Hard Carbon/SiO_x Composite Active Material Prepared from Phenolic Resin and Rice Husk for Li-ion Battery Negative Electrode

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The composite negative electrode active material of Li-ion batteries (LIBs) was fabricated using phenolic resin (PR) and agricultural waste of rice husk (RH). Because silicates were intrinsically composed in RH, the composite of hard carbon (HC) and SiO_x (HC/SiO_x composite) was readily prepared by carbonizing the mixture of PR and RH. Li-ion insertion and extraction capacity of the HC/SiO_x composite was evaluated in a half-cell configuration using Li metal as the counter electrode, in comparison with those of the carbonized RH and the commercial HC. It was revealed the HC/SiO_x composite exhibited 30% higher specific capacity of Li-ion insertion/extraction than did the commercial HC. In addition to this, its capacity retention was found to be approximately equal to that of the commercial HC. The performance comparison of the HC/SiO_x composite and the carbonized RH suggested that hybridization of HC and SiO_x was useful to alleviate the capacity fading of the SiO_x part with maintaining the increased specific capacity attributed to the SiO_x part. Cost-effective active material for the LIB negative electrode with acceptable performances could be realized by the simple carbonization of the mixture of PR and RH. The produced HC/SiO_x composite was promising for vehicle applications requiring excellent cycle performance and high cost effectiveness.

Keywords : Lithium-ion battery, negative electrode, anode, hard carbon, SiO_x, rice husk

1 INTRODUCTION

Li-ion batteries (LIBs) possessing high energy-storage density have been utilized for rechargeable power sources of electric vehicles and plug-in hybrid electric vehicles. Most of the negative electrode (NE, the term “anode” can be alternatively used in LIB studies) active materials in LIBs are carbonaceous materials such as graphite and hard carbon (HC). HC which is composed of amorphous structure can display long charge-discharge lifetime [1], indicating that HC is promising for the above vehicle applications.

HCs can be fabricated from various carbon sources such as petroleum pitch, biomass resources, and resins. HCs prepared from phenolic resins (PRs) have been explored for the use of LIB NEs because of high carbonization yield (>50 mass%) and lower production cost [2]. In recent years, Si/C nano-composite NEs in which PRs were utilized as carbon sources have been gathering attention to increase the specific capacity of LIB NEs [3, 4].

The theoretical Li-ion insertion capacity for Si in a form of Li₂₂Si₅ is 4200 mAh/g, which is about ten-times higher than those of HCs [5]. However, it is well known that Si suffers from huge volume expansion (>300%) upon Li-ion uptake and extraction, incurring fracturing and exfoliation of Si particles [6]. Hence, the Si-based NEs tend to allow a rapid capacity fading and poor cycle performance. To alleviate the volume expansion, silicon monoxide (SiO) and silicon dioxide (SiO₂) can be alternatively used in place of Si [7]. Si reduced from silicon oxides has been known to have sufficient functionality to accept the cycles of Li-ion uptake

and release. LiO₂ and Li₄SiO₄ formed as byproducts of Li-ion-induced reduction of silicon oxides can play a role as the buffer of alleviating the Si volume expansion [8].

Rice is a silicicolous plant which can adsorb silicate ions from paddy. Silicates adsorbed for the rice growth are accumulated in its husk in a form of amorphous silicon oxides with silanol (Si-OH) groups. A composite of lingocellulose and nano or micro-scale silicon oxides (about 20 mass%) is naturally composed in rice husk (RH) [9]. This characteristic material feature of RH is suitable for creating the nano-composite structure of carbon/silicon oxides (C/SiO_x) with simple carbonization process [10]. *x* in SiO_x means that the valence of Si is not determinable, but in the range of 0-2, because it is naturally-occurring compound and it takes amorphous structure when RH was carbonized under about 1200°C [11].

