



Short communication

The anode performance of the hard carbon for the lithium ion battery derived from the oxygen-containing aromatic precursors

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ABSTRACT

The hard carbon is attractive for the Li ion secondary battery because of its higher capacity than the theoretical value of 372 Ah kg^{-1} based on the composition of stage 1 Li-intercalated graphite, LiC_6 . However, the structure of hard carbon as an anode has not been optimized and the reaction mechanism also has not been clarified in detail. In the present study, the structure of hard carbon derived from oxygen-containing coal tar pitch was investigated by X-ray diffraction, small angle scattering and density measurement, and the relationship between the structure of hard carbon and its anode performance was discussed.

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1. Introduction

About 20 years have passed since the Li ion battery using a carbon as an anode was commercialized. During the first few years, the electrochemical performance of most carbons was investigated. Nowadays, the carbons are systematically classified into four groups from the viewpoint of charge/discharge performance. The first group consists of the graphitizable carbons prepared below ca. 1000°C . They show a higher capacity than the theoretical value of 372 Ah kg^{-1} owing to the presence of LiC_6 [1,2]. However, the cycle performance is notably poor and the initial coulombic efficiencies are less than ca. 80%. For this reason, their electrochemical characteristics are hardly studied now. The second group consists of what are called “artificial graphites”, which are graphitized above ca. 2500°C . Since such carbons have high crystallinities, natural graphite should also be included in this group. In general, these graphites show excellent cycle performance, high capacities of $350\text{--}370 \text{ Ah kg}^{-1}$, and coulombic efficiencies higher than 90%. Therefore, graphite is commercially used as the anode of most Li ion batteries which are used in many electronic devices such as mobile phones, computers, and digital cameras. The third group consists of graphitizable turbostratic carbons, heat-treated between ca. 1100 and 2500°C . In this temperature range, the discharge capacity shows a minimum value at ca. 1800°C . Very few researchers have, therefore, studied the characteristics of these carbons, and their detailed electrochemical performance have

been unknown. Recently, the author and Ozaki have found that such carbons, i.e., carbons heat-treated at $1800\text{--}2400^\circ\text{C}$, show excellent characteristics in terms of high-rate charge/discharge performance and cyclability [3,4] and have named it “ICOKE”. The last group is concerned with non-graphitizable carbon heat-treated at $1000\text{--}1100^\circ\text{C}$. It is also often called “hard carbon” and shows a higher capacity than 372 Ah kg^{-1} . It is firstly reported by Takahashi et al. and Sonobe et al. [5,6]. After that, several groups also reported the carbons with similar structure and electrochemical performances [7,8]. The hard carbon materials have been recently received much attention as an anode for the large scale Li ion battery for hybrid electric vehicles because of the excellent cyclability and high input/output performances. It is considered that such carbons accommodate the lithium species in the micropores as well as in the interlayer. Hence, it is important to characterize the pore structure for the optimization of carbon fine structure that is suitable for an anode.

In order to obtain the information for the pore structure, the density measurement and small angle X-ray scattering (SAXS) measurement will be available. In principle, the difference of the electron density between the scatterer and its circumference is required for the observation of the SAXS. Perret and Ruland et al. considered that the difference of the electron density comes from that between the crystallites and the pores in carbon, and estimated the pore volume ratio from the absolute scattering intensity for the carbon fibers [9–11]. The pore volume ratio obtained was in good agreement with that estimated from the helium absorption method. Johnson and Tyson also reported the same result [12,13]. Liu et al. applied SAXS technique for the analysis of carbon anode and estimated the pore size from the radius of gyration [8]. In the

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present study, the structure of the typical non-graphitizable carbon prepared by the heat treatment of oxidized coal tar pitch was investigated by means of the X-ray diffractometry, SAXS and density measurement, and the relationship between the structure and electrochemical properties was discussed.

