



A simple fabrication route of activated carbons from chicken droppings

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ABSTRACT

We report a simple fabrication route of activated carbons (ACs) from a waste biomass, chicken droppings without any additional activation process. The ACs with specific surface area up to $1618 \text{ m}^2 \text{ g}^{-1}$ with well developed micropore channels are successfully fabricated by pyrolysis followed by HCl treatment. The detailed analysis of pyrolysis behavior using thermogravimetry and gas chromatography reveals that activation of the precursor takes place through the catalytic gasification by CO_2 evolved from CaCO_3 during the pyrolysis. Electric double-layer capacitors (EDLCs) fabricated from the ACs show good specific capacitance up to 25 F g^{-1} due to well developed sub-nanometer sized pore channels.

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1. Introduction

Utilization of waste biomass such as animal wastes and sewage sludge is necessary for sustainable society since they are major industrial waste in many countries. Pyrolysis is considered as a promising alternative way of less acceptable disposal process including agricultural application, land fill and incineration. Especially, fast pyrolysis in air tight condition at low temperature can produce oil products applicable for fuel and chemical feedstock [1–6]. Carbonaceous residue is also obtained as byproduct of the pyrolysis, and their conversion into valuable products will contribute to promote the use of the waste biomass.

Activated carbons (ACs) are one of the useful products able to be fabricated from the organic resources, and have been receiving much attention because of their wide range applications involving adsorbents [7,8], catalysts and its support [9,10] and electric double layer capacitors (EDLCs) [11–14] due to particularly high specific surface area (SSA) with controlled porosity. ACs are commonly fabricated from synthetic and natural organic compounds through the activation process followed by pyrolysis. Although waste biomass resources have an advantage in low material cost compared to the synthetic resins, the conventional activation process to control the porosity makes ACs costly. Thus fabrication of ACs from the waste biomass without any additional activation process is beneficial from the view point of both reduction of material costs and exhausted amount of industrial wastes.

In this study, we demonstrate a simple fabrication process of ACs from a major waste biomass, chicken droppings. We found that activation takes place during pyrolysis of them without any additional activation process. The activation mechanism is discussed through the detailed analysis of the pyrolysis behavior. The ACs are attempted to be applied for electrodes of EDLC which is one of the promising energy storage devices in the growing renewable energy and electric vehicle markets [12].

2. Materials and methods

Table 1 shows the composition of the chicken droppings used in this study. Major inorganic components are Ca, K, and P. The ACs were fabricated through the following simple manner without conventional activation process. The droppings of 1 g were pyrolyzed between 600 and 1000 °C for 7 min in an air tight Pt crucible, and then cooled down to room temperature. The pyrolyzed samples were put into 1 M HCl solution and magnetically stirred at 80 °C for 1 h to remove ash components. The ash removed samples were washed with de-ionized water and then filtered. This washing sequence was continued until the filtrated water to be ~pH 7. The ACs were obtained after the drying of washed products in an oven at 107 °C for 24 h. Specific surface area (SSA) and micropore size distribution of the ACs were examined with N_2 adsorption at 77 K using Brunauer–Emmett–Teller (BET) and MICROPOR analysis (MP) methods, respectively. X-ray diffraction (XRD) measurement was performed to identify the crystalline phase in the samples before and after the acid treatment. The weight change during pyrolysis was investigated using thermo-gravimetry under Ar atmosphere with the flow rate of 100 ml/min. The gases evolved through the pyrolysis with a fixed bed reactor is collected by aluminum coated

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Table 1

Composition of the chicken droppings used in this study.

| Proximate analysis (wt% d.b.) | | | Ultimate analysis (wt%, d.a.f.) | | | | | Ash composition of Hen dropping (%) | | |
|-------------------------------|------|------|---------------------------------|-----|-----|-----|----------------------|-------------------------------------|------------------|-------------------------------|
| V.M. | Ash | F.C. | C | H | N | S | O _(diff.) | CaO | K ₂ O | P ₂ O ₅ |
| 59.0 | 28.4 | 12.6 | 45.3 | 5.5 | 3.7 | 0.3 | 45.2 | 87.94 | 3.65 | 3.06 |

d.b., dry basis; V.M., volatile matter; F.C., fixed carbon; d.a.f., dry ash-free basis.

gas sampling bag and analyzed by gas chromatography with flame ionization detector coupled with methane converter and thermal conductivity detector. EDLC electrodes were fabricated from the mixture of ACs, acetylene black and polytetrafluoroethylene with the weight ratio of 0.87, 0.10 and 0.03, respectively. The mixture of 34.4 mg was filled into metal die with the inner diameter of 13 mm and then uniaxially pressed to form the electrode pellets. The pellets were then immersed into electrolyte solution consisting of 0.5 M tetraethylammonium fluoroborate ($\text{N}(\text{C}_2\text{H}_5)_4\text{BF}_4$; TEABF₄) electrolyte in polypropylene carbonate solution under vacuumed atmosphere. The EDLC with two electrode setup was built in a grove box. Fourth charge (40 mA g^{-1}) and discharge (10 mA g^{-1}) cycles were performed to confirm the performance stability, and then specific capacitance (C_g) was calculated from the discharge profile of the fifth cycle.

