Journal of Power Sources 323 (2016) 166–173

Contents lists available at ScienceDirect

Journal of Power Sources

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

Preparation of hierarchical porous carbon from waste printed circuit boards for high performance electric double-layer capacitors

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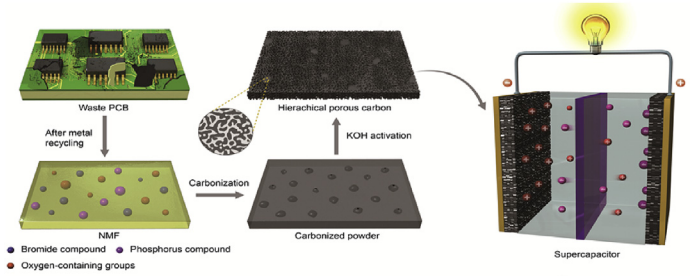
HIGHLIGHTS

- Non-metallic fractions (NMF) of waste PCB were recycled and prepared into carbon.
- Additives assisted to produce NMF-based carbon with hierarchical porous structure.
- NMF-based carbon showed high specific capacitance and stable cycling performance.
- The NMF-based carbon have good prospect in large-scale EDLC application.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 February 2016
Received in revised form
10 May 2016
Accepted 12 May 2016

Keywords:
Hierarchical porous carbon
Electric double-layer capacitor
Printed circuit board
Non-metallic fractions
Energy storage

ABSTRACT

Renewable clean energy and resources recycling have become inevitable choices to solve worldwide energy shortages and environmental pollution problems. It is a great challenge to recycle tons of waste printed circuit boards (PCB) produced every year for clean environment while creating values. In this work, low cost, high quality activated carbons (ACs) were synthesized from non-metallic fractions (NMF) of waste PCB to offer a great potential for applications of electrochemical double-layer capacitors (EDLCs). After recovering metal from waste PCB, hierarchical porous carbons were produced from NMF by carbonization and activation processes. The experimental results exhibit that some pores were formed after carbonization due to the escape of impurity atoms introduced by additives in NMF. Then the pore structure was further tailored by adjusting the activation parameters. Roles of micropores and non-micropores in charge storage were investigated when the hierarchical porous carbons were applied as electrode of EDLCs. The highest specific capacitance of 210 F g^{-1} (at 50 mA g^{-1}) and excellent rate capability were achieved when the ACs possessing a proper micropores/non-micropores ratio. This work not only provides a promising method to recycle PCB, but also investigates the structure tailoring arts for a rational hierarchical porous structure in energy storage/conversion.

1. Introduction

Electric double-layer capacitors (EDLCs), also known as supercapacitors, are new breakthrough in energy storage devices and have become research hotspots because of their high capacity, great

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http://dx.doi.org/10.1016/j.jpowsour.2016.05.054
0378-7753/

power density and long cycle life [1–3]. Thus EDLCs have been widely used in the information technology industry, electronic devices, electric vehicles, military equipment and so on. Carbon materials are the most commonly used materials for EDLC electrodes due to their high surface area, high conductivity and good physicochemical stability. Up to date, available carbon materials used for EDLCs electrode include activated carbons (ACs) [4], carbon aerogels [5], carbon nanotubes [6] and graphene [7], which possess a variety of microstructures, electrochemical properties and a wide range of costs. However, ACs enjoy the spotlight mainly because of their abundance, low-cost and mass-production. In recent years, to reduce the production cost of ACs, recyclable and waste resources have become attractive precursors to prepare ACs as electrode materials of EDLCs [8–10]. For instance, Jiang et al. [8] prepared ACs for electrochemical supercapacitors from ginkgo shells and the obtained specific capacitance was 178 F g^{-1} at 500 mV s^{-1} within a three-electrode cell. Domingo-Garcia et al. [10] used poly(ethylene terephthalate) (PET) waste from plastic vessels as precursor of carbon electrodes for supercapacitors. PET derived-ACs displayed specific capacitances of 197 F g^{-1} at current density of 1 mA cm^{-2} in 2 mol L^{-1} H_2SO_4.

Recycling today is not only driven by the scarcity of resources, but a great response to environmental concerns for a best way to protect all living things. Since the 20th century, the rapid development of electronic technology has led to shorter and shorter electronic product life cycles while discarding more and more waste electrical and electronic equipment (WEEE). It has been reported that 20–50 million tons of WEEE are generated worldwide each year [11,12]. Waste printed circuit boards (PCBs), which are the essential component of WEEE, are composed of various metals and non-metals e.g. thermosetting resins, reinforcing materials, brominated flame retardants (BFRs) and other additives. Therefore, recycling of waste PCBs have drawn much attention because it concerns two principal themes: the protection of environment and the recovery of valuable materials [13–16]. Currently, the metallic fractions (MFs) of waste PCBs can be effectively recycled through mechanical separation methods [16–18]. While the non-metallic fractions (NMFs), which are almost 70% weight content of waste PCBs, are generally treated by incineration or land filling. Incineration of the NMFs could cause the formation of highly toxic polybrominated dibenzodioxins and dibenzofurans [19,20]. Moreover, land filling of the NMFs would lead to secondary pollution caused by heavy metal residues and BFRs leaching to the groundwater [21]. Therefore, environmental friendly recycling of NMFs from waste PCBs remains a huge challenge.

