Short communication

Highly conductive bridges between graphite spheres to improve the cycle performance of a graphite anode in lithium-ion batteries

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Abstract

Spherical carbon-coated natural graphite (SCCNG) is a promising anode material for lithium-ion batteries, but the smooth surface of graphite spheres is difficult to wet with an aqueous binder solution, and lacks electrical contacts. As a result, the cycle performance of such a graphite anode material is not satisfactory. An effective method has been introduced to tightly connect adjacent SCCNG particles by a highly conductive binder, viz. acetylene black bridges. The effect of the conductive bridges on the cyclability of SCCNG electrode has been investigated.
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Keywords: Spherical natural graphite; Acetylene black; Cycle performance; Lithium-ion batteries; Anode material

1. Introduction

In the community of rechargeable lithium-ion batteries with high energy and power densities, natural graphite anode material has drawn extensive attention due to the following advantages: low and flat working potential, low cost, high reversible capacity and cycling stability in compatible electrolytes, and high electronic conductivity, etc. [1–10]. Nevertheless, the crude natural graphite flakes as obtained directly from mines could hardly be used for practical lithium-ion batteries [11]. It has two main shortcomings: intolerance towards propylene carbonate (PC)-based electrolytes [12–17] and high orientation of graphitic layers. The former will obstacle the utilization of lithium-ion battery at low temperature (melting point of PC, −49 °C) [18–20], while the latter can slugger the Li$^+$ motion between the electrolytes and graphite electrodes since the direction of current flow is just towards the inert basal-plane surface of graphite [21], and then decrease the power density remarkably.

Recently, the above problems have successfully been solved by folding small graphite fragments into balls and addition-ally coating the sphere surface with carbon [22–25]. This kind of spherical carbon-coated natural graphite (SCCNG) demonstrates excellent electrochemical performance in the terms of high reversible capacity, high rate capacity, high coulombic efficiency and low irreversible capacity in the PC-based electrolytes.

However, during the course of further performance evaluations, we found the new weak point of SCCNG. That is its poor cycling stability. To make SCCNG become a near perfect anode material for lithium-ion batteries, it is very urgent to solve this problem without the sacrifice of the comprehensive virtues of SCCNG. In this paper, we have investigated the reason for the capacity fading of SCCNG and explored effective ways to improve the cycle performance of SCCNG.

2. Experimental

2.1. Preparation and modification of SCCNG

SCCNG samples have been prepared by the method as described in Refs. [22,23]. To improve the cyclability of SCCNG electrode, we have attempted to modify SCCNG by the dispersion of a small amount of tiny AB particles onto the surface of SCCNG spheres prior to the preparation of slurry. This kind of modified SCCNG was named as ABD-SCCNG. The B.E.T.-specific surface area of AB is about 68 m^2/g, while the particle

size of AB is smaller than 1 μm. The weight percentage of AB to SCCNG is lower than 5%.

2.2. Fabrication of graphite electrode

For fabrication of the graphite electrode, the graphite (SCCNG or ABD-SCCNG) sample was mixed with a binder aqueous solution to make a slurry of a suitable viscosity. The binder consists in CMC (carboxy methyl cellulose, Daiseru Chemical Inc., Japan) and BM-400B (Zeon Ltd. Co., Japan). Then the slurry was spread onto a copper foil evenly. The electrode was allowed to stand in air overnight to evaporate most of the water and vacuum-dried at 80 °C for 1 day.

2.3. Electrochemical measurements on the graphite electrode

For electrochemical measurements, 1 M LiPF$_6$ dissolved into the mixed solvents of EC and DMC (1:2 by volume) was used as the electrolyte. The charge–discharge tests were performed in CR2032 coin-type half-cell (Li/graphite). Cells were composed of graphite electrode and a Li metal electrode separated by a porous polypropylene film (Celgard 3401) and two glass fiber mats. The graphite electrode generally consisted of 20 mg active material. In the charge process, the cell was generally tested by a CC–CV mode (CC, constant current; CV, constant voltage) as follows, unless otherwise specified. That is, graphite electrode was charged (corresponding to Li$^+$ intercalation) at the constant current density of 0.5 mA/cm^2 until the voltage reaches 3 mV against Li metal, and then the cell was held at this voltage for 2 h. In the discharge process, only CC mode was used. The graphite electrode was discharged until 1.5 V against Li metal at the constant current density of 0.5 mA/cm^2.

