

## Effect of Preheating Treatment on Electrochemical Performance of Phosphorus-Doped Soft Carbon Anodes

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Phosphorus-doped soft carbons were prepared by preheating treatment of phosphoric acid-incorporated petroleum cokes and subsequent carbonization at 900°C. To find optimum preparation conditions, the preheating process was performed at various temperatures between 150 and 600°C. It was found that the reversible capacities of the P-doped soft carbons significantly depended on the preheating temperature. The reversible capacities of P-doped soft carbons preheated above the decomposition temperature of H<sub>3</sub>PO<sub>4</sub> (158°C) increased, compared with those of soft carbons without preheat treatment, while the reversible capacities of P-doped soft carbons with preheating treatment at 600°C significantly decreased. It was found that the P-doped soft carbons preheated at 200°C showed the larger reversible capacities of 467 mAh/g at 0.2 C, compared with those of other carbons and retained decent reversible capacities of 379 mAh/g at 1 C after 50 cycles.

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

### 1. INTRODUCTION

Rechargeable lithium batteries have made a great contribution to the wireless revolution in cellular phones and portable computers and now triggered an international race for the development of electric cars. Currently, most lithium-ion batteries for electric cars applications provide limited performance in a cruising range and a charge rate[1]. It is thought that without significant improvement in the lithium-ion batteries, the full realization of electric cars will not be possible. The charging performance of the lithium-ion batteries depends on the kinetics of anode reactions. Lithium intercalation into graphite anode slowly proceeds during charging due to narrow interlayer distance of graphite[2-4]. Many alternative carbon materials with high capacity and fast charging performance have been presented. It was concluded from the electrochemical performance data of many kinds of

carbon materials that reversible capacities of soft carbons are directly proportional to the H/C ratio of carbons which depend significantly on carbonization temperature[5-7]. Very interestingly, it was recently proved that reversible capacities and rate capabilities of soft carbons were greatly improved by incorporating a small amount of phosphorus[8,9].

In this work, we report effect of pretreatment temperature on the performance of P-doped soft carbon anode. Petroleum cokes used as a precursor of soft carbons were mixed with a phosphoric acid at room temperature and then preheated at various temperatures between 150 and 600°C before carbonization at 900°C. The electrochemical properties of the resulting carbons were evaluated by using coin-type cells and compared with that of P-doped carbons without pretreatment.

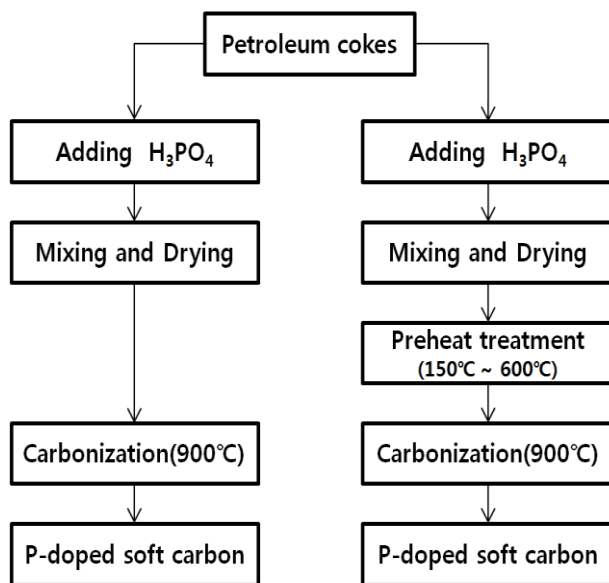
## 2. EXPERIMENTAL SECTION.

The phosphoric acid ( $\text{H}_3\text{PO}_4$ ) was mixed with petroleum cokes (GS Energy, Korea) in triple-distilled water for 10 h with the mass ratio between petroleum cokes and phosphorus (95:5) and dried by agitation at room temperature to get phosphorus-incorporated carbon precursors. The resulting materials were preheated at various temperatures of 150, 175, 200, 250, 400 and 600°C for 1.5 h and then carbonized in the flow of argon at 900°C for 1 h to make phosphorus-doped soft carbons, which are denoted as P-SC-150, P-SC-175, P-SC-200, P-SC-250, P-SC-400 and P-SC-600 (Fig. 1). For control experiment, the phosphorus-doped carbon (P-SC) without pretreatment was made by carbonizing the phosphorus-incorporated petroleum cokes under the same conditions.

