

Short Communication

Electrochemical performance of a novel surface modified spherical graphite as anode material for lithium ion batteries

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1. Introduction

Many anode materials like, for example, graphitic carbon, amorphous carbons, tin oxides, nitrides, nano oxides and phosphides have been studied with respect to their applicability in lithium secondary batteries since the mid 1970s [1], but only graphitic carbon materials have been widely used in practical applications. However, despite considerable efforts to improve the performance of these materials, the actually obtained reversible capacity of typical commercial synthetic graphites such as MCMB6-28 is usually $< 320 \text{ mAh g}^{-1}$ [1]. The rapid advance of electronic devices such as the third generation of mobile phones and electric vehicles demands power sources with higher energy density, and it is therefore, necessary to develop practical anode materials with higher reversible capacity.

It is known that natural graphite has a higher reversible capacity than commercial synthetic graphite [1]. However, co-intercalation of solvents, poor processing performance and poor rate capability due to the common flake shape limit the application of natural graphite. A variety of methods have been employed to tune the properties of natural graphitic materials, such as carbon coating, mild oxidation, deposition of metals and metal oxides and polymers [2–8]. However, while some progress has been made in each of these areas, only carbon coated natural graphite has been used in devices, and even in the case of carbon coating, it is not easy to control the uniformity of the product since the processing can easily destroy the carbon coating resulting in the separation of the coated film from the surface

of natural graphite [8]. In perhaps one of the most encouraging recent developments, Sodiff Co. Ltd. in South Korea has initiated distribution of a type of coated carbon on the market a few years ago. The material is obtained by making a strong shearing impact stress on natural graphite powder with incorporation of some coating binder; the specific capacity is as high as 350 mAh g^{-1} . The stability during cycling, however, appears to require some improvement.

Recently we developed a novel surface modified spherical graphite (SSG) [9] which offers very good electrochemical behavior. Here we report the primary electrochemical performance of this SSG in relation to the distribution of conductive additive particles on the coated electrode material.

2. Experimental

The preparation of the novel anode material SSG was carried out according to the following procedure. The common flake natural graphite (the content of carbon: $> 99.9\%$) from Nanshu Graphite Mining Plant, Shangdong Province, China, was mechanically reformed into a spherically shaped particle. Then the powder (100 g) was dipped in 500 ml solution of an epoxy resin (concentration 2%). After filtering, drying and heat-treating in an inert atmosphere, the composite obtained was pulverized. It was observed, that during pulverization some carbon coating was separated from the natural graphite particles. Consequently, in order to ensure full carbon coating of the natural graphite, a

second dipping of the composite into 500 ml solution of a phenol resin (concentration 2%) was carried out. After filtering, drying and heat-treating in the inert atmosphere once again, the pulverized product (SSG) was fully covered by a carbon coat.

The SSG powder was deposited on a copper current collector sheet (15 μm thick) with vapor grown carbon fiber (VGCF) as a conductor and poly(vinylidene fluoride) (PVDF) dissolved in *N*-methyl pyrrolidinone as a binder. The coated sheet was heat-dried, roll-pressed and punched into ~ 1 cm diameter disks, which were used as the working electrode (weight about 10 mg). The reference and counter electrodes were lithium metal foil; the electrolyte solution was 1 M LiClO_4 in EC/DMC (1:1 v/v). Discharge and charging of the three-electrode cells were performed using a constant current density in the voltage range $0.04 < E$ vs $\text{Li}^+/\text{Li} < 1.5$ V.

Scanning electronic microscopy (SEM) was performed with a microscope JEOL (JEM 2011). Measurements of cross-section were performed in the following manner. In a paper cup, a formaldehyde resin was stirred with a few drops of hardening agent and subsequently mixed with ~ 10 vol % graphite powder. The graphite paste became completely stiff after 1 day. The stiff material was broken into smaller fragments

with a hammer and a piece was investigated with the SEM to find the cross-section of a particle.

