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Template and binder free 1D cobalt nickel hydrogen phosphate electrode materials for supercapacitor application

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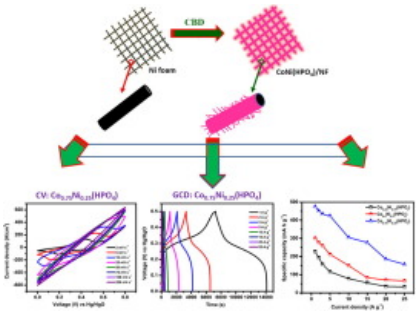
Abstract

Herein, we synthesized 1D bimetallic hydrogen phosphate [$Co_xNi_x(HPO_4)$] nanorods by using a simple and effective chemical bath deposition method for supercapacitor applications. The prepared $Co_xNi_x(HPO_4)$ was analyzed by Fourier transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD) pattern. The surface morphology was envisaged by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) methods. The porous nature and surface area of the materials were characterized by nitrogen sorption isotherm and a high specific surface area of 153 $m^2\ g^{-1}$ was found to be for $Co_{0.75}Ni_{0.25}(HPO_4)$. The $Co_{0.75}Ni_{0.25}(HPO_4)$ displays a maximum specific capacity of 475 $mAh g^{-1}$ at 1 A g^{-1} in a three-electrode configuration using 3M KOH as the electrolyte. $Co_{0.75}Ni_{0.25}(HPO_4)$ exhibits almost 94.8% of its initial specific capacity over 5000 GCD cycles at 10 A g^{-1}. Furthermore, the fabricated asymmetric supercapacitor (ASC) with $Co_{0.75}Ni_{0.25}(HPO_4)$ and activated carbon (AC) showed a high specific capacitance of 182.5F g^{-1} at 0.5 A g^{-1}. The ASC device delivered a maximum energy density of 64.88 Wh kg^{-1} at a power density of 800W kg^{-1}.

Graphical abstract



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Introduction

In recent years, with the ever-increasing demands for green energy, energy-storage devices with excellent outcomes, cheap prices, and eco-friendliness have attracted intense attention from both the academic and industrial domains [1], [2]. Supercapacitors (SCs) have been widely explored as one of the most promising energy storage devices due to their outstanding electrochemical characteristics, such as the high specific power and exceptional specific capacitance as well as the rapid charge–discharge process [3], [4].

An effective approach for improving the rate capability of metal oxide/hydroxide positive materials is to combine one or two metal ions into them to form multi-metal compounds, such as Co-Ni [5], [6], Al-Co [7], Ru-Co [8], Mo-Co [9], Co-Mn [10]and Zn-Ni-Co oxides or hydroxides [11], which can produce ample structural defects and ensure rapid redox reactions. Of these materials, nanostructured binary Co-Ni is considered being one of the prominent contenders due to its high theoretical capacitance (above 2000 F g^{-1}), excellent discharge level, favorite rate capability, and relatively rich redox reactions compared with unitary Ni or Co oxide [12], [13]. However, their energy storage capability still lowers the expected value, possibly restricting their practical applications.

Very recently, metal hydrogen phosphates (MHPs) have been attracted owing to their layered surface-interface structure, which provides facile access for electrolyte ions and good ion intercalation in electrochemical applications [14]. To the best of the author's knowledge, very few articles are published in MHP for supercapacitor applications. For example, Huan Pang et al. [14] have synthesized cobalt hydrogen phosphate ($CoHPO_4.3H_2O$) ultrathin nanosheets by a simple one-pot hydrothermal method for supercapacitor applications. The $CoHPO_4.3H_2O$/Nickel foam electrode displayed a maximum specific capacitance of 413F g^{-1} in a three-electrode configuration. Despite the prepared material was cobalt hydrogen phosphate ($CoHPO_4.3H_2O$) but the author stated cobalt phosphate only in the entire manuscript. Recently, Abdulmajid A. Mirghni et al. [15] synthesized bimetallic sodium–nickel phosphate/graphene foam composite ($NaNi_4(PO_4)_3$/GF) by a direct and facile precipitation method. The $NaNi_4(PO_4)_3$/GF composite electrode shown the highest specific capacity of 63.3 mAh g^{-1} at 1 A g^{-1} in a three-electrode system. Furthermore, a designed and fabricated hybrid $NaNi_4(PO_4)_3$/GF//AC (activated carbon) asymmetric supercapacitor exhibited the highest specific energy and specific power of 19.5 Wh kg^{-1} and 570 W kg^{-1}, respectively at a current density of 0.5 A g^{-1}. Yufeng Zhao et al. [16] reported NH_4-Co-Ni phosphates composed of $(Ni,Co)_3(PO_4)_2{\cdot}8H_2O$ ultrathin nanoslices and single crystal $(NH_4)(Ni,Co)PO_4{\cdot}0.67H_2O$ were synthesized through a mild hydrothermal sacrificial template method. The mixed phases existing a high specific capacitance of 1128 F g^{-1} at 0.5 A g^{-1}. An asymmetric supercapacitor exhibited high specific energy of 35.3 Wh kg^{-1} at low specific power of 101 W kg^{-1} and still holds 30.9 Wh kg^{-1} at 4400 W kg^{-1}, accompanied with excellent cyclic stability (retained 95.6% of its initial capacitance over 5000 GCD cycles).

