

The kinetics of the agglomerate-of-spheres model for the PbO₂ electrode

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Abstract

The structure of a particulate electrode may be modelled by an agglomerate-of-spheres, called the AOS model. For the particulate PbO₂ electrode this model assumes that the electronic connections between the particles are established through vase-like necks. The size of these necks determines the electronic conductivity of the electrode. It has been demonstrated that thermodynamically there is a tendency for a spontaneous growth of the neck at the expense of the particles. Finally, this should result in a three-dimensional network of PbO₂ strings. In the present paper it is shown that the transfer of material from sphere to neck can take place by an electrochemical path, established through discharge of the sphere and charge of the neck. Under this assumption the growth rate of the neck is calculated. Using suitable estimates of the constants involved it is found that in a few hours the neck diameter increases to ~0.2 times the particle diameter, however, the development to the final structure may take many days. © 1998 Elsevier Science S.A.

Keywords: Lead electrodes; Agglomerate-of-spheres; Kinetics

1. Introduction

The agglomerate-of-spheres (AOS) model was introduced by Winsel and co-workers [1–3] as a three-dimensional network of equally sized PbO₂ spheres connected by necks. The present work concerns primarily the electronic conductivity perpendicular to the surface of the electrode. From this reason only one-dimensional parallel strings of spheres are considered.

The structure is defined by three interdependent radii of curvature namely the sphere radius, r_s , the radius of the cylinder, which can be inscribed in the neck, r_n and the radius of the toroidal part of the neck, r_t , see Fig. 1.

The sphere radius can be estimated from specific surface area data, and therefore it is most convenient to use r_s and the ratios

$$a = \frac{r_n}{r_s} \quad \text{and} \quad b = \frac{r_t}{r_s} \quad (1)$$

as variables. According to Ref. [1] a is also the ratio between the electronic conductivity of the particulate mass and the bulk conductivity.

From the geometry of the sphere–neck configuration it can be found [1,4]

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

By thermodynamic analysis of the AOS model it was found [4] that the transfer of PbO₂ from the bulk of the sphere to the neck zone causes a change in partial molar free energy

$$\Delta G = \frac{\gamma V_0}{r_s} \left(\frac{1}{a} - \frac{1}{b} - 2 \right) \quad (3)$$

where γ is the interfacial tension between PbO₂ and the electrolyte and V_0 the molar volume of PbO₂.

Within the limits of the model ($0 < a < 1$, $b > 0$) it was shown that ΔG always is negative. Thus, if a path for transfer of PbO₂ from the sphere to the neck exists, a will continue to grow, finally causing the AOS structure to degenerate into a cylindrical string.

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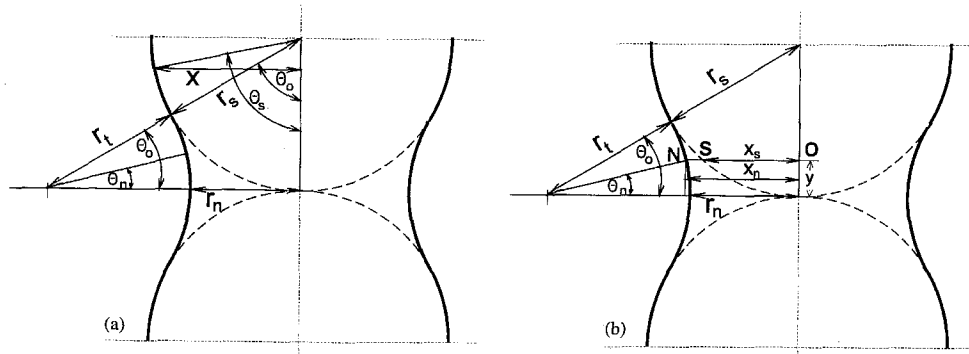


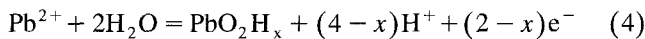
Fig. 1. (a), (b) Geometry of the AOS structure.

The importance of this development originates from the recognition that the electronic conductivity of the mass is proportional to a [1], and that it is likely that in some instances the conductivity is a dominating factor for determining the capacity of the PbO_2 electrode [5,6].

2. Electrochemical transfer

Both the sphere and the neck establish electrochemical exchange with an electrolyte containing Pb^{2+} , H^+ and H_2O combined with an electron source.

