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ELECTROLYTE ADDITIVE

FOR PROMOTING LOW-TEMPERATURE PERFORMANCE OF LAB

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LAB Additives

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Function

- Better Stability
- Better Performance
- Longer Lifetime

COMPOSITE

SYNERGISTIC EFFECT

Category

- PAM additives
- NAM additives
- Electrolyte additives

Battery component	Normal additives
PAM	4BS，staple fiber
NAM	lignosulfonate，carbon，$BaSO_4$
Electrolyte	Na_2SO_4, $Al_2(SO_4)_3$

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ENTERPRISE INTRODUCTION

1982

FOUNDED IN

- China’s industrial leader in LAB additive R&D;
- Additive supplier for Clarios, GS-Yuasa, Yadea, Tianneng, Chilwee;
- Certified CMA/CNAS laboratory for LAB testing;
- Collaboration with Borregaard, Cabot;
- International research advisory team;
- Active member of CBI;

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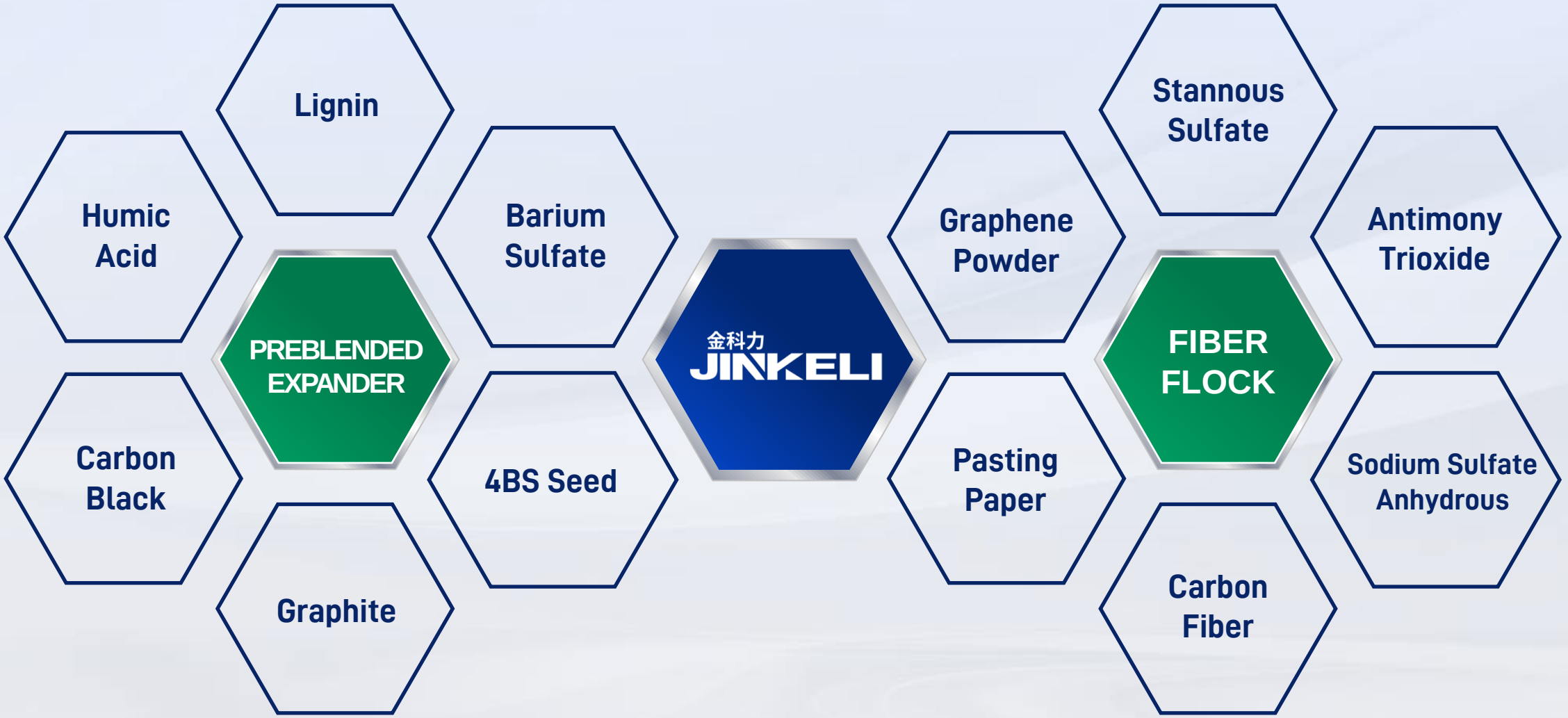

