

Theoretical calculations for using positive electrode compression to increase lead–acid battery life

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Accepted 22 September 1999

Abstract

Investigators have confirmed that applying a small amount of mechanical pressure, approximately 1 bar (10^5 Pa), to the face of the positive electrode can dramatically increase the life of deep cycled, lead acid batteries. In this paper, we calculate the pressures required to stabilize the active material in the positive electrode based on the “Agglomerate of Spheres” model. The calculations agree closely with the experimental observations. In addition to these calculations, we also provide another possible interpretation of the “Agglomerate of Spheres” model and give an improved estimate for the surface tension of lead dioxide, an important physical quantity for the model. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Lead–acid; Battery; Life; Compression; Gassing; Spheres

1. Introduction

For approximately 20 years, researchers have known that exerting mechanical pressure on the positive electrode of lead acid batteries helps to prevent shedding and increase cycle life. Shedding is the usual failure mode of deep cycled batteries and occurs when the positive active material softens and loses electrical contact with the electrode. In a series of papers, Alzieu et al. [1–3] found that the cycle life of lead acid batteries could be increased from approximately 300 cycles to 3000 cycles as the mechanical pressure, which we will refer to as compression, was increased from zero to 10^5 Pa (i.e., 1 bar). Applying mechanical pressure greater than this value, 10^5 Pa, did not significantly increase cycle life. This small amount of compression appears to prevent shedding and shifts the failure mechanism from shedding to grid corrosion.

Other investigators have also observed an increase in cycle life with mechanical compression. Takahashi et al. [4] found that the cycle life of the cells they were testing nearly doubled (i.e., 400–800 cycles) when the mechanical pressure was increased from 0.2×10^5 Pa to 0.4×10^5 Pa. They also reported that the maximum cycle life occurred at

a compression of 10^5 Pa and that increasing the compression to 3×10^5 Pa did not result in any further increase in cycle life. Landfors [5] determined that the cycle life of batteries could be increased from 90 cycles to 1150 cycles when the positive plates were subjected to a compression of 10^5 Pa. Atlung and Zachau-Christiansen [6], while studying the detrimental effect that BaSO_4 had on cycle life, also found that cycle life increased when the positive electrode was subjected to compression. These studies confirm that applying a small amount of compression to the surface of the positive electrode can dramatically improve cycle life.

It is surprising that such a small amount of mechanical pressure or compression on the positive electrode would have such an extraordinary effect on cycle life. In order to understand the beneficial effect of compression, we should first understand how shedding occurs. Unfortunately, investigators have not agreed on the fundamental causes for shedding.

In the past, shedding was thought to be associated with the volume change that occurs in the positive plate as PbO_2 , specific volume of $24.6 \text{ cm}^3/\text{mol}$, is transformed into PbSO_4 , specific volume of $48.2 \text{ cm}^3/\text{mol}$. This large change in volume was believed to stress the positive electrode and cause it to crumble with cycling. Alzieu et al. [1–3] and Takahashi et al. [4] both investigated the

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change in plate volume and the mechanical pressures exerted on the plates as their batteries were cycled. They found that after the first 20–50 cycles, the plates did not continue to expand and that the change in mechanical pressure over one cycle was approximately 0.01 to 0.04×10^5 Pa. This value is much lower than the optimal mechanical pressure or compression of 10^5 Pa required for greatly increasing the cycle life of these batteries. Apparently during the initial cycles, the change in volume of the active material creates stresses in the electrode and causes the electrode to expand. The porosity of the electrode increases until the active material volume changes can be accommodated in the porous structure [6]. If this is true, then shedding would not be associated with the volume changes of the positive active material.

Shedding appears to occur at the end of charge and beginning of discharge (see Bode [7]). If stresses associated with volume changes were responsible for shedding, then we would expect shedding to occur at the end of discharge where the volume change and stress is at its maximum. Wales and Simon [8] suggested that during discharge PbO_2 particles were isolated from the conductive part of the electrode. When the electrode is charged, the lead sulfate dissolves, leaving these PbO_2 particles unattached to the electrode. This explanation is consistent with the experimental observation that shedding occurs at the end of charge and that most of the shed particles ($\sim 90\%$) are lead dioxide. This explanation, however, is not completely consistent with other experimental observations. In discharged plates, only small amounts of PbO_2 particles are encapsulated and isolated by PbSO_4 crystals. Other researchers [9,10] have suggested that the PbO_2 particles undergo a morphological change in areas that are stressed and eventually lose contact with the conductive electrode. Unfortunately, none of these explanations for shedding has been successfully used to explain the increase in cycle life observed with the application of mechanical pressure to the electrode.