3. Results and discussion

From the viewpoint of effective suppression of hazardous electrolyte decompositions, the structure of SCCNG seems very beneficial since the outer surface is very inert. This virtue lies in the following fact: the outer surface of SCCNG mainly consists of the chemically inactive basal-plane surface. Unfor-

tunately, the inert basal-plane surface short of functional groups always suffers from the poor wet-ability with the aqueous binder solutions, which will slacken the electric contacts between the adjacent carbon-coated graphite spheres. Accompanying the charge–discharge cycling of the Li/SCCNG cells, each graphite spheres will inevitably experience volume changes during the course of Li$^+$ intercalation and de-intercalation. Consequently, corresponding stress on the outer surface of graphite particles is likely to break down the fragile binder bridges jointing the tiny contacting points between graphite spheres cycle by cycle. The loss in electrical contacts accumulates with charge–discharge cycles and leads to the capacity loss accordingly. The above expectation can be verified by comparison of the SEM graphs of the SCCNG electrodes before and after charge–discharge cycling as shown in Fig. 1. The interval spaces between the adjacent graphite particles on the graphite electrode become apparently widened only after 10 cycles of charge–discharge, which fact implies that the electric contacts are loosened.

To overcome the above "bottle-neck" problem, we have tried the following three ways: (1) increasing the amount of binder to enhance the adhesion forces between graphite spheres, (2) minimizing the particle size of graphite spheres to increase the number of contacting points, and (3) adding in acetylene black to raise up the electric conductivity. For the first measure, the effect of binder amount can be clearly observed in Fig. 2. With the rise in the binder amount, the trend for capacity fading is slowed down remarkably. However, the binder amount must be controlled below a certain threshold value since the increase in binder amount will decrease the weight portion of graphite in the composite anode and then lower the energy density of lithium-ion battery. Moreover, excess amount of binder may block the electric-conductive paths between the graphite particles and obstacle the contact of the electrolytes with graphite particles. For example, the climb-up of capacity within the initial several cycles in the case of 7 wt.% binder in Fig. 2 is a sign of inadequate contact between the electrolyte and graphite, which probably come from the excess in binder. As for the second measure, decrease in the particle size leads to the increase of surface area, so the irreversible capacity associated with electrolyte decomposition on graphite surface will rise up accordingly, which is unfavorable for lithium-ion batteries. Taking the above factors
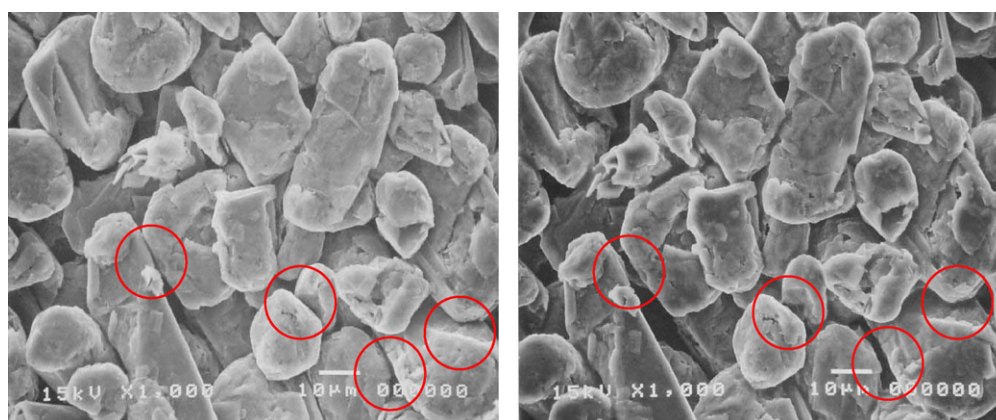

