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Material for Lithium-Battery Anodes

Spherical Carbon-Coated Natural Graphite as a Lithium-Ion Battery-Anode Material

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The great demand for high-energy-density rechargeable lithium-ion batteries has spurred extensive research on electrode materials. Natural graphite is an important anode material for Li-ion batteries by virtue of its advantages such as

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a flat and low voltage range, high reversible capacity (372 mA h g^{-1} with the stoichiometry of LiC$_6$), and low cost.[1–2] However, it has one big disadvantage that may obstruct its further use. That is, its sensitivity to propylene carbonate (PC)-based electrolytes.[3–7] PC is an essential solvent for the electrolytes of lithium-ion batteries for low-temperature use because of its low melting point of about −49 °C. But graphite electrodes are exfoliated in most PC-based electrolytes, and thus give rise to a very drastic decomposition of the electrolyte, which leads to a big irreversible capacity as well as low coulombic efficiency. Moreover, the product of PC decomposition, propylene gas, is potentially explosive. Thus, obtaining a method to effectively and safely use natural graphite in PC-based electrolytes is urgent.

In recent years, we have applied the thermal vapor decomposition (TVD) technique to coat carbon onto natural graphite surfaces to keep the natural graphite surface from direct contact with the electrolyte.[8–10] We found that the carbon coating can suppress the electrolyte decomposition remarkably and the carbon-coated natural graphite shows excellent electrochemical performance in lithium-ion batteries. Although "common" TVD carbon-coated natural graphite can meet most of the practical needs for anode materials in lithium-ion batteries and so has been commercialized, there is still a wide margin for improvement of its comprehensive performance. For example, it was proven that the inertness of the carbon-coated graphite to the electrolytes increases with an increase in the amount of carbon coating. Nevertheless, as the density of the carbon coating (about 1.86 g cm^{-3}) is lower than that of graphite (2.27 g cm^{-3}) the electrode density will decrease with an increase in the amount of carbon coating. The electrode density is also a very important factor for practical lithium-ion batteries, because it determines the energy density of the batteries. Therefore the trade-off between the electrode density and the inertness towards the electrolyte decomposition becomes problematic for carbon-coated natural graphite anode materials.

In this kind of core–shell structured composite, a small amount of carbon coating is favored in terms of a higher density, and the cost of TVD process is reduced if the inertness of the graphite core towards electrolyte decomposition could be guaranteed by itself to some extent. Besides, too much carbon coating will decrease the discharge capacity of the composite electrode material. So in this study we turned our attention to the carbon-coating shell, and initially focused on the design of the natural graphite core.

There are two kinds of planes on graphite crystallite surface, edge and basal. Edge planes show much more activities towards chemical reactions than basal planes. The exfoliation and decomposition of the electrolyte mainly occur on edge planes rather than basal planes. Figure 1 schematically compares the morphology designs of the natural graphite core of our previous work and the present one.

In our previous studies,[8–11] we tore natural graphite flakes into thin planar sheets and then stacked the planar graphite fragments into a shuttle-shaped core by vibration-rod milling before applying the TVD carbon-coating process. In such a case, there are considerable edge planes on the outer surface of the graphite core, and thus greater amounts of carbon coating is needed to cover these edge planes. In contrast, in the work presented herein, we succeeded in folding graphite fragments into a compact ball by applying pressure from both sides of the planar graphite fragments through impact milling. Considerable parts of the edge planes are bound inside the graphite balls and, predominantly, basal planes are exposed outside. Thus, only a very small amount of carbon coating is needed to cover the residue edge planes and the decomposition of the electrolytes is effectively suppressed.

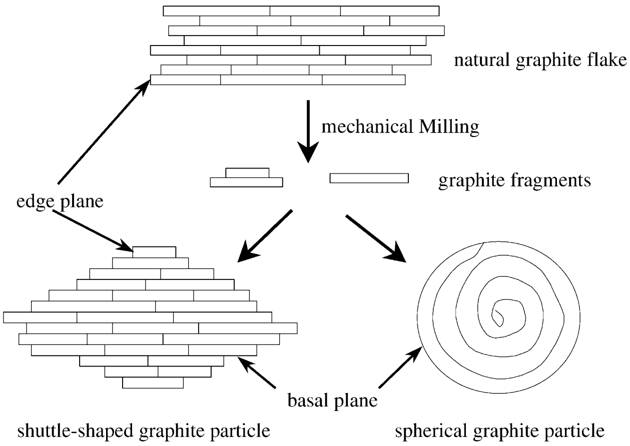

Figure 1. Schematic views for graphite morphology designs.

