Research & Development of Paste Additives for High-rate Discharge Batteries

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Outline

Part 1 Introduction
Part 2 Project Background
Part 3 Optimization of the Negative Expanders
Part 4 Battery Tests
Part 5 Conclusion

Part 1: Introduction

Company History

JINKELI

1982 Founded in Zibo / China;

2001 Humic acid was specially recommended by Battery Institute of Shenyang;

2005 ISO 9001 :2008 Certified;

2007 R&D center built;

2009 Drafter of additives standard for lead acid battery industry;

2012 Strategic partnership with Borregaard;

2013 R&D center acknowledged as Provincial R&D center;

2014 Strategic partnership with Cabot Corporation & Member of ALABC;

2015 Technology exchanges with Bulgarian Academy of Sciences & built joint laboratory with Cabot Corporation;

2016 ISO14000 ISO 18000&TS16949 & joint laboratory with Borregaard in August

Today

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- ※ Advanced battery R&D Center, continuous technical support and product development
- ※ The largest battery additives supplier in China and over 70% domestic market share
- ※ Global sales and service networks
- ※ Drafter of additives standard for lead acid battery industry in China
- ※ ISO 9001:2008 ,ISO14000, ISO18000 & TS16949
- ※ More than 180 employees
- ※ 53,334m² production and storage area
- ※ USD 9.2 million register capitals

R&D Center

Jinkeli R&D Center was founded in 2007, and consists of process lab, cell testing lab and battery testing lab.

Committed to continual development and improvement of additives for lead acid battery and provide battery technical support and service. Collaboration with Bulgarian Academy of Sciences, Borregaard, Cabot, ALABC and universities & colleges.

Technical & Engineering Team

Cao Guifa
Director of R&D center
Senior engineer

Hua Shounan
Professor
Senior consultant

Mike McDonagh
Consultant

Ban Taowei
Product manager
Assist Senior Engineer

Liu Wenlin
Product manager
Engineer

Zhou Yu
Project manager
Engineer

Lab Equipments

Atomic absorption spectrometer
Content of the Fe, Mn, Cu and other metal impurities of pre-blended expander, humic acid , graphite, etc.

Laser particle size analyzer
Particle size distribution of barium sulfate, graphite, carbon black, etc.

Simultaneous thermal analyzer
Analysis of the ingredients content in the Pre-blended expanders, and the decalescence, heat release, melting point of the ingredients

Electrochemical workstation
Measurement for different electrochemical constant

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Labs & Equipments

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Labs & Equipments

XRD

SEM

Battery Testing Lab

Battery Test Equipments

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Accuracy up to 0.02%

Cycle life test ,

Capacity test ,

Internal resistance test ,

Charge retention test ,

Battery performance under different temperature ,

Over-charge and over-discharge rate test ,

Etc.

Temperature range: -60℃~150℃

Collaborative Lab with Cabot & Borregaard

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Part 2: Project Background

Background

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High-power batteries

⇩

Number of batteries reduced

⇩

Space and cost save

1KVA PC
12V7Ah Batteries

Customers' Requirement

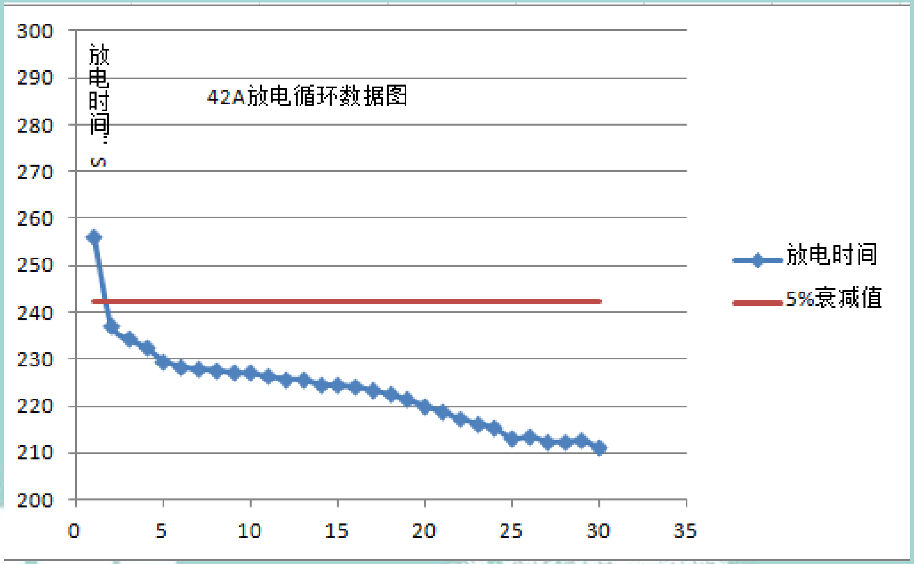
1. Battery capacity discharge for 10min improve 20%
   (battery weight remain the same)
2. The discharge time declines after 30cycles less than 5%

Current average situation in China:

Batteries(6-FM-7 Ah) discharge time @21A is 10-11min.

Current Situation of Leading Battery Producer A

1. Average discharge time @21A is 10’50” (**request ≥13min**)
2. Discharge @42A- time decline after 30cycles is about 17%(**request less than 5%**)



Part 3: Optimization of the Negative Expanders

Effects of Battery Additives to High Power Discharge

Carbon

Barium sulfate

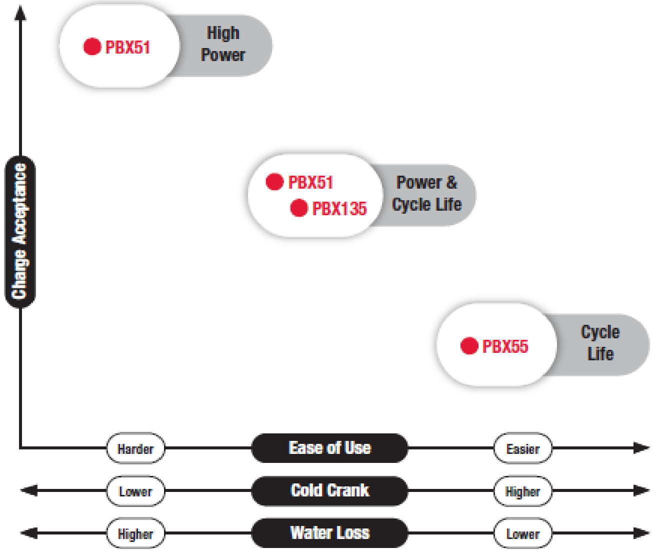
Lignin

Improve conductivity of lead sulfate

Recrystallization nuclear

Limits the growth of spongy lead and lead sulfate crystallization

Selection of Carbon and Mixing Ratio



Additives for Lead Acid Batteries

The primary function of Cabot additives for batteries is to improve the morphology of negative plates and enable better charge acceptance and cycle life for partial state of charge cycling applications.

- For applications that require superior dynamic charge acceptance, Cabot recommends high surface area grades such as PBX51. This grade is most suitable for valve regulated lead acid (VRLA) batteries or in applications where water loss and cold crank performance are less important or can be mitigated by battery design or system fixes.
- For applications that primarily require excellent cycle life, with minimal requirements on charge acceptance Cabot recommends low surface area grades such as PBX55.
- For applications where both high charge acceptance and cycle life are important, Cabot's multi-purpose grades PBX09 and PBX135 are recommended and can meet the requirements for a variety of applications.

Balancing Other Requirements

- High surface area grades may impact water loss, cold crank and deep discharge in some applications.
- Cabot can provide recommendations on how to select and optimize additives to achieve appropriate balance between various requirements.
- Cabot can also provide recommendations how to disperse and incorporate Cabot's additives into the negative plate.

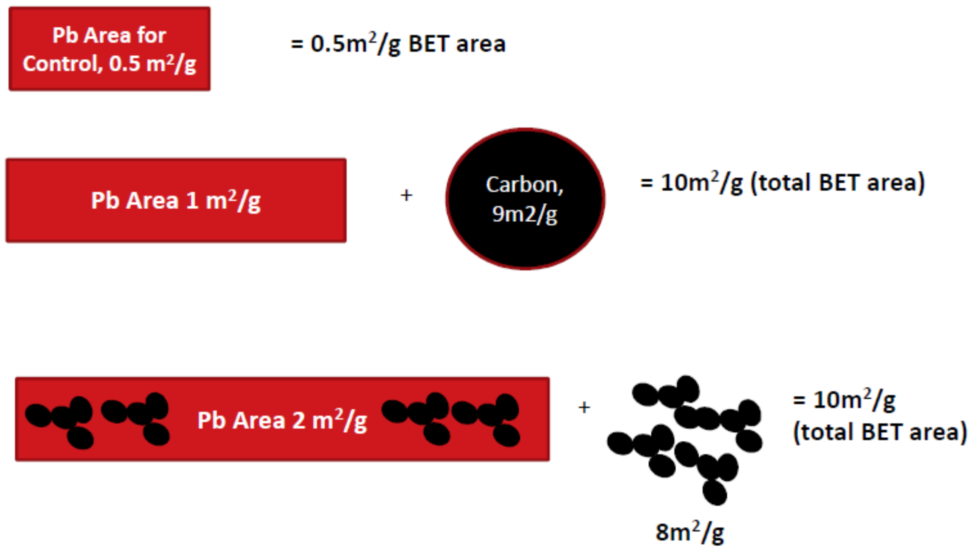
PBX™ Spec				
	PBX09	PBX51	PBX135	PBX55
BET（㎡/g）	210～260	1300～1550	120～180	45～60
OAN (cc/100g)	100～130	140～200	150～180	120～150
Fe (ppm)	＜20	＜40	＜20	＜20
Application	Telecom, Energy-storage, UPS	Start-stop, E-bike	EFB	EFB
Dosage	0.5%～1%	0.25%～0.5%	0.5%～1%	0.5%～1%

Cabot PBX™ high performance carbon features:
- •Improve dynamic charge acceptance
- •Excellent dispersion and easy operation
- •Improve cycle life at PSoC
- •Improve battery production and consistency

PBX™ products have been widely used in lead acid industry worldwide. PBX7 is the best substitute of acetylene carbon.