Fig. 1. SEM graphs of the SCCNG electrodes before (left) and after (right) 10 cycles of charge–discharge.
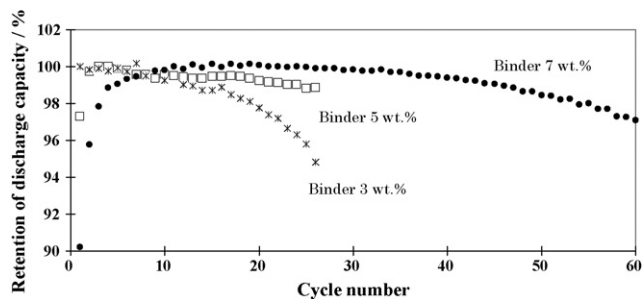
Fig. 2. Effect of binder amount on the cycle performance of SCCNG electrodes.

into account, we switched over to the third measure, the addition of highly electric-conductive acetylene black.

The common procedure for the acetylene black addition by simply mixing SCCNG, acetylene black and binder solution into slurry generally can't get satisfactory composite anode in lithium-ion batteries. It is because the big differences between some physical properties (say, density, morphology and adsorption ability of binder solution, etc.) of SCCNG and acetylene black are likely to lead to the inhomogeneous distribution in the slurry. Actually, the increase in acetylene black amount even causes trouble in spreading slurry onto the current collector (copper foil) since acetylene black may seize much more amount of binder solution from SCCNG smooth surface. Then the effective addition of acetylene black to construct sufficient electric-conductive paths becomes a very urgent task.

We have explored one method to fulfill the above task as schematically shown in Fig. 3. Small amount of tiny acetylene black particles was spread over the smooth surface of SCCNG prior to mixing with the binder solution. This kind of graphite is named acetylene black-dispersed SCCNG. Once the surface-modified SCCNG particles were immersed into the binder solution, the acetylene black "parasite" would detach from the surface of SCCNG and diffuse into the binder solution. The obtained slurry was coated onto copper foil and subject to drying process. During the drying process, the volume of the solvent in the anode slurry gradually decreased in the intergranular spaces where were surrounded by SCCNG particles. At the same time, the solvent would carry acetylene black and
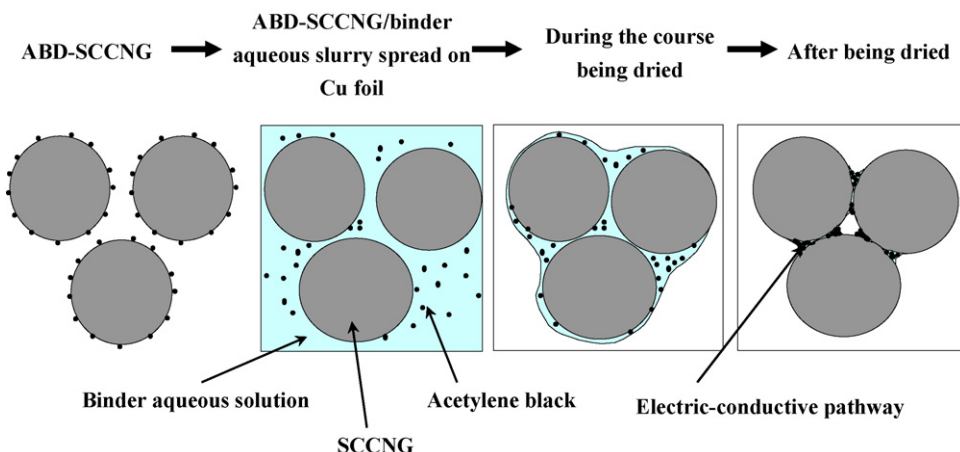

