Electrochimica Acta 168 (2015) 346–355

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Transmission X-Ray Microscopy of the Galvanostatic Growth of Lead Sulfate on Lead: Impact of Lignosulfonate

K.W. Knehr [a,*], Christopher Eng [b], Jun Wang [b], Alan C. West [a]

[a] *Department of Chemical Engineering, Columbia University, New York, NY 10027, USA*
[b] *Photon Sciences Directorate, Brookhaven National Laboratory, Upton, NY 11973, USA*

ARTICLE INFO

Article history:
Received 23 February 2015
Received in revised form 26 March 2015
Accepted 4 April 2015
Available online 6 April 2015

Keywords:
Lead acid battery
transmission X-ray microscopy
negative electrode
expander
nucleation and growth

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.

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 $PbSO_4$ crystals [17–23]. In these studies, the growth and reduction of $PbSO_4$ was controlled using potentiostatic and voltammetric techniques, while the $PbSO_4$

---

[*] Corresponding author. Tel.: +1 212 854 4546; fax: +1 212 854 3054.
E-mail address: kwk2111@columbia.edu (K.W. Knehr).

http://dx.doi.org/10.1016/j.electacta.2015.04.022
0013-4686/

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 $PbSO_4$ film on Pb in H_2SO_4 [24]. The present study seeks to expand this work by investigating the galvanostatic growth of $PbSO_4$ 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 $PbSO_4$ 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 $Hg|Hg_2SO_4$ 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 $\mu A\,cm^{-2}$ 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 × 40 μm (1600 μm^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 2k × 2k 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

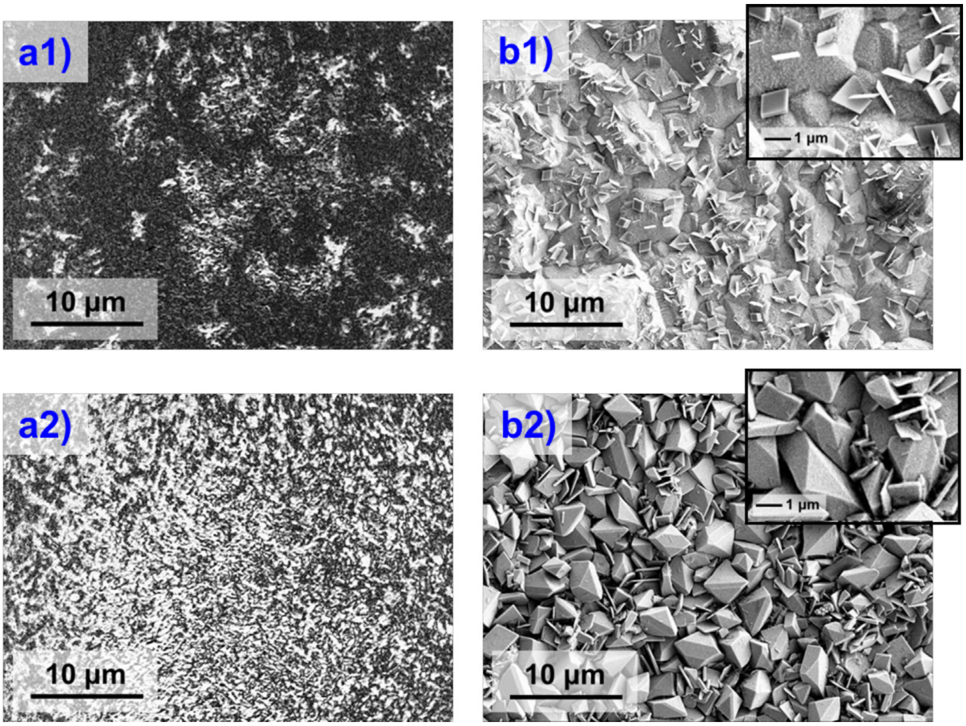

Fig. 1. a) TXM and b) SEM images taken during oxidation of Pb at 50 $\mu A\,cm^{-2}$ in 4.6 M H_2SO_4: 1) 3 minutes after the start of OCV (see Fig. 3); 2) passivation with $PbSO_4$.