

High-Performance Soft Carbons Prepared by Treatment with Various Phosphorus Acids

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Phosphorus-doped soft carbons were successfully prepared by carbonizing petroleum cokes treated with phosphorus acids, such as H_3PO_2 , H_3PO_3 , and H_3PO_4 . The effect of the type of phosphorus acids used on the composition, structure, and electrochemical performance of the soft carbons was extensively investigated. The soft carbons modified with H_3PO_3 and H_3PO_4 exhibited dramatically improved reversible capacities and outstanding rate capabilities.

Key Words : Soft carbons, Phosphorus acid, Reversible capacities, Rate capabilities

Introduction

There is an increasing need for advanced batteries to suit recent applications, such as converged digital devices and large-scale energy storage systems.^{1,2} It has been recognized that introducing new materials is without a doubt crucial to the successful development of advanced battery systems. A number of materials have been developed to replace the current anode materials of lithium-ion batteries.³⁻⁹ Lithium alloy based-carbon composites with high theoretical capacities are the primary candidates being considered, but the short cycle life and low rate capability of these composites remain unresolved issues.⁷⁻¹⁰ Conversely, attractive features of soft carbons, such as high rate capability and electrochemical stability, have drawn considerable attention from researchers.¹¹ Recently, it was reported that the low reversible capacity of soft carbons could be improved by treatment with phosphorus compounds, enabling characteristic advantages, such as high initial efficiency and rate capability, to be retained.¹²⁻¹⁴

In this work, the effect of phosphorus acids on the electrochemical performance of soft carbons was intensively examined.

Experimental

Preparation and Characterization. Petroleum cokes (GS Energy, Korea) were impregnated with three types of phosphorus acids, hypophosphorous acid (H_3PO_2 , Sigma-Aldrich), phosphorous acid (H_3PO_3 , Sigma-Aldrich), and phosphoric acid (H_3PO_4 , Sigma-Aldrich) by mixing the cokes with aqueous solutions containing the phosphorus acids in a cokes:phosphorus (P) mass ratio of 95:5 for 10 h. The resulting materials were carbonized at 900 °C for 1 h. The soft carbons prepared by treating with H_3PO_2 , H_3PO_3 , and H_3PO_4 were denoted by SC-PO2, SC-PO3, and SC-PO4, respectively. For comparison, the two soft carbons SC-900 and SC-1000 were prepared without treatment with

phosphorus acids at 900 and 1000 °C, respectively. Elemental analysis was performed using an elemental analyzer (Flash EA 1112 series, CE Instruments) to examine the content of C, H, N, and O in the prepared soft carbons. The P content was examined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Ultima 2, Horiba). X-ray diffraction (XRD) analysis was carried out with an X-ray diffractometer (Empyrean, PANalytical) to examine the structural changes in the composites after the phosphorus acid treatment.

Electrochemical Evaluation. The carbon electrodes used in this study were composed of soft carbons (90 wt %), carbon black (Super-P, 2 wt %), and polyvinylidene difluoride (PVDF, 8 wt %). The specific conditions used to prepare the carbon electrodes were well described elsewhere.^{13,14} The electrochemical properties of the carbon electrodes were examined with coin-type cells containing a lithium metal counter electrode. The electrolyte used was 1.0 M $LiPF_6$ in a mixture of ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (30/70, v/v, Panax Etec) with 2 wt % vinylene carbonate (VC). The test cells were evaluated using a galvanostatic instrument (BaSyTec, Germany) over the range of 5 mV to 1.5 V vs. Li/Li^+ . However, various cutoff voltages were used to obtain a deeper understanding of the lithium insertion mechanism occurring in the soft carbons. The other test conditions, including the rate and cycle performance, were described in detail elsewhere.^{13,14}

Results and Discussion

Elemental analysis of the soft carbons showed that the atomic ratio of hydrogen to carbon (H/C) was not affected by the phosphorus acid treatment, but the atomic ratio of oxygen to carbon (O/C) increased slightly from 0.001 to 0.008 regardless of the type of phosphorus acid used after the phosphorus acid treatment (Table 1). On the other hand, it was observed that the phosphorus (P) content determined by ICP-AES was heavily dependent on the type of phosphorus

