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Anodic performance of vapor-derived carbon filaments in lithium-ion secondary battery

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Abstract

The electrochemical characteristics of vapor-derived carbon filaments of diameter 0.1 μm were studied by charge–discharge testing of a lithium-ion secondary cell with a lithium metal electrode. After activation, followed by either nitridation or reduction in hydrogen, vapor-derived carbon filaments show high reversible charge and discharge capacities. An ordered structure and a large pore size are favorable for a high capacity, as shown by comparison of vapor-derived and pitch-derived carbons. The combination of a high specific surface area and a large amount of oxygen-containing surface functional groups results in a high irreversible capacity. To improve the anodic performance, it is important to control the surface microstructure by decreasing the surface oxygen content by nitridation or reduction in H_2, while maintaining order in the crystallographic structure with surface mesoporosity. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Lithium ion secondary batteries [1,2] are needed for electric and hybrid electric vehicles. The carbon anode in these batteries is one of the key components that strongly affect battery performance, particularly the specific charge/discharge capacity, i.e. the capacity per unit volume of the anode material during charge or discharge. The development of better carbon anode materials is a challenge due to the large variety of carbon materials available (including hard or non-graphitizable carbons, soft or graphitizable carbons, and graphites) and the complexity of factors that affect anode performance (including crystallinity, microstructure, surface chemistry and surface porosity). The intercalation of lithium in graphite has been extensively studied and is relevant to the understanding of the electrochemical intercalation of lithium in graphite, for which the theoretical specific capacity is limited to 372 mA h/g. On the other hand, some soft carbons which have been heat treated exhibit specific capacities as high as two to three times the theoretical value for graphite [3]. The reason for the high specific capacity is still not clear.

Much work has been done by numerous workers on the use of pitch-derived carbons and polymer-derived carbons as anodes [1–3]. Pitch-derived carbons include coke, microbeads, pitch-based carbon fibers and other soft carbons. Polymer-derived carbons include granular and filamentary carbons derived from poly *p*-phenylene, phenolic, polyfurfuryl alcohol and polyacrylonitrile, and other hard carbons. A third type of carbon that has received little attention in relation to batteries is vapor-derived carbons, i.e. carbons obtained from carbonaceous gases [4]. Vapor-derived carbons include soot and filamentous carbons, which differ from those derived from pitch or polymers in the much smaller value of the lower limit of the filament diameter. Fibers made from pitch or polymers are at least 5 μm in diameter, whereas those made from vapor can be as small as 50 Å in diameter. Vapor-derived carbons also differ from those derived from pitch or polymers in the microstructure. The pores in vapor-derived carbons (50 Å BJH or more) [5] tend to be larger than those in carbons derived from pitch or polymers (20 Å or less). Vapor-

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derived carbons without graphitization (without high temperature heat treatment) tend to be more ordered (interplanar spacing d_{002} as low as 3.37 Å) than carbons derived from pitch or polymers. Vapor-derived carbons are soft carbons like pitch-derived carbons, so the degree of crystallinity can be greatly increased upon high temperature heat treatment.

High crystallinity tends to be associated with high electrical conductivity, which is desirable for anode performance. The small size of vapor-derived carbon particles or filaments results in a high geometric specific surface area and good processability into thin foils. Due to the low cost of carbonaceous gases (such as natural gas) compared to pitch or polymers, vapor-derived carbons are expected to be the form of carbon that costs the least. Indeed, the price of vapor-derived carbons is decreasing and is expected to decrease rapidly when the currently small market is greatly enlarged by the use of vapor-derived carbons as anodes of batteries. Due to the low costs of the precursor and of the filament fabrication, the price of vapor-derived carbons may eventually drop below that of pitch-derived carbons.