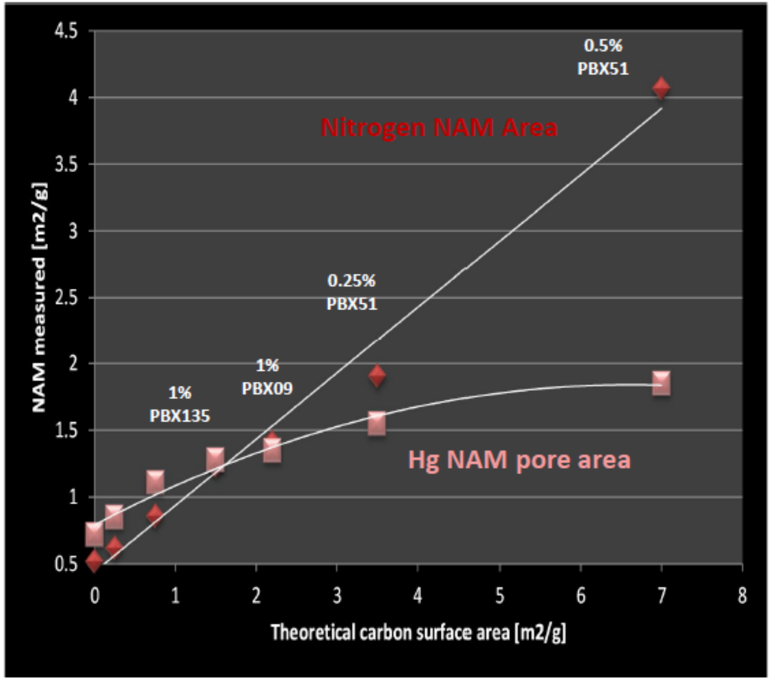
Selection of Carbon and Mixing Ratio

Carbons Could Act as Seed for $PbSO_4$/Pb Crystallites Growth and Change Pb Size and Surface Area



Selection of Carbon and Mixing Ratio

NAM Surface area – micro, meso vs. macro porosity



Selection of Carbon and Mixing Ratio

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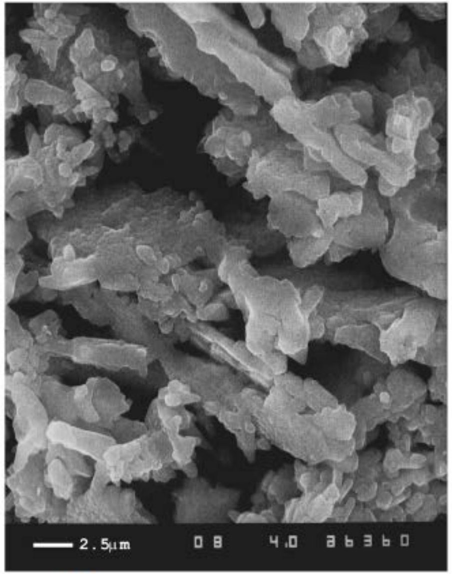
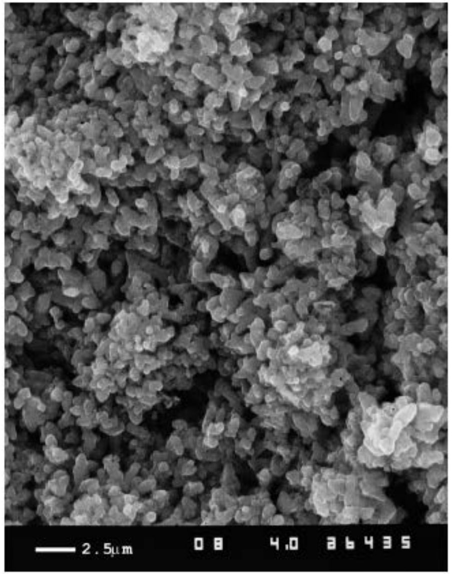
SEM Images of Negative Active Mass (NAM): Different Size Pb Crystallites

Without carbon additive



With 0.5% Carbon Black



Effects of Different Carbons on Battery Performance

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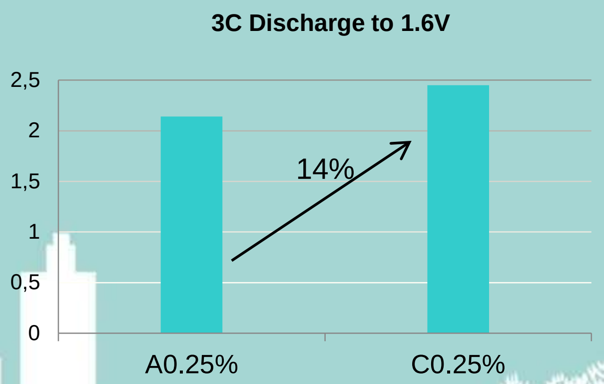
序号	0.3A放电至1.75V 放电容量Ah	-18℃,40A放电至1.0V 时间s	2.4V充电10min时 电流A	-15℃ 1.5A放电至1.75V 放电容量Ah	3C 放电至1.6V 放电容量Ah
A（0.25%）	4.059	181.000	0.626	2.535	2.142
A（0.5%）	4.266	195.200	0.993	2.708	2.282
A（1%）	4.189	198.800	1.214	2.350	2.182
B（0.25%）	4.113	204.000	0.704	2.512	2.430
B（0.5%）	4.230	193.500	0.882	2.598	2.261
C（0.25%）	4.028	193.000	0.898	2.508	2.449
D（1.0%）	4.143	175.400	1.059	2.495	2.224



We study the different carbon materials and confirmed the mixing ratio by repeated tastings.

Selection of Barium Sulfate and Mixing Ratio

The function of barium sulfate is to work as the crystallization of lead sulfate, preventing the plates shrink during the charging cycles and improving battery discharge performance and charge acceptance.

Due to different process technologies, the particle size and distribution as well as structure of barium sulfate vary a lot， which will have different effects on battery performance.

Selection of Barium Sulfate and Mixing Ratio

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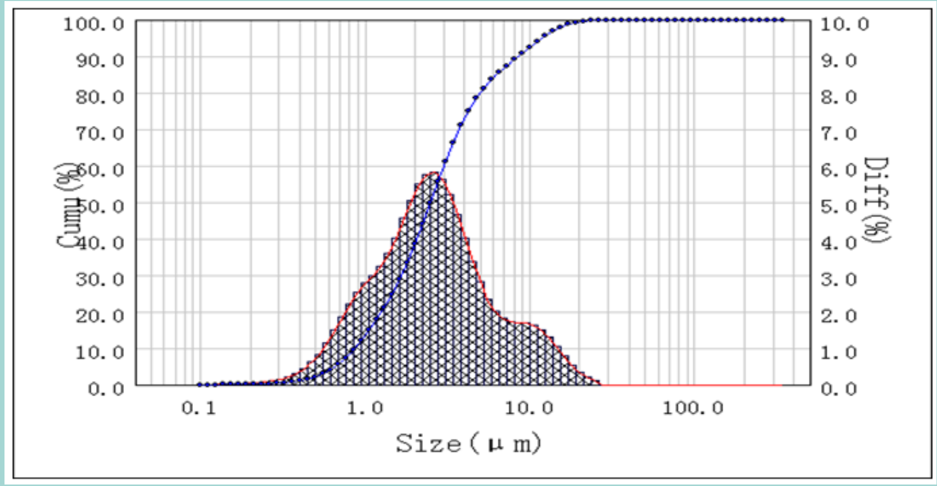
Particle Size Distribution



中位径:2.49um	体积平均径:3.68um	面积平均径:1.81um	遮光率:17.43
比表面积:1226.68m^2/kg	物质折射率:1.649+0.100i	介质折射率:1.333	跨度:3.07

D3:0.55um	D6:0.70um	D10:0.86um	D16:1.09um	D25:1.46um
D75:4.23um	D84:5.99um	D90:8.53um	D97:13.85um	D98:15.34um

中位径:1.03um	体积平均径:1.13um	面积平均径:0.93um	遮光率:14.75
比表面积:2374.27m^2/kg	物质折射率:1.649+0.100i	介质折射率:1.333	跨度:1.15

D3:0.44um	D6:0.52um	D10:0.59um	D16:0.67um	D25:0.77um
D75:1.38um	D84:1.58um	D90:1.79um	D97:2.35um	D98:2.54um

Sample N

Sample Y

Selection of Barium Sulfate and Mixing Ratio

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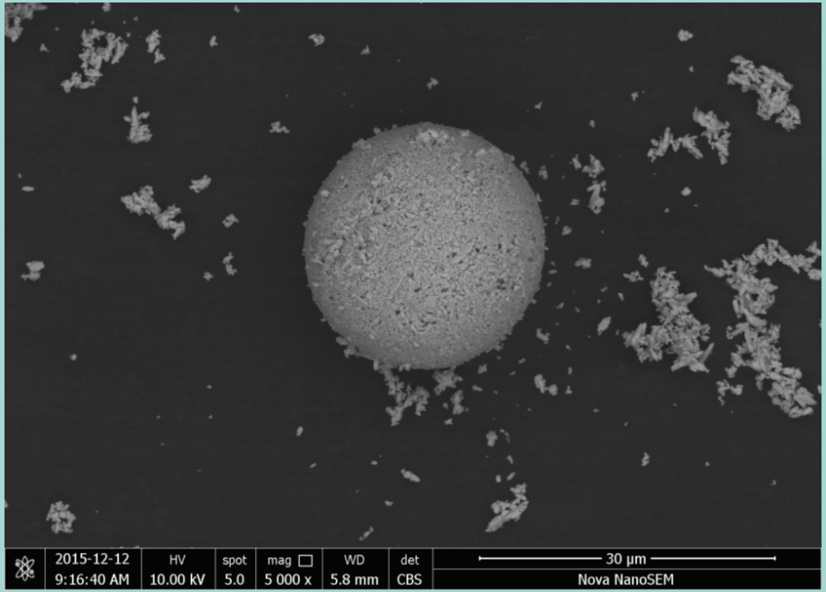
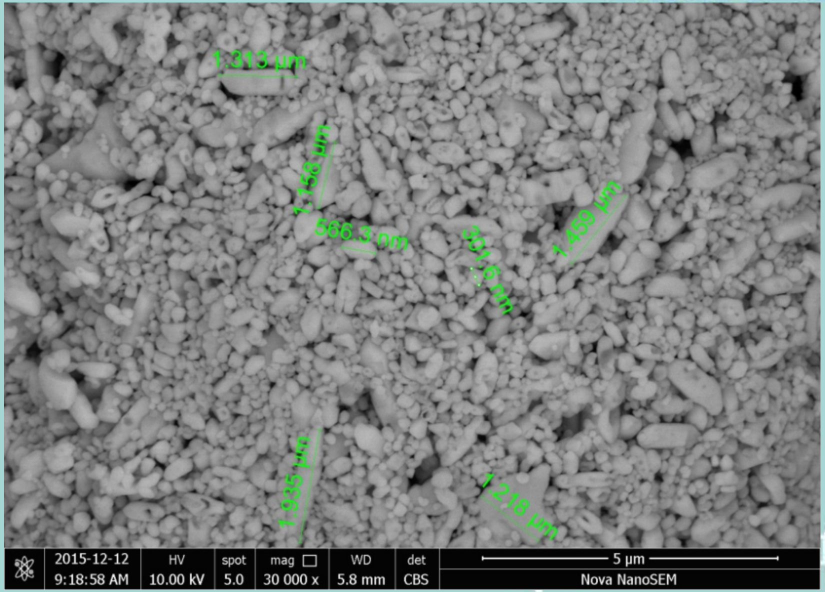
Particle size:

We made a comparison test between ultrafine barium sulfate and ultrafine precipitated barium sulfate with laser particle size analyzer.

