

SEM AND XRD STUDIES ON CARBON BASED ANODE MATERIAL

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ABSTRACT

Amorphous carbon derived from rice husk has been investigated as anode materials for lithium-ion battery. The electrode was prepared in pellet-shape using hand press. The sample was assembled in half-cell and cycled for charge-discharge using battery cycler system. The result showed initial higher capacity but reduced drastically upon further cycling test. SEM analysis showed that carbon particles agglomerated when the number of charge-discharge increased. XRD analysis indicated the deterioration of carbon structure occurred after cycling.

INTRODUCTION

Carbon material attracted great interest to be used as negative electrode over lithium metal in term of cycle performance and safety [1]. However, its capacity is limited up to 372 mAh/g. The effort to further improving capacity of anode materials with the cost effective factor is essential. Several series of amorphous carbon used as anodes have been prepared by pyrolysis of natural or agricultural precursors [2-4]. The capacity of these materials is dependent on the pyrolysis condition and precursor sources. In this study, carbon was produced from rice husk, which was regarded as agricultural waste and environmental hazard. The major content of rice husk are cellulose, which yield carbon when pyrolyzed under inert condition, and then followed by silica. Silicon-doped hard carbons were reported to improve cell capacity and cycle behaviour. [4].

EXPERIMENTAL DETAILS

Material synthesis and sample preparation

Rice husk (RH) obtained from a rice mill at Penaga, Penang, was thoroughly washed with water to remove dust and dried in an oven. The dried husk was treated with acid and base before it was washed with distilled water to a pH of 7. Then, the treated husk was heated in a tube furnace LT TF70-1200 at varied temperature of 700°C, 800°C, 900°C, 1000°C with a heating rate of 5° C/min. for 1 hour in an argon atmosphere. The black residues obtained were ground into powders by mortar and pestle. As a comparison, some residues were milled by planetary miller for 5 hours.

The powders were analysed using BRUKER D8 Advance X-ray diffractometer with the Cu-K α radiation and LEO 1525 FE-SEM. Carbon electrode was fabricated by mixing the carbon powder with acetylene black and PTFE, and then pasted on a steel mesh. The electrode was dried in an oven overnight at 100°C. Carbon content were analysed using FISON CHNS-O Elemental Analyser Model EA 1108.

Electrochemical performance XRD and SEM analysis

A teflon cell was used to assemble the carbon electrode with a lithium foil as the counter electrode in an argon filled glove box. The electrolyte used in this work was 1M LiPF₆ in EC:DMC (1:1). The charge/discharge test was performed using a Solartron 1470 Battery Testing System, at a constant charge and discharge current of 0.5mA with a voltage range of 0.05V – 3.0V. XRD and SEM analysis were carried out after 4 and 8 cycles of charge-discharge tests.

RESULTS AND DISCUSSION

The charge-discharge profile of RH, which was heated at 700°C, carbon electrode is shown in Figure 1. The discharge and charge capacity of the first cycle were observed at 1029 mAh/g and 356 mAh/g, respectively. These capacities were reduced to 420 and 330 mAh/g, respectively upon the second cycle, and further reduced upon the following cycle.

The sample shows higher discharge capacity at the first cycle, however the reversible capacity is only 34%. Initial irreversible losses are probably due to the formation of SEI layer. An improved coulombic efficiency is observed for the second (78%) and third cycle (85%).

