

Effect of morphology and texture on electrochemical properties of graphite anodes

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Abstract

Three different natural graphite powders (MPG, SPG and HPG) were used to make anode films of lithium-ion batteries by rolling technique. It was found that particle size and particle distribution of graphite, as well as particle orientation in the foil, show great influence on the electrochemical performance of graphite foil anodes. Different X-ray experiments were performed to study the mosaic distributions and coherence lengths of graphite crystallites. This study of the morphology and texture characteristics of anode foils reveals results that pertain to the understanding of electrochemical performance of cells. © 1997 Elsevier Science S.A.

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1. Introduction

Carbon materials have large variations in their structure and texture. It has been found that the micro- and macroscopic structures have large influences on the electrochemical properties of carbonaceous anode of lithium-ion batteries [1–3]. Powder grains of natural graphite typically have plate-like shapes with a shorter dimension along the crystallographic *c*-axis. In this paper, we present the results of an investigation where the degree of preferred orientation of graphite crystallites is determined in rolled foils and where the degree of orientation is correlated with the electrochemical behavior of lithium intercalation. To study the effect of morphology and texture of the graphite foils on the electrochemical properties, natural graphite powders having three different particle size distributions were used to make anode films for lithium-ion batteries by the rolling technique. Our study showed that the electrochemical performance of an Li-ion battery was influenced by particle size distribution and particle orientation.

2. Experimental

Three natural graphite powders (MPG, SPG and HPG) from the same origin of a graphite ore in Shandong Province

of China and only differing in their size distributions were used in this study. The centrifugal sedimentation technique and BET method were used to measure the particle size distributions and surface areas, respectively. To understand the mosaic distribution and crystallite orientation in the foils, X-ray experiments were performed using a laboratory diffractometer with a Cu rotating anode ($\lambda = 1.5406 \text{ \AA}$) and LiF monochromator. The analysis was done by studying 'rocking curves' (Fig. 1(a)) in which the detector angle 2θ is fixed at a particular graphite reflection and the sample angle ϕ is 'rocked' through some range of values. If the sample was a perfect crystal, intensity would be observed only when $\phi = \theta$, whereas the observed spread in ϕ reflects the real-space dispersion of crystallite orientation. This experiment was performed at two different reflections, the (004) and the (100). Since the average *c*-axis is normal to the plane of the foil, the (004) is observed in reflection while the (100) is seen in transmission, as shown in Fig. 1(a).

The crystal coherence lengths parallel (\parallel) and perpendicular (\perp) to the carbon planes were obtained by analysing the full width at half-maximum (FWHM) of reflections using the Scherrer formula

$$L = 0.94\lambda / [\text{FWHM} \cos(\theta)]$$

where the angles are in radians. Here the FWHM is the width in 2θ rather than ϕ , and is measured either from the starting powder in a capillary (Fig. 1(b)) or from the foil

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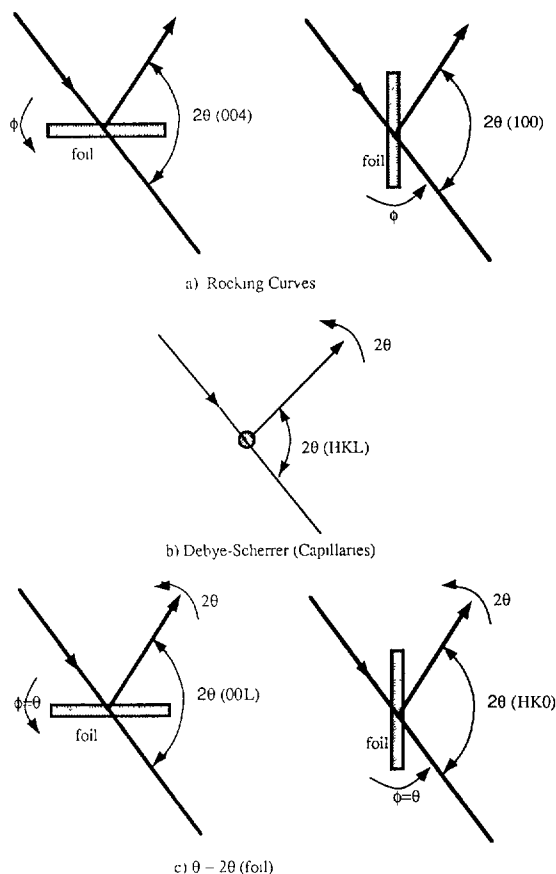


