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Highly Stable Performance of Supercapacitors from Phosphorus-Enriched Carbons

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A supercapacitor is an energy storage device storing the energy by accumulation of charges at the electrode/electrolyte interface.[1] Because the capacitance is proportional to the surface area of the electrode, porous carbons have attracted much attention for this application.[2] Oxygen functionalities are often present on the carbon surface, and their effect on the capacitive performance must be considered as they take part in the Faradic interactions and thus significantly increase the specific capacitance of carbons in acidic aqueous supercapacitors.[3] In addition, nitrogen-containing surface functional groups on carbon have attracted much interest due to their enhancing effect on capacitance in both aqueous[4] and organic electrolytes.[5a,b] Recently the negative impact of nitrogen heteroatoms in organic electrolytes was also reported.[5c]

We report herein the electrochemical performance of phosphorus-rich carbons (P-carbons) prepared by phosphoric acid activation of three carbon precursors of different origins, namely fruit stones (FS), styrene-divinylbenzene copolymer (SC) and bismelimido-diphenylmethane-divinylbenzene copolymer (BC) at 800 °C. The resultant samples are denoted as FS-P, SC-P, and BC-P, respectively. Their P-free counterparts synthesized from the same precursors and at the same temperature without addition of H_3PO_4 are named FS, SC, and BC, respectively. Commercial microporous carbon Norit (Norit RB3) is used as comparison.

As shown previously[6] and displayed in Table 1, H_3PO_4 activation introduces not only micropores but also phosphorus-containing functional groups to the carbon. The N_2 adsorption isotherms of P-carbons and Norit (Figure S1a in the Supporting Information (SI)) belong to a mixed type corresponding to microporous carbons with certain meso- and macroporosity. The CO_2 adsorption (Figure S1b, SI) revealed the presence of pores less than 1 nm wide in all samples but to different extents. The micropore volumes calculated from N_2 and CO_2 isotherms by the DR method ($V_{\mu pN_2}$, $V_{\mu pCO_2}$) indicate that SC-P possesses narrow microporosity with ultramicropores not accessible to nitrogen molecules. On the other hand, FS-P, BC-P, and Norit are characteristic of wide microporosity with a large volume of supermicropores not filled with CO_2 at 273 K below the atmospheric pressure.[7] These observations are supported by the pore size distribution curves calculated by the DFT method from N_2 adsorption (Figure S2a, SI) and CO_2 adsorption (Figure S2b, SI). The presence of phosphorus in carbon is confirmed by elemental analysis in moderately high amounts between 6.18% and 8.65%. Previously we understood that phosphorus in carbons is unambiguously present in the form of phosphate PO_4/polyphosphate $(PO_3)_n$ functional groups.[6a−c,8] Correspondingly high contents of oxygen are present in all samples (Table S1, SI). In addition to oxygen in phosphate groups, BC-P contains 15.5% of oxygen bonded to carbon.

Table 1. Structural Parameters, Phosphorus Contents, and Specific Capacitances Expressed per Single Electrode of P-Containing Carbons, P-Free Carbons, and Norit

sample	S_{BET} [m^2/g]	V_{total} [cc/g]	$V_{\mu pN_2}$ [cc/g]	$V_{\mu pCO_2}$ [cc/g]	P [wt%]	C [F/g]
FS	4	0.02	0.03	0.23	0.00	64
FS-P	1055	0.55	0.39	0.28	8.52	192
SC	351	0.38	0.14	0.20	0.00	36
SC-P	434	0.44	0.17	0.20	8.65	212
BC	247	0.17	0.10	0.22	0.00	12
BC-P	633	0.31	0.26	0.21	6.18	220
Norit	697	0.40	0.38	0.19	0.00	140

The specific capacitances expressed per single electrodes (C) calculated from the specific capacitances of cell ($C_{cell\text{-}spec}$) in 1 M H_2SO_4, at a current load of 1 A/g and cell voltage of 1 V, are also displayed in Table 1. Significantly higher capacitance values are obtained from P-carbons than from P-free carbons or Norit. The best performing BC-P possesses a capacitance of 220 F/g. On the other hand, Norit with similar S_{BET} and $V_{\mu pCO_2}$ but more total pore volume gives only 140 F/g. Most interesting and extraordinary is that the supercapacitors from P-carbons could operate at potentials larger than the theoretical decomposition potential of water (1.23 V). Figure 1a depicts the example of the cyclic voltammograms of BC-P recorded at cell voltages of 1.3 and 1.5 V. It is clear that BC-P provides almost rectangular shape voltammograms unlike Norit, which could not withstand 1.2 V as evidenced by the electrolyte decomposition peak above 1 V.

To investigate the extraordinary electrochemical stability of P-carbons, the galvanostatic cycling was performed. The cells were subjected to 5000 cycles at a voltage of 1 V followed by 5000 cycles at 1.2 V and finished by 5000 cycles at 1.3 V. A current load of 5 A/g was applied. The results summarized in Figure 1b confirm the very stable performance of P-carbons at such harsh conditions demonstrating their electrochemical robustness and stable capacitive performance. The particular stability of FS-P (Figure S3, SI) can be explained by the absence of oxygen groups such as quinone, which are electrochemically active[3a] but not stable and can cause capacitance deterioration. This is also supported by the highest capacitance of BC-P but with a poorer cycling performance. The capacitance drop of SC-P can result from the presence of ultramicropores limiting the accessibility to the surface[9] with cycling at a high current load. These findings imply that P-carbons with optimized porosity should be free of oxygen atoms bonded to carbon for stable and long cycle life performance.

