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7 **Transmission X-Ray microscopy of the galvanostatic growth of lead sulfate on lead: Impact**
8 **of lignonsulfonate**
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14 K. W. Knehr^{a,1}, Christopher Eng^b, Jun Wang^b, and Alan C. West^a
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19 ^aDepartment of Chemical Engineering, Columbia University, New York, NY 10027, USA
20

21 ^bPhoton Sciences Directorate, Brookhaven National Laboratory, Upton, NY 11973, USA
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¹Author to whom correspondence should be addressed: e-mail: kwk2111@columbia.edu; Phone: 1-212-854-4546; Fax: 1-212-
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Abstract

The galvanostatic growth of PbSO_4 on Pb in H_2SO_4 was studied using scanning electron microscopy and *in situ* transmission x-ray microscopy (TXM). Images from the TXM are used to investigate the effects of sodium lignosulfonate on the PbSO_4 formation and the initial growth of the PbSO_4 crystals. Sodium lignosulfonate is shown to retard, on average, the growth of the PbSO_4 crystals, yielding a film with smaller crystals and higher crystal densities. In addition, results from experiments with and without sodium lignosulfonate indicate an increase in the nucleation rate of the PbSO_4 crystals when the oxidation current is applied, which was attributed to an increase in the supersaturation of the electrolyte. Furthermore, an analysis of the growth rates of individual, large crystals showed an initial rapid growth which declined as the PbSO_4 surface coverage increased. It was concluded that the increase in PbSO_4 provides additional sites for precipitation and reduces the precipitation rate on the existing crystals. Finally, the potential-time transient at the beginning of oxidation is suggested to result from the relaxation of a supersaturated solution and the development of a PbSO_4 film with increasing resistance.

Keywords

Lead acid battery; transmission x-ray microscopy; negative electrode; expander; nucleation and growth

1. Introduction

One of the major factors limiting the widespread use of lead-acid batteries for smart-grid applications (*e.g.*, load-leveling, distribution deferral, and renewable energy storage) is a relatively short cycle life when compared to other electrochemical energy storage technologies [1]. The short cycle life can be attributed to a variety of aging processes, including: anodic corrosion, positive active mass degradation, active mass sintering, and the irreversible formation of PbSO_4 on the surface of the electrodes (*i.e.*, sulfation) [2]. The prevalence of each aging mechanism on the various components in the battery strongly depends on the operating conditions and design of the system. For one of the components, the negative electrode, one of the major life limiting factors is sulfation, which occurs when the PbSO_4 film becomes irreversible and cannot be fully converted back into Pb after a sufficient charge [3].

For over 70 years, attempts have been made to increase the lifetime of the battery by including chemical additives in the active mass of the negative electrode [4]. Out of all the additives, wood-derived lignosulfonates (*i.e.*, lignin) have been the most extensively studied and thorough overviews of the progress on this topic can be found in [5-7]. In recent years, further attempts to increase the lifetime have led to the development of novel chemical additives which are tailored to the specific applications of the battery. For batteries used in high-rate partial-state-of-charge applications, additions of polyaspartic acid, synthetic additive blends, and high amounts of carbon black have been shown to reduce sulfation and improve battery life [8-16]. While the results of these studies are impactful, the advances in performance typically result from trial and error testing of full-size batteries. In order to further identify methods for reducing sulfation, it would be beneficial to obtain a more fundamental understanding of the mechanisms of crystal formation, and how additives affect this process.

One promising method for researching the mechanisms of crystal formation is the use of imaging techniques to obtain *in situ* observations of the growth processes. Recently, several authors have utilized atomic force microscopy (AFM) to study the effects of operating conditions (*e.g.*, open circuit standing time and cyclic voltammetry sweep rate) and the impact of electrolyte additives on the morphology and growth rates of the PbSO₄ crystals [17-23]. In these studies, the growth and reduction of PbSO₄ was controlled using potentiostatic and voltammetric techniques, while the PbSO₄ crystals were simultaneously visualized using AFM. Further advancement of this work would require the use of a new technique which can overcome the relatively long acquisition time (52 seconds per image) associated with the AFM. In addition, it may be beneficial to utilize constant current (galvanostatic) operating conditions, which are typically used during the testing of full-scale batteries [10-12]. Galvanostatic operating conditions would make it easier to directly relate the observations and conclusions from the microscopic, *in situ* work with the full-scale, macroscopic battery performance.

