

Synthesis of Amorphous Carbon Materials for Lithium Secondary Batteries

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A new and effective approach to enhance electrochemical properties of amorphous carbons is presented. Phosphorus-doped amorphous carbons have been prepared by incorporating a phosphorus compound into petroleum cokes and carbonizing them at 850 °C for 1 h. It was observed that reversible capacity of amorphous carbons was greatly improved by incorporating a very small amount of phosphorus (around 1%), implying that extra lithium-storage-sites were created by phosphorus doping. In addition, the phosphorus-doped amorphous carbons showed outstanding rate capability (205 mA h/g at 5 C) and excellent capacity retention of about 90% after 50 cycles, comparable to that of undoped carbons. Very interestingly, a trade-off relation between capacity and cycle property, which is very common in electrode materials, was not found in the phosphorus-doped amorphous carbons.

Keywords: Amorphous Carbon, Phosphorus, High Capacity, High Rate Capability.

1. INTRODUCTION

Lithium-ion battery industry has been greatly expanded with the unprecedented growth of portable electronic devices such as mobile phones and laptops. At present, lithium-ion batteries are used as a power source in nearly every type of portable devices. Over the past 20 years, the cathode and the anode have used lithium metal oxides (e.g., LiCoO₂) and graphite, respectively. However, present lithium-ion battery technology was faced with several challenges such as cost and performance limitations such as capacity and rate capability.¹ The rapid growth of smart phones and tablet computers has been requiring the development of next generation batteries with high capacity and rate capability. Actual charge rate performance is limited by the lithium insertion rate into graphite. Recently, attractive anode materials, lithium-storage-materials and amorphous carbons, have been presented to replace graphite.²⁻⁴ Silicon-based composites among lithium-storage-materials

have great advantage in capacity, but still present poor performance in terms of cycle life and charge rate capability.⁵ Amorphous carbons have attracted much attention due to their excellent electrochemical properties such as high capacity and high rate capability.^{6,7} In general, it is well known that the reversible capacity and H/C ratio of amorphous carbons significantly decrease as carbonization temperature increases.^{8,9} Especially, it proved that the amorphous carbons with huge capacity show big hysteresis in charge/discharge curves and the reversible capacity is directly proportional to the H/C ratio of amorphous carbons prepared at the temperature below 1000 °C regardless of the type of amorphous carbons.⁹ On the other hand, the cycle property of amorphous carbons tended to be improved with an increase of temperature.

In this work, we report a new approach to improve the electrochemical performance of amorphous carbons. Petroleum cokes, a precursor of amorphous carbons, were impregnated with a phosphorus compound at room temperature and carbonized at 850 °C to make phosphorus-doped

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carbons. Their electrochemical properties were evaluated by using coin-type cells and compared with those of graphite and undoped amorphous carbons.

2. EXPERIMENTAL DETAILS

2.1. Preparation and Characterization of Phosphorus-Doped Amorphous Carbons

The $\text{PO}(\text{OC}_3\text{H}_7)_3$ was used as a doping agent of carbon, which was *in situ* prepared by reacting POCl_3 and isopropyl alcohol (35 mL) for 1 h at room temperature. $\text{PO}(\text{OC}_3\text{H}_7)_3$ was incorporated into petroleum cokes (GS Caltex, Korea) by simply dispersing petroleum cokes in the isopropyl alcohol solution containing $\text{PO}(\text{OC}_3\text{H}_7)_3$. The mixing ratios of POCl_3 and petroleum cokes were 10:90 and 20:80. The total weight of POCl_3 and petroleum cokes was 25 g. The resulting mixture was dried by agitation at room temperature and then carbonized at 850 °C under argon for 1 h to make phosphorus-doped amorphous carbons. The amount of phosphorus element in the carbons was analyzed by an inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Horiba Ultima 2). The two phosphorus-doped amorphous carbons, denoted as PD-AC-L and PD-AC-H, showed phosphorus contents of 0.78% and 1.2%, respectively. Undoped amorphous carbons (UD-AC) were prepared by carbonizing pure petroleum cokes under the same conditions to elucidate the effect of phosphorus doping into the amorphous carbons. The characterization of the prepared carbons was carried out through scanning electron microscopy (SEM), X-ray diffraction (XRD), and elemental analysis. SEM images were collected with a field emission scanning electron microscope (JEOL JSM-7000F). XRD patterns were taken in the 2θ range of 10~40 with a Rigaku Ru200B diffractometer using $\text{Cu K}\alpha$ radiation. The nitrogen sorption tests were carried out with a Micromeritics TriStar to get pore size distribution curves, which was determined by Barrett–Joyner–Halenda (BJH) analysis from the adsorption branch. Elemental analysis was performed by a Perkin Elmer 2400 Series II. The particle size of the prepared carbons was measured by a particle size analyzer (Microtrac S3500).

