



# Notable improvement of capacitive performance of highly nanoporous carbon materials simply by a redox additive electrolyte of *p*-nitroaniline



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## H I G H L I G H T S

- Magnesium citrate and nickel nitrate as carbon source and graphitization catalyst.
- Synchronous carbonization and graphitization method is simple and effective.
- Adding redox additive of *p*-nitroaniline can highly improve the performance.
- Redox additive into KOH electrolyte can be operated at ambient condition.

## A R T I C L E I N F O

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## A B S T R A C T

Highly nanoporous carbon materials have been produced by a synchronous carbonization/graphitization process, using magnesium citrate serves as the carbon source and nickel nitrate as graphitization catalyst. The carbonization temperature plays a crucial role in determining the porosity and graphitization. The lower temperature favors for the formation of larger porosity, whilst higher temperature for better crystallinity. Resultantly, a high BET surface area of 2587.13 m<sup>2</sup> g<sup>-1</sup> and large total pore volume of 4.64 cm<sup>3</sup> g<sup>-1</sup> appear, the case of **C-800** sample, thereby resulting in a large specific capacitance of 305.3 F g<sup>-1</sup> at 1 A g<sup>-1</sup> from the contribution of electric double layer capacitances. More importantly, we demonstrate a novel redox active additive of *p*-nitroaniline (PNA) into the 6 mol L<sup>-1</sup> KOH electrolyte to largely improve the capacitance by the quick self-discharge redox reaction of H<sup>+</sup>/e<sup>-</sup>. The **C-800-2** sample with the PNA concentration of 2 mmol delivers largely improved capacitance of 502.1 F g<sup>-1</sup> at 1 A g<sup>-1</sup>, which is almost 1.65 fold increase. Apparently, the present PNA is commercially available, and highly effective for elevating the specific capacitance and might be implemented for the wide supercapacitor application.

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## 1. Introduction

Recently, nanoporous carbon materials have caused the extensive concern because of various applications in scientific research, especially in the field of electric energy storage [1,2]. Generally speaking, nanoporous carbon materials with high surface areas are

favorable to the generation of the electrical double layer capacitances (EDLCs), which result from electrostatic attraction between the carbon surface and ions [3,4]. On the other hand, with the rapid increasing exploration about carbon materials, template carbonization method has been proved to be a simple and effective approach for producing highly nanoporous carbon materials. Templates refer to some nanostructured or self-assembled materials, which can give rise to the formation of pores during the carbonization process without any chemical or physical activation [5–7]. The resulting carbon materials commonly have sizable surface areas and controllable pore structures to meet the

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requirements of the electrostatic attraction, which thereby lead to the improvements of the EDLCs. As a typical example, magnesium citrate has exhibited its potential to produce nanoporous carbon with high electrochemical performance [8,9]. Nanoporous carbon prepared through carbonization of sole magnesium citrate displays excellent BET surface area of  $2322.00 \text{ m}^2 \text{ g}^{-1}$  and pore volume of  $1.33 \text{ cm}^3 \text{ g}^{-1}$ , and the specific capacitance of which is  $180.3 \text{ F g}^{-1}$  at  $0.5 \text{ A g}^{-1}$  [8]. Then followed by this study, Mg powder as hard template was incorporated into Mg citrate to modulate the pore structures and improve the capacitances of carbon samples. As a result, the obtained nanoporous carbon delivers a larger specific capacitance of  $236.5 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$ , which is derived from the high BET surface area ( $1972.12 \text{ m}^2 \text{ g}^{-1}$ ) and the large pore volume ( $1.33 \text{ cm}^3 \text{ g}^{-1}$ ) [10].

The examples mentioned above have evinced the significance/effectiveness of template carbonization method toward the formation of nanoporous carbon. However, most of these nanoporous carbons indicate poor rate performances probably incurred by their poorly graphitic structures, which might be difficult to satisfy the requirements of high performance supercapacitors. On the other hand, graphitic carbons normally have high electrical conductivities and good chemical stabilities, which make them to be superior candidates of electrode materials to some extent [10,11]. One of the most used methods for producing high graphitization degree carbon materials is the direct heating of carbon precursors at extremely high temperatures such as  $2000\text{--}3000 \text{ }^\circ\text{C}$ , in which the activity of the molecule to accelerate the crystallization [12,13]. Although porous carbon with a well-developed graphitic order can be formed after heat treatment, the surface area and the pore volume have also been reduced. For example, the BET surface area has reduced from  $185.00$  to  $115.00 \text{ m}^2 \text{ g}^{-1}$  when graphitized from  $1000$  to  $2500 \text{ }^\circ\text{C}$ , meanwhile the pore volume decreasing from  $1.63$  to  $1.12 \text{ cm}^3 \text{ g}^{-1}$  [13].

To circumvent the above disadvantages, some catalysts have been employed to give assistance *in situ* producing graphitic nanoporous carbon at relatively low carbonization temperature (usually below  $1000 \text{ }^\circ\text{C}$ ). Up to now, there are many reports about this catalytic graphitization approach using metal salts as catalysts, like cobalt nitrate [14], nickel nitrate [11,15] and nickelous hydroxide [16]. Note that nickel is a kind of rational and effective catalyst to favor the graphitization enhancement. An instance is that nickel nitrate was used as a catalyst to increase graphitization of carbon at  $1000 \text{ }^\circ\text{C}$  [11]. In contrast with nanoporous carbon without being graphitized, the resulting carbon show slightly decreased specific capacitances but better rate performances, namely a moderate decrease rate in capacitance [11].

