Journal of Power Sources 267 (2014) 635–640

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Performance of carbon material derived from starch mixed with flame retardant as electrochemical capacitor

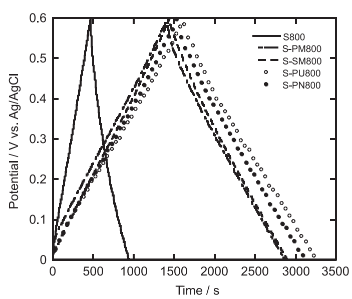
Toshiki Tsubota*, Masaki Morita, Naoya Murakami, Teruhisa Ohno

Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology, 1-1 Sensui-cho, Tobata-ku, Kitakyushu 804-8550, Japan

HIGHLIGHTS

- The properties of carbon derived from starch with an added flame retardant were investigated.
- The capacitance values were improved by the addition of the flame retardants.
- The N atoms derived from the flame retardants were incorporated in the synthesized carbon material.
- The P atoms or the S atoms were possibly incorporated in the synthesized carbon material.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 February 2014
Received in revised form
27 May 2014
Accepted 28 May 2014
Available online 6 June 2014

Keywords:
Electrochemical capacitor
Starch
Flame retardant
Carbon material
Nitrogen

ABSTRACT

Carbon materials derived from starch with an added flame retardant, such as melamine polyphosphate, melamine sulfate, guanylurea phosphate, or guanidine phosphate, were synthesized for investigating the performance as the electrode of an electrochemical capacitor. The yield after the heat treatment of the carbonization reaction increased by the addition of these flame retardants up to 800 °C. Although both the specific surface area and electrical resistivity are almost independent of the addition of the flame retardants, the capacitance values are improved with the addition of the flame retardants. The nitrogen atoms derived from the flame retardants are introduced to some extent into the synthesized carbon material. Moreover, the phosphorous atoms or the sulfur atoms derived from the flame retardants are doped into the synthesized carbon material. The method applied in this study, that is, the addition of flame retardants before the carbonization process can be used for the doping of the hetero atom such as N, P and S into the carbon material.

1. Introduction

Many research studies have been performed for the development of carbon materials as the electrode of electrochemical capacitors such as the electrical double layer capacitor (EDLC) because the electrode is the most important component for the electrical storage [1–5]. Many ideas have been proposed for improving the performance of the carbon material [1,6,7]. The addition of a hetero element, such as N, has been proposed as one of the approaches for improving the performance of the electrode for use in an electrochemical capacitor [8,9]. We have already reported that the addition of guanidine phosphate to starch before its heat treatment is effective for the improvement of the capacitive performance of the carbon material in an aqueous electrolyte [10,11]. It was confirmed that the N atom derived from the guanidine phosphate was incorporated to some extent into the synthesized carbon material. It is known that guanidine phosphate is one of the flame retardant for cellulose, which is a kind of

* Corresponding author. Tel.: +81 93 884 3324; fax: +81 93 884 3300.
E-mail address: tsubota@che.kyutech.ac.jp (T. Tsubota).

http://dx.doi.org/10.1016/j.jpowsour.2014.05.140
0378-7753/

polysaccharide like starch [12]. It is known that certain kinds of flame retardants for cellulose could be involved in the carbonization process of cellulose [12]. The chemical structure of starch is similar to that of cellulose. Therefore, these flame retardants are presumed to introduce the hetero atom to the carbon material derived from starch. Moreover, the chemical condition (chemical bond, networks of bonding, and so on) of the synthesized carbon material should be affected by the addition of the flame retardant, and the electrochemical property of the carbon material may be improved by the change its the chemical structure.

It is known that some reagents, such as melamine polyphosphate [13], melamine sulfate [14], and guanylurea phosphate [15], act as flame retardants. These flame retardants contain a hetero atom, such as N, P, and S, like guanidine phosphate. Therefore, it is presumed that these reagents would also be effective for improving the performance of the carbon material derived from starch for use in an electrochemical capacitor. Because the addition of a flame retardant before the heating process is simple, easy, safe, and inexpensive, this method should be important for practical use. Therefore, the investigation of the effect of the addition on the performance should be important for the development of a carbon material for use in an electrochemical capacitor. In this study, the effect of the addition of these reagents to starch on the performance of the electrode of an electrochemical capacitor was investigated in detail.