Fig. 3. Schematic view of the conductive bridge formation between graphite spheres during the preparation process of graphite electrode.
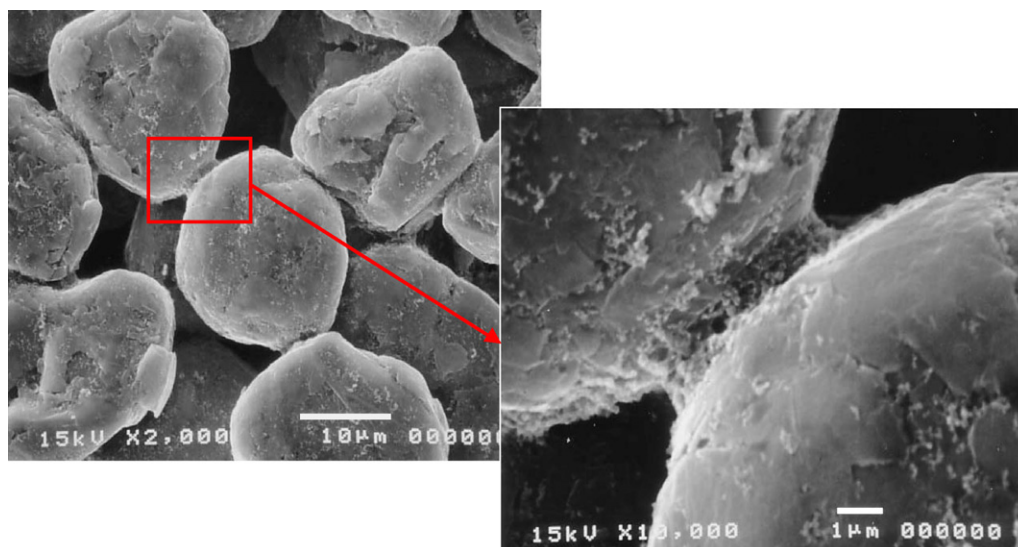

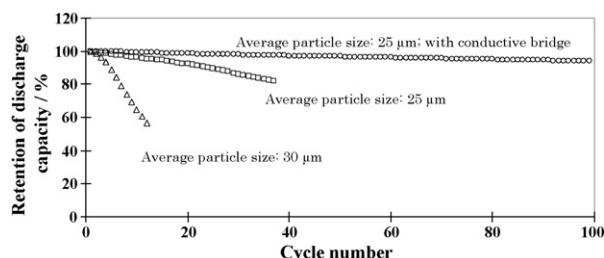Fig. 4. SEM graphs of the conductive bridge between graphite spheres.

Fig. 5. Improvement of the cycle performance of SCCNG electrodes after the conductive bridge being built between graphite spheres.

immigrate from SCCNG surface to the capillary space because of the liquid bridge forces in the narrow gulfs between adjacent SCCNG particles. Thus both the binder and acetylene black would condense near the contacting points between SCCNG particles as the solvent was evaporated. The electric-conductive pathway is effectively built up at the contacting points as evidenced in the SEM image of Fig. 4. As compared with the SEM image in Fig. 1, the interval gulf between the adjacent SCCNG particles disappears. Instead, there is a "neck" that fills this interval space and tightly connects two neighbored graphite spheres. This demonstrates a shape of a gourd. It is expected that this kind of inter-connective structure can guarantee good cycle performance of SCCNG since the concentrated distributions of acetylene black and binder at the "neck" connecting adjacent SCCNG particles have twofold merits, robust adhesion and high electric-conductivity. This assumption can be proved in Fig. 5. The cyclability of SCCNG modified by acetylene black is satisfactory, the retention rate of discharge capacity could reach 90% even after 100 cycles. By big contrast, the original SCCNG electrodes show much poorer cycle performance than the ABD-SCCNG electrode. In the case of SCCNG with the particle size of 25 μm, the retention rate drops to near 80% until 40 cycles. If the particle size of SCCNG rises to 30 μm, the deterioration trend in cycle performance of graphite electrode becomes more drastic, the retention rate even falls to less than 60% within 20 cycles. The great influence of particle size on the cycle performance of SCCNG electrodes actually can be ascribed to the following fact. The bigger particle size of SCCNG has, the fewer graphite particles are accumulated in the given volume, and the fewer contact points between graphite spheres.