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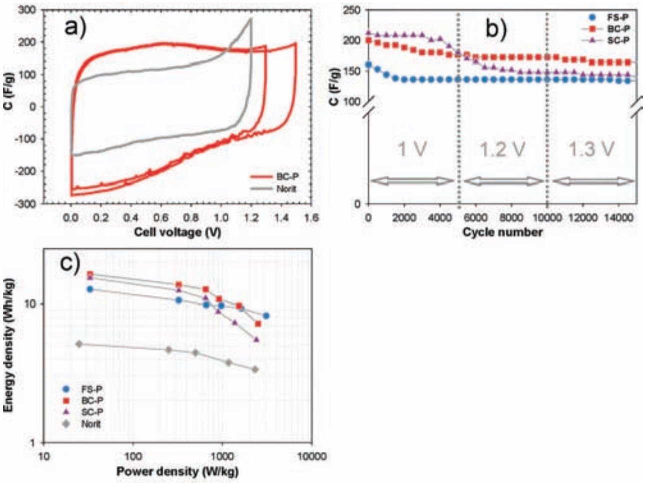

Figure 1. (a) Cyclic voltammograms of BC-P recorded at the 5 mV/s and the cell voltage of 1.3 and 1.5 V compared with Norit at 1.2 V. (b) Galvanostatic cycling at the current load of 5 A/g and cell voltage of 1, 1.2, and 1.3 V. (c) Ragone plots of P-carbons and Norit. Energy and power densities of P-carbons were calculated from $C_{\text{cell-spec}}$ obtained at a cell voltage of 1.3 V and current loads between 0.01 and 10 A/g. In the case of Norit, the cell voltage was kept at 1 V.

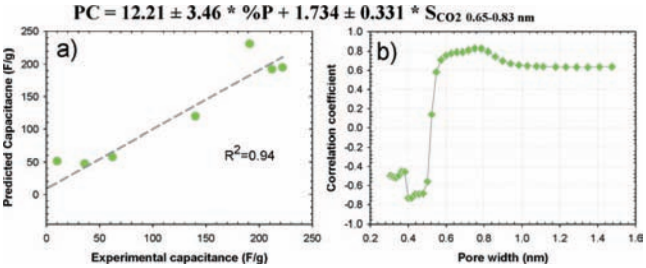

Figure 2. Results of the statistical analyses. (a) Predicted capacitance vs experimental capacitance for series of investigated carbons. (b) Dependence of the correlation coefficient between the surface area of pores of definite width from CO_2 adsorption and the experimental capacitance.

The widening of the cell voltage has a great impact on the energy density of the supercapacitor as it is proportional to the square of the cell voltage.[1] The combined effect of large capacitance and wide operational voltage of P-carbons results in energy densities 3 times larger than that of Norit and reaching 16.3 Wh/kg at the power density of 33 W/kg in BC-P (Figure 1c). FS-P shows the most stable performance maintaining 8.2 Wh/kg at 3100 W/kg.

To understand the key factor influencing capacitance and to confirm the effect of phosphorus on capacitive performance, we used statistical analysis with an intercept-free multiple linear regression model on the experimental data (Experimental section, SI). A significance test of individual regression coefficients shows that among all factors taken into account (% P, % O, surface area of pores of 0.5−0.6 nm, 0.77−0.84 nm, 1.34−1.55 nm, 6.5−8.2 nm from N_2 adsorption isotherms, the surface area of pores of 0.65−0.83 nm from CO_2 adsorption), the content of phosphorus (% P) and the surface area of pores of 0.65−0.83 nm from CO_2 adsorption ($S_{CO_2\,0.65-0.83}$) are the most significant for the prediction of capacitance. The corresponding correlation and the calculation for the predicted capacitance (PC) are shown in Figure 2a. The analysis corroborates the strongest impact of P on experimental capacitance implying the pseudocapacitance from phosphorus functional groups, the mechanism of which is yet to be fully understood. The pores between 0.65 and 0.83 nm from CO_2 adsorptions are confirmed to be the most effective in a double-layer formation in all carbons under investigation. This is supported by an independent analysis of correlation between the capacitance and the surface area of pores of definite width displayed in Figure 2b and Figure S4. The result relates well with the stable performance of FS-P and the latest understanding of the importance of pores less than 1 nm on the capacitive performance of carbons.[10] The exciting possibility of widening the potential window can be explained on the basis of enhanced oxidation stability of P-carbons at positive potentials due to the blockage of active oxidation sites by phosphate groups, the characteristics exploited in many applications,[11] and the adsorption of hydrogen at negative potential.[12]

In summary, we report the extraordinary supercapacitive performance of phosphorus-rich microporous carbons prepared by a simple H_3PO_4 activation method. Such supercapacitors are capable of stable operation at voltages larger than 1.3 V in H_2SO_4. Phosphorus has been confirmed to have the strongest influence on capacitance together with micropores 0.65−0.83 nm in width that are the most effective in forming the electric double layer. This is the first finding that carbons enriched with phosphorus groups and optimized porous structure have a uniquely high and stable performance in electrochemical energy storage devices such as supercapacitors.

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Supporting Information Available: Experimental section, gas sorption measurements, electrochemical characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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