Journal of Electroanalytical Chemistry 764 (2016) 45–55

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Nitrogen-doped nanoporous carbon materials derived from folic acid: Simply introducing redox additive of *p*-phenylenediamine into KOH electrolyte for greatly improving the supercapacitor performance

Zhong Jie Zhang [a,*], Xiang Ying Chen [b]

[a] College of Chemistry & Chemical Engineering, Anhui Province Key Laboratory of Environment-friendly Polymer Materials, Anhui University, Hefei 230601, Anhui, PR China
[b] School of Chemistry and Chemical Engineering, Anhui Key Laboratory of Controllable Chemistry Reaction & Material Chemical Engineering, Hefei University of Technology, Hefei, Anhui 230009, PR China

ARTICLE INFO

Article history:
Received 23 November 2015
Received in revised form 2 January 2016
Accepted 15 January 2016
Available online 16 January 2016

Keywords:
Folic acid
Template
Redox additive
p-Phenylenediamine
Supercapacitor

ABSTRACT

In the present work, we have demonstrated a simple but effective template carbonization approach to convert folic acid into highly nitrogenated nanoporous carbon materials, using $Mg(OAc)_2 \cdot 4H_2O$ as template. For the **C-800**/**900**/**1000** samples, the nitrogen contents can reach up to 9.03%, 6.81%, and 6.65%, respectively, and they also deliver large BET surface areas of 1242.2, 1559.1, and 1302.8 $m^2\ g^{-1}$, and high pore volumes of 1.36, 2.26, and 1.44 $cm^3\ g^{-1}$, respectively. On the other hand, it is revealed that the incorporation of *p*-phenylenediamine as a redox additive into KOH electrolyte has greatly improved the capacitances, mostly due to the occurrence of pseudo-capacitance derived from the redox reaction of *p*-phenylenediamine at the electrode/electrolyte interface. For instance, the capacitances of the **C-900-6/9/12** samples can reach up to 105.1, 232.8, and 317.6 $F\ g^{-1}$ at 5 $A\ g^{-1}$, respectively, and all of which are much higher than that of the pristine **C-900** sample (42. $F\ g^{-1}$). Obviously, we have provided a simple but highly efficient approach for the improvement of the supercapacitor capacitance by introducing the *p*-phenylenediamine into KOH electrolyte, which exhibits the advantages of low cost, easy operation, high efficiency, etc.

1. Introduction

Nitrogen-containing nanoporous carbon materials have attracted great attention with a wide range of technologically important applications, especially the areas of energy generation and storage application [1]. Generally, the nitrogen functionality has basic character, which can induce electron-donor properties. In addition, doping N atoms into carbon materials strengthens the wettability of the interface between the electrode and electrolyte [2]. Regarding the case of supercapacitor application, the incorporation of N species can also result in pseudo-capacitive effect that generally originates from Faradaic contribution by the substitution of heteroatoms, thereby benefiting the increase of overall capacitance. To date, nitrogen-containing functional groups can be introduced through reaction of carbon precursors with nitrogen-containing reagents (such as NH_3, melamine, urea, etc.) or direct carbonization (with or without activation) of nitrogen-rich carbon precursors. Obviously, the latter approach exhibits better advantages such as simplicity, easy processibility and low cost. So far, lots of nitrogen-rich carbon precursors such as ionic liquids [3], polypyrrole [4], *p*-nitrobenzenamine [5], and terephthalonitrile [6] have been documented for the production of N-doped carbon.

Apart from the aforementioned N-doping of carbon, another intriguing method for greatly improving the electrochemical performance is to incorporate redox additives into the conventional electrolytes (such as KOH, H_2SO_4), primarily thanks to the occurrence of pseudo-capacitances incurred by the redox reactions at the electrode–electrolyte interface [7]. Up to now, the redox additives can be usually categorized into inorganic and organic species. In the case of inorganic ones, the pseudo-capacitive effects mainly come from the redox pairs with various kinds of valence states during the electrochemical process. For instance, since iodide ion (I^-) can produce redox pairs of $3I^-/I_3^-$, $2I^-/I_2$, $2I_3^-/3I_2$, and I_2/IO_3^-, the KI has been implemented as a novel redox additive for greatly elevating the supercapacitor capacitances. In the mixed 1 M KOH + 0.05 M KI electrolyte, the specific capacitance and energy density of reduced graphene oxide is 500 $F\ g^{-1}$ and 44 $Wh\ kg^{-1}$, respectively [8], and nearly two-fold improved specific capacitance and energy density of 912 $F\ g^{-1}$ and 19.04 $Wh\ kg^{-1}$ were achieved when 0.08 M KI was added to 1 M H_2SO_4 electrolyte [9]. On the other hand, in the case of organic redox additives, the pseudo-capacitive capacitances stem from the contributions of hydroxyl and/or amine functionalities, which commonly release pairs of protons and electrons during the redox reaction process. Excellent organic redox additives include *p*-phenylenediamine and hydroquinone, and both of them can synchronously give two protons and two electrons, thus enabling the increase of total capacitances of supercapacitors. For example, adding 0.050 g *p*-phenylenediamine to 2 M KOH electrolyte can lead to a