Figure 2 shows the SEM images for the cross-sectional view of a spherical natural-graphite particle before TVD carbon coating. The concentric alignment of the graphite texture can be clearly observed in this compact natural graphite core, which is in good agreement with the structure model we proposed in Figure 1. The particle size of the

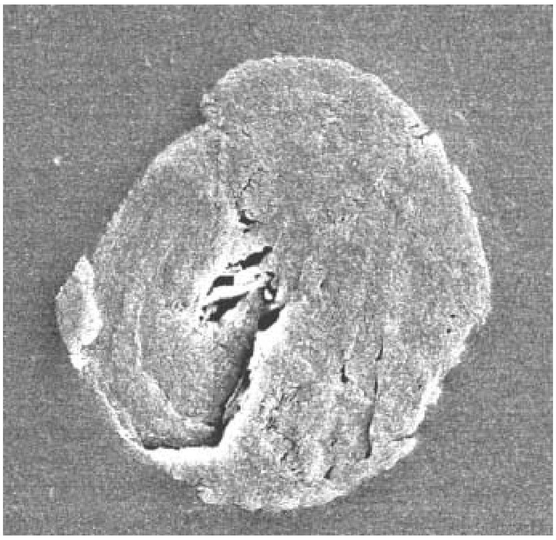

Figure 2. SEM images for the cross-section view of the spherical natural graphite core before TVD-carbon coating.

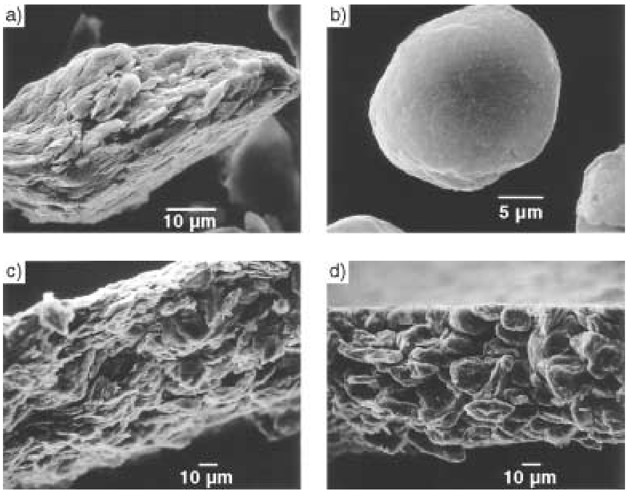

Figure 3. SEM images of TVD-carbon coated natural graphite particles: a) Shuttle-shaped and b) spherical graphite particles; c) shuttle-shaped and d) spherical-shaped graphite particles spread on a current substrate.

spherical natural-graphite core is about 20 μm. Figure 3 shows a comparison of the SEM images of the spherical carbon-coated natural graphite with the shuttlelike carbon-coated natural graphite. After TVD carbon coating, the surface of the spherical carbon-coated natural graphite particle is very smooth with respect to the surface morphology of shuttle-shaped one.

Because of the concentric alignment of planar graphite fragments in the core of spherical carbon-coated natural graphite, it is expected that each particle is isotropic, which is in contrast with the well-known anisotropic graphite flakes received directly from coal mines. Common natural graphite particles that are spread on a current substrate (such as copper foil) are highly orientated, with the basal planes parallel to the current substrate.[12] This kind of morphology may retard the rate capacity significantly, as the current flows in the direction perpendicular to the substrate whereas Li^+ intercalation and de-intercalation occur at edge planes from the directions parallel with the substrate. Therefore, the spherical carbon-coated natural graphite is more favorable than anisotropic graphite flakes in terms of the rate capacity.

Figure 4 shows a comparison of the XRD-patterns of the spherical and shuttle-shaped carbon-coated natural-graphite samples. The intensities of their (004) diffraction peaks were deliberately drawn equally. In the case of spherical sample, the diffraction peaks of (100), (101), (102), (103), (104), (110) and (112) can be clearly observed, which verifies the 3D structure. For the shuttle-shaped sample, these peaks are too weak to be labeled, mainly the (002), (004), and (006) peaks arising from the layered structure can be seen. If we take the intensity ratio of (002) to (110) as an orientation index, the shuttle-shaped sample has the value of 344.9 while the spherical sample has the value of 81.3. These values mean that graphitic layers in the spherical carbon-coated natural graphite are much less orientated than those in the shuttle-shaped carbon-coated natural graphite. Thus the rate capacity is likely to be increased in the former.

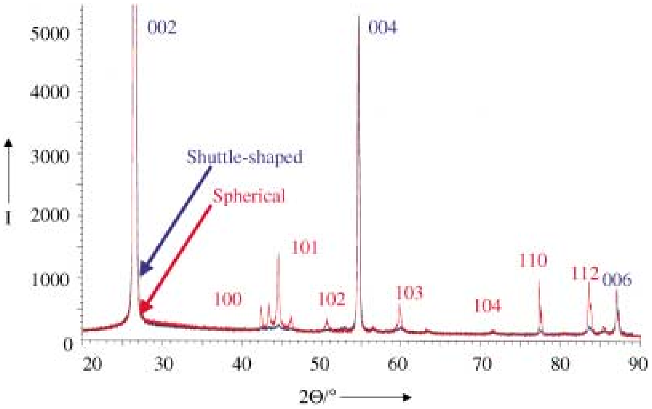

Figure 4. XRD-patterns of the spherical and shuttle-shaped TVD carbon-coated natural graphite samples. I = intensity.