In this paper, we will use the agglomerate of spheres model (AOS) and its explanation for shedding to estimate the mechanical pressures required to stabilize the electrode structure so as to increase its life. In Section 2, we will use tabulated thermodynamic data along with methods previously reported [15] to establish a better estimate for the surface tension of lead dioxide, an important parameter in the AOS Model. In Section 3, we will discuss the AOS model and provide an alternative explanation for some of the model's features. We will then use the AOS Model and the improved estimate for the PbO_2 surface tension in Section 4 to calculate the mechanical compressions required to stabilize the lead dioxide particles in the positive electrode. This calculation is based on the AOS model premise that a critical ratio between the sphere and neck radii exists and that the neck will disappear for ratios above this critical value. In Section 5, we will summarize our work and give our conclusions.

2. Surface tension calculations

In one of the first papers discussing the AOS model, Winsel et al. [11] provides an order of magnitude estimate for the surface tension of lead dioxide. This estimate, 1.0 J/m^2 , was selected in accordance with typical values of solids previously reported [12,13]. Although this order of magnitude estimate was sufficient for making some general predictions about the AOS model, one of the major uncertainties associated with investigating the kinetics of the positive electrode (see Atlung et al. [14]) was the value for this surface tension. Our analysis of the effects that mechanical compression has on the life of the positive electrode also depends on the surface tension of PbO_2 and so, in order to reduce the uncertainty in our analysis, we decided to develop a better estimate for this important parameter.

We use an approach invented by Tanaka et al. [15] and explained in their paper entitled "Application of Thermodynamic Databases to the Evaluation of Surface Tensions of Molten Alloys, Salt Mixtures and Oxide Mixtures." They derive relationships between the excess Gibbs energy in the bulk phase and that in the surface phase for molten alloys and molten ionic mixtures. They use these relationships with Butler's equation [16] to calculate the surface tension of some molten alloys and ionic mixtures. Unfortunately, they do not compute the surface tension for PbO_2 although they do estimate the surface tension for Pb, PbO, and PbCl_2 . The surface tensions of Pb and PbO are 0.52 J/m^2 and 0.15 J/m^2 , respectively, as reported by Tanaka et al. [15]. We will show that the surface tension of PbO is a better estimate for the surface tension of PbO_2 than the previous estimate of 1 J/m^2 .

We will use the method given in Ref. [15] to estimate the surface tension of PbO_2 . In this method, the surface tension γ of pure liquid metals and pure ionic melts at their melting points is determined by the following relation:

$$\gamma_x = (1 - \beta) \Delta_1^{\text{g}} H_{\text{m},x} / A_x \quad (1)$$

$\beta = 0.83$ for liquid metals, $\beta = 0.94$ for molten ionic mixtures including oxide mixtures, and $\Delta_1^{\text{g}} H_{\text{m},x}$ = evaporation energy at the melting point.

The expression for A_x is provided below:

$$A_x = LN_0^{1/3} V_x^{2/3}$$

where $L = 1.0$ for ionic mixtures including oxide mixtures, N_0 = Avogadro's number (6.02252×10^{23} atoms/mol), V_x = molar volume of substance.

Although the information on $\Delta_1^{\text{g}} H_{\text{m}}$ for molten oxides is not generally available in databases, $\Delta_1^{\text{g}} H_{\text{m}}$ can be associated with T_m , the melting temperature. When the evaporation energy is related to the melting temperature, the above equation can be written as

$$\gamma_x = \alpha T_m / A_x \quad (2)$$

where $\alpha = 14.2 \text{ J/K}$ and is an empirically measured value while A_x is defined as before.

We can use Eq. (2) to estimate the surface tension of PbO_2 . We will assume the “extrapolated” melting temperature for PbO_2 to be approximately 850 K, a value slightly higher than the melting temperature of PbO , 835 K [15]. We estimate the specific volume of PbO_2 at its melting point to be approximately $28.9 \times 10^{-6} \text{ m}^3/\text{mol}$. This number is estimated by assuming the ratio of the specific volumes of PbO and PbO_2 at the standard temperature is the same as at their melting temperature. We can now estimate the surface tension of PbO_2 at its theoretical melting point and use it in the AOS model because the model assumes the material to be in a condensed liquid phase [17].

When the above numbers are substituted into Eq. (2), we estimate the value for the surface tension of PbO_2 to be approximately 0.15 J/m^2 . This value is very close to the surface tension of PbO but considerably less than 1.0 J/m^2 . We use this improved estimate for the surface tension of PbO_2 in our analysis of the AOS model as well as to analyze mechanical compression.

