

Influence of Adhesive System on Performance of SiO/C Lithium-ion Battery

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Abstract. Silicon based anode material is turning into the research hot point of lithium-ion battery material field due to Si inside supporting higher capacity. Furthermore binder applied as major accessory material of anode system could bring anode material & current collector together, thus the influence given by binder system to battery performance becomes the key point. The paper describes the procedure of adopting commercial LiCoO₂, SiO/C as composite material & electrolyte, with using styrene butadiene rubber and acrylic acid copolymer as binder to figure out lithium-ion battery with 2.5Ah, which is testified to present better performance on cold temperature & cycle life plus having a little bit swelling compared with the lithium-ion battery using only styrene butadiene rubber as binder.

1 Introduction

It has been hard to get wide commercial application with silicon based anode material due to higher swelling rate of charging & discharging^{1,2}, it's easier to get material dropped from current collector as making electrode due to volume effect, which then have cycle life performance limited³⁻⁷, however binder applied into electrode of lithium-ion pole takes the significant role⁸, special for Si based anode material with huge volume effect, qualified binder system supports huge modulus of elasticity, which could prevent Si based anode material during charging & discharging from dropping with current collector, finally get cycle life performance improved.

The article mentions anode material adopting SiO/C composite material⁹, with referring the impact of different system SN307 & JSR104A on properties of SiO/C material, SN307 is one qualified & effective binder containing styrene butadiene rubber (C₁₂H₁₄). JSR104A identified as fresh designed binder owned by JSR co., which contains mainly acrylic acid copolymer, its molecular formula is butadiene styrene methyl methacrylate copolymer. Therefore we could judge comprehensively the influence of battery performance brought by using two types of binders from factors including adhesion, reservoir volume, high/low temperature, discharge rate, cycle life etc.

2 Experiment

2.1 Reagent and equipment

Cathode material (Beijing Easpring), anode material (Battery SiO/C, Si – 5%), separator – Ube PP/PE/PP 3layers 16 m, material list is below:

(1) Cathode material: LiCoO₂ (Beijing Easpring);

(2) Anode material: SiO/C material;

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(3) Anode conductive: Super-P;

(4) Binder: SN307 (butylbenzene) & JSR104A;

(5) Separator (Japan Ube);

2.2 Experiment & method

2.2.1 Cathode electrode making

The paper describes lithium cobalt oxide adopted as matched cathode material, first step is putting cathode material & conductive into oven with setting up temperature at 800C & baking for 4hours. Finally, getting cathode material mixed up, the mixing ratio is set as lithium cobalt oxide: super conductive carbon: PVDF at 95:2:3, sizing agent is NMP, taking solid : liquid at 1: 3 ratio for material mixing up, lasting over 5hours, then mixing up under vacuum condition for 5mins ahead of having slurry coated onto Al foil with 18m, passing electrode through oven with four steps of temperature from 60 °C, 80 °C, 100 °C, 120 °C for continuous baking, next is for electrode making as below processes:

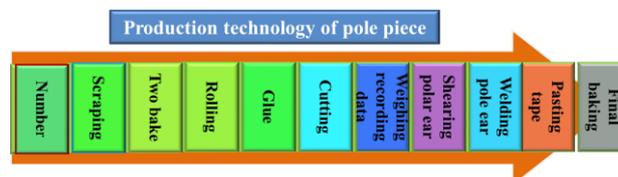


Figure 1. Cathode electrode making process chart.

2.2.2 Anode electrode making

Adopting Battery owned SiO/C as anode material; first step is getting little moisture forced out by baking anode material, conductive carbon Super-P and VGCF for 4hours at 150 °C. Then weighing accurately anode material, conductive, CMC, SBR, sizing agent to set up

mixing ratio at 90: 2: 3: 5 for anode material: Super conductive carbon: CMC: SN307 (JSR104A), taking deionized water of sizing agent to get raw material mixed up with solid Vs liquid at 1: 2.5 ratio lasting for 5hours, then mixing up under vacuum condition for 10mins ahead of having slurry coated onto Copper foil with 16 m, passing electrode through oven with four steps of temperature from 50 °C, 70 °C, 90 °C, 105 °C for lasting baking, next is for anode electrode making just repeat like cathode electrode making processes.

2.2.3 Battery producing

According to the following process, we used prepared anode and cathode electrode to produce polymer cells (without sealing and injection), and then number them to record.

