

On the thermodynamics of the agglomerate-of-spheres' model for the PbO₂ electrode

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Abstract

The agglomerate-of-spheres' model concerns the structure of particulate battery electrodes, in particular the positive lead/acid battery electrode. This model consists of an agglomerate-of-spheres of the active material electrically connected by vase-shaped 'necks'. It has been claimed that for electrodes made from non-stoichiometric compounds — in particular PbO₂ electrodes — there exists a certain combination of neck-and-sphere dimensions which, by the way of the non-stoichiometry, is thermodynamically stable. In the present paper this situation is discussed from a rigorous thermodynamic point of view. It is found that no sphere-neck configuration exists, representing an equilibrium state.

Keywords: Agglomerate-of-spheres; Lead dioxide electrodes; Thermodynamics

1. Introduction

It has been shown [1,2] that the electronic resistance in the PbO₂ battery electrode increases abruptly at the end of discharge and may be, therefore, a limiting factor for the capacity.

Considering the good electronic conductivity of the charged positive mass it is clear that this conductivity originates from some intergrowth structure between the particles.

The agglomerate-of-spheres (AOS) model [3,4] proposes that the particles are connected by a neck-like region, which acts as a bridge between the particles and establishes the electronic contact. It was calculated [4] that the specific conductivity of the mass is proportional to the ratio between the radius of the neck and the radius of the particle, independent of the size of the particle.

2. Geometry of the AOS structure

The main features are described in Refs. [3,4]. The particles are assumed to be spherical. With reference to Fig. 1 the structure is fully described by three radii of curvature: (i) the radius of the particle, r_s ; (ii) the inner radius of the cylindrical neck, r_n , and (iii) the radius of the outer concave curvature of the neck establishing a continuous transition to the spherical particle, r_t . This part of the neck is considered as a part

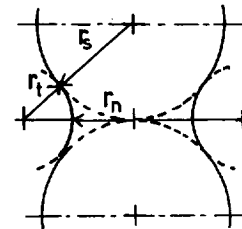


Fig. 1. Geometry of the AOS structure.

of the perimeter of a circular bended cylinder (a toroid) with a perimetrical radius, $r_n + 2r_t$, and a cylinder radius, r_t . It is important to realize that, whereas the centres for the particle and the neck are inside, the centre for the toroid is outside the structure.

The geometrical relation between the three radii can easily be found as [3,4]

$$r_t = \frac{r_n^2}{2(r_s - r_n)} \quad (1)$$

The ratio $a = r_n/r_s$ is important because it controls the electronic conductivity. The other ratio, $r_t/r_s = b$, determines to a large extent, as will be shown, the stability of the AOS configuration. The relation between these two ratios is

$$b = \frac{a^2}{2(1-a)} \quad (2)$$

Table 1
Calculated values for b and $r_t \cdot r_s = 60$ nm

a	b	r_t (nm)
0.90	4.05	243
0.70	0.82	49.0
0.50	0.25	15.0
0.40	0.13	8.0
0.30	0.06	3.6
0.20	0.025	1.5
0.10	0.006	0.36

Within the frame of the AOS model the definition range for a is $0 < a < 1$ whereas b is defined for all positive values. For $a \rightarrow 1$, $b \rightarrow \infty$ as the limit for the AOS model is a cylinder with a radius $r_n = r_s$.

Therefore, the particle size enters as a fundamental quantity in the AOS theory. Even if the particles in a real electrode are by no means spherical, it is used to illustrate the AOS model as a means of investigating the nature of the coherence and electronic conductivity of the electrode. The average sphere size can be calculated from the BET surface as a mean to estimate the characteristic size range.

For different preparations of the positive plate the specific surface area is about $5 \text{ m}^2/\text{g}$ and using the density of PbO_2 a spherical radius of about 60 nm can be calculated.

Some approximate values for b and r_t as function of a are given in Table 1. The unit cell for tetra- PbO_2 is about 0.4 nm, which should be a lower limit for r_t , and, therefore, the lower limit for a with a particle radius of 60 nm is 0.1–0.2.

3. Thermodynamics of the AOS model

Because of the high specific surface area of the PbO_2 particles the interfacial energy between the electrolyte and the solid must be considered in the thermodynamic functions. The basic relation for the inner energy is

$$dE = (T dS) - (p dV) + \sum (\mu dn) + (\gamma d\sigma) \quad (3)$$

which defines the interfacial tension, γ , as an energetic potential, similar to the chemical potential, μ . T , S , p and V have their usual significance; μ is the chemical potential of the components, n the transported amount of matter, and σ the interfacial surface.

The AOS system consists of a neck and the adjoining two half spheres. The external pressure and the temperature are kept constant.

