ANODIC PERFORMANCE OF SOME KINDS OF BIOMASS DERIVED CARBONS

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Abstract

In this study, four biomass derived carbon materials (bark (BC), rice husk (RC), Indonesia mangrove (IM) and Thailand mangrove (TM) charcoals) were evaluated as anodic materials for Li-ion batteries after optimistic heat treatment at 1000^{o}C. They showed excellent characteristics of hard carbons except for RC derived carbon. IM derived hard carbon showed the largest discharge capacity of 469mAh/g. Acid or alkali treatment before carbonization of IM charcoal increased the discharge capacity to 350mAh/g (to 0.5V) and 500mAh/g (to 2V).

Introduction

The cheap production of hard carbon with high discharge amount is most intensively studied for the application of Li ion battery to electric car (EV) and hybrid electric car (HEV). Volumetric abundance of cheap cost of wood bio sources are most charming raw materials for developing the cheap anodic carbons for Li-ion batteries. Several anodic carbons from the relatively cheap sources have been reported such as anthracite (Kim, 2003), sugar, rice husk, peanut shells (Fey, 2003), lignin, cotton and wool, pitch (Mochida, 2001), resin (Zheng, 1995).

In this study, the present authors selected four biomass charcoals to investigate their anodic performances and determine the best conditions for obtaining the best performance of hard carbon.

Experimental

Four biomass charcoals(BC, RC, IM and TM; Kansai electric power corporation) were used in the present study, BC was from bark carbon, RC from rice husk carbon, IM from Indonesian mangrove charcoal, and TM from Thailand mangrove charcoal.

After grinding into less than the size of 45μm, these four biomass charcoals were carbonized at 1000℃ (heating rate: 10K/min) for 1h under Ar atmosphere, named as BC1000, RC1000, IM1000 and TM1000, respectively. IM was also heat treated at 700~1050oC (heating rate: 10K/min) for 1h for determining the optimal conditions. For further enhancement of discharge amount, IM was immersed in 30% HNO_3 solution or 1 mol NaOH solution for 20 hrs with stirring, followed by washing with de-ionized water to pH 7, and vacuum drying at 120℃ overnight. It was also carbonized at 1000℃ (heating rate: 10K/min) for 1h under Ar atmosphere, named as IM$HNO_3$10 and IMNaOH10, respectively.

Test electrode was fabricated by spreading a slurry mixture of active material (90 wt.%) and PVdF (polyvinylidene fluoride, 10 wt.%), which were dissolved in NMP(1-methyl-2-pyrrolidone) solution, onto the copper foil, and rolling it after drying under vacuum for 12 hrs at 120oC. Two-electrode coin type cell was assembled by using lithium foil as the counter electrode with 1M $LiPF_6$ in EC/DEC(1:1, v/v) and polyethylene separator. The cell assembly was carried out in an argon-filled glove box.

Electrochemical evaluation was performed using TOSCAT-3000U battery testing unit (TOYO SYSTEM CO. LTD., Japan). Test methods consisted of CC (constant current) and CC-CV (constant current and constant voltage). In charge, CC method was performed from OCV to 0V at 30mA/g and continuously CV method was at 0V until current decreased to 3mA/g. In discharge, CC method was performed at 30mA/g until 2V.

Results and Discussion

Analysis and charge/discharge performance of various biomass derived carbons

Elemental analysis data of various biomass derived carbons are summarized in Table 1. Apparently, BC, IM and TM showed high oxygen contents over 20%. In spite of high oxygen contents, IM and TM derived carbons showed relatively high contents over 90%. RC showed low carbon contents with large ashes of silicone element (Figure 1).

Figure 2 shows the first charge/discharge profiles of various biomass derived carbons which were carbonized at 1000℃ under Ar atmosphere for 1h. RC showed the largest charge capacity of 1014mAh/g while discharge capacity was only 444mAh/g, and mainly located at 0.3-1.2V, which mostly exhibited anodic characteristics of Si-contained materials. BC1000, IM1000 and TM1000 exhibit typical charge/discharge characteristics of hard carbon. IM1000 showed the largest capacity of 593 and 467mAh/g for charge and discharge amounts, respectively, and the coulombic efficiency of 74.7%.

