

Molecular Mechanisms of Nucleation and Growth on Barite Expanders for Lead Acid Batteries

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Synopsis: Barite (BaSO_4) is a common additive in lead-acid batteries for promoting reversible formation and dissolution of PbSO_4 during battery cycling. However, little is known about the molecular-scale mechanisms that control these processes over battery's lifetime. Here, we explore responses of the barite (001) surface to cyclic changes in Pb concentration in 100 mM sulfuric acid solution using in-situ atomic force microscopy and high-resolution X-ray reflectivity.^[1] We find that PbSO_4 epitaxial films readily nucleate on the barite surface even from solutions that are undersaturated with respect to bulk PbSO_4 . These experimental results are compared with theoretical models, which reveal reduced strain and interfacial energies that stabilize the overgrowth phase. These insights into non-stoichiometric heteroepitaxy will enable better predictions of how barite affects PbSO_4 nucleation and growth in battery environments.

Background and Motivation

Lead acid batteries

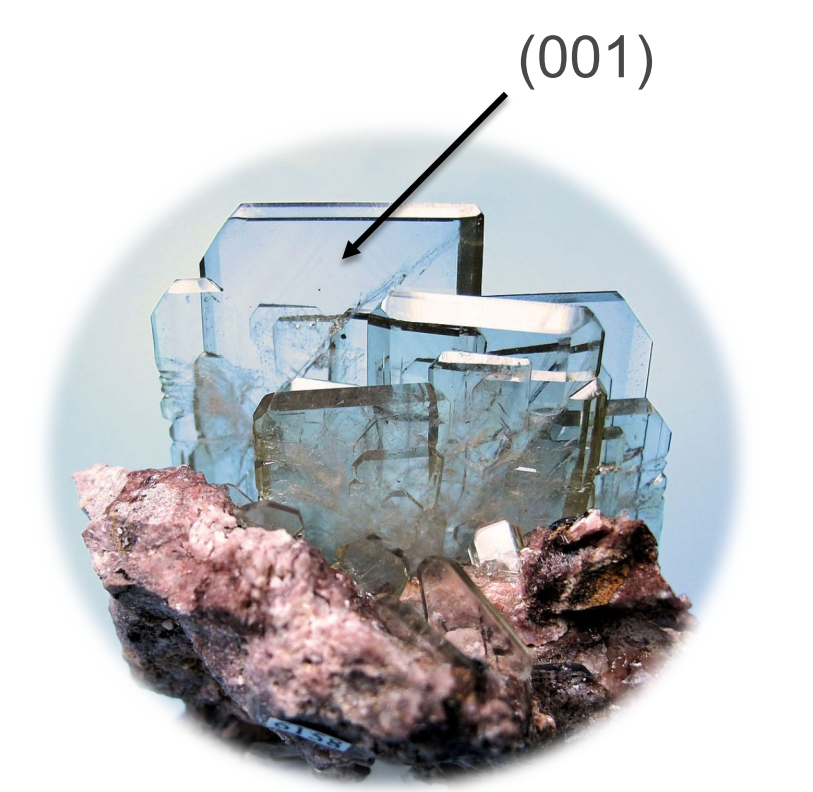
- Widely used for pulsed power applications and industrial power systems.
- Cost efficient: attractive for emerging long-term duration storage applications.
- Need for increased cycling ideally at greater depth of discharge.
- Requires understanding of controlling mechanisms at the atomic-scale.

Barite (BaSO_4): common additive promoting nucleation and stability of PbSO_4

- A major route toward tailored or directed PbSO_4 crystal growth.
- High effectiveness generally attributed to its identical crystal structure to the crystalline PbSO_4 phase, anglesite.
- However, molecular scale interactions between PbSO_4 and barite are poorly understood in sulfuric acid solutions that are relevant to lead-acid batteries.

Materials and Methods

- **Barite:** naturally occurs as large single crystals
 - Basal (001) plane: most dominant surface
 - Equal numbers of Ba^{2+} and SO_4^{2-} groups
- **X-ray reflectivity**
 - probes electron-density distribution at the interface.
- **Atomic force microscopy**
 - visualizes surface morphological evolution during cyclic changes in solution composition.
- **Density functional theory**
 - determines interfacial energetics at various stable configurations.



(Top) Euhedral barite crystal and (Bottom) its (001) plane structure.

