Characterization of Aquarefined Micro/Nanoporous Lead Material

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by

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Abstract

The process of aquarefining is an environmentally-friendly method for producing pure lead products that exhibit particularly low density. To observe the microstructures of these low-density forms of lead, scanning electron microscopy (SEM) was employed to examine aquarefined lead samples produced under three batches of processing conditions. Due to aquarefined lead's tendency to collapse under its own weight, careful measures were taken during transport and handling to avoid damaging the samples. Three types of microstructures were observed and correlated to changes in processing conditions: octahedron crystallites, microscales, and dendrites. Energy-dispersive x-ray spectrometry (EDS) was used to quantify the amount of oxygen in each of these microstructures, as the type of lead microstructure appears to vary with the amount of oxygen present. For each batch of processing conditions, the density of the samples produced under those conditions was measured using the Archimedes method. The density of the samples ranged from 1.30 to 3.62 g/cm³, which is significantly less than that of conventional lead (11.30 g/cm³). The decrease in density appears to be due to the formation of thinner dendrites and of hydrogen-filled pores during the aquarefining process. From our results, lead and free acid concentrations were determined as the most critical factors in determining the microstructure of the aquarefined lead, with applied current and temperature of secondary importance.
1. Introduction

Aquarefining is a room temperature, electrochemical process that efficiently recycles lead acid batteries. When compared to traditional lead smelting, aquarefining eliminates much of the solid waste and air emissions, while producing a higher yield of refined lead material which is then processed further to produce lead ingots for battery production. This project focuses on the processing and structural factors of the refined lead material produced from aquarefining, and attempts to explain the reason for the low density observed in the product [1].

The current problem that needs to be addressed is the lack of understanding of the microstructure of aquarefined lead. From the aquarefining solution, lead ions are reduced to form a solid, porous matrix consisting of pure lead, evolved hydrogen, and retained electrolyte solution. Prior work has shown that this matrix can have a density less than 5 g/cm$^3$, much less than typical pure lead, 11.3 g/cm$^3$ [2]. Thus, additional understanding of the microstructure and its formation mechanism is need. Another characteristic of aquarefined lead is that it tends to collapse on its own weight, making it challenging to transport and handle.

The main goals of this project are the following:
- Identify the best method of transporting samples from the aquarefineries to Cal Poly for analysis at the micron level
- Characterize the microstructure of aquarefined lead to explain its low density.

1.1. Lead Acid Batteries

1.1.1. Why Lead Acid Batteries?

The lead acid battery (LAB) is an old technology that dates back to the 1860s. As with any outdated technology the shortcomings of LABs, such as short life span and negative environmental effects, are widely known in the industry. Yet the demand for LABs continues to grow because their advantages such as reliability, familiarity, low cost, and robustness outweigh their disadvantages [3]. LABs have become a critical source of stored energy providing competitively low cost energy per kilowatt-hour, which is why they are the most commonly used batteries today. The most common application of LABs is starting, lighting, and ignition (SLI) batteries; and high power output for automobile applications like spark plugs and headlights [4]. These batteries are optimized to output high power densities, rather than the low, stable power output required for batteries that are used for energy storage.

Unlike most other battery chemistries, approximately 99% of all LABs are recycled, making LABs the nation’s most recycled commodity [5, 6]. This high recycling rate is possible
because the cost of recycling lead from batteries is significantly less than the cost of mining and processing lead from ore, and because the infrastructure and economies of scale necessary for collecting and transporting LABs to recycling facilities exists in North America [5]. While the regulations for recycling are growing, many American smelters are having trouble keeping up. In order to keep costs down, U.S.-generated spent LABs are being exported to Mexico for recycling to avoid the costs of the stricter environmental and health protection laws prevalent in the United States. According to the commission for environmental cooperation, 68% of US spent lead acid batteries are exported to Mexico to undergo secondary refining [5].

1.1.2. Components of Lead Acid Batteries

A lead acid battery consists of individual units called cells. These cells contain the four key components of a battery: a positive and a negative electrode, a separator, and an electrolyte (Figure 1) [7].