3. Results and discussion

Figure 1 shows the SEM micrographs of pellets of the SSG anode material and their cross-section. The shape of the SSG is spherical or potatoe-like, indicating that the formation process is successful. The carbon coating can be seen. However, the carbon coating is thin and not homogeneous, which is perhaps due to the non-uniform surface of the natural graphite. From its cross-section (Figure 1b), it can be seen that there are still some voids because the initial processing into the spherical shape could not produce enough pressure and the stacking of graphene sheets is not very tight. This is likely the reason that its tapping density is not as high as that of synthetic graphite, only about 0.95 g cm^{-3} .

Figure 2 shows the SEM micrographs of two prepared anodes. One shows poor dispersion of conductive VGCF, the other shows good dispersion. In the latter case, the surface of the SSG-particles was surrounded or encircled by VGCF.

The importance of a homogeneous dispersion of the conductive additive VGCF in the SSG matrix has been

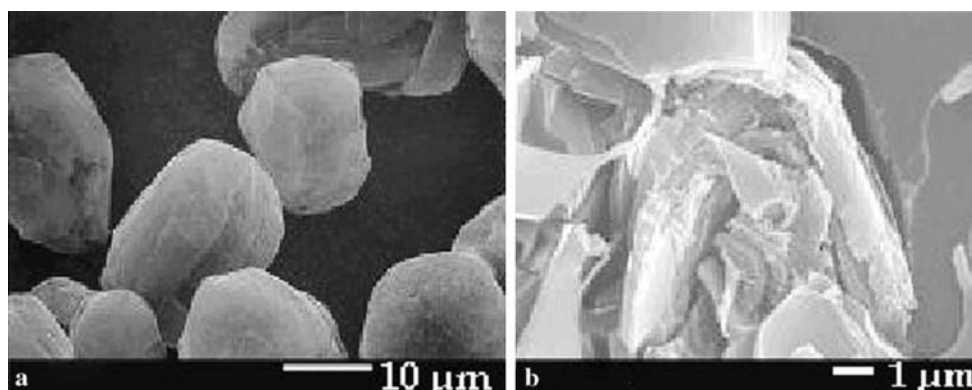


Fig. 1. SEM micrographs of (a) pellets of the produced anode material SSG and (b) cross-section of a similar product (DAG 40 of SODIFF Advanced Material Co., Ltd).

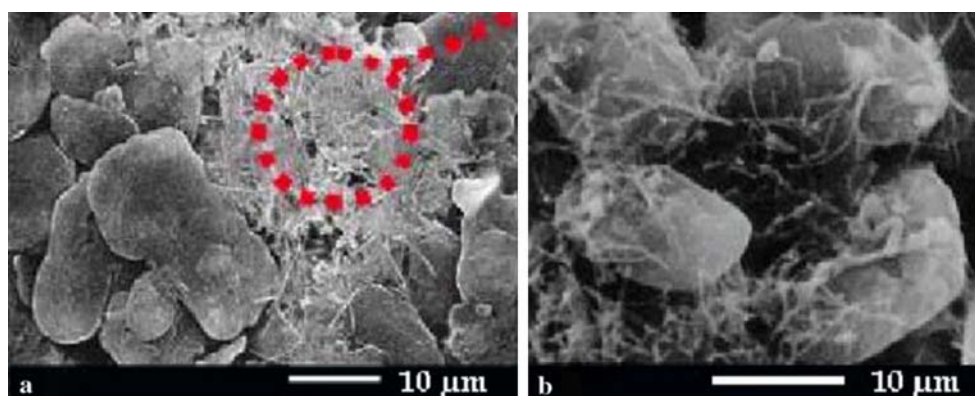


Fig. 2. SEM micrographs of the coated anode materials: (a) poorly and (b) well dispersed conductive additive.

stressed previously [8, 10], and this applies also to SSG. The cycling performance of anodes with good and poor dispersion of VGCF at a constant current density of 0.22 mA cm^{-2} (about 0.2C) is shown in Figure 3. The anode with poor dispersion of VGCF shows a sharp capacity fade during the first 50 cycles (Figure 3a); the reversible capacity in the 50th cycle is only 47% of its value in the 10th cycle. In contrast, the anode with good dispersion of VGCF shows good capacity retention after 50 cycles; the reversible capacity remains at 98% of the value in the 10th cycle (Figure 3b). Figure 3 also shows that poor dispersion of VGCF results in a decrease in reversible capacity (only 330 mAh g^{-1}) whereas the anode with good dispersion of VGCF shows a higher reversible capacity ($> 350 \text{ mAh g}^{-1}$).