3. AOS model

The agglomerate of spheres model was developed by Winsel et al. [11] 9 years ago. Since that time the model has been very successful in explaining some peculiar behavior exhibited by lead–acid batteries [18–25]. The AOS model takes the view that the positive electrode consists of spheres connected together through neck regions. Fig. 1 shows two spheres connected together by a neck, and this simple figure illustrates the important aspects of the model. The AOS model includes surface tension as one of the electrode reaction processes in a

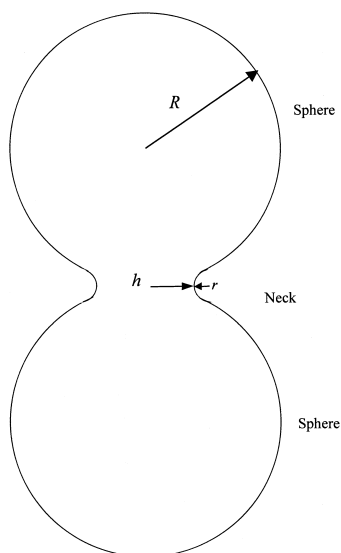


Fig. 1. Geometry of the AOS model.

manner similar to how surface tension is included in sintering processes [26]. Although the electrode consists of different size particles and necks, the surface of the electrode can still be characterized by different radii of curvature, and the AOS model provides a framework by which these curvatures and the surface tension associated with these curvatures can be analyzed.

In Fig. 1, we see the sphere has a positive radius of curvature (i.e., the radius lies within the body) and the Laplace pressure, P_S , associated with this curvature is

$$P_S = 2\gamma/R \quad (3)$$

where γ = surface tension of PbO_2 ; R = sphere's radius.

Similarly, at the neck the Laplace pressure, P_N , is

$$P_N = \gamma \left(\frac{1}{h} - \frac{1}{r} \right) \quad (4)$$

where h = neck's radius; r = radius of curvature between sphere and neck.

The negative sign in front of the second term occurs because the radius of curvature, r , lies outside the bodies of the sphere and neck. The Laplace pressure, P_N , is usually negative because the radius of curvature between the sphere and neck, r , is much smaller than the neck's radius, h .

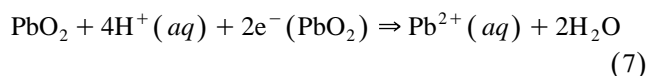
A Gibb's free energy term can be associated with these pressures so that the influence of surface tension and curvature can be quantified. The potentials E_S and E_N associated with the sphere's and neck's pressures, respectively, are

$$E_S = \frac{\gamma V_0}{RF} \quad (5)$$

$$E_N = \frac{\gamma V_0}{2F} \left(\frac{1}{h} - \frac{1}{r} \right) \quad (6)$$

where V_0 = specific volume of PbO_2 , F = Faraday's constant (96,485 C/mol). We will use these energy terms to investigate the effect surface tension has on the processes occurring at the positive electrode.

The standard reaction occurring at the positive electrode, written down in the cathodic direction, is given as



The electrode potential, E_{PbO_2} , that results from Eq. (7) is

$$E_{\text{PbO}_2} = E_{\text{PbO}_2}^0 - \frac{R'T}{2F} \ln(a_{\text{Pb}^{2+}}) + \frac{2R'T}{F} \ln(a_{\text{H}^+}(aq)) \quad (8)$$

where $E_{\text{PbO}_2}^0$ = standard potential of the lead dioxide electrode, $a_{\text{Pb}^{2+}}$ = thermodynamic activity of the plumbous ions in the electrolyte solution, a_{H^+} = thermodynamic activity of the hydrogen ions in the electrolyte solution, R' = gas constant ($8.3143 \text{ J (K mol)}^{-1}$), T = temperature.

At 298 K, and assuming the $[H^+]$ concentration is the same as its activity, Eq. (8) becomes

$$E_{\text{PbO}_2}(v) = 1.449 - 0.0295 \log(a_{\text{Pb}^{2+}}(aq)) - 0.118 \text{ pH} \quad (9)$$

When we include the potentials associated with the surface tension terms, the potentials for the sphere, $E_{\text{PbO}_2}^S$, and neck, $E_{\text{PbO}_2}^N$, become

$$E_{\text{PbO}_2}^S(v) = 1.449 - 0.0295 \log(a_{\text{Pb}^{2+}}(aq)) - 0.118 \text{ pH} + \frac{\gamma V_0}{RF} \quad (10)$$

and

$$E_{\text{PbO}_2}^N(v) = 1.449 - 0.0295 \log(a_{\text{Pb}^{2+}}(aq)) - 0.118 \text{ pH} + \frac{\gamma V_0}{2F} \left(\frac{1}{h} - \frac{1}{r} \right) \quad (11)$$

These two equations (Eqs. (10) and (11)) provide the basic relationships for our analysis.

From these two equations we see that a potential exists between the sphere and neck according to the following equation

$$\Delta E_{\text{PbO}_2} = E_{\text{PbO}_2}^S - E_{\text{PbO}_2}^N = \frac{\gamma V_0}{RF} - \frac{\gamma V_0}{2F} \left(\frac{1}{h} - \frac{1}{r} \right) \quad (12a)$$

or

$$\Delta E_{\text{PbO}_2} = \frac{\gamma V_0}{2F} \left(\frac{2}{R} + \frac{1}{r} - \frac{1}{h} \right) \quad (12b)$$

This potential is positive and shows that the material in the sphere will preferentially move to the neck. However, according to the AOS model, a neck is only stable if the difference in voltage potential does not become too large. When the ratio of sphere radius to neck radius becomes too large, a large voltage difference develops and causes the neck to disintegrate (see Winsel et al. [11]).