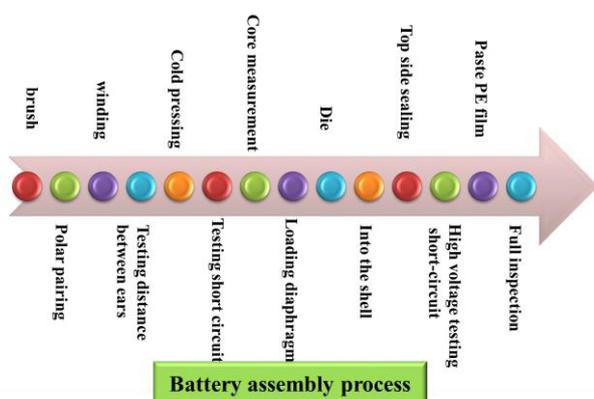


Figure 2. Battery assembling process flow.

After assembling, the polymer cells are going to double bake and weigh, and then inject electrolyte one by one on the injection machine; at last, weigh and record the sealed cells and store in the aging room for 24 hours. After aging, the polymer cells need to get further formation, and to be pre-charged, baked, second sealed and cut, folded and regularized; finally put into the aging room, capacity sorting and internal resistance measurement.

2.3 Measurement equipment and characterization

In this report, we use QUANTA 6000 scanning electron microscope of FEI Holland and TEM (transmission electron microscopy) of Hitachi Japan to analyze the particle's size and surface morphology of the samples. For charging and discharging test, we use BTS-5V20A battery testing device of Kinte Guangzhou.

3 Figures and tables

3.1 SiO/C material, characterization of the morphology of different adhesive system

Figure 3 are the photos of the coating electrode SEM when SiO/C material using SN307 as adhesive, we can see that the white spots on the graphite are conductive additive Super-P carbon granule, but we cannot see SN307 adhesive. Similarly, when SiO/C material using JSR104A as adhesive on the coating electrode SEM, we can also see Super-P carbon granule on the graphite, but we cannot see JSR104A adhesive. According to the comparison, we can see that the coating electrode using different two adhesives do not have obvious differences under the scanning electron microscope.

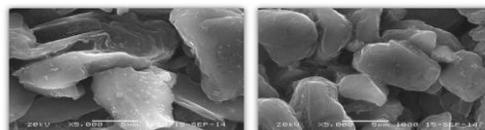


Figure 3. (1)SiO/C material using SN307 as adhesive on the coating electrode SEM, (2)SiO/C material using JSR104A as adhesive on the coating electrode SEM.

3.2 Analysis of electrode peeling strength when SiO/C material using different kinds of adhesive

In order to test the degree of adhesion of SiO/C material and current collector when SiO/C material using SN307 and JSR104A as adhesive; we tested electrode peeling strength when using these two adhesives. We cut the anode which finished one-side coating and baking into one large piece of electrode (see figure 4-4); and then we use paper cutter to cut a 15cm*2cm small piece of electrode, the longer side has to be paralleled to the two sides of the large piece of electrode. Then we use white double sided tape completely sticking to the small piece of electrode's dressing surface, then peel a little bit, and show the copper foil under the anode material. Then, use machine's two clips—one to clamp the copper foil and one to clamp the double sided tape, and start doing the peeling test. The ordinate is the needed strength that peel the dressing out of the copper foil, the abscissa is the moving distance of the clip which clamps the double-sided tape. The recorded data are the maximum strength during the test. In order to make sure the accuracy of the test, in this report we choose eight electrodes and test eight groups of parallel data. Maximum force is to record the maximum strength of each electrode's peeling process, the larger the average number means the firmer the dressing material sticking to the copper foil and the greater the peeling strength. According to the comparison of the testing data, we can tell that using JSR104A has slightly better adherence performance than using SN307. Because JSR104A has one more methyl acrylic acid monomer than SN307, and the carboxyl or carboxylic sodium in it has stronger binding force with Cu-O or Cu-OH on the surface of the copper foil, so it has greater peeling strength.

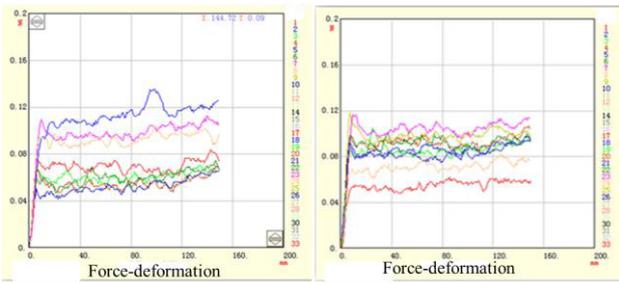


Figure 4. 1 Analysis of electrode peeling strength when SiO/C material using SN307 as adhesive; 2 Analysis of electrode peeling strength when SiO/C material using TRD104A as adhesive.

