



Short communication

Improvement of capacitance value as the electrode of an electrochemical capacitor by mixing starch with guanidine phosphate

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ABSTRACT

Starch or starch mixed with phosphoric acid, guanidine carbonate, or guanidine phosphate is heat-treated for use as an electrode in an electrochemical capacitor. In the case of starch, the capacitance value is low (31.2 F g^{-1} at 50 mA g^{-1}). However, the capacitance value significantly increases with the addition of guanidine phosphate, which can act as a flame-retardant (124.1 F g^{-1} at 50 mA g^{-1}). The method used in this study, which involves mixing with a flame-retardant by immersion, should be a promising candidate for improving of the capacitance value of starch-derived carbon.

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1. Introduction

Electrochemical capacitors, such as the electrical double layer capacitor (EDLC), have recently attracted much attention as energy-storage devices. Therefore, research has been carried out to increase the capacitance of these electrochemical capacitors. In particular, improvement of the electrode material is the most important approach for the capacitance enhancement. It has been reported that the addition of a hetero element such as N, P, etc., is effective for improving the capacitance [1–3]. As for N-containing electrodes, most of the research has involved using nitrogen-containing resins, such as melamine resin and polyacrylonitrile, as precursors [1–3]. As for the addition of P, inorganic compounds, such as phosphoric acid, have been used as the P source [4–6]. However, in most of the studies using phosphoric acid, the purpose of the addition was for activating the carbon material [5,6].

Flame-retardant is used to prevent fire disasters from becoming worse. It is known that guanidine phosphate has a flame-retardant effect on cellulose, including paper products. When guanidine phosphate is used as a flame-retardant, cellulose products, such as paper and wood, are dipped in a water solution of guanidine phosphate and then dried at room temperature. It is considered that guanidine phosphate encourages the dehydration reaction of cellulose, resulting in the formation of a C=C bond. As a result of this chemical reaction, the combustion reaction is retarded. Guanidine phosphate ($((\text{C}(\text{NH})(\text{NH}_2)_2)_2\text{H}_3\text{PO}_4)$) contains three N atoms and a P

atom in its chemical structure. If this flame-retardant treatment is effective for the reforming of a carbon material, it can also be used as a new approach to synthesizing the electrodes of electrochemical capacitors. In this letter, we report that the capacitance value of carbon materials derived from starch is significantly improved with the addition of guanidine phosphate.

2. Experimental

Starch (Starch, soluble; Wako) was mixed with guanidine carbonate or guanidine phosphate at the weight ratio of 20:1, and the mixed powder was then added to distilled water. The amount of the water added was sufficient to cover the mixed powder. The slurry mixture was manually mixed for ca. 3 min. In the case of phosphoric acid, the mole number of P in the added phosphoric acid water solution was the same as that in the added guanidine phosphate. The slurry was dried in a dryer at 80°C until the slurry became dry (approximately 72 h). The dried powder was then heated at 800°C for 1 h under flowing N_2 (50 mL min^{-1}). The heating rate was ca. $20^\circ\text{C min}^{-1}$. The samples prepared only from starch, and those prepared from starch mixed with phosphoric acid, guanidine carbonate, and guanidine phosphate are subsequently referred to as S-800, S-P800, S-N800, and S-PN800, respectively. Moreover, activated carbon (Charcoal, activated, powder; Wako) are referred to as AC, and as for the samples washed with hot water “W” is added after the reference, for example, S-PN800 → S-PN800W. The powders were used for the BET and CHN-corder measurements. The powder prepared by the heat treatment, acetylene black, and Teflon powder were mixed at a weight ratio of 8:1:1 to make the sheet. The sheet was cut ($20 \text{ mm} \times 8 \text{ mm} \times 0.5 \text{ mm}$) and then

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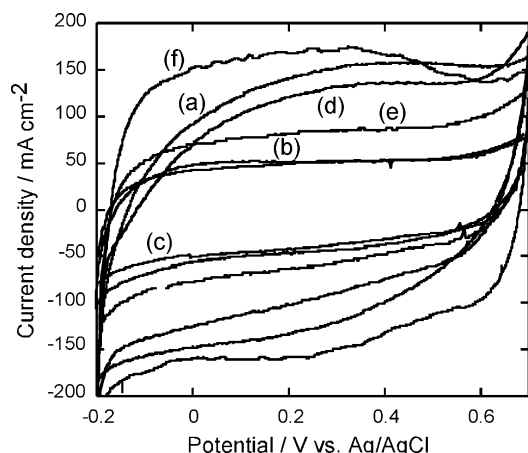