2. Experimental

As a starting material for the preparation of hard carbon, a coal tar pitch (Osaka Gas Chemical Company Co., Ltd.) was used. It was an isotropic pitch having a softening point of 280 °C. It was milled and classified, so that the median diameter, D50 was adjusted to ca. 5–6 μm. After that, it was oxidized by air at 300 °C for 1–5 h in order to avoid remelting during the carbonization process. The role of the oxidation is not only for the inhibition of remelting but also for the pore size control by the formation of three-dimensional cross-linking by oxygen atom. Thus obtained pitch was carbonized at 1100 °C. In order to investigate the effect of other oxidation method, P₂O₅ and (NH₄)₂S₂O₈ were selected as the oxidation agents. The concentration of oxidation agent was in the range of 1–20 wt.% against the amount of the pitch. The mixture of the pitch and oxidation agent was heated up to 270–310 °C in air and was kept for 1 h. Then it was carbonized at 1100 °C. Moreover, in order to investigate the effect of the amount of oxygen on the performance of carbon anode, three kinds of pitches with different oxygen contents made in Osaka Gas Chemical Co., Ltd. were also used for the raw material. Each oxygen content was 8.0, 9.4 and 15.2 wt.%, respectively. The material was milled and heat-treated at 1100 °C in the similar method.

The obtained hard carbons were analyzed by X-ray diffraction (XRD), SAXS and density measurement. The XRD profiles of carbons were measured with CuKα using RINT2500 diffractometer (Rigaku Denki Co., Ltd.). The measurement was carried out by a step-scanning technique with an interval of 0.1°. The tube-voltage and current were 40 kV and 200 mA, respectively. The diffraction profiles obtained were refined by the two-dimensional analysis method. The method is a least square refinement method by which the XRD profile is fitted with several hundreds of theoretical intensities of model crystallites with different *L*_a and *L*_c sizes based on the assumption that the carbon is an aggregate composed of various size crystallites. The detail procedure of the analysis method was described elsewhere [14]. The SAXS measurement was carried out using SAXS goniometer (2203E6 goniometer) attached to RINT2500 diffractometer in 2θ range of 0.08–8.00°. The sampling distance is fixed at 0.01°. The scattering curves measured were corrected by the smoothing, subtraction of back ground scattering and extrapolation to 2θ = 0°. Then, the distance distribution function (DDF), *p*(*r*) was calculated from the corrected scattering profile by Fourier transform,

$$p(r) = \frac{1}{2\pi^2} \int_0^\infty I(h) \cdot (hr) \cdot \sin(hr) dh, \quad h = 4\pi \sin \theta / \lambda \quad (1)$$

where θ and λ are the scattering angle and wave length of X-ray [15], respectively. DDF is generally interpreted as a physical function that expresses the pore size distribution in case of carbon materials. The density of carbon was measured using helium and butanol as a solvent according to the Japanese industrial standard R7212.

Electrochemical measurements were performed using three-electrode test cells made of glass. A lithium metal was used as a counter and a reference electrode. The electrolyte used was a 1 M LiClO₄/ethylene carbonate + diethyl carbonate (1:1). The cells were discharged down to 0.001 V at a constant current density of 1 mA cm⁻² and then kept at a potential of 0.001 V, so that the total discharging time was 12 h. Then, the cells were charged in

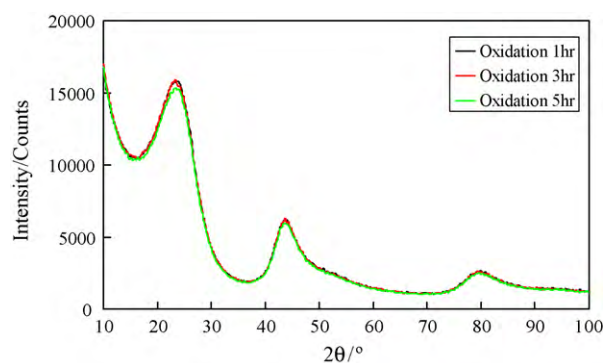


Fig. 1. X-ray diffraction profiles of hard carbons derived from coal tar pitch oxidized in air for 1, 3 and 5 h.

the potential range of 0.001–1.3 V vs. Li/Li⁺ at a constant current density of 1 mA cm⁻².