Some preliminary electrochemical studies of spherical natural-graphite samples with different amounts of carbon coating have been carried out in both ethylene carbonate-(EC) and PC-based electrolytes. The reversible (discharge) capacity of the spherical graphite samples are as high as around 360 mA h g^{-1}, which is very near to the theoretical value of 372 mA h g^{-1}. Moreover, most of the coulombic efficiencies are over 90%, so the spherical carbon-coated natural graphite is a very promising material for use as anodes in lithium-ion batteries.

Figure 5 shows the relationship between coulombic efficiency and the amount of carbon coating for both spherical and shuttle-shaped natural graphite samples. For both kinds of samples, the coulombic efficiency increases with the amount of carbon coating, in either EC-based or PC-based electrolytes. In addition, the spherical graphite samples demonstrate much higher coulombic efficiency values than the corresponding shuttle-shaped graphite samples with similar amounts of carbon coating. The curves for spherical graphite level off once the amount of carbon coating rises to about 10 wt.%, which means that this quantity of coating is

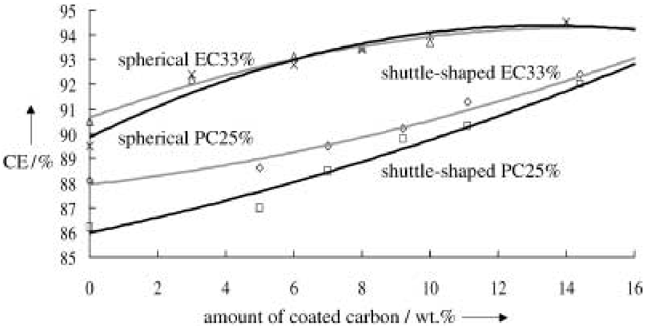

Figure 5. Relationship between coulombic efficiency and carbon-coating amount for both spherical and shuttle-shaped TVD-carbon coated natural graphite samples. Note: EC33% = the electrolyte of 1 M $LiPF_6$ dissolved in EC/DMC (1:2 by volume); PC25% = the electrolyte of 1 M $LiPF_6$ dissolved in PC/DMC (1:3 by volume). CE = coulombic efficiency.

sufficient to cover all the edge planes on the surface of the graphite core. On the other hand, the curves of shuttle-shaped graphite continue to climb even after the amount of carbon coating reaches 15 wt.%, which shows that more TVD carbon coating is needed to cover all the edge planes completely.

In conclusion, the spherical carbon-coated natural graphite is a promising candidate for use as an anode for lithium-ion battery, as it has high coulombic efficiency, high rate capacity, and low cost because of the abundance of natural graphite and low amount of carbon coating required.

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[1] M. Fujimoto, Y. Shoji, Y. Kida, R. Ohshita, T. Nohma, K. Nishio, *J. Power Sources* **1998**, *72*, 226–230.

[2] K. Fukuda, K. Kikuya, K. Isono, M. Yoshio, *J. Power Sources* **1997**, *69*, 165–168.

[3] A. N. Dey, B. P. Sullivan, *J. Electrochem. Soc.* **1970**, *117*, 222–224.

[4] M. Arakawa, J. Yamaki, *J. Electroanal. Chem.* **1987**, *219*, 273–280.

[5] R. Fong, U. von Sacken, J. R. Dahn, *J. Electrochem. Soc.* **1990**, *137*, 2009–2013.

[6] D. Aurbach, Y. Ein-Eli, O. Chusid, Y. Carmeli, M. Babai, H. Yamin, *J. Electrochem. Soc.* **1994**, *141*, 603–611.

[7] H. Nakamura, H. Komatsu, M. Yoshio, *J. Power Sources* **1996**, *62*, 219–222.

[8] M. Yoshio, H. Wang, K. Fukuda, Y. Hara, Y. Adachi, *J. Electrochem. Soc.* **2000**, *147*, 1245–1250.

[9] H. Wang, M. Yoshio, *J. Power Sources* **2001**, *93*, 123–129.

[10] H. Wang, M. Yoshio, T. Abe, Z. Ogumi, *J. Electrochem. Soc.* **2002**, *149*, A499–A503.

[11] H. Wang, T. Ikeda, K. Fukuda, M. Yoshio, *J. Power Sources* **1999**, *83*, 141–147.

[12] Z. X. Shu, R. S. McMillan, J. J. Murray, *J. Electrochem. Soc.* **1993**, *140*, 922–927.