INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 42 (2017) 28797–28806

Available online at www.sciencedirect.com

ScienceDirect

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

Design and synthesis of Ni-Co and Ni-Mn layered double hydroxides hollow microspheres for supercapacitor

M. Li [a,b], PengWei Yuan [a], SongHao Guo [a], F. Liu [a], J.P. Cheng [a,*]

[a] State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province, Zhejiang University, Hangzhou 310027, PR China

[b] Research Institute of Narada Power Source Co., Ltd, Hangzhou 311305, PR China

ARTICLE INFO

Article history:
Received 3 July 2017
Received in revised form
6 September 2017
Accepted 2 October 2017

Keywords:
Layered double hydroxides
Hollow microsphere
Electrochemical properties
Supercapacitors

ABSTRACT

The development of electrode materials with hierarchically porous structure and high electrochemical stability is crucial for the electric energy density of supercapacitors. Hollow microspheres of Ni-Co layered double hydroxides (LDHs) and Ni-Mn LDHs are fabricated with a simple co-precipitation method at low temperature using SiO_2 microspheres as a sacrifice template. The as-fabricated two LDH hollow microspheres possess a unique 3D architecture and exhibit high specific capacitance, as well as excellent rate and cycling performances as electrode materials of supercapacitors. A specific capacitance of 1766.4 F g^{-1} at 1 A g^{-1} is achieved for Ni-Co LDHs electrode, much higher than that of Ni-Mn LDHs. A hybrid capacitor composed of Ni-Co LDHs hollow spheres and activated carbon is fabricated and evaluated for practical application, providing an energy density of 44.3 Wh kg^{-1} at a power density of 0.425 kW kg^{-1}. This study indicates that the hollow LDH microsphere prepared by our method is a promising material for supercapacitors.

Introduction

With the rapid increase of energy depletion in the world, it is urgent for us to find eco-friendly energy storage devices for electric vehicles to reduce the use of fossil fuels. A supercapacitor can supply a high power, but can not store much energy and it can be applied as an auxiliary power in electric vehicle [1]. Supercapacitors store electrical energy by two main mechanisms, *i.e.* pseudocapacitance and electric double layer capacitance (EDLC) [2]. Pseudocapacitor usually exhibit higher energy densities than EDLC due to the reversible Faradaic reaction on the surface of electrode materials. Electrode materials are essential for the performance of supercapacitors and have received much attention [3–5].

Recently, a lot of research has been carried out on layered double hydroxides (LDHs) due to their unique layered structure, large specific surface area, tunable compositions, low cost and environmental friendliness [6–11]. They have attracted tremendous attention for the application in the fields of energy storage, catalysts, magnetic materials and material science [12–16]. In the past decade, LDHs containing transition metals have been considered as promising electrode materials for supercapacitors because of their high theoretical specific capacitance [8,17–19]. However, the electrochemical reactions of LDHs during the charge and

* *Corresponding author.*
E-mail address: chengjp@zju.edu.cn (J.P. Cheng).
https://doi.org/10.1016/j.ijhydene.2017.10.019

discharge processes are limited by the low charge transfer rate, slow electrolyte penetration, and unsatisfactory electrical conductivity. A lot of efforts have been thus devoted to enhancing their electrochemical performances, which can be generally divided into two strategies, *i.e.* combining LDHs with other highly conductive materials to form heterogeneous composites and designing reasonable porous nanostructures or architectures with high specific surface areas [16,20–23]. Previous reports have proved that the former can realize a synergistic effect through inducing large porosity, minimizing particle size, preventing LDHs from densely stacking, enhancing specific surface area, facilitating electron and proton conduction, delivering more active sites, extending the potential window, protecting active materials from mechanical degradation. The latter will provide short transport/diffusion path lengths for electrons and ions directly, leading to faster kinetics, more efficient contact of electrolyte ions, and more active sites for Faradaic reaction, resulting in high charge/discharge capacities even at high current densities [13,23,24].