Results and Discussion

□ Sorption structure of Pb on barite

- Structural changes at the barite-acidic aqueous solutions with and without Pb^{2+} were monitored by in-situ XR (Fig. 1).
- Pb^{2+} ions directly exchange with Ba^{2+} ions to create mixed $(\text{Ba,Pb})\text{SO}_4$ surfaces.
 - Dominant Pb uptake occurs in the topmost barite layers.
 - A small fraction of Pb incorporates into the surface (~10 Å in depth).

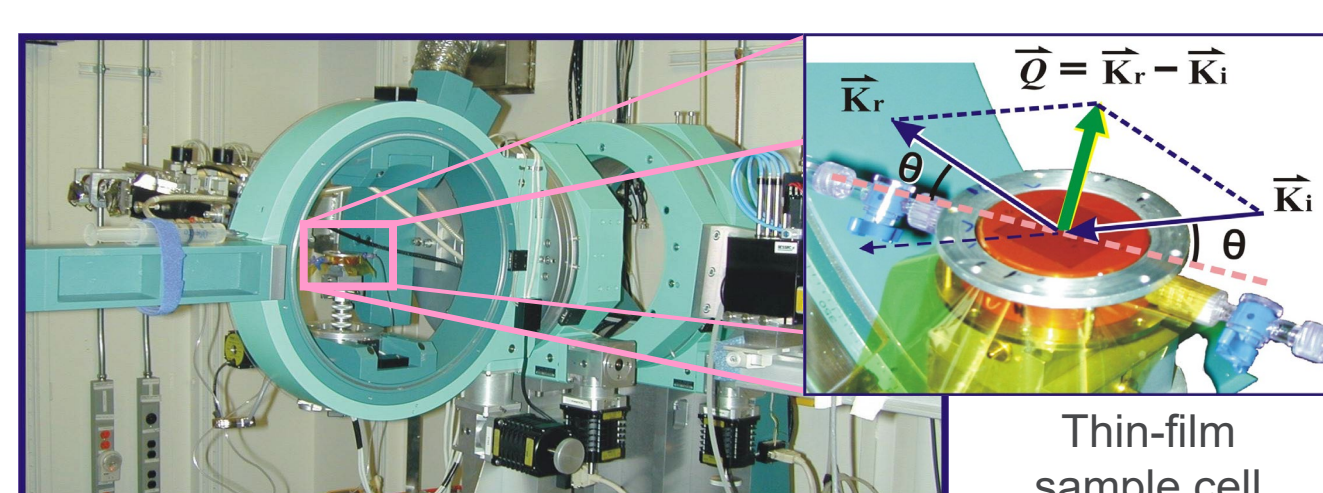


Figure 1. High-resolution XR at the barite-acidic aqueous solution interfaces. (Top) Experimental setup for in-situ XR measurements at Advanced Photon Source (APS) and the thin-film sample cell. K_i and K_r : incident and reflected X-ray beam vectors, Q : momentum transfer, and θ : incident angle of the X-ray beam on the sample surface.

(Bottom) *left*: Changes in XR pattern in 100 mM H_2SO_4 in the absence and presence of Pb (green and red) in comparison with that in barite saturated solution (BSS). *Middle*: The amplitude and phase for interfacial Pb. The values at the lowest Q correspond to the sorption coverage and average height, respectively. *Right*: The total electron-density (black) and sorbed Pb (red) profiles at the barite-solution interfaces. The total profile without Pb (green) is also shown.

□ Reactivity of monolayer PbSO_4 films on barite

- In-situ AFM observations of barite (001) reacted with $9 \mu\text{M}$ $\text{Pb}(\text{NO}_3)_2$ in 100 mM H_2SO_4 (Fig. 2)
 - Growth of secondary PbSO_4 films from the step edges of the barite (001) surface.
 - These films grow only laterally and stop advancing when they reach the subsequent steps.
 - Film growth and stability is facilitated by structural similarity to the substrate (i.e., epitaxy).
 - No multilayer growth or bulk precipitation.

