CHARGE/DISCHARGE CHARACTERISTICS OF MESO-CARBON MICROBEADS PREPARED FROM SYNTHETIC ISOTROPIC PITCH

Yong-gang Wang, Cha-hun Ku, S. Ishida, Y. Korai, and I. Mochida
Institute of Advanced Material Study, Kyushu University
Kasuga, Fukuoka 816, Japan

Introduction

Rechargeable lithium ion battery has been recognized as an important power source for electric vehicles because of its high energy density and safety. As anode materials, high specific capacity carbons have the promising application[1,2]. Among them, meso-carbon microbeads (MCMB) produced from coal tar pitch and petroleum pitch showed the high Faradaic capacity and long cycling life when they were heat-treated at low temperature. The present authors have prepared the homogenous size of MCMB from the synthetic isotropic naphthalene pitch in the absence and presence of carbon blacks[3]. In this study, the charge/discharge performances of these MCMBs were examined which were heat-treated at 600-800 °C to clarify the influences of carbonization temperature, stabilization and carbon blacks on the anodic performances.

Experimental

MCMBs used in this study were prepared from the synthetic isotropic naphthalene pitch which was heat-treated at 420 °C for 1 or 1.5 h in the presence of carbon blacks. Table 1 summarized the preparation conditions and some properties of MCMBs. MCMBs obtained by extracting the heat-treated pitch with pyridine and stabilized MCMBs at 230-300 °C for 1 h in the air flow were carbonized at 600 to 800°C for 1 h with a heating rate of 3 °C/min in the flow of argon.

Electrochemical measurements of MCMBs were made in a half cell by the constant current of 0.2 mA/cm^2 and cut-off voltage of 0 and 2 V. Lithium metal electrodes were used as counter and reference electrodes in 1 M $LiPF_6$-EC/DMC (1:1)solution. MCMB of ca.10 mg was mixed with PTFE binder for electrode preparation.

Results

Charge/discharge performance of MCMB Table 2 summarized the charge/discharge capacities of carbonized MCMB under the constant current of 0.2 mA/cm^2. The charge capacities of MCMB-HTT700 °C in the first cycle were between 640 and 710 mAh/g. Among them, MCMB prepared with 1 wt% BP2000 exhibited the highest capacity of 706 mAh/g. As the carbonization temperature increased from 600 to 800 °C, the charge capacities of MCMB with 3 wt% BP2000 decreased from 894 to 449 mAh/g.

The discharge capacities of MCMB-HTT 700 °C in the first cycle were between 320 to 420 mAh/g. The MCMB-HTT 700 °C prepared with 1 wt% BP2000 exhibited the best discharge capacity of 422 mAh/g. As the carbonization temperature increased from 600 to 800 °C, MCMB with 3 wt% BP2000 decreased the discharge capacity from 433 to 268 mAh/g. KB addition gave the slightly different charge/discharge capacities from MCMB with BP2000.

Table 3 listed the discharge capacities of carbonized MCMB under a short-circuit. The high discharge capacity of 786 mAh/g was obtained by the MCMB-HTT 700 °C with 1 wt % BP2000.

Effect of stabilization As shown in Table 4 , the stabilized MCMBs prepared with 3 wt% KB gave the different charge/discharge capacities than that without stabilization. As the stabilization temperature increased from 230 to 300 °C, the charge capacity increased from 726 to 755 mAh/g and the discharge capacity increased from 348 to 391 mAh/g, respectively, and its discharge capacity under short-current reached the 611 mAh/g at the stabilized temperature of 300 °C.

Irreversible capacity of MCMB in the first charging process Figure 1 showed the voltage changes of MCMB-HTT 700 °C in charge/discharge examination. Figure 2 showed the variation in discharge capacities of MCMBs with the cycle number. The irreversible capacity was estimated by the difference between the charging and the discharging capacity in the first cycle. The irreversible capacities of MCMBs-HTT 700 °C were about 310 mAh/g(table 2) and stabilized MCMB-HTT 700 °C gave the different value of irreversible capacities(table 4). From Fig.2, MCMB carbonized at 700 °C exhibited the good discharge cyclability.