In our previous work, transmission X-ray microscopy (TXM), an imaging technique with a fast acquisition time (up to one second per image), was used to study the initial growth, passivation, and reduction of the PbSO₄ film on Pb in H₂SO₄ [24]. The present study seeks to expand this work by investigating the galvanostatic growth of PbSO₄ in the presence of sodium lignosulfonate, an organic macromolecule which is the precursor to many commercial chemical additives (*e.g.* Vanisperse A and Vanillex N). In addition, this work seeks to further understand the mechanisms of PbSO₄ formation through an analysis of the growth of individual crystals, including an examination of the initial, galvanostatic potential-time transient. To accomplish this, both TXM and scanning electron microscopy (SEM) are employed.

2. Experimental Procedure

2.1 TXM experiments

The transmission X-ray microscopy (TXM) experiments were conducted using the same experimental set-up and procedure outlined in [24]. To study the impact of additives on the mechanisms of PbSO_4 growth, two separate experiments were conducted: one with and one without 26 ppm sodium lignosulfonate (*i.e.* lignin) added to the electrolyte. During each experiment, an electroplated Pb working electrode was assembled into an in-house designed, *in situ*, micro-electrochemical cell. The cell was placed in the transmission X-ray microscope with the X-ray beam penetrating through the Pb in a direction normal to the surface. An external half-cell compartment containing a $\text{Hg}|\text{Hg}_2\text{SO}_4$ reference electrode and a Pt counter electrode was placed outside the beam flight-path. The two compartments were connected via a tube, and the whole set-up was filled with 4.6 M H_2SO_4 (with and without lignin), which was deaerated for 3 hours with argon gas.

For both experiments, the electrochemical growth and reduction of the films were controlled using a BioLogic VMP3 potentiostat, which was connected to all three electrodes. Prior to each experiment, the ohmic resistance of the setup was determined using galvanostatic electrochemical impedance spectroscopy (EIS). This value was used to correct for ohmic drop between the reference and Pb electrodes (*i.e.*, iR compensation) during the galvanostatic experiments. After the EIS, the Pb electrode was held at constant voltages of -1.1 V and -1.2 V for 30 minutes in order to reduce any PbSO_4 that formed on the Pb while sitting in H_2SO_4 . Next, the working electrode was held at the open-circuit voltage (OCV) for 2 minutes, followed by a galvanostatic oxidation at $50 \mu\text{A cm}^{-2}$ with a cut-off voltage of -0.84 V (before correcting for ohmic drop).

The *in situ* transmission X-ray microscopy (TXM) was done at the X8C beamline of the National Synchrotron Light Source at Brookhaven National Laboratory. Imaging was performed at a X-ray energy of 8 keV with a $40 \times 40 \mu\text{m}$ ($1600 \mu\text{m}^2$) field of view and an exposure time of 20 seconds for each image. The moderate exposure time made it possible to generate a clear image by binning a 2×2 pixel region using the $2\text{k} \times 2\text{k}$ CCD camera, resulting in a pixel size of 39 nm [25]. Images collected from both TXM experiments were processed using a pixel-by-pixel normalization with five background images taken from the corresponding Pb sample. In addition, all images in this work underwent further refinement using ImageJ software in order to better visualize the nucleation and growth of the PbSO_4 films. A more detailed description of the image refinement procedure can be found in [24].