3.3 Analysis of electrode compaction and imbibition when SiO/C material using different kinds of adhesive

We re-test when SiO/C material using SN307 and JSR104A as adhesive, the electrode compaction and imbibition. The specific test methods are: after coating and baking both sides of the anode electrode, we use paper cutter to cut a 25cm*4cm small piece of electrode, the longer side has to be paralleled to the two sides of the large piece of electrode, 20 pieces in total, carefully remove the electrode which exposed the foil. Then we weigh those pieces by electronic balance, and use ball pen to mark on the electrode; and we use pressing machine to press the thickness that we need, the area of the electrode is 100 cm². At this moment, the mass of the copper foil is 0.728g, the thickness of the copper foil is 8μm. The calculation formula of compaction density is: $\text{Compaction density} = (\text{electrode mass} - \text{copper foil mass}) / (\text{thickness after pressing} - 8\mu\text{m})$. (5.1)

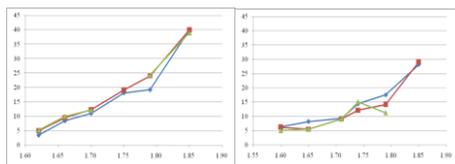


Figure 5. 1 Electrode compaction and imbibition when SiO/C material using SN307 as adhesive (The abscissa is compaction density, the ordinate is time), 2 Electrode compaction and imbibition when SiO/C material using JSR104A as adhesive (The abscissa is compaction density, the ordinate is time).

The electrode use different pressure distribution to press different compaction density. When using SN307 as adhesive, the electrode compaction densities are 1.63, 1.66, 1.70, 1.75, 1.79, and 1.85 respectively. Under the condition of same pressure, when using JSR104A as adhesive, the electrode compaction densities are 1.60, 1.65, 1.71, 1.74, 1.79, and 1.86 respectively. We use pipette to add a drop of about 50μL PC liquid on the right, middle, left areas of the electrode, and to stopwatch till the liquid is out of sight, parallel test three times under every condition of compaction density. Normally, the greater the compaction density is, the slower the rate of imbibition is. Under the same circumstance of

compaction density, the rate of imbibition is connected with the anode material, conductive additive and adhesive. As the following figure 5-1 and 5-2 show, when SiO/C material using SN307 and JSR104A as adhesive, the comparison of imbibition time under different compaction density. Firstly, we can see that under the same condition of pressure, compaction density of using SN307 has better consistency than using JSR104A; however using JSR104A has better performance of imbibition. So we can tell that when compaction density reaches 1.85g/cm³, using JSR104A, electrode’s time of imbibition is only 30 minutes; while using SN307 is 40 minutes. It is probably because JSR104A has a better wettability with electrolyte.

Table 1. The thickness changes before and after anode compaction when using different kinds of adhesive (Unit /μm)

Thickness after pressing	Thickness before winding	Thickness after injection	Thickness after full-charging	Total swelling rate
110	112	113		2.70%
111	112		143	28.83%
110	112	113		2.70%
111	112		142	27.93%

In the report, we test the electrode thickness changes of injection after pressing, before and after charging when using SN307 and JSR104A. We pick ten spots on the electrode to test, and then we calculate the average. Two electrodes measure the thickness changes before and after injection, two cells test the thickness before and after full charging, and the record show above (Form 1). When using SN307 and JSR104A, the total swelling rate of the electrode before and after injection all are 2.70%; while after full charging, the total swelling rate of using SN307 is 28.83%, and is 0.9% higher than that of JSR104A (27.93%). According to the comparison, the changes of swelling rate before and after injection and charging are basically the same when SiO/C composite using those two kinds of adhesive.

3.4 Analysis of the amount of remained electrolyte of whole battery when SiO/C using different kinds of adhesive

The amount of remained electrolyte of pouch cells means the actual amount of electrolyte within the cell after injection, aging storage, pumping and two times sealing. The amount of remained electrolyte is an important factor to guarantee the cell cycle performance. When the amount of remained electrolyte is enough, it can be avoided that cycle performance of the battery in a long time cycling because of the reduced amount of electrolyte and lead to sharp decline. So we hope that the amount of remained electrolyte is large enough, in order to avoid the situation that when the electrolyte is not enough, resulting

in battery performance fell sharply in the circulation process.

