T/V \Rightarrow dV = -\kappa V dp. \quad (2)$$

We can derive the change of the elastic energy, $E_{2,1}$, between two states of pressure from $dE = -pdV = \kappa V dp$ by integration:

$$E_{2,1} = \kappa V (p_2^2 - p_1^2)/2. \quad (3)$$

We choose a sphere with unlimited radius $1/R_1 = 0$ as the reference state. The elastic energy, E_ρ , of a sphere with

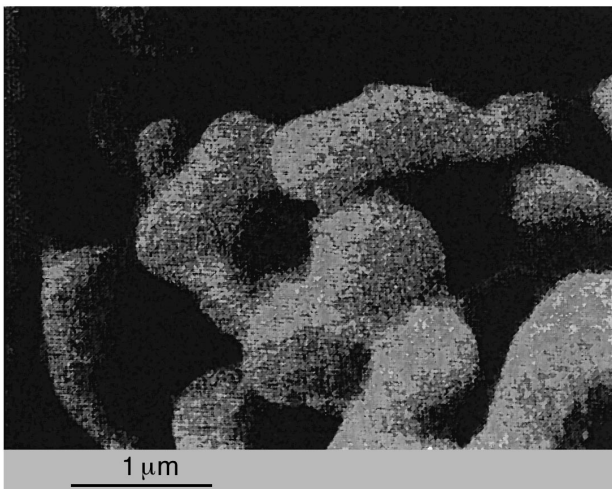


Fig. 4. Sample pressed from Co powder and sintered [8,9].

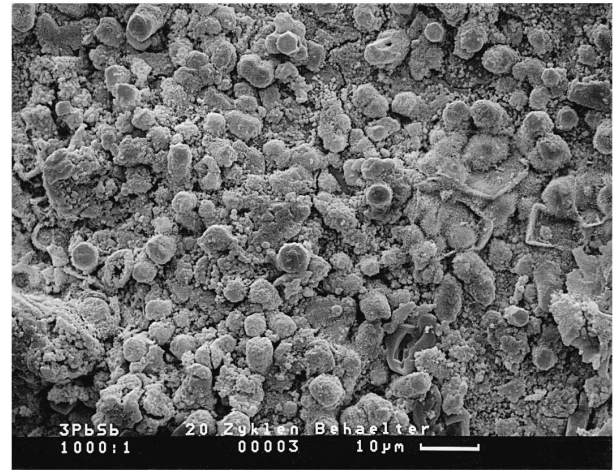


Fig. 5. SEM picture of a PbO_2 rupture plain immediately on top of the grid.

radius $R_2 = \rho$ that is exposed to the Laplace pressure $p = 2\sigma/\rho$ with interface tension σ is

$$E_\rho = \kappa(4/3\pi\rho^3)(2\sigma/\rho)^2/2 = (8\pi/3)\kappa\sigma^2\rho \quad (4)$$

According to Eq. (4), the energy of deformation is independent of the sign of the Laplace pressure. The material behaves like a spring that stores energy under pressure as well as under stress. Besides the volume energy in Eq. (4), the small spheres have interface energy, E_O , equal to the product of surface area, $O = 4\pi\rho^2$, and specific energy of the interface, σ . The unit for σ is N/m (dyn/cm) or J/m^2 (erg/cm^2).

The specific energy of the interface σ (i.e., interface tension σ) includes the specific electrostatic energy, $C\phi^2/2$, of the double layer capacity, C , of the interface. $C \approx 16 \mu\text{F/cm}^2$ is the capacity of the double layer at potentials more negative than the potential of zero charge. ϕ is the potential referred to the potential of zero charge (pzc). A double layer potential of $\Delta\phi = 1 \text{ V}$ will change the surface energy about $\Delta\sigma = 0.08 \text{ J/m}^2 \approx 8\% \cdot \sigma$. Other values for C are reported in the literature [12]. The surface energy of the sphere is

$$E_O = 4\pi\sigma\rho^2 \quad (5)$$

Now we have to calculate the energy of the neck, Fig. 1. We cut a small disc out of the neck-region with the neck-radius h and the throat radius r . Its volume, V_h , follows from a simple geometric calculation