2.2. Electrochemical Evaluation of Phosphorus-Doped Amorphous Carbons

Electrodes were composed of 90 wt% amorphous carbons or graphite (mesocarbon microbeads, MCMB) as an active material, 2 wt% carbon black (Super-P) as a conducting agent and 8 wt% polyvinylidene difluoride (PVDF) as a binder. To make a composite slurry, active material and carbon black were dispersed in the binder solution, which was prepared by dissolving PVDF in *N*-methyl-2-pyrrolidone (NMP) solvent. The slurry was coated on copper foil with a doctor blade and the carbon electrodes were dried in a convection oven at 120 °C for 1 h. After that, they were pressed, dried at 100 °C

under vacuum for 12 h and assembled into cells. The electrolyte was 1.0 M LiPF_6 in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3:7, v/v, Panax Etec) with 2 wt% vinylene carbonate (VC) as an additive. Coin-type cells (CR2016) were assembled with a lithium metal foil as a counter electrode in an argon-filled glove box. Charge/discharge tests of the cells were conducted in the voltage range between 0.005 and 1.5 V versus Li/Li^+ at 25 °C. A constant current–constant voltage (CC–CV) mode was used for the charge tests, whereas a constant current (CC) mode was used for the discharge test. The CC–CV tests were carried out in two steps: (1) charge to 5 mV under a constant current; and (2) subsequent charge at 5 mV until the current reaches the cut-off value of 0.02 C (1 C = 372 mA h/g). During the first two cycles, the charge (lithium insertion) and discharge (lithium deinsertion) were carried out at rates of 0.1 C and 0.2 C, respectively. Subsequently, the C rate was fixed at 1.0 C for the cycle performance tests. In this work, the third cycle is defined as the first cycle of the cycle tests. For rate capability tests, the charge rates were sequentially changed (0.2 C → 0.5 C → 1.0 C → 2.0 C → 5.0 C) after the first two cycles, whereas the discharge rate was fixed at 0.2 C. The charge rate tests were examined under a CC mode with cut-off voltages of 5 mV.

3. RESULTS AND DISCUSSION

Elemental analysis of the undoped amorphous carbons (UD-AC) and the two phosphorus-doped amorphous carbons (PD-AC-L and PD-AC-H) showed that the H/C atomic ratios were 0.08 in the three carbons (Table I). It was revealed from ICP-AES that PD-AC-L and PD-AC-H contained 0.78% and 1.2% phosphorus within each amorphous carbon, respectively (Table I).

This indicates that *ca.* 40% phosphorus at the PD-AC-L and *ca.* 30% phosphorus at the PD-AC-H remained after carbonization when considering the initial amount of phosphorus within POCl_3 used in the early mixing step. The particle size of the carbons was not affected by phosphorus doping, which was very similar to one another (Table I).

Figure 1 shows XRD patterns for the undoped amorphous carbon and the two phosphorus-doped amorphous carbons. The (002) peaks with similar full width at half maximum (FWHM) due to the stacking of carbon layers were observed at approximately $2\theta = 26^\circ$ in all the three

Table I. Results of composition and particle size analysis for the amorphous carbons.