3. Results and discussion

Fig. 1(a) shows XRD patterns of the pyrolyzed chicken droppings before ash removal. The crystalline phase of CaCO_3 and calcium phosphates are observed for the sample pyrolyzed at 600 and

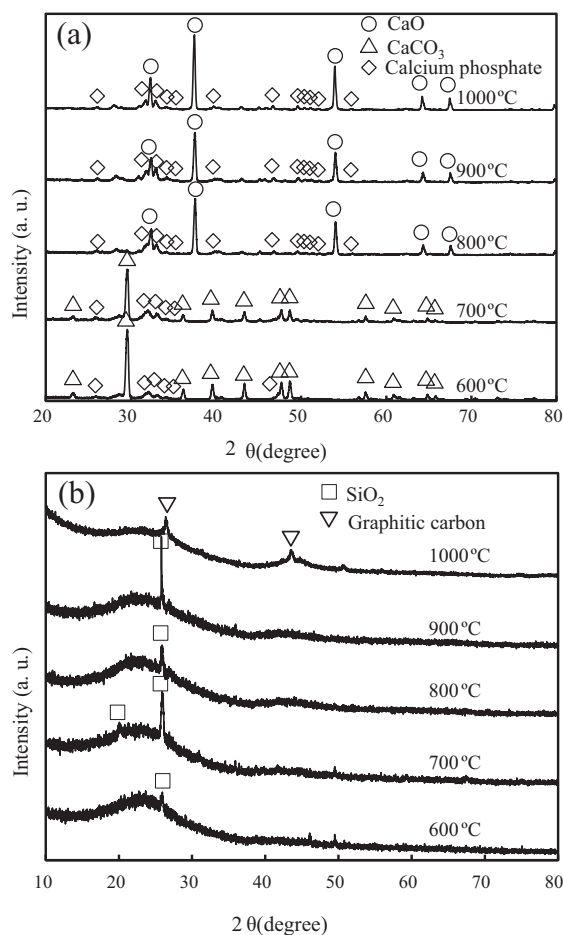


Fig. 1. XRD patterns of chicken droppings pyrolyzed at various temperatures: (a) before and (b) after HCl treatment.

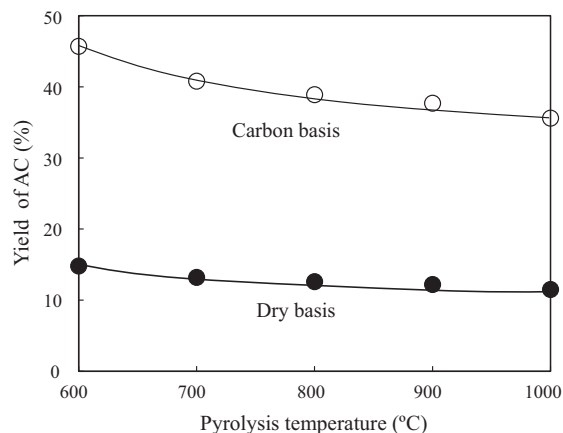


Fig. 2. Yield of chicken droppings derived ACs in dry and carbon bases.

700 °C. CaO phase appears instead of the disappearance of CaCO_3 phase at above 700 °C, indicating that major decomposition of CaCO_3 occurs between 700 and 800 °C. While calcium phosphate phase remains without noticeable change up to 1000 °C. Fig. 1(b) shows XRD patterns of the pyrolyzed chicken droppings after ash removal. Halo pattern centered at around $2\theta = 23^\circ$ is observed for all the samples, indicating that the obtained carbon material has amorphous structure. Although only a minor SiO_2 phase remains in the products, major ash components involving CaCO_3 , CaO and calcium phosphate are removed. In addition, graphitic carbon phase is observed in the sample pyrolyzed at 1000 °C, suggesting the occurrence of catalytic graphitization by the aid of ash components.

