

## A modified graphite anode with high initial efficiency and excellent cycle life expectation

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### Abstract

A new procedure was developed to prepare surface-modified graphite. First, spherical graphite (SG) particles were prepared through milling natural flake graphite (NFG). Then, surface-modified spherical graphite (MSG) was obtained by coating SG with a nanolayer of nongraphitic carbon. The SG exhibits better electrochemical performance than NFG, since there are significant decreases in the surface area and the probability of getting graphite basal planes parallel to the copper foil. It is also demonstrated that a nanolayer of nongraphitic carbon evenly covers the surface of SG. MSG with a core–shell structure shows higher initial coulombic efficiency and better cycle stability than SG because the carbon coating layer has improved its compatibility with electrolytes and protected the graphite against exfoliation.

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### 1. Introduction

After being introduced into the market as early as 1991, rechargeable Li ion batteries have become the key components of portable computing and telecommunication equipment required by an information-rich society. This is because they have the following advantages: high energy density, high operating voltage, good safety, and no memory effect [1–3] when compared with Ni–Cd or Ni–MH batteries. Although their advantages are prominent, investigation is still needed for reducing the thickness and weight of batteries and increasing their cycle stability. Therefore, the improvement of the anode material would advance the investigation one step further.

So far, the materials studied for lithium ion battery anode involve carbon materials, nitrides, tin oxides, and novel

alloys [2,4]. Only carbon materials are commercialized, despite the great progress made by researchers with other anode candidates. The main reason for this is that Li ions can be intercalated into and deintercalated from the carbon materials reversibly. On the basis of their structure, carbon materials are categorized in three types: graphite or graphitic carbons, soft carbon, and hard carbon [5–8]. Among them, graphite or graphitic carbon materials, especially natural graphite, is considered to be one of the most important anode materials because it is superior to other carbon candidates in terms of high capacity, low irreversible capacity at the first cycle, flat and low potential profile, large amounts of resources, and low cost. Nevertheless, its disadvantages, such as its low volumetric density, high sensitivity to electrolytes, and easy exfoliation, are also remarkable. In order to overcome these disadvantages, vigorous investigation on the surface modification of graphite has begun.

Some authors [9,10] pointed out that coke-coated graphite exhibited some smaller irreversible capacity and better cyclability than pristine graphite. However, it decreased the total reversible capacity of the anode because coke showed lower capacity than graphite. Some metals [11,12], such as

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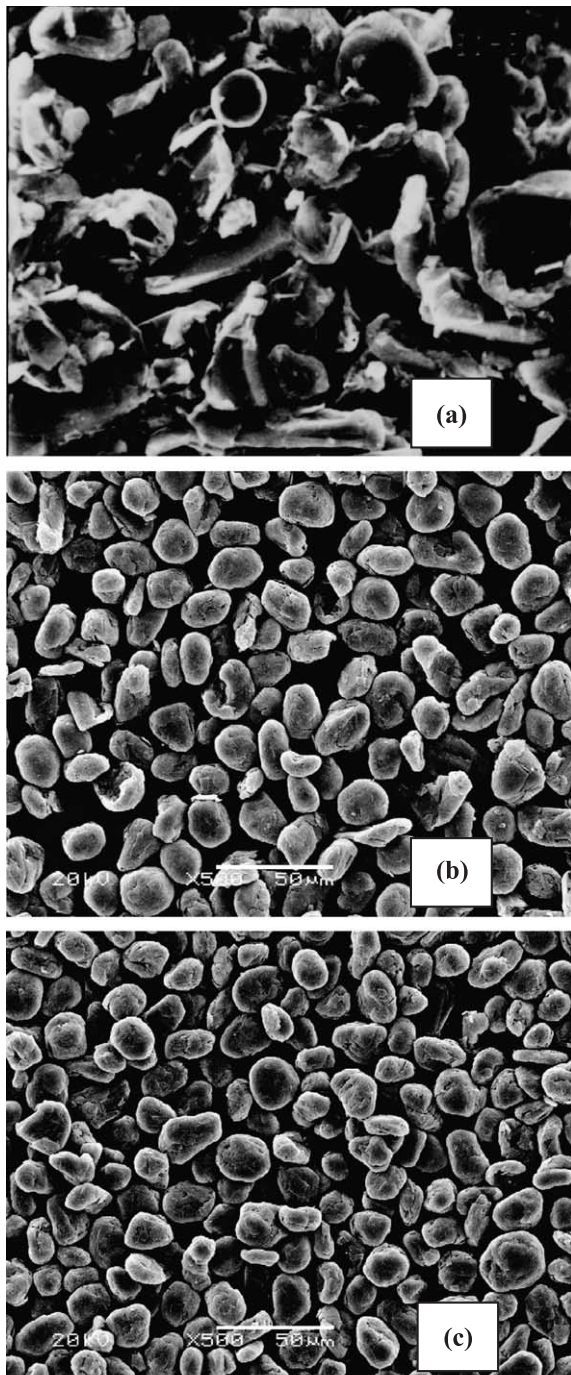