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Laser particle size analyzer

Detect and characterize the nanoparticle size and molecular size in different dispersion systems such as colloidal solutions, polymer solutions, microparticles, and nanoparticle suspensions and emulsions

Atomic absorption spectrometer

Materials quantitative analysis and impurity content analysis

BET

Determination of the specific surface and porosity of various powders, granules and sheet materials

DSC/TGA

Analyze the content of single materials in compound additives and the heat absorption, heat release, melting point and weight loss of other single materials

XRD

Test peak finding, phase identification, quantitative and linear analysis of powder samples

SEM

Observe the microstructure and morphology of materials, and to analyze the types and contents of components in the micro-regions of materials

Electrolyte Additive

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IMPORTANCE

- Important region for mass transportation;
- Interact with NAM and PAM to affect structure and composition of active materials.

MAJOR CATEGORIES

- Inorganic, organic and polymer additives;
- and the composites

REQUIREMENT OF SUITABLE ELECTROLYTE ADDITIVES

- Good solubility in sulfuric acid;
- proper pH range; stable under strong acids;
- inert in electrochemical redox process.

CATEGORY	EXAMPLE
Inorganic	Various sulfates
Organic	EDTA，Amino acids
Polymer	Polyacrylate, PEG, Cellulose

Organic Additives: Structural-based Evolution

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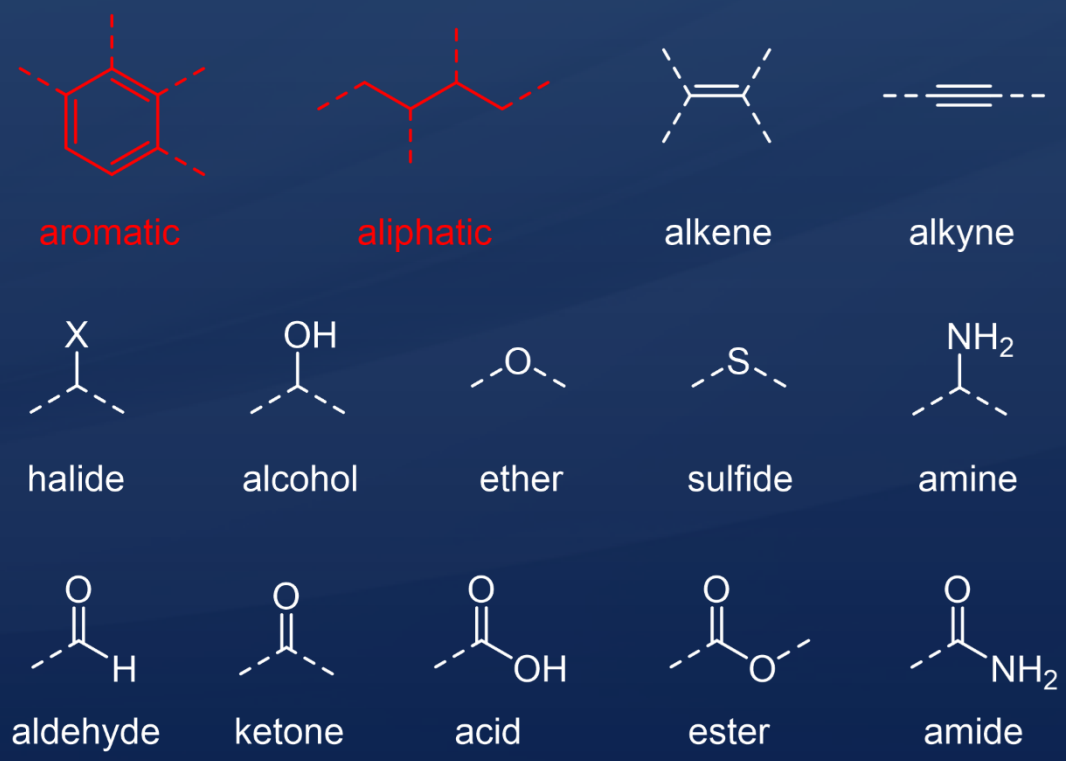
- Aromatic or aliphatic skeleton;
- Various functionalities;
- Numerous combinations.

