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Short Communication

The Influence of Preheating Time on the Reversible Capacities of P-Containing Soft Carbons

Seong Hun Jeong, Yongju Jung[*]

Department of Chemical Engineering, Korea University of Technology and Education
(KOREATECH), Cheonan, 330-780, Korea
[*]E-mail: yjung@koreatech.ac.kr

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The synthetic conditions of P-containing soft carbons were optimized in terms of heating rate and preheating reaction time. First, phosphoric acid-containing carbon precursors were heated to 950°C with two heating rates of 2.5 and 10 °C/min. Very surprisingly, it was found that the rapidly heated soft carbons showed relatively higher dischage (lithium extraction) capacities compared to the slowly heated soft carbons. It is thought that this feature may be caused by the difference in the bonding nature of phosphorus species at graphene edge which would depend critically on the oxygen content. Second, phosphoric acid-containing carbon precursors were preheated at 200°C for different reaction times of 30 to 120 min. It was observed that all preheated samples presented improved reversible capacities by about 10 to 20 mAh/g compared to the P-doped carbons prepared without the preheating step and the preheated carbons for more than 60 min exhibited reversible capacities similar to one another, indicating that optimum preheating reaction time would be 60 min when considering preparation costs and electrochemical properties.

Keywords: Phosphorus**,** Soft carbons, Petroleum cokes, Preheating time

1. INTRODUCTION

There have been strong efforts in the development of new energy production and conversion systems in order to mitigate the current environmental problems[1-3]. Currently, rechargeable batteries and fuel cells have been considered to be key devices for energy storage systems and electric cars[4,5]. As for fuel cells operating at ambient temperature, the major hindrance for electric cars applications is the lack of low-cost catalysts to allow fast electrode reactions. Rechargeable lithium-ion batteries have been wide used in cordless drills and electric wheelchairs as well as in portable devices such as cellular phones and tablet computers. In addition, lithium-ion batteries are without a doubt the main candidate of large-scale energy storage systems for electric vehicles, but capacity and charge rate issues slow down growth[4]. The latter is mainly due to slow lithium insertion rate at the graphite-based anodes[5-8]. For this reason, the quest for anode materials with rapid charge capability has become essential. Soft carbons, one of amorphous carbons, have drawn much attention due to their attractive features such as high charge rate and low cost. In general, it is well known that reversible capacities of soft carbons are strongly relevant to carbonization temperature[9-11]. Soft carbons prepared at low temperatures below 800°C show higher capacities, compared with that of graphite, but they are not implemented to the lithium batteries due to poor cycle life. On the other hand, soft carbons made at elevated temperatures above 900°C present low reversible capacities (< 300 mAh/g), but excellent cycle life. These features have limited their use in lithium-ion battery applications. Recently, it was revealed that reversible capacities of soft carbons could be significant enhanced by incorporating phosphorus into the carbon particles at 900°C[12]. In a recent study, we demonstrated that the reversible capacities of P-containing soft carbons were improved by a two-step process consisting of preheat treatment and carbonization at 900°C[13].

In this work, we examined the effect of preheating time on the electrochemical performance of P-containing soft carbons for optimizing synthesis conditions of high capacity soft carbons.

2. EXPERIMENTAL SECTION

Mixtures of petroleum cokes (GS Energy, Korea) with phosphoric acid (H_3PO_4) solution was agitated for 10 h and dried at ambient temperature. A 95:5 mass ratio of petroleum cokes to phosphorus was used to get phosphoric acid-containing carbon precursors. The resulting materials were heated to 950°C with two heating rates of 2.5 and 10 °C/min and carbonized in inert Ar gas at 950°C for 1 h to investigate the effect of heating rate on the electrochemical performance of phosphorus-containing carbons. In addition, the phosphoric acid-containing carbon precursors were preheated at 200°C for various reaction times of 30, 60, 90 and 120 min, and then carbonized at 950°C for 1 h in order to find optimal synthesis conditions in terms of preheating time. The resulting phosphorus-containing carbons are denoted as P-SC-30, P-SC-60, P-SC-90 and P-SC-120.

