Lattice-engineering of strontium enriched barite for enhanced nucleation in lead-acid batteries

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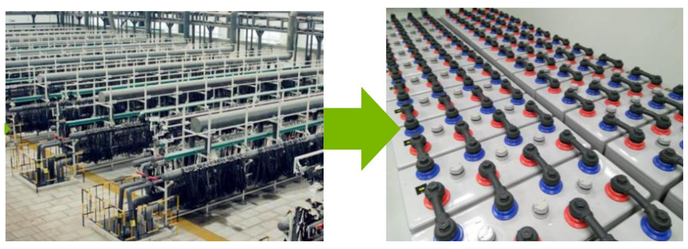
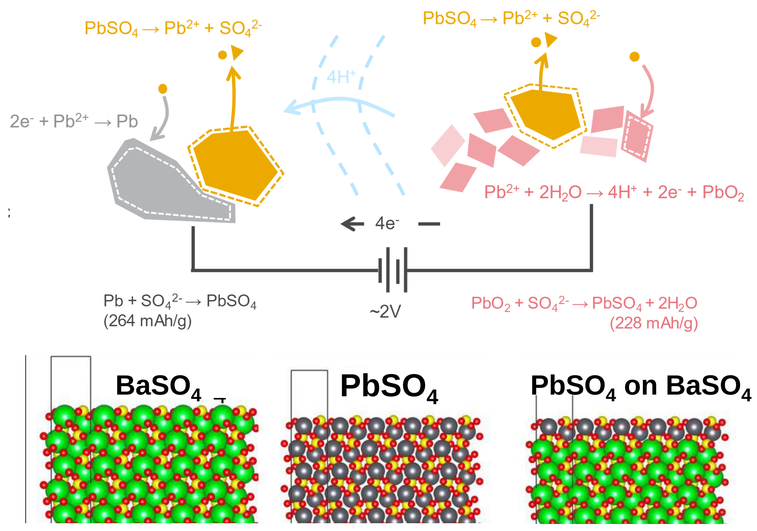
Introduction

Lead-acid batteries are comparable in installed cost to lithium-ion batteries for grid storage applications, but have a higher Levelized Cost of Storage (LCOS) due to their lower cycle life.[1] Extending the cycle life of lead-acid batteries, especially at high Depth of Discharge, would significantly improve their performance as a cost-competitive energy storage technology.



Operation of Pb-acid batteries depends on the reversible nucleation, growth, and dissolution of anglesite ($PbSO_4$). This is promoted through addition of barite ($BaSO_4$) particles, which provide an isostructural template for $PbSO_4$ nucleation.



Legg et al [2] demonstrated that $BaSO_4$'s effectiveness is limited by a large lattice-mismatch with $PbSO_4$. This work presents a new strategy for improving $BaSO_4$ effectiveness through lattice engineering.

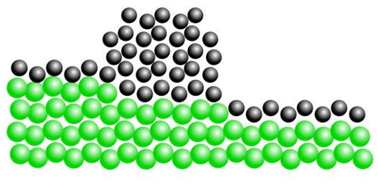
Synthesis of $(Sr,Ba)SO_4$ for improved lattice match.

Sr-doping can be used to systematically alter barite lattice parameters and provide improved lattice match. $(Sr,Ba)SO_4$ particles were synthesized hydrothermally to achieve varied Sr incorporation, as measured with ICP-MS. Single crystal XRD showed decreasing lattice-constants with Sr-incorporation, providing reduced lattice mismatch

Sample	*a*(Å) (misfit%)	*b*(Å) (misfit%)	*c*(Å) (misfit%)
0% Sr-barite	8.886 (+4.8%)	5.456 (+1.1%)	7.160 (+2.9%)
6% Sr-barite	8.865 (+4.5%)	5.458 (+1.1%)	7.149 (+2.7%)
17% Sr-barite	8.800 (+3.7%)	5.453 (+1.0%)	7.116 (+2.3%)

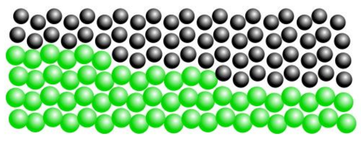
High strain (traditional barite)

Stranski Krastanov Growth
(Frustrated islands over monolayer)



Low strain (engineered barite)

Frank-Van der Merwe Growth
(Layer by layer)



Sr-doping is estimated to reduce lattice-strain energy by up to 30 to 40%, depending on crystal surface.