2.2 Experiments for SEM images

Additional electrochemical experiments with and without 26 ppm lignin in the electrolyte were performed in order to support the TXM results. Pb electrodes were formed by electroplating a 10- μm thick layer of lead onto a 38- μm thick copper substrate using the same plating procedure outlined in [24]. Prior to plating, the substrate was rinsed with isopropyl alcohol and de-ionized water. After plating, the electrode was rinsed with de-ionized water and dried with argon gas. The electrochemically active area of the Pb ($\sim 0.1 \text{ cm}^2$) was defined by melting paraffin wax onto the sample. The exact active area for each sample was obtained by analyzing an image of the electrode using the area selection tools available in the ImageJ software [26]. The electrochemical experiments were conducted using a three-electrode system with a $\text{Hg}|\text{Hg}_2\text{SO}_4$ reference electrode and a Pt counter electrode. All three electrodes were placed in a beaker containing 70 mL of 4.6 M H_2SO_4 (with and without 26 ppm lignin), which

was deaerated for 3 hours with argon gas. The entire beaker was blanketed with argon gas for 15 minutes and then sealed with paraffin wax for the entirety of the experiment.

The electrochemical experiments were controlled using a μ AutolabIII potentiostat (Metrohm USA, Inc.). The Pb electrode was first held at a constant voltage of -1.1 V for 30 minutes in an attempt to reduce any PbSO_4 that formed on the Pb while sitting in H_2SO_4 . Next, the working electrode was held at the open-circuit voltage for 2 minutes, followed by a galvanostatic oxidation at $50 \mu\text{A cm}^{-2}$. The end of the oxidation was either specified by a given amount of time (*e.g.*, 1 minute) or by allowing the electrode to passivate using a cutoff voltage of -0.85 V. Immediately after the oxidation, the sample was removed from the acid, rinsed with de-ionized water, and dried with argon gas. Scanning electron microscope (SEM) images were taken of the sample surface using a Hitachi 4700 microscope. A minimum of three regions was imaged for each sample.

3. Results and Discussion

3.1 Comparison of TXM and SEM images

In order to aid in the interpretation of the results from the TXM experiments, the images obtained from the TXM were compared to SEM images taken from separate experiments. Figures 1 and 2 show a comparison of TXM and SEM images of the PbSO_4 films grown with and without lignin in the electrolyte, respectively. Included in both figures are images taken 3 minutes after the start of the OCV procedure (images a1 and b1) and at passivation of the electrode (images a2 and b2). Good agreement is observed between the SEM and TXM images, especially for the images taken 3 minutes after the start of OCV (images a1 and b1) and for the experiments conducted with 26 ppm lignin in the electrolyte (Figure 2). In Fig. 2, both the TXM and SEM images at passivation (Fig. 2, images a2 and b2) depict a film containing a few, large

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4 crystals dispersed among many, smaller, PbSO_4 crystallites. In contrast, the SEM image taken at
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6 passivation from the experiment without lignin in the electrolyte (Fig. 1, image b2) shows a film
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8 containing many, large, overlapping crystals. It appears that these overlapping crystals were
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10 difficult to deconvolute using transmission X-rays (Fig. 1, image a2), resulting in an image
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12 without clearly defined crystallites.
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20 *3.2 Impact of lignin on PbSO_4 morphology and growth*

21 *3.2.1 Oxidation until passivation*

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25 The voltage responses of the open circuit voltage (OCV) and galvanostatic oxidation
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27 steps of the TXM experiments conducted with and without 26 ppm lignin are shown in Figure 3.
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29 All times in the remaining figures throughout the paper are reported in reference to this figure.
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31 The results show that addition of lignin to the electrolyte decreased the time to passivation in the
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33 experiment by ~15%; whereby passivation is indicated by the sudden increase in voltage. The
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35 decrease in passivation time caused by lignin can be attributed to the morphological differences
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37 in the PbSO_4 films. When comparing the two films at passivation, the SEM images (images b2 in
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39 Figures 1 and 2) indicate that the film formed with lignin in the electrolyte contains higher
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41 amounts of small crystals. High amounts of small crystals result in a more densely packed
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43 morphology when the film is relatively thin. The thin, dense film blocks the diffusion of
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45 reactants, passivating the electrode with minimal PbSO_4 . A similar observation was made by
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47 Hampson and Lakeman, who conducted potentiostatic oxidations on Pb at various potentials and
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49 recorded the charge required for passivation [27]. They also concluded that films with a higher
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51 crystal density and a smaller average crystal size resulted in a quicker passivation and a smaller
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(Insert Figure 3 here)