After putting the wound pouch cell into the pouch can, fold the pouch, and left three sides to be sealed. Firstly, seal the sides of cathode tab and anode tab, which is what we call top and side sealing; first sealing side has been remained, between first sealing side and cathode tab is air tank. Secondly, we put the cells into 80 degree centigrade baking oven to remove the moisture. After taking the cells out, we store them till they have cooled down, weigh it for the first time, inject 6.8g electrolyte from the unsealed side, and then repeat the first sealing. At this moment, the inner part of the cell has completely isolated from the outside. Store in normal temperature for three days to wait for the electrolyte completely infiltrate the cell. In pre-charging process, the SEI film formation generated gas will enter into the gas tank. The in second sealing process, the airbags will be impaled, take away the remained air between cell and pouch; at the same time, some of the electrolyte will be taken away inevitably, the second sealing side will be sealed and weigh for the second time. This number minus the first weigh number is the amount of remained electrolyte. The amount of taken away electrolyte has a relationship with the anode and cathode materials, diaphragm and the kind of electrolyte.

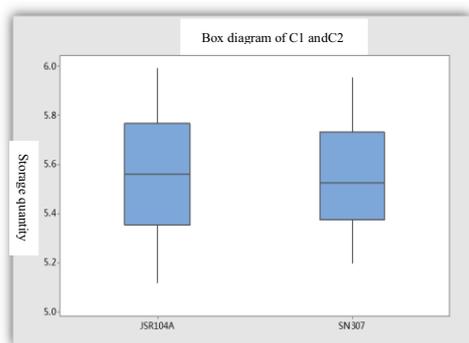


Figure 6. Comparison of electrode remained amount of electrolyte when using JSR104A and SN307.

3.5 Test of cell capacity when SiO/C using different kinds of adhesive

Firstly, test capacity of the cells which use SiO/C as anode material, and use JSR104A and SN307. We choose 20 cells respectively to test, and calculate the average. The specific testing methods are as below:

Pre-charge the cells with JSR104A and SN307, after full charging, aging the cells for three days under the condition of 45 degree centigrade; after aging, re-discharge the cell at 0.5C to 2.5V, and then charge the cell to 4.35V with 0.5C constant current. Charge the cell to 0.02A under the condition of 4.35 constant voltages, and then we have the charging capacity. At last, discharge at 0.5C constant current to 2.5V, and then we have the discharge capacity. The capacity can be recorded

as the discharging capacity; this testing process is called as capacity sorting in the industry.

Figure 7 is the testing box-plot, the average capacity sorting of JSR104A is 2500.4mAh, and 2496.8mAh of the cells using SN307.

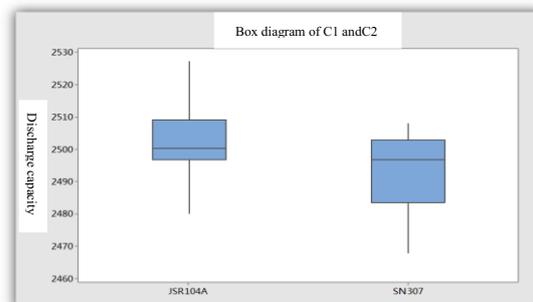


Figure 7. Comparison of capacity sorting when using SiO/C as anode material and JSR104A and SN307 as adhesive.

The volume energy density can be converted by the following formula: Volume energy density = discharging capacity * nominal voltage (3.8V) / cell length * width * thickness. (5.2) At last, we calculate that when using different adhesives the average volume energy density of two groups of 20 cells are 604.5Wh/L for SN307, and 606.7 Wh/L for JSR104A. We can see that the average volume energy density for JSR104A is a little bit higher than that of SN307. Figure 8 is volume energy density data compared with box plots.

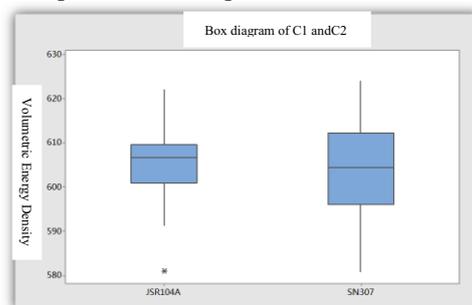


Figure 8. SiO/C Box-plot of pouch battery's Volume/Energy with different bond

3.6 SiO/C Battery's High/Low temperature performance and rate test

As consumption battery, pouch battery has higher demand in high/low temperature performance. Because of that, we do the test of batteries of SiO/C as negative electrode material but has different bond. Choosing 4 cells for each type for test, calculate the average value of the test result. Test method is as bellowing: Using SiO/C as negative electrode material, choose SN307 or JSR104A as the bond and make the two kinds of pouch battery. Taking 4 pcs cells for each type, measure the thickness first. Then put the batteries in the box at 60 °C for 7 days and measure the thickness again after that. The record is showing at figure 9 below. The 4 groups of data are almost the same, which shows that two different kinds

of bond have no big difference for swelling at high temperature.

