Growth Mechanisms of Nano-to Micro-Sized Lead Sulfate Particles

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ABSTRACT: PbSO₄ is a key component in the charging and discharging of lead acid batteries—such as the cycling of automotive batteries. PbSO₄ is a poor conductor that forms on the positive and negative electrodes during discharging and dissolves during charging of a lead acid battery. Over time, buildup of PbSO₄ occurs on the electrodes, ultimately reducing the efficiency of the battery. This study aims to determine the nucleation and growth mechanisms of PbSO₄ nanoparticles in various solutions to potentially reduce or control the buildup of PbSO₄ on battery electrodes over time. The time dependency of particle morphology was observed using various reaction conditions. PbSO₄ particles were created using premixed solutions at various times of reaction. H₂O, acetone, methanol, ethanol, and isopropanol were used to stop the reaction and development of the PbSO₄ particles. The structure of the nanoparticles was characterized via transmission electron microscopy, high-angle annular dark field scanning transmission electron microscopy, and selected area electron diffraction. This study provides insight into the mechanism by which PbSO₄ nanoparticles form in various solutions and reveals that the degree of complexity of the solution plays a large role in the nucleation and growth of the PbSO₄ nanoparticles. This insight can provide avenues to reduce unwanted buildup of PbSO₄ on battery electrodes over time, which can extend battery life and performance.

1. INTRODUCTION

1.1. Lead Acid Batteries. Although markets for alternative batteries such as Li-ion-based batteries are growing, Pb-alloy acid batteries still dominate the market due to their low cost and good functionality. The most prominent application of Pb-alloy acid batteries is for motor vehicles.² These Pb-alloy acid batteries typically contain cast Pb-alloy grids inside the battery. The reason for using Pb alloys is due to their low melting temperature, easy processability, cost efficiency, good functionality within the battery, and recyclability. These grids are then packed with varying Pb, PbO₂, or other active pastes to create positive and negative plates inside the battery after the paste has cured. As illustrated in Figure 1, the unpacked Pb-alloy grid is packed with a paste before being inserted into the battery.

Once packed with the corresponding paste, the positive cathodic and negative anodic plates are typically separated by a piece of porous, electrically insulating cloth.² A standard 12 volt car battery contains six 2 V cells linked in series where each cell contains cathodic and anodic plates. A molded polymer case is used to contain the cell components and the electrolyte solution with connected positive and negative plates, terminals, and venting arrangements.² Functionality of a Pb-alloy acid battery relies on a forward and reverse electrochemical reaction during charging/discharging. The forward and reverse electrochemical reaction during charg-

Figure 1. Schematic of a Pb-alloy grid, anodic Pb packed plate, and cathodic leady-oxide plate separated by microporous cloth.
\[
Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \\
\leftrightarrow 2PbSO_4(s) + 2H_2O(l)
\]  

(1)

During battery discharge, HSO\(_4^–\) ions migrate to the negative electrode and produce H\(^+\) ions and PbSO\(_4\).\(^2\) At the positive electrode, PbO\(_2\) reacts with the electrolyte to form white PbSO\(_4\) crystals and water. Both electrodes are discharged to Pb\(_{\text{SO}_4}\), which is a poor conductor, and the electrolyte is progressively diluted as the discharge proceeds.\(^6\) As the cell becomes discharged, the number of ions in the electrolyte decreases and the area of active material available to accept them also decreases because the plates become coated with PbSO\(_4\). On charging or converting electrical energy to chemical energy, the reverse electrochemical reaction occurs. The electrodes are converted back to Pb and PbO\(_2\) plates, while the electrolyte increases its H\(_2\)SO\(_4\) concentration.\(^2\) Buildup of PbSO\(_4\) forming on battery plates is a process known as sulfation, and it occurs naturally over the life of the battery due to the electrochemical reaction that occurs in the battery. Other variables can increase sulfation such as battery overcharge or battery storage in a high-temperature environment. This process is important to study due to PbSO\(_4\) crystals being a poor conductor. The crystal size and solubility of these crystals in the electrolyte affect the current in the battery, where crystal size plays a larger role in this effect.\(^1\),\(^1\),\(^3\),\(^1\),\(^6\)