Detailed investigation is still lacking!



Research Summary

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- 2020-2024, More than 200 organic additives tested so far;
- 1% additive was added in five 4Ah test cells;
- Room temperature discharge capacity at 2 hr or 20 hr were tested three times;
- Low temperature 10s、30s、90s cell voltage，1V discharge time，charge acceptance
- and capacity were tested.

Test Cell Data Set

			2hr and 10hr discharge, ended at 1.75V						-18℃ discharge（40A，24A）				2.4V charge 10min	2hr
Entry	1% additive	code	2hr Capacity 1	20hr Capacity 1	2hr Capacity 2	20hr Capacity 2	2hr Capacity 3	20hr Capacity 3	10s cell voltage/V	30s cell voltage/V	90s cell voltage/V	1.0V time/s	Charge acceptance/A	-18℃ capacity
1	Na_2SO_4	15-0-1	5.0278	5.3734	5.1221	5.5286	4.8551	5.3531	1.5159	1.4442	1.5959	141	0.9513	2.8497
2		15-0-2	4.8327	5.1107	4.9477	5.2674	4.8105	5.1975	1.4803	1.3931	1.5660	154	1.0567	2.7809
3		15-0-3	4.8686	5.1062	4.9421	5.2429	4.6955	5.0761	1.4926	1.4099	1.5766	146	0.9075	2.8075
4		15-0-4	4.8053	5.0373	4.9041	5.1811	4.6028	4.9431	1.4758	1.3849	1.5507	132	0.9634	2.8296
5		15-0-5	4.7550	4.9126	4.8867	5.1053	4.7460	5.0345	1.4926	1.4165	1.5785	134	0.9154	2.7727
		Average	**4.8579**	**5.1080**	**4.9605**	**5.2651**	**4.7420**	**5.1209**	**1.4914**	**1.4097**	**1.5735**	**141.4**	**0.9587**	**2.8081**

Amino Acids

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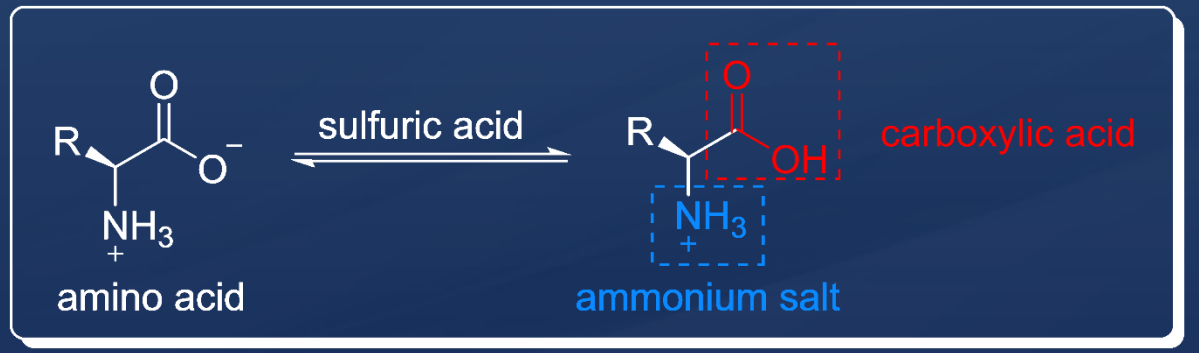
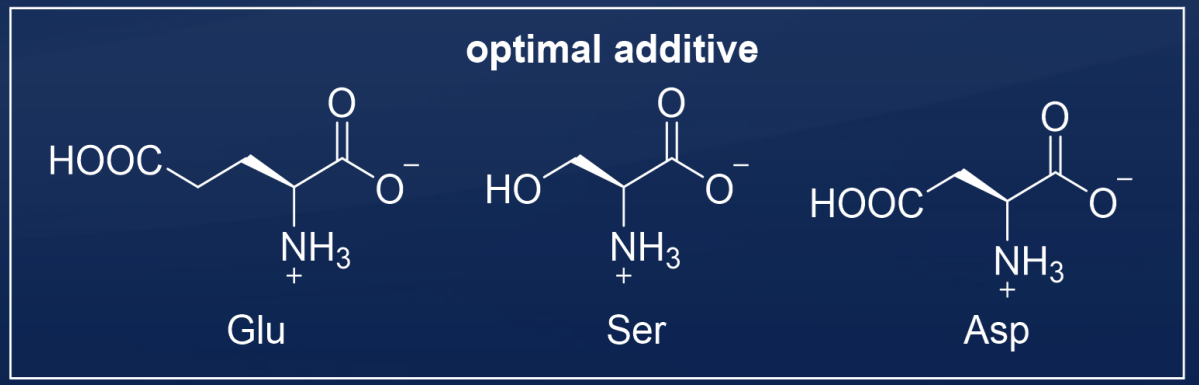
Design