The morphology and crystallinity of the prepared carbons were examined by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. SEM images were taken with a scanning electron microscope (Coxem CX-200TA). X-ray diffraction (XRD) experiments were performed in the  $2\theta$  range from 10° to 40° with a PANalytical Empyrean diffractometer.

Electrodes consisted of 90 wt% soft carbons, 2 wt% carbon black (Super-P) and 8 wt% polyvinylidene difluoride (PVDF). N-methyl-2-pyrrolidone (NMP) solvent was used to make homogeneous slurry with an appropriate viscosity. The slurry was casted on 20  $\mu\text{m}$  thick copper foil, dried at 120 °C for 1 h and assembled into coin-type cells (CR2016) with a lithium metal foil as the counter electrode. The mixture solution of ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3:7, v/v, Panax Etec) with 1.0 M  $\text{LiPF}_6$  and 2 wt% vinylene carbonate (VC) was used as the electrolyte.

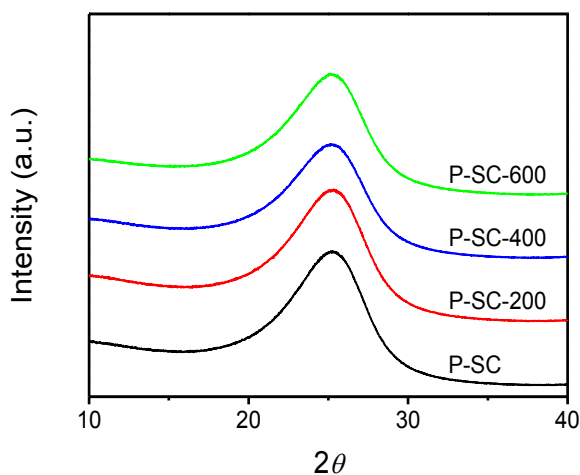
The cells were tested with galvanostatic charge and discharge method in the potential range between 0.005 and 1.5 V vs.  $\text{Li/Li}^+$ . A constant current-constant voltage (CC-CV) mode was applied with a cut-off current of 0.01 C (1 C = 372 mAh/g) at 5 mV vs.  $\text{Li/Li}^+$  during charging (lithium intercalation), whereas a constant current (CC) mode was used during discharging (lithium deintercalation). For the first two cycles considered as formation step in this work, the charge and discharge tests were carried out at a rate of 0.2 C. After that, the cycle performance was examined at 1.0 C for additional 50 cycles.