Scanning electronic microscopy micrographs of anodes after 50 cycles are shown in Figure 4. White deposits on the surface of the SSG particles can be seen. On the anode with the poor dispersion of VGCF (Figure 4a) the amount of surface deposits is much higher in comparison with the anode with good dispersion (Figure 4b). This implies, that good electrical contact inhibits formation of the deposits and ensures good cycling. Poor electrical contact, in contrast, accelerates the formation of deposits and capacity fade. The composition of the white deposits needs further

investigation. Conceivably they may consist of Li_2CO_3 , LiF [9] or other organic lithium carbonates [11].

The cycling behavior of the anode with good dispersion of VGCF is shown in Figure 5. Its initial reversible capacity is 348 mAh g^{-1} at a discharge rate of about 2C, higher than those of commercially used synthetic graphite (usually $< 320 \text{ mAh g}^{-1}$). After 500 cycles the residual capacity is 301 mAh g^{-1} , i.e., 86.5% of the initial capacity. This is an excellent cycling performance. The comparison of charge curves in Figure 5b shows, even after 500 cycles, a very good voltage plateau. In practical lithium ion batteries the cycling behavior will be much better because only 90–95% of the reversible capacity of the anode is utilized.

These results do not show any evident staging phenomenon for lithium deintercalation from SSG. This may be caused by the high charging rate. Figure 6 shows the charge curve of SSG at a lower rate (0.08C) in the first cycle. Under these conditions the staging phenomenon is evident. The apparent voltage plateaus correspond to formation of the compounds LiC_6 , LiC_{12} , LiC_{18} and LiC_{24} .

As has been pointed out elsewhere [8, 10] several factors affect the cycling performance of anode materials during practical application: type of conductive additive and its amount, electrode density and electrolyte

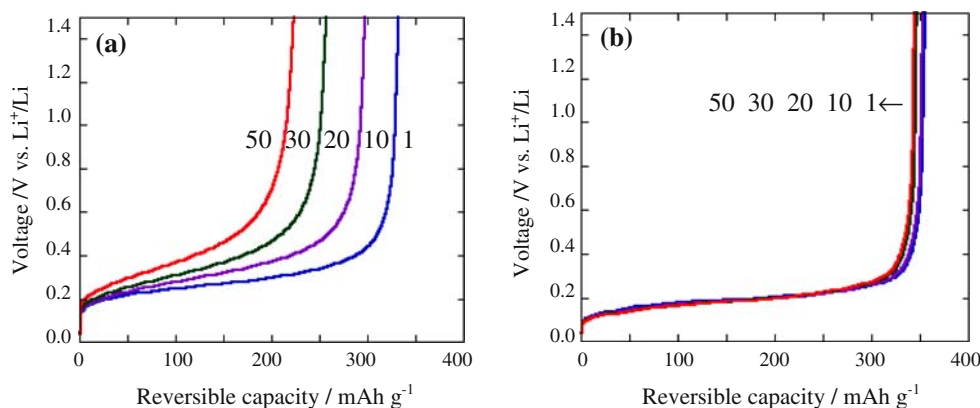


Fig. 3. Charge curves of the coated anode materials in different cycles at a rate of 0.2C: (a) poorly and (b) well dispersed conductive additive.

