ScienceDirect

Electrochimica Acta
Volume 426, 10 September 2022, 140763

A high-performance asymmetric supercapacitor consists of binder free electrode materials of bimetallic hydrogen phosphate ($MnCo(HPO_4)$) hexagonal tubes and graphene ink

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https://doi.org/10.1016/j.electacta.2022.140763
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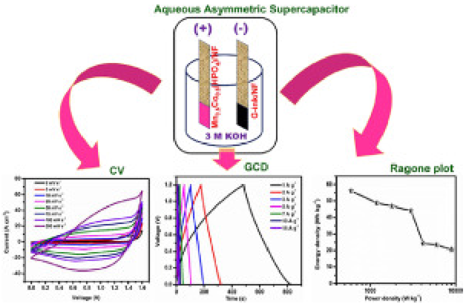
Abstract

Novel bimetallic manganese-cobalt hydrogen phosphate ($Mn_xCo_x(HPO_4)$) hexagonal tubes were efficiently prepared by a direct and simple chemical bath deposition (CBD) procedure. The prepared $Mn_xCo_x(HPO_4)$ materials have been analysed through Fourier transform infrared (FT-IR), thermogravimetric analysis (TGA), and X-ray diffraction (XRD) methods. The surface morphology and the particle size of the materials were studied using field emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM). The textural characteristics and elemental composition of the $Mn_xCo_x(HPO_4)$ were measured using nitrogen sorption isotherms and X-ray photoelectron spectroscopy (XPS) analysis. Owing to its unique hexagonal structures and porous nature, the $Mn_{0.5}Co_{0.5}(HPO_4)$ electrode is measured *via* a three-electrode system and achieved the highest specific capacitance of 1,727 F g^{-1} at the current density of 1.0 A g^{-1}. An aqueous asymmetric supercapacitor (AAS), $Mn_{0.5}Co_{0.5}(HPO_4)$//G-ink device based on $Mn_{0.5}Co_{0.5}(HPO_4)$ as the cathode and graphene ink (G-ink) as an anode material. The fabricated device might function well in a large operating potential window of +1.6 V. The $Mn_{0.5}Co_{0.5}(HPO_4)$//G-ink AAS exhibited the maximum power and specific energy of 9,000 W kg^{-1} and 56.16 Wh kg^{-1}, correspondingly at 1.0 A g^{-1}. Furthermore, the fabricated device could withstand 95.5% of its primary capacitance after 5,000 galvanostatic charge/discharge (GCD) turns, which illustrates that the materials could be a prominent contender for supercapacitor applications.

Graphical abstract



Introduction

In the present scenario, the rapid consumption of fossil fuels and the associated crucial environmental problems have forced scientists and engineers to find environment-friendly, less-cost, effective, and sustainable energy storage, and conversion technologies [1], [2]. Supercapacitors (SCs) are promising in a variety of areas, including telecommunications equipment, pulse laser technique, digital cameras, smartphones, power utensils, electric hybrid vehicles, uninterruptible electric supply to computers/laptops, and energy storage created by solar cells [3, 4]. Capable of existing with other electrochemical devices such as batteries, the specific energy of the SCs must be significantly boosted with the specific power and cyclic stability [5]. The specific energy (E_d) improves with the specific capacitance of the device (C_s) and the operating potential window (V) rendering to the following equation E=0.5 C_s x V^2 [6].