Atlung et al. [14] investigated the influence that surface tension had on the reactions of the positive electrode and these investigators were not able to verify the mechanism whereby the neck disintegrates. In fact, according to their analysis the action of surface tension should produce cylinder type structures, not spheres and necks. They also investigated the kinetics associated with the surface tension and found that the reactions are sufficiently rapid that within a few hours the surface tension will cause the diameter of the neck to grow from a point contact to $\sim 20\%$ of the particle diameter. From BET considerations, they assume the particle radius to be approximately 0.60×10^{-5} cm (0.06 μm). In addition to the uncertainty ascribed to this radius, they also assume a value for the surface tension, γ , of 1.0 J/m². In Section 2, we established an improved estimate for the surface tension so that some of the uncertainty in the kinetic analysis can be eliminated. In the remaining part of this section, we will also present an

alternative view of the ‘‘AOS’’ model that preserves the essential features of the model but answers some questions posed by these investigators.

We believe that the gassing or oxygen evolution reaction must be included in the ‘‘AOS’’ model to explain its main features. We will begin our analysis by treating the PbO₂ electrode as an oxygen electrode. Pohl and Rickert [27] showed that the PbO₂ electrode can be treated as an oxygen electrode in that oxygen is one of the components of lead dioxide and oxygen may be exchanged between the oxide and the electrolyte in a manner similar to the exchange of oxygen between an oxygen electrode and the solution. The only difference is that oxygen exists in the form of O₂ molecules at an oxygen electrode, whereas at the lead dioxide electrode, oxygen exists as a component of the compound PbO₂. The potential of the oxygen electrode can be written as

$$E_{\text{O}_2}(v) = 1.229 + 0.0148 \log(P_{\text{O}_2}/P_{\text{O}_2}^0) - 0.0592 \text{ pH} \quad (13)$$

where $P_{\text{O}_2}^0$ = standard pressure of 1 atm.

Starting with Eq. (13), Pohl and Rickert [27] derived the equation for the potential of the lead dioxide electrode (Eq. (8)), which can also be written as Eq. (15) as shown below.

These investigators studied the changes in stoichiometry of the lead dioxide electrode. They considered the lead dioxide electrode to have a chemical composition of PbO_{2- δ} ($x\text{H}_2\text{O}$). The index ‘‘2- δ ’’ provides for a variable deviation in the ideal stoichiometry, and the ‘‘ $x\text{H}_2\text{O}$ ’’ states that a variable amount of water is present in the electrode. These investigators experimentally established the range for this deviation to be $0.003 \leq \delta \leq 0.016$. This range for the deviation of the lead dioxide composition becomes extremely important in the ‘‘AOS’’ model. Pohl and Rickert also established an empirical relationship between the deviation, δ , and the equilibrium partial pressure P_{O_2} (PbO₂) as given below

$$\delta \approx [P_{\text{O}_2}(\text{PbO}_2)/P_{\text{O}_2}^0]^{-0.119}/82 \quad (14)$$

The equation is valid for partial pressures between the range of approximately 10^{-1} to 10^4 atm. When the partial pressure of Eq. (14) is substituted into Eq. (13), the resulting expression for the lead dioxide electrode becomes

$$E_{\text{PbO}_2}(v) = 0.991 - 0.124 \log \delta - 0.0592 \text{ pH} \quad (15)$$

This equation is also given by Winsel et al. in Ref [11]. As previously noted, Eq. (15) is an alternative way of writing the potential of the lead dioxide electrode as given by Eq. (8). We can now add the potentials associated with the surface tension of the sphere and neck to Eq. (15) giving

$$E_{\text{PbO}_2}^S(v) = 0.991 - 0.124 \log(\delta_s) - 0.0592 \text{ pH} + \frac{\gamma V_0}{RF} \quad (16)$$

and

$$E_{\text{PbO}_2}^{\text{N}}(v) = 0.991 - 0.124 \log(\delta_{\text{N}}) - 0.0592 \text{pH} - \frac{\gamma V_0}{2F} \left(\frac{1}{r} - \frac{1}{h} \right) \quad (17)$$

The equations given above (Eqs. (16) and (17)) are the lead dioxide potentials for the sphere and neck regions, respectively, for the chemical reaction given by Eq. (7) and represent the same potentials as given by Eqs. (10) and (11).

As previously discussed, we see that the sphere region has a higher potential than the neck region due to the positive contribution of its surface tension to the potential. This higher potential causes the discharge of the sphere region to be favored over that of the neck region. In this manner, the spheres are discharged while the necks are preserved. This prediction that the sphere region will discharge before the neck region is one important feature of the ‘‘AOS’’ model.