$$V_h \approx 2\pi rh^2. \quad (6)$$

For the surface of this torus we use the equation:

$$O_h = 2\pi h \cdot \pi r = 2\pi^2 rh. \quad (7)$$

In an earlier paper, we have derived the equation $r = h^2/[2(\rho - h)]$ between the throat radius r , the neck radius h , and the sphere radius ρ [6]. We get from Eq. (16):

$$V_h \approx \pi h^2 \cdot 2r = 2\pi h^2 \cdot h^2/[2(\rho - h)] \approx \pi h^4/\rho \quad (8)$$

Table 1
As list of symbols

Ideal property	Electrochemical	Ideal property	Electrochemical
Lead dioxide $\text{PbO}_{2-\delta}$ Weight per mole $\text{MG} = 339.21 \text{ g/mole}$ Density $D = 9.375 \text{ g/cm}^3$ Mole volume $V_o = 36.18 \text{ cm}^3/\text{mole}$ $[F/V_o] = \text{As/cm}^3$ $[F\eta/V_o] = [\text{J/cm}^3] = 10^7 \text{ rg/cm}^3$	$\delta = 0.02$ Porosität $P = 50\%$ BET-Oberfläche $2.5 < 10 \text{ m}^2/\text{g}$ $D_{\text{echt}} = 9.25 \text{ g/cm}^3$ $2F/V_o = 5334 \text{ As/cmcm}$	Neck's volume V_h in cm^3	$V_h = \chi h^2 2r = \pi h^4 / (\rho - h) \approx \pi h^4 / \rho$
Sphere's radius ρ		Volume energy of a neck	$E_{V,h} = V_h \rho_h = 2\pi\sigma h^2$ $E_{V,h} = \kappa V_h \rho_h^2 / 2$
Sphere's volume V_ρ	$4\pi\rho^3/3$	Number of spheres of radius ρ per mole $N_\rho = V_o / V_\rho$	$N_\rho = (3/4\pi)V_o / \rho^3$
Sphere's surface O_ρ	$4\pi\rho^2$	Number of nearest neighbours χ	
Spec. energy of interface σ Spec. double layer energy $C\phi^2/2$	$\sigma = \sigma^0 + C\phi^2/2$ in dyn/cm or erg/cm^2	Number of necks/mole in mole^{-1}	$N_h = (\chi/2)N_\rho$
Compressibility κ in $\text{cm}^2/\text{dyn} = 10^5 \text{ cm}^2/\text{N}$	$\kappa = -(\partial V/\partial p)r/V$	Surface per mole in cm^2/mole	$\Omega_\rho = 4\pi N_\rho \rho^2 = 3V_o / \rho$
Laplace pressure of the sphere p_ρ	$p_\rho = 2\sigma / \rho$ in $\text{dyn/cm}^2 = 10^{-5} \text{ N/cm}^2$	Surface energy per mole $E_o = E_\sigma N_\rho$	$3V_o(\sigma / \rho)$
Surface energy $E_o = O_\rho \sigma$ in erg	$E_o = 4\pi\sigma\rho^2$	Volume energy per mole $E_v = E_\rho N_\rho$	$4V_o \kappa (\sigma / \rho)^2$
Volume energy E_ρ in erg	$E_\rho = (16\pi/3)\kappa\sigma^2\rho$	Neck energy/mole $E_{VH} = E_h N_\rho$	$(3V_o/2)(\chi/2)\sigma h^2 / \rho^3$
Neck radius h in cm		Neck volume per mole V_h	$(3V_o/2)(\chi/2)(h / \rho)^4$
Throat radius $r = h^2/2(\rho - h)$ in cm		Neck surface per mole O_H	$(3\pi/2)(\chi/2)V_o hr \sigma / \rho^3$
Laplace pressure p_h in dyn/cm^2	$p_h = -2\rho\sigma / h^2$	Surface energy of the necks per mole $E_{O,h}$	$(3\pi/2)(\chi/2)V_o hr \sigma / \rho^3$

$$O_h = 2\pi^2 hr = 2\pi^2 h^2 / [2(\rho - h)] \approx \pi^2 h^3 / \rho \quad (9)$$