Electrodes were constituted of soft carbons (90 wt%), carbon black (Super-P, 2 wt%) and polyvinylidene difluoride (PVDF, 8 wt%). N-methyl-2-pyrrolidone (NMP) was used as a dispersion solvent of the mixture slurry, which was casted on a copper foil, dried at 120 °C for 1 h and pressed. Electrochemical properties of the resulting carbon electrodes were evaluated by using coin-type cells (CR2016) with a lithium foil as the counter electrode. A 1.0 M $LiPF_6$ solution of ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3:7, v/v, Panax Etec) with 2 wt% vinylene carbonate (VC) was used as the electrolyte. The cells were tested with the cut-off potentials of 0.005 and 1.5 V vs. Li/Li^+. Upon charging (lithium insertion), a constant current-constant voltage mode was used with a cut-off current of 0.02 C (current at 1 C = 372 mA/g) at 5 mV vs. Li/Li^+. Upon discharging (lithium extraction), a constant current mode was used. The first two cycles were charged and discharged at a rate of 0.2 C, which were considered to be a formation step in this work. Thereafter, the cycling tests were carrid out at 1.0 C for additional 50 cycles.

3. RESULTS AND DISCUSSION

In general, soft carbons made at temperatures above 900°C show rapid rate capability and excellent cycling performance which are very beneficial for large scale applications, but they present lower reversible capacities compared to graphite, which are a significant drawback to be overcome to allow for the use of these carbons in commercial lithium-ion batteries[5]. Recently, it was reported that reversible capacities of soft carbons could be significantly improved when they are incorporated with phosphoric acid[12]. It was found from a cross-sectional view of energy dispersive X-ray spectroscopy that the phosphorus moieties remained inside the carbon particles even after carbonization. It was suggested that the chemical bonding between the phosphorus moieties and graphene edges contributed to the formation of nanopores within carbon particles, which were responsible for the extra capacities of the soft carbons[12-14]. In the previous work, we reported that the electrochemical performance of P-doped soft carbons was strongly affected by the preheating treatment[15]. To find optimal preheating conditions, in this study, the influence of heating rate and preheating time was examined. As for heating rate, it was known that slow heating process helped somewhat to increase the reversible capacities of carbons[16,17]. Very interestingly, however, the rapidly heated soft carbons (P-SC-HH, heating rate = 10 °C/min) showed relatively higher dischage (lithium extraction) capacities compared to the slowly heated soft carbons (P-SC-LH, heating rate = 2.5 °C/min), as shown in Fig. 1.

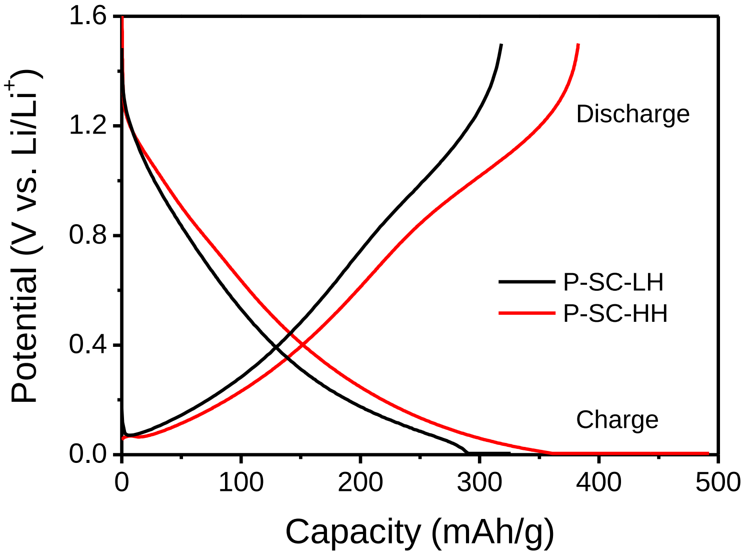

Figure 1. The first charge and discharge curves of the P-doped soft carbons (P-SC-LH and P-SC-HH).

It was reported that incorporated phosphorus was stable in the temperature regions of 500 and 1000°C and bound to carbon lattice by forming C-O-P or C-P-O bonds, resulting in the formation of nanopores to be able to store lithium[18-20]. It is recognized that the oxygen content greatly decreases with heating time during the carbonization process above 500°C. In fact, this feature may be ascribed to the difference in the bonding nature of phosphorus species at graphene edge[19,20]. It is thought that the nanopores directly connected to the extra capacities would be not formed well at slow heating rate. It should be noted that carbonization time (4 h) above 500°C at slow heating rate was much longer than that (1.75 h) at high heating rate. On the other hand, it was observed that the P-SC-HH exhibited larger capacities (313 mAh/g at 1C) after fifty cycles, but slightly lower capacity retention compared to the P-SC-LH (Fig. 2).