Fig. 1. Cyclic voltammetric measurements. (a) AC; (b) S800; (c) S-P800; (d) S-N800; (e), S-PN800; (f), S-PN800W.

used as the electrode for the electrochemical measurements, such as the cyclic voltammetric (CV) measurements and galvanostatic charge/discharge cycles. The CV measurements and galvanostatic charge/discharge cycles measurements were performed in a 1 M H_2SO_4 water solution, and a Pt plate was used as the counter electrode and the Ag/AgCl electrode was used as the reference electrode. A Pt plate was used as the collecting electrode. The electrical conductivity of the sheet samples was measured by the DC four-probe method. Other measurements were also performed (SEM, IR, XRD, XPS).

3. Results and discussion

The results of the cyclic voltammetric measurements are shown in Fig. 1. Most of the graphs are almost rectangular in shape with no distinct peaks. The reported CV graphs for the N-containing carbon show a deformed square with a slanted line in the lower section [1,3]. As for S-PN800W, the CV graph showed a slight deformation. However, the degree of deformation was small compared to the reported CV graphs. From Fig. 1, we can confirm that no electrolysis reaction of the electrolyte solution, which was water in this case, progressed in the voltage range utilized in the present study (from -0.2 V to 0.6 V vs. Ag/AgCl).

The experimental results of the galvanostatic charge/discharge cycles are shown in Fig. 2. The charge/discharge measurements were performed in the voltage range of 0 – 0.6 V vs. Ag/AgCl. At 50 mA g^{-1} , the capacitance slightly increased with the addition of phosphoric acid, and then significantly increased with the addition of guanidine carbonate or guanidine phosphate. These results seem to indicate that its immersion with the guanidine carbonate or guanidine phosphate is effective for enhancement of the capacitance.

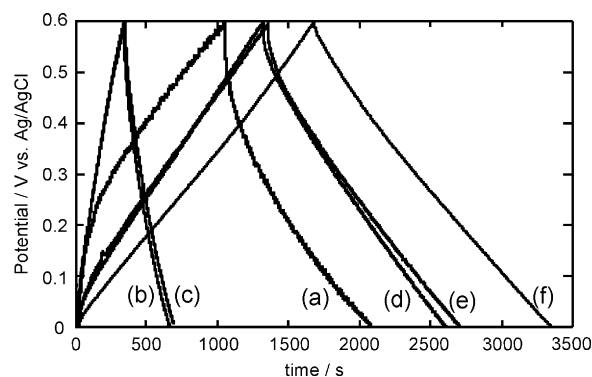


Fig. 2. Galvanostatic charge/discharge cycles. (a) AC; (b) S800; (c) S-P800; (d) S-N800; (e), S-PN800; (f) S-PN800W.

In order to quantitatively discuss the effects of the addition, the capacitances are summarized in Table 1. The capacitance value for the sample prepared from only starch is much lower than that for AC. The capacitance value was almost independent of the addition of phosphoric acid (S-P800). However, after the washing process with hot water, the capacitance values and specific surface area significantly increased (S-P800W). It is known that phosphoric acid can act as an activator for making activated carbon, which has a high specific surface area. The main reason for the low capacitance of S-P800, therefore, is likely the existence of impurities derived from the phosphoric acid. Moreover, the increase in the capacitance values and the increase in specific surface area with the washing process should be reasonable because the impurities which should have low specific surface areas were removed. When guanidine carbonate (S-N800) or guanidine phosphate (S-PN800) was added, the capacitance value increased fourfold. In particular, S-PN800 had the highest capacitance values. Moreover, the ratio of the capacitance calculated from the discharge process and the capacitance calculated from the charge process (C_-/C_+) increased with the addition of guanidine carbonate or guanidine phosphate. It has been reported that N-containing carbon material had high capacitance. For S-N800, the N doping may be the reason for the improvement. The performance of S-PN800 was further improved after washing with hot water (S-PN800W). We can therefore conclude that the performance as a capacitor electrode improves with the addition of guanidine carbonate or guanidine phosphate.