Samples	Ratio of POCl_3 to coke	H/C atomic ratio	Weight percent of phosphorous (%)	D_{50} (μm)
UD-AC	0:100	0.08	0	5.5
PD-AC-L	10:90	0.08	0.78	5.6
PD-AC-H	20:80	0.08	1.2	5.6

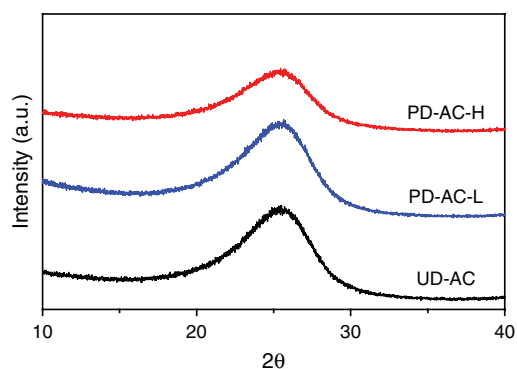


Figure 1. XRD patterns of the amorphous carbons.

carbon samples, implying that the crystallinity of carbon was not affected by the phosphorus doping.

SEM images of the phosphorus-doped amorphous carbons clearly show that the overall particle morphologies and sizes are very similar to those of undoped amorphous carbons (Fig. 2).

Moreover, any remaining phosphorus compounds were not found on the surface of the phosphorus-doped amorphous carbons, suggesting that phosphorus was successfully incorporated into the amorphous carbons. Furthermore, the effect of phosphorus doping on the microstructure of the amorphous carbons was analyzed from nitrogen sorption tests. Very interestingly, the pore size distribution curves showed the great increase in the pore size range of 2 to 4 nm with increasing phosphorus doping levels (Fig. 3).

Figures 4(a) and (b) show the charge (lithium insertion)/discharge (lithium deinsertion) curves of the three carbon samples in the first two cycles. The three carbons showed higher reversible capacities (discharge capacity in the first cycle) more than the theoretical capacity of graphite (372 mA h/g). The undoped amorphous carbon (UD-AC) showed the charge/discharge curves with large hysteresis related to high hydrogen content. The effect of hydrogen content on electrochemical properties of amorphous carbons was well described by Zheng et al.¹⁰ Very interestingly, it was found that the reversible capacity of the amorphous carbons was significantly increased as the content of incorporated phosphorus was increased. PD-AC-L and PD-AC-H showed the extra reversible capacities of 40 and 63 mA h/g, respectively. It is thought that this feature may arise from the nano-sized pores to store additional lithium which were generated by phosphorus doping. The extra capacities were observed in the high potential range between 0.6 and 1.5 V (Fig. 4(c)).

Table II summarizes the results of the charge/discharge tests for the carbon samples. The coulombic efficiency for the first cycle was about 75% as a result of the high irreversible reaction, which very typical for amorphous carbon samples with small particle sizes (*ca.* 5.5 μm). All the carbon samples showed very high coulombic efficiency (>97%) since the second cycle, indicating that