The observed decrease in passivation time contradicts the fact that lignin is known to increase the capacity of the negative electrode in a lead acid battery [4-6, 12, 28-32]. Currently, two main mechanisms have been proposed to explain why lignin increases the capacity, neither of which is expected to be a major factor in this study. First, lignin is known to increase the capacity during the forming of the electrode by producing a high porosity, high surface area structure, which improves utilization of the active mass [4, 12, 31, 32]. In the present study, these beneficial effects are not expected to occur because electroplated Pb was used, which did not undergo an electrode formation process. In the second mechanism, lignin in the electrolyte adsorbs onto the Pb surface, which causes the PbSO_4 to precipitate on top of the lignin instead of directly onto the Pb. This results in the formation of a more porous PbSO_4 film, which improves the capacity by leaving the active Pb available for further Pb^{2+} dissolution [5, 6, 28-30]. Before lignin can adsorb onto the Pb surface, it must first complex with Pb^{2+} ions in the solution to make an insoluble molecule [33]. In the present study, the potentiostatic reductions performed at the beginning of the experiment reduced any free Pb^{2+} ions. Therefore, the lignin was unable to complex and adsorb onto the Pb at the onset of the experiment. Without an initial layer of adsorbed lignin on the Pb surface, the beneficial effects on the PbSO_4 film are reduced and no increase in capacity is observed.

3.2.2 Crystal size distributions

In order to determine the mechanism by which lignin changes the morphology of the PbSO_4 film and decreases the capacity in this study, distributions of the crystal sizes at various times during the TXM experiments were obtained by analyzing the TXM images with ImageJ software. The size of each crystal was calculated by determining the maximum length of a

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4 straight line which could be drawn from one end of the crystal to another. The measurement
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6 represents the diameter for non-spherical particles.
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9 Figures 4 and 5 show the crystal size distributions obtained from the TXM and SEM
10 experiments without and with lignin in the electrolyte, respectively. In addition, the mean,
11 median, and mode of the distributions obtained from the TXM experiments are shown in Figure
12 6. For each histogram bar in Figures 4 and 5, the crystal size on the horizontal axis corresponds
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14 to the center of the bin. The distributions of the crystals from the TXM experiments (Figures 4a
15 and 5a) were normalized based on the total amount of crystals at $t = 160$ seconds. After this time,
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17 distributions were unattainable due to overlapping of crystals in the films, which obscured
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19 determination of individual sizes (image a1 of Figures 1 and 2). Each SEM crystal distribution
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21 (Figures 4b and 5b) was obtained from three separate images of the same sample and was
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23 normalized with respect to the total number of crystals used in the study. An example image for
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25 each experiment is shown in image b1 of Figures 1 and 2. The TXM data show good agreement
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27 with the distributions obtained from the SEM images.
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42 The mechanism of action of the lignin can be revealed from an analysis of the crystal
43 distributions. For instance, Figures 4a and 6a show that the number and average size of the
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45 crystals increases during the early growth of the film without lignin. This behavior corresponds
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47 to a progressive nucleation and growth mechanism, where new crystals are continually forming,
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49 and pre-existing crystals are continually growing. In contrast, Figures 5a and 6b show that in the
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51 presence of lignin the number of crystals increases while the size distribution remains relatively
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53 the same. This trajectory in morphology indicates that lignin retards the growth of the crystals.
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59 Myrvold has shown that lignin will quickly adsorb onto PbSO_4 , and it appears that this
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adsorption prevents the growth of the crystals [33]. Assuming the crystals grow due to precipitation of Pb(II) species from the electrolyte, the adsorbed lignin most likely prevents the growth by physically blocking the precipitation sites on the crystals [34].