改性超细硫酸钡（单位 um）							
未开超声	D90	D50	D25	开超声	D90	D50	D25
	22.31	4.12	1.97		5.15	1.81	1.04
	20.91	6.66	3.29		4.77	1.74	1.01
	16.63	4.08	1.97		3.69	1.66	0.98
	14.38	3.95	2.00		4.72	1.69	0.98
超细沉淀硫酸钡（单位 um）							
未开超声	D90	D50	D25	开超声	D90	D50	D25
	2.65	1.25	0.84		2.45	1.19	0.81
	2.56	1.23	0.83		2.40	1.16	0.80
	2.53	1.22	0.82		2.42	1.17	0.80

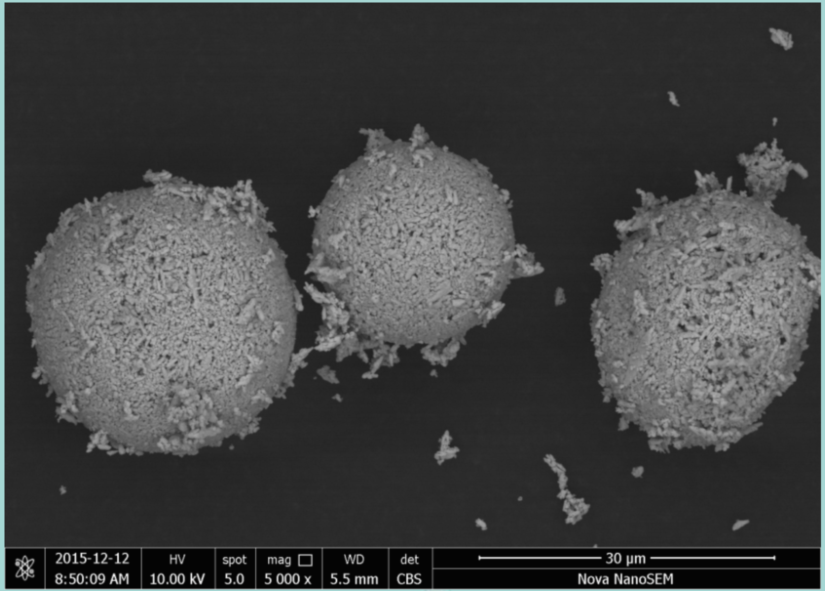
SEM Images of Different BaSO4

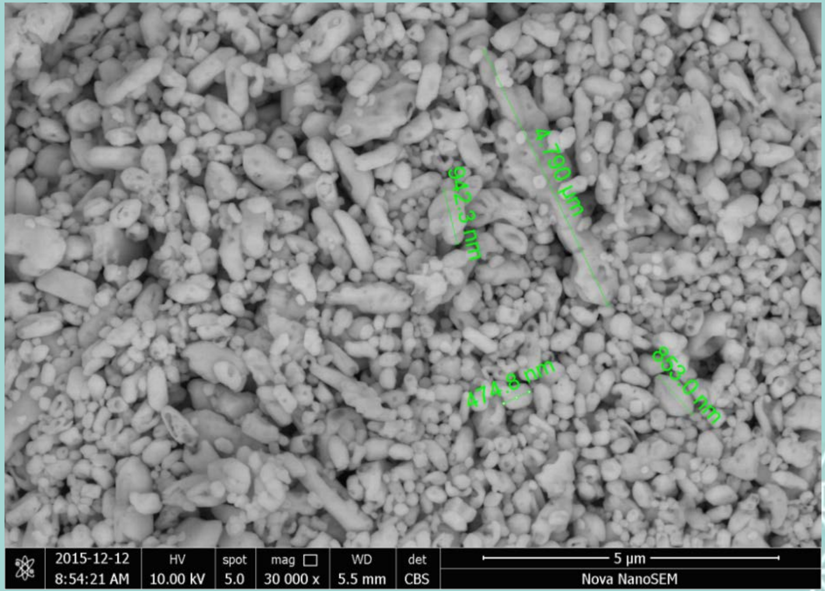




Part of ball structures of Sample X

SEM Images of Different BaSO4





All ball structures of Sample N

SEM Images of Different BaSO4

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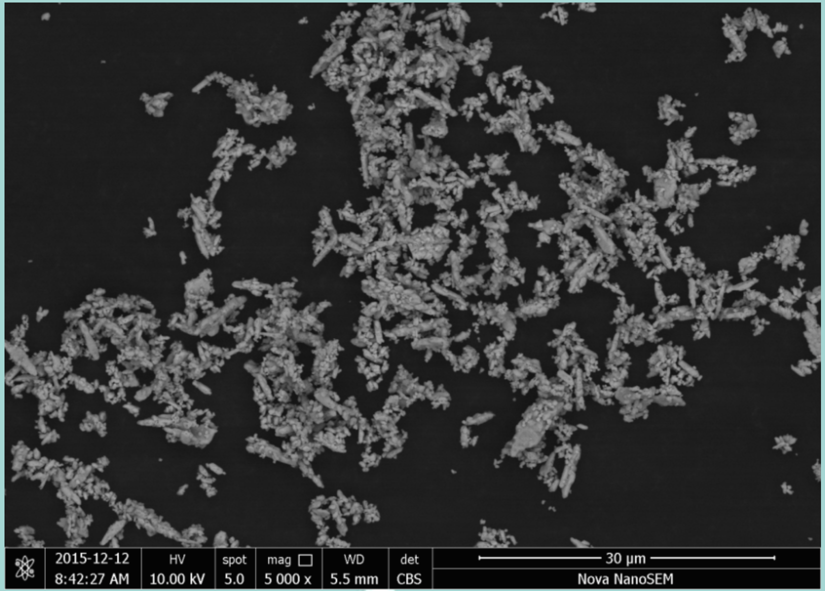
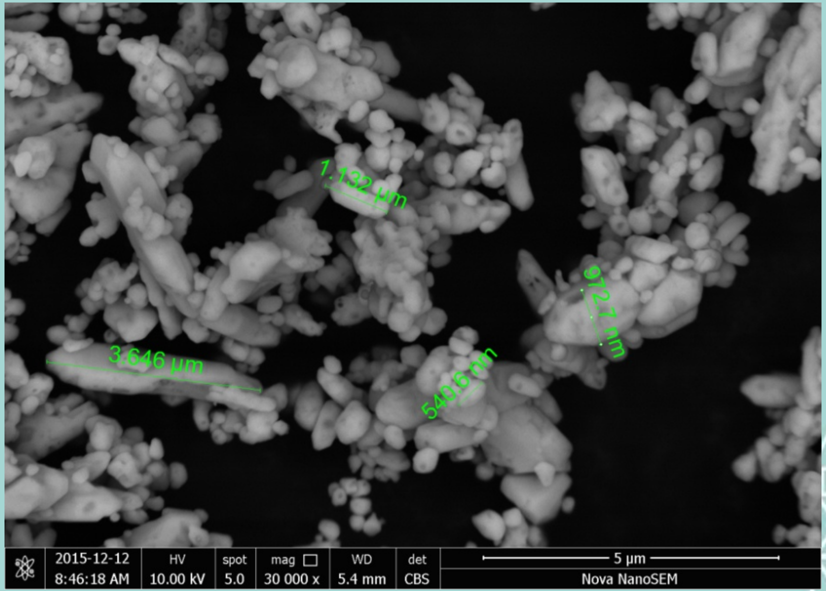
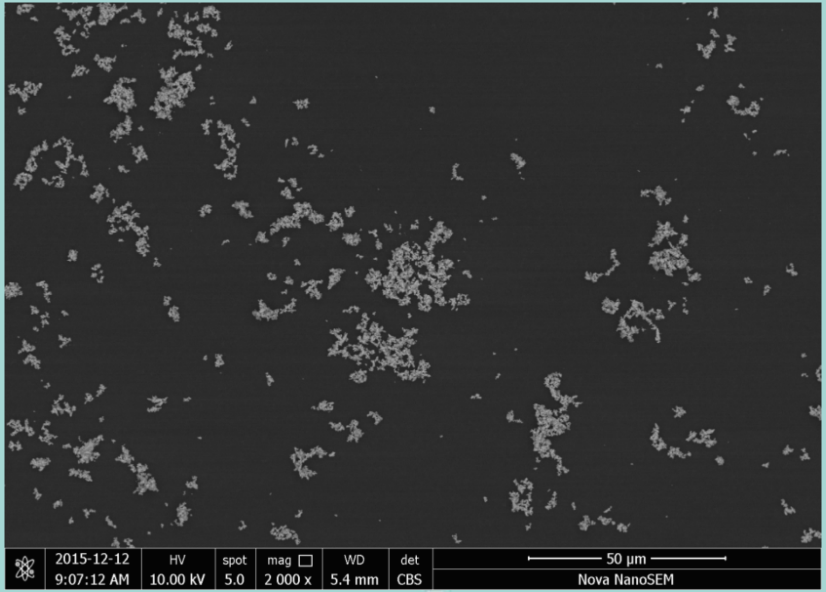
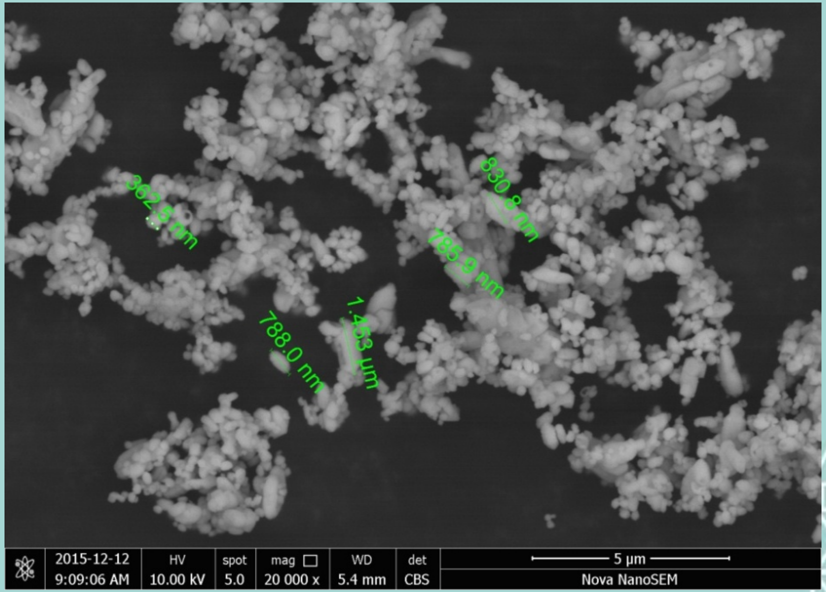