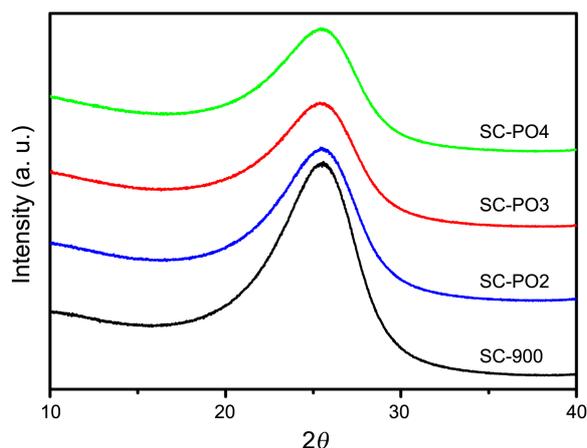


Figure 1. XRD patterns of the prepared soft carbons.

acid employed.

Figure 1 shows the XRD patterns of the prepared soft carbon samples. All of the samples showed broad (002) peaks near $2\theta = 26^\circ$, which is characteristic of highly disordered carbons. The full width at half-maximum (FWHM) of the (002) peaks became slightly wider after phosphorus doping. The average crystallite size along the c axes (L_c) was estimated from the (002) diffraction peaks using the Scherrer equation (Table 1).¹⁵ The L_c values were observed to be very similar to one another, indicating that the phosphorus treatment did not induce considerable changes in the crystallinity of the soft carbons.

Figure 2(a) shows the first charge (lithiation) and discharge (delithiation) curves of the soft carbons. The three P-doped carbons showed higher reversible capacities, defined as the discharge capacities of the first cycle, compared with those of the pure soft carbon (SC-900).

The reversible capacities of the soft carbons significantly increased from ~ 350 to ~ 440 mAh/g when they were treated with H_3PO_3 and H_3PO_4 . Quite interestingly, SC-PO3 and SC-PO4 showed nearly identical electrochemical behavior

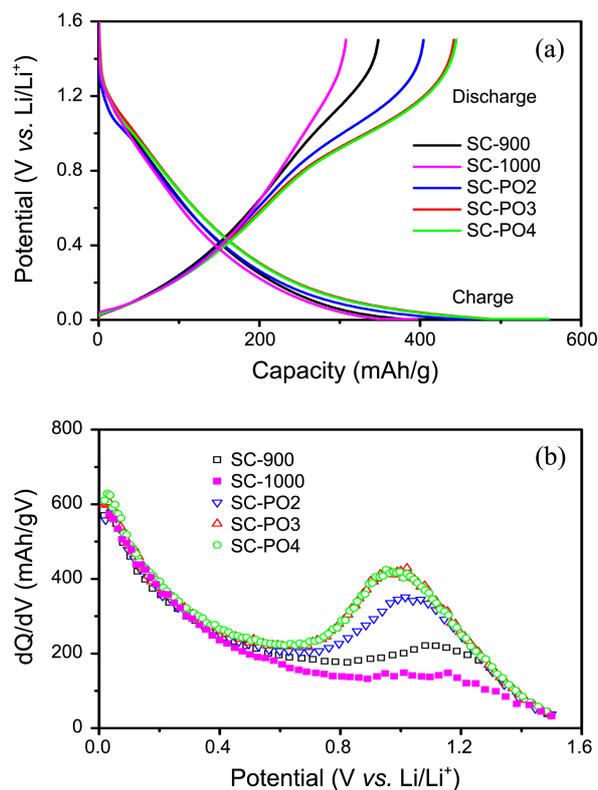


Figure 2. First charge and discharge curves of the soft carbons (a) and dQ/dV plots for the first discharge curve (b).

in terms of their voltage profiles and capacities. SC-900 as well as the P-doped carbons showed large hysteresis between the charge and discharge curves. It has been accepted that this hysteresis phenomenon is closely related to the hydrogen-terminated edges of carbon fragments and that the capacities of the 1-V plateau are directly proportional to the H/C atomic ratio.¹⁶

In fact, these features were confirmed again by comparing the H/C ratios of SC-900 (H/C ratio = 0.07) and SC-1000 (H/C ratio = 0.04). It is noteworthy that even though the H/C

Table 1. Results of characterization and charge/discharge tests of the prepared soft carbons