The process consists of several partial reactions [7]. At stationary conditions the total process is

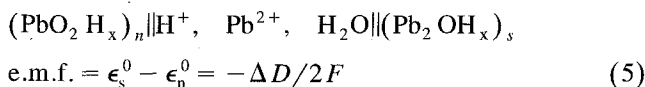


using the fact that PbO_2 is a non-stoichiometric oxide containing protons and electrons [8].

The equilibrium potential connected with Eq. (4) can be written as a standard potential ϵ^0 plus terms depending on the chemical potentials of Pb^{2+} and H^+ in the solution and H in the oxide. In fact only two of these are independent variables [9].

Considered separately ϵ^0 is different for the sphere and the neck as the change in the G function by adding PbO_2H_x is different because of the difference in interfacial energy. As there is chemical equilibrium between the sphere and the neck [4] it is clear that the equilibrium electrode potentials differ by an amount given by $\Delta G/2F$. (The denominator should correctly be $(2-x)F$, but x is negligibly small.)

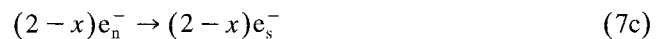
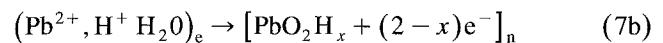
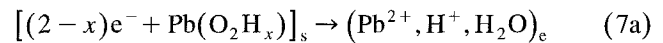
Indicating sphere and neck by 's' and 'n', respectively, we have for the cell



or using Eq. (3)

$$\text{e.m.f.} = -\frac{\gamma V_0}{2Fr_s} \left(\frac{1}{a} - \frac{1}{b} - 2 \right) \quad (6)$$

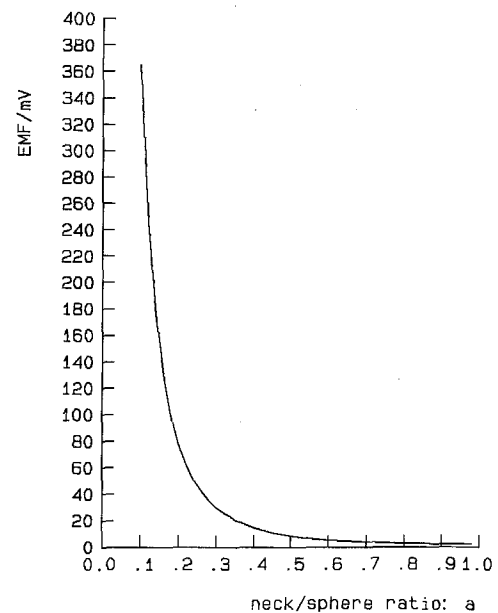
If an electronic connection exists between sphere and neck the non-zero value of e.m.f. will cause electrochemical transfer of PbO_2 and electrons



Eqs. (7a) and (7b) take place through the electrolyte (e) and Eq. (7c) through neck/sphere boundary.

The direction of Eqs. (7a–c) is given by the negative value of ΔG . The sphere is the positive, the neck the negative electrode in the cell. Eqs. (7a–c) cause the sphere to be discharged and the neck to be charged.

The e.m.f. is the driving force for the transfer and its magnitude together with the active areas determines the current associated with Eq. (7b). If b is expressed by Eq. (2), the value of the e.m.f. can be calculated as a function of the ratio a , using V_0 , γ and r_s as parameters.

Fig. 2. E.m.f. as a function of a (Eq. (6)), $r_s = 60$ nm, and $\gamma = 1 \text{ J m}^{-2}$.

V_0 is well known, being $24.6 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. Estimation of γ is quite arbitrary. No relevant literature data has been found. In Ref. [1] $\gamma = 1 \text{ J m}^{-2}$ is proposed. This is comparable with known data for metals.

Using the AOS model, r_s is estimated by approximating the PbO_2 electrode by an agglomerate of monodisperse spheres and equalizing their surface area to the known BET area. The reason for using the BET surface for calculating r_s is that the key point in the work is the use of interfacial energy, which is proportional to the total surface. Under the assumptions of the model this surface must be converted to sphere radii. With $5 \text{ m}^2 \text{ g}^{-1}$ as a typical value, r_s comes out as $\sim 60 \text{ nm}$.