The specific surface area of the S-PN800 was higher than those of the other samples mixed with the additives. This may be one of the reasons for the highest capacitance value of the sample. The reason for the high capacitance might be the combination of the effect of P (mainly activation) and the effect of N (N doping). After washing with hot water, the specific surface area significantly increased and the capacitance values slightly increased. The improvement, therefore, could mean that a soluble compound that cannot act as a capacitor was removed from the sample. The electrical resistances of the sheet-type electrodes, which contain acetylene black as an

Table 1
The capacitance values, electrical conductivities, and specific surface areas of the samples.

Sample	50 mA g^{-1}			500 mA g^{-1}			R ($\Omega \text{ m}$)	S ($\text{m}^2 \text{ g}^{-1}$)
	C_+ (F g^{-1})	C_- (F g^{-1})	C_-/C_+ (%)	C_+ (F g^{-1})	C_- (F g^{-1})	C_-/C_+ (%)		
AC	98.3	66.6	67.7	34.1	11.2	32.8	9.06	1433
S-800	31.2	19.9	63.7	13.4	5.5	41.0	0.0130	490
S-P800	32.4	21.4	65.7	14.4	7.5	52.1	0.185	376
S-N800	116.1	91.5	78.8	47.2	14.1	29.9	0.372	457
S-PN800	124.1	93.4	84.5	83.3	36.1	43.3	0.0201	871
S-P800W	87.3	76.6	87.7	75.4	47.0	62.3	0.243	827
S-N800W	115.1	100.0	86.7	93.2	42.9	46.1	0.142	564
S-PN800W	138.4	125.0	90.3	121.3	67.3	55.4	0.0410	1537

Table 2

The percentages of C, H, N, and others of the samples and the yields (weight after heat treatment/weight before heat treatment) of the samples.

Sample	C (wt.%)	H (wt.%)	N (wt.%)	Others (wt.%)	Yield (%)
AC	86.25	2.12	0.63	11.00	–
S800	90.25	1.25	0	8.50	12.20
S-P800	79.63	1.83	0	18.54	26.68
S-N800	76.41	1.89	4.10	17.60	16.30
S-PN800	75.56	1.55	3.98	18.91	25.86
S-P800W	78.05	2.21	0.75	18.99	–
S-PN800W	76.55	2.28	4.26	16.91	–

electrical conductive aid, are listed in Table 1. The values of the electrical resistance for all the samples treated from starch were lower than that for AC. The lower electrical resistance may be one of the reasons for the high capacitance value of S-PN800 because a low electrical resistance should suppress the IR drop and this suppression should result in an increased ratio of the capacitance calculated from the charging process to that from the discharging process (C_-/C_+).

The weight percents of C, H, and N in the samples were measured by a CHN-corder. The results are listed in Table 2. There is no N atom in S800 and S-P800. These results are reasonable because there is no N atom in these raw materials. The weight percentages of the other elements increased and that of carbon decreased with the addition of phosphoric acid. We can presume from the components of the raw material (starch mixed with phosphoric acid) that the “others” contained O and P. In the case of S-N800 and S-

