

Supporting Information

Preparation of Coating Artificial Graphite with Sodium Alginate as Negative Electrode Material for Lithium-ion Battery Study and Its Lithium Storage Properties

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1 Experiment

1.2 Phase and morphology characterization of materials

1.2.1 Scanning Electron microscope (SEM)

The SEM images of the electrode materials involved in this paper were used to observe the microscopic surface morphology and internal structure of the sample by using the SCANNING electron microscope (EVOMA10 ZEISS, Germany) of Jiangxi Province Key Laboratory of Power Battery and Materials. The acceleration voltage is 5.0-20kV and the amplification factor is 500-5000.

1.2.2 X-ray Electron Diffraction analysis (XRD)

The XRD diffraction pattern of the electrode materials involved in this paper was detected and analyzed by the Dutch Panaco X Pert Powder X-ray diffractometer. The tested tube voltage was 40kV, the tube current was 15mA, and the scanning speed was 0.328287° s⁻¹. The XRD scanning Angle is 10°-80° in the 2θ range, and the scanning speed is 10°min⁻¹.

1.2.3 RAMAN Spectroscopy (RAMAN)

The Raman spectra of the materials involved in this paper were tested by Thermo DXR microscopic optical Raman apparatus. Sample preparation method: take about 10mg powder sample and place it on the slide, put it on the spectrometer sample table for testing, use 532 nm laser exciter, exposure time 5s, exposure times 6, 50 times object environment, 10 times eyepiece, resolution 4 cm^{-1} Thermo DXR micro laser Raman, laser wavelength 532nm, the test range of wave number is 50-3500 cm^{-1} .

1.2.4 Specific surface area and Pore size test (BET)

In this paper, the specific surface area and pore size distribution curves of hard carbon materials were tested by bestor 3H-2000PS2 static volumetric specific surface area and pore size analyzer. When preparing samples, the mass of the sample tube is weighed first, and then the balance is zeroed and inserted into the funnel. Add the sample through a funnel into the sample tube, shake it slightly so that the sample volume exceeds 1/2 of the sample tube volume, and record the reading. The product of sample size and estimated surface area is best at 20 m^2 with 40 m^2 in between. The sample tube was installed in the degassing place, and the electric furnace was installed to set the temperature and time. In this experiment, the heating - vacuumizing mode was adopted to degassing at 200 $^{\circ}\text{C}$ for 2h. After degassing, take off the heating furnace, transfer the sample tube to the tester, input the sample quality and other parameters, pour liquid nitrogen, and start the test.

1.2.5 Transmission Electron Microscope (TEM)

The TEM used Japanese electron JEM-2100F, test acceleration voltage of 200 kV, point resolution of 0.19 nm, lattice resolution of 0.1nm, tilt Angle of $\pm 25^{\circ}\text{C}$, used to analyze the microstructure of solid materials, and observe the crystal structure and crystal defects for the preparation of new materials, properties and structure of the relationship between the study.

1.3 Preparation of electrode and electrochemical performance test

1.3.1 Preparation of electrode

The prepared materials SA/G-C, conductive carbon black (SP)(TIMCAL) and vinylidene fluoride (PVDF)(ARKEMA) were mixed at a mass ratio of 80:10:10 with a total weight of 1g to prepare the negative slurry. When the humidity is below 50, the paste is coated on the rough surface of the copper foil and placed in the electric heating oven at 120°C for more than 1 hour to ensure the full volatilization of NMP. After drying, start the double roll film rolling machine (HJZ-201, Shijiazhuang Hongxing Machinery Factory) for roller pressing; After completion, the use of special negative plate punching machine (SZ-50, Xingye Machinery Co., LTD.) will be pressed into the pole plate diameter of 14mm size. Weigh and record the data, and finally put the measured negative electrode pieces into the vacuum oven according to the number, and dry them for more than 12h at 60°C and -1Mpa.