Fig. 2 shows the yield of chicken droppings derived carbonaceous materials. The yield was slightly decreased with increasing pyrolysis temperature in the range between 14.8 and 11.5% in dry basis and 45.7 and 35.6% in carbon basis of the chicken dropping.

Fig. 3 shows the SSA evolution of the chicken droppings derived carbonaceous materials after the ash removal and the C_g of the EDLCs fabricated from them. The SSA increased linearly with

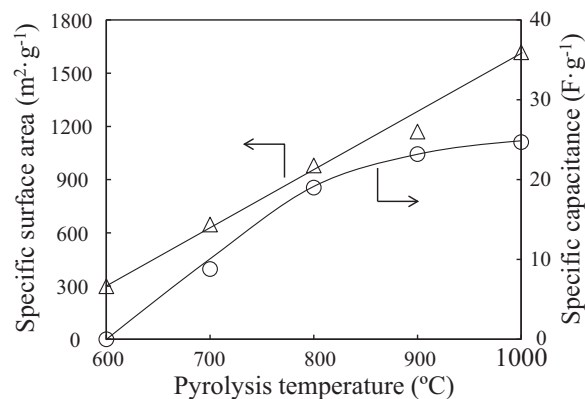


Fig. 3. Evolution of specific surface area of the chicken droppings derived ACs and specific capacitance of EDLCs fabricated from the ACs as the function of pyrolysis temperature.

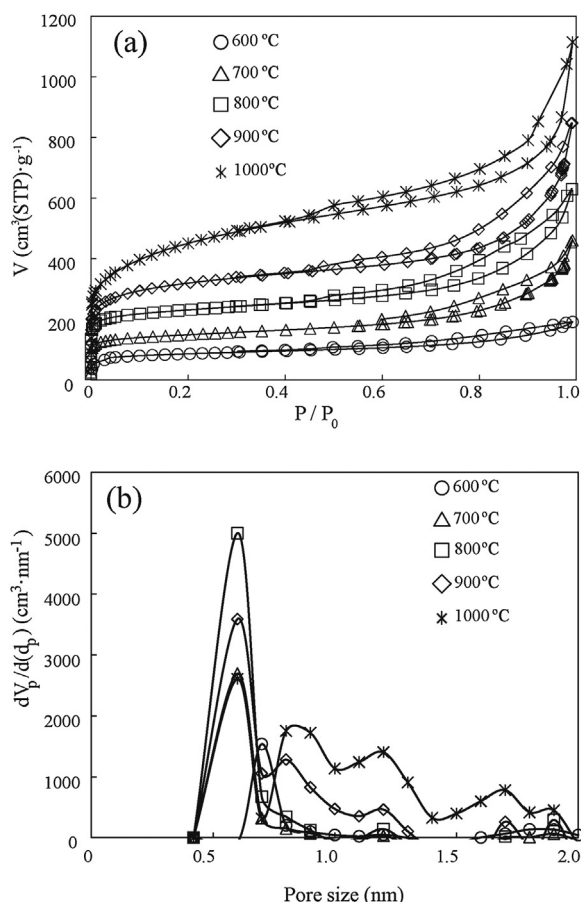


Fig. 4. (a) Nitrogen adsorption isotherms and (b) size distributions of micro-pores of the chicken droppings derived ACs fabricated from various pyrolysis temperatures.

increasing pyrolysis temperature, and reached to be $1618\text{ m}^2\text{ g}^{-1}$ at 1000°C . The fabrication of ACs with the proposed simple way without any additional activation process indicates that the pore channels evolve during the pyrolysis. The EDLCs fabricated from the ACs shows good C_g up to 25 F g^{-1} . The C_g dramatically increases with increasing pyrolysis temperature up to 800°C , and then the gain becomes dull above the temperature even though the continuous significant increase of the SSA. The result suggests that the major pore channels suitable for EDLC application evolves mainly between 600 and 800°C .

Fig. 4(a) shows the N_2 adsorption isotherms of chicken droppings derived ACs. The adsorption isotherms on the all ACs are a combination of types I and IV with an H4 hysteresis loop indicating contribution from mesopores. Adsorption volume at very low relative pressure gradually increased with increasing pyrolysis temperature, suggesting the increase of the micropore volume. Fig. 4(b) shows the size distribution of micropores of the ACs. The volume for the sub-nanometer sized pores increases with increasing pyrolysis temperature up to 800°C and then decreases. In contrast, those with the size of $0.7\text{--}2.0\text{ nm}$ start to evolve at 800°C and increases with increasing pyrolysis temperature. These facts suggest that the dramatic increase of C_g of EDLC from the ACs fabricated between 600 and 800°C is mainly due to the increase of pore channels with sub-nanometer size, while only the small gain of C_g at $>800^\circ\text{C}$ even though the significant increase of the SSA can be attributed to the evolution of larger pores instead of disappearance of these finer ones. Chmiola et al. found that sub-nanometer size pores can contribute to the dramatic increase of the capacitance of EDLCs, while the pore channels more than 1 nm less contribute to the increase of the performance when using TEABF_4 electrolyte