The objective of this project is to investigate the use of vapor-derived carbons for anodes of lithium ion cells. This investigation is focused on filamentary vapor-derived carbons, modification of these carbons through activation, reduction and non-carbon element (e.g. nitrogen) addition to surface, and charge–discharge testing using a lithium metal cathode for evaluation of carbon anode performance. The main purpose of the modification is to increase the specific capacity and decrease the irreversible capacity loss. The secondary purpose is to attain a better understanding of the factors that govern anode performance.

2. Experimental methods

Carbon filaments of diameter ~0.1 μm were provided by Applied Sciences Inc. (Cedarville, Ohio). They were fabricated from methane gas using an iron-based catalyst. Sample 1 was as-received carbon filaments. Sample 2 had been cleansed by acetone. Samples 3 and 4 had been cleansed by acetone and then activated as in Ref. [4] (heating in O_3 (0.3 vol.% in air) at 150°C for 3 min, followed by heating in N_2 to 970°C at 3°C/min and then heating in CO_2+N_2 in 1:1 volume ratio at 970°C for 30 min for Sample 3 and 20 min for Sample 4). Sample 5 was obtained from Sample 4 by reduction in H_2 at 800°C. Sample 6 was obtained from Sample 4 by (i) heating in O_3 (0.3 vol.% in air) at 180°C for 6 min for formation of oxygen-containing functional groups on the surface, and (ii) immersion in a 1 N solution of ammonium hydrogen phosphate, $(NH_4)_2HPO_4$, at room temperature, followed by drying in air at 105°C for 60 min, then heating in air at a rate of 10°C/min to 210°C and then held at 210°C for 30 min for formation of OH groups, and then at 418°C for 40 min in nitrogen for forming nitrogen-containing functional groups. Sample 7 was naphthalene-mesophase-based pitch (not fiber) which had been carbonized at 800°C and then reduced in H_2 at 800°C.

Charge–discharge testing was conducted in a dry box filled with argon gas. The test cell (Fig. 1) consisted of a carbon working electrode, a counter electrode (pure Li metal) and a reference electrode (pure Li metal). The carbon working electrode consisted of 96 wt.% carbon and 4 wt.% teflon. The carbon filaments were mixed with teflon and ethanol to form a paste, which was made into a foil. The electrode was cut from this foil to 1.0 cm diameter, dried, pressed at 30 kg/cm^2, and dried at 125°C under vacuum before assembling the test cell. Microporous polypropylene (Celgard 2500, Hoechst Celanese Corp., Charlotte, NC) was used as separator. The electrolyte was a solution consisting of $LiPF_6$ in a mixture of ethylene carbonate and dimethyl carbonate (1:1 by volume, 1 M). The cell was evacuated and then backfilled with the electrolyte in order to degas the porous separator and impregnate it with the electrolyte.

Galvanostatic measurement was performed by charge–discharge testing using a constant current method (0.2 mA/cm^2 at a potential range of 0–2 V). ESCA (Electron Spectroscopy for Chemical Analysis, with spot size 1000 μm, monochromatized Al Kα X-ray) was used to observe the surface elemental composition. The surface area, pore volume and pore size were determined by N_2 adsorption at 77 K, using ASAP 2010 analyzer produced by Micromeritics (Norcross, GA). Before adsorption, samples were degassed at 150°C in vacuum for 3 h. The crystallographic parameter d_{002} was measured by using a Siemens X-ray Diffractometer with Cu Kα radiation. The 2θ scan rate was 0.02° per second.

3. Results and discussion

Table 1 gives the surface composition from ESCA, surface pore information from BJH (Samples 1–6) and from BET (Sample 7) and the interplanar spacing d_{002} (with a low value reflecting a high degree of graphitiza-

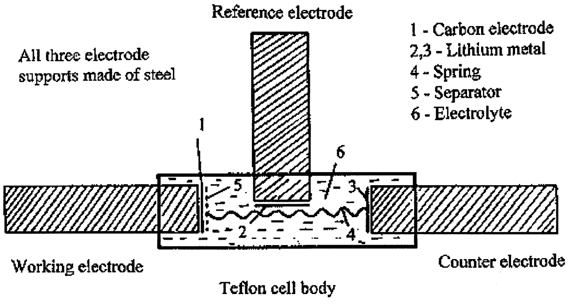

Fig. 1. Charge–discharge test cell configuration.