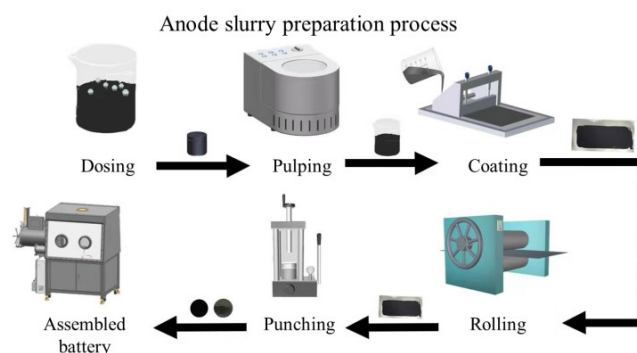


Figure 1.1 Anode slurry preparation process

After vacuum drying for 12h, the negative electrode piece was transferred to the glove box (LABSTAR, MBRAUN) in argon (purity 99.99%, Ganzhou Fengsheng Gas Co., LTD.) environment, and placed in sequence according to the negative shell, lithium metal, diaphragm, negative electrode piece, stainless steel washer and spring piece. Wherein, the electrolyte used is $1\text{mol}\cdot\text{L}^{-1}$ LiPF_6/DMC (dimethyl carbonate)/ EC (vinyl carbonate)/ DEC (methyl ethyl carbonate) were encapsulated into buckle batteries by sealing machine (MSK100, Hefei Science and Technology Material Technology Co., LTD.) for testing.

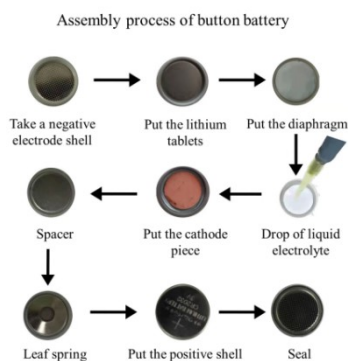


Figure 1.2 Assembly process of a button battery

1.3.2 Electrochemical performance test

The battery formation, cycling and multiplication were completed on the New Way battery tester (BTS-5V/10mA, Shenzhen New Way Electronics Co., LTD.). The cyclic voltammetry was tested in the Multi-channel electrochemical workstation in the Netherlands. The test voltage was 0.01-3V, and the scanning rate was 0.1mVs.Ac impedance test was carried out in Chenhua Electrochemical Workstation (CHI660E, Shanghai Chenhua Instrument Co., LTD.), in which the test frequency of EIS was 0.01-105Hz.

The battery formation condition is at room temperature 25°C, the formation of 12h, then constant discharge to 0.01V, 0.2C current constant charge to 2.5V, and then 0.2C discharge, the process is repeated three times, the end (the current size changes according to the active substance quality of the electrode). When the battery is cycling, the room temperature is kept at 25°C, the range of charge and discharge voltage is 0.01 ~ 2.5V, the cycle times are 70 ~ 600 times, the current is set according to the size of the battery charge capacity; The rate performance was performed at 100 mA·g⁻¹, 200 mA·g⁻¹, 300 mA·g⁻¹, 500 mA·g⁻¹, 1000 mA·g⁻¹ and 2000 mA·g⁻¹ charge and discharge test at electrochemical station.

2. Results and discussion

2.1 Influence of different temperatures on SA as anode material

In order to obtain better electrochemical properties, we explored the optimal heat

treatment temperature at the initial stage. For the material samples sintered at 800 、 1000 和 1100°C, formation, rate performance and cycle performance under different current density were carried out respectively.

It can be seen from the charge-discharge curve of pure SA sample in Figure 2.1(a-c) and the first charge-discharge specific capacity and coulomb efficiency of pure SA sample in Table 2.1 that the first charge-discharge specific capacity of SA-800 sample (Figure 2.1-a) is 71.996mA h·g⁻¹, and the discharge specific capacity is 161.332 mA h·g⁻¹ with a charge-discharge efficiency of 44.626% , and the discharge specific capacity of SA-800 sample is only 70.290 mA h·g⁻¹ in the third charge and discharge test; SA-1100 sample (Figure 2.1-c) has a first charge specific capacity of 138.478mA h·g⁻¹ and a discharge specific capacity of 583.349mA h·g⁻¹, corresponding to a first charge-discharge efficiency of 23.728%,and in the third charge and discharge test, the discharge specific capacity of SA-1100 is 217.567mA h·g⁻¹; For SA-1000 sample (Figure 2.1-b), its initial charge specific capacity is 240.912 mA h·g⁻¹, discharge specific capacity is 732.438 mA h·g⁻¹, the calculated first coulomb efficiency is 32.892%, after three cycles,its charge specific capacity is still 137.811 mA h·g⁻¹ charge specific capacity.