3. Results and discussion

3.1. Effect of oxidation in air on the structure and electrochemical performance of hard carbon

Figs. 1 and 2 show the XRD and SAXS profiles of hard carbons derived from the pitch oxidized in air for 1, 3 and 5 h. All the XRD profiles were perfectly superimposed indicating that all the samples have the same bulk structure. SAXS profiles were also the same as each other. SAXS profile of the carbon generally reflects the pore size distribution. Hence, it is concluded that the oxidation time does not affect on the bulk structure and pore size. Nevertheless, the charge/discharge curves were different from each other as shown in Fig. 3. The carbon with no oxidation did not show the plateau region below 0.25 V, whereas the oxidized samples showed plateau and the oxidation time of 1–3 h gave the maximum charge capacity. These results indicate that the oxidation process would affect only on the surface structure of hard carbon. That is, only the entrance sizes of the pores near the surface of carbon are different from each other. If the pore entrance size is optimized, so that only the lithium ion goes in and goes out from the entrance, the charge capacity becomes maximum. It will be discussed in detail in Section 3.4.

3.2. Addition effect of a phosphorous penta oxide

Fig. 4 shows XRD profiles of carbons prepared from P₂O₅-added pitch. The 0 0 2 diffraction line at ca. 23° shifted to higher angle side and its intensity decreased with increasing the amount of P₂O₅.

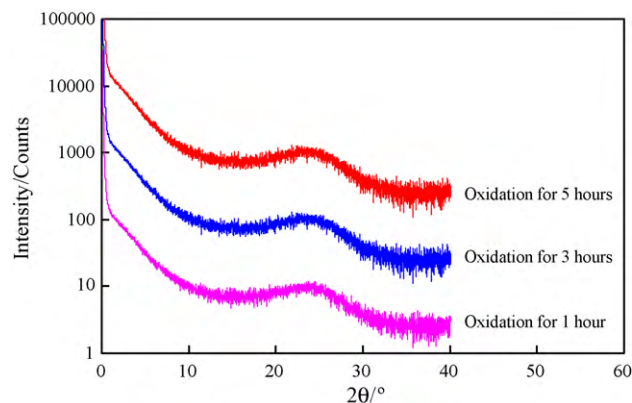


Fig. 2. SAXS profiles of hard carbons derived from coal tar pitch oxidized in air for 1, 3 and 5 h.

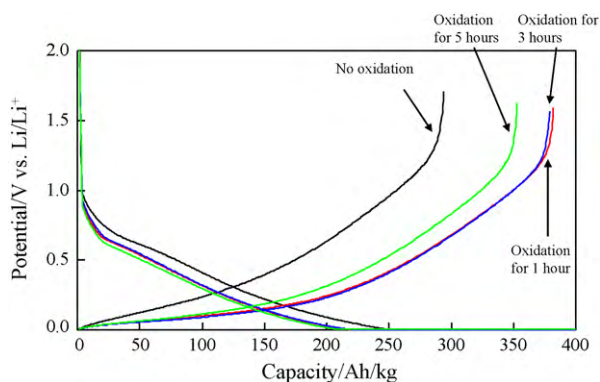


Fig. 3. Charge/discharge profiles of hard carbons derived from coal tar pitch oxidized in air for 1, 3 and 5 h.

