Battery characteristics with various carbonaceous materials

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Abstract

Various carbonaceous particles having a core–shell structure, produced from graphite and pseudo-graphite coated with pitch-blended phenol resin and green mesophase-pitch coated with phenol resin and ground graphite powder, were investigated as active materials for negative electrodes. The particles with natural graphite cores, as well as those with pseudo-graphite cores, were stable both in 1 M $LiClO_4$–PC:EC (50:50) electrolyte and in 1.5 M $LiBF_4$–PC:EC:BL (25:25:50) electrolyte, and showed excellent electrical capacities. Those produced from green mesophase-pitch cores were of markedly deformed configuration and showed large capacity gains with only small additions of graphite powder to the phenol coating material. Negative electrodes, in which the particles containing natural graphites cores were blended with petroleum coke in various ratios, showed that it may be possible to produce cells with specific discharge voltage curves, by varying the ratio of this blend.

Keywords: Carbonaceous materials; Negative electrodes

1. Introduction

Petroleum coke was adopted as a negative electrode active material for a rechargeable battery with 1 M $LiClO_4$–propylene carbonate (PC) in 1986 [1], in what is believed to be the first appearance in the industry of rechargeable lithium-ion batteries. Im 1988, the electrolyte solution was replaced by the more thermally stable $LiBF_4$ in PC:EC:BL (propylene carbonate: ethylene carbonate:gamma-butyrolactone) [2]. Lithium-ion batteries, still using coke as the main negative electrode material, are now recognized for the inherent safety of their basic charge/discharge mechanism, which consists essentially of the shuttling of lithium ions back and forth between the two electrode materials and, thus, involves no metal lithium [3,4].

The characteristics and utilization of coke as a negative electrode material have been studied extensively during the past few years [5–11], but the use of graphite for the same purpose has also become a subject of strong interest. The intercalation of lithium into graphite by vapour transport was discovered by Guerard in 1975, and many studies have recently been made, using electrochemical methods, to elucidate the structure and stageing of lithium-intercalated graphite [10,12,13]. The

decomposition of electrolyte during the first lithiation of graphite leads to gas evolution and the formation of a solid electrolyte interphase (SEI) film [14,15]. EC containing $LiPF_6$ electrolyte is apparently stable with graphite negative electrodes, while providing high energy densities and flat discharge voltage curves [16,17], but the charging rate of cells utilizing these is as yet too slow to permit practical applications in the consumer market.

In a different approach, we have been engaged in the development of carbonaceous materials having a core–shell structure, with the shell comprised of coke-like carbon and the core composed of graphite or pseudo-graphite, in the expectation that these will be stable in both the conventional $LiClO_4$–PC:EC (50:50) and the $LiBF_4$–PC:EC:BL (25:25:50) electrolyte systems in order: (i) to obtain a discharge curve with a tilt voltage that facilitates ready detection and indication of the residual cell capacity and also a higher energy density by blending the core–shell carbon with coke, and (ii) to obtain a carbonaceous material with a higher energy density than coke by coating a blend of phenol resin and fine-ground graphite on green mesophase-pitch beads. In this paper, we present the characteristics of cells containing these core–shell carbons as the negative electrode active material.

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2. Experimental

Each powder consisting of natural graphite, spherical artificial graphite and pseudo-graphite from heat-treated mesophase-pitch beads, or polyhedral artificial graphite from coal tar was coated with pitch-blended phenol resins (modified phenol resins) in a kneader and then heat-treated up to 1200 °C in a nitrogen gas atmosphere. For the characterization of the shell carbon, phenol resin and pitch-blended phenol resin were obtained by polymerization in the kneader followed by heat treatment in the same manner.