Samples	H/C atomic ratio	O/C atomic ratio	Weight percent of phosphorous (%)	L_c (Å)	Capacity (mAh/g)	
					Charge	Discharge
SC-900	0.07	0.001	0.04	16.2	453	348
SC-PO2	0.07	0.008	1.04	16.1	515	404
SC-PO3	0.07	0.008	1.57	15.8	560	442
SC-PO4	0.07	0.008	1.68	15.8	560	445

Table 2. Extra charge capacities of SC-PO2, SC-PO3, and SC-PO4 with respect to the charge capacity of SC-900 over the potential range of the second charge curve

Samples	Extra charge capacities (mAh/g)						Total
	1.5 V–1.0 V	1.0 V–0.5 V	0.5 V–0.2 V	0.2 V–0.1 V	0.1 V–50 mV	50 mV–5 mV	
SC-PO2	0	+1	+9	+12	+11	+13	+46
SC-PO3	0	+8	+17	+20	+17	+18	+82
SC-PO4	0	+10	+18	+20	+16	+17	+84

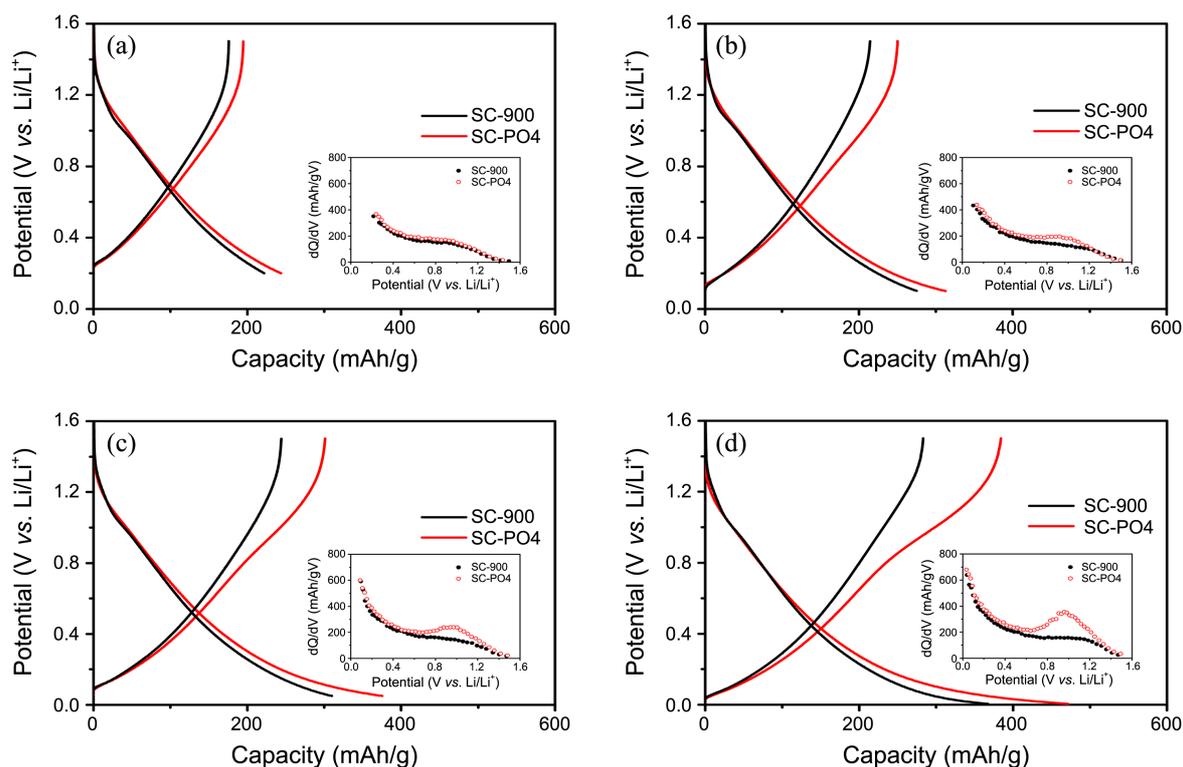


Figure 3. First charge and discharge curves of the SC-900 and SC-PO4 specimens at various cutoff voltages, and the dQ/dV plots (inset): (a) 200 mV, (b) 100 mV, (c) 50 mV, and (d) 5 mV.

ratios of these specimens were identical to one another, the P-doped soft carbons exhibited much larger capacities with respect to the capacity of SC-900, implying that additional sites to store lithium were generated after doping with phosphorus. It has been reported that the phosphorus moieties generated from the thermal decomposition of phosphoric acid could form C-O-P or C-P-O bonds at graphene edges, which would create micropores between crystallite domains.¹⁷⁻²⁰ It is suggested that the additional capacities of P-doped soft carbons may be caused by their micropores. The first discharge curves were analyzed in detail by creating differential capacity plots. Figure 2(b) clearly shows that the deinsertion of additional lithium ions occurred in the high potential

range of 0.6 to 1.2 V.