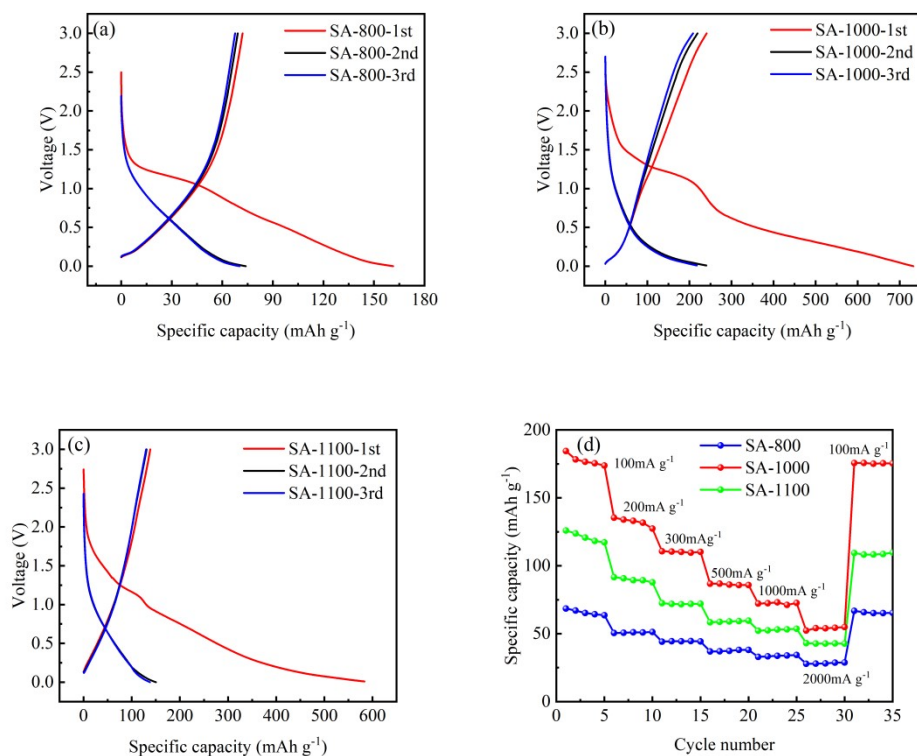
Comparatively, although SA-1000 sample consumed more irreversible lithium during the first cycle, thus a lower first Coulomb efficiency was observed, the capacity was about 4 times that of that of the SA-800 and SA-1100 samples. Figure 2.1-d compares the magnification performance curves at different temperatures,It can be seen that the SA-1000 negative electrode exhibits a great rate performance. At low current densities of 100、 200、 300 and 500 mA·g⁻¹, the capacity of SA-1000 negative electrode is 184.48, 135.41, 110.71 and 86.790 mA h·g⁻¹ respectively. It is particularly significant that the SA-1000 negative electrode maintains a capacity of 72.21 mA h·g⁻¹ and 52.376 mA h·g⁻¹, when the current density reaches 1000 and 2000 mA·g⁻¹. When the current density further returns to 100 mA·g⁻¹, the SA-1000 negative electrode recovers over 95% of its original discharge capacity (175.644 mA h·g⁻¹), exhibiting good capacity restoration performance.

Figure 2.1-(e,f) compares the cycling performance of SA-800, SA-1000 and SA-1100 at different current densities. At a small current density of 500 mA·g⁻¹, The initial specific capacities of SA-800, SA-1000 and SA-1100 are 117.203, 222.255 and 107.760mA h·g⁻¹.