Powder consisting of green mesophase-pitch beads was mixed with phenol resin and various amounts of finely ground graphite powder in the kneader, polymerized, and then heat-treated at various temperatures in a nitrogen atmosphere. Working electrodes were prepared by wet mixing the carbonaceous material with 2.8 wt.% of cross-linked rubber particles and carboxymethyl cellulose (CMC) as binder and laying the mixture on copper foil. Glass cells were constructed in a parallel plate configuration using these as negative electrodes, lithium foil as counter electrodes, microporous polyethylene as separators, and either 1.5 M $LiBF_4$ in a 25:25:50 mixture by volume of PC, EC, and BL or 1.0 M $LiClO_4$ in a 50:50 mixture by volume of PC and EC. Electrochemical behaviour was studied in galvanostatic charge/discharge cycling at a current density of 1.0 mA cm^{-2} maximum with a lower limit of 0.01 V for 8 h for the first charge and at 1.0 mA cm^{-2} and a voltage of 0.01–1.0 V versus Li/Li$^+$ for subsequent cycles. Prototype thin prismatic cells (thickness × width × length: 8.6 mm × 34 mm × 48 mm) were constructed with the separators and the $LiBF_4$ electrolyte system described above, positive electrodes composed of $LiCoMO_2$ on aluminum foil, and negative electrodes prepared as described above from the natural-graphite core–shell particles but with the admixture of petroleum coke in various amounts. Impedance measurements were made with the prototype thin prismatic cells. The average carbon layer spacing $d(002)$ and average crystallite thickness L_c of the carbonaceous materials were determined by X-ray diffraction.

3. Results and discussion

The stability of the 1.0 M $LiClO_4$–PC:EC and 1.5 M $LiBF_4$–PC:EC:BL electrolyte systems was examined as an indication of the extent of coating coverage on the core graphite. As shown in Table 1, the results indicate that the stability of the electrolyte is critically influenced by very small differences in $d(002)$ or the related L_c. With the $LiBF_4$–PC:EC:BL electrolyte system, even naked graphite showed good lithiation from the first charging, but separate unpublished studies have shown this combination of negative electrode and electrolyte to be unstable in storage at elevated temperatures, making it unsuitable for consumer-market applications. The discharge capacity and coulombic efficiency for each electrode–electrolyte combination are also shown in Table 1.

Further experimentation (not described here) showed that even the single coating on natural graphite was

Table 1
Electrolyte stability and extent of carbonaceous shell coating with the various core graphites 1 M LiClO₄–PC:EC(50:50) and 1.5 M LiBF₄–PC:EC:BL(25:25:50) during the first charge and discharge

Core material			Shell material		Core:shell wt. ratio	1 M LiClO₄ (PC:EC)		1.5 M LiBF₄ (PC:EC:BL)	
$d(002)$ (Å)	L_c (Å)	Graphite type	$d(002)$ (Å)	L_c (Å)		Capacity (mAh g^{-1})	First cycle efficiency (%)	Capacity (mAh g^{-1})	First cycle efficiency (%)
3.354	1000 <	Natural (polyhedral)			100:0	Decomposed	Decomposed	371	83
					87:13 [a]	Decomposed	Decomposed	336	81
					70:30 [b]	169	38	303	81
3.365	460	Artificial (spherical)	3.535	17	80:20	236	78	259	85
3.364	550	Artificial (polyhedral)			80:20	300	78	302	85
Carbon for shell					0:100			167	67
3.447	52	Petroleum coke			100.0	204	78	218	81

[a] Single coating.
[b] Double coating: first coating and heat treatment resulting in graphite (core):coke-like carbon (shell) ratio of 87:13 by weight, followed by second coating comprising 20% of total particle weight after heat treatment.

Table 2
Coulombic efficiency and capacity of core–shell carbons in 1.5 M LiBF$_4$–PC:EC:BL (25:25:50) electrolyte

Core material			Shell material		Core:shell wt. ratio	Capacity (mAh g^{-1})	First cycle efficiency (%)	Third cycle efficiency (%)
d(002) (Å)	L_c (Å)	Graphite-type	d(002) (Å)	L_c (Å)				
3.354	1000 <	Natural (polyhedral)			80:20	333	90	98
3.376	500	Artificial (spherical)			80:20	230	87	98
3.372	660		3.535	17	80:20	254	86	97
3.365	460				80:20	259	85	95
3.363	530	Artificial (polyhedral)			80:20	300	86	96
Carbon for shell					0:100	167	67	99

sufficient to stop decomposition of the 1.0 M LiClO$_4$–PC:EC electrolyte system by the third cycling, with only negligible discharge capacity thereafter.