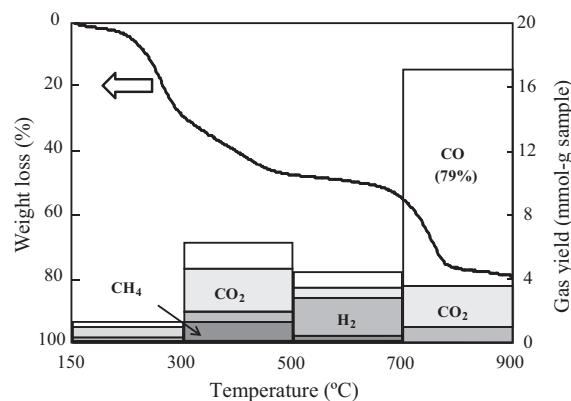


Fig. 5. Thermo-gravimetry and evolved gas analysis result during pyrolysis of the chicken droppings.

[15]. They have explained the mechanism of the significant contribution of pores with sub-nanometer size to the performance of EDLCs that the distortion of solvation shells of electrolyte ions in pore channels with the size approaching to the crystallographic diameter of the ions under the potential and subsequent closer approach of the ion center to the electrode surface. The distortion of the shell was also reported in the recent studies [16,17]. The pore size/capacitance relationship in this study agrees with the previous studies. Further performance enhancement is expected if pore channels with the sub-nanometer size can be increased through the understanding of the activation mechanism of chicken droppings.

Here, we discuss about the activation mechanism of the chicken droppings derived ACs. Fig. 5 shows weight loss and gas evolution behavior associate with the pyrolysis of the dried chicken droppings. The weight loss between 200 and 600°C can be attributed to the evolution of volatile matter. Although the significant weight change of 20% occurs between 200 and 300°C , only a few mmol/g -sample of evolved gas is obtained, since the most of volatile matter evolves as tarry matter due to the lack of thermal cracking at the temperature range and is collected at a condenser placed before gas sampling bag. Significant weight loss between 600 and 800°C is mainly attributed to the thermal decomposition of CaCO_3 with CO_2 evolution from the XRD patterns shown in Fig. 1(a). However, the majority of the evolved gas is CO rather than CO_2 in the temperature range. The fact indicates that CO_2 evolved from CaCO_3 in the droppings during pyrolysis is consumed for gasification of the fixed-carbon. The pore channels with sub-nanometer size start to evolve at 700°C and a dramatic increase in performance of EDLC is observed between 600 and 800°C . The temperature well agrees with the decomposition temperature of CaCO_3 . The fact indicates that activation of the chicken droppings during pyrolysis takes place through the gasification by CO_2 evolved from CaCO_3 . As can be expected, the SSA of ash removed (HCl treated) chicken droppings derived product pyrolyzed at 800°C is only $113\text{ m}^2\text{ g}^{-1}$. Although the SSA of the product from the mixture of ash removed chicken droppings and commercial CaCO_3 powder pyrolyzed at 800°C increases to be $318\text{ m}^2\text{ g}^{-1}$, it is significantly lower than that of the ACs from the as-received chicken droppings. These results suggest that the CO_2 gasification is catalyzed by highly active species including Ca , K and P formed by the digestion in chicken's body. Catalytic gasification to form the pore channels suitable for EDLCs takes place below 800°C . The heat treatment of the chicken droppings at this temperature range under flowing CO_2 atmosphere may increase the volume of sub-nanometer sized pore channels, thereby increase the performance of EDLCs. Further detailed mechanism of the catalytic gasification and subsequent evolution of micropore channels are under investigation, the understanding will aid to develop new activation process for

the fabrication of ACs from the various types of waste biomass with lower cost and energy consumption.

4. Conclusions

High surface area ACs with sub-nanometer sized pore channels are obtained from the chicken droppings through a simple route with the pyrolysis followed by acid treatment. The sub-nanometer sized pore channels contributed to significant increase of the C_g of EDLCs, while those of >1 nm shows minor contribution. The detailed investigation of the pyrolysis behavior reveals that the activation is achieved through the catalytic gasification with CO_2 evolved from decomposition of $CaCO_3$ in the droppings.

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