**Figure 1.** The preparation processes for the P-doped soft carbons

### 3. RESULTS AND DISCUSSION

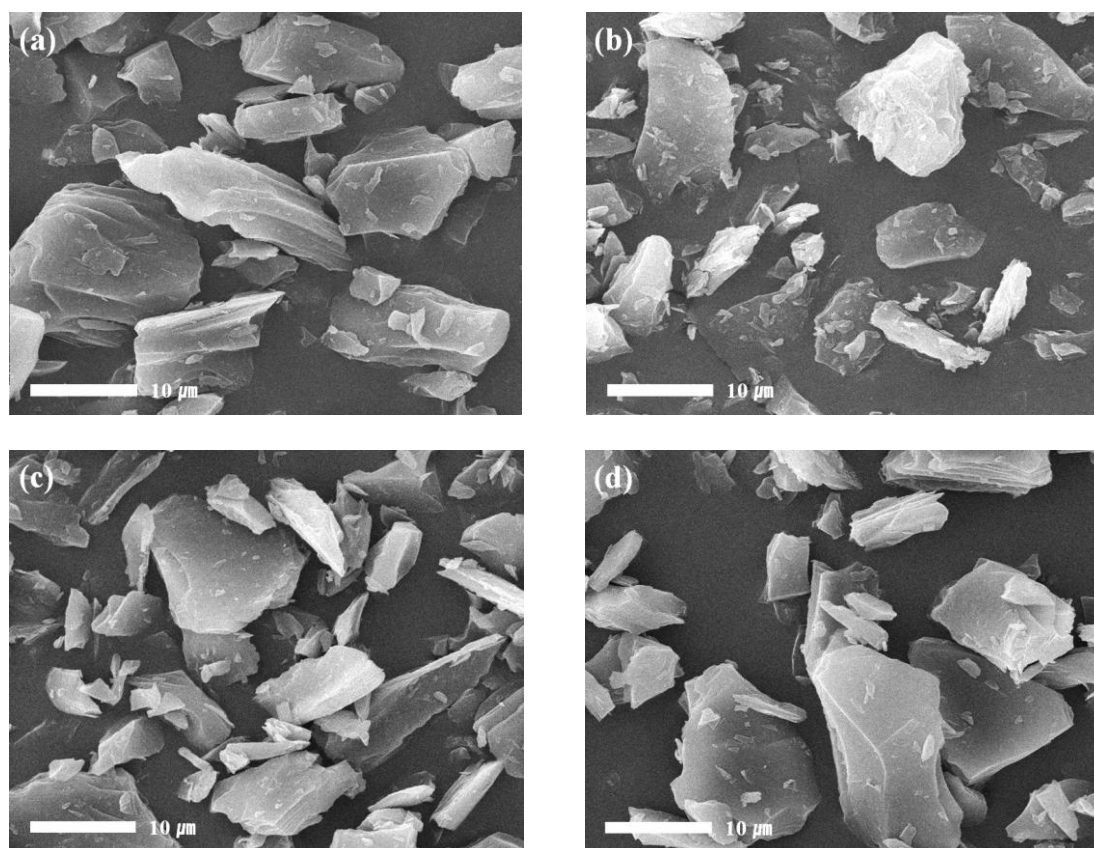
Significant increase in reversible capacities of soft carbons was reported when petroleum cokes used as a carbon precursor were mixed with phosphoric acid ( $H_3PO_4$ ) and then carbonized[8]. It was revealed by the X-ray photoelectron spectroscopy (XPS), high-resolution TEM with EDS spectroscopy and nuclear magnetic resonance (NMR) spectroscopy that the phosphorus moieties, the thermal decomposition products of phosphoric acid, remained in the form of C-O-P or C-P-O bonds at graphene edges[8,10-12]. XRD patterns showed that the crystallinity of soft carbons greatly decreased after the phosphorus doping. It was suggested that the decrease in crystallinity of the soft carbons was attributed to the chemical bonding between the phosphorus species and graphene edges, which created nanopores to store lithium between crystallite domains[8,13,14].



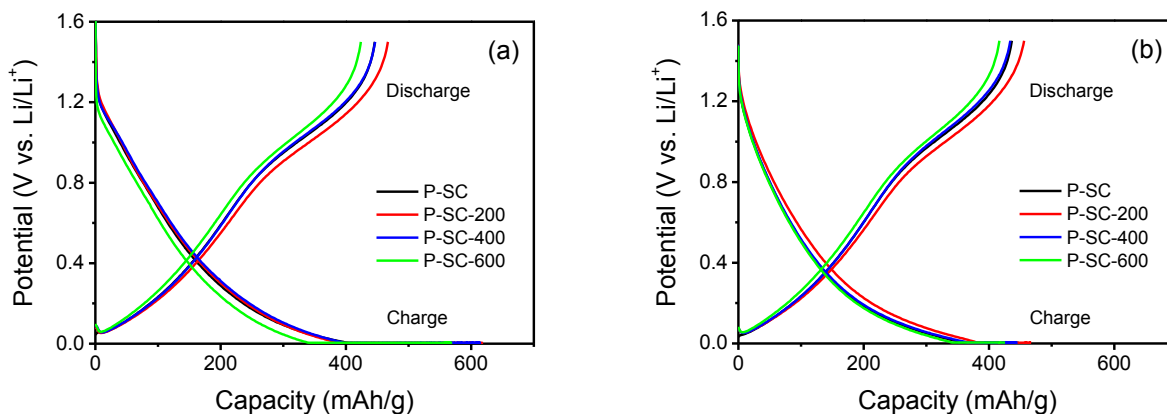
**Figure 2.** XRD patterns of the P-doped soft carbons

