Electrochimica Acta 213 (2016) 260–269

Contents lists available at ScienceDirect

Electrochimica Acta

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

ZIF-8@MWCNT-derived carbon composite as electrode of high performance for supercapacitor

Yanfang Wang[a,b], Bingwei Chen[a,b], Yi Zhang[b], Lijun Fu[b], Yusong Zhu[b,*], Lixin Zhang[a,*], Yuping Wu[a,b,*]

[a] New Energy and Materials Laboratory (NEML), Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, China
[b] College of Energy and Institute for Electrochemical Energy Storage, Nanjing Tech University, Nanjing 211816, China

ARTICLE INFO

Article history:
Received 10 May 2016
Received in revised form 30 June 2016
Accepted 4 July 2016
Available online 5 July 2016

Keywords:
supercapacitor
zeolitic imidazolate framework
ZIF-8
porous carbon

ABSTRACT

Carbon materials from zeolitic imidazolate framework (ZIF) present poor electrochemical performance as electrode materials for supercapacitors. In this work, well-intergrown ZIF nanocystals are strung on MWCNTs to form necklace architecture. After carbonization and chemical etching, porous carbons with necklace architecture and proper hierarchical micro-mesoporous structure were obtained. It exhibits excellent electrochemical performance as electrode material for supercapacitor in 1 M H_2SO_4 solution such as high specific capacitance up to 326 $F \cdot g^{-1}$ at 1 $A \cdot g^{-1}$, good rate capability and excellent cycling stability of 99.7% capacitance retention after 10000 cycles. The main reasons are due to the increased surface area, the improved electrical conductivity, and the combination of micro- and meso-porous structure. This provides another promising way to design porous carbons from ZIF materials for supercapacitors.

1. Introduction

Due to the increasing consumption of fossil fuels, developing renewable energy sources has become an extreme urgency. The utilization of renewable energy resources, such as solar, wind and tide energies, is limited by their intermittent features. In order to solve this problem, many energy storage facilities have been invented. In the previous works of our group and others, electrical energy storage (EES) devices, such as M-ion batteries (M = Li, Na, Zn, Al etc.) [1–7], M-ion capacitors [8–10] and supercapacitors [11–13] have been proved to be feasible candidates. Supercapacitors or electrochemical capacitors, which can store the unstable powers generated from the intermittent energies and output them in more stable ways, are projected to be one of the suitable suppliers for portable electronic devices and hybrid electric vehicles (HEVs).

Generally, supercapacitors can be classified into two types based on their charge storage mechanisms [14]. One is the Faradic capacitor, in which fast faradaic reactions occur during the charge storage and release processes [15–17]. The other is the electrochemical double-layer capacitor (EDLC), in which only electrostatic accumulation occurs during the charge and discharge processes. Many kinds of carbon materials have been reported as electrode materials for EDLCs including activated carbon [18], carbon nanotube [19] and graphene [20]. Lots of organic materials from the nature such as animal bones, [21] banana peels [22] and even human hairs [23] can be used as sources to obtain carbon materials through physical and chemical activations [24].

Recently, metal-organic frameworks (MOFs) or porous coordination polymers (PCPs), as typical inorganic-organic hybrids, have been used as precursors to prepare porous carbon materials due to their large specific surface areas and tunable pore sizes [15–31]. Zeolitic imidazolate framework (ZIF), which is a subclass of MOFs and combines highly desirable properties of zeolites and MOFs, has emerged as a novel type of crystalline porous materials [32,33]. Emerging functional applications of ZIFs in separation [34–36], catalysis, [37,38] sensing [39] and energy storage fields [40–42] have been reported in the past few years. Comparing with common MOFs, ZIFs with stable structures can be prepared easily under ambient temperature and pressure in methanol solutions or even in aqueous solutions [43–45].

ZIF-8 has a large number of pores with diameters of 1.16 nm and specific surface area of more than 1000 $m^2 \cdot g^{-1}$ [46]. Carbons

* Corresponding authors.
E-mail addresses: zhuys@njtech.edu.cn (Y. Zhu), lixinzh@fudan.edu.cn (L. Zhang), wuyp@fudan.edu.cn, wuup@fudan.edu.cn (Y. Wu).

http://dx.doi.org/10.1016/j.electacta.2016.07.019
0013-4686/

obtained through the carbonization of ZIF-8 have been used as electrode materials for EDLCs. However, most of the ZIF-derived carbon materials show discrete nanoparticles, highly porous structures, low graphitized degree and numerous defects. Consequently, these features result in poor electrical conductivity and inevitably limit the electrochemical activity required for fast electron transfer. In addition, the oneness of pore size also hinders them from presenting variable properties [47]. Generally speaking, the high end specific capacitance of a capacitive material is related to the availability of total specific surface area. Therefore, the abundant micropores in the ZIFs are very helpful to achieve large specific surface areas and consequently deliver high specific capacitances. However, the absence of meso- and macropores may lead to inferior rate capability [48,49]. In order to improve the properties of ZIF-8-derived carbons, many attempts have been done. Some additional carbon sources including sucrose, melamine, urea and xylitol were used to obtain ZIF-8 based composites. After carbonization, the carbon composite derived from the ZIF-8 and sucrose showed a high capacitance of 180 $F \cdot g^{-1}$ at 10 $A \cdot g^{-1}$ [50]. Some meso- and macropores as additional second-order structures were successfully introduced by ultra-sonication during the synthesis process and carbon derived from this kind of ZIF-8 showed a capacitance of 200 $F \cdot g^{-1}$ at 10 $A \cdot g^{-1}$ [51]. Carbon derived from the composite of ZIF-8 and 3D graphene were also explored and it showed a capacitance of around 130 $F \cdot g^{-1}$ at 5 $A \cdot g^{-1}$ when single layer ZIF-8 was embedded on the 3D graphene [52].