In recent years, metal phosphate (M-$(PO_3)^{2-}$) related electrode materials have drawn much interest due to their extreme electrochemical activity and layered architecture assembly [7, 8]. The two crucial factors, such as excellent chemical stability and superior conductivity are the primary criteria for any electrode resources in SCs or Li-ion batteries (LIB) [9]. In the solid form of open framework, M-$(PO_3)^{2-}$ have large networks and pores that can produce high ionic and charge densities when employed as pseudocapacitive electrode materials [10]. Furthermore, the oxyanion of pentavalent phosphorus can prime to various phases of M-$(PO_3)^{2-}$ [11]. Different types of valance states through surface reactions can increase the conductivity of M-$(PO_3)^{2-}$ electrodes [12]. Metal hydrogen phosphate (MHP; M-HPO_4) is the part of M-$(PO_3)^{2-}$ the family that has fascinating, layered surface/interface structures which are effortlessly available to ions in the electrolyte and have virtuous intercalation of ions in energy storage applications [13]. As far as we know, there are very few papers reported in M-HPO_4 electrode materials for supercapacitors. For instance, Huan Pang et al. [14] prepared $CoHPO_4.3H_2O$ nanosheets by a simplistic hydrothermal technique for SC applications. The synthesized $CoHPO_4.3H_2O$ was performed well in a 3-electrode cell and exposed the highest specific capacitance (413 F g^{-1}). Of late, Abdulmajid A. Mirghni et al. [15] have produced $NaNi_4(PO_4)_3$/GF composite *via* precipitation method and it displayed a maximum of 63.3 mAh g^{-1} at 1.0 A g^{-1} specific capacity in a three-electrode configuration. In addition, the constructed $NaNi_4(PO_4)_3$/GF//AC ASC revealed the high specific power with the specific energy of 570 W kg^{-1} and 19.5 Wh kg^{-1}, correspondingly at 0.5 A g^{-1}. Yufeng Zhao et al. [16] described ammonium cobalt-nickel phosphates electrode material consisting of $(Ni, Co)_3(PO_4)_2{\cdot}8H_2O$ and $(NH_4)(Ni, Co)PO_4{\cdot}0.67H_2O$ by hydrothermal method. The composite material delivers a maximum capacitance of 1,128 F g^{-1} at 0.5 A g^{-1}. Furthermore, the fabricated ASC delivered a high specific power and specific energy of 4,400 W kg^{-1} and 35.3 Wh kg^{-1} accompanied with outstanding cyclic stability (95.6% of capacitance retention after 5,000 galvanostatic charge/discharge - GCD cycles). Zhang et al. [17] stated that core-shell $Co_{11}(HPO_3)_8(OH)_6$-Co_3O_4 hybrids for supercapacitor electrode material with a maximum capacitance of 1.84 mF cm^{-3} at 0.5 mA cm^{-2}. In addition, the fabricated asymmetric device exhibited the highest power densities of 105 mW cm^{-3} at 1.5 mA cm^{-2}. Yang et al. [18] synthesized $Mn_3(PO_4)_2.3H_2O$ NSs/G (manganese phosphate nanosheets/graphene) composites for SCs studies. The assembled ASC exhibited a supreme specific capacitance of 152 F g^{-1} at 0.5 A g^{-1} along with specific energy (0.17 μWh cm^{-2} at 0.5 A g^{-1}) and specific power (46 μW cm^{-2} at 2.0 A g^{-1}). Furthermore, ASC displayed an exceptional cyclic steadiness and almost cent percent capacitance maintenance was achieved over 2,000 GCD cycles. Recently, Wang et al. [19] prepared cobalt-nickel phosphate composite for ASC applications. The ASC device presented the highest capacitance of 298.65 F g^{-1} at 1 A g^{-1} and could reach specific energy of 19.31 Wh kg^{-1} at a specific power of 163.42 W kg^{-1}. Liu et al. [20] synthesized

$Ni_3P_2O_8$-$Co_3P_2O_8{\cdot}8H_2O$ by a superficial chemical precipitation technique and it displayed the extreme capacitance of 1,974 F g^{-1} at 0.5 A g^{-1}.

Nevertheless, the aforementioned approaches require several complicated steps, such as the need for expensive equipment (high-pressure autoclave) for hydrothermal method consuming urea (COH_4N_2)/ammonium hydroxide (NH_4OH) as a reducing agent. Depending on the template method, removing the hard template, or selecting/embedding it in the appropriate solvent causes the final material impure and time-consuming. Though, in this current investigation, a simple chemical bath deposition (CBD) method was employed to yield $Mn_xCo_x(HPO_4)$ with good hexagonal tube morphology. CBD requires only a glass bottle with a lid and hot-air oven. In addition, the present synthesis method requires source materials of Mn, Co, and hydrogen phosphate with distilled water. Additionally, no reports are available to date for the preparation of (HPO_4) hexagonal tubes for supercapacitor applications.

Transition metal oxides (TMOs), such as iron oxides (Fe_2O_3), manganese oxides (MnO_2), cobalt oxides (CoO), nickel oxides (NiO), and are extensively studied as electrode materials for supercapacitor applications owing to their noble electrochemical outcome. However, the TMOs suffer inferior rate capability and poor cyclic performance of the electrode materials. To overcome these issues, manganese cobalt phosphates are considered a potential choice due to their cheap prices, lesser harmfulness, facile preparation method, and high theoretical specific capacity [21, 22]. In addition, generally HPO_4 ion exhibit three distinct *pKa* values of 2.16 ($H_2PO_4^-$), 7.21 (HPO_4^{2-}), and 12.67 (PO_4^{3-}). With a greater *pKa* value and sturdier nucleophilic ability, the above values govern their nucleophilic capability. So, MHPs may deliver an additional effective proton pair electron transfer method than metal phosphates [23, 24].