We shall investigate the effect of transferring a small amount δn of PbO_2 from the interior of the spherical part, indicated by s , to the interior of the neck part, indicated by n .

By constant temperature and outside pressure the change in Gibbs free energy is a good indicator for the possibility of a spontaneous process in the system or — if this change is zero — of the stability of the system.

Using partial molar quantities we get for the transfer of δn from the spherical part is

$$\Delta G_s = \gamma \frac{\partial \sigma_s}{\partial n} (-\delta n) + \mu_s (-\delta n) \quad (4)$$

A corresponding relation is valid for the change of G in the neck region but with $(+\delta n)$.

The $\gamma(\partial\sigma/\partial n)$ terms are evaluated by using the radii of curvature (see Appendix 1)

$$\frac{\partial \sigma_s}{\partial n} = \frac{2V_0}{r_s} \quad (5a)$$

$$\frac{\partial \sigma_n}{\partial n} = V_0 \left(\frac{1}{r_n} - \frac{1}{r_t} \right) \quad (5b)$$

where V_0 is the molar volume of PbO_2 .

The overall change in the partial molar free energy, ΔG_t , is the sum of changes in the sphere and the neck. Inserting Eq. (5) we get

$$\Delta G_t = \gamma V_0 \left(\frac{1}{r_n} - \frac{1}{r_t} - \frac{2}{r_s} \right) + \sum (\mu_n - \mu_s) \quad (6)$$

where the first term is the surface term, and the second a chemical term. These are discussed in Sections 4 and 5.

4. Surface term

By using the ratios $a = r_n/r_s$ and $b = r_t/r_s$ the term in the parentheses in Eq. (6) can be written

$$SFT = \frac{1}{r_s} \left(\frac{1}{a} - \frac{1}{b} - 2 \right) \quad (7)$$

and with Eq. (2) one gets¹

$$SFT = \frac{1}{r_s} \left(\frac{3}{a} - \frac{2}{a^2} - 2 \right) \quad (8)$$

Or rearranging

$$SFT = -\frac{1}{r_s a^2} (2a^2 - 3a + 2) \quad (8a)$$

It is easy to ascertain from Eq. (8(a)) that the surface term in Eq. (6) has no zero value or extremum in the definition range for a and is always negative.

5. Chemical term

In earlier papers on the AOS model it has been proposed that a positive value of the term $(\sum \mu_n - \sum \mu_s)$ could balance the negative surface term, creating a state of equilibrium and stability [1,4–6].

¹ This equation was derived in Ref. [4] using the Laplace pressure. The present derivation based on the G -function is preferred, because it stresses the fact that the transfer of matter takes place from and to the interior of the regions.

For discussing this possibility, the disorder structure of the non-stoichiometric PbO_2 is crucial. Based on early works it was assumed [4] that PbO_2 had a deficient oxygen lattice and that the disorder could be expressed by the formula PbO_{2-s} .

However, experimental investigations on the charge/discharge and relaxation behaviours showed that PbO_2 like other 'electroactive' oxides acts as a proton-insertion compound [7–9] which should be formulated as PbO_2H_x .

According to this view the non-stoichiometry is caused by protons on interstitial sites combined with quasi-free electrons, but the Pb–O lattice is complete.

In an equilibrium state at a given temperature, pressure and surface energy, the value of x is determined by the pH and the Pb^{2+} activity of the solution [7,8]. In sulfuric acid saturated with PbSO_4 x is small, less than 0.03.

Based on this disorder model the chemical term in Eq. (6) is

$$\Sigma(\mu_n - \mu_s) = (\mu_n - \mu_s)_{\text{PbO}_2} + x(\mu_{\text{H},n} - \mu_{\text{H},s}) \quad (9)$$

The disturbance of the lattice by the interstitial protons is probably negligible as the ionic radii of O^{2-} and OH^- in a tetragonal oxygen lattice are nearly equal (0.136 and 0.134 nm, respectively) [10].

According to this discussion it can safely be assumed that $\mu(\text{PbO}_2)$ has the same value in both the sphere and the neck region. A non-zero value of the chemical term must then be due to the existence of a difference in μ_{H} between the two regions.

However, the mobility of protons and electrons in the Pb–O lattice is high [9]. Measured on an electrodeposited sample a value of the chemical diffusion coefficient of about $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ was found [9]. Even allowing for a roughness factor of 10 the time constant (l^2/D) for transport of $\text{H} \approx (\text{H}^+ + e^-)$ in an AOS structure of 0.05–0.1 μm is in the order of seconds. Thus, independently of the possible non-stability of the system as such, H will be in equilibrium inside the system, i.e. $\mu_{\text{H},n} = \mu_{\text{H},s} = \mu_{\text{H}}$.