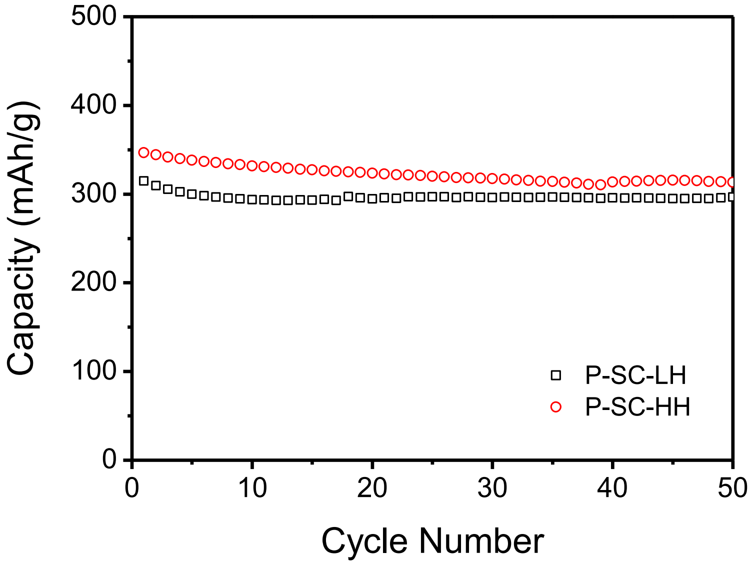

Figure 2. Cycling performance of the P-doped soft carbons (P-SC-LH and P-SC-HH).

An optimum range for preheating temperature was found to be between 175 and 250°C in the P-doped soft carbons in the previous work[15]. In order to make the best decision of the preheating reaction time, the phosphoric acid-treated petroleum cokes were heated at 200°C for 4 different reaction times of 30, 60, 90 and 120 min and carbonized at 950°C with a fixed heating rate of 10 °C/min.

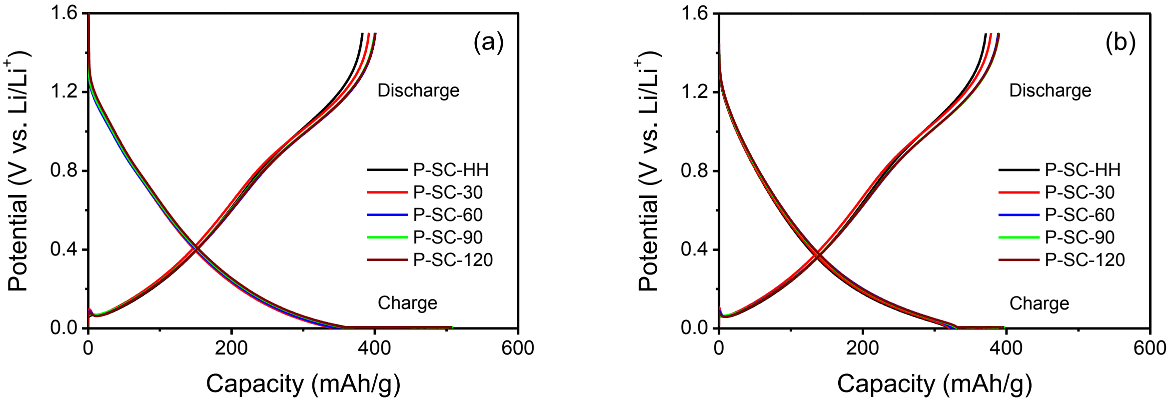

Figure 3. The first (a) and second (b) voltage profiles of the P-doped soft carbons (P-SC-HH, P-SC-30, P-SC-60, P-SC-90 and P-SC-120).

Fig. 3 shows the charge (lithium insertion)/discharge (lithium extraction) curves of the prepared carbon samples. It was observed that all preheated samples presented improved reversible capacities (the first discharge capacities) by about 10 to 20 mAh/g compared to the P-SC-HH prepared without the preheating step. The reversible capacities of the preheated carbons were not sensitive to the heating reaction time when it exceeded 60 min.

Table 1. Summary of electrochemical cell tests for the prepared P-containing soft carbons.