Herein, we provide a straightforward method to prepare a hexagonal tube of $Mn_xCo_x(HPO_4)$ in a chemical bath deposition procedure by applying $MnSO_4.H_2O$ and $Co(NO_3)_2.6H_2O$ precursors. In addition, we examined the electrochemical evaluation of the *as*-prepared materials *via* a traditional three-electrode configuration, and the $Mn_{0.5}Co_{0.5}(HPO_4)$ hexagonal tubes showed the superior electrochemical performance for energy storage. More importantly, the construction of an AAS device composed of the hexagonal tube structured manganese-cobalt hydrogen phosphate ($Mn_{0.5}Co_{0.5}(HPO_4)$) as a positive electrode and G-ink as a negative electrode in 3.0 M KOH as the supporting electrolyte. The constructed AAS device shows a supreme specific capacitance of 280.8 F g^{-1} at 1.0 A g^{-1}. The AAS demonstrated a high specific energy of 56.16 Wh kg^{-1} at a specific power of 599.92 W kg^{-1}. Furthermore, the assembled AAS shows a slight capacitance change after 5,000 charge/discharge cycles at 5.0 A g^{-1} (95.5% capacitance retention).

Section snippets

Materials

$Mn(NO_3)_2.6H_2O$ (99% of Manganese (II) nitrate hexahydrate) and $Co(NO_3)_2.6H_2O$ (99% of cobalt (II) nitrate hexahydrate) was procured from Daejung Chemicals, South Korea. Na_2HPO_4 (99% of sodium phosphate dibasic) was obtained from Sigma-Aldrich, USA. NF (nickel foam) was acquired from Sigma-Aldrich for electrode fabrication.…

Preparation of $Mn_xCo_x(HPO_4)$

$Mn_{0.25}Co_{0.75}(HPO_4)$ was prepared by a facile and efficient CBD method. In brief, the required amounts of $Mn(NO_3)_2.6H_2O$ (1.10 g), $Co(NO_3)_2.6H_2O$ (1.89 g), and deionized water (100…

Physicochemical characterizations of $Mn_xCo_x(HPO_4)$

The surface morphology of electrode materials derived for supercapacitor application is crucial because all electrochemical reactions take place on or close to the electrode surface, and distinct morphology has diverse ion transfer rates and electrode/electrolyte interface properties [25]. Hence, the morphology of the $Mn_xCo_x(HPO_4)$ governs its electrochemical properties.The surface morphology of the prepared materials was studied by SEM and TEM analysis. The SEM pictures (Fig. 1(a) - 1(c2))…

Conclusions

In summary, bimetallic hydrogen phosphate ($Mn_xCo_x(HPO_4)$) materials have been successfully prepared by the CBD method for electrochemical energy storage devices. The hexagonal tube-like morphology was established by SEM and TEM methods. The maximum surface area of 132 $m^2\ g^{-1}$ was achieved for $Mn_{0.5}Co_{0.5}(HPO_4)$. The maximum specific capacitance of 1,177, 1727, and 449 F g^{-1} was obtained for $Mn_{0.25}Co_{0.75}(HPO_4)$, $Mn_{0.5}Co_{0.5}(HPO_4)$, and $Mn_{0.75}Co_{0.25}(HPO_4)$, respectively at a specific current of 1.0 A g^{-1} …

CRediT authorship contribution statement

Kwang-Seon Ahn: Data curation, Writing – original draft. **Rajangam Vinodh:** Data curation, Writing – original draft. **Bruno G. Pollet:** Supervision, Visualization, Investigation. **Rajendran Suresh Babu:** Conceptualization, Methodology. **Vanaraj Ramkumar:** Conceptualization, Methodology. **Seong-Cheol Kim:** Software, Validation, Writing – review & editing. **Kungumaraj Krishnakumar:** Software, Validation, Writing – review & editing. **Hee-Je Kim:** Supervision, Visualization, Investigation.…

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.…

Acknowledgment

This research work was supported by BK21 Plus Creative Human Resource Education and Research Programs for ICT Convergence in the 4th Industrial Revolution, Pusan National University, Busan, South Korea.…

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