By using these geometric relations and assuming cubic compressibility, κ , we can derive the volume energy, $E_{V,h}$, and the surface energy, $E_{O,h}$, of the neck region as follows:

$$E_{V,h} = 8\pi\kappa\sigma^2\rho \quad (10)$$

$$E_{O,h} = O_h\sigma = \pi^2\sigma h^3/\rho \quad (11)$$

4. The agglomerate-of-spheres electrode as the sum of many particles

Per one mole of material, the AOS electrode contains f_ρ spheres in the interval $[\rho, \rho + d\rho]$. f_ρ is the distribution function of the radii, ρ . We can derive the following equations for the molar volume, V_o , the molar surface, O_M , and the molar number of spheres, N_M :

$$V_o = \int f_\rho V_\rho d\rho \quad (12)$$

$$O_M = \int f_\rho O_\rho d\rho \quad (13)$$

$$N_M = \int f_\rho d\rho \quad (14)$$

We summarise the contributions of spheres with radius ρ to the total energy under ψ_ρ which is the distribution function of energy per mole.

The mechanical energy per mole is

$$\psi_M = \int f_\rho \psi_\rho d\rho \quad (15)$$

If m is the number of moles in the electrode, we can derive the following expressions for the agglomerate-of-spheres

$$N = m \int f_\rho d\rho \quad (16)$$

$$V = mV_o = m \int f_\rho V_\rho d\rho \quad (17)$$

$$O = m \int f_\rho O_\rho d\rho \quad (18)$$

$$\psi = m\psi_M = m \int f_\rho \psi_\rho d\rho \quad (19)$$

In most cases, the spectrum of sphere's radii is narrow. This is shown for platinum in Figs. 2 and 3 [7]. The large shaped spheres are those of the active carbon. In the case of PbO_2 , Fig. 5, the spheres in the charged electrode are also almost equal in size. Without any doubt, larger particles are formed by deposition of PbO_2 on smaller ones. Therefore, we have to divide the total charging current, i , into those parts, di_ρ , that are correlated to spheres of a certain radius, ρ . We assume di_ρ to be proportional to the surface area of these spheres, O_ρ , and to $(\eta - \eta_\rho)$, the difference between the real over-voltage, η , and the crystallisation over-voltage, η_ρ , of the particles with radius ρ . We introduce proportionality factor, λ , as the specific

conductance of the interface. It is the reciprocal value of the specific interface resistance. The total current is

$$\int di_\rho = \lambda m \int f_\rho O_\rho (\eta - \eta_\rho) d\rho = i \quad (20)$$

In accordance with our observations, we assume that the distribution function, f_ρ , is independent of the charging time. Hence,

$$df_\rho/dt = 0 \text{ for } \rho \neq \rho_{\min} \cdot \rho_{\max} \quad (21)$$

Logically, nuclei with radius ρ_{\min} are precipitated first. These nuclei are growing as spheres quickly until their radii have reached the maximal values, ρ_{\max} . A sphere with ρ_{\max} becomes inactive and does not grow any longer. This is, because the small pressure exerted from the surface of a sphere with a large radius, ρ , on the bulk is no longer able to bring the bulk in a spherical shape. Instead of this, one or more planar nuclei are formed upon its surface that start to grow quickly to new spheres. On the average, as many planar nuclei are formed on a sphere as many nearest neighbours are found at the end. We call this number N_k . Each sphere originates from one neck but has $\chi = N_k/2$ necks as an average number, since each neck belongs to two spheres. According to our model, the sphere has reached its maximum radius ρ_M when the surface tension σ is no longer large enough to overcome the tensile strength ε_o of the material:

$$2\sigma/\rho \leq \varepsilon_o. \quad (22)$$

Therefore

$$\rho_M = 2\sigma/\varepsilon_o \quad (23)$$

From $it/(2F) = m$ and constant current i , it follows

$$dV/dt = iV_o/(2F) = i/(2F) \int f_\rho V_\rho d\rho + [it/(2F)] d[\int f_\rho V_\rho d\rho]/dt \quad (24)$$