2. Experimental

Commercial starch (Starch, Soluble, Wako Pure Chemical Industries, Ltd.) was mixed with a flame retardant at the weight ratio of (starch:flame retardant) = 10:1. In this study, melamine polyphosphate, melamine sulfate, guanylurea phosphate, and guanidine phosphate were used as the flame retardant. The mixtures were heated at 700–900 °C for 1 h under flowing N_2 (50 mL min^{-1}). The powders after the heat treatment were used for the measurements by the BET method (nova4200e, Quantachrome Instruments) and CHN-corder (CHN CORDER MT-5, Yanaco). The XPS measurements were performed for the analysis of the hetero atoms (N, P or S) derived from the flame retardants by using Shimadzu/KRATOS AXIS-NOVA. The peak of C 1s was used for the calibration as 284.6 eV. The powders prepared by the heat treatment, acetylene black, and Teflon powder were mixed at an 8:1:1 ratio to form sheets. The sheets were cut and then used as the sample for the measurement of the electrical resistivity and the electrode for the electrochemical measurements. The electrical resistivity was measured by the DC four-probe method. The sheets were placed in a three-electrode cell, and Pt plates were used as the counter electrode and collector electrode and a Ag/AgCl electrode was used as reference electrode. The capacitance values were calculated from the data for the charging process. In this study, starch, melamine polyphosphate, melamine sulfate, guanylurea phosphate, and guanidine phosphate were abbreviated S, PM, SM, PU, and PN, respectively. Moreover, the information about the treatment temperature was described on the label of the samples. In the case of the sample washed with water, "W" was used for the label. For example, when starch mixed with melamine polyphosphate was heated at 800 °C and the sample was washed with water, the label of the sample was S-PM800W.

3. Results and discussion

In order to estimate the yield of the sample, the weights were measured before and after the heat treatment. The yields, the value of 100 × (the weight after the heat treatment)/(the weight before the heat treatment), are shown in Fig. 1. The yield of S700 was

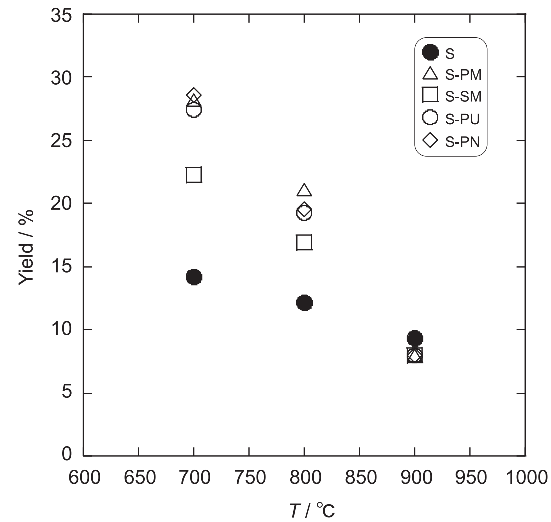


Fig. 1. Heating temperature dependence of yield.

14.2%. The yields decreased with the increasing heating temperature, and reached 9.3% at 900 °C. The yields of S-PM700, S-PU700, and S-PN700 were *ca.* 28%, and the yield of S-SM700 was 22.3%. When the heating temperature was less than 800 °C, the yields for the samples with the added flame retardants were greater than that for only the starch sample. On the other hand, when the heating temperature was 900 °C, the yields for the samples with the added flame retardants were slightly lower than those for only the starch sample. There was no effect of the flame retardants on the enhancement of the yield at 900 °C.

The CV graphs of the samples are shown in Fig. 2. The area of the CV curves for the samples derived from only starch was relatively small, which should mean that the capacitance values are lower than those of the other samples. Therefore, the addition of the flame retardants could enhance the capacitance values. Some CV curves of the samples, such as S-PU800, had broad peaks, which may be derived from the pseudocapacitance. All the CV graphs of the samples treated at 900 °C had a rectangular shape, which should mean that there was no pseudocapacitance.

The heating temperature dependence of the specific surface area is shown in Fig. 3. The specific surface area of all the samples increased with the increasing heating temperature. At 700 °C, the samples with added flame retardant except for S-SM had lower specific surface areas than the sample derived from only starch. On the other hand, at 900 °C, all the samples with the added flame retardant had higher specific surface areas than the sample derived from only starch. This result should be one of the facts that the flame retardants affected the carbonization process of the starch. However, the specific surface area values did not drastically change by the addition of the flame retardants. Some of the flame retardants used in this study were phosphates, which contain the phosphoric acid component. It is known that phosphoric acid acts as an activator for the synthesis of activated carbon. Although it might be postulated presume that the flame retardants used in this study act as the activator, the specific surface areas of the samples with the added flame retardants had values similar to that of the starch only sample. Liu et al. [16] reported that the specific surface area of the carbon material derived from a lotus stalk with added guanidine phosphate was much lower than that with added phosphoric acid when the heat treatment temperature was 450 °C. Therefore, these phosphates have a low activity as the activator for the synthesis of activated carbon.