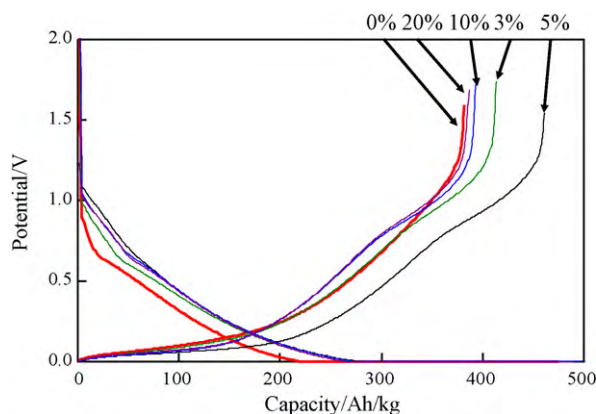


Fig. 6. Charge/discharge curves of hard carbons derived from P₂O₅-containing coal tar pitch.

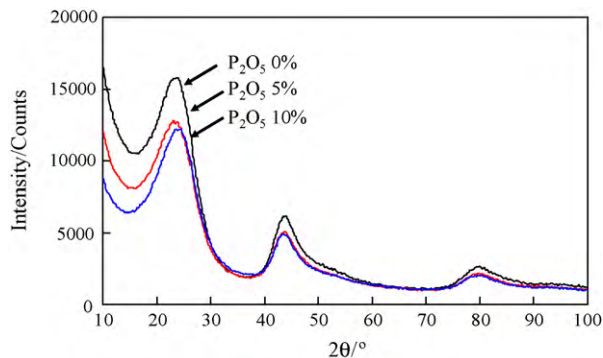


Fig. 4. X-ray diffraction profiles of hard carbons derived from P₂O₅-containing coal tar pitch.

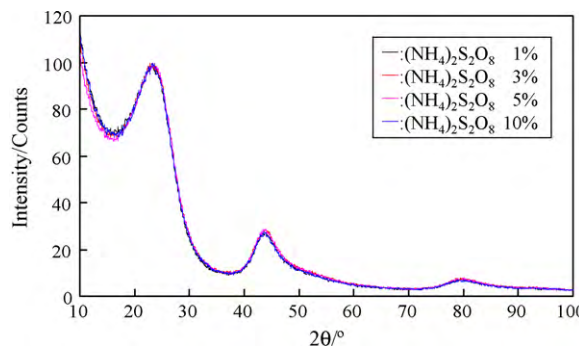


Fig. 7. X-ray diffraction profiles of hard carbons derived from coal tar pitch containing ammonium peroxosulfate.

Not only the 002 line but also the two-dimensional *hk* diffraction lines at 43° and 80° become weak. It indicates that the addition of P₂O₅ interferes with the crystallite growth. Fig. 5 shows the crystallite size distributions of carbons derived from the precursor with P₂O₅-addition by 0, 5 and 10 wt.%. The accumulation histograms projected onto *La* and *Lc* axes represent the *La* and *Lc* size distributions, respectively. The *La* size distribution shifted toward the lower size as the amount of P₂O₅ increased showing the inhibition of enlargement of carbon layer planes. And also, the concentration of carbons contained in carbon layer stacking decreased from 58.8 to 53.8 wt.%. Since the addition of P₂O₅ caused the complicated structure change, the charge/discharge profile was largely affected

by the P₂O₅ addition. Fig. 6 shows the charge/discharge curves of P₂O₅-added hard carbons. The turning point at ca. 0.8 V appears in the charge curve by the P₂O₅ addition, and the capacity apparently increased above the potential of the point. However, the capacity below 0.8 V decreased by the higher addition than 10 wt.%. The optimized amount of P₂O₅ seems to lie on 3–5 wt.%.