3.2.3 Crystal density and surface coverage

Because lignin impedes the growth of the existing PbSO₄, it is anticipated that the number of crystals will increase in the presence of lignin in order to provide enough precipitation sites for the Pb(II) species. This hypothesis is verified in Figure 7, which shows PbSO₄ crystal densities for the images obtained from the TXM and SEM experiments. Each crystal density was determined by manually counting the number of crystals using ImageJ software and dividing that number by the area of the image. Similar to the crystal size distributions in Figures 4 and 5, the crystal densities for TXM images after $t = 160$ seconds were unattainable due to the overlapping of crystals and the coalescing of the films (images a1 of Figures 1 and 2). The data points for the SEM experiments were determined from the averages of three separate images of the same sample. The error bars represent the maximum and minimum values obtained from the sample. An example image for each SEM experiment is shown in image b1 of Figures 1 and 2.

In Fig. 7a, the experiments without lignin show good agreement between the TXM and SEM data. Extrapolation of the TXM data to $t = 180$ seconds results in a crystal density of $\sim 80 \times 10^6 \text{ cm}^{-2}$, which is only 1.1 times higher than the average crystal density reported for the SEM experiments ($\sim 70 \times 10^6 \text{ cm}^{-2}$). For the experiments with lignin, there is less of an agreement between the TXM and SEM data. Extrapolation of the TXM data results in a crystal density of $\sim 90 \times 10^6 \text{ cm}^{-2}$, which is 1.3 times smaller than the average crystal density obtained from the SEM images ($\sim 120 \times 10^6 \text{ cm}^{-2}$). Despite this discrepancy, the TXM extrapolation for the experiment with lignin still resides within the error bars of the SEM data.

(Insert Figure 7 here)

Figure 7b shows the crystal densities for the TXM experiments. The results further confirm that lignin increases the crystal density. In addition, Fig. 7b shows that the rate of crystal nucleation approximately doubles in both experiments when the oxidation current is applied. The increase in crystal nucleation rate can be attributed to an increase in the oxidation rate, which increases *i*) the supersaturation concentration of Pb^{2+} in the electrolyte and *ii*) the overpotential. Both of these factors decrease the critical nucleus size, which increases the rate of nucleation [35].

The supersaturation can increase when the current is applied because the oxidation rate exceeds that at OCV. For this system, the oxidation of Pb at OCV is balanced by the following proton reduction reaction:

When the current is applied, the proton reduction rate decreases due to the increase in the electrode potential. The change in the proton reduction rate can be determined by performing a Taylor series expansion of the Tafel equation. This results in the following:

$$\Delta i = \frac{|i_{corr}| \alpha_c F}{RT} \Delta \phi \quad (4)$$

where α_c is the cathodic charge transfer coefficient ($\alpha_c = 0.5$), R is the ideal gas constant, T is the temperature, F is Faraday's constant, and $\Delta \phi$ is the change in potential applied to the electrode. $\Delta \phi$ is ~20 mV at the beginning of oxidation (Figures 3 and 12). i_{corr} is the steady state corrosion rate, which for this system is $50 \mu\text{A cm}^{-2}$. [24]. According to Eq. 4, Δi is equal to $+20 \mu\text{A cm}^{-2}$ at the beginning of oxidation, indicating that the reduction rate changes from -50

$\mu\text{A cm}^{-2}$ at OCV to $-30 \mu\text{A cm}^{-2}$ when the current is applied. Therefore, in order for the applied current to reach $50 \mu\text{A cm}^{-2}$, the actual oxidation rate can be estimated to be $\sim 80 \mu\text{A cm}^{-2}$, which is ~ 1.6 times higher than expected from the applied current.

To further understand the mechanism of growth of the PbSO_4 crystals, the surface coverage vs. time and overpotential vs. surface coverage are plotted in Figure 8. Fig. 8a indicates that the electrode is fully covered with PbSO_4 within the first 3 to 5 minutes of oxidation. The remainder of the oxidation corresponds to a thickening of the film [24]. In addition, both experiments (without and with lignin) have similar trends in overpotential (Fig. 8b), suggesting a similar mechanism of growth. The higher overpotential observed for the experiment with lignin can be attributed to the retardation in growth of the crystals. The trends in overpotential resemble the analytical expressions derived by Hills *et. al.* for the two dimensional growth of cylindrical crystals under galvanostatic conditions [36]. However, a rigorous analysis of the data to distinguish between instantaneous and progressive nucleation was not possible due to the scatter of the TXM results.