We can also see from Eqs. (16) and (17) that a potential exists between the sphere and neck under open circuit conditions. If we assume that the stoichiometry between the sphere and neck equalize under these conditions (i.e., $\delta_{\text{S}} = \delta_{\text{N}}$), then the difference in potential between the sphere and neck regions is simply the potential difference attributed to the surface tension terms as given by Eqs. (12a) and (12b). Under these conditions, the necks will grow at the expense of the spheres. The rate of growth associated with this process will be dependent upon the sphere’s radius and the surface tension [14]. The prediction that the neck region will increase under open circuit conditions is another important feature of the ‘‘AOS’’ model.

In order to explain the other main features of the ‘‘AOS’’ model, we believe that the oxygen evolution reaction must be included with the charging reaction of the lead dioxide electrode. We will use the Pourbaix diagram from [27] (see Fig. 2) to show the interaction between these two reactions. The oxygen evolution equation is established by plotting the potential of the oxygen electrode (Eq. (13)) with the partial pressure of oxygen set equal to one atmosphere and is shown as line 1 in Fig. 2. Note that the potential of the lead dioxide electrode, Eq. (9), as a function of pH is shown as line 0 on the figure where the concentration of the Pb^{2+} ion is held constant (i.e., 1 mol/dm³). In order to understand what occurs during the charging process, we must determine under what conditions the oxygen evolution reaction is favored over the lead dioxide reaction.

During charge, a voltage, V_{C} , is applied to the positive electrode to overcome the potentials given by Eqs. (16) and (17). In the sphere region, the surface tension potential favors the discharge of PbO_2 and works against this charging voltage. In the neck region, however, the surface tension term works with the charging voltage so that the

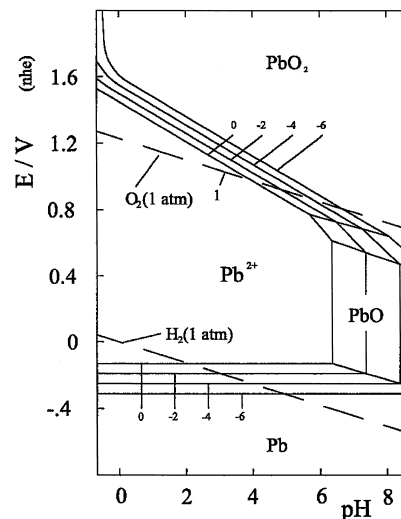


Fig. 2. Pourbaix diagram of the lead/water system (0, -2, -4, -6 lines indicate Pb^{2+} concentrations of 1, 10^{-2} , 10^{-4} , 10^{-6} mol/dm³, respectively).

effective voltage being applied to the neck is more positive than at the sphere. We can show this difference by moving the two surface tension potentials to the left hand side of Eqs. (16) and (17) as given below

$$V_{\text{C}} - \frac{\gamma V_0}{RF} = 0.991 - 0.124 \log(\delta_{\text{S}}) - 0.0592 \text{pH} \quad (18)$$

$$V_{\text{C}} + \frac{\gamma V_0}{RF} \left(\frac{1}{r} - \frac{1}{h} \right) = 0.991 - 0.124 \log(\delta_{\text{N}}) - 0.0592 \text{pH} \quad (19)$$

From these equations and the Pourbaix diagram (Fig. 2), we see that the effective potential at the neck is higher than at the sphere. Due to this higher potential, gas evolution will be more favored at the neck than at the sphere.

For both the neck and sphere to be charged simultaneously, the difference in voltage due to surface tension must be accommodated by the difference in deficiencies, δ , of the PbO_2 electrode. Since the neck region has the higher potential, the deficiency, δ_{N} , associated with this region must be smaller (Eq. (19)) than the sphere’s deficiency, δ_{S} (Eq. (18)). This assumes that the electrolyte values in these regions are the same. If we subtract these two equations, we find

$$\frac{\gamma V_0}{2F} \left(\frac{1}{r} - \frac{1}{h} + \frac{2}{R} \right) = 0.124 \log(\delta_{\text{S}}/\delta_{\text{N}}) \quad (20)$$

The deficiencies in the lead dioxide electrode have a relatively narrow range, $0.003 \leq \delta \leq 0.016$, so that the maximum potential difference occurs when $\delta_{\text{N}} = \delta_{\text{min}} = 0.003$ and $\delta_{\text{S}} = \delta_{\text{max}} = 0.016$. Substituting these values for δ_{N} and δ_{S} into the above equation gives

$$\frac{\gamma V_0}{2F} \left(\frac{1}{r} - \frac{1}{h} + \frac{2}{R} \right) \leq 0.124 \log(\delta_{\text{max}}/\delta_{\text{min}}) \quad (21)$$

This equation gives the maximum difference in potential that can be supported by deficiencies in the PbO_2 lattice.