To get the same distribution of spheres anywhere in the electrode, the term $d[\int f_\rho V_\rho d\rho]/dt$ within Eq. (24) has to be zero. The integral has fixed borders: the upper one is ρ_M , the lower one is the radius of the nuclei. Therefore, $d(f_\rho V_\rho)/dt = 0$ and $f_\rho V_\rho = \text{constant}$. On the average, as many necks must grow, as spheres are formed. The total energy for this process is equal to the energy of formation of the necks and of the grown-up spheres. We define the number of necks per mole by $\chi = N/2$. The electric energy for the formation of one mole of PbO_2 is equivalent to the additional elastic energy for the formation of necks and spheres:

$$\psi = N_\rho \left[(8\pi/3) \kappa \sigma^2 \rho + 4\pi\sigma\rho^2 + \chi(4\pi\kappa\sigma^2\rho + \pi^2\sigma h^3/\rho) \right] \quad (25)$$

$$N_M = \int f_\rho d\rho = N_\rho = V_o/(4\pi\rho^3/3) = 3V_o/(4\pi\rho^3) \quad (26)$$

$$\psi = V_o \left[(2 + 3\chi) \kappa \sigma^2 / \rho^2 + (3 + 3\pi\chi\rho^3/4h^3) \sigma / \rho \right] \quad (27)$$

Eq. (27) expresses the additional energy that is necessary for the formation of one mole of PbO_2 spheres of radius ρ . Therefore, ψ is equal to the product of charge, $2F$, and over-voltage, $(\eta - \eta_p)$:

$$(2 + 3\chi)\kappa\sigma^2/\rho^2 + 3(1 + (\pi\chi/4)h^3/\rho^3)\sigma/\rho = 2F(\eta - \eta_p)/V_0 \quad (28)$$

The first term is that part of the additional energy which is based on the compression of the volume, the second one is that of the surface. For a numerical treatment, we can write Eq. (28) as follows:

$$\kappa(\sigma/\rho)^2 + 3[(1 + (\pi\chi/4)h^3/\rho^3)/(2 + 3\chi)](\sigma/\rho) = 2F(\eta - \eta_0)/[V_0(2 + 3\chi)] \quad (28a)$$

This quadratic equation allows the calculation of (σ/ρ) for a given polarisation, $(\eta - \eta_0)$, and a given coordination number, χ , if the quotient h/ρ is known. We try two different approaches:

4.1. Approach 1

In mechanical equilibrium, the ratio of neck radius h to sphere radius ρ is given as

$$h/\rho = [(\sigma/\rho)/(2\varepsilon_0)]^{1/2} \quad (29)$$

A sphere reaches the maximum radius, ρ_M , as soon as the tension, $2\sigma/\rho_M$, exerted by the surface is equal to the tensile strength, ε_0 , of the material: $\varepsilon_0 = 2\sigma/\rho_M$. By inserting $\rho_M = 2\sigma/\varepsilon_0$, $\sigma/\rho = \varepsilon_0/2$, we get

$$h/\rho = [(\varepsilon_0/2)/(2\varepsilon_0)]^{1/2} = \sqrt{1/4} = 1/2$$

From Eqs. (28) and (29), we can derive

$$(2 + 3\chi)\kappa\sigma^2/\rho^2 + 3(1 + (\pi\chi/4)[(\sigma/\rho)/(2\varepsilon_0)]^{3/2})\sigma/\rho = 2F(\eta - \eta_p)/V_0 \quad (30)$$

$$\varepsilon_0^2 + 6(1 + \pi\chi/32)/[(2 + 3\chi)\kappa]\varepsilon_0 = [8F(\eta - \eta_p)/V_0]/[(2 + 3\chi)\kappa] \quad (31)$$