In Fig. 2 e.m.f. is shown as a function of a . It is noticeable that e.m.f. decreases to rather small values for $a > 0.5$.

3. Transfer current

During the flow of the transfer current the e.m.f. is balanced by the transfer overvoltages at the PbO_2 electrolyte boundaries in combination with the ohmic voltage drop between the sphere and the neck and a possible concentration overvoltage. As an approximation (the validity of which is discussed later) only the transfer overvoltage is considered significant. Then

$$\text{e.m.f.} = \eta_n - \eta_s \quad (8)$$

where η stands for the transfer overvoltage ($\eta_n > 0$, $\eta_s < 0$). The transfer current is given by these overvoltages and the electrochemical active areas of the sphere and neck, respectively. Owing to the magnitude of the e.m.f. the non-linear Volmer–Butler relation between the current densities and the overvoltages must be used. Indicating the areas for neck and sphere, respectively, by A_n and A_s the currents to the neck and the sphere, i_n and i_s are

$$\begin{aligned} i_n &= A_n i_0 \left[\exp\left(\frac{2F}{RT} \alpha \eta_n\right) - \exp\left(-\frac{2F}{RT} \beta \eta_n\right) \right] \\ i_s &= A_s i_0 \left[\exp\left(\frac{2F}{RT} \alpha \eta_s\right) - \exp\left(-\frac{2F}{RT} \beta \eta_s\right) \right] \end{aligned} \quad (9)$$

where the exchange current i_0 is defined with respect to the electrolyte; α and β are the anodic and cathodic transfer coefficients.

The currents in the electrolyte at the neck and the sphere are numerically equal, but of opposite sign

$$i_n = -i_s \quad (10)$$

By combining Eqs. (8)–(10) and inserting values for e.m.f., A_n and A_s , the overvoltages can be found. Then, by inserting a value for i_0 in Eq. (9) the current transferring PbO_2 from the sphere to the neck can be found as function of a . Finally, from the relation between the volume of the neck and a , the rate of the increase in neck size and consequently a , can be found.

4. Experimental

The constants i_0 , α and β in Eq. (9) were determined experimentally.

Two commercial positive plates, 2 mm thick, were cut into $5 \text{ cm} \times 8 \text{ cm}$ surface area. The active mass in each was 29 g. They were cycled 5 times in parallel against an oversize negative in $3.5 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$. The cycling procedure was: discharge with 24 A/kg to 1.5 V and IUI charge with the same current to 20% overcharge. They delivered 90–100 Ah/kg PbO_2 . To ensure the presence of PbSO_4 they were both discharged with 20 Ah/kg . In this way $\sim 9\%$ of the total amount of PbO_2 was converted to PbSO_4 .

With one plate as reference electrode the other was discharged and charged potentiostatically in the same acid against a negative plate. The potential range was $\pm 16 \text{ mV}$ and the geometrical stationary current density was less than 1 A m^{-2} .

5. Results

Initially at the potential step the current was larger than noted above. This is due to the hydrogen insertion/extraction reaction [7,9] having a much larger rate constant than

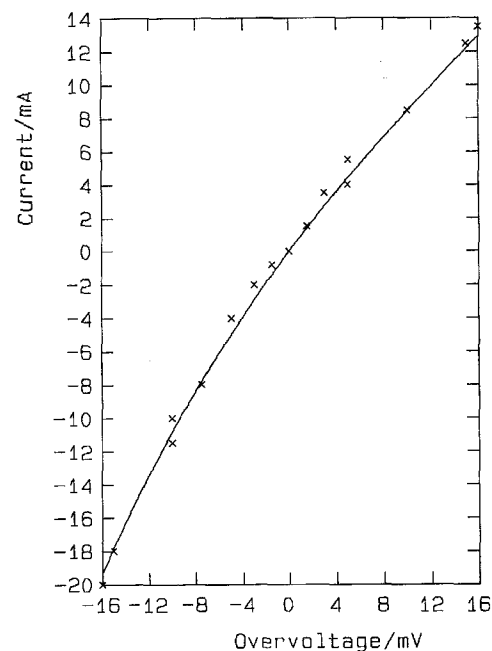


Fig. 3. Anodic and cathodic current on positive plate 40 cm^2 . \times : experimental values; (—) Volmer–Butler approximation with $i_0 = 12.2 \times 10^{-3} \text{ A}$ and transfer coefficients 0.34 (anodic) and 0.66 (cathodic).

the lead dissolution/deposition reaction [7]. Within 5 to 10 min the value of x at the surface is adjusted to the given overvoltage and the current acquires a constant value representing the rate of the stationary Eq. (4). It is the rate constant of this reaction, which should be used in Eq. (9). During the measurements less than 1% of the PbO_2 and the acid in the pores was used. Due to the high electronic and ionic conductivities, compared with the low exchange current found, it is estimated, that the influence of the porous structure can be neglected.