---

* Corresponding author.
E-mail addresses: zhangzj0603@126.com (Z.J. Zhang), cxyhfut@gmail.com (X.Y. Chen).

http://dx.doi.org/10.1016/j.jelechem.2016.01.017
1572-6657/

large capacitance and energy density of 605 F g^{-1} at 1 A g^{-1} and 19.8 Wh kg^{-1}, much higher than without *p*-phenylenediamine addition (144 F g^{-1} and 4.5 Wh kg^{-1}) [10]; when hydroquinone was incorporated into H_2SO_4 electrolyte, the performance has been greatly enhanced by quick Faradaic reaction, whose results (with the largest one at 901 F g^{-1} ever reported so far) are nearly three folds higher than the original one [11]. Thereby, the redox additive of *p*-phenylenediamine that has clearly exhibited the merits of low dosage, high efficiency, ambient operation, etc. still remains fascinating for quick but effective improvement of capacitances.

In the present work, we demonstrated a simple but efficient template carbonization method to produce nanoporous carbon materials containing nitrogen species, using folic acid as carbon/nitrogen source, and $Mg(OAc)_2 \cdot 4H_2O$ as template. Folic acid as a typical kind of vitamin displays an interesting unit structure, as shown in Fig. 1a, which commonly contains phenyl group (serving as carbon source) and, in particular, many groups containing nitrogen (acting as nitrogen source). That is the reason why we chose folic acid as carbon precursor. However, when solely heating folic acid at elevated temperatures such as 800 °C, only seriously sintering carbon samples appeared, and, therefore, certain amount of template needs to be introduced for circumventing this shortcomings. Herein, we adopted $Mg(OAc)_2 \cdot 4H_2O$ as template to form the pores within carbon matrix, for the following reasons: (1) it is commercially available but more inexpensive, compared with other templates (SiO_2, $CaCO_3$, ZnO, etc.) commonly used for pore formation; (2) it is quite soluble in H_2O, therefore it can be mixed with folic acid (also soluble in water) more homogeneously when adding a little water in the grinding process, which guarantees the homogeneity in composition and phase; (3) it can decompose into MgO, and lots of gases during the carbonization process, in which MgO serves as hard template (usually for the formation of mesopores and/or macropores), and the gases in situ produced as soft template (usually for the formation of micropores) [12]; (4) the removal of MgO in the final carbon product can be readily carried out by milder/greener acid such as HCl solution, while other kinds of templates such as SiO_2 to be removed need highly toxic/erosive HF solution. Actually, this kind of multi-template carbonization approach has been proved to be effective for producing hierarchically nanoporous carbon, usually with superior electrochemical performance for supercapacitors [13].