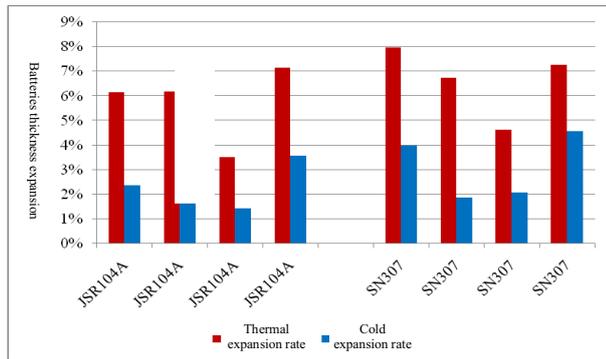


Figure 9. The change of thickness when use different kinds of bond at high temperature.

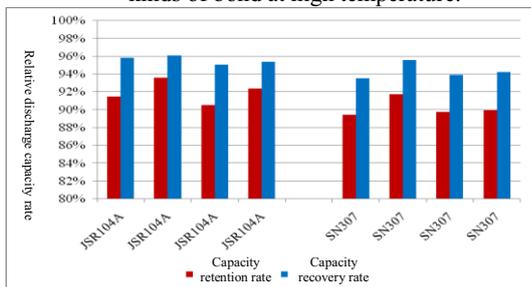


Figure 10. The change of capacity when use different kinds of bond at high temperature

Also measure the left energy and regain capacity after the test. The residual rate of energy means that during high temperature storage, the left energy's rate of nominal capacity. The regain capacity rate means that when temperature is down to RT, the release capacity's rate of nominal capacity. Judging the records, we can know about the self-discharge. First, measure the discharge capacity at high temperature, and then calculate the rate. The data is showing as figure 10 above. According to the data, the residual rate is almost the same, but when using JSR104A, the regain capacity rate is 96%, which is higher than that using SN307.

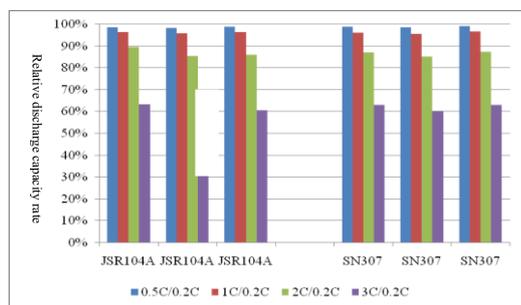


Figure 11. The relative capacity of two kinds of battery.

Then measure the rate discharge test. As figure 11, discharging at 0.5C, 1C, 2C and 3C, charging at 0.2C, chose 3 pcs of each type to test. It shows that discharging at 0.5C, 1C, 2C and 3C, the two kinds of batteries has similar performance, which means they have similar influence to the inner resistance.

At the same time, do the high temperature test again, then test the discharge capacity at -20 °C, -10 °C, 0 °C, 45 °C and 60°C (charging at 25 °C). Test 3 groups of battery as figure 12. Judging the result, the capacity is higher than 70% at -20 °C. When using JSR104A, the capacity is higher than 80%, which is better than SN307. The capacity is almost 100% at 60 °C for both two kinds of battery. Therefore, two kinds of bonds have same capacity holding rate at high temperature, but JSR104A is better than SN307 at low temperature.

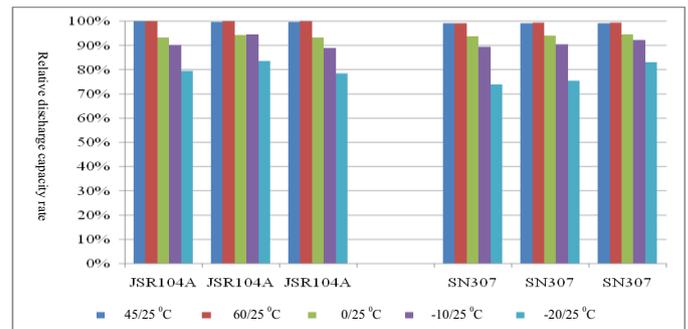


Figure 12. Judging the capacity of two kinds of battery under different temperature.