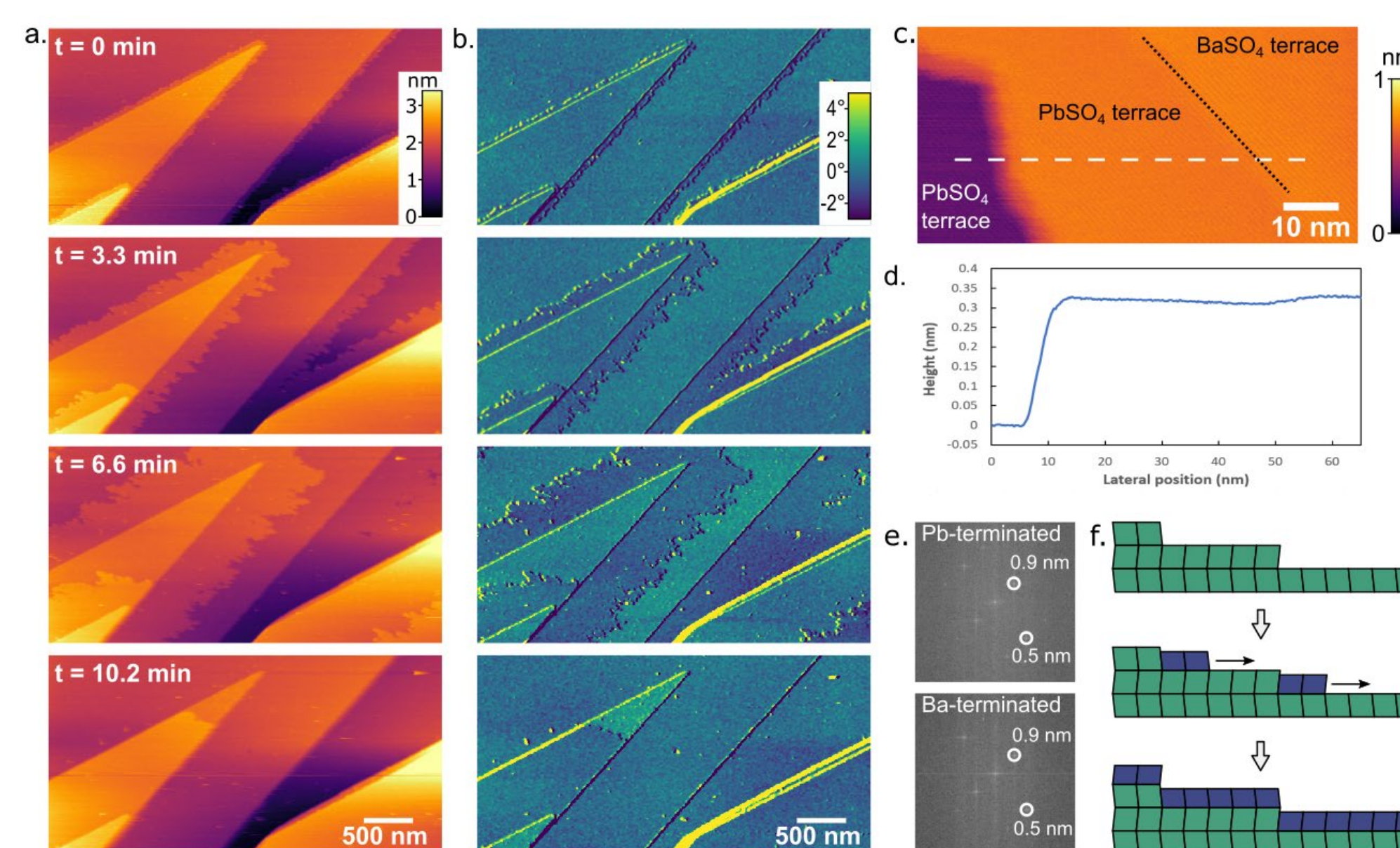


Figure 2. AFM imaging of lead-sulfate epitaxial overgrowth on barite (001). (a) In-situ AFM height images showing the nucleation and growth of ~ 3.5 Å thick monolayer films on the barite surface. (b) Corresponding AFM phase-shift images where clear contrast is observed between the original BaSO_4 surface and the PbSO_4 overgrowth. (c) High-resolution AFM height image of three terraces: two PbSO_4 terminated terraces on the left and one BaSO_4 terminated terrace on the right, with lattice resolution visible. (d) height line-profile across the three terraces in c, showing a ~ 0.02 nm height difference. (e) Fast Fourier transforms (FFTs) obtained from subfigure c, showing the matching lattice periodicities between the Pb and Ba terminated surfaces. (f) Schematic of the indicated growth processes for strained epitaxial overgrowth monolayers.