1.2. Small Particles. Efforts have been made to optimize the electrochemical reaction by studying the sulfate material created in the batteries to improve overall battery performance.\(^3\),\(^1\),\(^4\),\(^14\) Based on these efforts, it is clear that the surface structure and morphology of the sulfate are an important factor in improving battery performance.\(^15\) The surface properties of the sulfate crystals depend on the crystal faces that are exposed and their relative sizes, which both correlate to engineering desired surface properties, i.e., catalysis of sulfate crystals in a battery.\(^15\) Additives have also been shown to modify the structure and size of crystals that grow during the formation process in these battery cell reactions.\(^1\),\(^1\),\(^1\),\(^1\) PbSO\(_4\) formation has been observed to occur through a dissolution/recrystallization mechanism.\(^1\),\(^1\),\(^2\),\(^1\),\(^4\),\(^1\),\(^7\) This process proceeds at the solution/crystal interface, so the PbSO\(_4\) crystals that form have well-pronounced walls and edges.\(^5\) Sulfation of lead-oxide pastes has been reported to depend on the size of the lead-oxide crystals.\(^1\),\(^1\),\(^6\),\(^1\),\(^7\) While many studies have examined the microscopic behavior of these PbSO\(_4\) crystals,\(^1\),\(^1\),\(^1\),\(^1\) few studies have examined the nanoscopic behavior of crystals at the onset of formation.\(^1\),\(^1\),\(^7\) Moreover, fewer studies have investigated the effect of various solutions on nucleation and growth of these PbSO\(_4\) crystals at the nanoscale.

In this study, the growth mechanisms of PbSO\(_4\) nanoparticles at the nanoscale are examined. The PbSO\(_4\) nanoparticles are created using premixed solutions. The nucleation and growth of these PbSO\(_4\) nanoparticles are stopped or preserved by dropping them in a solution of H\(_2\)O, acetone, methanol, ethanol, or isopropanol and removing them at 10 s and 1 and 5 min. Thus, it is possible to identify the role the degree of complexity of the preserving solution plays in the growth of the PbSO\(_4\) nanoparticles. The time dependency of particle size and morphology due to these various reaction conditions are examined. The structure of the nanoparticles was characterized via transmission electron microscopy, high-angle annular dark field scanning transmission electron microscopy, and selected area electron diffraction. This study provides insight into the nucleation and growth mechanisms by which PbSO\(_4\) nanoparticles form in various solutions.

2. EXPERIMENTAL METHODS

Containers of PbCl\(_2\) powder and Na\(_2\)SO\(_4\) powders were used to create predissolved solutions for this experiment. Na\(_2\)SO\(_4\) (100 mg) was stirred in a polypropylene container with 100 mL of distilled H\(_2\)O to create a 7 mM Na\(_2\)SO\(_4\) predissolved solution. PbCl\(_2\) (100 mg) was mixed in a polypropylene container with 100 mL of distilled water to create a 3.6 mM PbCl\(_2\) predissolved solution. Predissolved solutions of PbCl\(_2\) and Na\(_2\)SO\(_4\) were mixed to create a 1 mM mixture of PbSO\(_4\) nanoparticles in polypropylene containers where the mixture was continually, magnetically stirred during the reaction time to prevent larger particles from sinking to the bottom and creating a bias in particle distribution. Similar preparation methods in a study of nucleation and growth of BaSO\(_4\) nanoparticles by Ruiz-Agudo et al.\(^1\) were used to prepare the mixture studied in this experiment. To study the potential growth mechanism of these particles, a liquid was mixed with the PbSO\(_4\) solution to potentially stop the growth of the PbSO\(_4\) particles. Acetone, methanol, ethanol, and isopropyl alcohol were used as preserving agents in this experiment to potentially stop the growth of the PbSO\(_4\) nanoparticles. H\(_2\)O was also used as a baseline for the preserving agents for comparison. Water (H\(_2\)O) (10 mL), acetone ((CH\(_3\)_2CO), methanol (CH\(_3\)OH), ethanol (CH\(_3\)CH\(_2\)OH), and isopropyl alcohol (CH\(_3\)CHOHCH\(_3\)) were filled into small vials prior to creating the PbSO\(_4\) solution. Once the PbSO\(_4\) solution was created, 10 mL of the solution was drawn from the main container at varying time intervals of mixing ranging from immediately after combining the two predissolved solutions, which will be referred to as the 10 s experiment, 1 min after mixing, and 5 min after mixing and applied to the prefilled vials of preserving agents. Different time intervals were used to test if the specific preserving agent ceased the growth of the PbSO\(_4\) nanoparticles. Shorter time intervals were used to investigate the mechanistic formation of the particles. Images were also collected a day later to determine if particles continued to grow after mixing with the preserving agents. TEM was used to study the different stages of particle growth after preserving the reaction where the particles ranged from nano- to micron-sized particles (nanoparticles and microparticles). A pipette was used to apply a drop of the varying time interval solutions to TEM gold 400 mesh grids with formvar and a carbon membrane to collect the particles. The grids were allowed to dry for roughly an hour before the TEM experiments, and the grids were analyzed using an FEI Tecnai TEM. High-resolution transmission electron microscopy (HRTEM), high-resolution scanning transmission electron microscopy (HRSTEM), Brightfield (BF), high-angle annular dark field (HAADF), and selected area electron diffraction (SAED) methods were used to image and characterize the particles. Nano- and microparticles were measured along the short axis of the particles and averaged over a minimum of five particles each. Electron diffraction patterns were analyzed with CrysTBox, Crystallography Open Database, and JEMS software.\(^1\),\(^8\)–\(^2\)
3. RESULTS