$$\varepsilon_0^2 + (A/\kappa)\varepsilon_0 = (B/\kappa)(\eta - \eta_p) \quad (32)$$

$$A = 6(1 + \pi\chi/32)/[(2 + 3\chi)] \quad (33)$$

$$B = [8F/V_0]/(2 + 3\chi) \quad (34)$$

The following Eq. (35) is the solution of the quadratic Eq. (32) for ε_0 :

$$\varepsilon_0\kappa = -(A/2) + \sqrt{\{(A/2)^2 + B\kappa(\eta - \eta_p)\}} = \xi \quad (35)$$

$$\rho = 2\sigma\kappa/\xi \quad (36)$$

We have displayed the results of the preceding calculations with the aid of the PC program EXCEL. We shall discuss the results later.

4.2. Approach 2

Winsel et al. [13] have shown that the necks in PbO_2 are stable only for values $R/h \leq 6$. This follows from the limited range of stability of $\text{PbO}_{2-\delta}$. If we use this value in Eq. (31), we get

$$\varepsilon_0^2 + 6(1 + \pi\chi/864)/[(2 + 3\chi)\kappa]\varepsilon_0 = [8F(\eta - \eta_p)/V_0]/[(2 + 3\chi)\kappa] \quad (31a)$$

$$A = 6(1 + \pi\chi/864)/[(2 + 3\chi)] \quad (33a)$$

5. The compressibility κ as a result of our experiments

Following the agglomerate-of-spheres model, the necks are controlling the macroscopic strength of the PbO_2 active material. Neckes are also expected to capture metal ions from the corroding grid alloys and modifying their physical properties. To demonstrate this, we have displayed in Fig. 6 some rupture curves measured on samples of PbO_2 [14] in grids made from different lead alloys. The samples had been cycled 15 times. In all cases, the rupture occurred within the PbO_2 active material. The diagram shows the variation of the force, K [p], as a function of the variation of the length, l [mm]. There is no dilatation in the point (0;0) when the force is zero. Negative values of the force mean ‘pressing’, positive values mean ‘stretching’ the sample. From the Hooks’ part of the curves, we can derive $\partial K/\partial l = 1000/0.03 \text{ p/mm} = 1/310^6 \text{ p/cm}$. The rupture force is about 1000 p to 2000 p, the rupture plane, Q , being $Q = 0.5 \text{ cm}^2$. From these data, we can calculate the compressibility, κ , as follows:

$$\kappa = -(\partial V/\partial p)_T/V = -[Q\partial l/\partial(K/Q)]/(Ql) = -QQ/Q/l(\partial l/\partial K) \quad (37)$$

$$\kappa = (Q/l)\partial l/\partial K \quad (38)$$

Since $Q = 0.5 \text{ cm}^2$ and $l = 0.2 \text{ cm}$, we have $Q/l = 2.5$

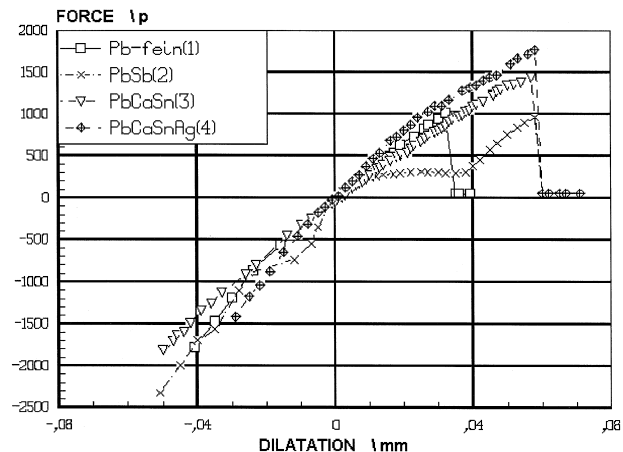


Fig. 6. Rupture curves of four PbO_2 samples. The force [p] is the coordinate, active on 0.5 cm^2 rod area. The dilatation is on the abscissa.

