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One-step route synthesis of active carbon@La_2NiO_4/NiO hybrid coatings as supercapacitor electrode materials: Significant improvements in electrochemical performance

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ABSTRACT

Active carbon@La_2NiO_4/NiO hybrid coatings are synthesized using different molar ratios of La/Ni to improve the electrochemical performance of active carbon materials. The morphology and microstructure of the composites are investigated via scanning electron microscopy (SEM), X-ray diffraction (XRD), and high-resolution transmission electron microscopy (HRTEM). Cyclic voltammetry (CV), galvanostatic charge/discharge test (GCD), and electrochemical impedance spectroscopy (EIS) are performed to characterize electrochemical performance. At a molar ratio of La/Ni 1:2, the electrochemical electrode shows that the resistance of the composite is 2.97 Ω, which is half of that in pure active carbon. The highest energy density of 70.37 W h kg^{-1} is obtained at a current density of 1 A g^{-1}, whereas the highest power density of 32.4 kW kg^{-1} is achieved at a current density of 10 A g^{-1}. The CV results present a high specific capacitance of 710.48 F g^{-1} at a scan rate of 1 mV s^{-1} in 7 M KOH aqueous solution.

1. Introduction

Given the increasing demand for power sources that deliver in high-power energy [1,2], studies on electrochemical capacitors (ECs) mostly focus on electrode materials and electrolytes [3–5], which affect the performance of ECs. Given their key function in ECs, electrode materials are crucial in determining the properties of ECs [6].

Many studies have investigated carbon-based materials [7–12]. Carbon has four nanostructures [13], namely zero-dimensional carbon nanoparticles (i.e., active carbon, carbon nanospheres, and mesoporous carbon) [14], one-dimensional nanostructures (i.e., carbon nanotubes and carbon nanofibers) [15], two-dimensional nanosheets (i.e., graphene and reduced graphene oxides) [16], and three-dimensional porous carbon nano-architectures [17].

Studies have investigated various carbon/metal oxide composite electrodes by focusing on different carbon nanostructures with metal oxide depositions [18–20]. Active carbon (AC) is used as the electrode material for ECs. This material provides several advantages, such as a high specific surface area, high porosity, and moderate electronic conductivity. AC also has an excellent cyclic stability and a long service lifetime considering the absence of any chemical reaction during its charge/discharge processes [21]. The accumulation of electrons on an electrode is a non-faradaic process [22]. However, the maximum specific capacitance and energy density of AC are lower than those of an electrochemical battery [23]. The electrochemical performance of AC is also limited by its electronic conductivity [24]. Surface modification of AC is necessary because it cannot fulfill the demand for power sources that deliver high-power energy. Multivalent metal oxides, graphene [25], and conductive polymers (i.e., polypyrrole [26,27] and polyaniline [28,29]), are usually blended with AC to minimize the internal resistance and to improve the electrochemical performance of the electrode. However, graphene oxide is a poor electrical conductor because of the disruption in the π-orbital structure during oxidation [30]. Polypyrrole is insoluble and infusible, which restrict its processing and applications [31]. The use of polyaniline as a conducting additive is hindered by structural defects [32–34]. However, the properties of metal oxides are relatively more stable than those of the abovementioned conducting materials [35,36]. Thus, active carbon/metal oxide composite materials are mainly studied in this paper.

Various transition metal oxides, such as MnO_2 [37,38], NiO [39–41], Co_3O_4 [42,43], and RuO_2 [44–46] are deposited on carbon materials to obtain large specific capacitance and high energy

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density. NiO is a promising electrode material that provides a higher specific capacitance than carbon-based active materials. However, the high resistivity of NiO causes a large IR loss at a high current density [47–49]. Moreover, the power density and the rate capability of NiO are not ideal, which hinder its practical application. As a result, the poor conductivity of NiO remains a great challenge.

La_2NiO_4 has several advantages such as favorable chemical stability and high conductivity of ions and electrons [50,51]. La_2NiO_4 has a layered structure that is formed by the perovskite layer of $LaNiO_3$ and the halite layer of LaO [52–54]. These two structures are alternately stacked [55]. Given the excellent transmission performance of electrons, La_2NiO_4 is a conductive oxide with a low electrical resistivity [56]. Therefore, La_2NiO_4 is expected to become a promising material for improving the conductivity of the carbon-based electrode materials. The co-existed La_2NiO_4 and NiO produce highly reduced IR loss at a high current density to provide a high power density.

It is logical to produce a composite containing both La_2NiO_4/NiO and AC to combine the advantages and mitigate the shortcomings of all the components. In the composite, the AC structure not only serves as the physical support of La_2NiO_4/NiO but also provides the channels for charge transport [57]. La_2NiO_4 plays a beneficial conductive role. Capacitance is produced by the combination of the double-layer capacitance of AC and the pseudocapacitance of NiO. A synergistic effect of La_2NiO_4/NiO and AC could be expected.

