ANODIC PERFORMANCE OF MODIFIED SUBMICRON CARBON FILAMENTS IN LITHIUM-ION SECONDARY BATTERY

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Introduction

The lithium-ion rechargeable battery, utilizes a carbon anode, a Li_xMnO_4, Li_xCoO_4, Li_xClO_4 or Li metal cathode and an organic electrolyte [1,2]. Despite great progress, improvement is needed in terms of the capacity, stability and voltage profile. For this purpose, most attention is focused on the anode. The carbon anode materials can be classified into three groups: graphite, hard (non-graphitizable) carbon and soft (graphitizable) carbon. The specific capacity of soft carbon which has been heat treated is about 2-3 times higher than the theoretical capacity of graphite, 372 mAh/g [3]. However, the reasons are still not well understood.

In this study, catalytically-grown submicron surface-modified carbon filaments and pitch-based carbon were used as the anode. The anode performance of the carbon electrodes was investigated in relation to the structural factors, surface area and functional groups.

Experimental Methods

Carbon filaments of diameter ~ 0.1 μm were provided by Applied Sciences Inc. (Cedarville, Ohio). Sample 1 was as-received carbon filaments. Sample 2 had been cleaned by acetone. Samples 3 and 4 had been activated as in Ref. 4 (heating in N_2 to 970°C at 3°/min, then activation by 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 after reduction in H_2 at 800°C. Sample 6 was naphthalene-mesophase-based pitch (not fiber) which had been treated 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 consists 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 to 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 $LiPF_6$/EC and DMC (1:1 by volume, 1 M), where EC stands for ethylene carbonate and DMC stands for dimethyl carbonate. 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 under a constant current (0.2 mA/cm^2 at a potential range of 0-2 V). ESCA, BET specific surface area measurement and x-ray diffraction (XRD) were also performed for structural analysis.

Results and Discussion

Table 1 gives the surface composition from ESCA, surface pore information from BET and the interplanar spacing d_{002} from XRD. Table 2 gives the charge/discharge capacities. Among Samples 1 to 5, carbon filaments without any treatment (Sample 1) exhibited the lowest charge and discharge capacities. Acetone cleaning (Sample 2) helped. Activation (Samples 3-5) helped even more. Samples 1 and 2 (without activation) showed a smoother surface (low BET specific surface area and absence of C=O surface functional groups) and higher crystallographic order (low d_{002}) than the three activated samples (Samples 3-5). 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.

That the capacity of Sample 1 was higher than that of Sample 2 is because of the formation of tar oil on the surface during the filament growth [5] and the tendency of the tar oil on the carbon to protect the surface of the carbon from the electrolyte.

All the activated carbons (Samples 3-5) exhibited relatively large irreversible capacities. 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 is one of the causes for an increased irreversible capacity, because these

Table 1 Properties of carbon anodes

Sample No.	C-H (at. %)	C-O (at. %)	C=O (at. %)	Surface area (m^2/g)	Pore size (Å)	Pore volume (cm^3/g)	d_{002} (Å)
1	95.5	4.5	0	50.5	81.9	0.10	3.37
2	96.0	4.0	0	57.1	81.9	0.12	3.37
3	82.7	13.6	3.7	533	52.6	0.58	3.42
4	83.1	14.1	2.8	220	55.2	0.26	3.40
5	89.3	8.8	1.9	226	55.2	0.26	3.41
6	86.2	3.0	0.8	88.2	19.3	0.05	3.49

Table 2 Charge/discharge capacities at constant current

Sample No.	1st cycle capacities (mAh/g)			2nd cycle capacities (mAh/g)		
	Charge	Discharge	Irreversible	Charge	Discharge	Irreversible
1	315	165	150	245	103	142
2	374	220	154	336	179	157
3	521	254	378	397	216	209
4	617	294	323	439	274	165
5	656	405	251	488	368	120
6	298	154	144	212	111	101

surface functional groups lead to the formation of a passivation layer during charging and discharging. This layer is electrically insulating, permeable to Li ions but impermeable to the other electrolyte components.

The second cycle results show that the reproducible charge capacities of the activated carbon (Samples 3-5) were around 450 mAh/g – larger than 372 mAh/g, the theoretical capacity of graphite (LiC_6). This means that x of LiC_x in this case is smaller than 6, which is similar to the behavior of soft carbon [6].

After reduction in H_2 (Sample 5), the charge and discharge capacities were increased. 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.

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

Conclusion

After activation and then reduction in H_2, catalytically grown submicron 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 between filaments and pitch. 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 increasing the pore size and decreasing the surface oxygen content, while maintaining order in the crystallographic structure.

References

1. Young-Min Choi, Su-Il Pyun and Jens Martin Paulsen, Electrochimica 44, 623-632 (1998).
2. D.H. Jang and S.M. Oh, Electrochemica 43, 1023-1029 (1998).
3. K. Sato, M. Noguchi, A. Demachi, N. Oki and M. Endo, Science 264, 556-558 (1994).
4. W. Lu and D.D.L. Chung, Carbon 35(30), 427-430 (1997).
5. X. Shui, C.A. Fryz and D.D.L. Chung, Carbon 33(12), 1681-1698 (1995).
6. G. Pistoria, Lithium Batteries, Elsevier, The Netherlands, 1994.