Table 1
Properties of carbons studied

Sample No.	$(C–H)_n$ [a] (at.%)	C–O [b] (at.%)	C=O [c] (at.%)	Surface area (m^2/g)	Pore size (Å)	Pore volume (cm^3/g)	d_{002} (Å)	L_c (Å)
1	95.5	4.5	0	50.5	81.9	0.10	3.37	89.2
2	96.0	4.0	0	57.1	81.9	0.12	3.37	89.2
3	82.7	13.6	3.7	533	52.6	0.58	3.42	50.7
4	83.1	14.1	2.8	220	55.2	0.26	3.40	63.4
5	89.3	8.8	1.9	226	55.2	0.26	3.41	60.1
6 [d]	81.7	13.0	1.7	221	55.2	0.26	3.40	59.2
7	86.2	3.0	0.8	88.2	19.3	0.05	3.49	112.3

[a] $(–C–H–)_n$: C–C; C–H; C_{1s} occurs at 285.0 eV.

[b] C–O: C_{1s} occurs at 286.2 eV.

[c] C=O: C_{1s} occurs at 288.0 eV for –C=O and 289.8 eV for –COOH, –COOR.

[d] Surface nitrogen content=3.6 at.%.

tion) from XRD. Fig. 2 gives the charge (deintercalation) and discharge (intercalation) characteristics. Among Samples 1 to 6, carbon filaments without any treatment (Sample 1) exhibited the lowest discharge capacity (E in Fig. 2). Acetone cleansing (Sample 2) helped. Activation (Samples 3–6) helped even more. Samples 1 and 2 (without activation) showed a smoother surface (low specific surface area and absence of C=O surface functional groups) and higher crystallographic order (low d_{002}) than the four activated samples (Samples 3–6). The porous structure obtained after activation allows easy penetration of the electrolyte, thereby enhancing the capacity. A less ordered structure after activation may help in a similar manner.

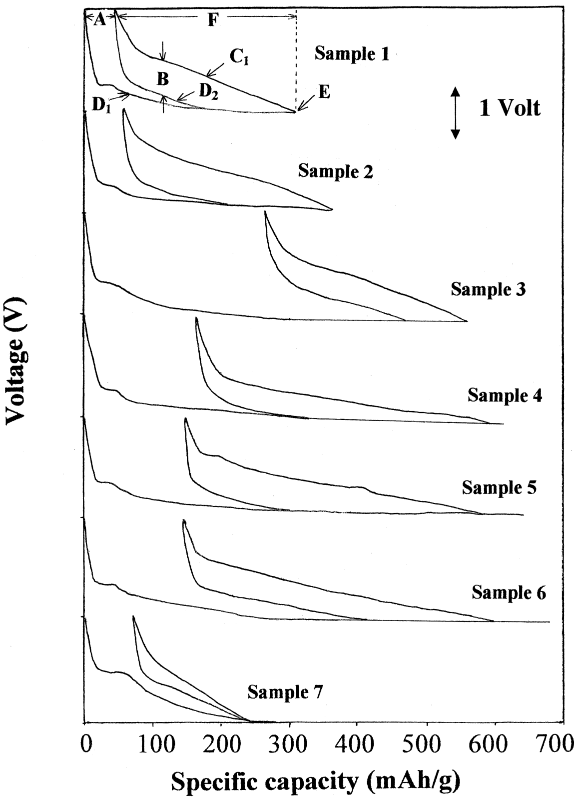

Fig. 2. Voltage profiles of each of Samples 1–7. The voltage ranges from 0 to 2 V for each panel. A: irreversible capacity; B: hysteresis; C: 1st charge (deintercalation) curve; D_1: 1st discharge (intercalation) curve; D_2: 2nd discharge curve; E: 1st discharge capacity; F: reversible capacity.