![Figure 1. A diagram of the key components of a lead acid battery [7].](image)

The negative electrode is composed of spongy porous lead and is a source of electrons during discharge. This negative electrode, or the anode, has the following overall reaction: \( Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^- \). These emitted electrons are accepted by the positive electrode or cathode, which is a lead electrode coated with lead dioxide (PbO\(_2\)). The overall cathode reaction is PbO\(_2\) + 4H\(^+\) + 2e\(^-\) + SO\(_4^{2-}\) \( \rightarrow \) PbSO\(_4\) + 2H\(_2\)O. This reaction between the anode and cathode plates in a LAB is a spontaneous redox reaction [8]. In order to develop an electric potential and transfer electrons across the two electrodes, the electrodes must be made of different materials. To complete the internal circuit, the electrodes are submerged in an electrolyte solution, which supplies ions to both the negative and positive plates. The electrolyte is typically dilute sulfuric acid (H\(_2\)SO\(_4\)) with a concentration of approximately 25% sulfuric acid and 75% water by volume [8].

The separator electrically separates the positive and negative plates, preventing a short circuit.
(Figure 1). Separators are typically made of a porous polymer such as perforated PVC or glass fiber material to allow diffusion of the electrolyte [8]. Individual cells are divided with a cell divider and protected with an outer plastic case. Each LAB is made up of several cells in series.

1.1.3. Lead Acid Battery Optimization

Despite lower production costs, ease of production, and recyclability, conventional LABs suffer from relatively low capacity and power, short life span, and heavy weight. A typical SLI car battery is as heavy as 14 kg; the internal circuit system constitutes about 60% of total weight, with about half of this weight coming from the positive and negative lead electrodes. One way to improve SLIs is to increase the internal surface area or the porosity of the lead electrode, which reduces the weight of LABs and increases the surface area, which controls power output. This change in internal electrode surface area reduces the electrode weight by 21%, and increases the utilization efficiency of the positive active material up to 50%, which is much higher than the conventional grid electrode [9].

1.1.4. Lead Foam Structure

There are several methods for developing lead with high internal surface area. This includes powder metallurgy, sintering, and casting using silica or salt particles as a space holder, machining ribs or grids into the active material plate, preparation of metallic foams using blowing agents, and gas evolution [10, 11]. Lead electrodes can be processed to have both submillimeter and millimeter pore sizes, and porosities of 50 to 75% [12]. The ultimate goal of LAB research is to produce open cell lead foams with a microstructure that can allow high current discharge densities with mechanical properties that can sustain certain secondary operations including fastening, rolling, bending, and cutting without any brittle deformation or fracture.

1.2. Lead Refining Methods

1.2.1. Lead Smelting

Lead smelting is a technique developed thousands of years ago to produce pure lead from primary and secondary lead. Primary lead is from lead ore, primarily galena or lead sulfide [8]. Secondary lead is found in recycled sources like used batteries [13]. Smelting is a metallurgical process that heats lead and lead oxides up to 1600 °C, which are then mixed with reducing agents to produce commercial lead. The main difference between smelting processes for primary and secondary lead is the initial sintering phase, where sulfur is removed from the lead sulfide ore that becomes primary lead. Although lead smelting is the main technique for
producing pure lead today, it significantly pollutes the environment by generating solid, liquid, and airborne waste. Sintering plant air emissions include sulfur and particulates. These emissions are usually burned in the blast furnace and eliminated. Particulate emissions from blast furnaces include lead oxides, quartz, limestone, iron pyrites, iron-limestone-silicate slag, arsenic, and other metallic compounds [12]. Due to increasing pollution problems, many lead smelters are shut down in Western countries, including the United States [13]. Smelting plants are also very expensive and difficult to run, making the operation hardly profitable for small companies. Due to these reasons, many different approaches have been taken to devise a more environmentally friendly method.

1.2.2. Electrodeposition

Electrodeposition refers to a precise and relatively low-cost method which enables synthesis of different microstructures of pure metals and alloys by easy control of electrolysis parameters such as current density, applied overpotential, electrolysis temperature, solution composition, type of working electrode, and addition of additives [15, 16]. When electrodeposition is used to extract pure metal from an ore dissolved in acid, it is referred to as electrowinning. The critical challenge in the development of micro- and nanomaterials is the synthesis of controlled microstructures, because it determines not only physical and chemical properties, but also its viability for applications of these materials. Electrodeposition is a suitable method to obtain microstructures of the desired shape and size.

Important prerequisites for electrolytic deposition of lead are highly soluble lead and anion stability under hydrolysis. Typical electrolyte solutions that were used in the past are fluoroborate- and fluorosilicate-based electrolytes, but the currently preferred electrolyte is methanesulfonic acid [9]. Nitric acid was also considered as a possible electrolyte but it causes a cathodic reaction, which results in the electrodeposited metal plating on the cathode and the deposition of lead sulfite on the anode [17].

