



# Highly microporous carbons derived from a complex of glutamic acid and zinc chloride for use in supercapacitors



Xiao-Ling Dong, An-Hui Lu, Bin He, Wen-Cui Li\*

State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, PR China

## HIGHLIGHTS

- L-glutamic acid is a new carbon precursor with nitrogen functionality.
- Pyrolysis of a complex from L-glutamic acid and ZnCl<sub>2</sub> leads to carbon formation.
- Carbon is highly microporous due to the evaporation of zinc species.
- Carbon as electrode for EDLC possesses stable cycle life and low leakage current.

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## ABSTRACT

The selection of carbon precursor is an important factor when designing carbon materials. In this study, a complex derived from L-glutamic acid and zinc chloride was used to prepare highly microporous carbons *via* facile pyrolysis. L-glutamic acid, a new carbon precursor with nitrogen functionality, coordinated with zinc chloride resulted in a homogeneous distribution of Zn<sup>2+</sup> on the molecular level. During pyrolysis, the evaporation of the *in situ* formed zinc species creates an abundance of micropores together with the inert gases. The obtained carbons exhibit high specific surface area ( $S_{\text{BET}}$ : 1203 m<sup>2</sup> g<sup>-1</sup>) and a rich nitrogen content (4.52 wt%). In excess of 89% of the pore volume consists of micropores with pore size ranging from 0.5 to 1.2 nm. These carbons have been shown to be suitable for use as supercapacitor electrodes, and have been tested in 6 M KOH where a capacitance of 217 F g<sup>-1</sup> was achieved at a current density of 0.5 A g<sup>-1</sup>. A long cycling life of 30 000 cycles was achieved at a current density of 1 A g<sup>-1</sup>, with only a 9% loss in capacity. The leakage current through a two-electrode device was measured as 2.3 μA per mg of electrode and the self-discharge characteristics were minimal.

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## 1. Introduction

Supercapacitors (also referred to as electrical double layer capacitors – EDLCs), have attracted considerable interest due to their potential use in electrical vehicles, digital devices and pulsing techniques [1–3]. Due to the high electrical conductivity, ease of processability, controllable heteroatom doping, excellent electrochemical stability and good capacitive performance, porous carbons are regarded as first choice candidate electrode materials for supercapacitors which store energy *via* the accumulation of electrical charges across the electrode/electrolyte interface [4,5]. To date, various porous carbons including carbon spheres [6,7], carbon tubes [8], carbon fibers [9,10], carbon nanosheets [11,12] and

graphene [13,14] have been studied as electrodes in supercapacitors. It has been generally accepted that micropores in these porous carbons are crucial sites for strengthening the electric double layer for high capacitance. The specific capacitance undergoes a sharp increase in carbons with pore sizes of <1 nm [15,16]. In addition, pores with sizes of 0.7–1.2 nm generate an optimum specific capacitance in aqueous electrolyte on account of the pore size being close to the desolvated electrolyte ions, thus leading to a maximum electrical double-layer capacitance [17–22]. However, supercapacitors based on microporous carbons are known to suffer from electrode kinetic problems that are related to the limitation of electrolyte ions penetrating the inner pores of electrodes [23]. To address this problem, one effective solution is to introduce heteroatoms into the microporous carbon skeleton, thus increasing the wettability of the electrode surface and the accessibility of the micropores [24,25]. The focus of the current work is

\* Corresponding author.

E-mail address: [wencuili@dlut.edu.cn](mailto:wencuili@dlut.edu.cn) (W.-C. Li).

therefore to develop a synthesis approach for a microporous carbon integrating a narrow micropore size distribution and heteroatom modification in order to simultaneously achieve properties of a high capacitance, good rate performance and long cycle life.

To achieve this goal, herein we propose the use of L-glutamic acid as a new and single carbon precursor. L-glutamic acid, which contains abundant functional groups such as  $\text{-NH}_2$  and  $\text{-COOH}$ , has a strong tendency to coordinate with inorganic cations, e.g.  $\text{Zn}^{2+}$ . The advantage of using L-glutamic acid as a carbon precursor therefore is that the zinc cations can be homogeneously distributed on a molecular level. The synthesized carbon materials are expected to possess abundant micropores from the evaporation of the in situ-formed and uniformly dispersed Zn species during the carbonization process [26,27]. When such microporous carbons are used as supercapacitor electrodes, they show an excellent capacitive performance. It is anticipated that this synthesis can be relatively easily scaled up to an industrial level.

## 2. Experimental section

### 2.1. Chemicals

L-glutamic acid (99%) was purchased from J&K Scientific Ltd. Zinc chloride (98%) was purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

### 2.2. Synthesis of microporous carbons

In a typical synthesis procedure, L-glutamic acid was first dissolved in water to form a clear solution with vigorous stirring at 60 °C. Afterwards, zinc chloride dispersion was added to the above solution and stirred until the reaction solution was again homogeneous. Subsequently, the water in the homogeneous solution was removed by reduced pressure distillation and the obtained compound was transferred to an oven at 90 °C for 12 h followed by pyrolysis at 910 °C (the evaporation temperature of metal Zinc) for 2 h under an argon atmosphere to obtain porous carbon. By varying the molar ratio of zinc chloride to L-glutamic acid (2:1, 1:1 and 0.5:1), three samples (denoted as Glu-Zn-2, Glu-Zn-1 and Glu-Zn-0.5) with different pore volumes were prepared. As a control experiment, one sample (denoted as Glu-Zn-0) was also prepared by direct pyrolysis of L-glutamic acid at 910 °C in an argon atmosphere.

