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Review

Composition, microstructure and performance of cobalt nickel phosphate as advanced battery-type capacitive material

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ABSTRACT

A series of cobalt nickel phosphates are prepared via a mild chemical precipitation method followed by calcination at a low temperature. With variation of Co/Ni molar ratio, the compositions and microstructures of the as-prepared samples are modulated and their electrochemical performances as battery-type materials are optimized. Electrochemical measurements by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) technique and electrochemical impedance spectroscopy (EIS) reveal that the flower-like $CoNi_2(PO_4)_2$ with the molar ratio of Co/Ni = 1:2 exhibits a high specific capacity of 630.4 C g^{-1} at the current density of 1 A g^{-1}, and an excellent cycling stability of 84.3% capacity retention after 1000 cycles. Furthermore, a hybrid supercapacitor, fabricated with the $CoNi_2(PO_4)_2$ as positive and graphene as negative electrode material, exhibits a high specific capacitance of 103 F g^{-1} at the current density of 1 A g^{-1}, along with a high energy density of 32.2 Wh kg^{-1} at the power density of 377.6 W kg^{-1}, and even 21.7 Wh kg^{-1} at 4.9 kW kg^{-1}. These figures demonstrate that cobalt nickel phosphates as electrode materials with the optimized composition and microstructure may hold promising application in energy storage devices.

Contents

1. Introduction

Shortage of oil resources and exhaust emission from combustion of diesel engine have brought about increasingly serious social and ecological problems. Therefore, development of the clean and renewable power resources, such as those from solar and wind energy are in urgent demand [1–3]. Accordingly, advanced energy storage devices with the merits of high energy/power density, cost-efficiency and environment-friendliness are inevitably required. Supercapacitors (SCs), also named electrochemical capacitors, are considered as the most promising system to bridge the power/energy gap between traditional dielectric capacitors and lithium-ion batteries because of their high power density, fast charge/discharge and long lifespan [4,5].

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Two categories of SCs with different charge storage mechanism are designated as electric double layer capacitors (EDLCs) and pseudocapacitors (PCs) [6,7]. While EDLCs based on carbon electrodes store energy through electrostatic accumulation at the electrode/electrolyte interface, charge storage in pseudocapacitors are derived from the electron transfer of faradic mechanism. The fast and reversible redox reaction on the surface or near-surface region of the electroactive materials, such as transition metal oxides and conductive polymers, may deliver a high energy density, rendering a fairly larger theoretical specific capacitance than carbon-based materials [8,9]. RuO_2 [10,11] and MnO_2 [12,13] are thought to be typical pseudocapacitive materials, because they have the similar electrochemical profiles to activated carbon in EDLCs, for which a linear dependence of the charge storage on the variation of the potential within the window of interest are observed. During the past years, electrode materials composed of transition metal oxides/hydroxides or their composites have been widely investigated as pseudocapacitive mechanism [14–16]. Very recently, Thierry et al. presented a different opinion about the previous investigation on pseudocapacitive materials [17]. They correctly pointed out that most Ni/Co/Mn-based compounds should be attributed to battery-type electrodes, because both their kinetics and electrochemical profile do not follow Conway's original definition of pseudocapacitance [18]. The fundamental differences between the battery-type electrodes and the pseudocapacitive MnO_2 or RuO_2 lie in the redox reaction at a particular potential and the continuous redox reaction within a potential range, respectively [19–22].

Battery-type materials, such as transition metal oxides, hydroxides and sulfides, exhibit much higher energy density than pseudocapacitve electrodes and would be excellent candidates for numerous electronic device applications if their cycle lifespan could be further enhanced but not sacrificing the power density and energy density [23–26]. Thus, structurally stable compounds including transition metal-phosphates, sulfates and carbonate have attracted increasingly attentions [27,28]. Besides the similar merits to the corresponding oxides, such as good electric conductivity, large theoretical specific capacitance, non-toxicity and low cost, transition metal phosphates present an excellent electrochemical stability [29–31]. Liu et al. [32] synthesized a series of nano-sized cobalt nickel phosphates. By tuning the molar ratio of Co/Ni in the starting materials, a high specific capacity of 1974 $F\,g^{-1}$ at 0.5 $A\,g^{-1}$ was achieved in the sample of $Ni_3P_2O_8$-$Co_3P_2O_8 \cdot 8H_2O$. When the current density was elevated to 8 $A\,g^{-1}$, the capacitance of 67.7% could be retained. Tang et al. [33] reported the properties of honeycomb-like mesoporous $Co_{0.86}Ni_{2.14}(PO_4)_2$ electrode, which showed a high specific capacity of 1049.8 $F\,g^{-1}$ at 0.25 $A\,g^{-1}$. Omar [34] and co-workers have synthesized amorphous nickel phosphate, which showed a specific capacity of 620 $C\,g^{-1}$ at the current density of 0.4 $A\,g^{-1}$ but a poor rate capacity of 32% in the range of 2 to 0.4 $A\,g^{-1}$. These researches demonstrated that for cobalt nickel phosphates with faradic charge storage mechanism, the electrochemical performances could be optimized by adjusting the Co/Ni ratio [35–38].