3.1. Preserving Agent: Water. Figure 2 shows TEM images of the sulfate solution mixed with water after 10 s of stirring where (a) is a HRSTEM image of small congregations of PbSO₄ nanoparticles, (b) shows a diffraction pattern from a large cluster of nanoparticles, (c) shows 1-D radial integration from the nanoparticle rings of (b), (d) shows TEM imaging of a large, rhombohedral sulfate microparticle, and (e) shows a SAED pattern of the (214) zone axis from the highlighted area in (d). These small congregations and even larger clusters of nanoparticles are found in many locations on the Au TEM grid. The diffraction pattern in (b) is similar to the diffraction patterns of large clusters of nanoparticles observed in the other preserving agents, so it is representative of the general structure of nanoparticles seen throughout this study. In water, the rhombohedral microparticle observed in (d) has jagged vertices on the short axis, while the longer axis has flatter vertices. Also, in this sample, multiple microparticles were observed on the Au TEM grid. The diffraction pattern observed in (e) gives evidence that the microparticle is crystalline as well and matches the (214) zone axis in PbSO₄.

Figure 3 displays TEM images from the sulfate solution mixed with water after 1 min of stirring where (a) shows a HAADF image of a large agglomeration of PbSO₄ particles, and (b) shows TEM imaging of a crystalline, rhombohedral sulfate microparticle. Agglomerations, such as those in (a), are observed in other locations of the Au TEM grid. The microparticle observed in (a) is a more developed microparticle as compared to the image in Figure 2b, which indicates that the longer stirring time allows for more of the sulfate microparticles to develop.

Figure 2. Sulfate solution mixed with water after 10 s of stirring. (a) HRSTEM image of small congregations of PbSO₄ nanoparticles. (b) Diffraction pattern from a large cluster of nanoparticles. (c) 1-D radial integration from the nanoparticle diffraction pattern shown in panel (b). (d) TEM image of a large, rhombohedral sulfate microparticle. (e) SAED pattern of the (214) zone axis from the highlighted area in panel (d).

Figure 3. Sulfate solution mixed with water after 1 min of stirring. (a) HAADF image of large agglomeration of PbSO₄ particles. (b) TEM image of a large, crystalline rhombohedral sulfate microparticle.
Figure 4 shows TEM images from the sulfate solution mixed with water after 5 min of stirring with (a) showing a BF image of a large agglomeration of PbSO₄ particles and (b) HRTEM image of the highlighted area in panel (a).

Figure 4. Sulfate solution mixed with water after 5 min of stirring. (a) BF TEM image of a large agglomeration of PbSO₄ particles. (b) HRTEM of the highlighted area in panel (a).

The BF image shows different orientations of nanoparticles with some amorphous regions observed throughout the agglomeration. The HRTEM image displays two nanoparticles, which appear to be combining where an amorphous interface is observed to be forming between them suggesting that the nanoparticles proceed through a reorientation, combination, and recrystallization to reduce their surface area (i.e., free energy) to form more stable microparticles.

3.2. Preserving Agent: Acetone. Figure 5 displays images from the sulfate solution mixed with acetone after 10 s of stirring where (a) exhibits a HRSTEM image of a large clustering of PbSO₄ nanoparticles, (b) exhibits a HRSTEM image of the highlighted region in (a) of PbSO₄ nanoparticles, and (c) shows TEM imaging of a PbSO₄ microparticle. The nanoparticles are on the same size-scale as the microparticles. This result is similar to that of water as a preserving agent, where the unstable clusters of nanoparticles reorient, combine, and recrystallize to create more stable microparticles.

Figure 5. Sulfate solution mixed with acetone after 10 s of stirring. (a) HRSTEM image of a large clustering of PbSO₄ nanoparticles. (b) HRSTEM image of the highlighted region in panel (a) of PbSO₄ nanoparticles. (c) TEM image of a PbSO₄ microparticle.