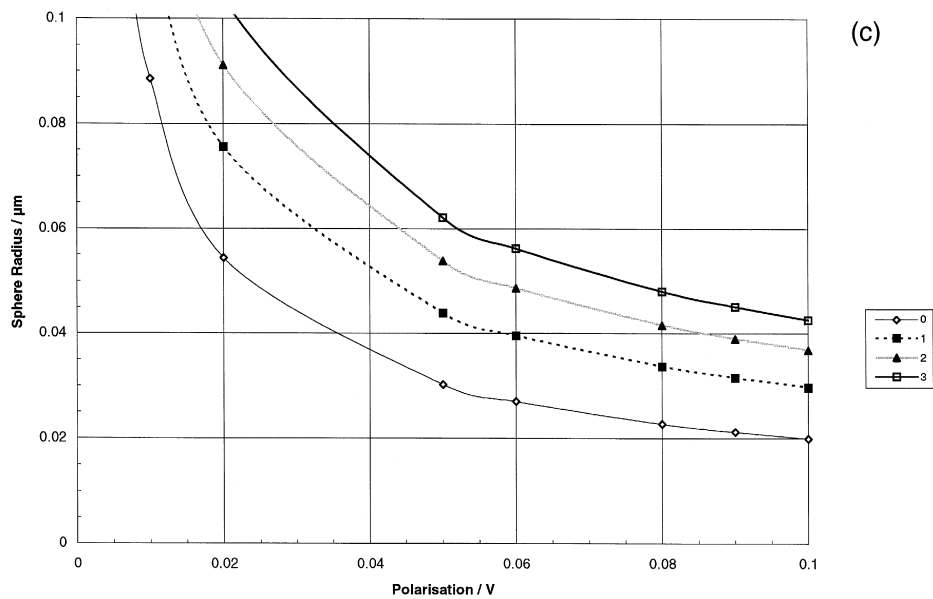
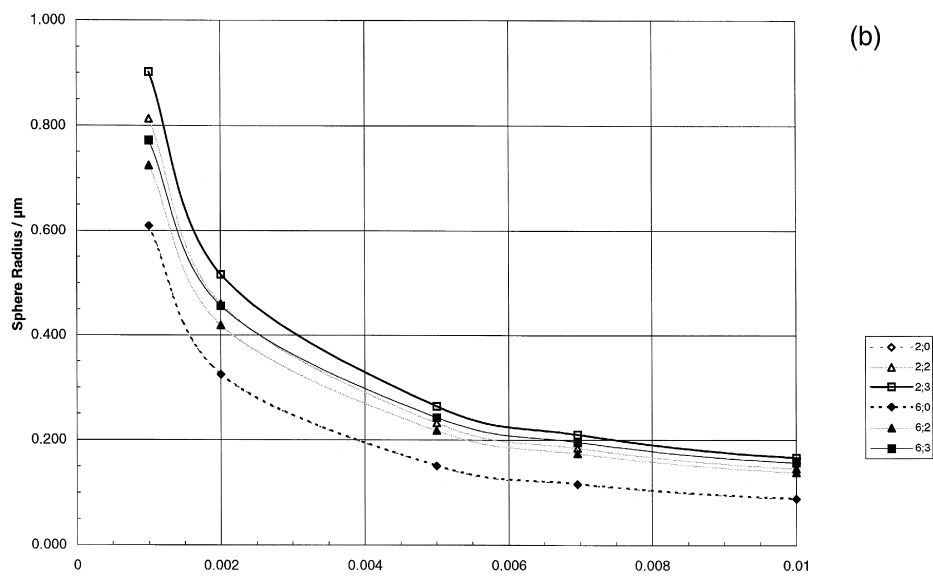
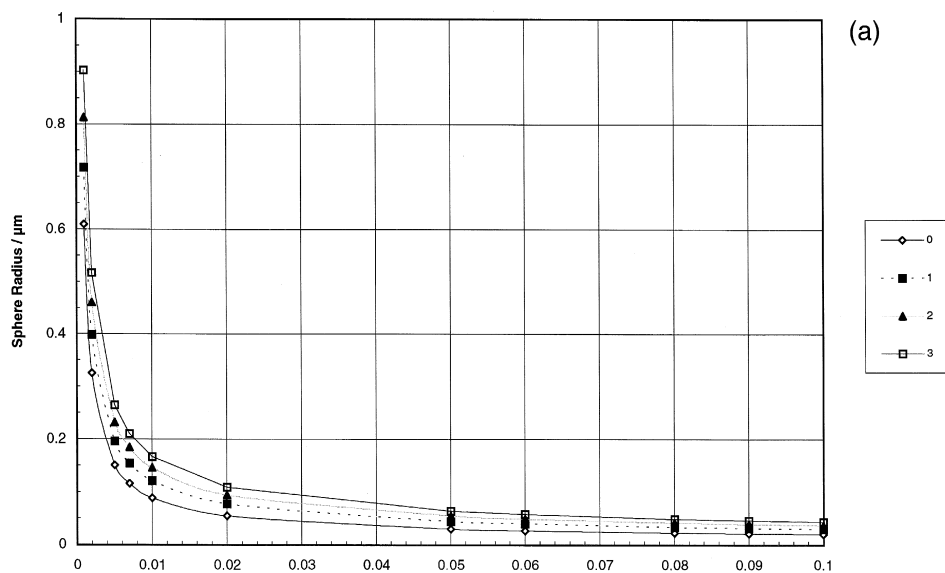