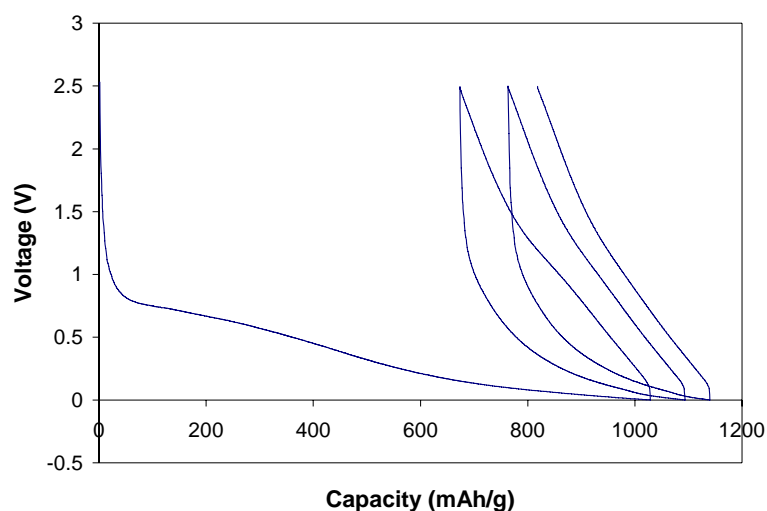
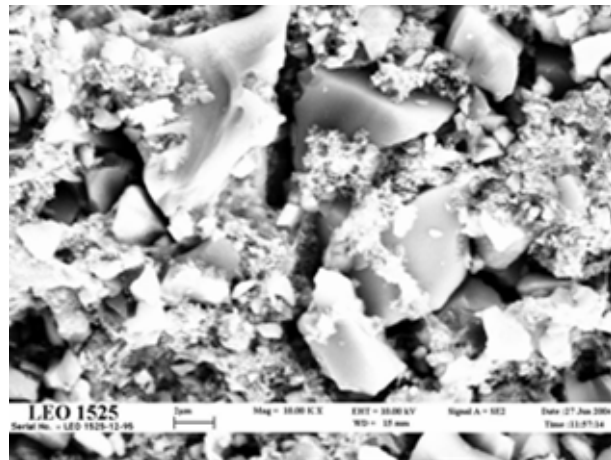
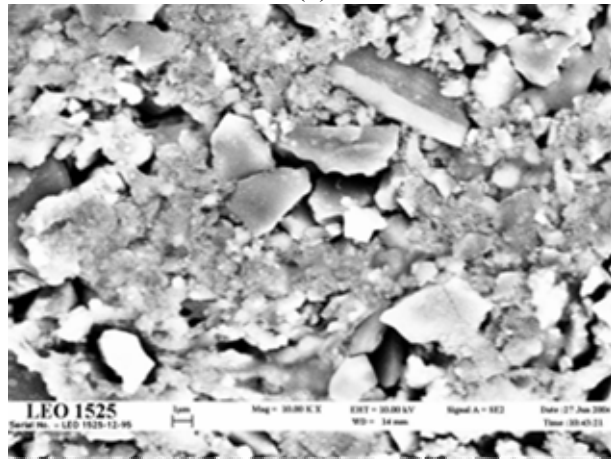


Figure 1: Charge-discharge curves of RH carbon electrode.

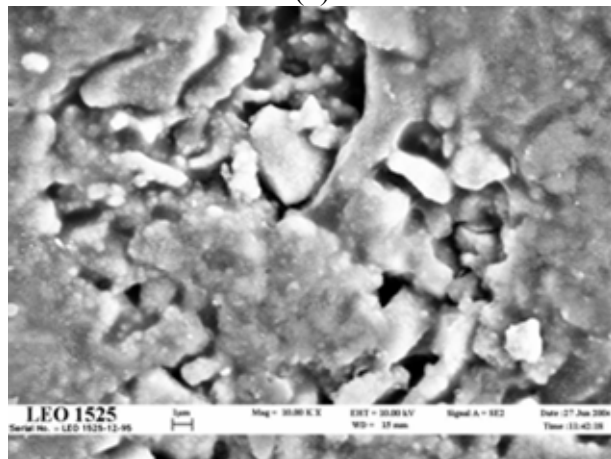
Higuchi et al reported that when discharge capacity increased, the cycle characteristics deteriorated [5]. An initial capacity cut-off was applied to minimize the deterioration of capacity in carbon anode. SEM micrograph of RH carbon electrode in Figure 2 shows the changes of carbon particles before and after charge-discharge test.



(a)



(b)



(c)

Figure 2: SEM micrograph of Rice Husk carbon electrode a) before charge-discharge, b) after 4 cycle of charge-discharge and c) after 8 cycle of charge-discharge

These figures indicate that the particles form agglomerates which is a form of defect resulted from the charge-discharge process. According to Yu-Ping Wu et al, the unstable defect structure breaks the C-C bond [6] that eventually causes the carbon structure to collapse. This has resulted in a formation of small particles. The micrographs showed evidence that the size of carbon particles become smaller with the increased cycle number of charge-discharge.

Figure 3 shows X-ray diffraction curve of RH carbon electrode before and after charge-discharge test. The figure indicated that the structure of carbon collapse after charge-discharge. Prolong the charge-discharge cycle, caused carbon content reduced. The XRD results also indicated the deterioration of carbon structure occurred after cycling.

