international journal of hydrogen energy XXX (2016) 1–11



Available online at www.sciencedirect.com

ScienceDirect



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

Nitrogen doped superporous carbon prepared by a mild method. Enhancement of supercapacitor performance

María José Mostazo-López ^a, Ramiro Ruiz-Rosas ^a, Emilia Morallón ^{b,*}, Diego Cazorla-Amorós ^a

^a Departamento de Química Inorgánica e Instituto Universitario de Materiales, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain

^b Departamento de Química Física e Instituto Universitario de Materiales, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain

ARTICLE INFO

Article history: Received 20 January 2016 Received in revised form 10 March 2016 Accepted 14 March 2016 Available online xxx

Keywords: Activated carbons Surface chemistry Nitrogen doped carbons Supercapacitors

ABSTRACT

Nitrogen functionalization (ca. 4 at. % N_{XPS}) of a highly microporous activated carbon ($S_{BET} > 3000 \text{ m}^2/\text{g}$) has been achieved by two different approaches at mild conditions: (i) oxidation and post-reaction with nitrogen reactants, and (ii) direct reaction of pristine carbon material with nitrogen reactants. Interestingly, the introduction of nitrogen functionalities allows full preservation of the microporosity when pathway (ii) is followed. The electrochemical performance of the carbon materials as electrodes for supercapacitors was evaluated by using symmetric and asymmetric configuration in 1 M H₂SO₄. Both nitrogenfunctionalized carbon materials showed larger stability and energy efficiency than the pristine carbon material when working at 1.4 V. The non-oxidized and functionalized activated carbon evidences the best performance as electrode for supercapacitor, providing energy and power density of 14.5 Wh/kg and 61.2 kW/kg and keeping 83% of original capacitance after 5000 charge–discharge cycles. This improvement is related to the presence of surface nitrogen functionalities that provide a higher electrochemical stability, avoiding the formation of detrimental oxygen groups during the operation of the supercapacitor.

Copyright ${\ensuremath{\mathbb S}}$ 2016, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Supercapacitors have attracted considerable interest as energy storage devices thanks to their high power density, a key missing feature of fuel cells and electrical batteries. They are based on the formation of an electrical double layer on the extensive surface of porous carbon materials, which is profited to store energy that can be delivered in few seconds. This energy storage mechanism is often complemented with pseudocapacitive processes produced by fast redox reactions occurring in electroactive surface functional groups. The development of electrode materials with large surface area,

* Corresponding author.

E-mail address: morallon@ua.es (E. Morallón).

http://dx.doi.org/10.1016/j.ijhydene.2016.03.091

0360-3199/Copyright © 2016, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Please cite this article in press as: Mostazo-López MJ, et al., Nitrogen doped superporous carbon prepared by a mild method. Enhancement of supercapacitor performance, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.03.091

electroactive functional groups and high electrochemical stability is crucial for the improvement of the energy density and durability of these devices [1,2].

Activated carbons are the most employed materials as electrodes for supercapacitors, mainly due to their large apparent surface area, proper electrical conductivity, high electrochemical stability and competitive production cost [2]. Also, their surface chemistry can be conveniently modified to introduce surface functionalities that could improve the performance of these materials by an increase of electrochemical stability, conductivity, wettability or pseudocapacitance [3]. For instance, oxygen groups and in aqueous electrolytes can increase the wettability of the surface, improving the electrolyte-electrode interaction and rendering a larger amount of the surface accessible for the formation of the electrical double layer, and can also participate in reversible faradaic reactions that contribute to the energy storage through pseudocapacitance [4]. Likewise, the presence of nitrogen on the surface of activated carbons improves the performance of activated carbon as electrodes of supercapacitors by increasing the wettability of the surface, the electrochemical stability, the conductivity or the contribution of pseudocapacitive processes [5–8]. Inversely to the ubiquity of surface oxygen groups, nitrogen functionalities are not as easily introduced in the structure of carbon materials, and the development of new procedures for obtaining nitrogencontaining porous carbons has therefore attracted a great interest.