Fig. 1 X-ray measurements geometries

(Fig. 1(c)). By analysing both (h/l) and ($00l$) type reflections, one can estimate the crystallographic coherence length in two orthogonal directions, namely parallel and perpendicular to the graphite layers, respectively. The instrumental resolution was determined by measuring an NBS silicon standard powder. It was found that data thus obtained from the laboratory diffractometer were judged to be of low accuracy since the instrumental resolution and sample widths in 2θ were comparable. We therefore repeated all the coherence length measurements (foils and powders) using the much higher resolution available at the Brookhaven synchrotron (NSLS National Synchrotron Light Source). We used beam-line X7A equipped with a perfect crystal monochromator and analyser operating at a wavelength of 1.2103 \AA .

The graphite powders were mixed with 8 wt.% of polytetrafluoroethylene (PTFE) emulsion solution (containing 60 wt.% of PTFE), then rolled into foils of $100\text{--}150 \mu\text{m}$ in thickness. The foil was pressed onto a nickel foam as the current collector with the pressure of 30 MPa. The foils were completely dried in vacuum at $150 \text{ }^\circ\text{C}$ for 48 h. A two-electrode button cell was assembled in a dry box and then used for the charge/discharge cycle tests. Different graphite foils were used as the working electrode, lithium metal foil as the counter electrode, and $1 \text{ M LiClO}_4/\text{EC-DMC}$ (1:1) as the electrolyte. The charge/discharge performance was galvanostatically tested with the current density of 0.3 mA/cm^2 in a voltage range from 0.010 to 2.00 V.

3. Results and discussions

As powder grains of graphite are typically plate-like shapes, the centrifugal sedimentation method is not suitable to analyse real particle size, however, for the particle size distributions this method can give useful information. The particle size distributions measured by a SA-CP3 centrifugal particle size analyser are shown in Fig. 2. In Fig. 2 the maximum value of particle distributions was normalized to 100. It can be seen that the particle sizes of MPG and SPG are almost the same, the median diameters are 6.27 and $6.31 \mu\text{m}$, respectively, but the distribution of SPG is broad. However, the particle size of HPG is much larger, the median diameter is $15.5 \mu\text{m}$. As seen in Fig. 2, the HPG powder appears to be a mixture of some large graphite particles ($> 40 \mu\text{m}$) mixed with a small graphite powder having a Poisson distribution.

The surface areas measured by the BET method for MPG, SPG and HPG powders were 25.9 , 12.6 and $5.0 \text{ m}^2/\text{g}$, respectively. The HPG particles are large, and have small surface area. The MPG powder has almost the same median diameter as SPG, but twice the surface area, which suggests that the particles of MPG are thinner and have a larger aspect ratio than SPG particles.