The results are shown in Fig. 3. A reasonably good fit, shown by the full line, is obtained with $\alpha = 0.34$ and $\beta = 0.66$. The exchange current for the plate came out as 12.2×10^{-3} A, corresponding to 3.0 A m^{-2} geometrical area.

Using the BET area $5 \text{ m}^2 \text{ g}^{-1}$ as an estimate of the true active surface, from the reasons given above, renders a value of the exchange current density, i_0 , for PbO_2 equal to $93.5 \times 10^{-6} \text{ A m}^{-2}$.

The values, in particular for i_0 , found here are in considerable disagreement with literature data [10–12]. i_0 is considerably smaller than the values cited in Refs. [10,11]. Better agreement is found with the value given in Ref. [12] for a comparable plate. This disagreement with literature data may originate from the large difference in the rate constants between the hydrogen insertion [7] and the stationary reaction, which is not discussed in the literature.

One may question the validity of using data for small overvoltages for the e.m.f. range, which is relevant for the AOS structure. The reason for this was that in order to minimize the influence of the porosity of the electrode, the current density should be small.

As will appear from the following, the time scale for the growth of the neck is inversely proportional to i_0 . Thus, the choice of this parameter is important, but for the reasons given above the experimental value found here is used in the following.

6. Calculations

The data and relations given so far allow a calculation of how the ratio a should increase spontaneously with time.

The first step is calculation of e.m.f. for a chosen value of a according to Eq. (6). Then combination of Eqs. (8)–(10) give

$$\begin{aligned} & A_n \left\{ \exp\left(\frac{2F\alpha}{RT} \eta_n\right) - \exp\left(-\frac{2F\beta}{RT} \eta_n\right) \right\} \\ & - A_s \left\{ \exp\left[\frac{2F\alpha}{RT} (\eta_n - \text{e.m.f.})\right] \right. \\ & \left. - \exp\left[-\frac{2F\beta}{RT} (\eta_n - \text{e.m.f.})\right] \right\} = 0 \end{aligned} \quad (11)$$

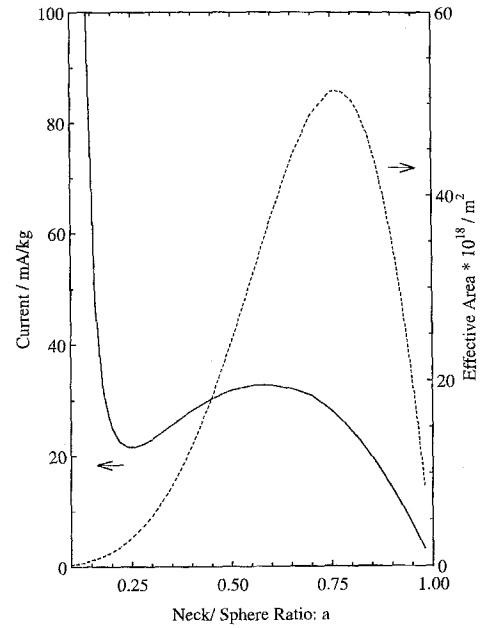


Fig. 4. Transfer current in $10^{-3} \text{ A kg}^{-1} \text{ PbO}_2$ and combined active area in 10^{-18} m^2 as a function of a .

The solution of this equation for η_n for a given e.m.f. requires knowledge of the areas A_n and A_s . These are found from the geometry (Fig. 1) by suitable integrations (see Appendix A)

$$A_s = 2\pi r_s^2 \frac{1}{1+b} \quad (12)$$

$$A_n = 2\pi r_s^2 b \left\{ (a+b) \arcsin \frac{1}{1+b} - \frac{b}{1+b} \right\} \quad (13)$$

From these, η_n can be found as a function of a by an iteration procedure.