Prior literature shows several types of lead nanostructures produced by electrodeposition. When single crystals are deposited, wires with rectangular cross section are produced. When there is multiple twinning, triangular or hexagonal plates will develop [18]. When applied potential is much higher than the H\(^+\) overpotential, the nanostructures produced transition from particles to microscale needles due to a combination of hydrogen adsorption and the evolution of hydrogen gas bubbles to form honeycomb-like porous thin films [19]. These films have pores of hydrogen about 50-100 microns in size, and the needles have a diameter of about 0.1 micron depending on the process parameters. This process is called the gas bubble dynamic template and is able to produce porous microstructures via concurrent fast metal deposition and hydrogen evolution arising from H\(^+\) reduction. Due to the inherent similarity of this process to
Aquarefining, it gives significant insight into controlling the growth mechanism in aquarefined lead.

1.2.3. Aquarefining

Aquarefining is a method of producing high-purity lead from LABs (Figure 2). LABs undergo a series of processing steps to separate the plastics, sulfates, separators, and solid lead plates so that pure lead can be extracted from an electroprocessing solvent. The electroprocessing solvent, a combination of an alkane sulfonic acid and a chelator, contains lead ions which are reduced on a cathode to form high-purity lead. A collection of the high purity lead is then compressed into lead ingots for use [9].

Figure 2. Aquarefining is a new continuous process used to recycle lead acid batteries (left) into their component parts. While some of the aquarefining steps remove sulfates, metallic lead, and plastics, the only outputs of the aquarefining modules (center) are air emissions, such as carbon monoxide, sulfur dioxide, and greenhouse gases, and the aquarefined lead product (right).

Due to the similarity of electrodeposition and aquarefining, their processing parameters are similar. The tracked aquarefining parameters were lead concentration in solution, free acid concentration, average temperature of electroprocessing solvent, and applied current. The solubility of lead in solution is controlled by the concentrations of lead and free acid in solution; hence their ability to precipitate out of solution to form aquarefined lead are also affected by these factors. Temperature is critical to any thermodynamic process and hence is important to the deposition rate of lead. According to Faraday’s first law of electrolysis, the quantity of ions transferred is proportional to the quantity of charges transferred. The parameter that controls this in aquarefining is the current, or charges transferred from the anode to cathode over time.
1.3. Characteristics of Aquarefining

1.3.1. Low Density Lead Material

During aquarefining, a unique low density lead is deposited from the lead ion-enriched electroprocessing solution onto a rotating cathode wheel. Some observable characteristics of this lead are a dark gray color with a spongy texture, along with hydrogen bubbles that gradually evaporate from the lead. When compressed, the solvent and hydrogen are expelled and the resulting low density lead material returns to a light metallic gray color with hard texture, the familiar traits of conventional lead. Due to this, researchers hypothesize the possibility of the low density lead exhibiting a micro- or nanoporous structure that stores the solvent and hydrogen prior to their expulsion [9].

![Figure 3. Aquarefined lead deposited onto the cathode wheel that has folds created from scraping. In this stage, the length of aquarefined lead samples harvested from the cathode is approximately 10 cm.](image)

Furthermore, when aquarefined lead is left to dry upon exiting the aquarefining module, it immediately experiences oxidation. If the duration of drying is prolonged, a light metallic gray color similar to the color of compressed lead material is exhibited.

1.2.3.2 Electroprocessing Solvent

An aqueous solution of the alkane sulfonic acid used to dissolve the desulfurized lead in the aquarefining process was a combination of methanesulfonic acid (MSA) and a chelator, ethylenediaminetetraacetic acid (EDTA). The recommended amounts range between 5 - 50 wt
% for the MSA and 0.5 - 20 wt% for the EDTA [9].

MSA is a common alkane sulfonic acid that is soluble in water, oxygenated solvents, and hydrocarbons. It is made by oxidizing the product of a methanol and sulfur reaction (Figure 4). As an aqueous solution, MSA is completely ionized, becoming a relatively strong acid. MSA is widely used in industries as a catalyst in organic reactions for its solubility and acidity [20].