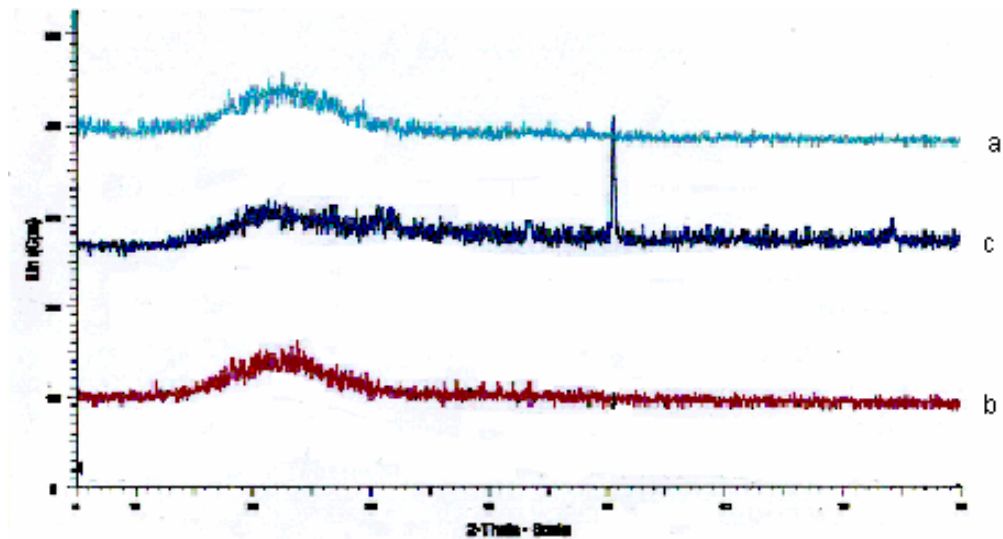


Figure 3: X-Ray Diffraction Curve of RH carbon electrode a) before charge-discharge, b) after 4 cycle of charge-discharge and c) after 8 cycle of charge-discharge

Meanwhile, varied heat treatment temperature has affected RH carbon structure as shown in Figure 4.

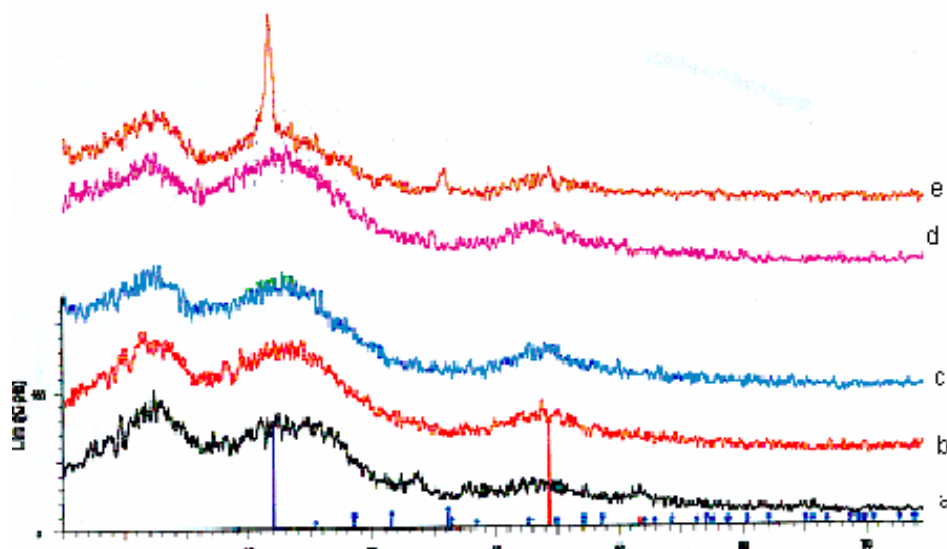


Figure 4: X-Ray Diffraction Curve of Rice husk carbon at Heat Treatment Temperature of a) 700°C, b) 800°C, c) 800°C (milled) d) 900°C e) 1000°C.

XRD graph shows those carbon peaks were observed in all of the RH carbon at 2θ of 23° and 44° . However RH which is pyrolysed at 1000°C shows peak of Silica (SiO_2) at 22° and 36° . Meanwhile milling process of RH (c) in planetary miller did not show any significant compared without milling (b). From XRD result, RH pyrolysis at 1000°C increased silica (SiO_2) content in pyrolysed RH powder.

