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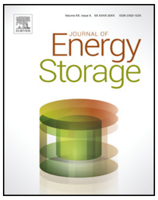

Methodology for synthesizing the nickel cobalt hydroxide/oxide and reduced graphene oxide complex for energy storage electrodes

Sheng-Sian Yang[a,1], Lu-Yin Lin[a,*,1], Xin Li[b,*], Cheng-Wei Ma[b], He-Xin Lai[a], Lu-Ying Lin[a]

[a] *Department of Chemical Engineering and Biotechnology, National Taipei University of Technology (Taipei Tech), Taipei 10608, Taiwan*
[b] *School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100084, PR China*

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ABSTRACT

Reduced graphene oxide (RGO) and nickel cobalt hydroxide/oxide complex is one of the promising electrocapacitive materials for the energy storage devices, in which RGO provides high conductivity and nickel cobalt hydroxide/oxide possesses high electrochemical activity toward conducting multiple Faradic reactions. The low-cost and simple hydrothermal reaction is the mostly used synthesis method for preparing the RGO and nickel cobalt hydroxide/oxide nanomaterials on the nickel foam. However, the methodologies based on the hydrothermal reaction are barely discussed in considering of the morphology of the nanomaterial and the electrochemical performance of the energy storage electrodes. The methodology includes the one-step and two-step hydrothermal reactions, direct growth and indirect deposition of the electroactive material on the nickel foam, and the post-thermal treatments. The highest specific capacitance value of 5.61 F/cm^2 corresponding to the capacity of 1.25 mAh/cm^2 are achieved for the nickel cobalt oxide and RGO complex electrode prepared by depositing the powder of the complex prepared using the one-step hydrothermal method and the post-thermal treatment on the nickel foam. This study discusses a rarely investigated subject and provides a blueprint for choosing the methodology to synthesize efficient electroactive material for the energy storage devices.

1. Introduction

The renewable energy has attracted much attention to satisfy the energy demand and solve the serious environmental problems. The energy storage device is of the same importance as the energy generation device like solar cells, in which the battery and the supercapacitors are the most promising energy storage devices to be developed in recent years [1,2].

Carbon materials store charges by using the electrochemical double-layers for the supercapacitor (SC) electrode, which presents a better cycling stability but a smaller specific capacitance than those for the pseudo-capacitor electrode, which stores charges by using the Faradic reactions [3]. Graphene is two-dimensional (2D) with carbon atoms bonded using the sp^2 orbital to form the six-hexagonal carbon ring, which lead to the solid and flexible nature, high specific surface area (2630 m^2/g), high thermal conductivity (5300 W/m K), and high electron mobility (>15000 cm^2/V s at room temperature). Since Hummer et al. used H_2SO_4, $KMnO_4$ and Na_2NO_3 to produce the reduced graphene oxide (RGO) in 1957 [4], numerous studies have applied or modified this method to produce RGO, a graphene-like material, for the SC electrodes [5–7]. On the other hand, the metal oxide storing charges via the Faradic reactions is one of the most promising materials for the charge-storage devices, among which the transition metal oxides are commonly used due to their semi- or full- empty d-orbitals for forming multiple valence states, *e.g.*, ruthenium oxides [8], cobalt oxides [9], nickel oxides [10], nickel cobalt oxides [11,12], iron oxides [13,14], and magnesium oxides [15,16]. To achieve high energy-storage ability and excellent long-term stability, the composites of carbon materials and metal oxides were intensively synthesized for the application on the charge-storage devices. Liu et al. used the modified Hummer's method to make RGO and applied a solution method to prepare the RGO and Fe_3O_4 composite paper for the SC electrode. The best charge-storage ability was obtained for the electrode containing 64.8% Fe_3O_4 in the composite [13]. Min et al. used the modified Hummer's method to prepare graphene oxide (GO) and applied the hydrothermal method to make the RGO and nickel hydroxide composite on the nickel foam. The electrode presents a specific

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[*] Corresponding authors.
E-mail addresses: lylin@ntut.edu.tw (L.-Y. Lin), klkxlx@163.com (X. Li).
[1] The first authors contributed equally.