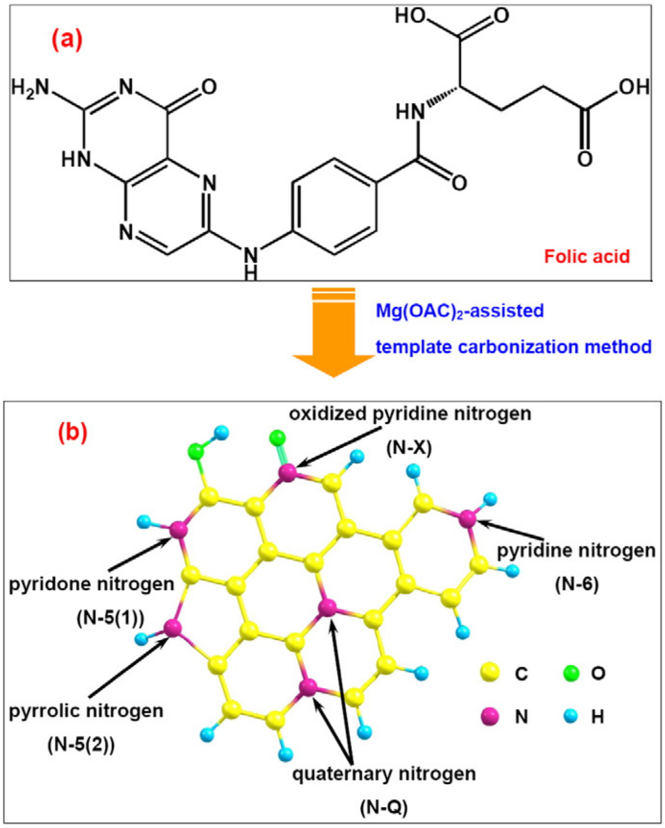

Fig. 1. (a) Unit structure of standard folic acid; (b) nitrogen species usually existent within the N-doped carbon matrix.

On the other hand, there exist several types of nitrogen species usually occurring within the N-doped carbon matrix, as illustrated in Fig. 1b, basically including pyridine nitrogen (N-6, the binding energy of ca. 398.5clearly eV), pyridone nitrogen (N-5(1), the binding energy of ca. 400.3 eV), pyrrolic nitrogen (N-5(2), also the binding energy of ca. 400.3 eV), quaternary nitrogen (N-Q, the binding energy of ca. 401.2 eV), and oxidized pyridine nitrogen (N-X, the binding energy of ca. 402.9 eV) [14]. Herein, due to the relatively large nitrogen content (22.2 wt.%; 13.7 at.%) in the raw material of folic acid ($C_{19}H_{19}N_7O_6$), so it is anticipated to produce highly nitrogenated carbon materials with the help of $Mg(OAc)_2 \cdot 4H_2O$ as template.

What's more, we used *p*-phenylenediamine as an efficient redox additive to highly enhance the capacitive performance of carbon-based supercapacitors when incorporated into 6 mol L^{-1} KOH electrolyte. The intrinsic reaction mechanism for the incremental capacitances is derived from the electron and proton transfer during the electrochemical process, which can of course give rise to the formation of pseudo-capacitive behaviors. Moreover, the molar concentration of *p*-phenylenediamine in KOH electrolyte was deeply investigated, clearly revealing the crucial role of redox additive for improving capacitances in the mixed electrolyte. Notably, although many research works were documented on the usage of *p*-phenylenediamine as redox additive in conventional KOH electrolyte, genuine but systematic illustrations concerning the highly nitrogen-doped nanoporous carbon materials (also producing pseudo-capacitances from the dopant of nitrogen species), as much as we know, have been rarely reported so far.

2. Experimental

2.1. Synthesis protocol

First, we used folic acid as carbon precursor (also as nitrogen source) to produce nitrogen-containing nanoporous carbon materials by a simple but effective $Mg(OAc)_2$-assisted template carbonization approach. When performed at 800, 900, or 1000 °C, a series of carbon materials named the **C-800/900/1000** samples appeared. Next, considering the fact that *p*-phenylenediamine can simultaneously give rise to proton and electron during the redox reaction process, therefore, in this work, a certain amount of *p*-phenylenediamine serving as redox additive has been incorporated into 6 mol L^{-1} KOH electrolyte to improve the electrochemical performances (mostly owing to the additional pseudo-capacitance produced from *p*-phenylenediamine). Besides, we emphatically investigated the effect of *p*-phenylenediamine concentration upon the variation of electrochemical behaviors. For all of the **C-800/900/1000** samples, the *p*-phenylenediamine concentrations were designated as 6, 9, and 12 mmol L^{-1}, and the resulting samples are called the **C-800-6/9/12**, **C-900-6/9/12**, and **C-1000-6/9/12** samples, respectively.

2.2. Typical template carbonization synthesis procedure for carbon samples

Folic acid ($C_{19}H_{19}N_7O_6$) and $Mg(OAc)_2 \cdot 4H_2O$ with the designated mass ratio of 1:1 were ground together in an agate mortar for 20 min, and then placed in a porcelain bowl, flushing with Ar flow for 30 min, and further heated in a horizontal tube furnace up to 800, 900, or 1000 °C at a rate of 5 °C min^{-1} and maintained at this temperature for 2 h under Ar flow. The resultant product was immersed with 1 mol L^{-1} HCl solution to remove soluble/insoluble substances, subsequently washed with adequate deionized water. Finally, the sample was dried under vacuum at 110 °C for 12 h to obtain the **C-800/900/1000** samples.