The first charge profiles with the 1.0 M LiClO$_4$–PC:EC electrolyte and core–shell particles composed of the natural graphite core and the carbonized shell in the weight ratio of 70:30, as compared with those of the same electrolyte and naked natural graphite, are shown in Fig. 1. Those of spherical and polyhedral coated particles having cores of natural or artificial graphite, in the 1.5 M LiBF$_4$–PC:EC:BL electrolyte, are shown in Fig. 2. The coulombic efficiency and capacity per gram in the first cycle for similar core–shell particles (80:20 core–shell weight ratio) with the 1.5 M LiBF$_4$–PC:EC:BL electrolyte are shown in Table 2, and the first discharge curves of several of similar particles with various core–shell weight ratios and the same electrolyte are shown in Fig. 3.

Unexpected results were obtained in both the preparation and the capacity of the core–shell particles produced with green mesophase-pitch beads and phenol resins containing ground graphite. Following kneading, the coated beads were subjected to heat treatment at
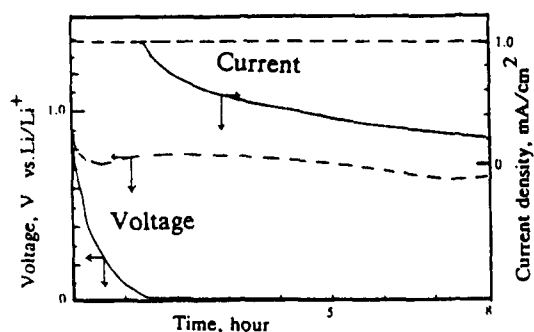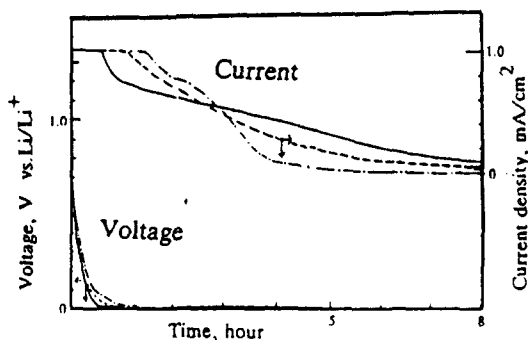

Fig. 2. First charge profiles of negative electrode core–shell materials from various graphites, in 1.5 M LiBF$_4$–PC:EC:BL (25:25:50) electrolyte; (——) polyhedral natural graphite core:shell, 70:30; (– –) spherical artificial graphite core:shell, 80:20, and (– · –) polyhedral artificial graphite core:shell, 80:20.
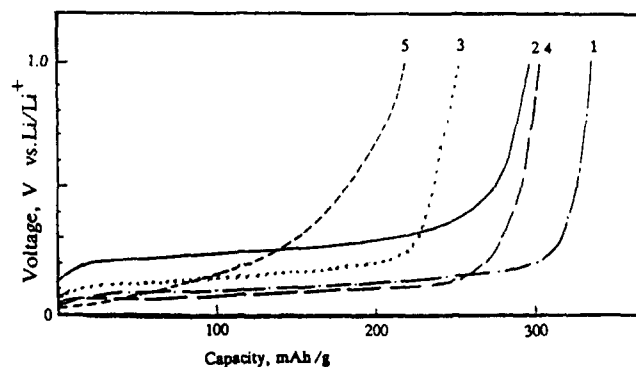

Fig. 3. First discharge curves of carbonaceous core–shell materials in 1.5 M LiBF$_4$–PC:EC:BL (25:25:50) electrolyte at 1 mA cm^{-2} and voltage cutoff at 1.0 V with lithium metal counter electrode: (1) natural graphite core:shell, 87:13; (2) natural graphite core:shell, 70:30; (3) spherical artificial graphite core:shell, 80:20; (4) polyhedral artificial graphite core:shell, 80:20, and (5) petroleum coke.