Li-ion insertion/extraction properties of nano-Si reduced from SiO_x which was prepared from calcination of RH have been evaluated, exhibiting very high specific capacity of 2500 mAh/g [12]. However, a preparation of nano-Si particles and a fabrication of nano-scale Si/C composite structure are time-consuming and expensive. High surface area C/SiO₂ composites were fabricated by chemically activating RH using ZnCl₂ at 500-650°C [13]. Although activation agent and the involved processes were required, and very high initial irreversible capacity (<50% coulombic efficiency) was observed, high specific capacity of >800 mAh/g was attained within 360 cycles at the current density of 100 mA/g.

The present study aims at realizing more cost-effective active materials for LIB NEs with acceptable rate and cycle

performances. Thus, biomass resource of RH and an inexpensive plastic of PR were employed as the source materials. Then, Li-ion insertion/extraction property of the HC/SiO_x composite prepared by carbonizing the mixture of PR and raw RH was evaluated in comparison with those of carbonized RH and commercial HC, which is a first-time challenge in the field of LIB studies. Finally, feasibilities and perspective of the HC/SiO_x as the active material of LIB NE were discussed based on the results of rate and cycle performances.

2 EXPERIMENTAL SECTIONS

2.1 Fabrication of Active Materials

RH was collected in Akita Prefecture, Japan and dried at 100°C for > 5 h. RH was carbonized at 1000°C in nitrogen gas flow (500 mL/min) for 1 h. The mixture of the above RH and a PR (PR-50731, Novolak type, Sumitomo Bakelite Co., Ltd.) in a similar mass (50: 50 in mass) was also carbonized at 1000 °C in nitrogen gas flow (500 mL/min), providing the HC/SiO_x composite. The carbonized samples were pulverized using a planetary ball mill. The pulverized samples and the commercial PR resin-based HC (LBV-1001, Sumitomo Bakelite Co., Ltd., Japan) were tested as the active materials of LIB NEs. Pore properties of active materials were evaluated based on the nitrogen gas adsorption-desorption isotherms at -196°C using a gas adsorption analyzer (Autosorb-3B, Quantachrome Instruments, USA). The SiO_x contents of the active materials were evaluated by burning out them in air. Thermogravimetry system (Thermo plus EVO TG8120, Rigaku Corp., Japan) was used for heating the active material up to 850°C in air flow (500 mL/min). The SiO_x content was determined by the residual ratio of the burnout. Pore properties and SiO_x contents of the active materials are shown in Table 1.

2.2 Electrode Preparation

A slurry was prepared by mixing the active material (90 mass%), acetylene black as a conductive agent (5 mass%, Denka Co., Ltd., Japan), polyacrylic acid binder (5 mass%, Aquacharge, Sumitomo Seika Chemicals Co., Ltd., Japan) with a suitable amount of distilled water to provide appropriate coating. The slurry was coated on a Cu foil current collector (t20 µm) by using an applicator. The copper foil coated with the active material was dried in an oven controlled at 100°C for >8 h. Then, it was pressed with a pressure of 2 MPa using a press machine for 1 min and punched out into a circle electrode (φ15 mm). Three-types of electrodes coated with active materials of HC/SiO_x composite, carbonized RH and commercial HC were degassed at 140°C for >4 h. Details of the prepared electrodes are shown in Table 2.

2.3 Cell Assembly and Performance Evaluation

The prepared electrode, a polypropylene-based separator (2500, Celgard LLC., USA, t25 µm), a Li metal disk (φ15 mm, t0.2 mm, Honjo Metal Co., Ltd., Japan) and LIB electrolyte (1 mol/L LiPF₆ dissolved in a 50/50 vol/vol% mixture of ethylene carbonate and diethyl carbonate, Kishida Chemicals Co., Ltd., Japan) were sealed in the SUS304 testing cell (HS flat cell, Hohsen Corp., Japan), realizing a half-cell configuration. The cell assembly was conducted in an argon-filled glove box. The three electrodes incorporating the HC/SiO_x composite, the carbonized RH, and the commercial HC were subjected to Li-ion insertion/extraction under different current densities (first rate testing): 50, 100, 200, 500, 1000 mA/g-active mass (10 cycles for each current density)