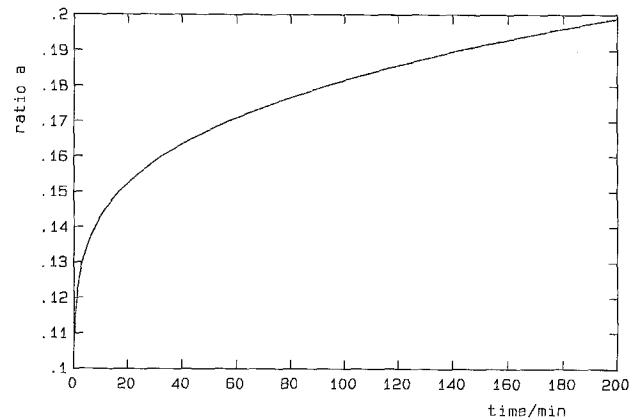
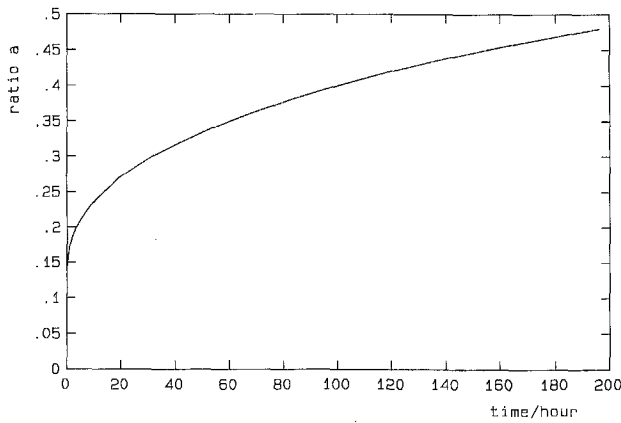


Fig. 5. a as a function of time 0–200 min.

Fig. 6. a as a function of time 0–200 h.

The transfer current, i is then found as a function of a using Eq. (9). i is influenced by the e.m.f. (Eq. (6)) as well as by the magnitude of the two areas A_n and A_s . The smaller of these has the major influence. A combined active area is defined as

$$\frac{1}{A_r} = \frac{1}{A_n} + \frac{1}{A_s} \quad (14)$$

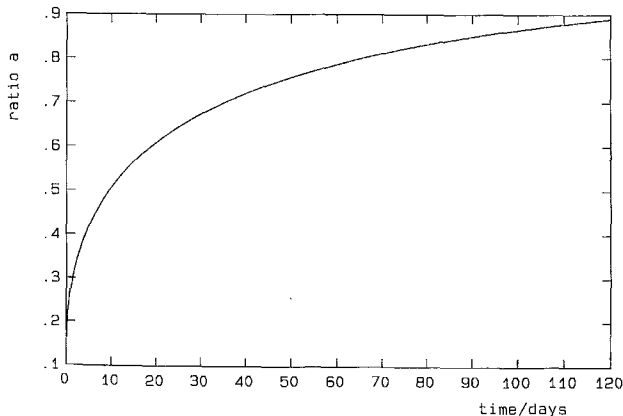
A_r increases to a maximum at $a = 0.8$ and therefore counteracts the decrease in e.m.f.

i (expressed as mA/kg PbO_2) and A_r as functions of a are shown in Fig. 4. The S shape of i is due to the interaction between e.m.f. and A_r .

The transfer current indicates the rate by which PbO_2 is transferred from the sphere to the neck, increasing the neck volume and diameter. The time dt to increase the volume by dV is then

$$dt = \frac{2F}{iV_0} dV \quad (15)$$

In order to pass to a as variable, the neck volume is found as a function of the angle θ_0 (Fig. 1(b)) and a and b (see Appendix B)

Fig. 7. a as a function of time 0–120 days.

$$V = \pi r_s^3 b \left\{ \left[(a+b)^2 + b^2 \right] \sin \theta_0 - b(a+b) \right. \\ \left. \times (\sin \theta_0 \cos \theta_0 + \theta_0) - b^2 \sin \theta_0 \right\} \quad (16)$$

with

$$\sin \theta_0 = \frac{1}{1+b}; \quad \cos \theta_0 = \frac{a+b}{1+b}; \quad \theta_0 = \arcsin \frac{1}{1+b}$$

Integration was performed by a stepwise numerical procedure using a as independent variable, calculating ΔV and i and inserting in Eq. (15). The results are shown with a as a function of time in Figs. 5–7.