Nitrogen compound can form ammonium salt in sulfuric acid solution, increase conductivity, help ion transfer.



Conclusion

Amino acids with acidic side chain showed the best result, which improved low-temp capacity and charge acceptance by 5-10%.



Question: nitrogen group and carboxylic acid, which functionality is necessary?

Nitrogen Compounds

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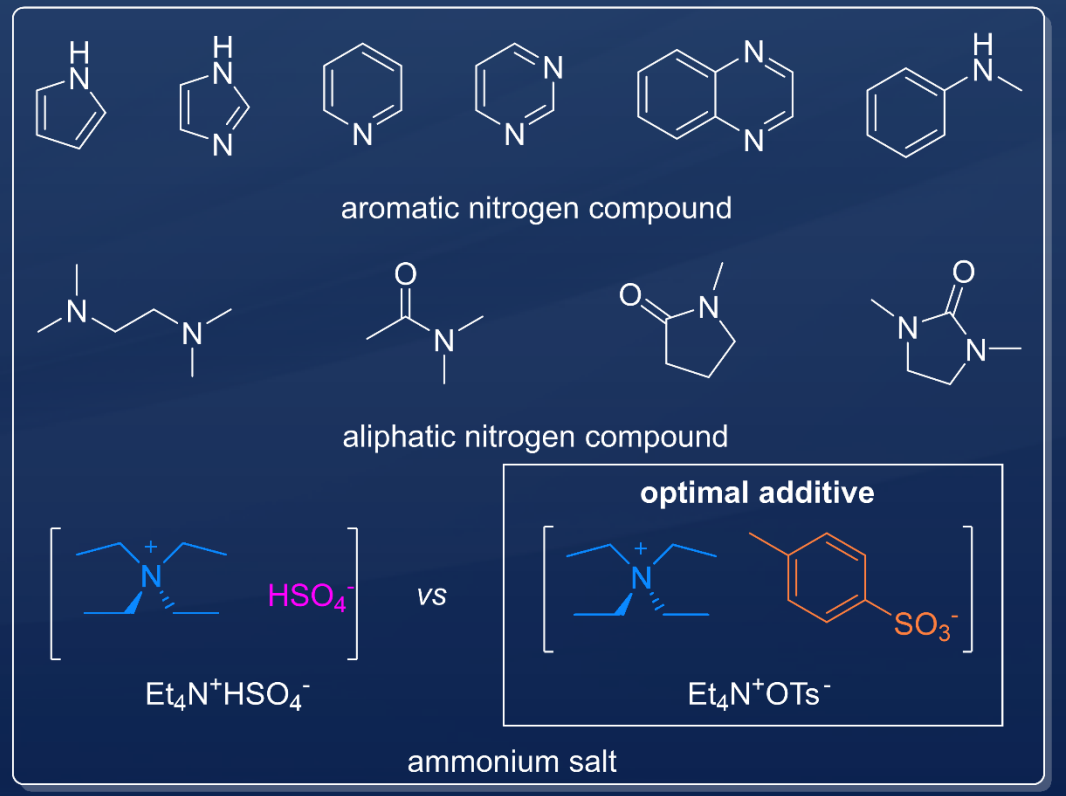
Design

Sulfonic acid can increase acidity and conductivity, possibly interact with lignosulfonate in PAM to reduce overpotential.