Compared with SA-800 and SA-1100, the initial specific capacities of SA-1000 is significantly increased, about twice as much as those of them. The capacity of SA-1000 is still 201.374 mA h g⁻¹ after 100 charge–discharge cycles, and the capacity retention rate is 90.60%. When the current density increases to 2000 mA g⁻¹, the initial specific capacity of SA-1000 is 107.295 mA h g⁻¹. After 200 cycles, the capacity of SA-1000 is still 93.093 mA h g⁻¹, and the capacity retention rate is 84.73%. However, the capacity of SA-800 and SA-1100 electrodes was only 38.033 and 33.707 mA h g⁻¹, which almost failed and could not maintain the normal charge and discharge cycle.

Table 2.1 Initial charge and discharge specific capacity and initial charge and discharge efficiency at different temperatures

Sample	First specific charge capacity (mA h g ⁻¹)	First specific discharge capacity (mA h g ⁻¹)	Charge-discharge efficiency (%)
SA-800	72.996	161.332	44.626
SA-1000	240.912	732.438	32.892
SA-1100	138.478	583.349	23.728



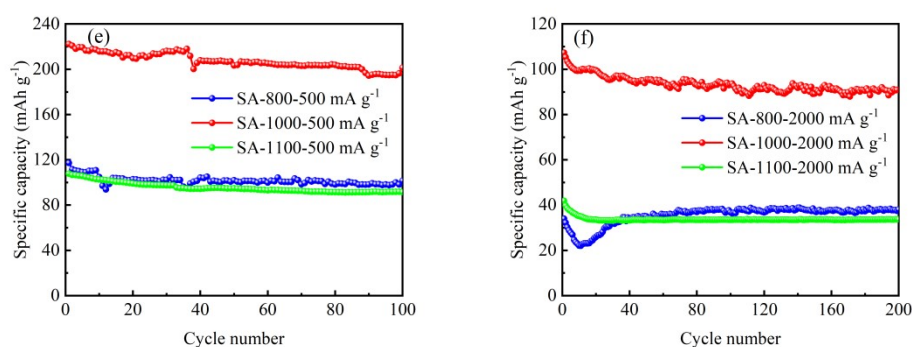


Figure 1.1 Charge-discharge curve (a)SA-800 (b) SA-1000 (c)SA-1100;(d)Rate performance curves at different temperatures; (e,f)Cycle curves at different current densities

To sum up, based on the three typical electrochemical test results of formation curves, rate capability and cycling performance, we chose 1000°C as the best heat treatment temperature in the material preparation stage, under which a better electrochemical performance can be obtained.

2.2 Study on different proportions of SA-1000 coated graphite as anode material

In order to further explore SA-1000 coated graphite as anode material, we investigated the XRD diffraction analysis of composite samples under four coating ratios of 2.5% SA-1000, 5.0% SA-1000, 7.5% SA-1000 and 10% SA-1000 (Fig. 2.2-c). The results showed that the diffraction characteristic peaks only appeared around 26.4°, 42.2°, 44.4° and 54.5°. Among them, the diffraction peak intensity near 26.4° is the highest, the distribution is the widest, and the difference is the largest. The peak values of the composites corresponding to the coating ratio from low to high are $2\theta=26.414^\circ$, 26.413° , 26.443° and 26.446° respectively. According to Bragg's formula $2d\sin\theta=n\lambda$, and through theoretical calculation, the lattice spacing of coated samples in different proportions were 3.3715Å, 3.3719Å, 3.3679Å and 3.3674 Å. Because the coating amount of SA is small and the whole process of coating graphite is only a physical change process, the diffraction characteristic peaks of SA and other phases are not detected in composite samples.