Nitrogen-doped porous carbon materials can mainly be obtained by two pathways: reaction of the carbon material with a nitrogen-containing reagent (NH₃, HCN, etc) or carbonization/activation of nitrogen-rich carbon precursors (urea, polyaniline, etc.) [6,9]. However, these approaches are usually carried out at high temperatures and, in the case of post-treatments, these conditions strongly modify the porosity of the pristine carbon material [10,11]. Also, the control of the nitrogen functionalities that are formed during post-treatments is a challenge. Therefore, post-modification treatments at low temperature are highly desirable for obtaining different nitrogen functional groups while preserving the characteristic porous texture of the original carbon material.

In our previous work [11], we proposed the modification of the surface chemistry of a highly porous activated carbon using organic chemistry reactions. Briefly, this treatment consisted in the oxidation of the carbon material in order to introduce oxygen functionalities that, afterwards, were converted into nitrogen functionalities through an amidation treatment. In a last step, the post-conversion of the formed amides into amine functional groups was achieved by a Hofmann rearrangement [12]. The modification protocol allowed the incorporation of different nitrogen functionalities. Interestingly, this method also leads to the formation of pyridines, pyridones and pyrroles, which have a positive impact in the electrochemical behavior of carbon materials [6,8], but are only introduced using high temperature treatments. However, the oxidation treatment carried out during the first step of the functionalization protocol produced a remarkable decrease of the microporosity along with the generation of non-desirable functional groups (CO₂-evolving groups) from the point of view of the capacitor performance. In this work, we propose a modification of this approach that allows the introduction of nitrogen on carbon materials but preventing the previous incorporation of oxygen functional groups. The electrochemical performance of the pristine and the nitrogenfunctionalized activated carbons has been assessed as electrodes for supercapacitors.

Experimental

Activated carbon

A highly microporous activated carbon prepared in our laboratory has been used as the starting material for nitrogen incorporation via organic chemical modification. The pristine material, henceforth named KUA, has been obtained by chemical activation of a Spanish anthracite (11 wt% of ash content) with KOH using an impregnation ratio of activating agent to raw material of 4:1 and an activation temperature of 750 °C under inert atmosphere, which was held for 1 h. More details about the preparation process are available elsewhere [13].

Chemical functionalization of activated carbon

Synthesis of KUA-CONH2

In our previous work [11], an approach for the incorporation of amides over activated carbon was satisfactorily developed. Also, other nitrogen functional groups were introduced on the surface of the carbon material via secondary reactions. The amidation treatment was carried out as follows:

- (i) Chemical oxidation with HNO₃ in order to introduce oxygen functional groups on the surface of KUA [14].
- (ii) Generation of acyl chloride functionalities by reaction of the activated carbon obtained on step (i) with SOCl₂ in toluene under Ar atmosphere.
- (iii) Reaction of the activated carbon obtained in step (ii) with 2 M NH_4NO_3/DMF solution and pyridine.

The obtained activated carbon was named KUA-CONH2. More details about the preparation process are available elsewhere [11].

Synthesis of KUA-N

In this case, step (iii) is directly carried out over activated carbon KUA, in order to obtain nitrogen functional groups by using a single treatment via reaction with the existing CO_2 and CO-evolving groups in the pristine material. In this step (iii), 400 mg of KUA were added into 140 mL of 2 M NH₄NO₃/ DMF solution (activated carbon to solution ratio of 1 g/ 300 mL) in a round bottom flask. Then, 140 mL of pyridine were added slowly to the round bottom flask under continuous stirring at room temperature. The mixture was stirred at 70 °C for 65 h. The obtained sample (KUA-N) was washed with abundant water and ethanol, filtered and dried at 100 °C overnight.

Please cite this article in press as: Mostazo-López MJ, et al., Nitrogen doped superporous carbon prepared by a mild method. Enhancement of supercapacitor performance, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.03.091

Download English Version:

https://daneshyari.com/en/article/5147465

Download Persian Version:

https://daneshyari.com/article/5147465

Daneshyari.com