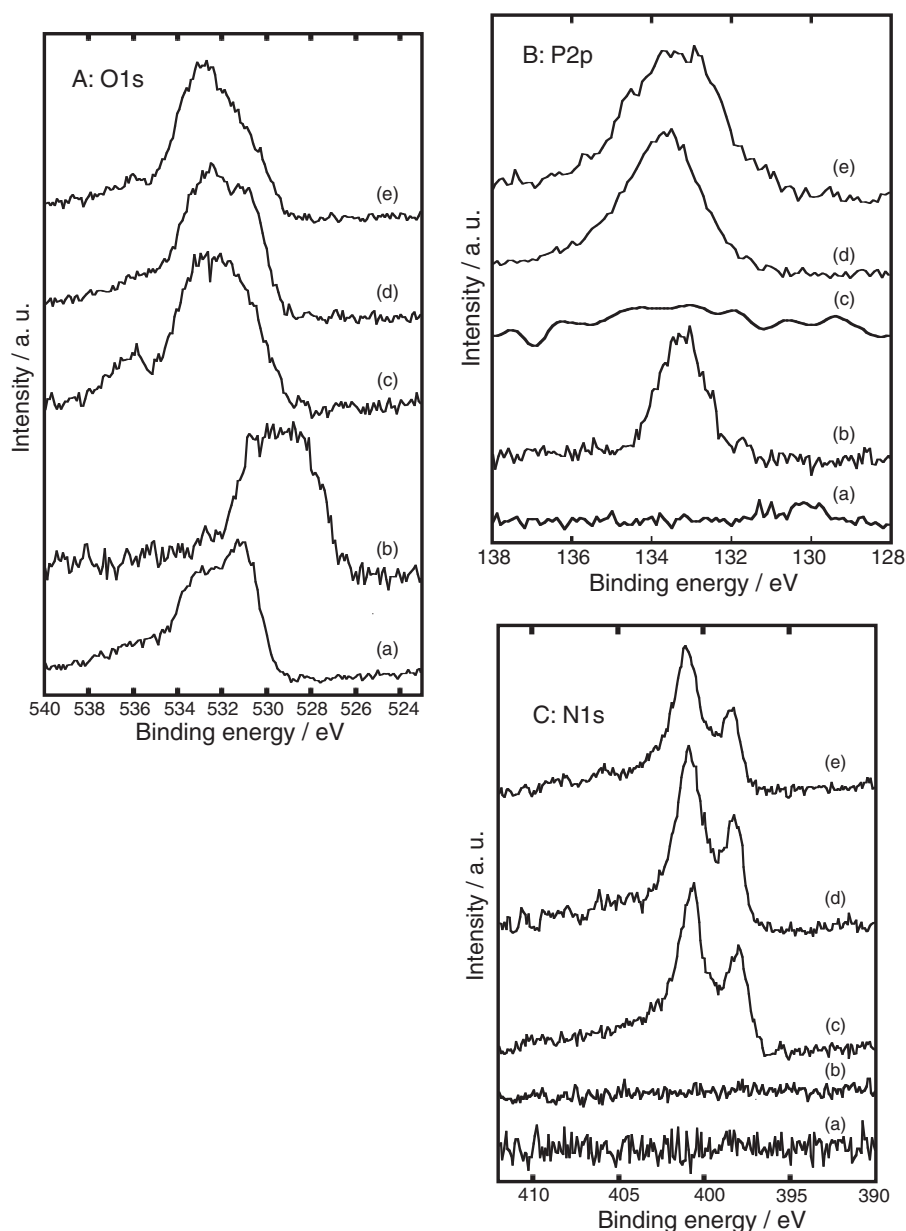


Fig. 3. XPS spectra of the samples. (a) S800; (b) S-P800; (c) S-N800; (d) S-PN800; (e) S-PN800W.

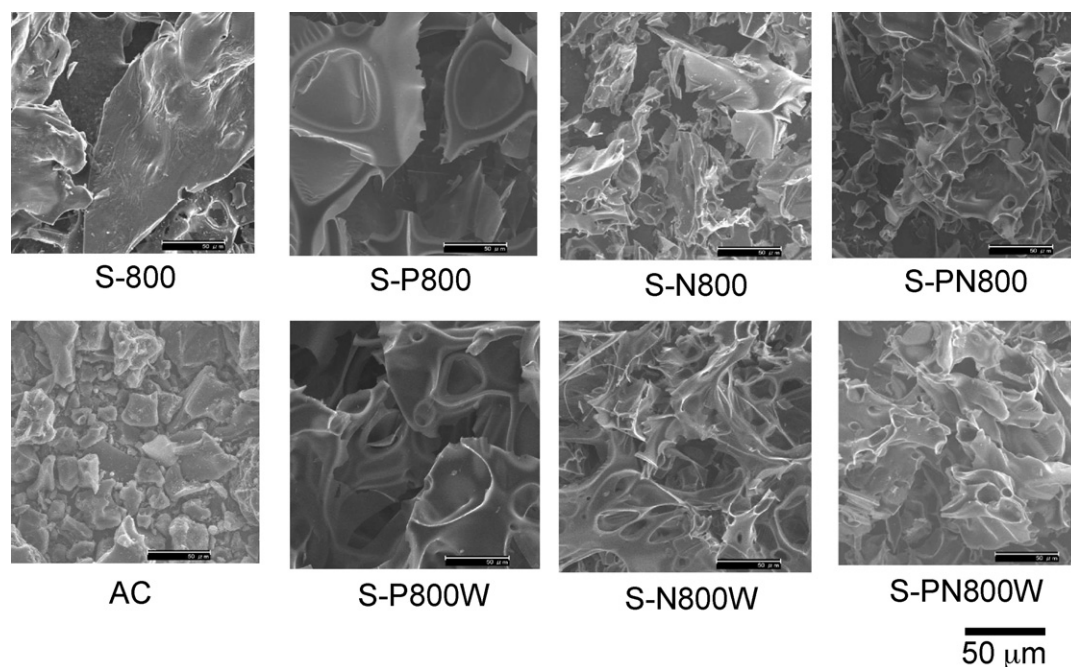


Fig. 4. SEM images of the samples.