(Insert Figure 8 here)

3.3 Growth of individual crystals

In Section 3.2.2, trends in crystal size obtained from the TXM images illustrated how lignin impacted the morphology of the PbSO_4 . Although useful, the analysis cannot be applied to individual particles because size distributions (*i.e.*, mean, median, and mode) are heavily influenced by the continued nucleation of new crystals. In this section, we use TXM to track the evolution of individual PbSO_4 crystals. A select group of crystals from the experiments without and with lignin were identified whose growth evolution was visualized by the TXM. Due to the

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4 need to easily visualize the crystals, the selected crystals tended to be the largest in the films.
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6 They are highlighted in images b1 and b2 of Figure 9.
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13 In Figure 9, graphs a1 and a2 track the increase in area of the crystals (*i.e.*, the projections
14 on the substrate) during the early stages of growth. For each crystal, the two-dimensional
15 projections could not be tracked past $t = 340$ seconds due to crystal overlap and coalescence of
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17 the films. The crystals with and without lignin appear to have a similar growth pattern. Both sets
18 of crystals appear to grow in two stages. In the first stage, the crystal area increases rapidly
19 during the initial 50 to 150 seconds of growth. After this period, the growth rates appear to slow,
20 signifying the second stage. This trend is most noticeable for crystals a, c, and d in the
21 experiment without lignin and for crystals 1, 3, and 6 in the experiment with lignin. Note that the
22 transition between the rapid and slow stages of growth occurs between $t = 140$ seconds and $t =$
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24 180 seconds for these crystals. This is close to the time ($t = 180$ seconds) when the crystal sizes
25 and crystal densities could no longer be determined in Figures 4a, 5a, and 7 due to coalescence
26 of the film. It suggests that the decrease in growth rate from the first to the second stage may be
27 attributed to an increase in the surface coverage of the PbSO_4 . An increase in PbSO_4 increases
28 the available precipitation sites and causes overlap between the diffusion zones of individual
29 crystals. Both of these factors limit the amount of precipitation on the existing crystals [37].
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52 To highlight the two observed stages of growth, Figure 10 shows magnified TXM images
53 of crystals 3 and 6 in image b2 of Fig. 9. In order to aid in the interpretation of this figure, these
54 crystals can be compared to the crystals in the SEM image shown in the magnified portion of
55 image b1 in Fig. 2. The crystal on the right in Fig. 10 (crystal 6) resembles a thin, flat crystal that
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4 appears to be growing in a planar direction along the surface of the Pb electrode. Meanwhile, the
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6 crystal on the left (crystal 3) more closely resembles a thin crystal growing in both the normal
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8 and planar directions.
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11 Referring back to Fig. 10, during the first stage of growth (up to $t = \sim 160$ seconds), the
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13 two white PbSO₄ crystals appear to grow rapidly on the predominantly black Pb background.
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15 Based on the SEM comparison, the crystals are thin and flat. For the crystals to have this
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17 structure, their growth is likely two-dimensional. After $t = \sim 160$ seconds, additional small, white,
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19 PbSO₄ crystals become visible, especially around the crystal on the left (crystal 3). These times
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21 correspond well to the slowing of the growth rates observed in Fig. 9, further suggesting that the
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23 slowdown in growth during the second stage is due to the presence of other crystals on the
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25 surface. Although crystal growth slows in the planar direction during the second stage, the SEM
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27 images in Fig. 2 suggest that crystal growth increases in the normal direction. For instance, a
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29 comparison of SEM images b1 and b2 in Fig. 2 shows that the large crystals at passivation
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31 (image b2) contain a more three-dimensional, pyramidal structure than the large crystals at the
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33 beginning of oxidation (image b1). In order for the large crystals in image b2 to have grown from
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35 large crystals similar to those in image b1, their growth in the normal direction would have to be
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37 greater-than-or-equal to their growth in the other two dimensions.
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50 To further investigate the growth processes of the crystals, the projected area of each
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52 crystal was plotted versus time on a logarithmic plot. These graphs are shown in Figure 11. For
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54 both experiments (without and with lignin), no clear power-law dependence ($A \propto t^n$) is
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56 observed. This suggests that the growth mechanism is complex and cannot be explained by a
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58 simple diffusion-limited or kinetics-limited growth model.
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3.4 Explanation for the voltage dip