### 2.3. Structure characterization

Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 instrument. Transmission electron microscopy (TEM) images were recorded on a FEI Technai F30 equipment operating at 200 kV. The samples for TEM analysis were prepared by placing a droplet of the products in EtOH onto carbon-coated copper grids and drying at room temperature. The X-ray diffraction (XRD) patterns were obtained on a Rigaku D/Max 2400 diffractometer by using  $\text{CuK}\alpha$  radiation (40 kV, 100 mA,  $\lambda = 1.5406 \text{ \AA}$ ). The specific surface area and porous structure were determined by nitrogen sorption on a Micromeritics ASAP 2020 device at 77 K, and prior to analysis, all samples were degassed under a pressure of 0.05 mbar at 200 °C for 12 h. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas ( $S_{\text{BET}}$ ). Total pore volumes ( $V_{\text{total}}$ ) were calculated from the amount of nitrogen adsorbed at a relative pressure,  $P/P_0$  of 0.99. The pore size distribution was obtained using the Non-Local Density Functional Theory (NLDFT) method. Elemental analysis was carried out on a CHNO elemental analyzer (Vario EL III,

Elementar). The weight ratio of zinc was determined through inductively coupled plasma optical emission spectrometry (ICPOES, Perkin Elmer, Optima 2000 DV ICP-OES). X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALAB250 electron spectrometer.

### 2.4. Electrochemical measurements

The working electrodes were prepared by mixing porous carbons, Ketjen Black and polytetrafluoroethylene (PTFE) binder with weight ratio of 8:1:1. The slurry of the mixture was rolled into a film, cut into suitable shapes and placed into an oven at 90 °C for 10 h, followed by placing it on a foam nickel current collector with an area of 1  $\text{cm}^2$  under a pressure of 10 MPa to fabricate an electrode. The mass loading of the active material was approximately 4  $\text{mg cm}^{-2}$ . The capacitive performance of the single electrode was carried out on an CHI660D electrochemical workstation (CH Instruments Inc., Shanghai, China) using a standard three-electrode test system composed of Hg/HgO as a reference electrode and a Pt plate as a counter electrode in 6 M KOH electrolyte at 25 °C. Cyclic voltammetry (CV) and galvanostatic charge-discharge cycling (GC) measurements were employed in the evaluation of the electrode electrochemical performance. Electrochemical impedance spectroscopy measurements were carried out in the range of 0.01 Hz–100 kHz with ac amplitude of 5 mV. The specific gravimetric capacitance based on the GC test was calculated using the following equation:  $C = I\Delta t/m\Delta V$ , where  $I$  (A),  $t$  (s),  $\Delta V$  (V) and  $m$  (g) are the discharge current, the discharge time, the voltage window from the end of the internal resistance (IR) drop to the end of the discharge process, and the mass of active material, respectively. The cycle life, leakage current and self-discharging performances were measured by a multichannel electrochemical workstation (Arbin Instruments USA).

## 3. Results and discussion

To synthesize desired microporous carbons, the selection of carbon precursor is crucial. In this study, we use L-glutamic acid as a single carbon precursor based on the consideration that it contains abundant functional groups such as  $\text{-NH}_2$  and  $\text{-COOH}$ , and has a strong tendency to coordinate with zinc cations. The FTIR spectrum of the as-prepared carbon precursor in Fig. S1 is evidence that the L-glutamic acid can indeed coordinate with  $\text{Zn}^{2+}$ . Moreover,  $\text{Zn}^{2+}$  can combine with the lone pair electrons of the nitrogen atom in nitrogen-containing ligands such as  $\text{-NH}_2$  [28]. This in turn facilitates the immobilization of the nitrogen atoms in the carbon framework. Based on the above, we used L-glutamic acid and  $\text{ZnCl}_2$  as the starting materials, with the expectation that the highly dispersed Zn cations would act as facile porogens by volatilization of *in situ* formed Zn clusters and thus lead to the formation of an abundance of micropores [27].

By varying the molar ratio of zinc chloride to L-glutamic acid (2:1, 1:1 and 0.5:1), three carbon samples were prepared with a carbonization yields of ca. 19 wt% (910 °C). The synthesized carbon materials were characterized by TEM, to gain an insight into the microstructures. Since the structures of all the samples are very similar from TEM observations, representative TEM images of Glu-Zn-2 are shown in Fig. 1a and b. It can be seen that the carbon skeleton of Glu-Zn-2 is highly amorphous and homogeneous in absence of visible Zn clusters. To check the homogeneity of the  $\text{Zn}^{2+}$  distribution in the carbon precursor, the carbon product derived from the Glu-Zn-2 precursor carbonized at 600 °C (denoted as Glu-Zn-2-600) was characterized using Energy-dispersive X-ray spectroscopy (EDX). As shown in Fig. S2, the element mappings of the representative regions show a concordance of the Zn, C, and O

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