That the capacity of Sample 2 was higher than that of Sample 1 is because of the formation of tar oil on the surface during the filament growth [6], the tendency of the tar oil on the carbon to protect the surface of the carbon from the electrolyte, and the removal of the tar oil by acetone [6].

All the activated carbons (Samples 3–6) exhibited relatively large irreversible capacities (A in Fig. 2). Although a high surface area increases the contact area between carbon and the electrolyte, it also increases the amount of the oxygen-containing surface functional groups. A large amount of oxygen-containing surface functional groups (Table 1) is one of the causes for an increased irreversible capacity, because of the reaction of lithium with these surface functional groups. The main reason for the irreversible capacity for Samples 1 and 2 (with relatively little oxygen-containing surface functional groups) is the reaction of lithium with the electrolyte to form a passivation layer [7]. This layer is electrically insulating, permeable to Li ions but impermeable to the other electrolyte components. However, the hysteresis (B in Fig. 2) was decreased after activation, as shown by comparing Samples 1–2 with Samples 3–6 (Fig. 2). This is believed to be related to a lower hydrogen content after activation [8].

After reduction in H_2 (Sample 5), the charge and discharge capacities were increased, as shown by comparing the results of Samples 4 and 5. This suggests that a carbon with the same specific surface area and the same porous structure, but lower amount of oxygen containing functional groups, shows higher capacities. Moreover, reduction in H_2 caused the irreversible capacity to decrease. The mesoporous surface structure and decreased amount of oxygen-containing surface functional groups may be responsible for the lower irreversible capacity. The C–O and C=O functional groups may not be stable in the electrolyte.

The plateaux at around 0.5 V on the first discharge curves (D_1 in Fig. 2) for Samples 1–6 are characteristic of passivation layer formation, as in the case of soft carbons [9,10]. The passivation layer is one of the causes of the high irreversible capacity [4,9]. The first charge characteristics (C_1 in Fig. 2) of Samples 1–6 are such that the charge potential increased monotonicly and showed a step at around 1.0 V for each sample. Only Sample 5 (reduction in H_2) showed a plateau at around 0.5 V, as in the first discharge, possibly due to the presence of hydrogen on the surface enabling further reaction between lithium and the electrolyte.

After nitridation (Sample 6), the charge and discharge capacities were increased, as shown by comparing the results of Samples 4 and 6. Furthermore, nitridation caused the irreversible capacity to decrease. Hence, surface nitrogen (Table 1) was beneficial. Comparison of the results of Samples 5 and 6 shows that nitridation was slightly more effective than reduction in H_2, as it gave slightly higher capacities and slightly lower irreversible capacity.

Both irreversible capacity and hysteresis were decreased by nitridation, as shown by comparing the results of Samples 4 and 6 in Fig. 2. This is probably because oxygen and hydrogen were removed in the form of H_2O during nitridation [11]. The chemical composition and structure of nitrogen in the material have not been determined, but they may be responsible for the increased capacity during first discharge.

Pitch-based carbon (Sample 7) showed very low charge and discharge capacities (Fig. 2). Its lower structural order (high d_{002}) compared to the carbon filaments may be mainly responsible for this.

4. Conclusion

After activation and then either nitridation or reduction in H_2, vapor-derived carbon filaments show high reversible charge and discharge capacities. An ordered structure and a large pore size are favorable for a high capacity, as shown by comparison of vapor-derived and pitch-derived carbons. The combination of a high surface area and a large amount of oxygen-containing surface functional groups, as in the case of Samples 3 and 4, results in a high irreversible capacity. To improve the anode performance, it is important to control the surface microstructure by decreasing the surface oxygen content by nitridation or reduction in H_2, while maintaining order in the crystallographic structure.

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