Structures of Sample Y

SEM Images of Different BaSO4





Structures of Sample A

Selection of Barium Sulfate and Mixing Ratio

From the SEM images, we can find some samples of $BaSO_4$ are part or all ball structures. Average particle size is around 20μm. While Sample A is 1-3μm, and uniformly dispersed without agglomeration.

We use ultrasonic in the particle size analysis and we found Sample A is no big difference of reaction to the ultrasonic, which means it has good dispersion and no agglomeration , good for battery performance.

Effects of Different BaSO4 on Battery Performance

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序号	1.5A放电至1.75V 放电容量Ah	-18℃,40A放电至1.0V 时间s	2.4V充电10min时 电流A	-15℃ 1.5A放电至1.75V 放电容量Ah	3C 放电至1.6V 放电容量Ah
硫酸钡A 0.7%	4.809	153	1.243	2.004	2.976
硫酸钡A 1%	4.784	166	1.270	2.287	3.305
硫酸钡B1%	4.693	159	1.270	2.440	3.237
硫酸钡C 0.7%	4.610	101	1.416	2.418	-
硫酸钡C1%	4.746	105	1.400	2.509	-
硫酸钡D1%	4.603	119	1.405	2.633	-
硫酸钡D0.7%	4.556	130	1.570	2.801	-

We study the different Barium sulfate and confirmed the mixing ratio by repeated tastings.

Selection of Lignin and Mixing Ratio

The dissolution degree of organic expander(lignin) has obvious correlation with high-rate discharge performance.

The below is the test of dissolution degree.

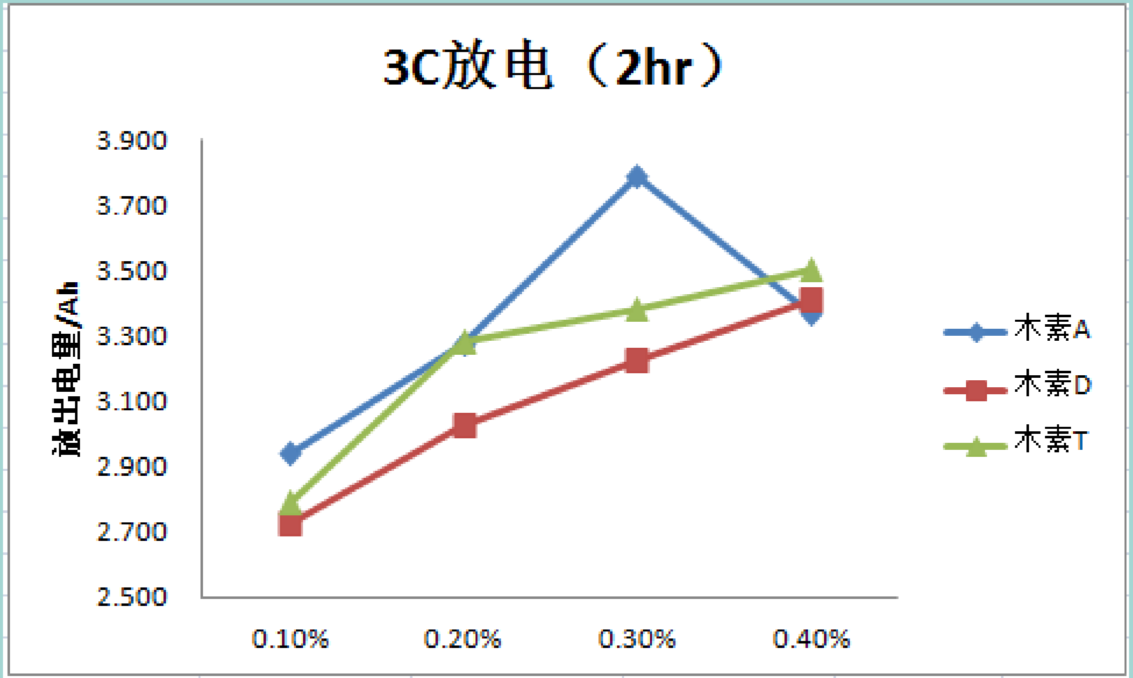
Test procedure: 1. Sulfuric acid 100ml 1.32g/cm^3(25℃)

2. Put 0.5g different kinds of organic expander into the acid and stand for 7days, and then filter & weigh.

No.	Bulk density (g/ml)	Residue on sieve(0.125mm)	%	%	PH	Alkali insoluble %	Water soluble at room temperature%	Acid solubility at room temperature%			High temperature acid solubility%		
			Moisture	Ash	PH			1.05 g/ml	1.28 g/ml	1.35 g/ml	1.05 g/ml	1.28 g/ml	1.35 g/ml
1	0.341	18	3.7	2	6.34	0.1	17	6	3	5.5	9	8	9
2	0.509	16	6.5	12.5	7.54	0.1	99.5	23	13	20	22	22	23
3	0.596	32	12.8	22.6	9.05	0.1	99.6	96	48	46	38	39	40
4	0.515	1	4	22	7.94	0.1	99.7	93	86	49	42.5	43	44
5	0.584	4	13.5	20	8.55	0.1	99.6	96	95.5	15	38	38	39

Chart 1: Comparison of the acid insolubles of different organic expanders

Effects of Different Lignin on Battery Performance



Different types of lignin and different mixing ratio will have different effects on battery performance.

Negative Expanders Mixing Effects on Battery Performance

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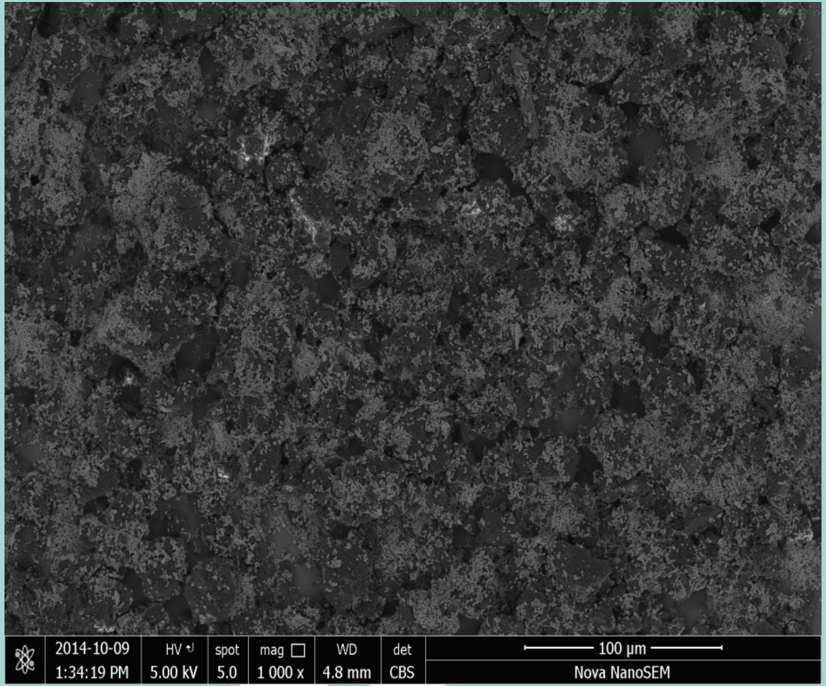
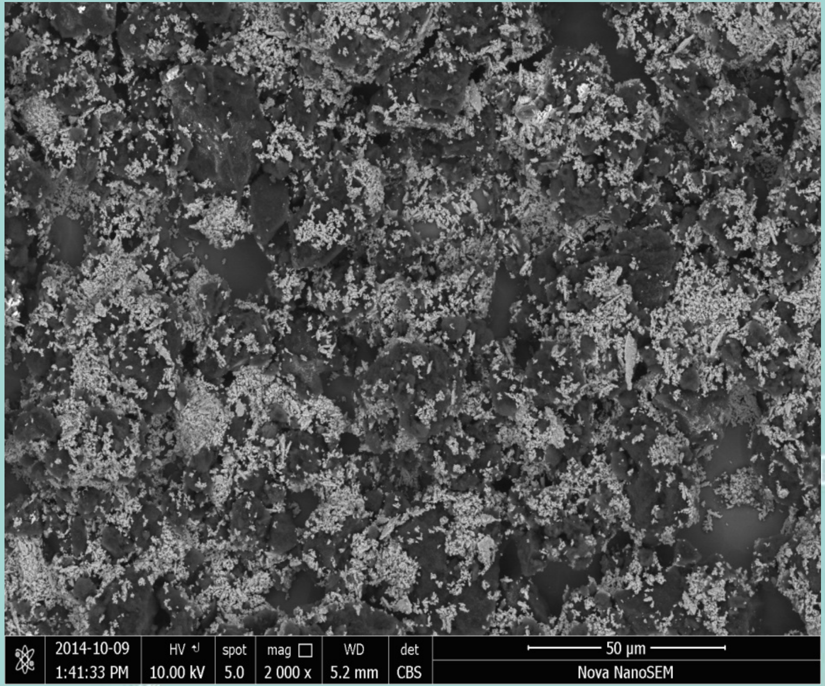
SEM Images of Expanders Mix