Samples	Heating rate (℃/min)	Preheat temperature (℃)	Capacity (mAh/g)				Coulombic efficiency (%)		Cycle performance		
			1st cycle		2nd cycle						
			Charge	Discharge	Charge	Discharge	1st cycle	2nd cycle	1st cycle^{a} (mAh/g)	50th cycle^{b} (mAh/g)	Capacity retention^{c} (%)
P-SC-LH	2.5	-	430	330	326	318	77	98	315	297	94
P-SC-HH	10.0	-	492	383	379	371	78	98	347	313	90
P-SC-30	10.0	200	502	392	386	378	78	98	358	316	88
P-SC-60	10.0	200	507	401	396	389	79	98	369	329	89
P-SC-90	10.0	200	509	400	398	390	79	98	370	332	90
P-SC-120	10.0	200	508	401	397	389	79	98	366	331	90

[a] The first cycle after the formation step.
[b] The 50th cycle after the formation step.
[c] The capacity retention at the 50th cycle.

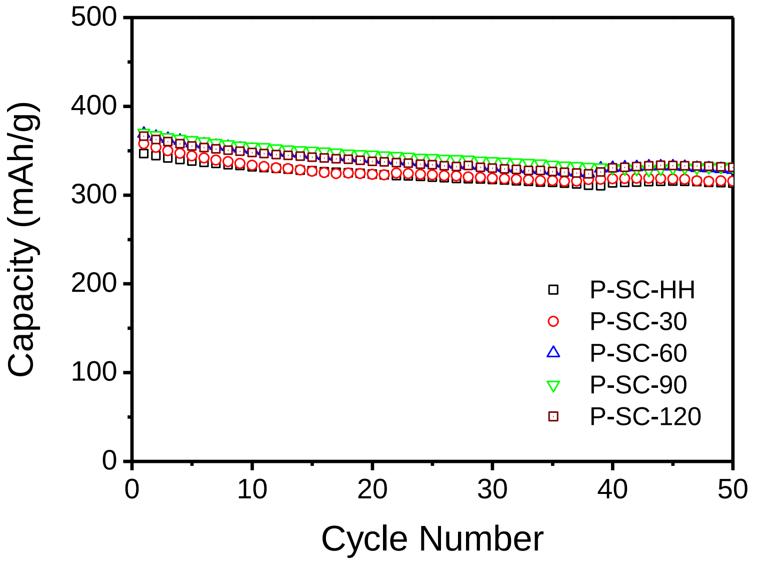

Figure 4. Cycling performance of the P-doped soft carbons (P-SC-HH, P-SC-30, P-SC-60, P-SC-90 and P-SC-120).

Table 1 compares the charge and discharge capacities and cycle life data of the soft carbons prepared. All the preheated carbon samples showed greater reversible capacities (390~400 mAh/g) than that of graphite (360 mAh/g) and very high coulombic efficiency (>98%) after second cycles. Fig. 4 shows cycling behavior of the prepared soft carbons. P-SC-60, P-SC-90 and P-SC-120 showed very large capacities of about 330 mAh/g at 1.0 C after 50 cycles with excellent capacity retention of 90%. It is concluded that optimum preheating reaction time is 60 min in the aspects of preparation costs and electrochemical properties.

4. CONCLUSION

Optimization study for preparation conditions of P-containing soft carbons was carried out in terms of heating rate and preheating reaction time. In order to examine the effect of heating rate on the electrochemical performance of P-doped soft carbons, phosphoric acid-incorporated petroleum cokes were heated to 950°C with two kinds of heating rates of 2.5 and 10 °C/min. Very surprisingly, it was found that dischage (lithium extraction) capacities of the rapidly heated soft carbons were much larger than those of the slowly heated soft carbons. It is thought that the unprecedented result may be originated from the difference in nanostructure such as nanopores which can be controlled by the bonding nature of phosphorus and graphene edges. Furthermore, phosphoric acid-incorporated petroleum cokes were preheated at 200°C for different reaction times of 30 to 120 min and subsequently carbonized at 950°C. All preheated samples showed increased reversible capacities by about 10 to 20 mAh/g compared to the simply heated P-doped carbons without preheating. It was observed that the preheated carbons exhibited similar reversible capacities to one another when heated at 200°C for more than 60 min. In result, optimum preheating reaction time appeared to be 60 min in terms of preparation costs and electrochemical properties. As for cycling performance, the carbons preheated for more than 60 min very large capacities of about 330 mAh/g at 1.0 C after 50 cycles, comparable to those of current graphite anode materials.

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