This study investigates the electrochemical performance of AC@La_2NiO_4/NiO hybrid coatings with different molar ratios of La/Ni to determine how these coatings can achieve a low resistance and a high specific capacitance. In the composite, La_2NiO_4 plays an excellent conductive role to improve the conductivity of composite and NiO is mainly to provide a high specific capacitance in the composite. The structure, morphology and composition of the composites are obtained via scanning electron microscopy (SEM), X-ray diffraction (XRD), and high-resolution transmission electron microscopy (HRTEM). Cyclic voltammetry (CV), galvanostatic charge/discharge test (GCD), and electrochemical impedance spectroscopy (EIS) are used to characterize electrochemical performance.

2. Experiment

2.1. Preparation of AC@La_2NiO_4/NiO hybrid coatings

All chemicals were of analytical grade and were used without further purification. $La(NO_3)_3{\cdot}6H_2O$ and $Ni(CH_3COO)_2{\cdot}4H_2O$ were dissolved in 25 mL of CH_3COOH and 25 mL of 2,4-pentanedione by using a magnetic stir bar at a temperature of 80 °C, at molar ratios of La/Ni 1:1, 1:2, 1:3, and 1:4. Afterwards, 1 g of AC was evenly mixed into the obtained solution and was placed in a vacuum oven for 2 h. The resulting suspension was stirred at 60 °C for an additional 24 h. The solid suspension was filtered and dried at 80 °C. The as-prepared samples were pre-heated at 400 °C to remove residual materials, were heated up to 650 °C, and were then cooled down to room temperature by using a N_2 oven.

2.2. Characterization

The surface morphologies and nanostructures of the AC@La_2NiO_4/NiO hybrid coatings were observed using an FE-SEM system (Inspect F, FEI Co., U.S.) at 20 kV and using an HRTEM (Libra 200FE, Germany). The XRD patterns of the products were determined by an X-ray diffractometer (D-Max-γ type A, Rigaku Co., Japan) with a Ni-filtered Cu Kα radiation and a 0.15406 nm wavelength that was operated at 40 kV and 40 mA. Data were obtained from $2\theta = 20°$ to $90°$ at a scan rate of 4° per step.

The textural characterization of the materials was based on the N_2 adsorption/desorption isotherms from Brunauer–Emmett–Teller (BET) theory, and was determined using a high-speed surface area and pore size analyzers (NOVA 2000e, Quantachrome Instrument, US).

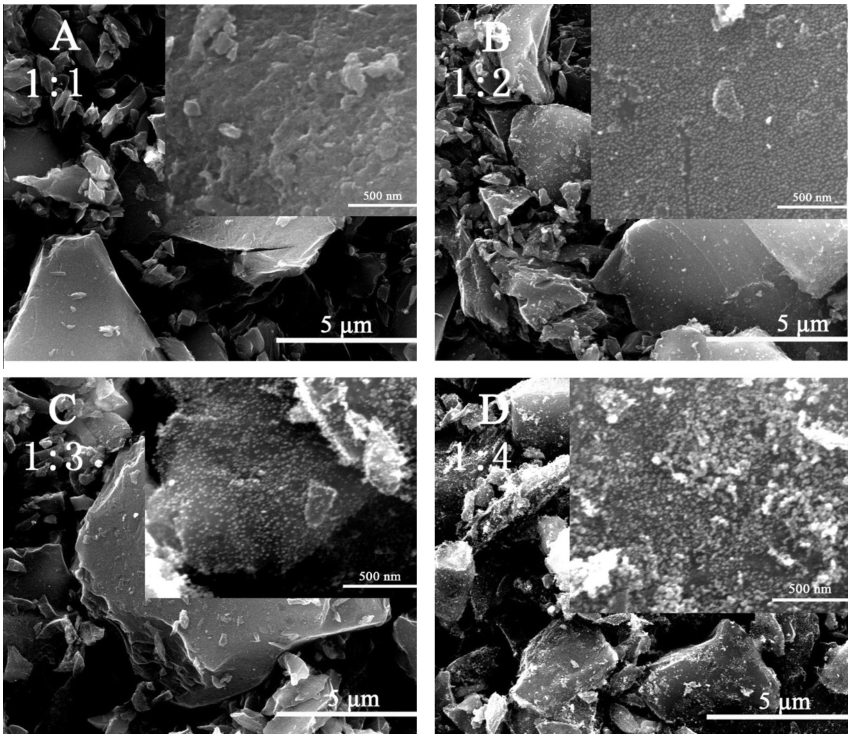

Fig. 1. SEM images of the composites at different molar ratios of La/Ni.