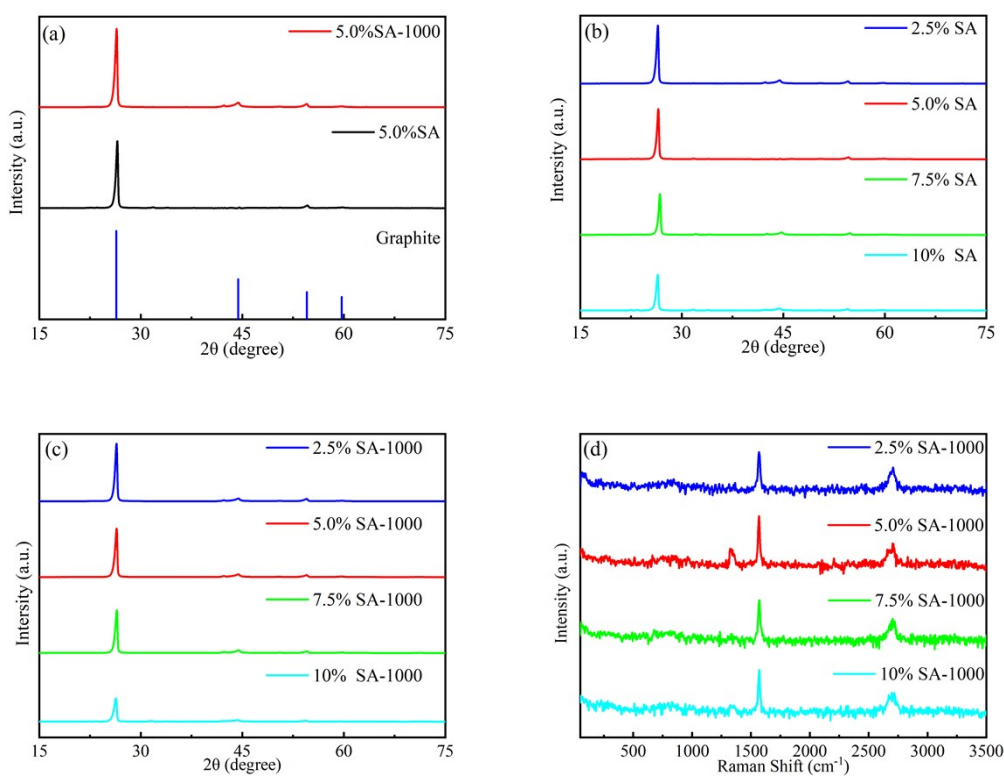


Figure 2.2 (a) XRD of graphite, graphite coated directly by SA and graphite after SA carbonization at high temperature

(b) XRD of graphite coated directly with different proportions of SA

(c) XRD of composite samples with different coating ratios (d) Raman of composite samples with different coating ratios

In order to further explore the order degree of SA/G composites under the four coating ratios and analyze their modification mechanism, we carried out Raman spectrum characterization (Fig.2.2-d).The results show that the intensities and positions of D and G peaks of 2.5% SA-1000, 5.0% SA-1000, 7.5% SA-1000 and 10% SA-1000 are very similar, both of them have ordered structure and disordered structure,which is very beneficial to the insertion and release of lithium ions.