Hierarchically hollow structures with well-defined micro/nanostructures, mesoporous pore-size distribution, high surface areas, preferable electrolyte permeability and favorable charge transfer have been confirmed to possess great potential to enhance the electrochemical performance of LDHs. Despite so, synthesizing hollow architecture with well-defined cavity and exterior surface is still challenging. In the reports, except a few template-free techniques such as tert-butanol (TBA) as a structure directing agent for the synthesis of α-$Ni(OH)_2$ hollow microspheres [25] and directly synthesizing hollow Co-Al LDHs spheres with a hydrothermal method [26], template-assisted technique is popularly used to synthesize LDHs. LDHs nanosheets were usually *in situ* grown on spherical templates such as SiO_2 [27–29], Fe_3O_4 [30,31], carbon nanospheres [32] and polystyrene (PS) [33,34] to obtain core-shell structures first. Then, the core materials were removed to produce hollow structures with well controllable shape and size. For example, Yan et al. [35] deposited an AlOOH layer on the surface of SiO_2 microspheres for the following *in situ* growth of Ni-Co double hydroxides. After removal of SiO_2 spheres, hollow structured Ni-Co double hydroxides with a high specific capacitance of 2275.5 F g^{-1} at 1 A g^{-1} were thus obtained. Shao et al. [28] reported that Ni-Al LDHs microspheres with tunable (core-shell, yolk-shell, and hollow) interior architectures could be synthesized by a similar *in situ* growth method. The hollow structured product had the advantage of very good capacitive performance, including high specific capacitance and rate capability, excellent charge/discharge stability and long-term cycling life, superior to the yolk-shell and core-shell structure. Yang's group [36] fabricated a hollow double-shelled carbon-based composite with enriched nitrogen through the same synthetic strategy.

All above reports show us a hint that using spherical SiO_2 templates to fabricate hollow LDHs spheres is a feasible way to obtain electrode materials with enhanced electrochemical performances. But, there are two defects for the template-related methods. First, all above structures were obtained by the synthesis of AlOOH as an intermediate product, which were time-consuming and complex. So, Xu [37] has improved the synthetic strategy by directly depositing Ni-Co LDHs on hollow carbon nanospheres more recently. Second, all the hollow LDHs were synthesized by a time-/energy consuming hydrothermal process, which is not suitable for large scale production. Not only that, to the best of our knowledge, most of hollow micro/nanostructures were obtained by a time/energy-consuming hydrothermal process or under heating processes [25,38].

In this work, in order to obtain high-performance electrode materials for supercapacitor, we demonstrate a well-designed fabrication of hollow Ni-Co LDHs and Ni-Mn LDHs with a simple co-precipitation method without using any intermediate product under low temperature, below 50 °C, even at room temperature. This unique method uses SiO_2 spheres as sacrifice cores and deposits Ni-Co and Ni-Mn LDHs nanosheets directly onto the surface of SiO_2 spheres as exterior shells. After a final process to remove SiO_2 spheres, hollow LDHs spheres possess unique architecture and high electrochemical performances are thus obtained. This work introduced a facile method to fabricate hollow LDHs under low temperatures and the as-prepared LDHs hollow structures exhibited high potential for energy storage.

Experimental

Preparation of LDH materials

The mono-dispersed silica microspheres were prepared by a modified Stöber method, *i.e.*, hydrolysis of tetraethyl orthosilicate (TEOS) in an alcohol medium with the presence of water and ammonia, as reported by Hsu et al. [39]. To prepare the intermediate product of SiO_2@LDHs, 200 mg of as-prepared SiO_2 spheres were dispersed in 100 mL alcohol with ultrasonic for 1 h. Then, total 4.5 mmol metal nitrates (containing 3 mmol $Ni(NO_3)_2$ and 1.5 mmol $Co(NO_3)_2$ or $Mn(NO_3)_2$) were dissolved into above suspension. A co-precipitation process was carried out to deposit Ni-Co LDHs or Ni-Mn LDHs nanoplates shell onto the surface of SiO_2 spheres. In this process, 23 mL ammonia (1 mol L^{-1}) was dropwisely added into the suspension of SiO_2 and metal nitrates under continuous magnetic stirring for 1 h. After filtration and washing thoroughly with deionized water and alcohol, the intermediate product was thus obtained. Then core-shell structured SiO_2@Ni-Co LDHs and SiO_2@Ni-Mn LDHs microspheres were dried at 80 °C for 10 h. It should be pointed out that the deposition of Ni-Co LDHs was carried out at room temperature, while for Ni-Mn LDHs was at 50 °C.

Hollow LDHs microspheres could be easily obtained by immersing above SiO_2@LDHs products into 0.5 M KOH solution for 1 h. 0.2 g SiO_2@LDHs could produce 0.12 g LDHs hollow spheres, indicating that the content of SiO_2 in SiO_2@LDHs was about 40 wt%.

Materials characterization

The phase, composition and morphology of the samples were characterized by a powder X-ray diffractometer (XRD, Shimadzu, LabX XRD-6000) with a secondary graphite monochromator, a scanning electron microscope (SEM, Hitachi S-