Table 2

Polarisation $\eta - \eta_p$ [V]	$\rho/h = 2$				$\rho/h = 8$			
	$\chi = 0$	1	2	3	$\chi = 0$	1	2	3
0.001	0.609	0.718	0.814	0.903	0.809	0.671	0.725	0.773
0.002	0.325	0.399	0.461	0.517	0.325	0.377	0.420	0.457
0.005	0.151	0.197	0.233	0.265	0.181	0.189	0.218	0.243
0.007	0.116	0.155	0.185	0.211	0.119	0.149	0.175	0.190
0.01	0.089	0.121	0.146	0.167	0.089	0.117	0.139	0.157
0.02	0.054	0.077	0.094	0.109	0.064	0.078	0.091	0.104
0.05	0.030	0.045	0.055	0.064	0.030	0.044	0.054	0.082
0.06	0.027	0.040	0.050	0.058	0.027	0.040	0.049	0.058
0.08	0.023	0.034	0.042	0.049	0.023	0.034	0.042	0.048
0.09	0.021	0.032	0.040	0.046	0.021	0.032	0.039	0.045
0.1	0.020	0.030	0.037	0.044	0.020	0.030	0.037	0.043

cm. Therefore, $\kappa = 2.5 \text{ cm}/(10^6/3 \text{ p/cm}) = 7.5 \times 10^{-6} \text{ cm}^2/\text{p} = 7.5 \times 10^{-6} \text{ cm}^2/(981 \text{ dyn})$;

$$\kappa = 7.56 \times 10^{-2} \text{ cm}^3/\text{J} \quad (39)$$

We could not find values for the surface tension of PbO_2 . We are able to determine its values from data of ρ_M that we could determine by a SEM analysis. Instead of this, we use for our calculations $\sigma = 10^{-4} \text{ J/cm}^2$. This value is reported for solid oxides [15]. Table 2 shows calculated values for ρ_M as a function of the polarisation $\eta - \eta_p$ and of the coordination number χ . We have displayed the same facts in Fig. 7a–c. The results of our calculations can be summarised as follows: (I) Small over-voltage favours the formation of large spheres (particles). (II) Above of 10 mV over-voltage the sphere's radii are in the observed range. (III) A larger coordination number reduces the sensitivity against the over-voltage. We can read these findings from the curves in Fig. 7a–c.

6. Interface tension σ and particle size ρ

Eqs. (35) and (36) together describe the relationship between sphere radius, ρ , and interface tension, σ , for any over-voltage. To solve the problem completely, we need one more independent equation between ρ , σ and η . For this purpose, we can determine ρ from SEM pictures. Thus, the interface tension, σ , of the agglomerate-of-spheres body can be calculated. Or we can determine σ from another experiment and calculate ρ . Here, we have supposed a value for σ and have calculated ρ .