A typical rocking curve, for the (100) reflection of HPG films, is shown in Fig. 3. This establishes the general trend that rolling induces preferred alignment of the c -axis normal to the plane of the foil. The solid curve is the best fit to a

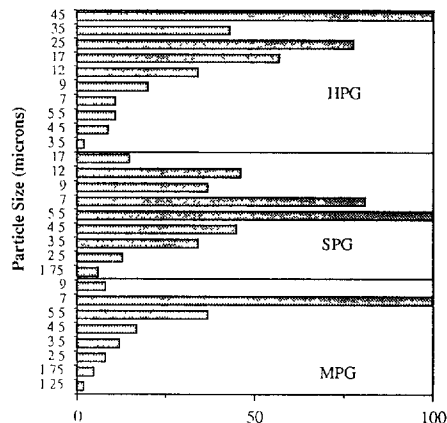
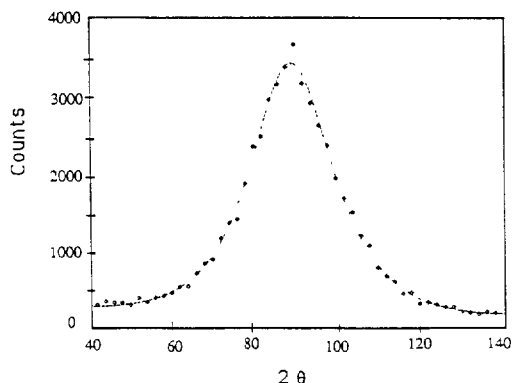


Fig. 2. Particle size distributions of MPG, SPG and HPG powders.

Fig. 3. (100) Rocking curve of HPG foil.

mixed Gaussian–Lorentzian line shape, yielding a FWHM of 25.5° . If the graphite particles reoriented stochastically in response to the anisotropic shear induced by rolling, then the orientation of individual grains would follow Poisson statistics and the rocking curve would be a pure Gaussian. The main difference between Gaussian and Lorentzian functions is their asymptotic behavior far from the center of the rocking curves. The Gaussian decays exponentially while the Lorentzian is a slower power law dependence. A Lorentzian component (called as Lorentz fraction L_l) in rocking curves is generally taken as evidence for a fraction of particles which respond less well to the anisotropic strain. The rocking curve FWHMs and Lorentz fractions are collected in Table 1. We notice that the FWHMs are about the same for MPG and SPG but significantly smaller for HPG, indicating a greater degree of preferred orientation in the latter material. The largest Lorentz fraction, 0.92, is observed in the (100) rocking curve from HPG sample, while the (004) reflection from the same sample yields a much smaller Lorentz fraction, 0.59. The difference is probably due to small-scale inhomogeneities, such that the (100) transmission and (004) reflection measurements perform different averagings over different sampled volumes. There is no systematic variation in the Lorentz fraction among the three materials studied.

Coherence lengths obtained from the initial powders and rolled foils are collected in Tables 2 and 3. Comparing the entries in Tables 2 and 3, it appears to be generally true for both powders and foils that the coherence length parallel to the layers is greater than perpendicular to the layers. We also note from Table 3 that $L(\perp)$ is not dramatically affected by the rolling process since it is about the same in the powder and foil for all three grades. This implies that the rolling process does not induce cleavage along basal planes, which would reduce the foil $L(\perp)$ relative to the parent powders.

However, Table 2 shows that for the HPG $L(\parallel)$, particle size is 15 750 Å, over twice as large as the 6850 Å value for the parent powder, just the opposite of what we expected. In-plane grain growth during foil processing is highly unlikely given the ambient temperature involved. A strong clue is the fact that this effect also appears in HPG (SPG showing very similar $L(\parallel)$'s for foils and powders) and that the HPG powder appears to be a mixture of some large particles ($>40 \mu\text{m}$) mixed with a small graphite powder as mentioned above. For powder samples, all grains/crystallites contribute to $L(\parallel)$ in proportion to their bulk population distribution regardless of their orientation, while for the foil $L(\parallel)$ is dominated by the grains/particles whose c -axes are well aligned

Table 1
Mosaic FWHM and Lorentz fractions (L_l) of three different graphite foils

(hkl)	MPG		SPG		HPG	
	FWHM	L_l	FWHM	L_l	FWHM	L_l
100	33.2	0.50	31.1	0.69	25.5	0.92
004	31.7	0.78	26.6	0.77	22.6	0.59