Transition metal phosphates may represent an important family of electrode materials with high energy density, long cycling lifespan and environment-friendly behavior. However, at present, there is still a large gap between the performance measured and the theoretical prediction for the phosphate electrodes. In this report, a series of cobalt nickel phosphates are prepared by a template-free chemical precipitation method followed by calcining in the muffle furnace. By varying the Co/Ni molar ratios, the composition and microstructure are modulated and the capacitive performances of the as-prepared samples are optimized. Moreover, hybrid supercapacitor is assembled with the cobalt nickel phosphate as positive and graphene as negative electrode, and its energy storage properties is well investigated. It is expected that by rational designing and tailoring the composition and microstructure, the transition metal phosphate as electrode material may exhibit high energy density, power density and capacity retention for production of high-performance energy storage devices in practical application.

2. Experimental

2.1. Synthesis of cobalt nickel phosphate

All the reagents or chemicals were commercial products without further purification. In a typical synthesis, a 100 mL aqueous solution containing $CoCl_2 \cdot 6H_2O$ (5.0 mmol), $NiCl_2 \cdot 6H_2O$ (10.0 mmol) was added into H_3PO_4 and hexamethylenetetramine (HMTA) at the ratio of n(Co+Ni)/n(P) = 1:1 and n(Co+Ni)/n(HMTA) = 1:3 respectively. The purple precipitate occurs promptly after mixing. This mixture was continuously stirred at room temperature for 5 h until a pink precipitate was obtained. Then, the precipitate was separated by filtration, washed with deionized water and ethanol several times. After dried in vacuum condition overnight, the sample was calcined at 300 °C for 3 h in the muffle furnace. A similar process was conducted by varying the Co/Ni ratios at Co/Ni = 3:0, 2:1, 1:1 and 0:3. The obtained samples were denoted as cobalt phosphate, nickel phosphate, cobalt nickel phosphate, respectively.

2.2. Preparation of graphene

Firstly, graphite oxide (GO) was synthesized by the modified Hummers' method using natural graphite powder as raw materials [39,40]. Then, the viscous GO hydrogel was centrifuged and washed using deionized water to pH 2. The GO solution was transferred into autoclave and kept at 160 °C for 10 h. After the reaction autoclave was cool down to room temperature, the product was filtered, washed with deionized water and ethanol several times, and then it was dried in an oven at 60 °C for 12 h.

2.3. Characterization and analysis

The microstructure and morphology of the cobalt nickel phosphate were characterized by scanning electron microscope (SEM, JMS-6700F). The crystal structure and the phase of the solid sample were determined by X-ray diffraction (XRD, Rigaku D/Max-2200) with Cu Kα X-rays. The thermal stability and phase transition were investigated by thermogravimetric analysis and differential thermal analysis (TG/DTA, DT-60). The surface electronic state was inspected by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ESCA). The metal ions contents were determined by inductively coupled plasma optical emission spectra (ICP, Varian VISTA-MPX) The surface area and porosity were measured by N_2 sorption analyzer (BET, Micromeritics ASAP 2020).

2.4. Fabrication of work electrode and electrochemical test

To prepare the work electrode, the cobalt nickel phosphate, acetylene black and polyvinylidene difluoride (PVDF) in a mass ratio of 8:1:1 were dispersed in N-methyl-2-pyrrolidone (NMP) to form a paste, which was then dropped onto nickel foam, dried in vacuum oven at 60 °C overnight and pressed under 10 MPa. The mass loading of the active materials on each electrode is about 3.0–4.0 mg. A three-electrode system was used to evaluate the electrochemical properties of the cobalt nickel phosphates, in which platinum foil ($1.0 \times 1.0\,cm^2$) and a saturated calomel