Fig. 1. First charge profiles of (——) negative electrode core–shell material (natural graphite (core): coke-like carbon (shell), 70:30 by weight) and (– – –) naked natural graphite in 1 M LiClO$_4$–PC:EC (50:50) electrolyte.

various temperatures with the intended purpose of altering the thin surface layer of beta-resins. This treatment, however, unexpectedly resulted in markedly deformed particle configurations quite unlike the regular

Table 3
Effect of graphite addition on capacity of mesophase-pitch (core)–phenol resin (shell) particles [a]

Graphite amount (%)	Carbon from phenol resins (%)	Heat-treatment temperature (°C)	$d(002)$ (Å)	L_c (Å)	Capacity (mAh g^{-1})	First cycle efficiency (%)
0	0	1200	3.512	29	213	78
0.7	5	1080	3.535	21	215	75
5.8	5	900	3.533	21	268	68
4.6	14	1200	3.539	24	227	80
5.5	14	900	3.570	18	382	61

[a] Obtained by coating green mesophase-pitch beads with phenol resin with or without finely ground graphite in a kneader and then heat-treating.

Fig. 4. SEM micrograph of core–shell particles obtained from green mesophase-pitch beads and phenol resins containing small amount of ground graphite.
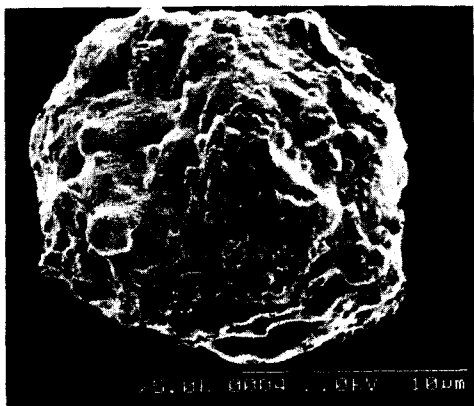
Fig. 5. SEM micrograph of core–shell particle obtained by heat-treating mesophase-pitch beads at 2300 °C followed by phenol resin coating and heat treatment at 1200 °C.

core–shell particle configurations that had been obtained with beads that had been heated to 2300 °C or higher prior to kneading, as shown by the scanning electron micrographs of Figs. 4 and 5. As shown in Table 3, furthermore, the addition of only small amounts of ground graphite to the kneading mixture resulted in surprisingly large capacity gains, particularly when the kneading was followed by a heat treatment at about

900 °C. The large size of the capacity gain would seem to imply that the comparatively high electric conductivity of the overall carbon under these conditions of preparation promotes the transport of Li$^+$ dopant to carbon sites that otherwise would remain latent and inactivated.

We next fabricated a series of prototype thin prismatic cells, with positive electrodes composed of LiCoMO$_2$, 1.5 M LiBF$_4$–PC:EC:BL as the electrolyte solution, and negative electrodes fabricated from a mixture of the core–shell particles (80:20 weight ratio; core from nat-
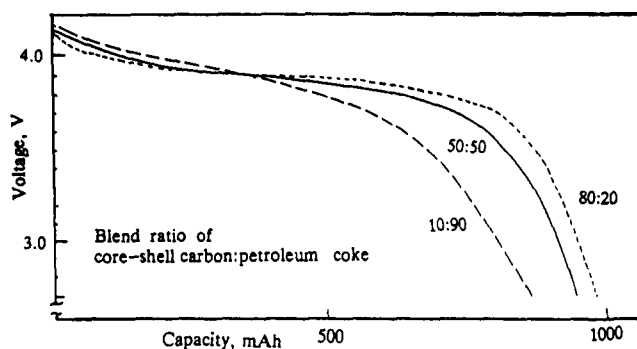