7. Discussion

In the calculations r_s has been assumed constant. However, in the range of interest the decrease of r_s is completely negligible. At $a = 0.6$ (after 500 h) the sphere radius is still 99% of the initial.

In the derivation of Eq. (8) the ohmic voltage drop within the AOS structure was neglected. Due to the low resistivity of PbO_2 ($1.2 \times 10^{-6} \Omega \text{ m}$) and the short distance—taken as r_s —the ohmic drop is orders of magnitude smaller than the overvoltages.

The same applies to a possible contribution of an ohmic voltage drop in the acid and a possible overvoltage caused by a concentration gradient between sphere and neck. Using the solubility of PbSO_4 (2 mg dm^{-3}) and the diffusion coefficient for Pb^{2+} ($0.9 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$), a diffusion length equal to r_s and the values for the transfer-current density at the neck, it can be calculated that even for $a = 0.1$ the concentration overvoltage is less than 10^{-3} times the transfer overvoltage.

The largest uncertainty in the calculation is due to the values ascribed to γ and r_s . However, this does hardly invalidate the conclusions drawn on the basis of the AOS model.

One may question the validity of the model for the actual PbO_2 electrode in the lead/acid battery. The assumption about spheres of the same size arranged in a one-dimensional array is, of course, not realistic. Expansion of this simplified AOS model to a three-dimensional network is mathematically possible but requires assumptions about the coordination number in the model [13]. This expansion would influence the time scale of the growth, but would not change the overall picture significantly. More questionable would be the influence of a statistical distribution of the sphere sizes, which would complicate the mathematical treatment. This problem is worked on elsewhere.¹

¹ A. Winsel, personal communication.

However, it is clear that in a particulate electrode consisting of one component only, the electrode structure will exhibit concave as well as convex surfaces in order to have electronic conductivity and mechanical coherence. The AOS model should be considered as an approximation to this fundamental property.

8. Conclusions

One conclusion of this work is that even if there is only a point contact—of unit cell dimensions—between two particles it should only take a few hours for the neck to grow to a diameter which is $\sim 20\%$ of the particle diameter (Fig. 5). This should ensure an interparticle conductivity sufficient for most applications.

After this initial phase the growth rate is slow. On a practical time scale one may consider the range 0.3–0.5 for the ratio (a) between neck and sphere diameter as a ‘pseudostable’ state (Fig. 6). Afterwards the growth rate becomes extremely slow (Fig. 7).

From the expression for e.m.f. Eq. (6), it can be seen that particle sizes larger than used here, delay the growth. This would also be the case for a smaller value of γ .

Tacitly it has been assumed that the electrode is at rest. However, the considerations above are also valid during discharge and charge conditions. As the concentrations at the sphere and neck surfaces are equal (see above) the e.m.f. is caused by a difference in the standard potentials (Eq. (5)), therefore the overvoltages associated with the transfer current adds to the overvoltage caused by the discharge or charge currents. The AOS overvoltage at the neck is positive, and calculation shows that in the range of interest it constitutes more than 90% of the AOS e.m.f. Therefore, in particular for small values of a (Fig. 2), during discharge the total overvoltage and thus the current density at the neck is smaller than the current density at the sphere. At charge the current density on the neck is larger. The exponential dependence of the current on overvoltage (Eq. (9)) for overvoltages in the practical range of discharge/charge currents amplifies this effect. From this reason the growth of the neck should be favored by cycling.

The development of the electronic resistance of the positive mass has been reported [2,3]. During most part of the discharge this resistance remains approximately constant, which agrees with the reasoning above. However the resistance increases abruptly at the end of discharge. Also during repeated cycling the resistance increases [2]. This cannot be explained easily by the AOS theory as presented here. Attention is drawn to the degradation phenomena (sludge formation) associated with the expansion of the electrode [14]. This degradation apparently takes place, although the increase in neck size should improve the coherence of the electrode, and therefore counteract a mechanical disruption.