It has been reported that the recycling methods of NMFs from waste PCBs mainly include both physical and chemical recycling methods [11]. For the physical method, NMFs can be used as fillers or reinforcing fillers for various products, such as construction materials, decorating agent, adhesives and insulating materials [20,22,23]. While the chemical recycling methods of NMFs are employed during and after the stage of chemical separating process for MFs and NMFs. Chemical recycling methods include pyrolysis, gasification, depolymerization with supercritical fluids and hydrogenolytic degradation, etc [24–29]. Among these methods, pyrolysis as a promising recycling method has been widely investigated [11,28,29]. Pyrolysis of the organic fraction of PCBs usually leads to the formation of gases, oils and chars, which can be used as chemical feedstocks, fuels, advanced carbonaceous materials (ACMs) and so on [23,30]. For instance, Quan et al. [30] prepared ACMs by pyrolysis oil from glass fiber reinforced epoxy resin in waste PCBs. The BET surface area and micropore volume of the prepared ACMs are 1214 m^2 g^{-1} and 0.41 m^3 g^{-1}, respectively. Although a number of researches have been carried out for handling NMFs in waste PCBs using pyrolysis, few research focused on the use of residue chars.

In this paper, for the first time NMFs in waste PCBs are employed as the raw material to produce hierarchical porous carbons used for EDLCs. The preparation of NMFs-based AC and its EDLC application is schematically shown in Fig. 1. The NMFs of waste PCBs contains a high concentration of oxygen-containing groups, providing many reactive sites for activation. Furthermore, NMFs of PCBs usually contain some additives e.g. brominted epoxide resin and triphenyl phosphate as fire retardant. These additives are unstable and can decompose during heat treatment, which can assist in creating additional pores. These characteristics should make NMFs of waste PCBs a promising candidate for producing hierarchical porous carbons with simple preparation process. The ACs derived from NMFs in waste PCBs are applied in EDLCs and excellent rate capability is obtained. This supplies a new approach to recycling the NMFs in waste PCBs avoiding environment pollution caused by their inappropriate disposal. Besides, the use of NMFs of waste PCBs as precursor also can reduce the large-scale production cost of ACs and EDLCs.

2. Experimental section

2.1. Preparation of NMFs-based carbon materials

Waste PCBs were obtained from Xingsong Flexible Printed Circuit Co., Ltd., Guangdong, China. After separating metals completely, the remained NMFs were washed by deionized water thoroughly and dried. Then ground NMFs with particle size less than 75 μm were carbonized under N_2 flow at 600 °C for 1 h and designated as NMFC6. Portions of NMFC6 sample were chemically activated by KOH with the KOH/sample weight ratio range from 3 to 5. The mixtures of NMFC6 and KOH were pyrolyzed in a horizontal tubular furnace under N_2 flow at 800 °C for 1 h with a heating rate of 5 °C min^{-1}. The activated NMFs (ANMFs) were washed in 1 mol L^{-1} HCl, rinsed in distilled water, filtered and then dried at 80 °C for 24 h. Then these ACs were labeled as NMFC followed by the carbonization temperature, activation temperature and KOH/sample weight ratio; for example, NMFC684 represented carbonization temperature of 600 °C, activation temperature of 800 °C and KOH/sample weight ratio of 4.

2.2. Material characterization

Thermal gravimetric analysis (TGA) coupled with derivative thermogravity analysis (DTG) was conducted with NETzsCH STA449 analyzer in order to determine the pyrolysis behaviors of NMFs. The sample (5–8 mg) was heated from room temperature to 800 °C with a heating rate of 10 °C min^{-1} in flowing nitrogen. X-ray diffraction (XRD) was carried out on a Rigaku Smartlab system with CuKα radiation (λ = 1.5406 Å). The surface morphologies of NMFs and NMFs-based carbon materials were characterized by field JSM-6700F scanning electron microscopy (SEM). TEM images were obtained with a JEM-2010 microscope operated at 200 kV. Fourier transform infrared spectra (FTIR) of NMFs and NMFs-based carbon samples were recorded from an Nicolet Magna-IR 560 FTIR spectrophotometer using the KBr disk method. Thirty-two scans were taken of each sample recorded from the range 4000–800 cm^{-1} at a resolution of 2 cm^{-1} in the transmission mode. The N_2 adsorption-desorption isotherms of NMFs and NMFs-based carbons were measured at 77 K using ASAP2020 (Micromeritic, USA) in order to determine the specific surface areas and pore structure parameters. Prior to measurement, samples were outgassed overnight at 300 °C in a vacuum oven.