Conclusion

Aromatic and aliphatic nitrogen compound showed adverse effect; with the same Et_4N^+ ammonium ion, HSO_4^- salt showed no effect while OTs^- salt showed dramatic improvement.



Serendipitous discovery: organic sulfonic acids as efficient electrolyte additive is feasible.

Sulfonic Acids

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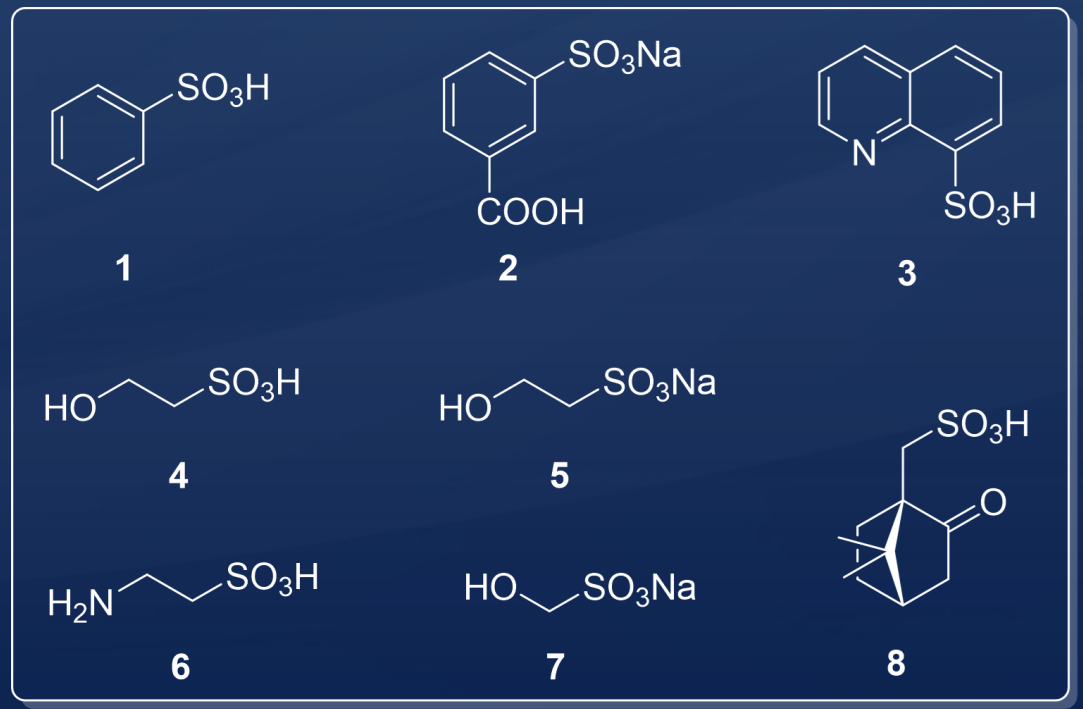
Design

Amino acids can increase conductivity; possibly form complex with lignosulfonate in PAM to reduce overpotential; coordinate with Pb^{2+} ion to inhibit sulfation.

Conclusion

Both aromatic/aliphatic sulfonic acids promoted low-temp capacity up to 10% and charge acceptance up to 30%.



Jin Wang，Houwen Wang，Yanchao Xing et al，‘Electrolyte Additives for Lead-Acid Battery , the Corresponding Electrolytes and Preparation Method’, CN 114243125 A

Composite: sulfonic acid with inorganic sulfates/amino acids

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Design

Additional sulfate ion prevents sulfation.

Conclusion

charge acceptance increased up to 34%, low-temp capacity up to 7%.