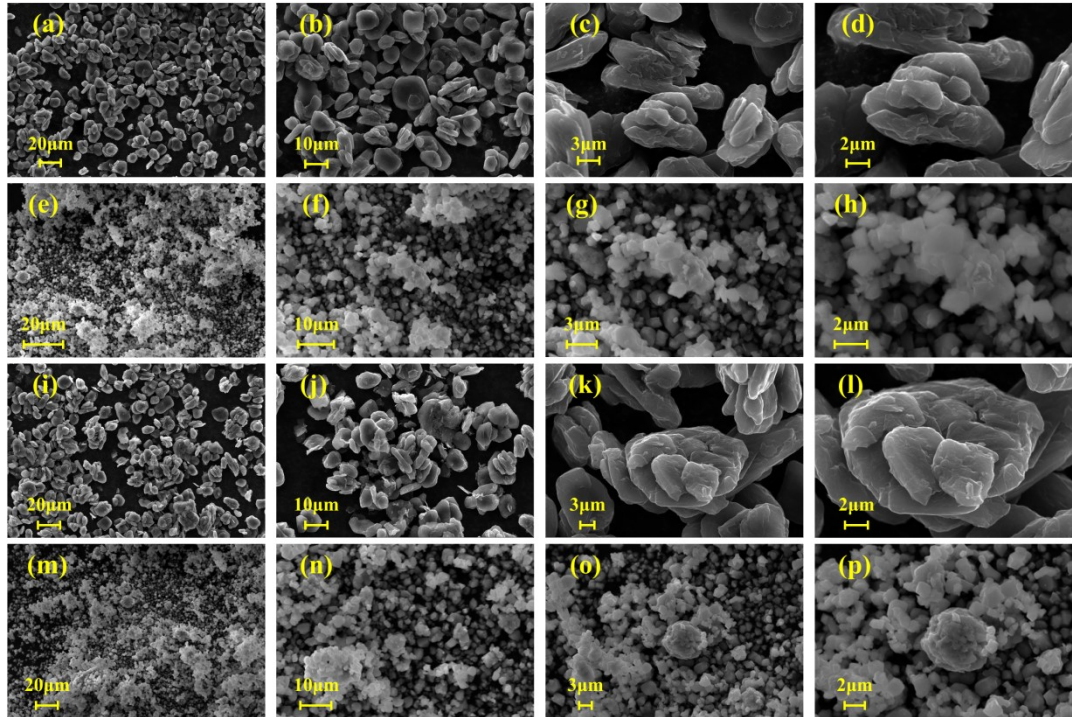


Figure 2.3 SEM of composite samples with different coating ratios

(a-d) 2.5% SA-1000 (e-h) 5.0% SA-1000 (i-l) 7.5% SA-1000 (m-p) 10% SA-1000

In order to observe the internal structure of four composites, we conducted SEM analysis (Fig. 2.3). It can be seen that the composite materials with the ratio of 2.5% SA-1000 and 7.5% SA-1000 are dominated by elliptic particles with large size, regular shape and narrow particle size distribution while the composite materials with the ratio of 5.0% SA-1000 and 10% SA-1000 showed a "pot-like" distribution and their particle size is smaller and unevenly distributed. Moreover, due to the small particle size, more active sites would be exposed, and it will be conducive to the capacity improvement.

Based on the above characterization results, electrochemical tests were performed on the composite samples with different coating ratios (Table 2.2). It can be seen from the first cycle of charge discharge curve (Fig. 2.4) that the charge discharge curves are U-shaped. Combined with XRD analysis, the graphitization degree of the cathode material prepared by the experiment is high, and the graphite layer structure is well developed.

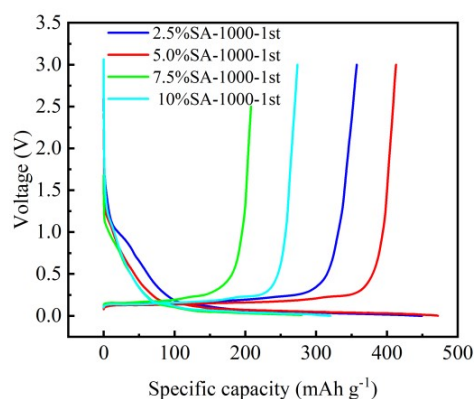


Figure 2.4 Initial charge-discharge curves under four cladding ratios

Table 2.2 Initial charge and discharge specific capacity and initial charge and discharge efficiency under the four coating ratios

Sample	First specific charge capacity (mA h·g ⁻¹)	First specific discharge capacity (mA h·g ⁻¹)	Charge-discharge efficiency (%)
2.5%SA-1000	357.418	449.476	79.519
5.0%SA-1000	412.809	472.067	87.447
7.5%SA-1000	208.097	279.832	74.365
10%SA-1000	353.369	402.014	87.900