9. List of symbols

$A_{n,r,s}$	Active areas of neck, neck/sphere and sphere, respectively
a	ratio r_n/r_s (see below)
b	ratio r_t/r_s (see below)
e.m.f.	electromotive force
F	Faraday constant
ΔG	change in partial molar Gibbs free energy
i, i_n, i_s	transfer currents
i_0	exchange current
R	gas constant
r_n	radius of neck (Fig. 1)
r_s	radius of sphere (Fig. 1)
r_t	radius of toroidal part of neck
x	stoichiometric coefficient
V	volume of neck

V_0 molar volume of PbO_2

Greek letters

α, β	anodic, respectively cathodic transfer coefficients
γ	interfacial tension
ϵ^0	standard potential
η	overvoltage
θ, θ_0	angles (Fig. 1)

Subscripts

n	subscript for neck
s	subscript for sphere

Appendix A

A.1. Active area of the sphere

With reference to Fig. 1(a) x is the distance from the centerline to a point on the periphery of the sphere, and θ_s is the angle between radius to that point and the centerline. Then

$$dA_s = 2\pi r_s d\theta_s \quad (\text{A1/1})$$

and

$$x = r_s \sin \theta_s \quad (\text{A1/2})$$

Then

$$A_s = -2\pi r_s^2 \int_{\theta_0}^{\pi/2} \sin \theta_s d\theta_s = 2\pi r_s^2 \cos \theta_0 \quad (\text{A1/3})$$

where θ_0 is the angle to the point where the neck touches the sphere; $\cos \theta_0$ is found from the figure

$$\cos \theta_0 = \frac{r_s}{r_s + r_t} = \frac{1}{1 + b} \quad (\text{A1/4})$$

Then

$$A_s = 2\pi r_s^2 \frac{1}{1 + b} \quad (\text{A1/5})$$

A.2. Active area of the neck

With reference to Fig. 1(a) θ_n is the angle between the basis line and a radius in the toroid to a point at the neck. Then

$$dA_n = 2\pi r_t d\theta_n \quad (\text{A1/6})$$

and

$$y = r_n + r_t - r_t \cos \theta_n \quad (\text{A1/7})$$

Then

$$A_n = 2\pi r_t \left[(r_n + r_t) \int_{\theta_0}^{\theta_n} d\theta_n - r_t \int_{\theta_0}^{\theta_n} \cos \theta_n d\theta_n \right] \quad (\text{A1/8})$$

where θ_0 is the complement to the θ_n used above. Introducing $\theta_0 = \arcsin[1/(1+b)]$ and a and b one finally gets

$$A_n = 2\pi r_s^2 b \left[(a+b) \arcsin\left(\frac{1}{1+b}\right) - \frac{1}{1+b} \right] \quad (\text{A1/9})$$

Appendix B

B.1. Volume of the neck

With reference to Fig. 1(b) a secant perpendicular to the centerline at point O is drawn in the distance y from the basis line. The secant cuts the sphere at S and the neck at N.

With $OS = x_s$ and $ON = x_n$ a volume element in the neck is

$$dV = \pi (x_n^2 - x_s^2) dy \quad (\text{A2/1})$$

Introducing as integration variable the angle θ between the radius in the toroid to N and the basisline we get

$$x_n = r_n + r_t - r_t \cos \theta = r_s (a + b - b \cos \theta) \quad (\text{A2/2})$$

and

$$y = r_t \sin \theta = r_s b \sin \theta \Rightarrow dy = r_s b \cos \theta d\theta \quad (\text{A2/3})$$

and

$$x_s^2 = r_s^2 - (r_s - y)^2 = r_s^2 (2b \sin \theta - b^2 \sin^2 \theta) \quad (\text{A2/4})$$

then

$$-2b(a+b) \int \cos^2 \theta d\theta - 2b \int \sin \theta \cos \theta d\theta \quad (\text{A2/5})$$

Integrating from 0 to θ_0 gives

$$V = \pi r_s^3 b \left\{ [(a+b)^2 + b^2] \sin \theta_0 - b(a+b) \times (\sin \theta_0 \cos \theta_0 + \theta_0) - b^2 \sin \theta_0 \right\} \quad (\text{A2/6})$$

with

$$\sin \theta_0 = \frac{1}{1+b}; \cos \theta_0 = \frac{a+b}{1+b}; \theta_0 = \arcsin \frac{1}{1+b}.$$

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