Table 1 Pore properties and SiO_x contents of active materials

Sample	BET specific surface area (m ² /g)	Total pore volume (cm ³ /g)	SiO _x content (mass%)
HC/SiO _x composite	215	0.22	33.7
Carbonized RH	90	0.24	54.6
Commercial HC	8	0.04	0

Table 2 Active materials tested for the LIB NEs

Active materials	Coating thickness (µm)	Active mass (mg)	Coating density of active material (g/cm ³)
HC/SiO _x composite	48	3.33	0.39
Carbonized RH	40	3.11	0.44
Commercial HC	31	3.06	0.56

within the electrode potential range of 0-2.5 V vs. Li⁺/Li (Li metal immersed in the electrolyte). The active mass means the mass of the active material incorporated in the electrode. Specific capacity was used to evaluate the Li-ion insertion or extraction property by dividing the electric charge spent for Li-ion insertion or extraction by the active mass. Then, the cell shorted for 24 h for the full doping of Li-ions into the active materials. The full doping of Li-ions was expectantly executed to maximize the specific capacities of active materials by completing the full reduction of SiO_x with formation of lithium silicates, Si and Li₂O [14] and by eliminating inactive portions where Li-ions were not fully delivered. The Li-ion insertion/extraction properties of the active materials were again evaluated at different current densities in the similar manner (second rate testing). After the second rate testing, the cells were again shorted for 1 h to supply the active materials sufficient Li-ions. Finally, the cycle performances were evaluated by repeating the Li-ion insertion/extraction for 500 times at the constant current density of 1000 mA/g-active mass (hereafter simply presented in mA/g) within the electrode potential range of 0-2.5 V vs. Li⁺/Li (cycle testing). All the performance evaluations were carried out at 25°C.

3 RESULTS AND DISCUSSION

The first rate testing of 50 cycles was performed under different current densities. Figure 1 shows the specific capacity-potential curves of the active materials at the specified cycles. When the active material accepted the Li-ion insertion, its potential decreased with the specific capacity representing the amount of inserted Li-ions. Thus, the specific capacity at the potential of 0 V vs. Li⁺/Li indicates the amount of accepted Li-ions in the tested active material. It was also found that the potential increased with the specific capacity in the Li-ion extraction process, suggesting that the release of Li for the active material was responsible for the enhancement of the potential difference against the Li metal. The specific capacity at the potential of 2.5 V vs. Li⁺/Li means the amount of Li-ions released from the active material. The HC/SiO_x composite and the carbonized RH showed similar specific capacity-potential curves at all the current densities, while the commercial HC showed different curve patterns in which almost the specific capacity was allocated at the potential lower than 1.0 V vs. Li⁺/Li. The gradual increase or decrease in the potential with the specific capacity for the HC/SiO_x composite and the carbonized RH was a characteristic nature of RH-derived LIB NEs [10, 13, 15]. It was obvious that the higher specific capacity was obtainable from the

Figure 1 Specific capacity-potential curves in the first rate testing (without the full Li-ion doping). (a) HC/SiO_x composite, (b) carbonized RH, (c) commercial HC.

Table 3 Li-ion insertion/extraction specific capacities and coulombic efficiencies of active materials at the first cycle.

Sample	Insertion specific capacity (mAh/g)	Extraction specific capacity (mAh/g)	Coulombic efficiency (%)
HC/SiO _x composite	515	275	53.4
Carbonized RH	510	263	51.5
Commercial HC	271	192	70.8

HC/SiO_x composite and the carbonized RH rather than from the commercial HC at all the current densities. The good performance provided by the RH-derived components was active in the HC/SiO_x composite.