□ Theoretical model for film stability

▪ DFT calculations

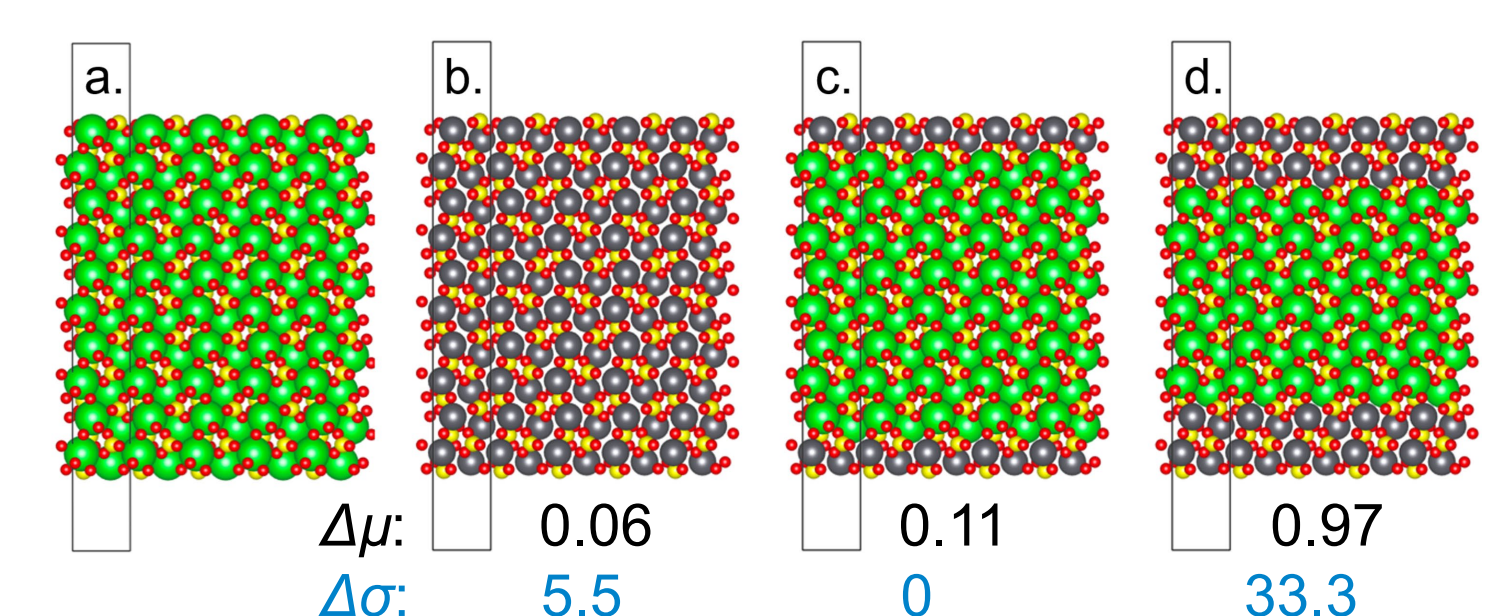


Figure 3. DFT-based thermodynamic model for the stability of strained overgrowth films. Schematic representation of the slab surface models for (a) BaSO_4 , (b) strained PbSO_4 , (c) monolayer of PbSO_4 on BaSO_4 and (d) bi-layer of PbSO_4 on PbSO_4 . $\Delta\mu$: excess chemical potential for strained growth. $\Delta\sigma$: solution saturation index to drive growth with respect to PbSO_4 monolayer (e.g., >0 : less stable, i.e., higher $[\text{Pb}]$ and $[\text{SO}_4]$ required). Green, gray, yellow and red spheres represent Ba, Pb, S and oxygen, respectively.