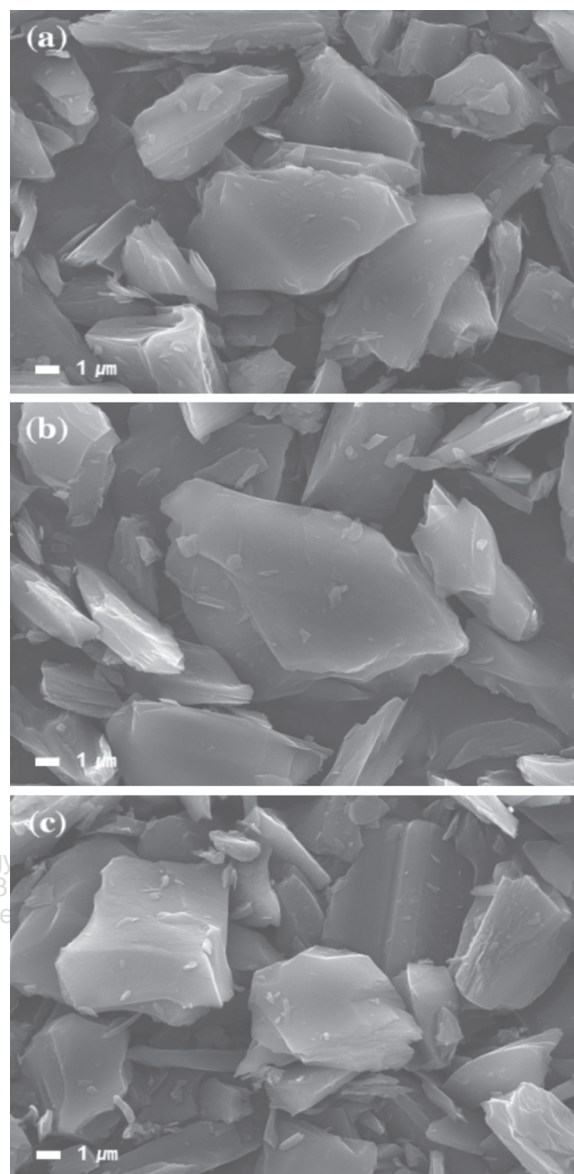


Figure 2. SEM images of the amorphous carbons: (a) UD-AC; (b) PD-AC-L; (c) PD-AC-H.

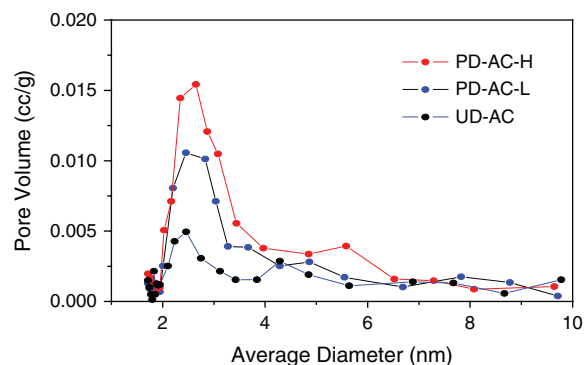


Figure 3. Pore size distribution of the amorphous carbons.

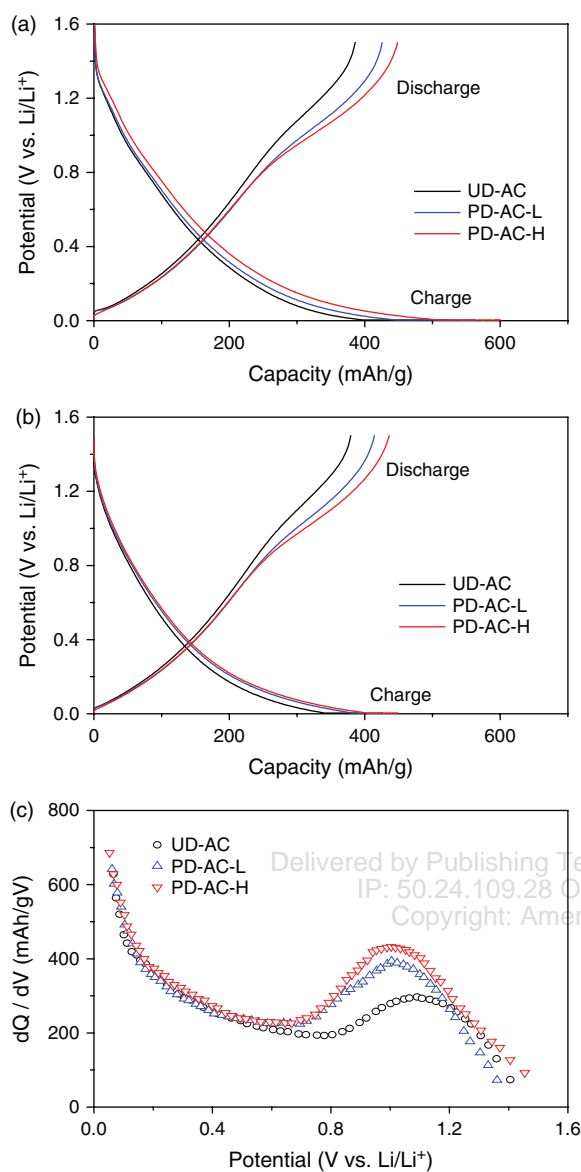


Figure 4. First (a) and second (b) charge/discharge curves of the amorphous carbons, and dQ/dV plots (c) for the first discharge curve.

a stable solid electrolyte layer was generated during the first charge. Charge rate capability of the three amorphous carbons was examined with varying C rates and compared with that of graphite.