Eq. (21) can be simplified because the radii of curvature are not independent and are geometrically related (see Fig. 1) as shown below

$$R^2 + (h + r)^2 = (R + r)^2 \quad (22a)$$

$$r = h/2 \left(\frac{R}{h} - 1 \right) \quad (22b)$$

When this relationship between the radii of curvature is substituted into Eq. (21), it becomes

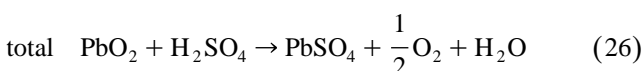
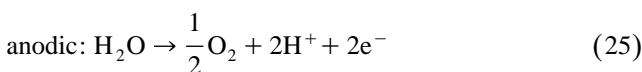
$$\frac{\gamma V_0}{RF} \left[\left(\frac{R}{h} \right)^2 - \frac{3}{2} \left(\frac{R}{h} \right) + 1 \right] \leq 0.124 \log(\delta_{\max}/\delta_{\min}) \quad (23)$$

For a given sphere radius, R , the maximum ratio of sphere to neck radii, R/h , is constrained. When the neck is small in comparison with the sphere, the potential difference associated with the surface tension between the sphere and neck exceeds the potential term associated with the difference in deficiencies between the sphere and neck. The value for the potential difference associated with the lattice deficiencies (i.e., right side of Eq. (23)) is 0.09 v which, for the small distances involved, is substantial.

Our interpretation of the ‘‘AOS’’ model predicts that the sphere and neck can be charged simultaneously, so that no oxygen evolution occurs, when the ratio for R/h is less than a critical value. The value of R/h which makes the left and right terms in Eq. (23) equal, will be called the critical (R/h) ratio or $(R/h)_{\text{crit}}$. For a sphere having a radius of $R = 10^{-5} \text{ cm}$, $(R/h)_{\text{crit}}$ equals 16.2. The value of $(R/h)_{\text{crit}}$ for different size particles or spheres will be used in Section 4 to analyze the effects of compression on the positive electrode.

What happens when (R/h) exceeds $(R/h)_{\text{crit}}$? We believe that when $(R/h)_{\text{crit}}$ is exceeded and the potential difference between the sphere and neck becomes too large, then oxygen evolution is favored over the PbO_2 charging reaction in the neck region.

From the Pourbaix diagram (Fig. 2), we see that thermodynamically, the oxygen evolution reaction is indeed favored in the range of pH values where charging occurs. After the deficiencies in the neck reach the minimum value, any additional increase in voltage produces oxygen at the neck. According to Garche [28], the oxygen evolution reaction can be written as



The reaction shows oxygen being liberated while lead ions, Pb^{2+} , dissolves into the electrolyte. Once in solution, the lead ions migrate to the sphere where they are converted back into PbO_2 , reverse reaction of Eq. (24). In this fashion, lead ions are transferred from the neck to the sphere.

As lead ions leave the neck, the neck becomes smaller, causing a larger potential difference between the sphere and neck. With this unstable situation, the neck quickly deteriorates, causing the sphere to separate from the electrode. We believe that this is the physical process that produces ‘‘shedding.’’ The ‘‘AOS’’ model, when considered with the oxygen evolution reaction, predicts that the lead ions in the neck will be transferred to the sphere and that the neck will be destroyed when $(R/h) \geq (R/h)_{\text{crit}}$.

We will now consider the case where the electrode is being overcharged. In this situation the electrode is charged and the lead ions are depleted in the electrolyte. The low concentrations require higher voltages for the charging reaction to proceed. Fig. 2 shows the higher voltages associated with the different Pb^{2+} concentrations. The higher voltages can cause gassing to occur in both the neck and sphere regions. Therefore, under overcharge conditions, the necks can deteriorate even when $(R/h) \leq (R/h)_{\text{crit}}$. The AOS model, when coupled with the oxygen evolution reaction, predicts that shedding can occur even when $(R/h) \leq (R/h)_{\text{crit}}$ during overcharge. Hollenkamp et al. [29] observed that battery life was reduced by half when the amount of overcharge was doubled. This observation is consistent with our explanation of the processes that cause the necks to deteriorate when plates are overcharged.

In this section, we gave an alternative explanation to the standard ‘‘AOS’’ model. Our explanation couples the oxygen evolution reaction to the ‘‘AOS’’ model to describe the processes occurring at the positive electrode during charge and overcharge. This new explanation shows how surface tension and gas evolution work together to produce shedding but still preserves the main features of the standard ‘‘AOS’’ model. These features are the following.

(1) The spheres have more of a tendency than the necks to discharge.

(2) Under open circuit conditions, the necks have a tendency to grow at the expense of the spheres.