Figure 6 shows a TEM image of a large clustering of PbSO₄ nanoparticles surrounding larger PbSO₄ microparticles from the sulfate solution mixed with acetone after 1 min of stirring. The very large clustering of nanoparticles provides enough material to form multiple microparticles as observed in the SEM image. These microparticles are slightly smaller than the ones observed in Figure 2b, Figure 3b, and Figure 5c where these have sharper vertices.

Figure 7 displays TEM images from the sulfate solution mixed with acetone after 5 min of stirring where (a) exhibits a SEM image of a large agglomeration of PbSO₄ particles and (b) exhibits a HRSTEM image of multiple congregations of PbSO₄ nanoparticles. The agglomeration observed here is similar to the agglomeration displayed in Figure 3a for water
after 1 min of stirring. These congregations observed in (b) are seen in multiple areas of the Au TEM grid, and they act as sites for PbSO$_4$ nanoparticles to grow and gather to form the microparticles.

3.3. Preserving Agent: Methanol. Figure 8 exhibits images from the sulfate solution mixed with methanol after 10 s of stirring where (a) shows a HRSTEM image of large congregations of PbSO$_4$ nanoparticles and (b) shows the HRSTEM image of the highlighted region from (a) of PbSO$_4$ nanoparticles. The congregation of the PbSO$_4$ nanoparticles follows similar trends to those observed in the water and acetone samples (Figures 3 and 5, respectively).

Figure 9 displays images from the sulfate solution mixed with methanol after 1 min of stirring with (a) showing the HRSTEM image of a large clustering of PbSO$_4$ nanoparticles, (b) showing a HRSTEM image of large PbSO$_4$ aggregate formations surrounded by clusters of PbSO$_4$ nanoparticles, and (c) showing SAED of the highlighted region from (b) of PbSO$_4$ aggregates. Like the previous preserving agents (water and acetone), the clustering of nanoparticles and other microparticles is also observed in methanol. One unique quality that methanol brings as a preserving agent is the morphology of the PbSO$_4$ microparticles observed in (b) as compared to prior microparticles observed in water and acetone (Figures 2, 5, and 6, respectively). These aggregates are longer and more rectangular/needlelike star-shaped microparticles and correspond well with the morphology reported previously by others.$^{10,16}$ The SAED pattern in (c) shows that the star-shaped microparticles are crystalline and match well with the (210) zone axis of PbSO$_4$. This morphology difference of the microparticles formed in methanol compared to the microparticles formed in water and acetone could be correlated with varied pH levels of PbSO$_4$/methanol solution.$^{16}$

Figure 10 shows images from the sulfate solution mixed with methanol after 5 min of stirring with (a) showing the HRSTEM image of a large clustering of PbSO$_4$ nanoparticles...
and (b) showing the HRSTEM image of large PbSO₄ aggregate formations. The aggregate formation for methanol after 5 min of stirring has more needlelike appendages as compared to the thicker aggregates observed in Figure 9b for methanol after 1 min of stirring. This could be related to a large cluster of nanoparticles acting as multiple sites for aggregate formation and the methanol’s single hydroxyl functional group. Growth along a preferred orientation is observed in Figure 10b, which also indicates that the solution changes the preferred orientation growth to slow or activating secondary orientation growth.

3.4. Preserving Agent: Ethanol. Figure 11 exhibits TEM images from the sulfate solution mixed with ethanol after 10 s of stirring where (a) shows a HRSTEM image capturing small congregations of PbSO₄ nanoparticles, (b) displays a BF SEM image of small congregations of PbSO₄, and (c) shows HRTEM of the highlighted region in (b). Congregations of nanoparticles are observed throughout the sample, and, in ethanol, the nanoparticles still have orthorhombic/rhombohedral morphology. The HRTEM image highlights an intersection of three nanoparticles where an amorphous interface is observed between the three particles, similar to the HRTEM image for water in Figure 4b.

Figure 12 shows a HRSTEM image capturing large clusters of PbSO₄ nanoparticles from the sulfate solution mixed with ethanol after 1 min of stirring. This clustering of nanoparticles correlates with the images observed in Figure 2a, Figure 5b,c, Figure 7b, and Figures 8, 10, and 11.