In general, the voltage of button cell decreases linearly at the initial discharge stage, and there is almost no transfer of Li⁺. When the voltage drops to 1.5V, the downward trend slows down, indicating that a small amount of Li⁺ begins to embed into the graphite layer. When the voltage drops below 0.13V, a longer voltage platform appears, indicating a large amount of Li⁺ embed in graphite layer and the lithium embedding is over. The charging stage shows Li⁺ emerging from a layer of graphite layer. When the voltage rises to 0.25V, there is only a small part of Li⁺ does not break out of the graphite layer. The curve shows that the overall voltage rises linearly. The maximum charging voltage of 7.5% SA-1000 is only 2.5V, while the other coating proportion rises to 3.0V by the end^[20]. With the increase of cladding ratio, the battery capacity increased firstly but then decreased, and 5.0% SA-1000 was the highest, 7.5% SA-1000 was the lowest, but 10% SA-1000 decreased and then increased. In addition, the first charge and discharge efficiency of 2.5% SA-1000 and 7.5% SA-1000 composite samples were

below 80%, showing poor reversibility, while the first charge and discharge efficiency of 5.0% SA-1000 and 10% SA-1000 composite samples were above 87%, showing good reversibility. The conversion rate is better when chemical energy is converted to electricity, and the battery does the most work.

In order to determine the best coating ratio, we conducted in-depth study on 5.0% SA-1000 and 10% SA-1000 which have good reversibility. From the initial charge-discharge curves of 5.0% SA-1000 and 10% SA-1000 composite samples (Fig. 2.8a-c), the initial charge and discharge specific capacities of 10% SA-1000 are $353.369 \text{ mA h} \cdot \text{g}^{-1}$ and $402.014 \text{ mA h} \cdot \text{g}^{-1}$ while the specific capacities of initial charge and discharge of 5.0% SA-1000 composite samples are $412.809 \text{ mA h} \cdot \text{g}^{-1}$ and $472.067 \text{ mA h} \cdot \text{g}^{-1}$, which are higher than those of 10% SA-1000 composite sample, but their first Coulomb efficiency are almost equal.

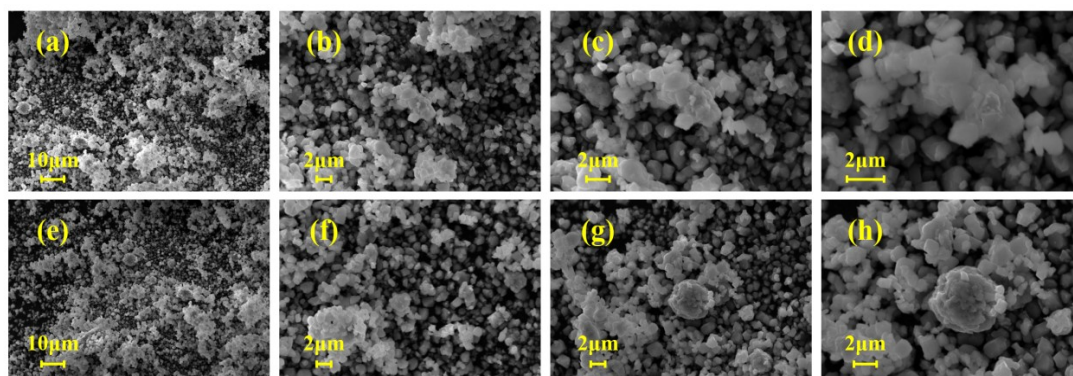


Figure 2.5 SEM of composite samples with different coating ratios

(a-d)5.0% SA-1000 (e-f)10% SA-1000

Because when the addition amount of SA-1000 is 10%, the coating amount is too much. During the sintering process, SA is completely melted and wrapped outside the graphite, making the sample easy to agglomerate and not conducive to the transportation of lithium ions. When the addition amount of SA-1000 is 5.0%, combined with SEM (Fig. 2.5) analysis, the sample formed by magnetic stirring and heat treatment process has a fluff appearance and complete graphite to obtain an ordered disordered structure, which greatly improves the specific surface area of the composite, thus, more active sites are exposed, which plays a crucial role in improving the specific capacity of the composite material^[25].

Then, the ratio performance curves of 5.0% SA-1000 and 10% SA-1000 composite samples under the two coating ratios were compared. (Fig. 2.6-d) It can be seen that the rate

capability of 5.0% SA-1000 composite material is higher than that of 10% SA-1000 composite material under different current densities, indicating that 5.0% SA-1000 can give full play to the advantages of good rate performance of composite material and significantly improve the rate capability of raw materials.