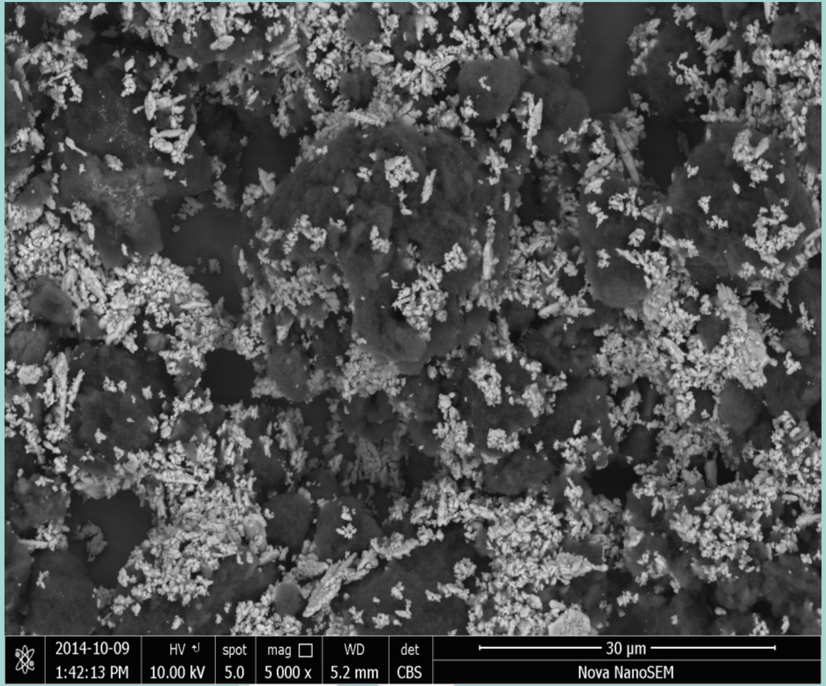


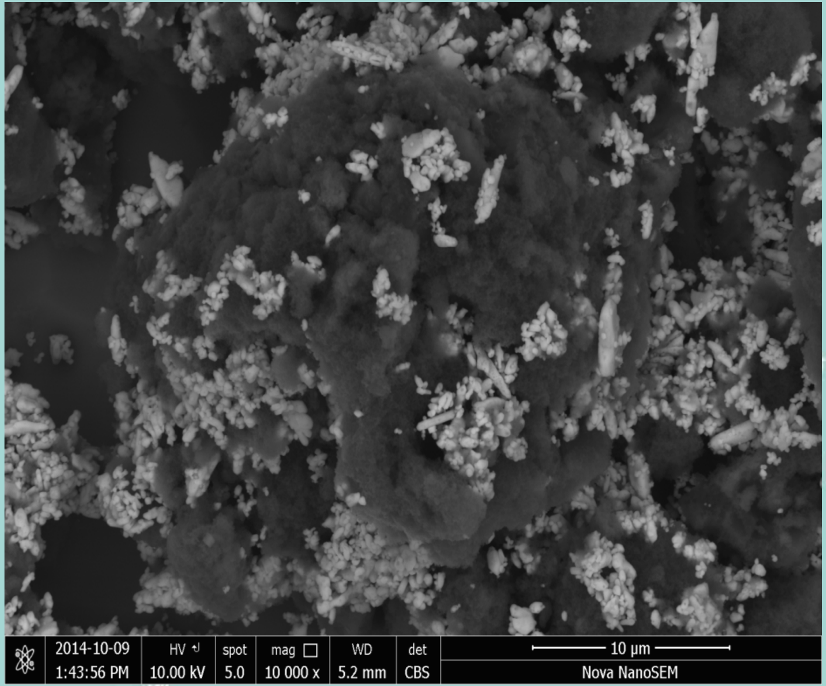


Manually Mixing

Negative Expanders Mixing Effects on Battery Performance

SEM Images of Expanders Mix

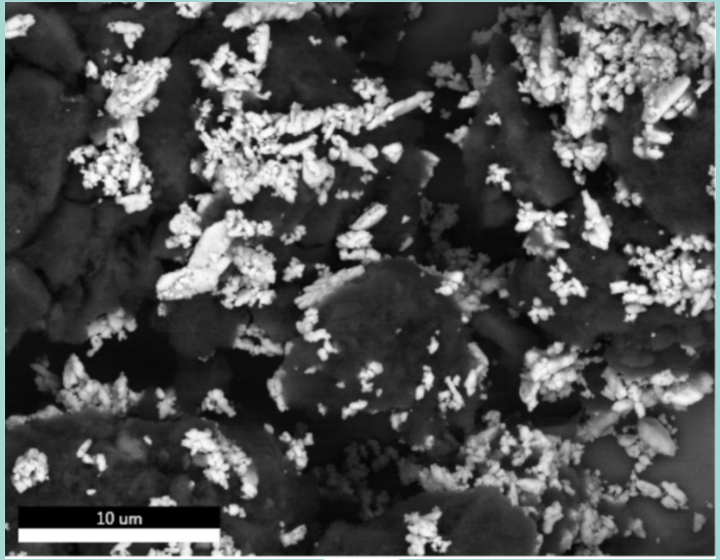


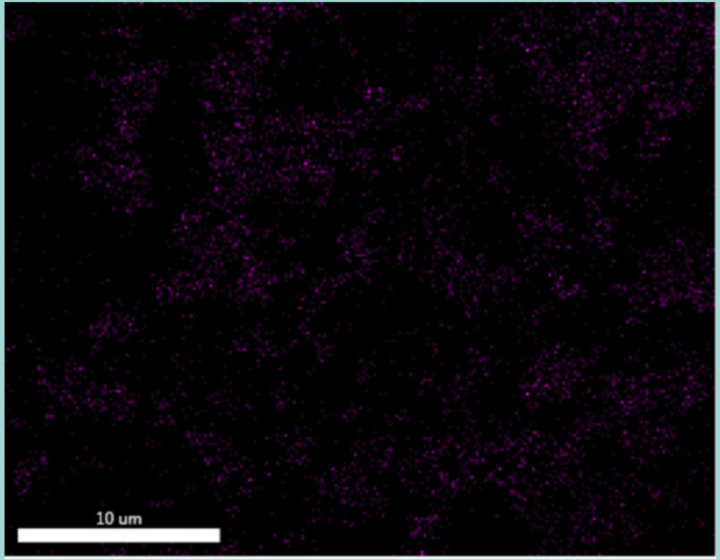


Manually Mixing

Negative Expanders Mixing Effects on Battery Performance

SEM Images of Expanders Mix





Ba distribution

Manually Mixing

Negative Expanders Mixing Effects on Battery Performance

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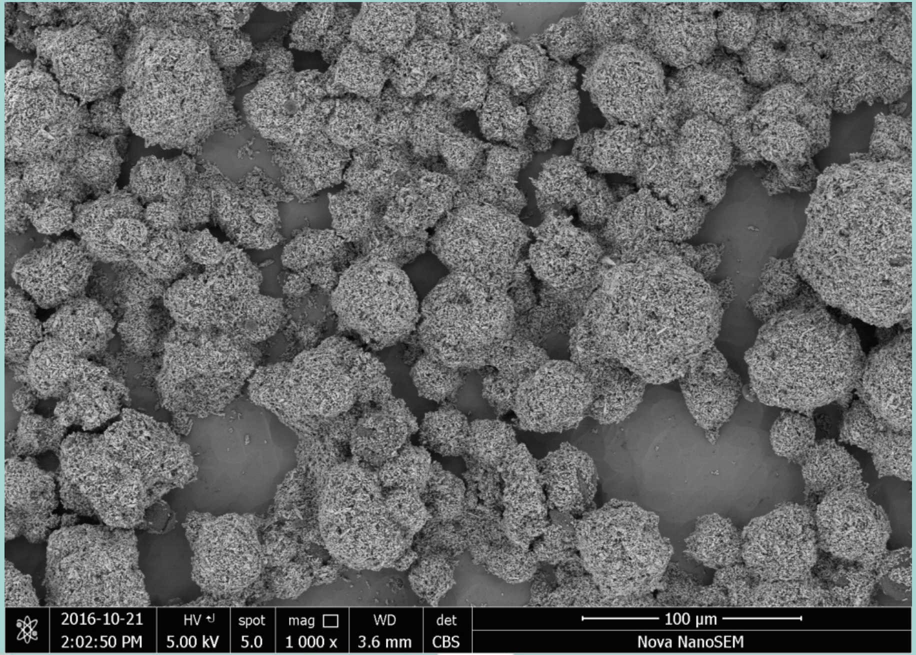
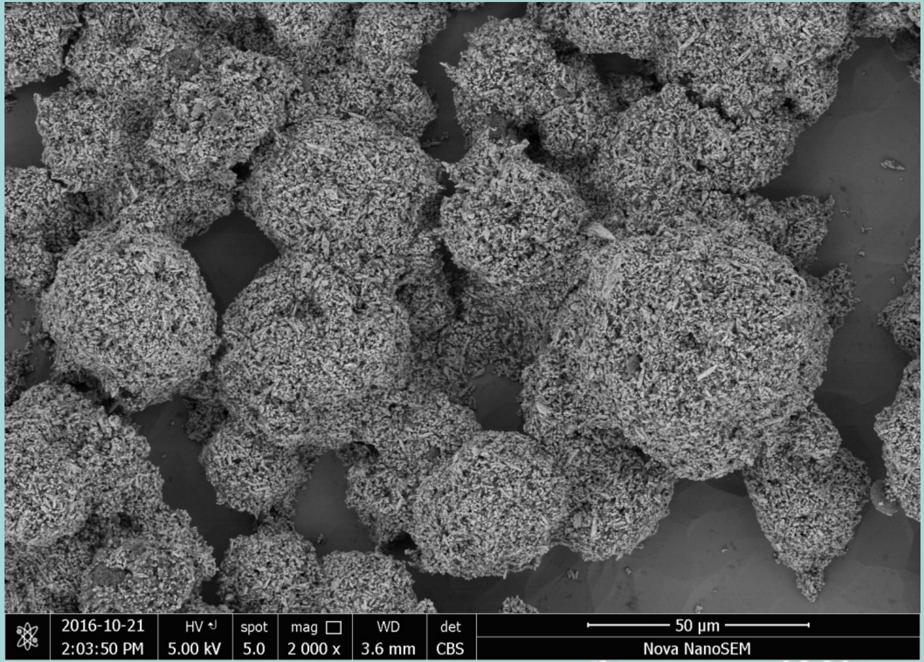
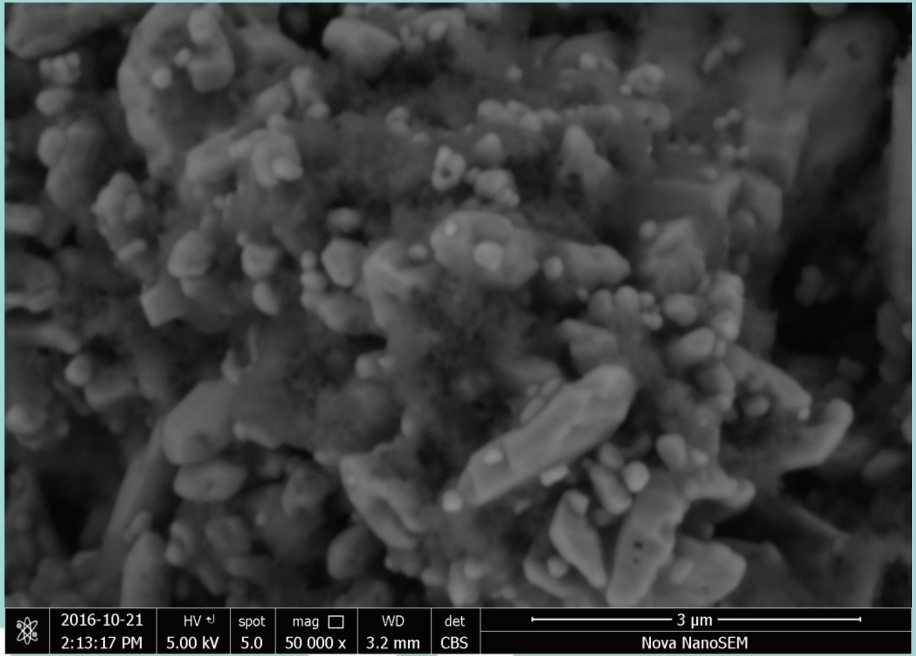
SEM Images of Our Pre-mixed Expanders