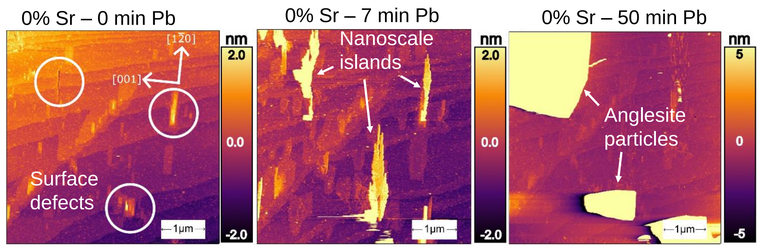
Sr-content in barite	Epitaxial strain energy (210) (eV/formula Unit)	Epitaxial strain energy (001) (eV/formula Unit)
0%	0.036	0.057
6%	0.033	0.053
17%	0.023	0.038

In-situ Atomic Force Microscopy of $PbSO_4$ nucleation and growth

Time-resolved, nanoscale imaging of barite surfaces exposed to Pb-enriched 100 mM $H2SO_4$ reveals molecular-scale mechanisms of nucleation and growth.

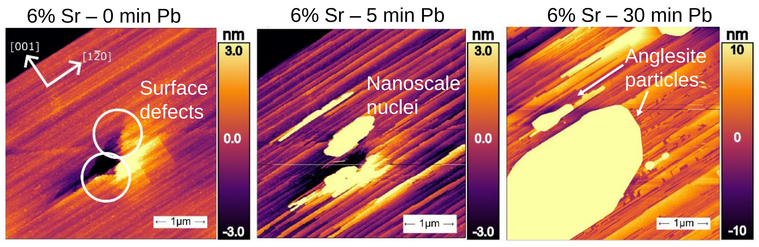
Pure Barite (0% Sr)

Nucleation of nanoscale-islands on surface-defects is followed by nucleation of 'bulk' $PbSO_4$ particles



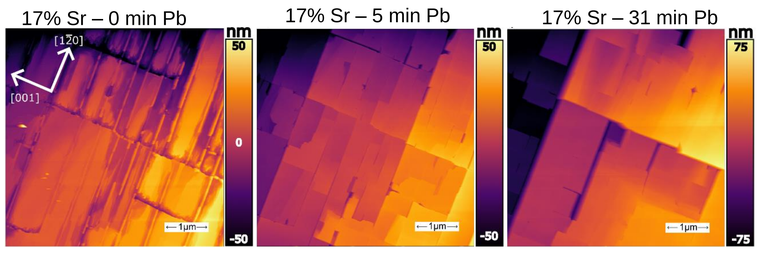
Lightly-doped barite (6% Sr)

Similarly to pure barite, nucleation of nanoscale-islands on surface-defects is followed by nucleation of 'bulk' $PbSO_4$ particles.



Heavily-doped barite (17% Sr)

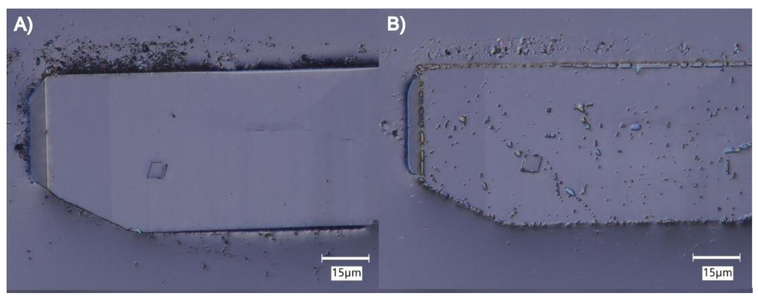
Initial pitted surface is evenly covered via layer-by-layer growth of $PbSO_4$.



Optical Microscopy

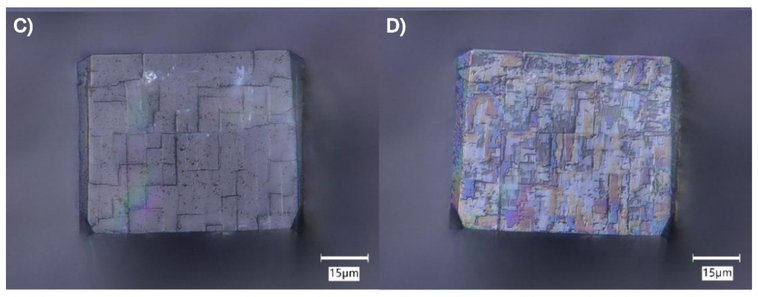
Pure Barite (0% Sr)

$PbSO_4$ nuclei are scattered sparsely across surface on defects, and at specific crystallographic features (i.e. facet edges).