7. The generation of planar nuclei called 'necks'

At the end of a deep discharge, the neck connections within the agglomerate-of-spheres electrode are corroded

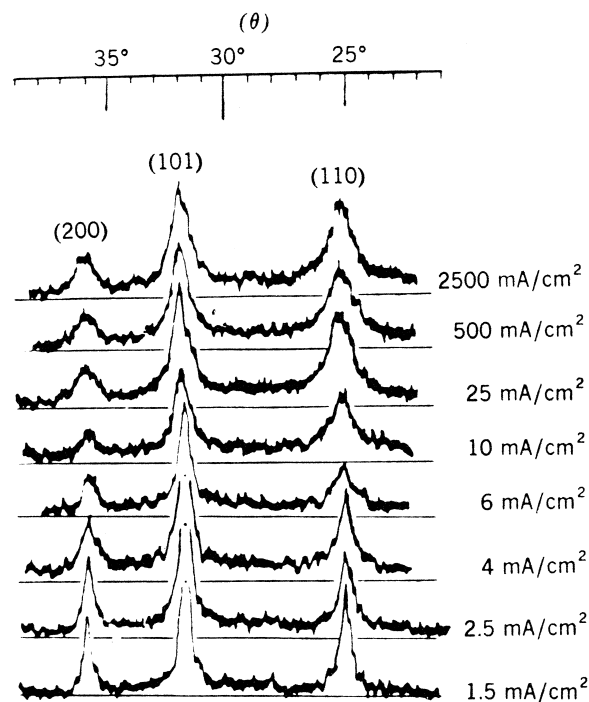


Fig. 8. Broadening of lines in the X-ray goniometer diagrams of PbO_2 , precipitated in acidic solution, as a function of the current density (Ikari and Yoshizava [18,19]).

or destroyed by the mechanical stress exerted by the generated PbSO_4 . In this case, the necks as nuclei must be regenerated during the very first step of recharge. Thus, if we recharge with constant current, we have to apply the first quantum of charge at an elevated over-voltage to pay for the larger elastic energy of the necks. This, as we believe, we have observed in our special unpublished experiments.

Many authors have described the process of nucleation [16], see Bode [17]. In this context, we want to draw attention to the book of Bode [17]. We have reproduced Fig. 8 from his book, showing broadening of the lines in the X-ray goniometer diagram of PbO_2 with increasing current density of formation in acidic solution. The increased current density requires a higher over-voltage. The broadening of the lines expresses a lower degree of order of the structure. It represents an increased error rate by the process during formation of the lattice and an increased elastic energy.

The agglomerate-of-spheres model is a phenomenological model to describe and to understand the observed phenomena during sintering of metal powders. It is useful for understanding many properties of electrochemically produced electrodes. Mainly, the model can interpret those problems of the PbO_2 electrode that are involved in the 'RIMU' as 'Relaxable Insufficient Material Utilisation',

Fig. 7. (a) Calculated sphere radii, $\rho(\equiv R)$, as a function of the polarisation, $\eta - \eta_p$. Parameter is the coordination number, χ . (b) Calculated spheres radii, $\rho(\equiv R)$, as a function of the polarisation, $\eta - \eta_p$. Parameter is the coordination number, χ . 6;2 means $R/h = 6$; $\chi = 2$. (c) Calculated spheres radii, $\rho(\equiv R)$, as a function of large polarisation values, $\eta - \eta_p$. Parameter is the coordination number, χ . $\rho/h = 6$.

s.a. Meissner et al. [20]. Our simple calculation, presented in this paper, supports the observance that low current densities generate a PbO_2 material with larger particles whereas higher current densities are effecting smaller particles. According to the AOS model small particles are beneficial for a better apparent conductivity of the PbO_2 electrode. Therefore, it explains why high charging currents keep the capacity better than low ones that cause the formation of coarse granulated material with a low capacity and a tendency for weakening and mud formation.

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