![Figure 4. Structure of methanesulfonic acid, a colorless liquid that is used as the electrolyte in aquarefining [20].](image)

2. Materials and Methods

2.1. Lead Sample Preparation

Samples of low density lead were prepared from a test scale aquarefining module. The module is like an electrowinning cell and is made up of a cathode, an anode, and lead ion-enriched electroprocessing solvent (alkane sulfonic acid and a chelator in deionized water). High purity lead samples were harvested from the module’s cathode using small polymer strips. Much care was taken to physically stabilize the harvested samples, as they are very fragile and have a tendency to collapse upon themselves. Harvested samples were deposited into a 50 mL transfer tube filled with deionized water such that the volume of water in the tube was twenty times the sample volume. A single specimen was contained in each tube that was capped and sealed with PTFE tape to prevent leaks. Specimens were prepared for shipping by wrapping individual tubes in polypropylene sorbent pads and then sealing the wrapped tubes together in plastic bags. Inside the shipping box additional plastic lining and sorbent material were used to immobilize the sealed specimen bags. Specimens inside the shipping box were arranged horizontally such that the aquarefined lead specimen sat along the inside walls of the tube (Figure 5). The shipping box was handled with great care to minimize the forces on the specimens. This includes applying “Fragile” stickers, force gauges, and “this side UP” stickers to the shipping box. Three batches of aquarefined lead samples were prepared in this way and shipped to Cal Poly.
2.2. Processing Parameters of Sample Batches

Samples were delivered in three separate batches, denoted A, B and C. Each batch produced multiple samples under constant processing parameters listed in Table I. Sample batch A had a relatively high solution temperature and lead concentration in solution, moderate applied current, and low free acid concentration. Sample batch B had moderate values for all of its processing parameters (solution temperature, lead concentration in solution, applied current, and free acid concentration). Sample batch C had a higher current and free acid concentration than the other sample batches. Sample batch C also had relatively low values for temperature and lead acid concentration. All samples were processed using the same voltage. Denoting time $t = 0$ as the time when the aquarefining process is begun, samples within each batch were harvested from the cathode wheel at various times, as seen in the ‘Acquisition Times’ of Table I.

2.3. Sample Conditions Upon Delivery

Initial examination of as-received specimens showed a dissimilarity in their conditions. Batch A specimens had mostly crumbled into fine powder and several chunks while specimens in batch B and C mainly retained a long foil shape (Figure 6). The general color of batch A specimens also deviated from the other batches, displaying light gray and white particles compared to the dark gray foils of the batches B and C. The aforementioned harvesting folds and ridges were observed in specimens from batch B and C length by comparing the pre- and post-transport images (Figure 7). The crumbled lead specimens served as a reference to gain experience with handling aquarefined lead and for initial analysis.
Table I. Processing Parameters for Batches A, B, and C

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead Concentration (g/L)</td>
<td>33</td>
<td>22</td>
<td>16</td>
</tr>
<tr>
<td>Free Acid Concentration (g/L)</td>
<td>89</td>
<td>175</td>
<td>211</td>
</tr>
<tr>
<td>Current (A)</td>
<td>159</td>
<td>158</td>
<td>180</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>37</td>
<td>31</td>
<td>26</td>
</tr>
<tr>
<td>Acquisition Times (min)</td>
<td>60, 60, 90</td>
<td>34, 90, 95, 146</td>
<td>30, 38, 60</td>
</tr>
</tbody>
</table>

Figure 6. Example of an as-received specimen from the batch A (left) compared to an as-received specimen from batches B and C (right).
2.4. Handling and Drying Procedure

Upon arrival, all three batches of specimens underwent visual inspection for signs of damage and oxidation, and were compared with images of the specimens taken before delivery for any physical changes during transport. After passing initial inspection, the specimens went through a drying procedure to prepare for microscopy.

The drying procedure involved replacement of the solution in the tube with a series of ethanol solutions, before leaving the final ethanol solution to volatilize in air. For all ethanol solution preparations, the quantity was measured by volume. A 50 mL aqueous solution of 70% ethanol and a 100 mL aqueous solution of 95% ethanol were first prepared for each sample. 13.5 mL of deionized water was then removed and replaced with anhydrous ethanol to make a 30% ethanol solution. The tubes were recapped and rested for 10-15 minutes, and the excess liquid waste was disposed afterwards. After 15 minutes, the 30% ethanol solution was almost entirely removed and immediately replaced with the prepared 70% ethanol solution. The tube was resealed and rested for another 10-15 minutes and the excess ethanol solutions were disposed of appropriately. This process was repeated with the 95% ethanol solution and then the anhydrous grade 99.7% ethanol. After the ethanol replacement process was completed, the specimen was carefully placed into a weighing boat using stainless steel tweezers. Using powder-free nitrile gloves, the specimen was grabbed from opposite ends and pulled until it fractured. The sample was mounted on a scanning electron microscope (SEM) stub with the
fracture surface facing up and transported in a closed container to either a light microscope or to the SEM for analysis.