Heavily-doped barite (17% Sr)

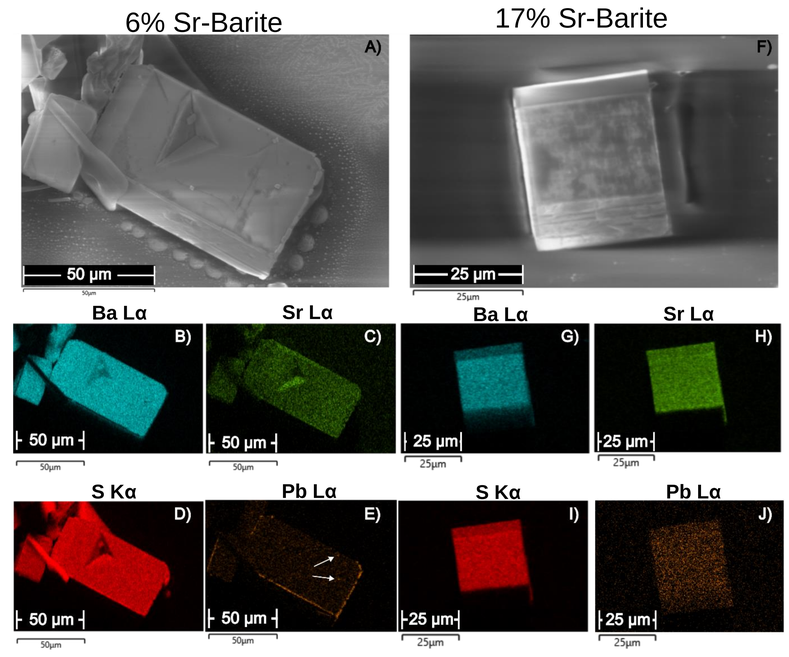
No particles are observed. Iridescent pattern indicates thin film of $PbSO_4$, growth, distributed evenly across surface.



[1] Vilayanur Viswanathan, Kendall Mongird, Ryan Franks, Xiaolin Li, Vincent Sprenkle, Richard Baxter, 2022. "2022 Grid Energy Storage Technology Cost and Performance Assessment" Publication No. PNNL-33283

[2] Legg, B. A.; Lee, S. S.; Garcia, J. C.; Iddir, H.; Fister, T. T.; Murugesan, V. *ACS Appl. Mater. Interfaces* **2023**, *15* (8), 10593–10605. https://doi.org/10.1021/acsami.2c18399.

Scanning electron microscopy and elemental analysis



EDS mapping of post-nucleation 6% Sr-barite particles (A – E) shows lead-rich particles at defect sites and barite particle edges. In contrast, EDS mapping of a similarly exposed 17% Sr-barite particle (F – J) shows even distribution of Pb on the surface.

Conclusions

Strontium doping can be used to obtained reduced lattice mismatch, and fundamentally alter nucleation and growth mechanisms.

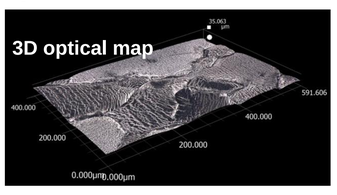
Future Work

Introduction of engineered barite into working Pb-acid battery pastes will allow systematic understanding of its influence on battery cycle life and charging/discharge properties.

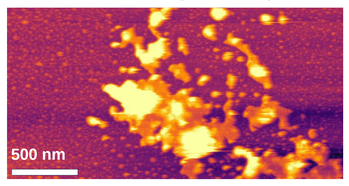
- Developing in-situ optical and AFM-based electrochemical cells will allow direct observation of electrochemically-driven nucleation and growth mechanisms.

in-situ electrochemical cell

polished lead surface



- Investigation of additional additives (i.e. lignosulfates and selected small-molecule lignosulfonate analogues) will allow investigation of cooperative interactions between barite and organic ligands.



Lignosulfonate film adsorbed on barite imaged w/ in-situ AFM

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