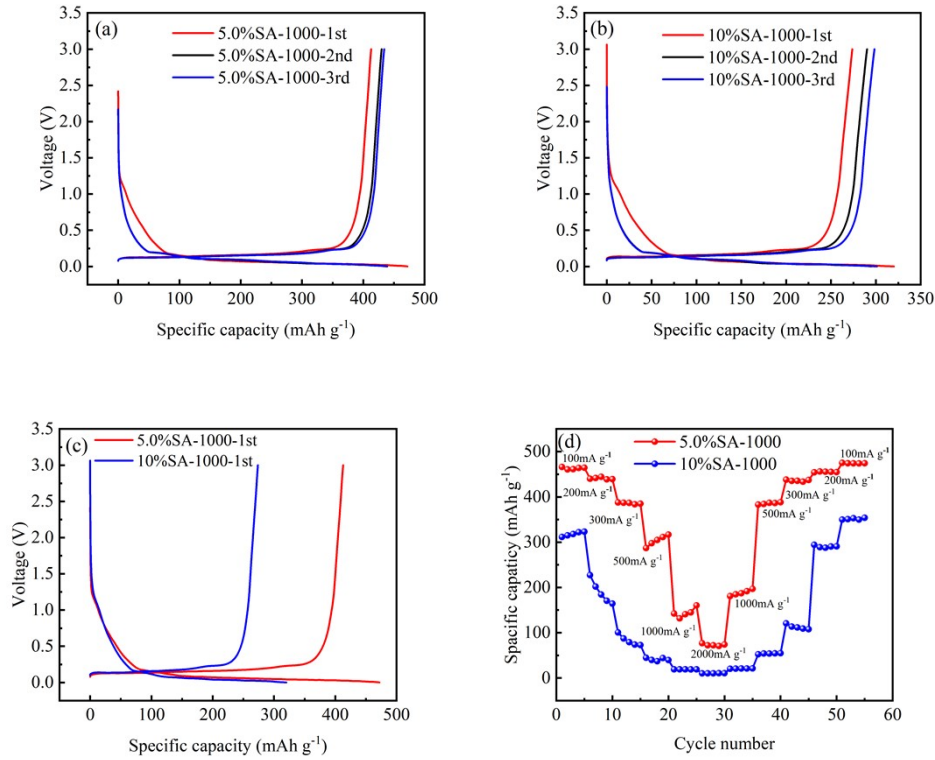


Figure 2.6 Charge and discharge curves of the first three cycles

(a)5.0% SA-1000 (b)10%SA-1000 (c) Initial charge-discharge curves under two cladding ratios

(d) Ratio performance curves of 5.0% SA-1000 and 10%SA-1000

Compared with 10% SA-1000, when the current density are $100 \text{ mA} \cdot \text{g}^{-1}$, $200 \text{ mA} \cdot \text{g}^{-1}$, $300 \text{ mA} \cdot \text{g}^{-1}$, $500 \text{ mA} \cdot \text{g}^{-1}$, $1000 \text{ mA} \cdot \text{g}^{-1}$, and $2000 \text{ mA} \cdot \text{g}^{-1}$, 5.0% SA-1000 showed high specific capacities, which are $464.449 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$, $439.265 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$, $385.012 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$, $316.750 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$, $160.416 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$, and $73.974 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$. When the current density goes back to $100 \text{ mA} \cdot \text{g}^{-1}$, the specific capacity is $474.269 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$. It can be seen that the specific capacity loss of 5%SA-1000 is small after charging and discharging at high rate.

The excellent rate performance of 5.0% SA-1000 is mainly attributed to the appropriate disordered structure contained in 5.0% SA-1000, which provides more migration channels for lithium ion transport and shortens its transmission path, which is conducive to improving the

rate of lithium ion insertion and removal and making it perform the best rate performance.

Therefore, based on the characterization of the material, the charge-discharge curve of the first three cycles, the first Coulomb efficiency and the rate performance, we concluded that 5.0% SA-1000 is the best coating ratio, and better electrochemical performance can be achieved under this condition.