PN800, the samples contained approximately 4 wt.% of the N atom. It has been reported that an N-containing carbon material has a high performance as the electrode of an electrochemical capacitor [1]. One of the reasons for the considerable enhancement of the capacitance is the existence of nitrogen in the samples. The number of N atoms in this study (*ca.* 4 wt.%) was much lower than that of the reported sample (*ca.* 7–30 wt.%) [1]. For the reported sample, the CV graph showed a distinctive shape, that is, a deformed square with a slanted line in the lower section. The CV graph of S-PN800W showed minimal deformity. Because the amount of nitrogen in S-PN800W is lower than that in the reported samples, the degree of deformity may be small. One of the reasons for the capacitance enhancement, therefore, should be the existence of nitrogen. The origin of the N atoms was likely the additive, that is, guanidine carbonate or guanidine phosphate. The remaining efficiency of the N atom for guanidine carbonate, therefore, should be almost the same as that for guanidine phosphate. Moreover, the weight percentages of C, H, N, and the other elements of S-N800 are almost the same as those of S-PN800. In the case of S-N800, the “others” could contain O. On the other hand, in the case of S-PN800, the “others” could contain O and P. No existence of P in S-N800 may be the reason for the low “others” value of S-N800 compared with those of S-P800 and S-PN800. As for S-PN800, all the weight percentages were almost unaffected by the washing process. The reason for the enhancement of the capacitance by the washing process may be that the residues that cannot contribute to the storage, the amount of which should be small, dissolve into the hot water. We think that the residue derived from the addition existed in small pores, so the volume is not very large, but the specific surface area significantly increases when the residue is removed.

So far, several explanations have been proposed as the reasons for the enhancement of the capacitance by N doping [7], that is, (i) an improvement in wettability, (ii) a decrease in the equivalent series resistance of a capacitor cell, (iii) the occurrence of a space-charge-layer capacitance, and (iv) the occurrence of a pseudocapacitance. XPS measurements were performed for the investigation of the binding state of elements. XPS spectra for the samples are shown in Fig. 3. All the samples had the peak assigned to O atom in the XPS spectra (Fig. 3a). However, the position of the

peak assigned to O atom for SP800 was different of those for other samples. As shown in Fig. 3b, the samples which contained no P atom in starting material, that is, S800 and S-N800, had no peaks assigned to phosphorus. The peak position of S-PN800 was different from that of S-N800, and the peak of S-PN800 was broader than that of S-N800. The peak condition of S-PN800 was independent of the washing process by hot water. As shown in Fig. 3c, the samples which contained no N atom in starting material, that is, S800 and S-P800, had no peaks assigned to nitrogen. On the other hand, the samples which contained the N atoms in starting material, that is S-N800 and S-PN800, had the peaks assigned to nitrogen. Moreover, the XPS spectrum of S-PN800W was similar to that of S-PN800. This should mean that the state of the N atoms in S-PN800 is stable in hot water. We can confirm that the spectra of S-N800, S-PN800, and S-PN800W consist of two peaks (401 eV, 398.5 eV). Some research works reported the peak identification of the peaks [3,7]. The peak at 401 eV could be attributed to the quaternary nitrogen, which is surrounded by three carbon atoms in the graphitic-layered structure. The peak at 398.5 eV could be assigned to pyridinic nitrogen, which exists at the edge part of the graphitic structure, or the nitrogen in nitrile group. Kawaguchi et al. reported that pyridinic nitrogen has a possibility of the pseudo-faradaic reaction [8]. Deradji et al. reported that the presence of nitrile group induces many ruptures in graphitic network, resulting in enhancing the electrical resistivity [9]. Most part of the peak at 398.5 eV for S-N800 and S-N800W could be assigned to nitrogen in nitrile because the electrical resistivity increased with the addition of guanidine carbonate. On the other hand, most part of the peak at 398.5 eV for S-PN800 and S-PN800W could be assigned to pyridinic nitrogen because the electrical resistivity decreased with the addition of guanidine phosphate. In the case of this study, the CV graphs do not show any sharp peaks as shown in Fig. 1. Kwon et al. [7] reported that the absence of evident peaks can be explained by the faradic process that consists of many complex reactions with a variety of onset potentials rather than a single reaction. This may be the reason for the enhancement of the capacitance with the addition of the N-containing reagent in this study.