Figure 13 displays images from the sulfate solution mixed with ethanol after 5 min of stirring where (a) shows a HRSTEM image capturing a PbSO₄ microparticle with trailing clusters of nanoparticles, and (b) shows a HRSTEM image of multiple PbSO₄ microparticles coupled with clusters of nanoparticles. The trails of nanoparticles coming off of the microparticles are also observed for water in Figure 5c. The nanoparticles cluster around the microparticles in ethanol as compared to the individual microparticles observed in water (Figure 2b). The two microparticles in Figure 13b are at different orientations, and another microparticle appears to form from combining nanoparticles to the right of the two microparticles.
3.5. Preserving Agent: Isopropyl Alcohol. Figure 14 exhibits images from the sulfate solution mixed with isopropyl alcohol after 10 s of stirring with (a) showing a BF SEM image of a cluster of PbSO₄ nanoparticles with a small agglomerate formation occurring and (b) showing SAED of the agglomerate region highlighted in (a). The SAED pattern shows that the agglomeration is crystalline and matches well with the (102) zone axis of PbSO₄.

Figure 15 shows images from the sulfate solution mixed with isopropyl alcohol after 1 min of stirring where (a) shows a BF SEM image capturing a cluster of PbSO₄ nanoparticles where agglomerations are observed, similar to the agglomeration observed in Figure 14b, and (b) shows SAED of the agglomerate region highlighted in (a). The SAED pattern shows that the agglomeration is crystalline and matches well with the (121) zone axis of PbSO₄.

Figure 16 displays images from the sulfate solution mixed with isopropyl alcohol after 5 min of stirring with (a) showing a BF SEM image capturing a large agglomeration of PbSO₄ nanoparticles.
particles with trailing nanoparticles and (b) showing a TEM HAADF image of the agglomerate region highlighted in (a). The agglomeration has trailing nanoparticles similar to those observed for water in Figure 4a and for ethanol in Figure 13a. The HAADF image of the highlighted region from (a) shows nanoparticles forming together to create this large agglomeration, which can be related to the growth method mentioned above in which the nanoparticles combine, reorient, and recrystallize to create microparticles.10

Chart 1 shows the average size of nanoparticles for different preserving agents at varying times of mixing. The average size of the nanoparticles remains consistent throughout all preserving agents and mixing times. Chart 2 displays the average size of microparticles for different preserving agents at varying times of mixing.

4. DISCUSSION

Water shows large agglomerations and crystalline particles with clusters of nanoparticles surrounding them at the three different times when water is used as a preserving agent (Figures 2–4). The nanoparticles have a similar morphology to the microparticles, and, as the reaction proceeds, microparticles are created through unstable nanoparticles clustering together for coagulation and reorientation, combining or attaching together, and recrystallizing to create a more stable microparticle.10 Studies have shown that the particle surfaces are covered with a layer of tightly bound water molecules during mixing, which acts as an effective activation barrier to nucleation, thus preventing cations in solution from reaching the particle surface.24 This leads to the idea that desolvation of the particle surface and cations (Pb\(^{2+}\)) can be a rate-determining kinetic step in crystal growth, but the barrier for the diffusion of anions (SO\(_4^{2-}\)) to the crystal surface is smaller, thus leading to the anions effectively catalyzing the cation desolvation.24 This is the assumed process throughout all preserving agents used. The mechanism during recrystallization from nano- to microparticles is quite ambiguous, and the observations from this study cannot exclusively determine the process. Further study is underway to unveil this mechanism. Other studies have shown that a dissolution–precipitation reaction is responsible for the monocrystalline microparticle formation, but the exact mechanism remains unclear.10,25,26

Similar to the samples using water as a preserving agent, the samples where acetone is used as a preserving agent show large agglomerations and crystalline particles at different times (Figures 5–7). The microparticles preserved by acetone in Figure 6 have sharper edges as compared to the microparticles during mixing, which acts as an effective activation barrier to nucleation, thus preventing cations in solution from reaching the particle surface.24 This leads to the idea that desolvation of the particle surface and cations (Pb\(^{2+}\)) can be a rate-determining kinetic step in crystal growth, but the barrier for the diffusion of anions (SO\(_4^{2-}\)) to the crystal surface is smaller, thus leading to the anions effectively catalyzing the cation desolvation.24 This is the assumed process throughout all preserving agents used. The mechanism during recrystallization from nano- to microparticles is quite ambiguous, and the observations from this study cannot exclusively determine the process. Further study is underway to unveil this mechanism. Other studies have shown that a dissolution–precipitation reaction is responsible for the monocrystalline microparticle formation, but the exact mechanism remains unclear.10,25,26

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preserved by water in Figures 2, 3, and 5. Compared to water, acetone has additional methyl and carbonyl functional groups. These additional groups in the chain cause a decrease in solubility with water, which can reduce the creation of microparticles compared to water. Additionally, acetone is a polar aprotic solvent, meaning that it cannot donate protons (H\(^+\)) since it lacks a hydroxyl group, which sets it apart from the other alcohols.\(^{27}\) This lack of hydrogen donation in the acetone leads to less interaction with the anions (SO\(\textsubscript{4}^{2-}\)) in the solution. Also, the oxygen in the carbonyl group can interact via hydrogen bonding with water that surrounds the nanoparticles, cations, and anions in the solution, which is related to desolvation described above.\(^{24}\) This allows more anion interaction with cations (Pb\(^{2+}\)) on particle surfaces or in the mixture, thus leading to increased nucleation and growth of the nano- and microparticles.