Performance / Additives	1.0V time/s	Increase by%	Charge Acceptance /A	Increase by%	-18℃ Capacity	Increase by%
Control (1% Na_2SO_4)	144	--	1.296	--	3.166	--
1% $PhSO_3H$ (0.5%$Al_2(SO_4)_3$)	170	18	1.403	8	3.267	3
1% $PhSO_3H$ (0.5% K_2SO_4)	147	2	1.544	19	3.191	1
1% $PhSO_3H$ (0.5% $KHSO_4$)	157	9	1.421	10	3.203	1
1% $PhSO_3H$ (0.5% $(NH_4)_2SO_4$)	156	8	1.738	34	3.385	7
1% $PhSO_3H$ (0.5% Glu)	153	6	1.469	13	3.282	4
1% $PhSO_3H$ (0.5% Val)	155	8	1.659	28	3.277	4

Jin Wang，Houwen Wang，Yanchao Xing et al，‘Electrolyte Additives for Lead-Acid Battery , the Corresponding Electrolytes and Preparation Method’, CN 114243125 A

Carboxylic Acids

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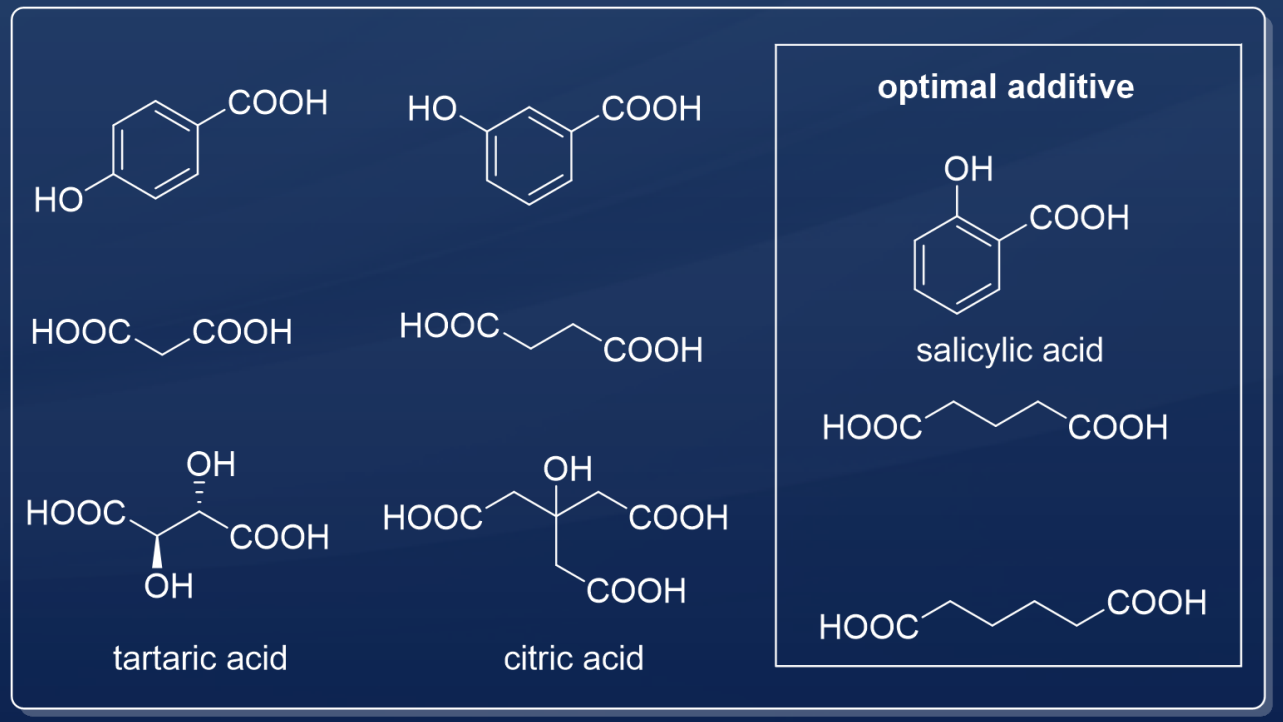
Design

Carboxylic acids are abundant in nature, possibly coordinate or chelate with Pb2+ ion to prevent sulfation.

Conclusion

Aliphatic acids showed better effect than aromatic acids. Multiple acid/hydroxyl group increased solubility and improved low-temp capacity by 12%.



Conclusion

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- Amino acids, sulfonic acids, carboxylic acids are effective additive to promote LAB low temperature performance;
- The structure, amount and composite of additives need to be further optimized;
- More tests are required to verify the lifetime and performance on larger batteries;
- An in-depth electrochemical and surface analysis is necessary to figure out the working mode of organic additives.

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THANKS

BUILD A WORLD-LEADING COLLABORATIVE INNOVATION PLATFORM

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