3.7 SiO/C Test for cycle life of two different kinds of bond

At last, we test cycle life of the battery of SiO/C as negative electrode material using two different kinds of bond at RT. At 25°C, charging at 0.5C until the voltage is 4.35V; the discharging end voltage is 2.75V. The cycle life is like figure 13 below. The blue is the battery with JSR104A and the red is SN307. Judging the first cycle and the other cycle, calculate the rate. According to the test result, the cycle life of JSR104A is much better than SN307. After 200 times cycle, JSR104A's capacity can hold at 85%, but SN307 only has 81%.

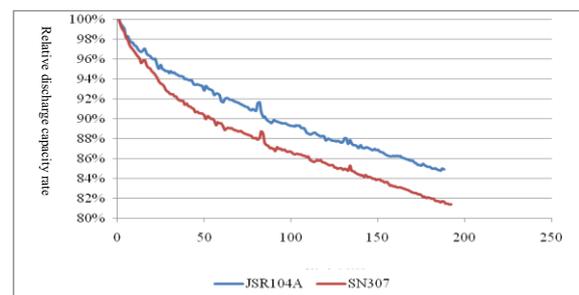


Figure 13. The cycle life of polymer cell on different kinds of adhesive.

4 Conclusion

In summary, this paper adopts the SiO/C composite material as cathode, through the investigation of the use of JSR104A adhesive and SN307 adhesive peeling strength of the electrode, and compaction density after electrolyte filling, thickness changes before and after

charge and discharge, battery liquid quantity, high and low temperature storage and the capacity retention rate performance, cycle performance respectively comparison test.

Through the comparison of test data of eight groups of pole piece of peel strength can be seen, the use of JSR104A SiO/C composite binder adhesion on copper foil in SN307 binder; when the battery charging battery for SEI film formation and decomposition of electrolyte gas due to the expansion of the use of two kinds of binder, the expansion of the battery consistent; Under the same pressure, the use of JSR104A binder SiO/C composite absorption time was significantly shorter in the use of SN307 binder; by contrast, the two kinds of bonded with SiO/C composite soft package battery storage liquid cathode are basically the same; in addition the use of JSR104A binder battery expansion is significantly less than the use of SN307 binder the battery in the charge and discharge; expansion through the comparison of high and low temperature conditions of the battery, there is no obvious difference between two kinds of binder on the battery at high and low temperature expansion. Test two kinds of binder as binder battery negative rate performance, battery capacity two relatively consistent, there was no significant difference between these two kinds of binder, illustrate the influence of the internal resistance of the battery is basically the same. In the high and low temperature performance, the use of two kinds of binder battery high capacity retention rate is basically the same, but the low temperature performance of JSR104A is superior to the use of SN307 as the adhesive. Finally, after testing the two kinds of materials of battery for long time cycle, found that the cycle performance of battery using JSR104A binder was better than using SN307 binder circulation, nearly 190 times the battery capacity can be maintained at 85% relative ratio, compared with SN307 binder battery capacity is only 81%. Overall industrial production line in the preparation of cathode cell with SiO/C composite, the performance in the use of TRD104A binder is better than that of the cell using SN307 as binder, and cycle life from the point of view, basically can reach 300 times the commercial application of the requirements of 80%.

- 8 Y. Yao, M. T. McDowell, I. Ryu, et al. Nano lett. **11**, 7 (2011).
- 9 X. Zhao, C. M. Hayner, M. C. Kung, et al. Adv. Ener. Mat. **1**, 6 (2011).

References

- 1 B. Guo, J. Shu, Z. Wang, et al. Electro. Commu., **10**, 12 (2008).
- 2 Y. S. Hu, R. Demir - Cakan, M. M. Titirici, et al. Ange. Chem. Inter. Edi. **47**, 9(2008).
- 3 Z. Huang, K. D. Harris, M. J. Brett. Adv. Mater. **21**, 29(2009).
- 4 J. K. Lee, K. B. Smith, C. M. Hayner, et al. Chem. Commu. **46**, 12(2010).
- 5 H Li, X L Wu, H Sun, et al. J. Phy. Chem. C, (2015).
- 6 X. Su, Q. Wu, J. Li, et al. Adv. Ener. Mat. **4**, 1 (2014).
- 7 Y. Yao, M. T. McDowell, I. Ryu, et al. Nano lett. **11**, 7 (2011).