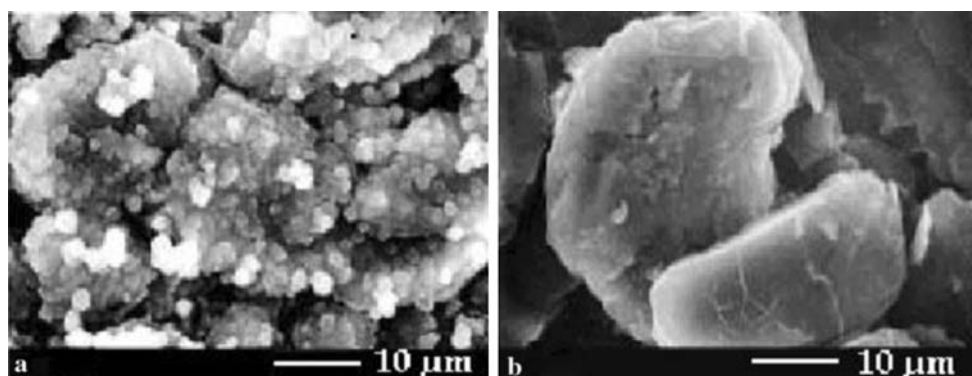


Fig. 4. SEM micrographs of coated anode materials after 50 cycles: (a) poorly and (b) well dispersed conductive additive.

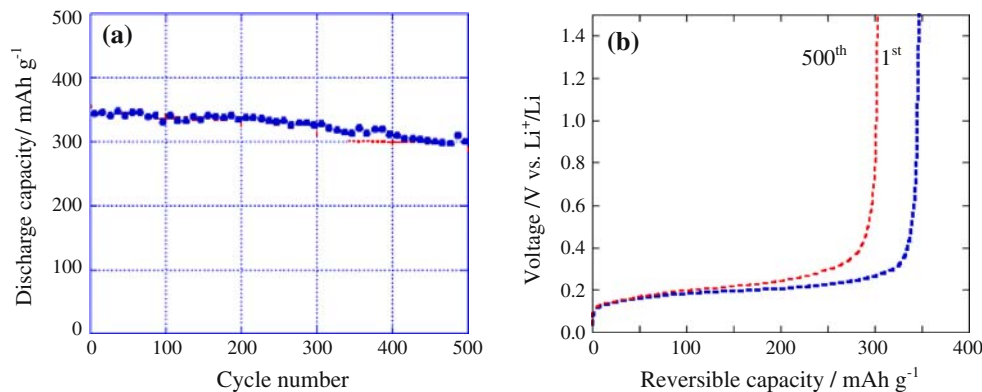


Fig. 5. Electrochemical performance of anode materials at constant current (about 2C) charge and discharge: (a) cycling behavior and (b) charging curves in the 1st and 500th cycle.

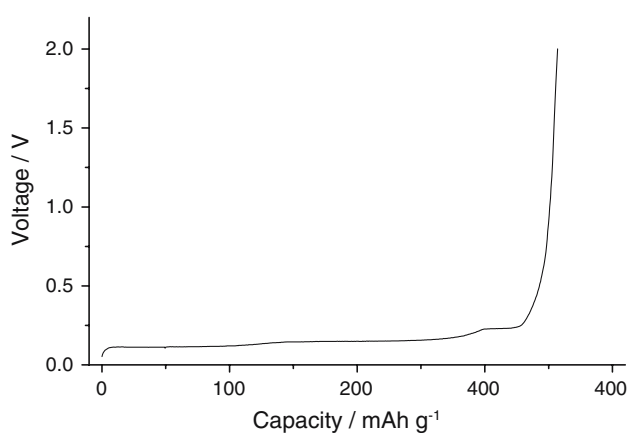


Fig. 6. Charging curve of the anode material SSG in the first cycle at low current (about 0.08C).

composition. These factors need further investigation and results will be reported later.

4. Conclusions

We prepared a new anode material, SSG (special spherical graphite), for lithium ion batteries by reforming natural graphite into spherical shape, and two coatings with polymers on its surface followed by heat-treatment in inert atmosphere after each coating step. The dispersion of conductive additive markedly influenced the cycling behavior. With good dispersion the cycling performance was excellent. The initial reversible capacity was 348 mAh g^{-1} at a rate of about 2C, greater than that of commercial synthetic graphite, and remained at 86.5% after 500 cycles in a cell with lithium

metal as counter and reference electrodes. With poor dispersion numerous white deposits were produced; lower reversible capacity and rapid capacity fade were observed. At low rate (0.08C) the charge curve showed evidence of a staging phenomenon.

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