In this work, we postulated that the chemical bonding and microstructure of the soft carbons can be affected by the chemical nature of the phosphorus moieties that depend on the decomposition temperature. For this reason, a preheating treatment step at various temperatures between 150°C and 600°C was introduced just before carbonization (Fig. 1). Fig. 2 shows some examples of XRD patterns of the prepared carbons. Any appreciable change in the full width at half maximum (FWHM) of the (002) peaks at  $2\theta = 26^\circ$  was not found after the preheating treatment, implying that the sizes of crystallite were retained before and after the preheating process[15]. SEM images of the phosphorus-doped soft carbons clearly show that the particle morphologies of preheat-treated carbons are very similar to that of the phosphorus-doped carbon without preheating(Fig. 3).

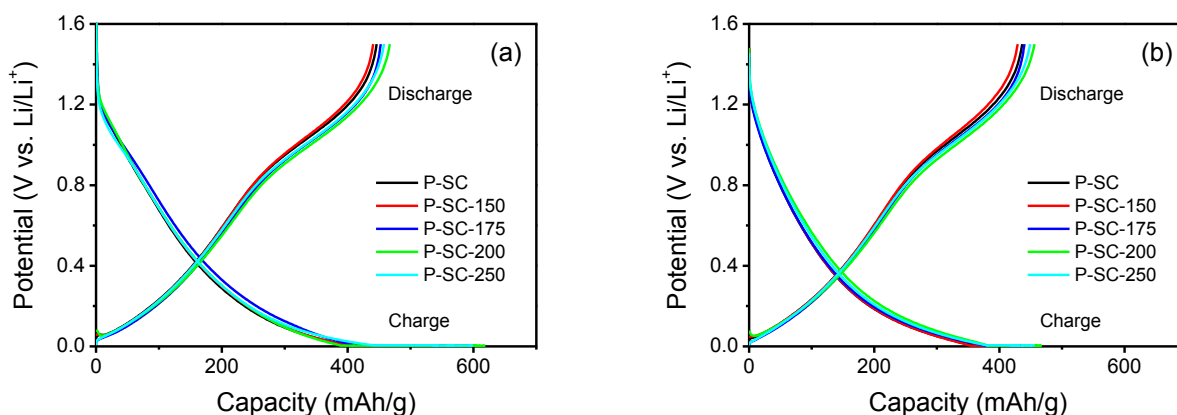
Fig. 4 shows the charge (lithium intercalation)/discharge (lithium deintercalation) curves of the four carbon samples (P-SC, P-SC-200, P-SC-400, P-SC-600) in the first two cycles. It was observed that the reversible capacities (the first discharge capacities) were significantly dependent on the preheating temperature, even though any noticeable difference was not found in the crystallinity and surface morphology of the soft carbons. P-SC-200 showed higher reversible capacities, compared with those of other carbons. On the other hand, P-SC-600 pretreated at 600°C showed the lowest reversible capacities. It is believed that this feature would be attributed to the content of oxygen sensitive to heating temperature which may directly contribute to the formation of C-O-P or C-P-O bonds near graphene edges when considering that the content of phosphorus remains almost constant up to about 1000°C[12].



**Figure 3.** SEM images of the P-doped soft carbons: (a) P-SC; (b) P-SC-200; (c) P-SC-400; (d) P-SC-600

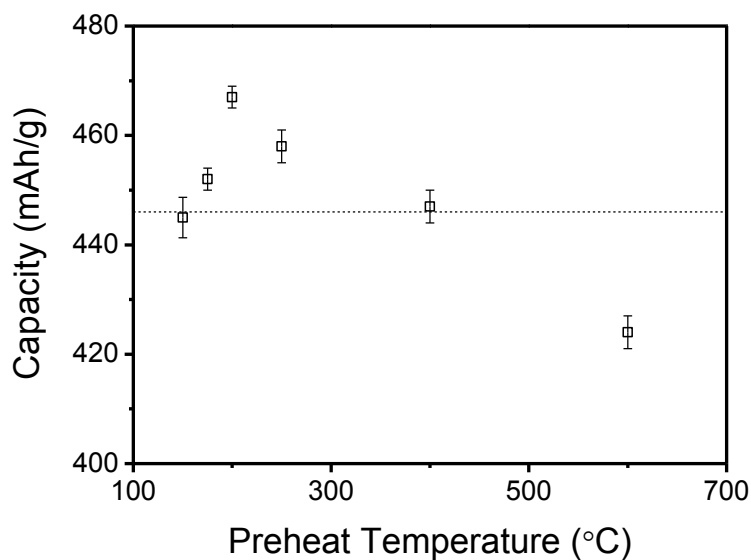


**Figure 4.** The first (a) and second (b) charge/discharge curves for the P-doped soft carbons (P-SC, P-SC-200, P-SC-400 and P-SC-600).