However, the above-mentioned methods need intricate multiple steps, such as the template method, the requirement of stainless steel autoclave for hydrothermal synthesis, using urea or ammonium hydroxide for reducing agent. The removal of hard templates or selective etching in a suitable solvent, which would make the product contaminated and time tedious process. However, in this present study, we used the simple chemical bath deposition (CBD) method to produce bimetallic hydrogen phosphate, $Co_xNi_x(HPO_4)$ with one dimensional (1D) nanorod structures. Only a glass container with a top and temperature-controlled oven is needed for the CBD method. Furthermore, we used only three precursor materials (Mn, Co, and hydrogen phosphate source) along with deionized water to synthesize $Co_xNi_x(HPO_4)$. To the best of the author's knowledge, there are no reports on the synthesis and application of cobalt–nickel hydrogen phosphate 1D nanorod structures for supercapacitor applications to date.

Considering the above facts in our mind, $Co_xNi_x(HPO_4)$ nanomaterials with 1D nanorod morphologies were successfully synthesized for the first time by a simple one-step chemical bath deposition method without a template. The present synthesis protocol not only avoids the conservative accumulation and confirms appropriate ion diffusion, but also decreases the charge-transfer resistance, ensuing in high electrical conductivity for electron transfer. Therefore, by designing the Co and Ni doping ratio, the attained $Co_{0.75}Ni_{0.25}(HPO_4)$ electrode possesses a higher specific capacity of 475 mAh g^{-1} at a current density of 1 A g^{-1} and exceptional cycling stability with capacity maintenance of 94.8% over 5000 cycles.

Section snippets

Materials

Nickel nitrate ($Ni(NO_3)_2.6H_2O$, 99%) and Cobalt nitrate ($Co(NO_3)_2.6H_2O$, 99%) were procured from Junsei chemicals, Japan and Samchun chemicals, South Korea, respectively. Sodium phosphate dibasic (Na_2HPO_4) and nickel foam (NF) was purchased from Sigma-Aldrich, USA. All the materials/reagents were used as received.…

Preparation of bimetallic hydrogen phosphate, $Co_xNi_x(HPO_4)$

Bimetallic hydrogen phosphate, $Co_{0.25}Ni_{0.75}(HPO_4)$ was synthesized by the chemical bath deposition method. In a typical synthesis, $Co(NO_3)_2.6H_2O$ (0.94g) and $Ni(NO_3)_2.6H_2O$ (2.82g) were…

Results and discussion

The FT-IR spectra of cobalt nickel-hydrogen phosphates were shown in Fig. 1. All the three spectra were showing the same features, thus confirming the same compound involving the isomorphic substitution of nickel by cobalt or vice-versa. Even, there is no peak shifting, as nickel and cobalt have nearly the same mass ($Co_{0.5}Ni_{0.5}(HPO_4)$). The sharp peak at 3437cm^{-1} owing to its stretching vibration of water coordinated to either cobalt or nickel or both. It is also confirmed by its bending…

Conclusions

As a whole, we successfully synthesized 1D bimetallic hydrogen phosphate nanorods grown directly on nickel foam by a facile chemical bath deposition method without a template. The $Co_{0.75}Ni_{0.25}(HPO_4)$ shows a maximum specific capacity of 475$mAhg^{-1}$ at 1 A g^{-1} in a three-electrode configuration using 3M KOH as the electrolyte. Furthermore, it exhibits almost 95% of specific capacity retention over 5000 GCD cycles and 98.6% coulombic efficiency at 10 A g^{-1}. In addition, the fabricated ASC…

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

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References (35)

R. Vinodh *et al.*
J. Ind. Eng. Chem. (2021)

H. Wang *et al.*
J. Power Sources (2010)

X. Guan *et al.*
Chem. Eng. J. (2019)

Y. Pan *et al.*
Nano Energy (2019)

K. Tao *et al.*
Nano Energy (2019)

J. Li *et al.*
New Carbon Mater. (2020)

Y. Zhong *et al.*
J. Alloys Compd. (2021)

R. Atchudan *et al.*
J. Ind. Eng. Chem. (2021)

I. Kim *et al.*
J. Energy Storage (2021)

R. Vivekanandan *et al.*
Ionics (2020)

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Cited by (24)

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2023, Journal of Energy Storage

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