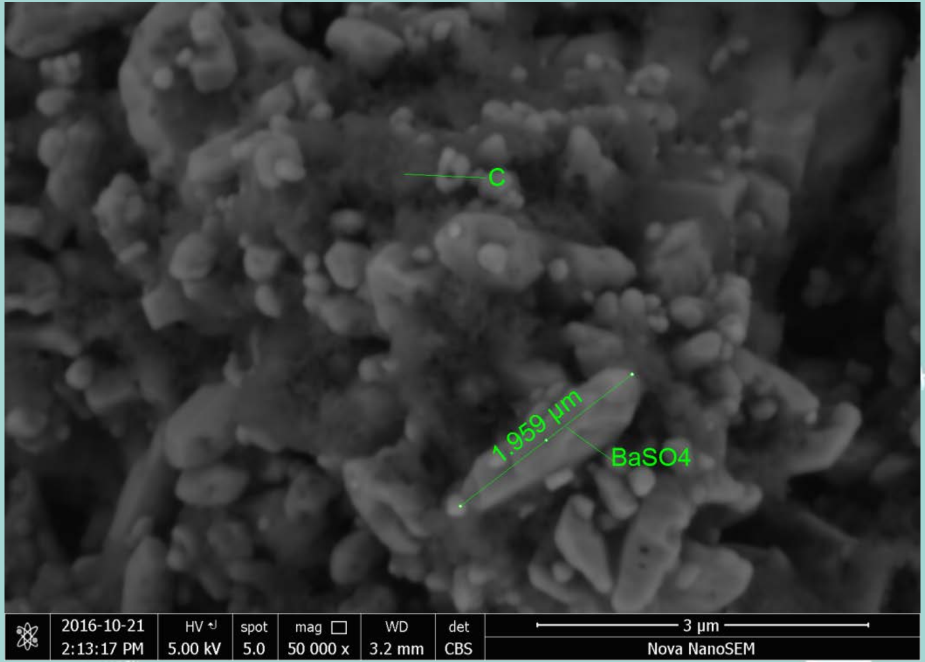




Negative Expanders Mixing Effects on Battery Performance

SEM Images of Our Pre-mixed Expanders





Negative Expanders Mixing Effects on Battery Performance

1. There are agglomeration of expanders in the manual mixing, which is bad to chemicals functioning.

2. With our pre-mixed expanders, all the chemicals will disperse uniformly around lignin without agglomeration. All chemicals will fully function and battery performance will improve accordingly.

Part 4: Battery Tests

Test Design

- 1. Orthogonal test of additives mixing ratio or dosage
- 2. Laboratory cells:

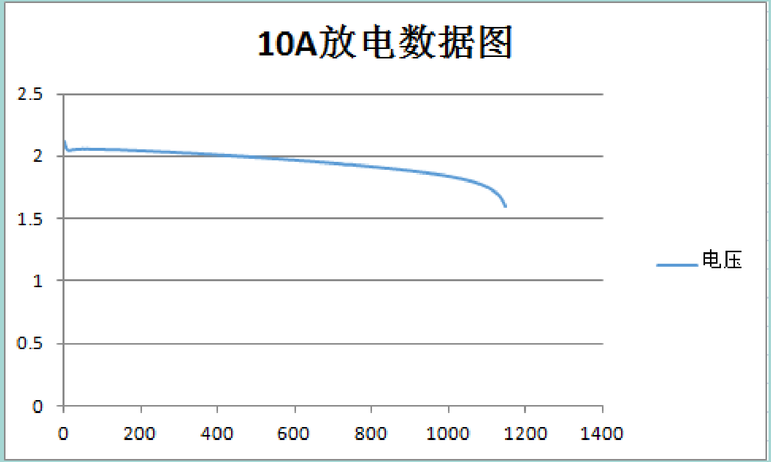
  Assemble cells(3positive&2negative) to compare the electrical performance of the negative plates

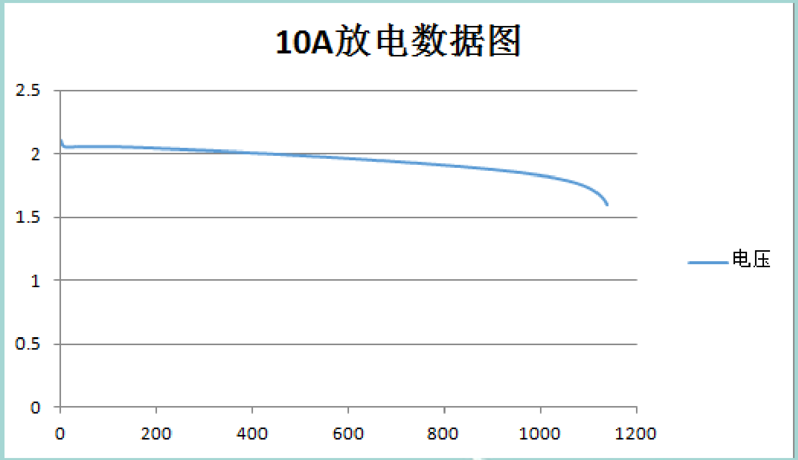
- 3. Test procedure

  1). Discharge @10A to 9.6V

  2). Constant voltage of 2.47V charge for 10h with current limit of 0.6A

Discharge Curve(with existing expanders)





Lab cells test data: discharge @10A time is around 1200s.

Discharge Curve(with our optimized expanders)

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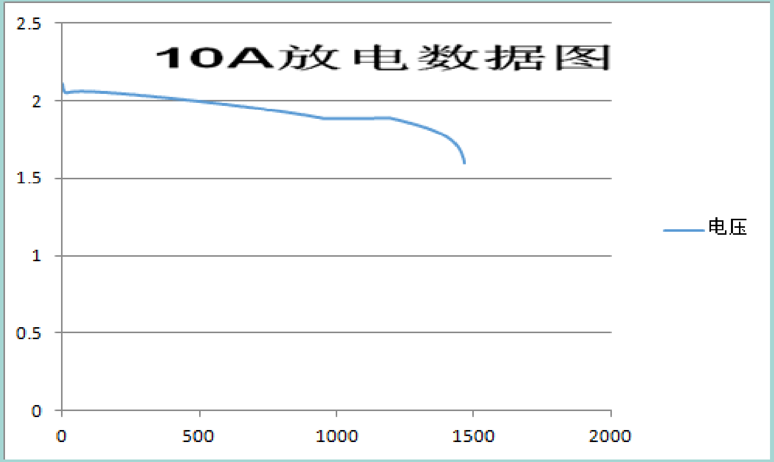
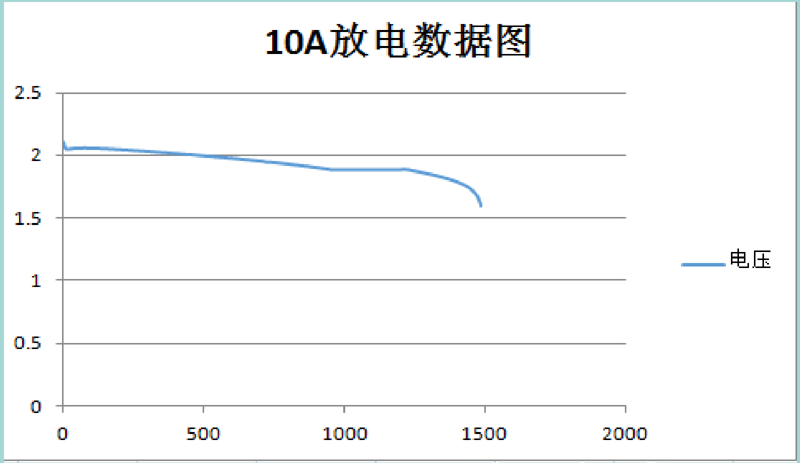
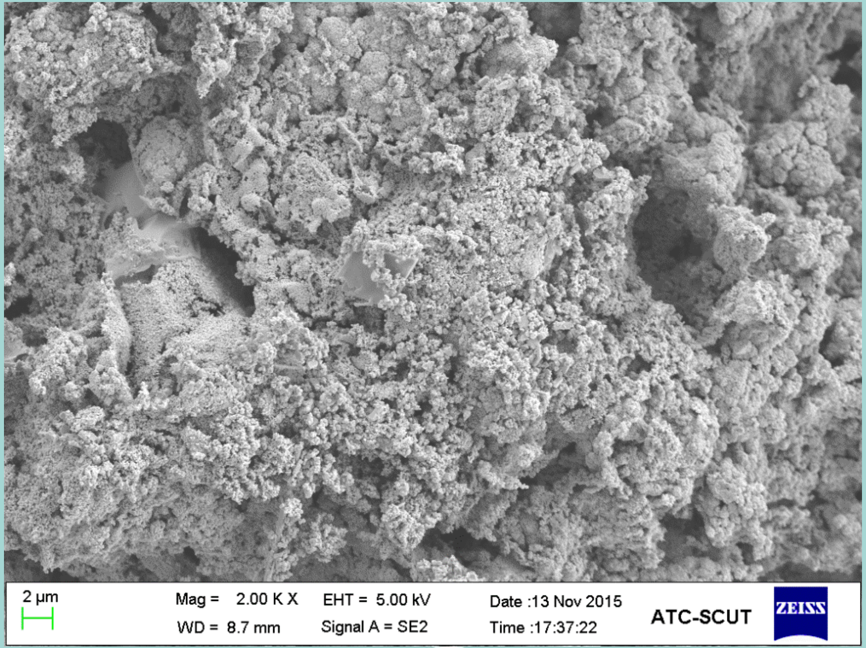