Fig. 1. SEM images of NFG (a), SG (b) and MSG (c).

Ag, Au, and Zn, were introduced onto the surface of graphite, too, and the rate capability and cycling behavior were improved. Obviously, these metals would decrease the power density of the graphite electrode due to their much higher atomic weight. In all of this literature, graphite without any pretreatment was directly coated with another kind of substance.

Presently, a new process for modified graphite is being developed. Natural flake graphite (NFG) was first milled to prepare spherical graphite (SG), which was then coated with

a layer of nongraphitic carbon to prepare surface-modified spherical graphite (MSG) with a core–shell structure. Because the MSG holds quite a low surface area and probability of getting graphite basal planes parallel to the copper foil in the anode, the shell (nongraphitic carbon) protects the graphite core from exfoliation. Therefore, the MSG anode shows excellent electrochemical performance in comparison with NFG and SG, such as an initial reversible capacity of 365 mA h/g, which is close to the theoretical capacity of graphite, and a high initial coulombic efficiency of 93%.

## 2. Experimental

To prepare the SG sample, NFG was milled in a self-made miller for 12 h and then the milled graphite particles were sieved with a series of sizing devices. MSG was prepared as follows: SG was first dispersed in a solvent that contains the precursor of nongraphitic carbon and then the solvent was evaporated. Finally, the residue was treated at 900–1200 °C for 2 h under nitrogen atmosphere.

The average size of the carbon particles in the powders was measured with a Malvern laser diffraction analyzer. Surface areas of carbon particles were determined by nitrogen adsorption according to the BET method. The X-ray diffraction (XRD) patterns, which were obtained with a Philips PW1730 diffractometer using Cu K $\alpha$  radiation, were utilized to analyze the crystal structure of graphite, and Raman spectroscopy was performed using an argon ion laser to analyze the surface structure.

The graphite composite electrode was fabricated as follows. First, 94% of active graphite, 3% of carbon black, and 3% of the binder LA132 were homogeneously mixed in an agate mortar and then the slurry was spread onto a 10- $\mu$ m-thick copper foil to form an electrode. Next, the

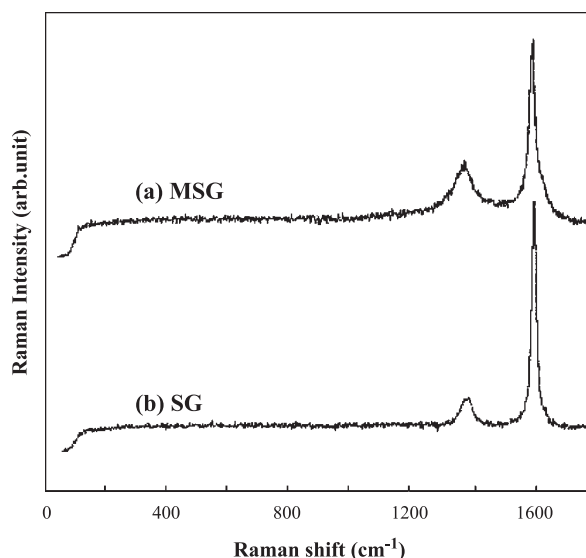


Fig. 2. Raman spectra of SG and MSG materials.

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