When methanol is used as a preserving agent, similar micron-sized particles and, more uniquely, star-shaped monocrystalline aggregates, in addition with large clusters of nanoparticles surrounding the microparticles, were observed at 1 min and 5 min mixing times. Since methanol has a hydroxyl group, it can donate a proton, thus increasing the interaction with anions in the solution and at the liquid/particle interface.\(^{27}\) This increased anion interaction will hinder the nucleation of nanoparticles and interaction at their surface by reducing cation interaction. Also, since it is a longer chain, there is a slight decrease in the solubility of methanol with water. As stated above, desolvation can occur with the alcohol preserving agents when the hydrogen is extracted from the hydroxyl group, leaving a slightly negative oxygen atom.\(^{24}\) This allows water to hydrogen bond with the oxygen atoms, which results in desolvation of the nanoparticles or cations/anions, allowing interactions to continue although at a reduced rate due to the additional reactions of the hydroxyl group. The aggregates have a much different morphology when compared to the microparticles observed in water and acetone. These star-shaped microparticles react with the methanol to produce varied morphologies that show preferential growth directions, which could be caused by a varying oriented aggregation of nanoparticle clusters.\(^{10}\) It is suggested that at the later stages of the precipitation process, continued growth of microparticles occurs at the expense of clusters of nanoparticles and smaller microparticles via Ostwald ripening to reduce surface energy.\(^{10}\)

When ethanol is used as a preserving agent, microparticles with large clusters of nanoparticles surrounding the microparticles were observed at the 5 min mixing time, which is similar to the samples using water and acetone as a preserving agent (Figures 2–7). These microparticles have a little more

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**Figure 16.** Sulfate solution mixed with isopropyl alcohol after 5 min of stirring. (a) BF image capturing a large agglomeration of PbSO\(_4\) particles with a trail of nanoparticles. (b) HAADF of the agglomerate region highlighted in panel (a).

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**Chart 1. Average Size of Nanoparticles for Different Preserving Agents at Varying Times of Mixing**

![Chart showing average size of nanoparticles for different preserving agents at varying times of mixing.](https://doi.org/10.1021/acsomega.0c05722)
consistent morphology when compared to the microparticles observed in water and acetone opposed to the star-shaped microparticles in methanol. The microparticles from the ethanol samples are not as sharply shaped near the edges and symmetrical as compared to the microparticles observed in acetone and water. Microparticles were not seen at mixing times below 5 min most likely due to the hydroxyl group increasing the interaction with anions in the solution and at the liquid/particle interface similar to methanol.\textsuperscript{27} Also, ethanol has an additional alkyl group in the chain compared to methanol, which also makes it slightly larger than methanol. This additional alkyl group also makes the chain less reactive with water, which can be related to reduced formation of microparticles at lower intervals of mixing times.

Agglomerations with large clusters of nanoparticles surrounding the agglomerations were observed at the 5 min mixing time for the samples using isopropyl alcohol as a preserving agent. These agglomerations show some consistency with the morphology of the microparticles observed in water, acetone, and ethanol. The agglomerations are not as well-shaped due to an incomplete reaction occurring due to isopropyl alcohol’s hydroxyl group increasing the interaction with anions in the solution, structural size, and the additional methyl group compared to methanol and ethanol.\textsuperscript{27} This additional proton donation, again, can be related to reduced growth of nano- and microparticles at lower intervals of mixing times. At the 5 min mixing time, the large agglomeration seen in Figure 16a is partially transitioned into a microparticle due to isopropyl alcohol’s ability to slow the creation of microparticles.