Table 1. Elemental analysis of as-received and carbonized biomass carbon materials

Sample	Elemental analysis(wt%)				Atomic ratio	
	C	H	N	O	H/C	N/C
BC	75.29	2.47	1.07	14.42	0.394	0.012
RC	32.59	1.10	0.30	8.72	0.405	0.008
IM	70.56	3.63	0.38	23.71	0.617	0.005
TM	68.32	4.01	0.15	25.50	0.704	0.002
BC1000	84.15	0.48	1.13	6.31	0.068	0.012
RC1000	35.48	0.26	0.50	3.33	0.088	0.012
IM1000	91.51	0.45	1.13	4.01	0.059	0.011
TM1000	88.89	0.54	0.52	6.65	0.073	0.005

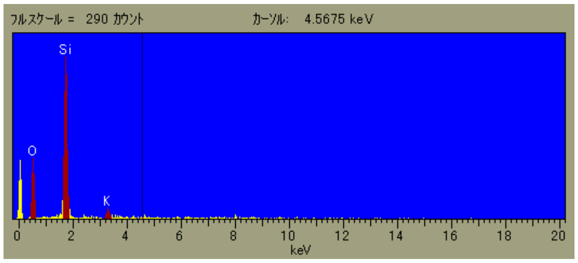

Figure 1. SEM-EDX of RC which was firstly oxidized under air.

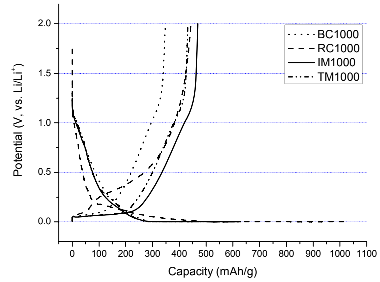

Figure 2. The first charge/discharge profiles of various biomass carbon materials carbonized at 1000℃.

Analysis and charge/discharge performances of IM series

Table 2 shows elemental analysis data of as-received and heat-treated IMs. With the increase of carbonization temperature, H and O content decreased while C and N content increased correspondly. For HNO_3 treated IMs, N and O contents increased largely but ash content decreased from 1.72% to 0.01%. after carbonization at 1000℃, IMNaOH10 obtained a highest C content of 96.13%.

Figure 3 shows STM photographs of IM1000. Small granular of 10 nm basic units arranged linearly can be observed, which may induced from the nano-fibrils in wood biomass.

Figure 4 shows the charge/discharge profiles of IM which was carbonized at various temperatures under Ar atmosphere for 1h. IM700 exhibited the highest charge/discharge capacities of 783 and 527mAh/g, respectively, nevertheless, a majority of discharge capacity located at around 1.0V, which decreased with the increase of carbonization temperature accompanying with the prolong of plateau at around 0.1V. When the carbonization temperature increased to 1050℃, discharge plateau at around 1.0V completely disappeared, showing the discharge plateau of 258mAh/g at around 0.1V with increasing Coulombic efficiency to 80.7%.

Table 2. Elemental analysis of as-received and heat-treated IMs

Sample	Elemental analysis (wt%)				Atomic ratio	
	C	H	N	O	H/C	N/C
IM	70.56	3.63	0.38	23.71	0.617	0.005
$IMHNO_3$	59.08	2.41	4.6	33.90	0.490	0.067
IMNaOH	72.03	3.53	0.38	23.82	0.588	0.005
IM700	89.38	1.00	0.72	5.82	0.134	0.007
IM800	90.00	0.75	0.74	5.50	0.100	0.007
IM900	90.95	0.55	1.17	4.34	0.073	0.011
IM1000	91.51	0.45	1.13	4.01	0.059	0.011
$IMHNO_3 10$	94.04	0.4	3.37	2.08	0.051	0.031
IMNaOH10	96.13	0.43	1.36	1.65	0.054	0.012

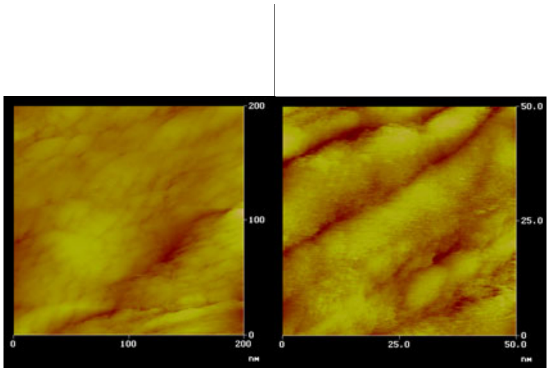

Figure 3. STM photos of IM1000.

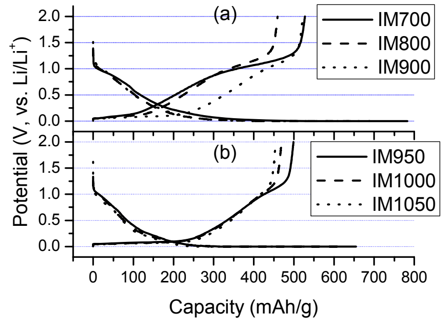

Figure 4. The first charge/discharge profiles of IM carbonized at different temperatures.