The yields after the heat treatment are also listed in Table 2. The yield of starch was 12.2 wt.% in this study. Starch contains oxy-

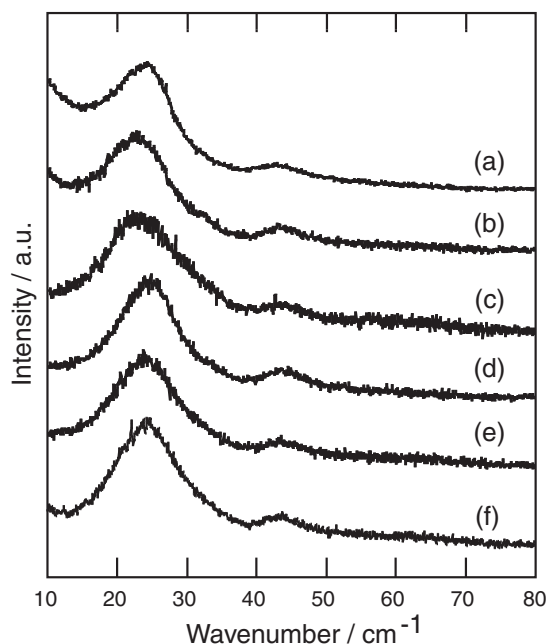


Fig. 5. XRD patterns of the samples. (a) AC; (b) S800; (c) S-P800; (d) S-N800; (e) S-PN800; (f) S-PN800W.

gen atoms in its molecular structure ($(C_6H_{10}O_5)_n$). The low yield, therefore, is reasonable because the oxygen atoms act as an oxygen source for the oxidation reaction of C and H in the molecule. The yield slightly increased with the addition of guanidine carbonate. The yields of S-P800 and S-PN800 significantly increased, and the values are *ca.* 25 wt.%. Both phosphoric acid and guanidine phosphate contain a P atom in their chemical structure. We can presume from these results that the existence of P in the additive may act to enhance the yield. However, the residues of the phosphoric compounds, such as phosphorous oxide, which can dissolve in hot water, may not be the main reason for the change in the yield because the decrease in the wt.% of “others” for S-PN800 after the washing with hot water was small. The phosphorus in S-P800 and S-PN800 may exist not as phosphorous oxide but as a functional group or covalently bonded in the frame network. It is known that guanidine phosphate has a flame-retardant effect on cellulose materials, such as paper products. The chemical structure of cellulose is similar to that of starch, and both of them are polysaccharides. The flame-retardant effect could be caused by formation of the C=C bond, which is formed via a dehydration reaction. Therefore, the

significant enhancements in the case of S-PN800 could result in an enhancement of the C=C bond.

We performed additional measurements. Scanning electron microscopy (SEM) images indicated that all the samples derived from starch had a flake-like structure, as shown in Fig. 4. The samples derived from starch were dissolved in water and then dried before the heating process. The flake-like structure should be formed during the drying process. At this time, the relationship between the flake-like structure and the high capacitance value is unclear. X-ray diffraction (XRD) patterns showed that no peaks were derived from additives in the spectra (Fig. 5). The IR spectra indicated that the samples treated with the additives had C=O bonds, like activated carbon (attached as [supplementary data Fig. S1](#)). These experimental results cannot directly explain the high capacitance. However, the preparative method in this study appears to have the potential as a technique for the synthesis of high-performance carbon materials for use as capacitor electrodes.

4. Conclusions

The capacitance value of the carbon material made from starch was significantly improved by a simple preparative method, that is, mixing in water and then drying before heat treatment. Moreover, the capacitance value of the sample increases by washing with hot water. The simple method used in this study should be effective for improving the capacitance value of starch-derived carbon.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jpowsour.2011.02.043](https://doi.org/10.1016/j.jpowsour.2011.02.043).

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