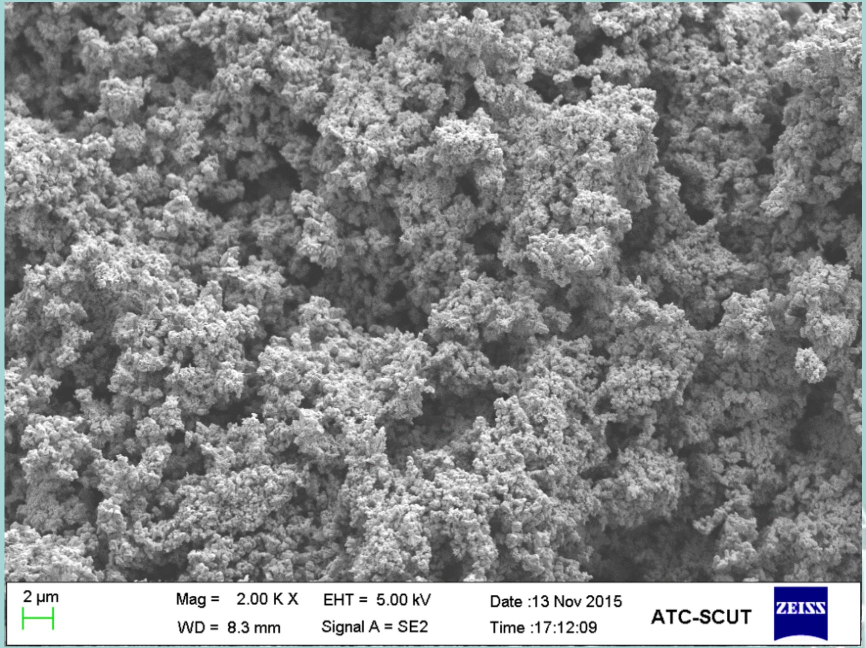


Lab cells test data: discharge @10A time improves to 1500s.

SEM Images of Negative Plates



Plates using existing expanders



Plates using optimized expanders

From the SEM images, we can find that plates using optimized expanders is much better in both surface area and porosity.

Porosity

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Negative Optimized							
No.	1st weigh	After punching	2nd weigh	3rd weigh	Soak for 3h	Weight after soaking	Porosity
1st plate	70.185	70.103	70.113	70.114	72.860	56.178	71.10%
2nd plate	70.247	70.174	70.185	70.185	72.361	57.703	66.45%
3rd plate	70.881	70.801	70.815	70.815	73.392	57.992	67.88%
						Average value	**68.60%**

Existing negative							
No.	1st weigh	After punching	2nd weigh	3rd weigh	Soak for 3h	Weight after soaking	Porosity
1st plate	74.327	74.261	74.286	74.287	76.032	61.145	64.24%
2nd plate	71.918	71.845	71.873	71.873	73.571	59.670	63.08%
3rd plate	72.761	72.695	72.720	72.720	74.550	59.990	64.41%
						Average value	**64.70%**

From the data, we can see that the plates porosity has been improved from 64.7% to 68.6%.

Battery Performance

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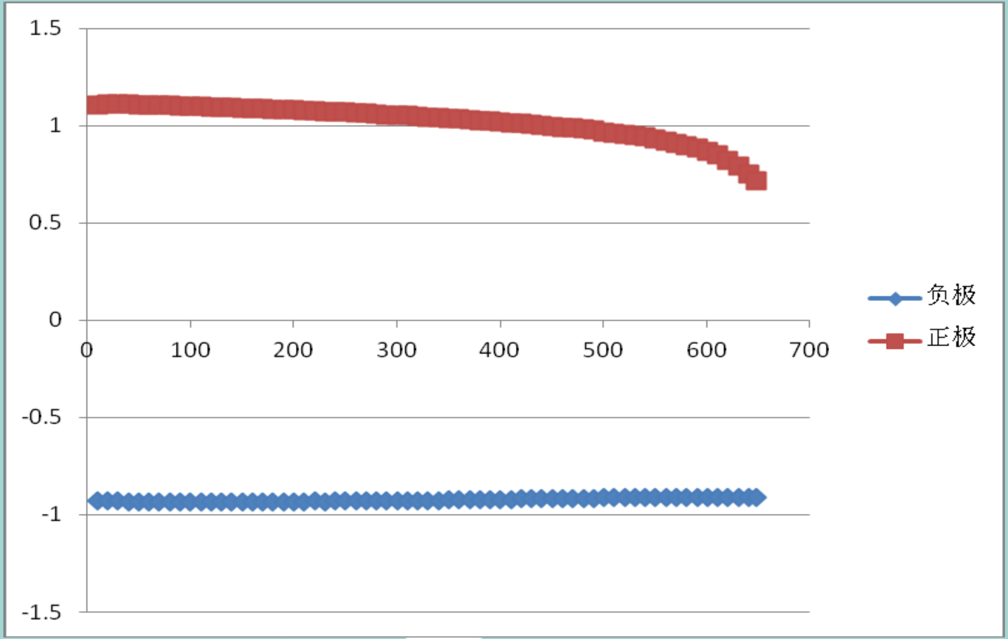
No.	Discharge time @21A (s)	
	Existing expanders	Optimized expanders
1	679	725
2	682	710
3	674	728
4	686	714
5	680	717

Assemble batteries and discharge @ 21A, we found that the discharge time improve from around 680s to 720s, but still fail to reach the expectation of 780s.(13min)

Electrode Potential Test



Use Ag/AgSO4 as reference to find out the limiting electrode affecting the capacity when discharge @21A.

From the picture we can see the problem lies in the **positive**.
Then the next step is trying to improve the positive additives.

Optimization of Positive Additives

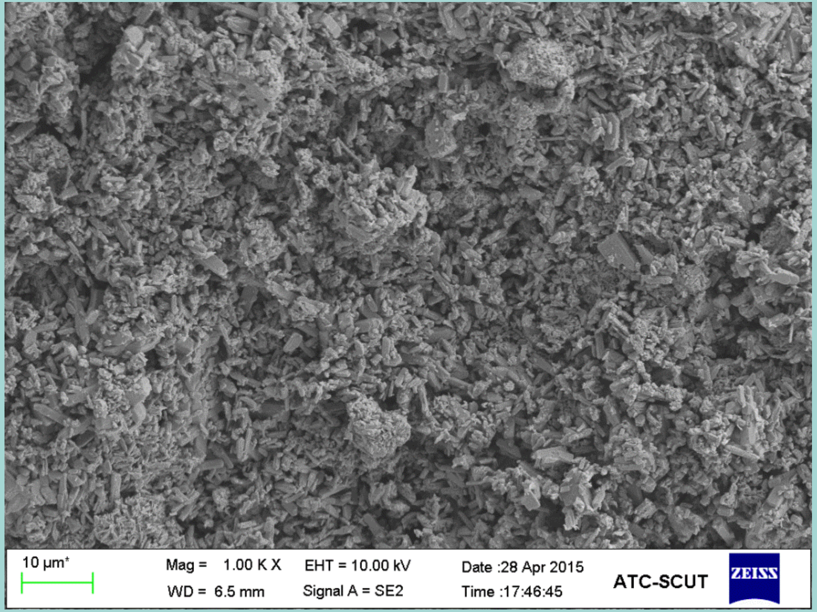
Aim:

- 1. Improve plates high-rate discharge capacity
- 2. Improve plates pore radius
- 3. Improve the conductivity

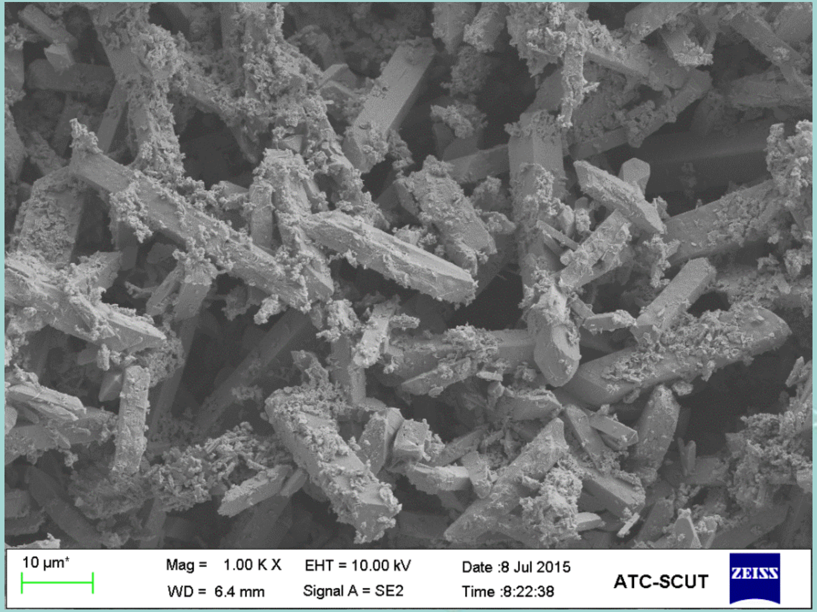
Solution:

- 1. Add new additive to improve the utilization of active material
- 2. Add new carbon to improve the conductivity
- **3. Add new additive to improve the high-rate discharge performance**

SEM Images of Positive Plates



Plates using existing additives



Plates using optimized additives

We can see from the SEM images that the pore radius of plates using optimized additives have been significantly improved and have stronger structure.