3.3. Addition effect of an ammonium peroxosulfate

Figs. 7 and 8 show the XRD profiles and charge/discharge profiles of carbon prepared from the (NH₄)₂S₂O₈-cotaining pitch. The XRD profiles of all the samples were almost the same, and

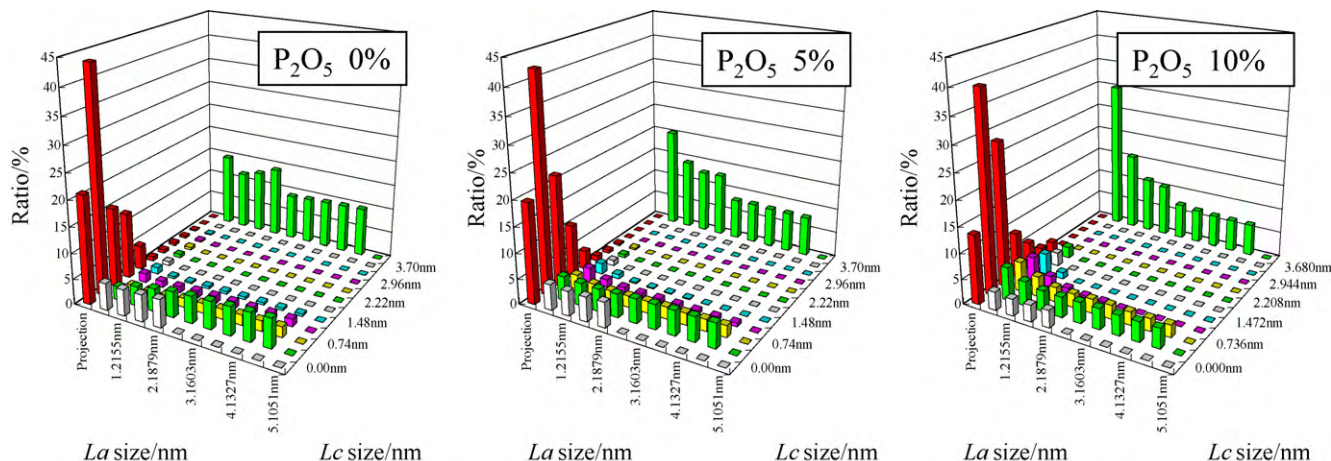


Fig. 5. Results of two-dimensional analysis of hard carbons derived from P₂O₅-containing coal tar pitch.

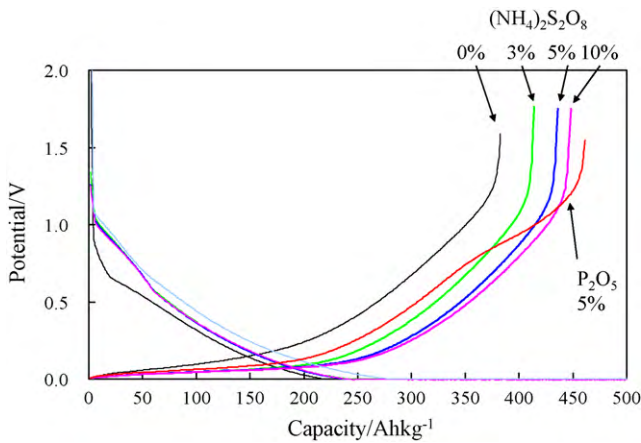


Fig. 8. Charge/discharge profiles of hard carbons derived from coal tar pitch containing ammonium peroxosulfate.

it is concluded that the bulk structure was not affected by the addition of ammonium peroxosulfate as well as in the case of air oxidation. However, the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ -added carbons exhibit the different charge/discharge profiles from those of P_2O_5 . They did not show the turning point at ca. 0.8V regardless the added amount, but the capacity and plateau below 0.25V increased with the added amount. Fig. 9 shows the relationship between the amount of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and reversible capacity. The carbon without $(\text{NH}_4)_2\text{S}_2\text{O}_8$ shows 380 Ah kg^{-1} , and the capacity increased with the amount of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ up to 470 Ah kg^{-1} . The temperature of $300\text{--}310^\circ\text{C}$ and the concentration of $10\text{--}20 \text{ wt.}\%$ were found as optimum oxidation condition.