Fig. 6. Discharge curves of prototype thin prismatic cells with LiCoMo$_2$ positive electrode, 1.5 M LiBF$_4$–PC:EC:BL electrolyte, and negative electrodes obtained from mixture of natural graphite core:shell (80:20 by weight) and petroleum coke in various ratios.
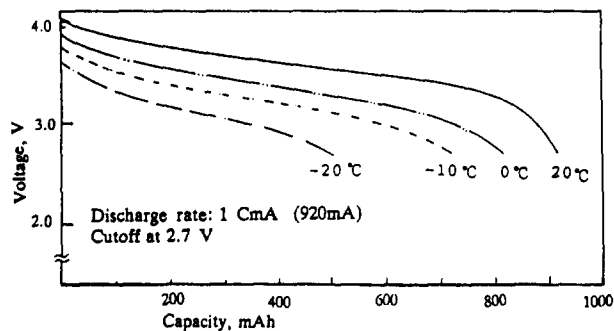

Fig. 7. Typical discharge curves of prototype thin prismatic cell with LiCoMo$_2$ positive electrode, 1.5 M LiBF$_4$–PC:EC:BL electrolyte, and negative electrode obtained from mixture of natural graphite core:shell (80:20 by weight) and petroleum coke in weight ratio of 65:35 at various temperatures.
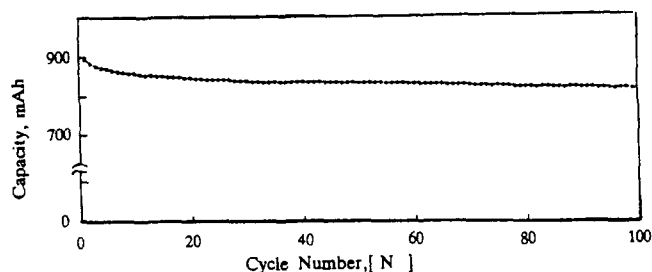
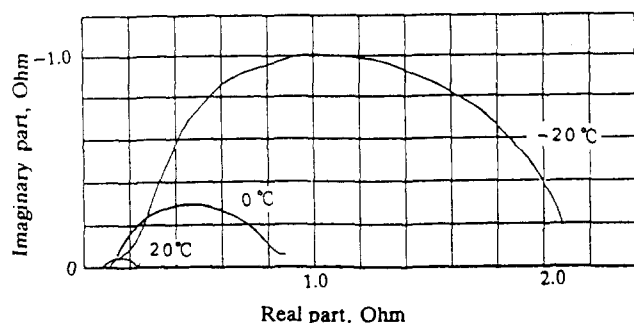Fig. 8. Cycle life of prototype thin prismatic cell (composition as in Fig. 7).

Fig. 9. Nyquist plot of the impedance spectra in the 10000–0.01 Hz range in prototype thin prismatic cell (composition as in Fig. 7).

ural graphite, shell from pitch-blended phenol resins) and petroleum coke in various ratios. The discharge curves of three of these cells with different ratios of core–shell carbon to petroleum coke are shown in Fig. 6. Typical discharge curves at various temperatures are shown in Fig. 7 for the cell with a negative electrode composed of core–shell carbon (80:20 weight ratio) and petroleum coke in the weight ratio of 65:35. In cycle-life tests, as indicated by Fig. 8, this cell showed excellent capacity retention.

The impedance spectra in the range 10 000–0.01 Hz at various temperatures were determined for this cell, and yielded the semicircular Nyquist plots shown in Fig. 9, and demonstrate the increase in the interfacial resistance between the negative electrode material and the electrolyte solution with decreasing ambient temperatures.

4. Conclusions

The morphology of core–shell structured carbons and their electrochemical behaviour were studied and found to be compatible with conventional petroleum coke. The findings may be useful for the design of rechargeable lithium-ion cells with a better balance of performance particularly in batteries for 3 V LSI (large-scale-in-

tegration) systems, in which higher energy densities will be desired and the tilt voltage around 3 V will be important to facilitate cutoff and annunciator initiation by the relatively simple means currently in wide use.

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