2.5. Analytical Techniques

SEM was performed using an FEI Quanta 200 SEM in high vacuum mode with a thermionic tungsten filament. The secondary electron (SE) detector was used to analyze topographical features and the backscattered electron (BSE) detector was used to confirm pure lead regions. An accelerating voltage of 15 kV and a spot size of 4 were used. Energy dispersive X-ray spectrometry (EDS) was also conducted in the SEM in an attempt to determine the composition of the different microstructures.

Light microscopy was performed using an Olympus BH2 UMA microscope with bright and dark field capability to determine the color of the lead samples and obtain an initial estimate of the sizes of their microstructures.

3. Results

3.1. Lead Density Calculation

The density of aquarefined lead was calculated using the Archimedes principle with water. The densities of three representative specimens from each set were selected, measured, and recorded in Table II. In order to compare our measured porosity values with those from the literature, density was converted to percent porosity by dividing the measured density by the density of conventional, fully-dense lead (11.30 g/cm$^3$) [2].

<table>
<thead>
<tr>
<th>Sample Batch</th>
<th>Density (g/cm$^3$)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.67</td>
<td>67.5</td>
</tr>
<tr>
<td>B</td>
<td>2.60</td>
<td>77.0</td>
</tr>
<tr>
<td>C</td>
<td>1.30</td>
<td>88.5</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>2.52</strong></td>
<td><strong>77.5</strong></td>
</tr>
</tbody>
</table>

3.2. Light Microscopy

Light microscopy was used as a tool to examine the color and shapes of the aquarefined samples. Light microscopy showed color differences between several specimens across
batches: yellow, light metallic gray, and dark gray (Figure 8). These results led to the hypothesis that microstructural changes may correspond to each color, making SEM analysis of microstructure of prime importance.

Figure 8. Light microscope images of lead specimens displaying variations in color. The images are in order of yellow, light metallic gray, and dark gray from left to right.

3.3. SEM

Through SEM analysis, three distinctive microstructures were revealed from the lead specimens: octahedral crystallites, microscales, and dendrite microstructures. These structures correspond to the three colors; yellow, light metallic gray, and dark gray, respectively.

3.3.1. Dendrite Microstructures

Dendrites were one of the microstructures observed in the aquarefined lead samples. The key characteristics of dendrites are their size and the number of branches per dendrite. Intriguingly, the sizes of the dendrites and the number of branches changed according to each batch (Figure 9). Specimens from batch A displayed thick dendrites that are about 50 µm in length with lots of branches. Specimens from batch B had dendrites that are thinner than specimens from batch A, and have fewer branches. Lastly, batch C specimens displayed the thinnest dendrites of the three batches, with dendrites around 5-10 µm in length and with almost no branches.
These dendrites are later discussed as the main microstructure contributing to the low density and high porosity of aquarefined lead.

### 3.3.2. Octahedral Crystallite Microstructure

The second microstructure observed from SEM analysis was octahedral crystallites. From examining specimens of batch A, the octahedral crystallites were clumped together and did not have distinct edges around the crystallites. Formation of scales was also present in this specimen. In contrast, specimens from batch B had crystallites with more distinguishable octahedron shapes that were arranged more uniformly and loosely. Specimens from batch C exhibited some octahedra, but resembled more closely the specimens from batch A than batch B (Figure 10).

### 3.3.3. Microscale Microstructures

A third microstructure observed is microscales, which seemed to grow on top of existing dendrites and crystallites. These scales generally appeared to grow on the dendrite and covered most of the surfaces of the dendrite. Specimens from batch A had microscales growing on most
surfaces of interior and exterior structures, but still had the underlying dendrites and pores visible. Specimens from batch B had an abundance of scales that covered almost the entire surface microstructure and had fewer and smaller microscale structures on the interior fracture surfaces. In contrast to batch A and B, specimens from batch C did not have any microscales present. While this may be due to less downtime between the drying step and SEM analysis, it cannot be said for certain.