Electrical Performance Comparison Test

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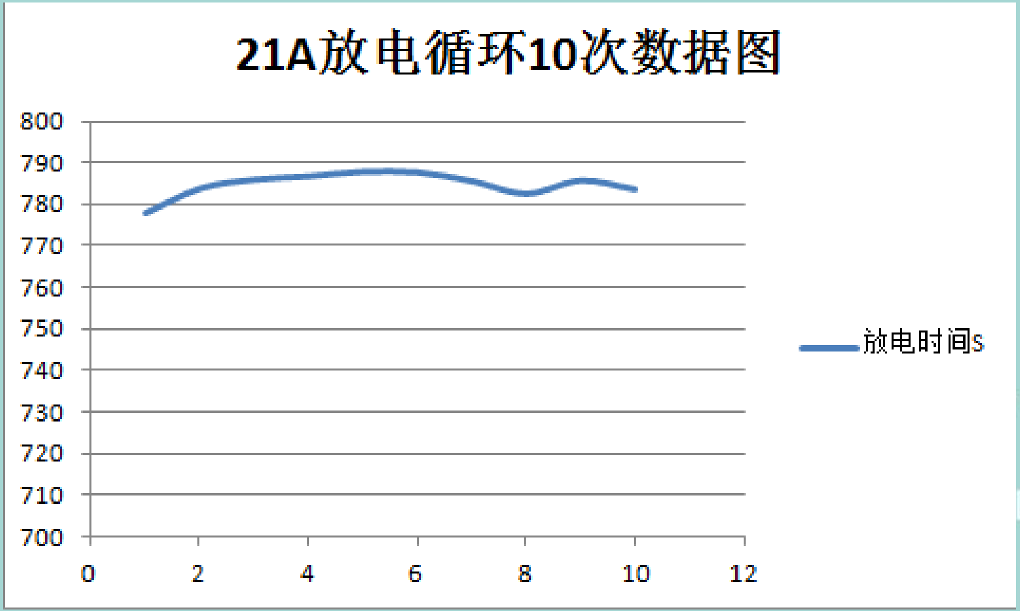
Cycle	Discharge time (s)	Discharge time (min)
1	777.8723	12.96454
2	783.8846	13.06474
3	786.0373	13.10062
4	786.8637	13.11440
5	787.9873	13.13312
6	787.7844	13.12974
7	785.6783	13.09464
8	782.6209	13.04368
9	785.8010	13.09668
10	783.6817	13.06136

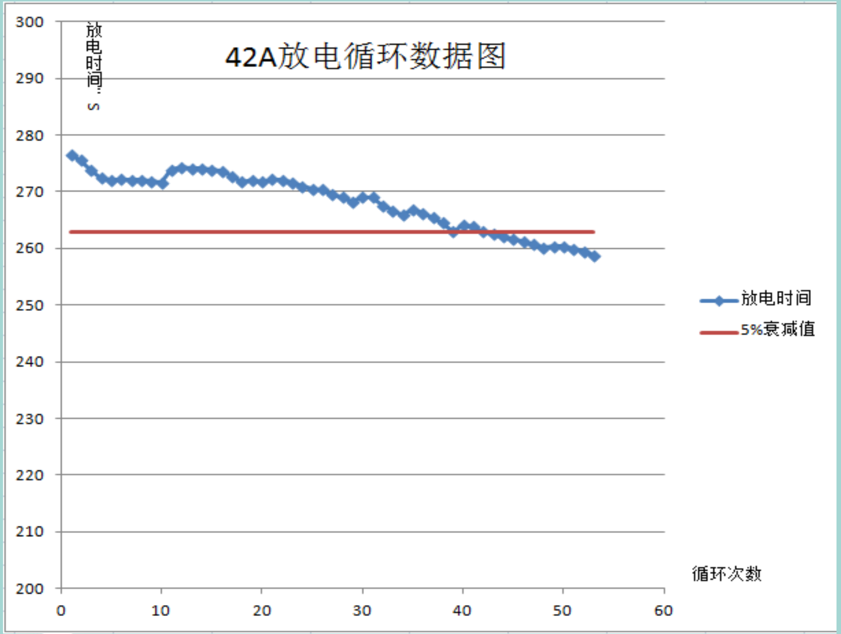


Discharge @21A 10 cycles

Discharge @21A time(s) ≥13min
10cycles≥9min

Electrical Performance Comparison Test

JINKELI



Discharge @ 42A- 40cycles, time decline 5%
meet the requirement of discharge time decline less than 5% after 30cycles

Test Results of 100Ah Batteries

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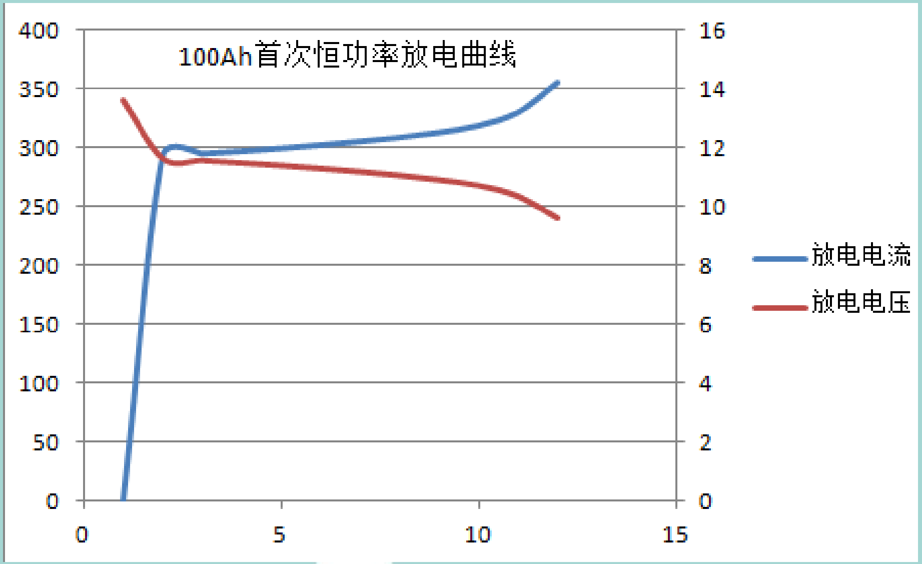


Battery Performance

No.	Test Items	Results
1	Weight (kg)	31.5
2	C10 (Ah)	105.6
3	Discharge for 10min (1.6V/cell) (568W)	10min36s
4	Discharge for 15min (1.6V/cell) (418W)	16min21s
5	10min rate after 30cycles discharge time(min)	9min35s

Electrical Performance Comparison Test

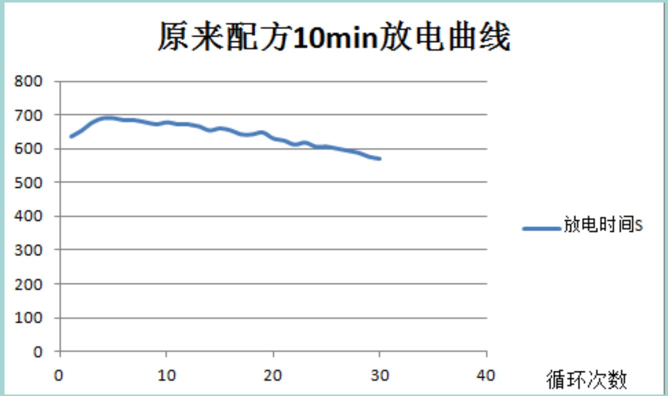
1. Test procedure:

Discharging: discharge @ 568W to 1.6V/cell

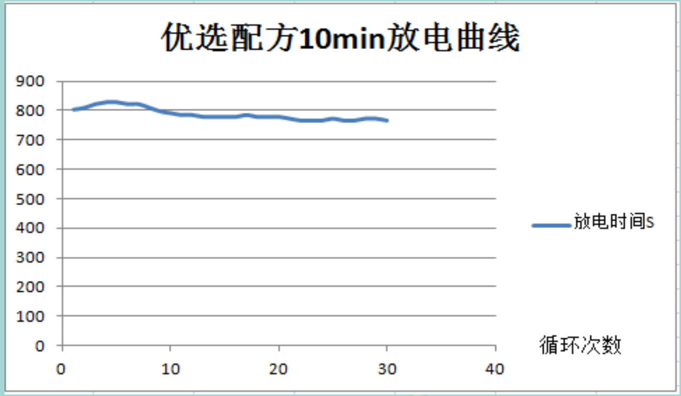
Charging: Constant voltage of 13.8V charge for 8h with current limit of 15A

2. Results:

Discharge Curve of the Existing Additives



Discharge Curve of the Optimized Additives



Item	Existing additives	Optimized additives	Improvement
10min Discharge capacity （average level)	642S	788S	**22.7%**
30cycles decline	10.38%	4.48%	

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Part 5: Conclusion

Conclusion:

With the application of our optimized positive and negative additives for high-power applications, the battery performance especially the high-rate discharge performance have been significantly improved and the customer’s requirements have also been satisfied.

Different Types of Pre-blended Additives for Different Applications

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Product series	Applications	Features
JSS	Start-stop batteries	Better starting ability, charge acceptance and deep cycle life, meet the requirements of both AGM and EFB batteries
JS	Starter batteries	Meet high and low temperature applications, and extend battery life
JEV	Motive batteries	Better charge acceptance and low –temperature performance, low water loss and longer cycle life
JV	Traditional back up power	Low rate discharge, discharge current lower than 0.5 CA, time 60min-6h
	High-rate discharge back up power	**High-rate discharge, current more than 0.5CA, time 3min-1h**
JSP	Energy-storage batteries	Meet high or low temperature applications, high endurance to sulfation and low self-discharge

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