To closely examine the lithium insertion and deinsertion process in the P-doped soft carbons, both the SC-900 and SC-PO4 electrodes were charged at various cutoff voltages, such as 200, 100, 50, and 5 mV, and discharged to 1.5 V. It was observed that the additional discharge capacities significantly increased as the cutoff voltage decreased, with additional capacities of ~ 80 mAh/g measured at a cutoff voltage of 5 mV.

Regardless of the cutoff voltage, most of the additional capacities were observed to occur within the range of 0.6-1.2 V, as shown in the insets of Figure 3. On the other hand, it was observed from the analysis of the second charge curve that the majority of additional lithium insertion occurred in the low range of 0.5 V to 5 mV (Table 2). The prepared soft

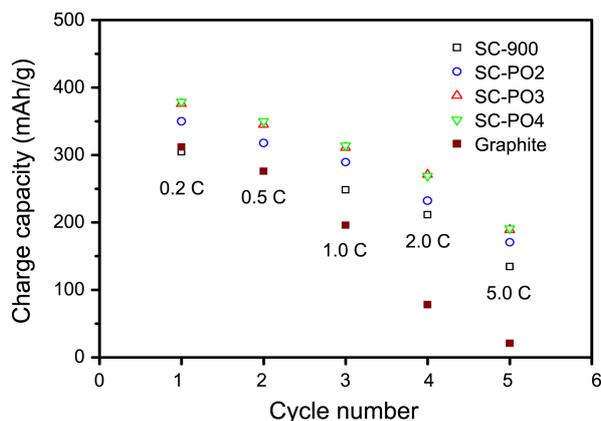


Figure 4. Charge rate capabilities of the soft carbons and graphite.

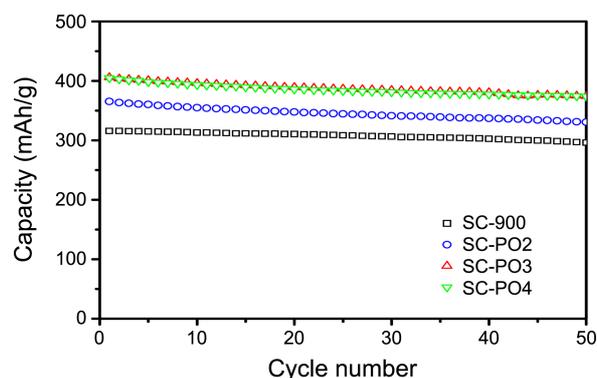


Figure 5. Cycling performance of the soft carbons.

carbons showed excellent charge rate performance at high rates of 2C and 5C compared to graphite (a control experiment) electrodes (Figure 4). In particular, SC-PO3 and SC-PO4 exhibited substantially larger charge capacities (~190 mAh/g) at 5C compared with that (~20 mAh/g) of graphite.

The outstanding rate capability of the soft carbons can be attributed to the rapid insertion of lithium into graphene layers with a broad interlayer distance.

Figure 5 shows the cycle performance of the soft carbon samples. SC-PO3 and SC-PO4 maintained higher capacities (~375 mAh/g) and showed similar capacity retention (~92%) to that of SC-900 after 50 cycles without a trade-off between high capacity and cycle life.

Conclusion

The electrochemical performance of soft carbons was observed to be greatly dependent on the type of phosphorus acids used to treat the carbons. Additional reversible capacities were observed in all of the P-doped soft carbon specimens prepared in this study. In particular, the soft carbons formed by treatment with H₃PO₃ and H₃PO₄ exhibited enormous additional capacities of ~90 mAh/g and excellent capacity retention comparable to that of pure soft carbon. In addition, the phosphorus-doped soft carbons exhibited outstanding charge rate capabilities (~190 mAh/g at 5C).

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