(3) Both the sphere and neck can be charged if $(R/h) \leq (R/h)_{\text{crit}}$. When $(R/h) \geq (R/h)_{\text{crit}}$, oxygen is evolved at the neck and lead ions from the neck pass into the electrolyte where they participate in the charging reaction at the sphere. In this manner, lead ions are moved from the neck to the sphere until the neck is destroyed and shedding occurs.

(4) During overcharge, oxygen can evolve in the neck region and the neck can be destroyed even when $(R/h) \leq (R/h)_{\text{crit}}$.

Our interpretation of the AOS model clearly describes how surface tension and the oxygen evolution reaction

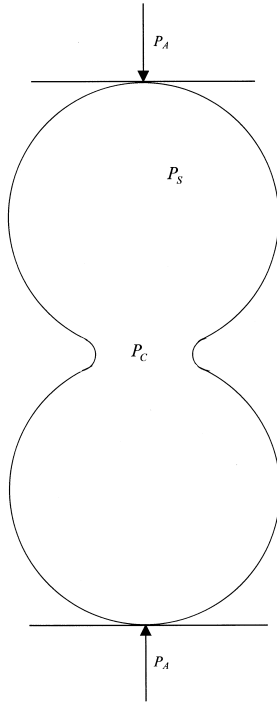


Fig. 3. Mechanical compression and the AOS model.

produces shedding. However, more experimental work is needed to verify this explanation of shedding and to provide a more quantitative understanding of battery life.

4. Mechanical pressure explanation

In this section, we provide a quantitative explanation for the beneficial effects on cycle life achieved by applying mechanical compression to the face of the positive electrode. The explanation relies on the concept that a critical value exists for the ratio of the sphere to neck radii, $(R/h)_{\text{crit}}$. This concept is a central feature of the AOS model. Our analysis of mechanical compression does not depend on the exact physical process by which the neck disintegrates when $(R/h) \geq (R/h)_{\text{crit}}$. We only assume that $(R/h)_{\text{crit}}$ exists and that mechanical compression helps to stabilize the neck so that $(R/h) \leq (R/h)_{\text{crit}}$.

In Fig. 3, we show mechanical pressure, P_A , being exerted on two spheres which are connected through a neck region. The mechanical pressure is applied over an area of $(2R)^2$ while the pressure in the neck exists over an area of πh^2 . At equilibrium, the force on the sphere must be equal to the force being transmitted through the neck so that

$$P_C = \frac{4}{\pi} \left(\frac{R}{h} \right)^2 P_A \quad (27)$$

where P_C = contact pressure in the neck.

When the force causing the axial pressure is initially applied, the stress at the point of contact between the spheres is equal to the material's yield stress, σ_{yield} . The

material continues to yield until the area of the neck increases to a value where the forces are balanced (i.e., $P_C = \sigma_{\text{yield}}$). When this occurs, the forces are balanced but the system is not in thermodynamic equilibrium since the contact region is at a higher stress than the Laplace pressure of the sphere, P_S . Due to surface tension, the material in the spheres will have a tendency to flow to the neck region until the contact pressure equals the Laplace pressure (i.e., $P_C = P_S$). This process is aided by the addition of energy, either thermal or electrochemical. When thermal energy is used, the process is called sintering. However, as previously discussed, in order for the neck to be stable during charging, the ratio of the sphere and neck radii must be constrained so that $(R/h) \leq (R/h)_{\text{crit}}$. In our analysis, we will assume that the pressure in the neck due to the application of mechanical pressure is the yield strength of lead dioxide, $P_C = \sigma_{\text{yield}}$.

Under the above assumptions, we can calculate the axial pressure needed to produce a neck so that $(R/h) = (R/h)_{\text{crit}}$. For a given radius, R , we can use Eq. (23) to solve for $(R/h)_{\text{crit}}$.

$$\frac{\gamma V_0}{RF} \left[\left(\frac{R}{h} \right)_{\text{crit}}^2 - \frac{3}{2} \left(\frac{R}{h} \right)_{\text{crit}} + 1 \right] = 0.124 \log(\delta_{\text{max}}/\delta_{\text{min}}) \quad (28)$$

Once $(R/h)_{\text{crit}}$ is determined, we find the axial pressure from Eq. (27)

$$P_A = \frac{\pi}{4} \frac{\sigma_{\text{yield}}}{\left(\frac{R}{h} \right)_{\text{crit}}^2} \quad (29)$$

We use the tensile stress of PbO_2 , $(300 \pm 200) \times 10^5$ Pa as given in Refs. [30,31], to approximate the yield stress of PbO_2 . Although the yield stress is lower than the tensile stress of a material, for a brittle material such as PbO_2 , the yield stress should be close to the tensile stress.

We use the nominal value of 300×10^5 Pa for σ_{yield} but show the uncertainty in P_A (see Table 1) due to the uncertainty in the tensile stress of PbO_2 . The largest sphere shown in Table 1 has a radius of 1 μm and can be stabilized with a very low amount of compression. The smallest sphere, $R = 0.01$ μm , requires a much larger amount of compression to be stable. As the radius of the sphere decreases from 1 to 0.09 μm , the compression needed to give a stable neck increases from 10^4 Pa (0.1 bar) to 10^5 Pa (1 bar).