Discussion

It was found that MCMB prepared from the synthetic naphthalene isotropic pitch exhibited the high charge/ discharge capacities. Especially, the discharge capacity of 786 mAh/g was obtained at short-circuit by the MCMB-HTT700°C with 1 wt % BP2000. The morphology and composition of MCMB were expected to have the influences on anode performance. BP2000 may decrease the microdomains of the sphere and enhanced the doping capacity of lithium ion, and the further work is needed to optimize the BP2000 amount.

Oxidative stabilization made the sphere infusible to inhibit their expansion when they are carbonized. The

higher stabilized temperature in the range of 230-300 °C changed the microdomains of MCMB and provided the carbons with easier chemical interaction of lithium ions although it is not clear about the mechanism yet.

Reference

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Table 1 Some properties of MCMB prepared from the synthetic pitch

code	Heat-treatment		Carbon black (wt%)	Diameter (μm)	H/C
	Temp.(°C)	Time(h)			
No.1	420	1	BP2000-1	1-4	0.55
No.2	420	1.5	BP2000-3	1-3	0.50
No.3	420	1	KB-1	1-5	0.55
No.4	420	1.5	KB-3	1-3	0.47

Table 2 Charge/discharge capacities of MCMB under a constant current

Sample	Heating temp. (°C)	Charge/discharge capacity (mAh/g)	Irreversible capacity (mAh/g)
No.1	700	706/422	284
No.2	700	637/324	313
No.3	700	645/334	311
No.4	700	680/368	312
No.2	600	894/433	461
No.2	800	449/268	181

Table 3 Discharge capacities of MCMB under the short-current of 0.25 mA until 0 v and 40 h at 0 v.

Sample	Heating temp. (°C)	Discharge capacity (mAh/g)
No.1	700	786
No.2	700	769
No.3	700	662
No.4	700	666

Table 4 Charge/discharge capacities of stabilized MCMB

Sample	Stabilized temp. (°C)	Heating temp.(°C)	Charge/discharge capacity (mAh/g)	Irreversible capacity (mAh/g)
No.4	230	700	726/348	461
No.4	270	700	698/353	345
No.4	300	700	755/391	181

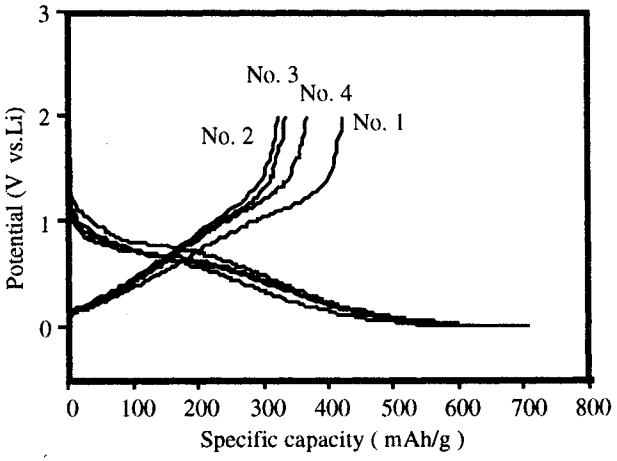

Fig.1 Charge/dischar ge characteristics of MCMB prepared from the synthetic naphthalene pitch (700 °C, 1 h)

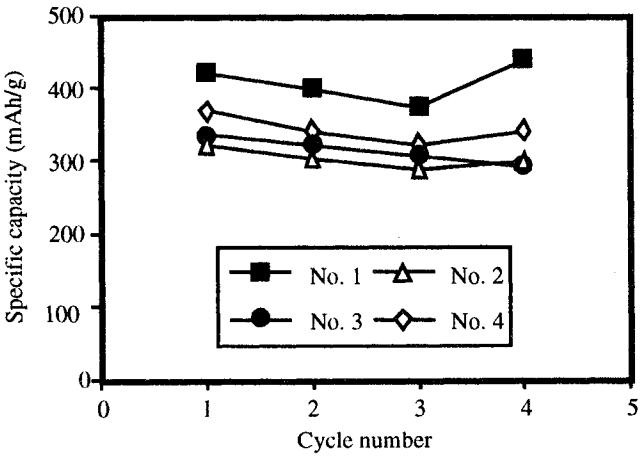

Fig.2 Variation in discharge capacities with cycle number (700 °C,1 h)