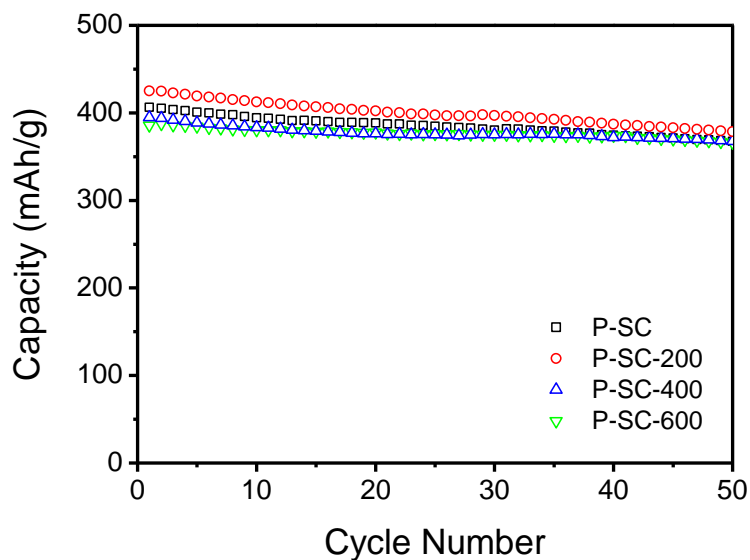


**Figure 5.** The first (a) and second (b) charge/discharge curves for the P-doped soft carbons (P-SC, P-SC-150, P-SC-175, P-SC-200 and P-SC-250).

To find optimum preheating temperature, in addition, the effect of preheating treatment was more closely examined at temperatures (150°C ~ 250°C) near 200°C. P-SC-150 showed very similar voltage profiles and reversible capacities to those of P-SC, while P-SC-175, P-SC-200 and P-SC-250, which were prepared with preheating treatment above the decomposition temperature of H<sub>3</sub>PO<sub>4</sub> (158°C), showed enhanced reversible capacities (Fig. 5), suggesting that the extra reversible capacities may be closely related to the environment of decomposition of H<sub>3</sub>PO<sub>4</sub>. It is suggested that C-O-P or C-P-O bonds would be formed by the reaction between graphene edges and the decomposed products of phosphoric acid[10-12]. The reversible capacities of the pretreated soft carbons were enhanced at the three preheating temperatures (175, 200, 250°C), as shown in Fig. 6. It is estimated from the overall results that the optimum preheating temperature for the P-doped soft carbons may exist around 200°C. A detailed understanding of the optimum preheating temperature on the electrochemical performance of the P-doped soft carbons is not easy and needs multidisciplinary studies.



**Figure 6.** The reversible capacities of the preheated P-doped soft carbons (□) and P-SC (···) prepared without preheating.



**Figure 7.** Cycling performance of the P-doped soft carbons.

Table 1 summarizes the electrochemical performance data of the carbon samples. All the carbon samples showed coulombic efficiency of about 75% at the first cycle and very high coulombic efficiency (>98%) at the second cycle. Fig. 7 shows some examples of cycle performance data of the prepared soft carbons. P-SC-200 and P-SC-250 showed more considerable capacities of about 380 mAh/g at 1.0 C after 50 cycles, compared with other carbons, while their capacity retentions were slightly lower than P-SC, reflecting a general trade-off relation between capacity and cycle life.