Table 1
Compression analysis results

Sphere radius R (μm)	$(R/h)_{\text{crit}}$	P_A (10^5 Pa)
1.00	49.7	0.10 ± 0.07
0.50	35.3	0.19 ± 0.13
0.10	16.2	0.91 ± 0.61
0.09	15.4	1.00 ± 0.66
0.05	11.7	1.76 ± 1.13
0.01	5.2	7.62 ± 5.80

From BET surface area calculations, investigators [11] have estimated the average radius of the lead dioxide particle to be approximately 0.1 μm while other investigators [14] have estimated this radius to be approximately 0.06 μm . At low mechanical pressures, only the larger particles are stabilized. As the pressure is increased to approximately 10^5 Pa (1 bar), most of the particles ($R \geq 0.09$ μm) are stabilized. Any further increase in pressure will not have a substantial increase in life since most of the particles are stabilized. These calculations are in agreement with the experimental observations and provide an explanation for how such a small amount of mechanical compression can substantially improve cycle life.

5. Summary and conclusions

In this paper, we provide an improved estimate of the surface tension of PbO_2 . The surface tension is an important parameter in the AOS model and was initially given an approximate value of 1.0 J/m^2 . Although this value was sufficient for helping to develop the general outline for the model, a better estimate is needed for more detailed analysis. Using techniques developed by other researchers, we estimated the PbO_2 surface tension to be approximately 0.15 J/m^2 . We use this improved estimate to analyze the effect that mechanical compression has on the life of the positive electrode.

During our investigations into the AOS model and mechanical compression, we developed an alternative explanation for some features of the AOS model. In this alternative explanation, oxygen evolution in the neck region must be considered along with surface tension when charging the positive electrode. When the difference in the lattice deficiencies between the neck and sphere produces a potential difference large enough to equalize the potential difference caused by the surface tension between these two regions, then both the neck and sphere can be charged simultaneously. This requirement reduces to a condition on the ratio of the sphere to neck radii such that $(R/h) \leq (R/h)_{\text{crit}}$. When $(R/h) \geq (R/h)_{\text{crit}}$, the potential in the neck region favors oxygen evolution. Oxygen is produced in the neck region and Pb^{2+} ions dissolve from the neck into the electrolyte and are eventually converted to PbO_2 at the sphere. In this manner, when $(R/h) \geq (R/h)_{\text{crit}}$, the lead ions are transferred from the neck to the sphere and the neck disintegrates causing “shedding.”

During overcharge, the lead ions in the electrolyte disappear so that the PbO_2 charging reaction requires higher voltages and oxygen evolution can occur in both the sphere and neck. The oxygen that is evolved in the neck region causes the neck to disintegrate. Overcharging therefore causes shedding even for situations where $(R/h) \leq (R/h)_{\text{crit}}$.

The $(R/h)_{\text{crit}}$ parameter is central to the AOS model and also serves as the basic assumption for our analysis of

mechanical compression. Additional experimental work needs to be performed in order to better understand the physical processes involved with the disintegration of the neck. Certainly, a better understanding of what occurs in the neck and sphere region during charge is essential for verifying our interpretation of the AOS model.

The primary goal of our research was to use the AOS model to analyze the effect that mechanical compression has on the life of the positive electrode. We base our analysis on the concept that a critical ratio exists for the sphere and neck radii, $(R/h)_{\text{crit}}$. The analysis shows that mechanical compression helps to improve life because it causes a broadening of the necks and reduces the (R/h) ratio. Applying axial pressure of about 10^5 Pa, (1 bar), to the face of the positive electrode causes the (R/h) ratio of spheres having a radius of 0.09 μm to be less than $(R/h)_{\text{crit}}$. From BET measurements, the size of PbO_2 particles is typically close to this value. The application of this amount of compression therefore stabilizes most of the PbO_2 particles in the positive electrode.

Our analysis agrees closely with experimental observations. The magnitude of the mechanical compression we calculate for long battery life is similar to what has been observed, approximately 10^5 Pa (1 bar). Our analysis predicts that life should increase with an increase in mechanical compression until most of the particles are stabilized. This prediction also agrees with experimental observations. The close correlation between our analysis and the experimental observations not only helps to explain the beneficial effect of mechanical compression on life but also helps to validate the AOS model.

Acknowledgements

The authors would like to thank Prof. Winsel, Dr. Bashtavelova, and Dr. Willer for the many enjoyable conversations we had concerning the Agglomerate of Spheres Model. Also, we would like to thank the Institut für Solare Energieversorgungstechnik e.V., ISET, the University of Kassel, and the University of Idaho for supporting the sabbatical of Dr. Edwards at the University of Kassel and ISET.

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