An analysis of the early formation of PbSO_4 on Pb in H_2SO_4 may also provide insight into the potential-time transient behavior at the beginning of oxidation. Specifically, the anodic overpotential initially decreases, goes through a minimum, and then begins to increase. [38]. In a lead acid battery, a similar behavior, termed the *coup de fouet*, is observed at the beginning of discharge, but it is attributed to the positive electrode, where PbO_2 is reduced to PbSO_4 [39]. Similar phenomena occur at the negative electrode, where Pb is oxidized to PbSO_4 , but it is of smaller magnitude.

(Insert Figure 12 here)

The transient at the start of oxidation in the TXM experiments is shown in Figure 12. The initial increase in overpotential likely corresponds to an increase in *i)* the double layer capacitance of the electrode and *ii)* the supersaturation of the solution with Pb^{2+} ions. The supersaturation provides a driving force for crystallization and may be written as a concentration overpotential (η_c) [34]:

$$\eta_c = \frac{RT}{2F} \ln \left(\frac{c_{\text{Pb}^{2+}}}{c_{\text{Pb}^{2+}}^e} \right) \quad (5)$$

where $c_{\text{Pb}^{2+}}$ is the Pb^{2+} concentration in the solution, and $c_{\text{Pb}^{2+}}^e$ is the saturated Pb^{2+} concentration at equilibrium. Based on this equation, the decrease in overpotential from the initial spike to the plateau voltage is due to a relaxation in $c_{\text{Pb}^{2+}}$ back to the equilibrium value.

The relaxation in $c_{\text{Pb}^{2+}}$ can be related to the increase in the surface coverage of PbSO_4 on the electrode (Fig. 8). For instance, the increase in surface coverage increases the number of available sites for precipitation of Pb^{2+} species. This increases the precipitation rate of Pb^{2+} ,

which causes $c_{Pb^{2+}}$ (and η_c) to decrease. This analysis implies that the rate of Pb^{2+} dissolution, which is equal to the applied current, may not equal the rate of $PbSO_4$ precipitation. This agrees with the explanation provided by Bernardi for the *coup de fouet* at the positive electrode [40].

In addition to the relaxation of the supersaturated concentration, the plateau voltage may correspond to the coalescence of the $PbSO_4$ film. For instance, Figure 12 highlights the occurrence of three specific events during the formation of the film. All three events occur close to the time when the plateau voltage is reached. The first mark at $t = 160$ seconds corresponds to the time when the crystal size distributions in Figures 4 and 5 and the crystal densities in Fig. 7 were unattainable due to overlapping of the crystals. The second mark signifies the region where the growth of the crystals in Fig. 9 began to slow due to the presence of other crystals on the surface. Finally, the third mark corresponds to the time when the film is fully coalesced [24].

4. Conclusions

This study examined the effects of an organic additive on $PbSO_4$ growth and analyzed the early growth mechanisms of $PbSO_4$. Addition of sodium lignosulfonate to the H_2SO_4 was shown to impede, on average, the growth of the $PbSO_4$ crystals, which resulted in a $PbSO_4$ film with smaller crystals and an increased crystal density. For experiments with and without lignin, an increase in the crystal nucleation rate was observed when the oxidation current was applied. This was attributed to an increase in the supersaturation of the electrolyte. In addition, the early growth of the large $PbSO_4$ crystals was examined with and without lignin. For both cases, there was an initial, rapid growth rate, which declined after 50 to 150 seconds. The decline in growth rate was attributed to an increase in the $PbSO_4$ coverage, which increased the number of precipitation sites competing for $PbSO_4$. Finally, the potential-time transient at the beginning of

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4 oxidation was suggested to result from the relaxation of a supersaturated solution and the
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6 development of a PbSO_4 film with increasing resistance.
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b)

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