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capacitance (C_F) value of 7 F/cm^2 at the current density of 20 mA/cm^2 [17]. In addition, it has been widely reported that the electrode composed of bimetallic compounds can exhibit better energy storage ability due to the more Faradic reactions occurring at the interfaces between the bimetal compounds and the electrolyte [18–21]. Among the bimetal species, cobalt and nickel are considered to be two of the most studied transition metals owing to the high redox activity of their metal ions [21,22]. The binary nickel cobalt oxides/hydroxides have been greatly studied as the electroactive materials for pseudocapacitors. Comparing to the pure nickel oxides/hydroxides or cobalt oxides/hydroxides, the binary nickel cobalt oxides/hydroxides cannot only provide multiple oxidation states for the Faradaic redox reactions, but also possess higher electronic conductivity because of the coupling of bimetallic transition metal species. Patil et al. prepared nickel cobalt hydroxides on the graphene foam by using the chemical vapor deposition and chemical bath deposition methods. A C_F value of 1280 F/g was obtained for the optimized electrode [23]. Qu et al. used the hydrothermal and electrochemical deposition methods to prepare the cobalt oxide nanobrushes, nickel cobalt hydroxide, and graphene composite on the nickel foam. The electrode shows a C_F value of 2579 F/g at the current density of 1 A/g [24]. Xu et al. used the modified Hummer's method to prepare GO and applied the hydrothermal method to combine the nickel cobalt oxide with the as-prepared GO. The resulting electrode presents a C_F value of 490 F/g at the current density of 0.5 A/g [25]. Cai et al. synthesized nickel cobalt double-layered hydroxide nanosheets and grew RGO on the sheets to reduce the aggregation by using the hydrothermal method and applied on the SC electrode [26]. Mostly the hydrothermal method was applied to make the complex of carbon material and the nickel cobalt compound. However, there is no literature comparing the methodology based on the hydrothermal reaction for making the nickel-cobalt binary compounds/carbon composite on the physical properties of the nanomaterials and the electrocapacitive performance of the pertinent electrodes. Hence, this work focuses on comparing the methodology to synthesize the nanomaterial other than merely pursuing the high performance of the electrode.

In this study, different methodologies based on the hydrothermal reaction were used for synthesizing the RGO and nickel cobalt hydroxide/oxide complex. The methodologies include the one-step and two-step hydrothermal reactions, the direct growth and indirect deposition of the electroactive material on the nickel foam, as well as the post-thermal treatment. When the nanomaterial grew directly on the nickel foam, the nanosheet structures were obtained regardless of the one-step or two-step hydrothermal reactions were applied for the synthesis. The 2D nanostructure was also obtained when the nanomaterial was synthesized in the powder form by using the one-step hydrothermal reaction, and the sample was found to arrange in the parallel direction after being deposited on the nickel foam. The highest C_F value of 5.61 F/cm^2 corresponding to the capacity of 1.25 mAh/cm^2 were obtained at the scan rate of 10 mV/s for the nickel cobalt oxide and RGO complex electrode, prepared in the powder form by using the one-step hydrothermal method and the post-thermal treatment.

2. Experimental section

2.1. Materials

Cobalt(II) chloride hexahydrate ($CoCl_2·6H_2O$, 99+%), cetyltrimethylammonium bromide ($C_{19}H_{42}BrN$, CTAB, 99%), graphite power, nickel(II) nitrate hexahydrate ($Ni(NO_3)_2·6H_2O$, 99%) and sodium nitrate ($NaNO_3$, 99 wt%) were purchased from Acros. Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2·6H_2O$, 99.0%), hexamethylenetetramine ($C_6H_{12}N_4$, HMT, 99%), and potassium permanganate ($KMnO_4$, 100 wt%) were brought from Showa. Potassium hydroxide (KOH, analytical reagent grade) was brought from Fisher. Hydrogen peroxide (H_2O_2, 30 wt%), methanol (CH_3OH, 99.9%), and sulfuric acid (H_2SO_4, 96%) were obtained from Aencore.