3.4. Result of density measurement

Franklin investigated in detail the densities of non-graphitizable carbons obtained by the heat treatment of coals using several solvents with different molecular sizes, and found that the density become maximum at the heat treatment temperature (HTT) of $800\text{--}1000^\circ\text{C}$ and the HTT at the maximum increases with decreasing the molecular size of the solvent used for the density measurement [16]. She concluded that the entrance size of micropores in the vicinity of carbon surface become smaller above HTT of 800°C and finally, even the helium atom does not penetrate therein. As a result, the ink-bottle type pores increase and the density apparently decreases above 800°C . Hence, it is very important to estimate

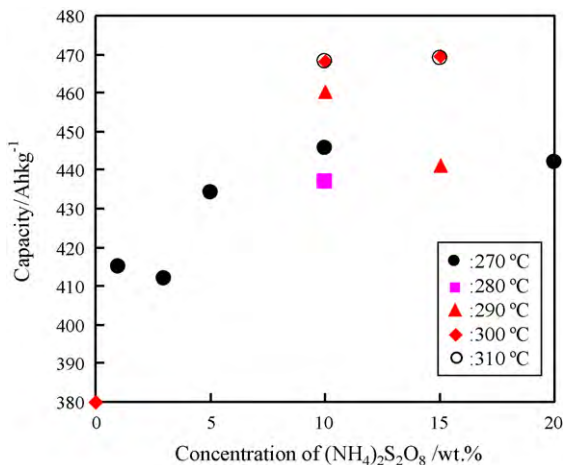


Fig. 9. Reversible capacities of hard carbons derived from coal tar pitch containing ammonium peroxosulfate.

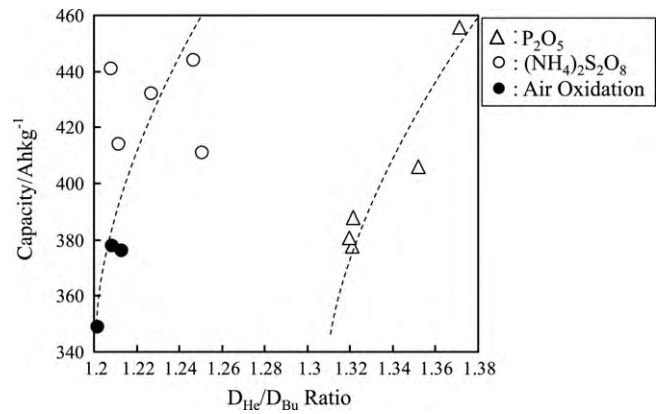


Fig. 10. Relationship between helium/butanol density ratio and reversible capacities of hard carbons.

the ratio between the densities with helium (D_{He}) and other solvent such as butanol (D_{Bu}). That is, as the $D_{\text{He}}/D_{\text{Bu}}$ value become large, the number of ink-bottle type pores increases whose entrance size would be suitable for the insertion/deinsertion of Li ion. Fig. 10 is the plots of the $D_{\text{He}}/D_{\text{Bu}}$ values vs. reversible capacities. In the case of oxidation by air and ammonium peroxosulfate, the plots lie on the same curve, and it seems that they have the same electrochemical behavior. On the other hand, the plots for the carbons derived from P_2O_5 -contained precursor lie on another curve indicating that they have a quite different behavior. The air and ammonium peroxosulfate mildly oxidize only the surface of the carbon so that pore entrance is suitable for the insertion/deinsertion of Li ion, whereas the oxidizing ability of P_2O_5 is so strong that the carbon structure would be destroyed. The result is supported by the calculation results of DDF. Fig. 11 shows the DDF of carbons derived from the pitch oxidized by air and P_2O_5 . The first peak at 0.76 nm for the carbons air-oxidized for 1 and 3 h are almost the same. However, the intensity of the peak for the carbons derived from P_2O_5 -containing pitch decreased with the amount of P_2O_5 indicating that the pore was destroyed. It is not clear whether the pore size directly come into an important play for the anode performance. However, the oxidation by P_2O_5 surely interferes with the crystallite growth and destroys the pores. Probably, the pore with the size of 0.76 nm would be important for the appearance of the plateau below 0.25 V.