Table 3 shows the specific capacities and the coulombic efficiencies, which are the specific capacity ratio of Li-ion insertion and extraction, of the active materials at the first cycle. The HC/SiO_x composite and the carbonized RH exhibited about 20% lower coulombic efficiency than did the commercial HC. One reason is

a formation of nano-size pores resulting in the passivation of Li-ions adsorbed therein. The other reason is a consumption of Li-ions caused by the reduction of SiO_x. The following reactions to form lithium silicates, Si and Li₂O could be supposed [6, 16-18].

The reduced Si has a high reversible specific capacity of 3580 mAh/g for the Li-ion insertion/extraction at room temperature in a form of Li₁₅Si₄ [7]. The above two reasons can be supported by the high porosity and the high SiO_x content shown in Table 1.

Li-ion extraction specific capacities of the active materials without full-doping of Li-ions are shown in Figure 2. A similar Li-ion extraction specific capacity was observed on the HC/SiO_x composite and the carbonized RH at the first cycle. The specific capacity of the carbonized RH increased with the cycle number, within the initial 10 cycles at the lowest current density (50 mA/g). SiO_x parts in the carbonized RH were gradually reduced to generate Si which provided high specific capacity. Owing to the abundant reduced Si, the carbonized RH showed the highest specific capacity at all the current densities. The HC/SiO_x composite exhibited a little lower specific capacity. It is clear that the RH-derived active materials had higher specific capacities and superior rate performances when compared with the commercial HC.

Following the first rate testing, all the cells shorted for 24 h in order to attain the full-doping of Li-ions into the active materials. Then, the Li-ion insertion/extraction properties of the active materials were evaluated at different current densities (second rate testing). Significant differences between the patterns (shapes) of the specific capacity-potential curves at the first and second rate testing were not observed. All the active materials were confirmed to attain high coulombic efficiency of >98%. Thus, only the extraction specific capacities of the active materials in the second rate testing are provided (Figure 3). Maximum extraction capacities were measureable from the results of the first cycle because the acceptable amount of Li-ions could be delivered to the active materials by keeping their potential equal to that of Li metal. The maximum extraction capacities of the HC/SiO_x composite and the carbonized RH were identically 440 mAh/g, while that of the commercial HC was 340 mAh/g. Owing to the full-doping of Li-ions, all the active materials allowed the increases in the specific capacity. In particular, the specific capacity of the carbonized RH was highly increased, which was related to the highest content of SiO_x. It was also found that the HC/SiO_x composite after the full

Figure 2 Li-ion extraction specific capacities of the active materials without full-doping of Li-ions during the first rate testing.

Figure 3 Li-ion extraction specific capacities of the active materials after the full Li-ion doping.

Li-ion doping attained ca. 30% higher specific capacity than did the commercial HC.

After the second rate testing, the active materials in which Li-ions were sufficiently provided were subjected to the cyclic Li-ions insertion/extraction (500 cycles) at the current density of 1000 mA/g. Figure 4 shows the specific capacity-potential curves at the specified cycles during the cycle testing. The carbonized RH showed the highest specific capacity all through the testing. However, it allowed a certain capacity fading, in particular at >100th cycle. About the half specific capacity of the HC/SiO_x composite and the carbonized RH was generated at high potential of >1.0 vs. Li⁺/Li, regardless of the number of cycles. It was also found that the capacity fading of the carbonized RH, which increased with the cycling number, was chiefly caused by the decrease in the specific capacity at >1.0 vs. Li⁺/Li. The capacity loss at >1.0 vs. Li⁺/Li was also observed on the HC/SiO_x composite. However, the loss degree was smaller than that of the carbonized RH and was similar to that of the commercial HC. Judging from the curves of the commercial HC excluding SiO_x, the capacity fading of the carbonized RH was due to the SiO_x parts produced by simple carbonization of RH.