Figure 11. SEM images of microscale microstructure from batch A and B (from left to right).

3.4. EDS

Energy dispersive X-ray spectrometry was performed for a representative specimen of each microstructure. Each spectrum was taken to determine the composition associated with the microstructure. EDS confirmed the presence of lead (Pb), oxygen (O), and traces of arsenic (As). The composition measured by EDS was converted to atomic percent and recorded in Table III. Each scan was performed over areas of the same size, and all images were taken at 3000x magnification.

Table III. EDS Results of Compositions of Observed Microstructures (in atomic %).

<table>
<thead>
<tr>
<th>Element</th>
<th>Octahedral Crystallites</th>
<th>Microscales</th>
<th>Dendrites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>39.68</td>
<td>28.86</td>
<td>50.52</td>
</tr>
<tr>
<td>O</td>
<td>60.00</td>
<td>71.14</td>
<td>49.48</td>
</tr>
<tr>
<td>As</td>
<td>0.32</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

In our initial hypothesis, we considered a correlation between the microstructure and the color of the sample. An EDS spectrum was taken of a typical dendrite microstructure, shown in Figure 12. The region where an EDS spectrum was taken from a microscale-covered surface was found and is shown in Figure 13. Using a specimen known to be yellow in color, EDS was
performed on a representative sample containing octahedral crystallites (Figure 14).

Figure 12. An SEM image of the representative sample of the dendrite microstructure taken from a sample from batch B. EDS was conducted over an area representative of the dendrite structure, as indicated in the image.

Figure 13. An SEM image of the surface of a sample from batch B. EDS was conducted over an area representative of the microscale structure, as indicated in the image.
4. Discussion

4.1. Results of Microstructural Analysis

4.1.1. Dendrites

Dendrites constituted the bulk of the microstructure in samples in all of the batches, making it the microstructure of interest in this research. Depending on the batch, the dendrites had differing morphologies. For example, batch A had long dendrites with many branches per length of dendrite, whereas batch C had short dendrites with few branches per length of dendrite.

There are two factors that changed with dendrite morphology. The density of each batch changed with the amount of porosity present. The porosity of each batch changed with the thickness of the dendrites. From batch A to batch B, the amount of branching did not change but the thickness of each branch decreased. Branches in batch B were also much longer and thinner than batch A. While the current used in processing batches A and B did not change, the lead concentration, free acid concentration, and temperature were different between these batches. As lead concentration correlates to the amount of lead in solution, it is critical to the diffusion mechanism that is favored. The concentration of free acid in solution controls the
solubility of lead in the aquarefining solution. These differences in processing parameters result in changes in the thickness of dendrites and their amount of branching.

The thick dendrites seen in batch A (Figure 9) have no or few pores, and small amounts of void space between dendrites. Dendrites with thinner branches show decreased density over dendrites with thick branches, and had higher amounts of void space. An accumulation of thin dendrites therefore forms a microstructure with high porosity. Void spaces, ranging from 10-500 µm in diameter, develop when hydrogen gas is liberated from acid (Figure 15). Pores show signs of expansion because dendrites around the edges of the pore appear compacted, meaning they experienced pressure from the hydrogen gas.

![SEM image of a sample from batch C. Edges of large pores are compacted due to pressure from hydrogen gas.](image)

At low current, lead will grow into a large single crystal. In aquarefining however, smaller, thinner dendrites rapidly grow under high currents. Consequently, high current can limit the growth to a few crystallographic directions that are favored, resulting in the short 5-10 µm dendrites with small amounts of branches seen in batch C.

When looking at the branching of dendrites, current seems to have the largest effect. Dendrites
with more branches are grown when the current is lower. This can best be seen when comparing batches A and C. As current defines the driving force of diffusion by Faraday’s law of electrolysis, the increase in current allows multiple crystallographic directions to be favored, producing long, thin dendrites and branches that grow orthogonally to each other. Branches of these dendrites are generally 1 - 10 µm in length.