As the chemical potential of both components are equal in the sphere and the neck no chemical work can be connected with the transfer of PbO_2H_x .

One may argue if the different Laplace pressures in the sphere and the neck surfaces may influence the chemical potentials.

However, this contribution to the free energy is fully accounted for in the surface energy terms in Eq. (8)². Thus, under the above-mentioned assumptions the contribution of the chemical term (Eq. 9) to ΔG is negligible. For this reason we prefer to consider the chemical term to be zero.

² This view is supported by the discussion by Adam [11] who advocates that surface free energy is the basic property of surfaces and that surface tension only is a convenient mathematical transformation of the energy, and "The view that there is some skin in the surface pulling parallel to it leads to great difficulties ..."

6. Conclusions

According to the above-mentioned discussions the partial molar free energy associated with the transfer of PbO_2H_x from the sphere to the neck is

$$\Delta G_t = \frac{\gamma V_0}{r_s} \left(\frac{2}{a^2} - \frac{1}{a} - 2 \right) \quad (10)$$

which is always negative. Therefore, this transfer represents a spontaneous process with the affinity $-\Delta G$.

For reasons of thermodynamics it is not possible to locate a stable state for a sphere–neck configuration. The final 'pseudo-stable' state will be a cylinder at the end of the definition range for the AOS model ($a = 1$). This should be a structure consisting of PbO_2 strings, with a maximum conductivity.

The practical importance of these findings depends, however, on the reaction path, which can make the spontaneous transfer possible. Apparently sintering — in analogy with metal powders — was considered as the transfer path [4]. This seems hardly possible for a high melting compound at ambient temperature. However, an obvious possibility for the transfer is an electrochemical reaction between sphere and neck caused by different equilibrium potentials. The kinetics of this reaction will be the subject of a following work [12]. In this context it should be observed that the affinity decreases very fast as a increases. The rate constants for a possible transfer reaction may well determine a range for a — and thus the conductivity — which is relevant for the properties of the PbO_2 electrode in the battery.

7. List of symbols

a	ratio of neck radius to sphere radius: r_n/r_s
b	ratio of torus radius to sphere radius: r_t/r_s
E	internal energy of system
$\Delta G_{s,n}$	change in Gibbs free energy of sphere and neck
ΔG_t	change in partial molar free energy
n	amount of matter (PbO_2)
p	external pressure on system
r_n	radius of neck
r_s	radius of sphere
r_t	radius of toroidal part of neck
S	entropy
SFT	surface term in Eq. (6)
T	absolute temperature
V	volume
V_0	molar volume of PbO_2

Greek letters

δn	small amount of matter
γ	surface tension
μ	chemical potential of indicated component
σ	surface area

Subscripts

n, s indices for neck and sphere, respectively

Appendix A

Consider a sphere with radius r_s . The surface σ is

$$\sigma_s = 4\pi r_s^2 \text{ giving } d\sigma = 8\pi r_s dr_s \quad (\text{A1})$$

The amount n of PbO_2 in the sphere is

$$n = \frac{4}{3}\pi r_s^3 \frac{1}{V_0} \text{ giving } dn = 4\pi r_s^2 \frac{1}{V_0} dr_s \quad (\text{A2})$$

Eqs. (1(a)) and (2(a)) give

$$\frac{d\sigma_s}{dn} = \frac{2V_0}{r_s} \quad (\text{A3})$$

In case of the neck, one may consider a small rectangular surface element on the double-curved surface of the neck. Let the sides be p and q . The area is then pq . p has a radius of curvature, r_n , and its centre inside the neck. q has a radius, r_t , and its centre outside the neck.

Displace the surface element parallel to itself a small distance δx away from p 's centre. The new radii of curvature are then $r_n + \delta x$ and $r_t - \delta x$, respectively. The sides of the surface element are then changed to $p(1 + \delta x/r_n)$ and $q(1 - \delta x/r_t)$. The area increase becomes

$$\Delta\sigma_n = pq\{(1 + \delta x/r_n)(1 - \delta x/r_t) - 1\} \quad (\text{A4})$$

Neglecting second-order quantities we obtain

$$\Delta\sigma_n = pq\left(\frac{1}{r_n} - \frac{1}{r_t}\right)\delta x \quad (\text{A5})$$

The amount of PbO_2 in the neck is increased by

$$\Delta n = pq \delta x \frac{1}{V_0} \quad (\text{A6})$$

Combining Eqs. (5(a)) and (6(a)) and going to the limit we obtain

$$\lim \frac{\Delta\sigma_n}{\Delta n} = \frac{\delta\sigma_n}{\delta n} = V_0 \left(\frac{1}{r_n} - \frac{1}{r_t} \right) \quad (\text{A7})$$

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