All the amorphous carbons exhibited so much higher charge capacities more than 160 mA h/g even at 5 C,

Table II. Results of the charge/discharge tests for the amorphous carbons.

Samples	Capacity (mA h/g)				Coulombic efficiency (%)	
	1st cycle		2nd cycle		1st cycle	2nd cycle
	Charge	Discharge	Charge	Discharge		
UD-AC	523	386	391	379	74	97
PD-AC-L	563	426	427	414	76	97
PD-AC-H	601	449	449	436	75	97

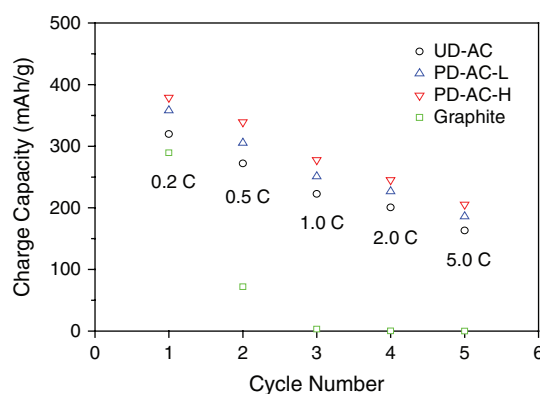


Figure 5. Rate capability of the amorphous carbons.

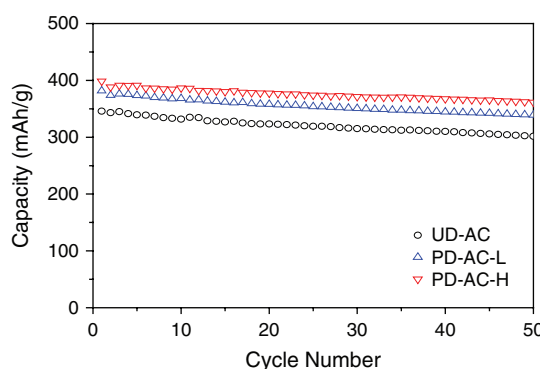


Figure 6. Cycle performance of the amorphous carbons.

which correspond to > 50% of capacities measured at 0.2 C (Fig. 5). Especially, the PD-AC-H showed a huge charge capacity (205 mA h/g) at 5 C. This suggests that the P-doped amorphous carbons may be usefully used in the electronic devices (e.g., smart phones, electric vehicles) to need a short charge time. Similar capacity reduction (< 50%) was observed in the three amorphous carbons regardless of phosphorus doping when the C rate was changed from 0.2 to 5 C. In contrast, graphite showed very poor capacities less than 20 mA h/g even at 1.0 C. It is thought that the outstanding rate capability of the amorphous carbons may arise from the relatively fast lithium insertion into amorphous carbons with much bigger interlayer distance.

Figure 6 shows the cycle performance of the three amorphous carbons. After 50 cycles, the two phosphorus-doped amorphous carbons showed an excellent capacity retention

of about 90% which is similar to that of undoped carbon. In general, there is a trade-off between high capacity and high cycle life. It is noteworthy that the phosphorus doping method developed in this work did not show the trade-off relation.

4. CONCLUSION

We have developed a new method to improve electrochemical performance of amorphous carbons. Petroleum cokes were used as a precursor of amorphous carbons. $\text{PO}(\text{OC}_3\text{H}_7)_3$ prepared by reacting POCl_3 and isopropyl alcohol was incorporated into petroleum cokes and then the resulting petroleum cokes were carbonized at 850 °C to make phosphorus-doped amorphous carbons. The amorphous carbons containing 1.2% phosphorus showed much higher reversible capacity (449 mA h/g), compared to that of undoped carbons (386 mA h/g). It was observed that the extra capacity of the amorphous carbons was increased with an increase of the content of incorporated phosphorus. The P-doped amorphous carbons presented outstanding rate capability, compared to graphite, suggesting the possibility of applying the P-doped carbons to anode materials for high-power-density battery as well as high-capacity battery. In addition, the P-doped

amorphous carbons (P content = 1.2%) showed an excellent capacity retention (>360 mA h/g) after 50 cycles.

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