In view of the decreased electrochemical performance, some researches about introducing redox active additive into electrolyte have been reported in order to further enhance the performances of supercapacitors [17,18]. In general, the performance enhancement caused by redox active additive is probably due to the quick self-discharge redox reaction between the electrode and electrolyte, whether the redox-additive is inorganic or organic species [19]. As a typical inorganic redox-additive, KI is a kind of universal redox-additive in  $\text{H}_2\text{SO}_4$  electrolyte system on account of the plentiful possible redox reactions between the pairs of  $3\text{I}^-/\text{I}_3^-$ ,  $2\text{I}^-/\text{I}_2$ ,  $2\text{I}_3^-/3\text{I}_2$  and  $\text{I}_2/2\text{IO}_3^-$  [17]. In the case of some common organic redox-additives, such as benzoquinone–hydroquinone [18], indigo carmine [20] and *p*-phenylenediamine [21], they all contain functional groups like  $-\text{OH}$ ,  $-\text{CH}_3$  and  $-\text{NH}_2$ , which can ionize hydrogen ion give rise to the redox reaction of  $\text{H}^+/\text{e}^-$ . For example, the specific capacitance measured in KOH electrolyte with the redox-additive of *p*-phenylenediamine (PPD) has an almost fivefold increase than in the conventional KOH electrolyte (from  $144.0$  to  $605.2 \text{ F g}^{-1}$  at the same current density of  $1 \text{ A g}^{-1}$ ) [22]. Therein,

PPD contains two functional groups of  $-\text{NH}_2$  around the benzene ring, providing two protons in the redox process. As a whole, introducing redox active additive is promising method for highly improving the capacitances and further exploring new kinds of redox active additives are still meaningful and significant for achieving high performance supercapacitors.

Herein, we demonstrate a facile template carbonization approach for producing highly nanoporous carbon materials, accompanied with synchronous catalysis graphitization process. We chose magnesium citrate as the carbon source, because of its potential to produce nanoporous carbon with high electrochemical performance [8,9]. It is notable that the decomposition of magnesium citrate can produce MgO as the hard template and mixture gases as the soft template [9]. Simultaneously, nickel nitrate is employed as catalyst in order to enhance the graphitization of nanoporous carbon in the carbonization process. The obtained highly nanoporous carbon with high BET surface areas and large pore volumes exhibit superior electrochemical performances in KOH electrolyte. Furthermore, *p*-nitroaniline (PNA) is a kind of organic matter with one functional group of  $-\text{NH}_2$ , which can make it applicable redox active additive *via* the transfer of electron and proton. The electrochemical performance of the highly nanoporous carbon has been measured in KOH electrolyte with different amounts of PNA. By comparison, introducing PNA into KOH electrolyte indeed facilitates the enhancement of the electrochemical performance.

## 2. Experimental section

### 2.1. Typical synchronous carbonization/graphitization for carbon sample

In this work, certain amount of magnesium citrate tetradecahydrate ( $\text{C}_{12}\text{H}_{10}\text{Mg}_3\text{O}_{14} \cdot 14\text{H}_2\text{O}$ ) and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with the mass ratio of 3:1 have been converted into nanoporous carbon materials *via* a straightforward template carbonization method. Typically, magnesium citrate tetradecahydrate and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were first mixed and ground. The mixture were placed in a horizontal tube furnace, and heated up to  $800/900/1000 \text{ }^\circ\text{C}$  at a rate of  $5 \text{ }^\circ\text{C min}^{-1}$  in Ar atmosphere for 2 h, respectively. Then, the products were ground into powder and washed with  $1 \text{ mol L}^{-1}$  HCl solution to remove soluble/insoluble impurities. Finally, the resulting carbon samples were obtained after dried at  $120 \text{ }^\circ\text{C}$  overnight under vacuum. These as-obtained carbon samples were named as **C-800/900/1000** samples, respectively.

### 2.2. Structure characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX2500 V diffractometer using  $\text{Cu K}\alpha$  radiation ( $40 \text{ kV}$  and  $40 \text{ mA}$ ) at a scan rate of  $2 \text{ }^\circ/\text{min}$ . Raman spectra were recorded at ambient temperature on a Spex 1403 Raman spectrometer with an argon-ion laser at an excitation wavelength of  $514.5 \text{ nm}$ . High-resolution transmission electron microscope (HRTEM) images and selected area electron diffraction (SAED) patterns were performed with a JEM-2100 F unit. The samples for HRTEM were prepared by ultrasonic dispersing the powder products in ethanol, which were then deposited and dried on a holey carbon film on a copper grid. The specific surface area ( $S_{\text{BET}}$ ) and pore structure of the carbon samples were determined by  $\text{N}_2$  adsorption–desorption isotherms at  $77 \text{ K}$  (Quantachrome Autosorb-iQ) after being vacuum-dried at  $150 \text{ }^\circ\text{C}$  overnight. The specific surface areas were calculated by the BET (Brunauer–Emmett–Teller) method. Cumulative pore volume and pore size distribution were calculated by using a slit/cylindrical nonlocal density functional theory (NLDFT) model.

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