Besides the merit of improvement in cyclability, the interconnective structure of ABD-SCCNG electrode can also enhance rate capability. This advantage may originate from two reasons: first, the high electric-conductivity at the "neck" position is very helpful for improving high rate performance; second, the point-joint SCCNG particles leave adequate channel space for the electrolyte to intrude freely. Since the binder mainly focuses on the contacting points between SCCNG particles, most of the SCCNG surface can get in touch with the electrolyte without the blockage of binder. So the rate performance is improved. This expectation can be somehow evidenced in Fig. 6. Fig. 6 compares the initial charge–discharge curves of SCCNG and ABD-SCCNG electrodes. The ABD-SCCNG electrode apparently shows superior performance to the SCCNG electrode in the terms of higher discharge capacity, low irre-
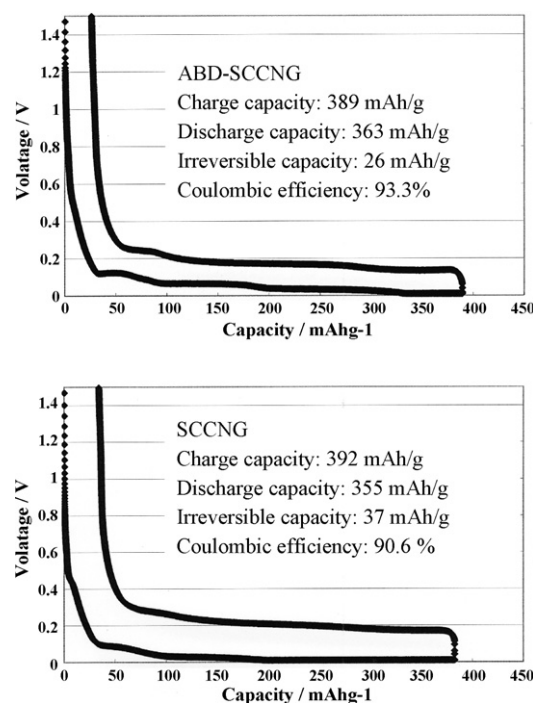

Fig. 6. Initial charge–discharge curves of SCCNG and ABD-SCCNG electrodes (constant current density: 1 mA/cm^2; cutoff voltage range: 0.01–1.5 V; constant voltage charge at 0.01 V for 4 h; electrolyte: 1 M LiPF$_6$-EC:DMC (1:2 by volume)).

versible capacity and higher coloumbic efficiency. Furthermore, the polarization between the charge and discharge curves corresponding to ABD-SCCNG is much smaller than that of SCCNG. This phenomenon implies that the effective conductive AB bridges connecting graphite spheres contribute to the enhancement of electricity of the graphite electrode.

4. Conclusion

In conclusion, although the spherical carbon-coated natural graphite have many merits as a lithium-ion battery anode material, it may experience capacity fading during long cycles due to the lack of contact between the graphite spheres. We have succeeded in tailoring the smooth surface of graphite spheres by tiny acetylene black particles. During the preparation process of graphite–binder composite electrode, the acetylene black and binder may become concentrated near the contact points between two adjacent graphite spheres because of the capillary effect of binder solution. The conductive bridge (acetylene black/binder) thus constructed between graphite spheres is very effective for improving the electric contact between graphite spheres during long cycles. Accordingly, the cycle performance of spherical carbon-coated natural graphite anode material is greatly enhanced without the sacrifice of other merits.

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