Carbon nanotube (CNT) has also been widely investigated as a candidate for EDLC due to its excellent electrical conductivity, good mechanical strength and theoretically ultrahigh specific surface area. However, obtaining single-walled carbon nanotubes (SWCNTs) is not an easy work. What is worse, it is economically infeasible to use SWCNTs for EES applications. Therefore, in order to make better use of the appealing properties of CNTs, researchers tend to explore composites based on multi-walled carbon nanotubes (MWCNTs) in which some other functional materials are introduced.

Herein, we report a kind of carbon derived from ZIF-8@MWCNTs composite, in which the ZIF-8 nanocrystals are strung on the MWCNTs to form necklace-like structures. Benefiting from the rational combination of the proper hierarchical micro-mesoporous structures and the synergistic interaction between porous carbon and MWCNTs, the ZIF-derived carbon material in our tailored necklace-like structure could deliver superior performances in terms of high specific capacitance (326 $F \cdot g^{-1}$ at 1 $A \cdot g^{-1}$), high rate capability (91.6% capacitance retention of that at 1 $A \cdot g^{-1}$ for 10 $A \cdot g^{-1}$) and excellent cycling stability (capacitance retention of 99.7% after 10000 cycles) for EDLCs.

2. Experimental

2.1. Synthesis and materials

All of the chemicals were used without further purification. All of the synthesis solutions followed the molar ratio of Zn^{2+}: 2-methlyimidazole (MeIn): methanol = 1: 8: 700.

2.2. Preparation of pure ZIF-8 and ZIF-8/MWCNT mixture

To obtain pure ZIF-8 crystals, $Zn(NO_3)_2 \cdot 6H_2O$ and 2-methlyimidazole (MeIn) were dissolved in methanol and stirred for 0.5 h, then the solution was kept still for 24 h. The product with white color was collected by centrifuging and then washed with methanol for several times. The ZIF-8/MWCNTs mixture was prepared under the same conditions except for adding MWCNTs (with a molar ratio of Zn^{2+}: MWCNTs = 5: 1) into the solution.

2.3. Preparation of ZIF-8@MWCNT "necklace" composite

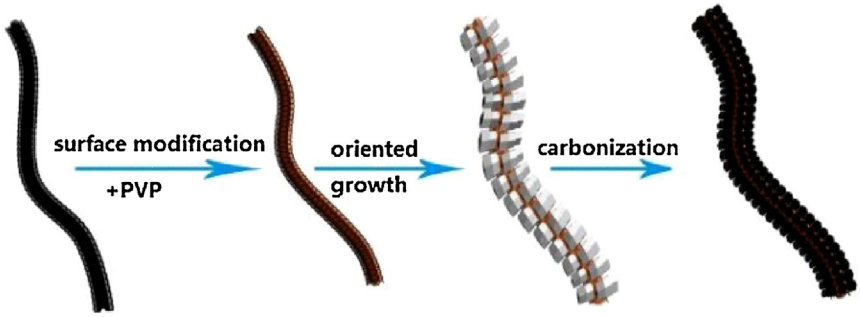
The ZIF-8@MWCNTs "necklace" composite was prepared following the processes shown in Scheme 1. Firstly, the MWCNTs were dispersed in PVP methanol solutions (in a mass ratio of MWCNTs: PVP = 1: 4) and stirred for 30 minutes. After centrifugation (10000 rpm, 10 minutes), the MWCNTs were collected and dispersed in the 2-MeIn methanol solution and the dispersion was added into the Zn^{2+} methanol solution later. The product was collected and washed as the above process.

2.4. Preparation of carbon materials

The anneal temperature was chosen to be 800 °C according to the thermogravimetric (TG) curves (Fig. S1). All of the products were placed in a tube furnace and annealed at 800 °C under nitrogen gas flow for 3 h with a heating rate of 2 °C·min^{-1}. The products were collected and etched with HCl (3 M). Finally, the carbon samples were rinsed with distilled water until the filtrates turned to be neutral and then dried at 80 °C for 12 h. The obtained carbon materials were noted as C-ZIF-8, C-ZIF-8/MWCNTs mixture and C-ZIF-8@MWCNTs necklace, respectively. Notably, in the final products, the weight ratio of MWCNTs in the mixture and necklace were calculated to be 55% according to the weight losses in the anneal process.

2.5. Characterizations

X-ray diffraction (XRD) patterns were collected by using a BrukerD4 X-ray diffractometer (Bruker, Germany) with Ni-filtered



Scheme 1. Schematic illustration for the synthesis of ZIF-8@MWCNTs necklace derived carbon.