Figure 5 shows the first charge/discharge profiles of IM carbonized at 1000℃ under Ar atmosphere for 1h by different heating rates. The lower heating rate, the higher Coulombic efficiency.

Effect of different charge-discharge rate

Figure 6 illustrates the first charge/discharge profiles of IM carbonized at 1000℃ by different charge/discharge rate. When the testing current was 3mA/g, IM1000 showed the largest discharge capacity of 507mAh/g and a highest coulombic efficiency of 82.9%.

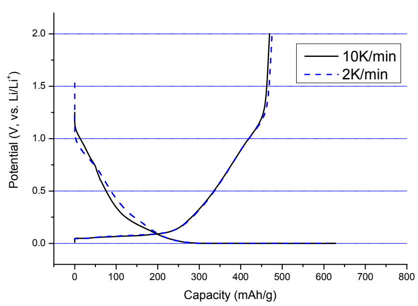

Figure 5. The first charge/discharge profiles of IM carbonized at 1000□ by different heating rates -10K/min and 2K/min.

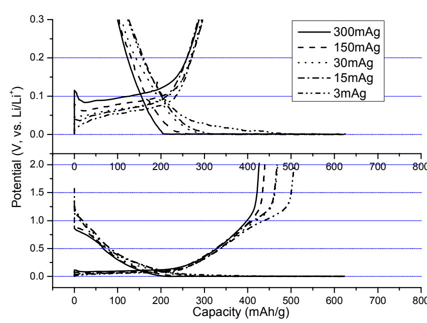

Figure 6. The first charge/discharge profile of IM carbonized at 1000℃ by different charge/ discharge rates(testing method: CC--- constant current method (300, 150, 30, 15, 3mAh/g), CV--- constant voltage method (at 0V until current decrease from 300, 150, 30,15, 3 to 0.3

Effect of acid and alkaline treatments

Figure 7 shows the first charge/discharge profiles of IM$HNO_3$10 and IMNaOH10. Discharge capacity of IM$HNO_3$10 and IMNaOH10 increased by 40 and 68mAh/g compared to non-treated IM1000, respectively. The Coulombic efficiency of IMNaOH10 also increased from 74.7% to 78.7%.

Figure 8 shows cyclic characteristics of IM1000, IM$HNO_3$10 and IMNaOH10. Apparently, IM1000 showed best cyclic performance which could hold the discharge amount above 90% of that of the 1st cycle, while IM$HNO_3$10 did the discharge capacity about 70% after 50 cycles.

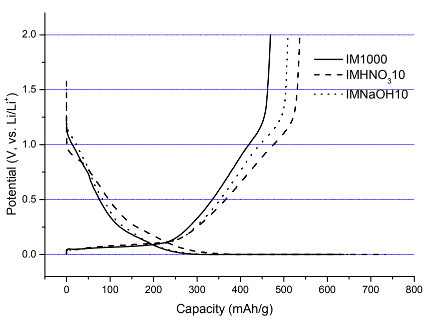

Figure 7. The first charge/discharge profiles of IM$HNO_3$10 and IMNaOH10.

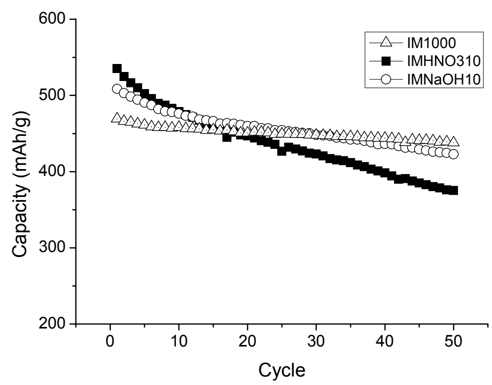

Figure 8. cyclic characteristics of IM1000, IM$HNO_3$10 and IMNaOH10.

Conclusion

(1) Among of four biomass derived carbons, IM1000 showed the largest discharge capacity of 467mAh/g, the highest coulombic efficiency of 74.7% and very good cycle ability.

(2) Under various carbonization conditions, IM carbonized at 1050℃ obtained a largest available capacity (under 0.5V) of 343mAh/g and a highest coulombic efficiency of 80.72%.

(3) HNO_3 and NaOH treatment can improve the discharge capacity of the 1st cycle.

Indonesian Mangrove charcoals should be a promising candidate for Li ion battery anode due to its low cost and abundance.

References

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