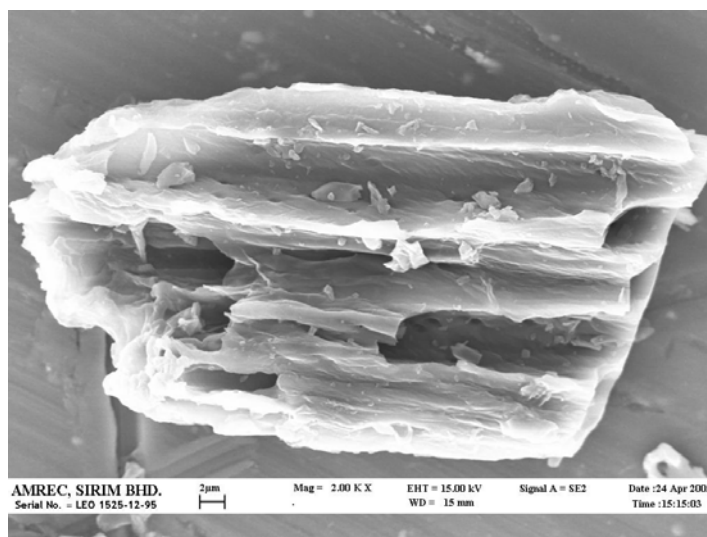
The content of carbon and silica in RH residue were confirmed by CHNS-O analyzer and gravimetric method. The charge and discharge capacities of RH electrode which were effected by carbon and silica content are tabulated in Table 1.

Table 1: Charge-discharge capacity of RH carbon electrode

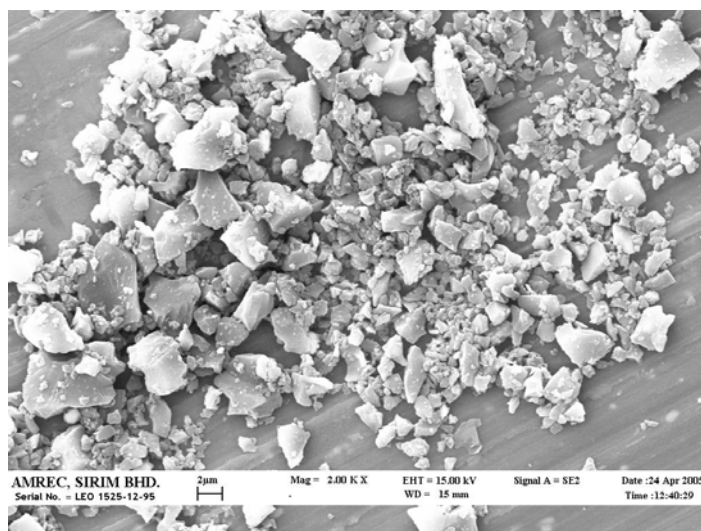
Sample	Pyrolysis Temperature/T°C	Capacity/mAh/g		Efficiency (%)	2 nd cycle discharge capacity/mAh/g	Carbon content (%)	Silica Content (%)
		1 st cycle discharge	1 st cycle charge				
RH1	700	658	148	22	199	81%)	-
RH2	800	633	146	23	254	79%)	0.2
RH3	900	622	172.9	26	265	76%	0.8
RH3 milled	900	633	157	25	208	78	-
RH4	1000	634	199	31	242	68	8.5

The table shows that carbon content are reduced while silica content increased with the increase of pyrolysis temperature. Capacity of the cell were also effected by carbon content as it decreases when carbon content decreased. However the reversible capacity or efficiency of the cell increased when carbon content decreased.

The table also shows that capacity of RH3 increased after milling process, which reduces carbon particle size from about 30 to average 6 μm as shown by SEM analysis in Figure 5.



(a)



(b)

Figure 5: SEM micrograph of RH3 carbon electrode a) before and b) after milling process

CONCLUSION

The initial irreversible capacity was due to the formation of the SEI layer. The following reversible capacity fades with increased cycle numbers due to the damaged carbon structure. Repeated lithium reaction with carbon electrode caused defect in the carbon structure that leads to the collapse of the C-C bond. Capacity of the cell also was effected by carbon content and its size.

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