Table 2
(100) reflection: in-plane coherence lengths, $L(\parallel)$ (in Å)

Carbon type	Foil (θ - 2θ , transmission)		Powder (capillary)	
	FWHM	$L(\parallel)$	FWHM	$L(\parallel)$
MPG	0.021°	11000	0.023°	6850
SPG	0.023°	8650	0.023°	8000
HPG	0.019°	15750	0.025°	6850

Table 3
(002) reflection: C-axis coherence length, $L(\perp)$ (in Å)

Carbon type	Foil (θ - 2θ , reflection)		Powder (capillary)	
	FWHM	$L(\perp)$	FWHM	$L(\perp)$
MPG	0.061°	1350	0.058°	1400
SPG	0.056°	1500	0.049°	1800
HPG	0.034°	3050	0.027°	4400

normal to the foil since these are the only ones detected in the θ - 2θ scan. We conclude that the larger particles which typify HPG are more likely to be well aligned, resulting in a significant larger 'effective' $L(\parallel)$ for HPG foil compared to HPG powder. The particle distribution of MPG is broad, some large particles are well aligned, also resulting in larger $L(\parallel)$ for foil than powder. The powder SPG has normal particle distributions, and $L(\parallel)$ is about the same for the foils and powders.

From X-ray results, it is concluded that the plate-like shape of graphite grains gives rise to anisotropic flow properties under shear during the rolling process. The large particles tend to align more readily than smaller particles, leading to increased orientation. Therefore, the larger c -axis oriented particles in HPG foils would have their edges less accessible for lithium intercalation compared with the smaller, less oriented SPG- and MPG-based anodes.

The quantity of lithium intercalated into the carbon with a constant current of 0.30 mA/cm^2 occurs within the voltage range from 0.010 to 2.00 V and is given in the 'effective' capacity for anodes containing SPG, MPG and HPG, shown in Fig. 4. It can be seen that the HPG foil stored less lithium

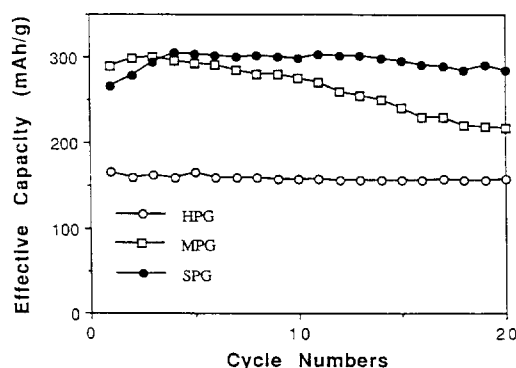


Fig. 4. Effective capacities of MPG, SPG and HPG anode films. Charge/discharged current: 0.30 mA/cm^2 , voltage range: 0.010–2.00 V.

than did the foils composed of SPG and MPG. The HPG anode foil had significantly lower lithium uptake, resulting from the higher degree of crystallite orientation and large particle size. The higher degree of orientation with *c*-axis perpendicular to the electrode surface increases the path length for the lithium diffusion to the edges of the crystallites. Compared with the smaller particle of SPG and the less oriented SPG foil, the HPG graphite particles were not fully intercalated. As seen in Fig. 4, the electrochemical reversibility of the anode foil containing MPG is worse than that of SPG, since the MPG particles are thinner and have a larger aspect ratio than SPG particles, as mentioned above.

4. Conclusions

Our findings show that since lithium intercalation occurs at the edges of the graphite plate-like crystallites the rate of

lithium intercalation can be significantly decreased by the size and orientation (crystallites with *c*-axis perpendicular to the electrode surface) of the particles used in making anodes for Li-ion batteries. This can decrease the performance of an Li-ion battery by limiting charge and discharge currents or limiting the 'effective' capacity due to a lower lithium intercalation rate. The graphite powders with a uniform particle distribution and smaller aspect ratio, and the foils with less orientation would show better electrochemical performance.

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