Based on Chart 1, it can be noted that water and acetone did not prevent the reaction from occurring at any time of mixing as discussed above and seen in Figures 2–7. In the case of acetone, although it is relatively long and nonpolar compared to methanol and ethanol, it does not provide proton donation, which decreases its interaction with the anions in the solution. Additionally, the oxygen in the carbonyl group can hydrogen bond with water and cause desolvation of the particles, thus increasing interaction of anions with cations in the solution and at particle surfaces. For methanol, microparticles are not observed in the 10 s mixing time (Figure 8), but they are observed in the 1 min and 5 min mixing (Figures 9 and 10). For ethanol and isopropyl alcohol, microparticles are only captured in the 5 min mixing times (Figures 13 and 16) where all 5 min solutions’ microparticles/agglomerations range from 1.5–2.5 \( \mu \)m in size. One reason for why microparticles are not observed at the 10 s time for methanol and 10 s and 1 min times for ethanol and isopropyl alcohol is due to the proton donation from the hydroxyl group of the preserving agent causing increased interactions with anions. Additionally, methanol has a methyl group compared to water, regarding chemical composition. Ethanol has one more alkyl group than methanol, and isopropyl alcohol has one more methyl group than ethanol. From this trend, it is observed that proton-donating functional groups in the preserving agent and longer molecules in the preserving agent perform better at stopping the reaction, i.e., stopping microparticles from forming.

5. CONCLUSIONS

In this study, we examine the growth mechanisms of PbSO\textsubscript{4} nanoparticles at the nanoscale. PbSO\textsubscript{4} particles were created by mixing PbCl\textsubscript{2} solution + Na\textsubscript{2}SO\textsubscript{4} solution, which was then mixed for varying amounts of time with the preserving agents: water, acetone, methanol, ethanol, and isopropyl alcohol. Samples were collected from the mixed solutions at 10 s and 1 and 5 min and analyzed using TEM to study the different stages of particle growth after preserving the reaction where the particles ranged from nano- to micron-sized particles.

The growth mechanism of PbSO\textsubscript{4} proceeds through unstable nanoparticles clustering together for coalignment and reorientation, combining or attaching together, and recrystallizing to create a more stable microparticle. PbSO\textsubscript{4} nanoparticles form consistently within the 30–50 nm range, irrespective of which preserving agent is used. Microparticles also formed in most solutions with varying size where the 5 min solutions formed microparticles ranging 1.5–2.5 \( \mu \)m. Water and acetone do not show signs of ceasing the reaction from occurring, and they show agglomeration of nanoparticles and large microparticles through all time intervals. Additionally, acetone does not provide proton-donating functional groups during the reaction, which suggests less interaction with anions in the solution and on liquid/particle surfaces compared.
to the alcohol preserving agents. Methanol, ethanol, and isopropyl alcohol perform better as a preserving agent of the PbSO₄ nanoparticles relative to water and acetone. This result suggests that proton-donating functional groups in the molecules and longer molecules hinder the reaction of particle nucleation and growth.

This study provides insight into the formation of PbSO₄ nanoparticles and methods for preventing their growth to larger agglomerations and microparticles. These results are especially important to understanding reactions in lead acid batteries, where battery lifetimes can be extended by preventing or slowing these PbSO₄ microparticles or agglomerations from forming.

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**Notes**

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### REFERENCES

(1) Prengaman, R. D. Lead Alloys. *Kirk-Othmer Encyclopedia of Chemical Technology*. John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2000.

(2) May, G. J.; Davidson, A.; Monahov, B. Lead batteries for utility energy storage: A review. *J. Energ. Storage* 2018, 15, 145–157.

(3) Prengaman, R. D. Battery alloys for automated battery production. *MBAT* 1991, 1–10.

(4) Siegmund, A.; Prengaman, R. D. Grid alloys for automobile batteries in the new millennium. *JOM* 2001, 53, 38–39.

(5) Torcheux, L.; Vaurijoux, J. P.; De Guibert, A. Improvement of the formation efficiency of the tetrasaccharide lead sulfate for lead/acid batteries. *J. Power Sources* 1997, 64, 81–89.

(6) Shin, J. H.; Lim, Y. T.; Kim, K. W.; Ahn, H. J. Effects of synthesized 4PbO·PbSO₄ on the initial capacity and cycle performance of lead dioxide electrode prepared by cementation leady oxide. *Met. Mater. Int.* 2001, 7, 485–492.

(7) Prengaman, R. A Guide to the Selection of Marine Materials; 3 European Lead Battery Conference, 1973.

(8) Prengaman, R. Handling procedures for Pb-Ca-Sn-Al alloys; 3 European Lead Battery Conference, 1977.

(9) Burashnikova, M. J.; Zotova, I. V.; Kazarinov, I. A. Pb-Ca-Sn-Ba Grid Alloys for Valve-Regulated Lead Acid Batteries. *Engineering* 2013, 05, 9–15.