**Table 1.** Results of the charge and discharge tests for the soft carbons.

Samples	Preheat temperature (°C)	Capacity (mAh/g)				Coulombic efficiency (%)		Cycle performance		
		1 <sup>st</sup> cycle		2 <sup>nd</sup> cycle		1 <sup>st</sup> cycle	2 <sup>nd</sup> cycle	1 <sup>st</sup> cycle <sup>a</sup> (mAh/g)	50 <sup>th</sup> cycle <sup>b</sup> (mAh/g)	Capacity retention <sup>c</sup> (%)
		Charge	Discharge	Charge	Discharge					
P-SC	-	600	446	447	437	74	98	406	368	91
P-SC-150	150	597	445	439	429	75	98	395	360	91
P-SC-175	175	598	452	447	440	76	98	407	364	89
P-SC-200	200	619	467	467	456	75	98	425	379	89
P-SC-250	250	600	458	456	449	76	98	416	378	91
P-SC-400	400	614	447	444	434	73	98	395	368	93
P-SC-600	600	568	424	426	417	75	98	386	366	95

<sup>a</sup>The first cycle after the formation step consisting of initial two cycles.

<sup>b</sup>The 50th cycle after the formation step consisting of initial two cycles.

<sup>c</sup>The capacity retention at the 50<sup>th</sup> cycle.

#### 4. CONCLUSION

Influence of preheat treatment on the electrochemical performance of P-doped soft carbons was intensively examined. Petroleum cokes and phosphoric acid were used as a precursor of soft carbons and doping agents, respectively. To find optimum pretreatment conditions, phosphorus-incorporated petroleum cokes were preheated for 1.5 h in a wide temperature range from 150 to 600°C and subsequently carbonized under argon atmosphere at 900°C. The reversible capacities of the soft carbons increased when preheated in the temperature range of 175 to 250°C, while the reversible capacities of soft carbons greatly decreased when preheated at 600°C. It was found that when preheated at 200°C, the P-doped soft carbons showed the largest reversible capacities of 467 mAh/g at 0.2 C and considerable reversible capacities of 379 mAh/g at 1 C after 50 cycles.

#### ACKNOWLEDGMENTS

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#### References

1. J.-M. Tarascon, M. Armand, *Nature* 414 (2001) 359.
2. Y. Yu, C.-H. Chen, Y. Shi, *Adv. Mater.* 19 (2007) 993.
3. P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.-M. Tarascon, *Nature* 407 (2000) 496.
4. Y. Idota, T. Kubota, A. Matsufuji, Y. Maekaw, T. Miyasaka, *Science* 276 (1997)1395.
5. T. Zheng, J. S. Xue, J. R. Dahn, *Chem. Mater.* 8 (1996) 389.
6. J. R. Dahn, T. Zheng, Y. Liu, J. S. Xue, *Science* 270 (1995) 590.
7. T. Zheng, W. R. Mckinnon, J. R. Dahn, *J. Electrochem. Soc.* 143 (1996) 2137.
8. Y.-N. Jo, E.-Y. Lee, M.-S. Park, K.-J. Hong, S.-I. Lee, H.-Y. Jeong, Z. Lee, S. M. Oh, Y.-J. Kim, *J. Kor. Electrochem. Soc.* 15 (2012) 207.

9. B. O. Jeong, S. H. Jeong, M.-S. Park, S. Kim, Y. Jung, *J. Nanosci. Nanotechnol.* in press.
10. A. M. Puziy, O. I. Poddubnaya, R. P. Socha, J. Gurgul, M. Wisniewski, *Carbon* 46 (2008) 2113.
11. Y. J. Lee, L. R. Radovic, *Carbon* 41 (2003) 1987.
12. R. Imamura, K. Matsui, S. Takeda, J. Ozaki, A. Oya, *Carbon* 37 (1999) 261.
13. K. Tatsumi, T. Akai, T. Imamura, K. Zaghbi, N. Iwashita, S. Higuchi, Y. Sawada, *J. Electrochem. Soc.* 143 (1996) 1923.
14. A. Mabuchi, K. Tokumitsu, H. Fujimoto, T. Kasuh, *J. Electrochem. Soc.* 142 (1995)1041.
15. Y. Jung, M. C. Suh, H. Lee, M. Kim, S. I. Lee, S. C. Shim, J. Kwak, *J. Electrochem. Soc.* 144 (1997)4279.