2.2. Cleanness of nickel foam and synthesis of GO

The nickel foam (110PPI, thickness = 1.05 mm, Innovation Materials Co., Ltd, Taiwan) was cut in the size of 1 cm in width and 3 cm in length, and cleaned before being used in the hydrothermal reaction. First the nickel foam was soaked in 6 M HCl for 30 min under ultrasonic vibration, and then washed by using deionized water (DIW) and EtOH alternatively. Finally the cleaned nickel foam was dried in a vacuum oven for 1 h [27].

The self-synthesized GO was made as follows. In a typical synthesizing process, 5 g graphite power and 2.5 g $NaNO_3$ were dissolved in a 115 mL aqueous solution containing 18 M H_2SO_4 in an ice bath. Then 15 g $KMnO_4$ was gradually added in the resulting solution under stirring and then the solution was kept stirring at 35 °C for 4 h. Subsequently 230 mL DIW was slowly added in the solution under stirring at 98 °C for 15 min. The solution was then diluted to 700 mL and stirred for another 30 min. Following 12 mL H_2O_2 (35 wt%) was added in the resulting solution under stirring at the room temperature. The precipitate was collected and washed by using DIW for several times, and finally the sample was dried at 40 °C for 24 h to obtain the self-synthesized GO.

2.3. One-step hydrothermal synthesis of the nickel cobalt hydroxide/RGO electrode

Chemicals of 0.21 mmol $Ni(NO_3)_2·6H_2O$, 0.14 mmol $CoCl_2·6H_2O$, 0.5 g CTAB and 5 mL GO dispersion were mixed in the solvent containing 3 g DIW and 12 g CH_3OH under stirring for 1 h. Then the resulting solution and the cleaned nickel foam were transferred to a 100 mL Teflon-lined autoclave which was then heated in an oven at 180 °C for 3 h. After cooling the autoclave to the room temperature, the electrode was rinsed by using DIW and ethanol for several times and dried in a vacuum oven at 50 °C for 12 h. The $Ni_xCo_y(OH)$/RGO@Ni foam was therefore obtained.

2.4. Two-step hydrothermal synthesis of the nickel cobalt hydroxide/RGO electrode

The two-step hydrothermal synthesis was conducted as follows. The first step of the hydrothermal synthesis is to prepare RGO on the nickel foam (RGO@Ni foam). The cleaned nickel foam and the GO aqueous solution were transferred to a 100 mL Teflon-lined autoclave which was then heated in an oven at 180 °C for several hours. After cooling the autoclave to the room temperature, the electrode was rinsed by using DIW and ethanol for several times and dried in a vacuum oven at 50 °C for 12 h. The RGO@Ni foam was therefore obtained.

The second step of the hydrothermal synthesis is to prepare the nickel cobalt hydroxide and RGO complex on the nickel foam ($Ni_xCo_y(OH)$/RGO@Ni foam). Chemicals of 0.21 mmol $Ni(NO_3)_2·6H_2O$, 0.14 mmol $CoCl_2·6H_2O$ and 0.5 g CTAB were mixed in the solvent containing 3 g H_2O and 12 g CH_3OH. The resulting solution and the RGO@Ni foam prepared in the first step of the hydrothermal reaction were then transferred to a 100 mL Teflon-lined autoclave which was then heated in an oven at 180 °C for 24 h. After cooling the autoclave to the room temperature, the electrode was rinsed by using DIW and ethanol for several times and dried in a vacuum oven at 50 °C for 12 h. The $Ni_xCo_y(OH)$/RGO@Ni foam was hence obtained.