Figure 5 shows the specific capacities of the active materials during the cycle testing, as a function of cycle number. The specific capacity of the HC/SiO_x composite was confirmed to be lower than that of the carbonized RH. SiO_x derived from natural-occurring silicates in RH had a function to increase in the capacity through the reduction process involving with Li passivation, which was explainable from the level of SiO_x content in the active materials (Table 1). However, the capacity retention of the HC/SiO_x composite was comparable to that of the commercial HC. High capacity retention (ca. 77-79%; specific capacity at the 10th cycle was defined to be 100% as the stabilized initial value) was observed on the HC/SiO_x composite and the commercial HC. It was acceptable that Si produced by the reduction of SiO_x allowed a decrease in the specific capacity during the cycling of Li-ion insertion/extraction, which was due to the volume expansion and/or cracking of SiO_x parts reducing electrical contact with the binders or the conductive agent, and with the Cu foil current collector. However, when SiO_x derived from RH was hybridized with the HC prepared from PR, the capacity fading of the active material was alleviated.

The results of material characterizations (Table 1) indicated that the highest BET specific surface area was observed on the HC/SiO_x composite, while the largest total volume was observed

Figure 4 Specific capacity-potential curves in the cycle testing at the current density of 1000 mA/g. (a) HC/SiO_x composite, (b) carbonized RH, (c) commercial HC.

Figure 5 Li-ion extraction specific capacities of active materials as a function of number of Li-ion insertion/extraction cycles at the current density of 1000 mA/g.

on the carbonized RH. It was also shown that the pore structure was hardly developed in the commercial HC. In addition to this, the SiO_x content of HC/SiO_x composite was lower than that of

carbonized PR (about 60% lower). Those results suggested that hybridization of PR and RH produced abundant nano-size pores in the HC/SiO_x composite, which were also verified from its lowest coating density mentioned in Table 2. Inorganic silicates in RH might restrict aggregation or densification of PR-originated amorphous carbon during the carbonization process.

After full Li-doping, the carbonized RH displayed the highest specific capacity at all the current densities. This means that SiO_x parts in the RH-derived active material contributed to an increase in the specific capacity and all the SiO_x parts could not be activated unless Li-ions were once fully supplied to them as mentioned in (1). On the other hand, the specific capacity of the carbonized RH with the highest SiO_x content allowed greater capacity fading with the cycle number of Li-ion insertion/extraction. It is thereby reasonable to interpret that the superior cycle performance of the HC/SiO_x composite was connected with the produced nano-free spaces acting as the buffer to accept the volume expansion of SiO_x in the process of Li-ion insertion.

In order to verify the above mechanisms and more appropriately explain the Li-ion insertion/extraction behaviors of the LIB NE active materials, surface morphology, dispersion degree of active material powder, and adhesion strength between the powder and the current collector for the pristine and aged NEs should be explored. Those will be executed in the future.

4 CONCLUSIONS

The rate and cycle performances of the HC/SiO_x composite upon the Li-ion insertion/extraction were evaluated in comparison with the carbonized RH and commercial HC. The HC/SiO_x composite subjected to full Li-ion doping displayed ca. 30% higher specific capacities than did the commercial HC at all the current density of 50-1000 mA/g. The capacity retention of the HC/SiO_x composite was revealed to be similar to that of the commercial HC. It was thereby shown that low-cost LIB NEs with acceptable performances could be realized by the simple carbonization of the mixture of inexpensive plastic of PR and agricultural waste of RH.

From the aspect of material science, the behaviors of Li-ion insertion/extraction in nano-free spaces produced in amorphous C and SiO_x composite structure were studied. Although the SiO_x part in the carbonized RH was shown to play a role of enhancing the specific capacity, the capacity fading of the SiO_x part was remarkable. The results regarding the HC/SiO_x composite and the carbonized RH suggested that hybridization of HC and SiO_x was useful to alleviate the capacity fading of the SiO_x part with maintaining the specific capacity increased by the SiO_x part. These findings indicate that, after the optimization of material properties, HC/SiO_x composites produced from PR and RH could be applied to vehicle applications requiring excellent cycle performance and high cost effectiveness.

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