4.1.2 Octahedral Crystallites

The science behind this structure is that each crystal nucleates homogeneously within the solution. The reason for the octahedral shape is due to the face-centered cubic crystal structure of lead. This structure leads to a crystallite shape of an octahedron whose faces are the \{111\} planes, which minimizes the surface energy of small particles. As face-centered cubic crystallites grow, they often transform to a thermodynamically stable, truncated octahedron structure with \{100\} planes at what would be the vertices of the octahedron. Because the current used in the aquarefining process is especially high, the rate of crystal growth is too fast for it to transform to the truncated octahedron structure. The result is the formation of high surface energy octahedral crystallites that are generally around 5-10 µm in size.

A peculiar characteristic of octahedral crystallites that varied significantly between batches was their population. Batch A had thousands of crystallites that agglomerated together in large clumps, such that only the edges of the crystallites were visible. The primary reason for the clumping is that individual crystallites nucleate simultaneously and can quickly lower their surface energy by adhering to each other. Batch B by comparison had smaller clumps of crystallites of varying sizes. Of course, the size of each crystallite is determined by the amount of time it has to grow, but fluctuations in where and when they grow were not easily determined by our data.

This brings us to the effect of temperature on the crystallites. The limitation with our temperature data is that it relies only on the average temperature of the fluid in the aquarefining module, not the localized fluid temperature which could be critical to the growth of certain microstructures. As we have observed, the octahedral crystallites must nucleate homogeneously in comparison to the heterogeneous nucleation of the dendrites. For this to occur, there must be some change in the electroprocessing solution. The parameters which best relate to these changes are lead concentration and temperature. Batch A showed the highest quantity of octahedral crystallites; Batch B showed a moderate amount of octahedral crystallites, but a mixture of wiry dendrites as well; Batch C showed nearly no octahedral crystallites. The movement of fluid through the aquarefining module and the increased lead concentration show how these two parameters result in the mixture of octahedral crystallites and thin dendrites (Figure 16).
4.1.3. Microscales

Although all microscales formed on the surfaces of specimens and were light metallic gray in color, the magnitude and quantity of scales on any given specimen had some variation to them. Specimens from batch A had the largest range in size, some even reaching the macroscale. Another notable quality of microscales was that it blurred some of the SEM images. Because oxides are non-conductive, the presence of a large number of microscales is thought to correspond to oxide microscales causing specimen charging in the SEM.

The sizes of the microscales differed based on the type of lead material that was harvested from the aquarefining process. Batch A, which had a high lead concentration, produced crystallized lead that already contained visible macroscales or facets to the naked eye upon delivery. Batches B and C did not have any large scales because the lead concentration was lower, resulting in a lower density structure.

The range in quantity of microscales correlates to the length of the oxidation period.
Aquarefined lead experiences oxidation immediately after harvesting, leading to the presence of some amount of oxides. But during the drying procedure, the length of time the specimens were left to dry allows oxygen atoms to come and bind to the surface of the specimens, ultimately forming microscales. Because the dendrites in batch B are thinner than the dendrites from batch A, they have a higher surface area where more oxygen atoms can bind, potentially forming larger quantities of microscales.

4.2. Composition Analysis

EDS results have shown that oxygen content is non-zero for all samples, confirming the oxidation of aquarefined lead after harvesting it from the cathode wheel. Initially, the changes in color were hypothesized to be related to oxygen content with the yellow sample having the massicot structure, PbO. But the spectra revealed a Pb:O ratio closer to 1:2, or lead dioxide. From these results, there is currently no evidence that sample color is related to oxygen content, but EDS does show that the dark gray dendrites have a lower amount of oxygen than the yellow octahedral crystallites or the light metallic gray microscales.

5. Conclusions

The low density of aquarefined lead is attributed to the presence of void spaces and pores between dendrites. Batch A had thick dendrites with large branches that almost had no gaps in between, resulting in the highest density of 3.67 g/cm\(^3\) and the lowest porosity of 67.5% among the aquarefined samples. Batch B measured 2.60 g/cm\(^3\) in density and 77% porosity, and was observed to have thinner dendrites with a similar amount of branches as Batch A. Lastly, Batch C exhibited the thinnest dendrites with almost no branches that produced a density measurement of 1.30 g/cm\(^3\) and 88.5% porosity. Batch C most notably had low lead concentration and high free acid concentration in its processing parameters, suggesting that these processing conditions produce spongy lead of high porosity that results in low density. Octahedral crystallites are thought to be formed at higher temperatures or higher lead concentrations. Microscales were shown to be associated with post-processing oxidation. EDS was not able to show a relationship between sample composition and color, suggesting that any variations in sample color may be due to unknown post-processing effects.
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