□ Interfacial evolution during cycling

▪ Barite surface after four lead cycles

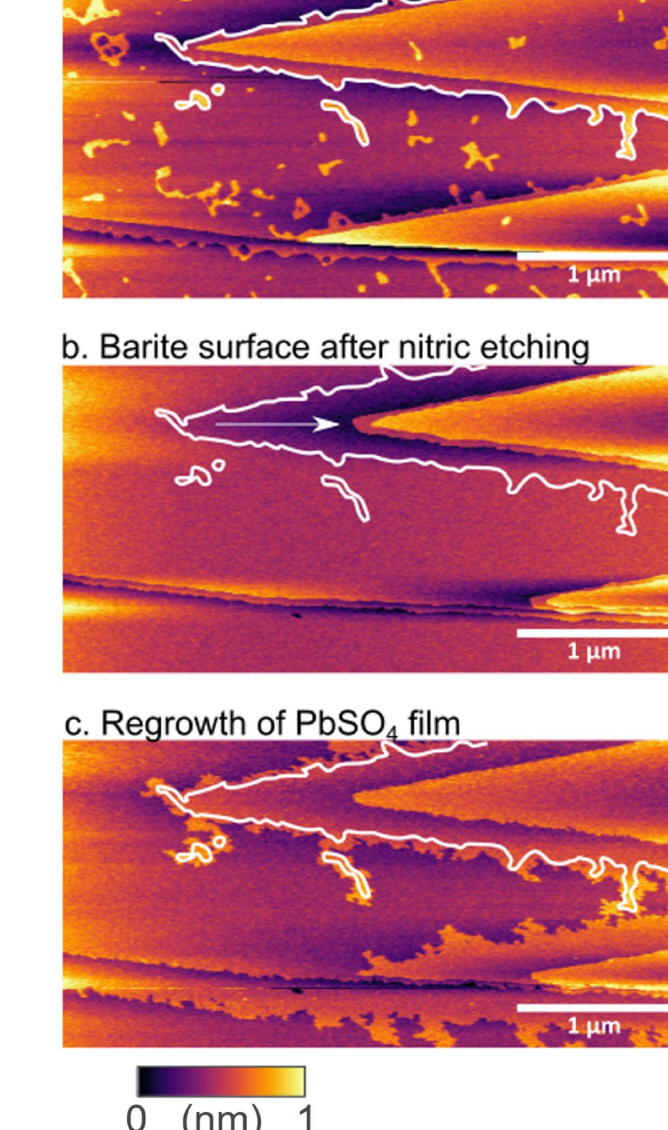


Figure 4. (a) AFM image of the barite (001) surface after four lead cycles exposures to lead solution and lead-free H_2SO_4 , showing retained islands. Selected step edges are outlined in white, to enable easier comparison to subsequent subfigures. (b) AFM image after ~ 6 min exposure to 100 mM nitric acid, which removed retained islands and caused retreat of barite steps to expose the fresh barite surface. (c) Image of the barite surface after re-exposure to $9 \mu\text{M}$ Pb -100 mM H_2SO_4 solution shows regrowth of PbSO_4 films. These films grow rapidly across the freshly exposed barite surface, but their advancement slow when they reach surfaces that have been previously exposed to Pb.

Significance and Impact

- New in-depth molecular-scale observations of non-classical behaviors at the barite-Pb-containing acidic aqueous interface provide a much-needed understanding of the impact of the mineral surface on the growth of Pb-enriched secondary films and their stability during repeated reaction cycles.
- The theoretical models developed based on these experimental results have a wide applicability to various systems that display heteroepitaxial growth in energy storage materials.

On-Going and Future Studies

- Understanding the individual reaction processes between Pb and barite in sulfuric acid solutions
 - Kinetic and thermodynamic controls over Pb incorporation vs. thin-film growth.
- Impact of chemical/structural heterogeneities of seeding materials on interfacial reactivities
 - Different crystallographic planes: e.g., 001 vs. 210.
 - Inclusion of chemical dopants.
 e.g., Use of chemically mixed surfaces (e.g., Sr-doped barite) to control the behavior of heteroepitaxial processes at mineral-acidic solution interfaces.

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Reference

[1] Legg, B.A., Lee, S.S., Garcia, J.C., Iddir, H., Fister, T.T., and Murugesan, V., Uptake of Pb and formation of mixed $(\text{Ba,Pb})\text{SO}_4$ monolayers on barite during cyclic exposure to lead-containing sulfuric acid. *ACS Appl. Mater. Interfaces*, **15**(8), 10593-10605 (2023). DOI: [10.1021/acsmi.2c18399](https://doi.org/10.1021/acsmi.2c18399).