3.5. Hard carbon prepared from a pitch containing high content oxygen

As discussed above, the oxidation process is considered as a crucial process to obtain higher capacity. Hence, it is considered that

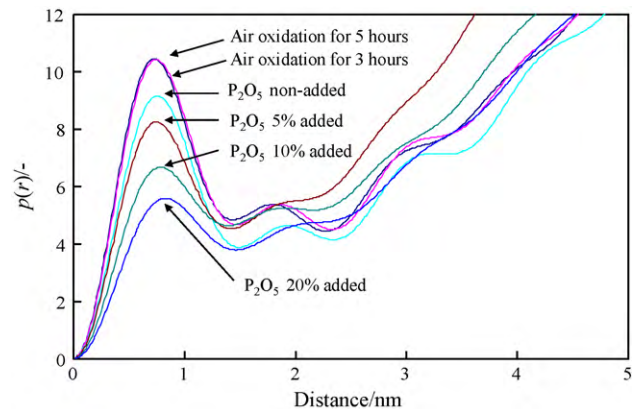


Fig. 11. Distance distribution function calculated from the SAXS profiles of hard carbons.

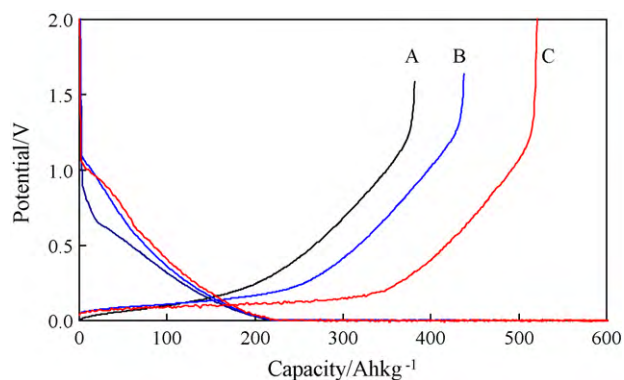


Fig. 12. Charge/discharge profiles of hard carbons derived from the pitch with different oxygen contents. A: 8.0 wt.%, B: 9.4 wt.% C: 15.2 wt.%.

a pitch with high oxygen concentration would also yield a high capacity hard carbon. In order to verify the assumption, a pitch with high oxygen concentration was used for the preparation of carbon. Fig. 12 shows the charge/discharge profiles of three kinds of carbon derived from the pitches with different oxygen contents. The carbon derived from the highest oxygen-containing pitch yielded a reversible capacity of more than 500 Ah kg⁻¹.

3.6. The other electrochemical properties of hard carbon

As discussed above, the focal issue in the present study was the relationship between the carbon structure and its reversible capacity. Concerning the other electrochemical properties such as the initial coulombic efficiency and cycle performance, all the samples show fairly good performance with the coulombic efficiency of 83–85% and cyclability within 10% degradation at 50 cycles in half-cell. Remarkable relationship was not observed between the carbon structure and these electrochemical behaviors.

4. Conclusion

The oxidation effect of carbon precursors on the carbon structure and its anode performance for Li ion battery was investigated. In the case of the mild oxidation by the air and ammonium peroxy-

sulfate, only the surface of carbon was oxidized so that the suitable pore entrance for the insertion/deinsertion of Li ion was formed, whereas the strong oxidation with P₂O₅ interfered with the carbon crystallite growth. It is concluded that the oxidation process is a crucial process to obtain higher capacity. Moreover, it is found that a pitch with high oxygen concentration would also yield a high capacity hard carbon.

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