(10) Ruiz-Agudo, C.; Ruiz-Agudo, E.; Putnis, C. V.; Putnis, A. Mechanistic Principles of Barite Formation: From Nanoparticles to Micron-Sized Crystals. *Cryst. Growth Des.* 2015, 15, 3724–3733.

(11) Bernardi, D. M. Nucleation of Lead Sulfate in Porous Lead-Dioxide Electrodes. *J. Electrochem. Soc.* 1990, 137, 1670–1681.

(12) Gruneo-Dewaele, H. D.-V. S.; Laruelle, S.; Torcheux, L.; Tarascon, J. M. Optimization of the Positive Active Material Capacity in Lead-Acid Cells Through Control of the Basic Lead Sulfate Precursor. *J. Electrochem. Soc.* 1998, 145, 3358.

(13) Lam, L. T.; Ozgun, H.; Cranwski, L. M. D.; Rand, D. A. J. Pulsed-current formation of tetrabasic lead sulfate in cured lead/acid battery plates. *J. Power Sources* 1993, 42, 55–70.

(14) Lam, L. T.; Vecchio-Sadus, A. M.; Ozgun, H.; Rand, D. A. J. Conversion of tetrabasic lead sulfate to lead dioxide in lead/acid battery plates. *J. Power Sources* 1992, 38, 87–102.

(15) Snyder, R. C.; Doherty, M. F. Faceted Crystal Shape Evolution During Dissolution or Growth. *AIChe* 2007, 53, 1337–1348.

(16) Pavlov, D.; Rusevs, S.; Rogachev, T. Soaking of Cured Plates Before Formation. *J. Power Sources* 2011, 46, 407.

(17) Gruneo-Dewaele, S.; Leriche, J. B.; Tarascon, J. M.; Delahaye-Vidal, A.; Torcheux, L.; Vaurijoux, J. P.; Henn, F.; De Guibert, A. Soaking and formation of tetrabasic lead sulfate. *J. Power Sources* 1997, 64, 71–80.

(18) Klinger, M. More features, more tools, more CrysTBox. *J. Appl. Crystallogr.* 2017, 50, 1226–1234.

(19) Quirós, M.; Gražulis, S.; Girdžiauskaitė, S.; Merkys, A.; Vaitkus, A. Using SMILES strings for the description of chemical connectivity in the Crystallography Open Database. *Aust. J. Chem.* 2018, 10, 6.

(20) Merkys, A.; Vaitkus, A.; Butkus, J.; Okulič-Kazarinas, M.; Kairys, V.; Gražulis, S. COD::CIF::Parser: an error-correcting CIF parser for the Perl language. *J. Appl. Crystallogr.* 2016, 49, 292.

(21) Gražulis, S.; Merkys, A.; Vaitkus, A.; Okulič-Kazarinas, M. Computing stoichiometric molecular composition from crystal structures. *J. Appl. Crystallogr.* 2015, 48, 85–91.

(22) Gražulis, S.; Daškevič, A.; Merkys, A.; Chatiegnier, D.; Lutterotti, L.; Quirós, M.; Serebryanaya, N. R.; Moeck, P.; Downs, R. T.; LeBail, A. Crystallography Open Database (COD): an open-access collection of crystal structures and platform for world-wide collaboration. *Nucleic Acids Res.* 2012, 40, D420–D427.

(23) Gražulis, S.; Chatiegnier, D.; Downs, R. T.; Yokochi, A. T.; Quiros, M.; Lutterotti, L.; Manakova, E.; Butkus, J.; Moeck, P.; Le Bail, A. Crystallography Open Database — an open-access collection of crystal structures. *J. Appl. Crystallogr.* 2009, 42, 726–729.

(24) Piana, S.; Jones, F.; Gale, J. D. Assisted Desolvation as a Key Kinetic Step for Crystal Growth. *J. Amer. Chem. Soc.* 2006, 128, 13568–13574.

(25) Qi, L.; Cölfen, H.; Antonietti, M. Crystal Design of Barium Sulfate using Hydrophilic Block Copolymers. *Angew. Chem., Int. Ed.* 2000, 39, 604–607.

(26) Inumaru, K.; Ito, T.; Misono, M. Porous aggregates of unidirectionally oriented microcrystallites of heteropoly compounds. *Microporous Mesoporous Mater.* 1998, 21, 629–635.

(27) Kwong, K. C.; Chin, M. M.; Davies, J. F.; Wilson, K. R.; Chan, M. N. Importance of sulfate radical anion formation and chemistry in heterogeneous OH oxidation of sodium methyl sulfate, the smallest organosulfate. *Atmos. Chem. Phys.* 2018, 18, 2809–2820.