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Fabrication of porous nickel (hydr)oxide film with rational pore size distribution on nickel foam by induction heating deposition for high-performance supercapacitors



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HIGHLIGHTS

- A room thermal substrate method was used to fabricate Nickel (Hydr)oxide Film.
- The film possessed a microstructure with rational pore size distribution.
- The film showed a very high capacitance of 4.5 and 3.2 F/cm² at 6 and 30 mA/cm².
- The film exhibited a high rate capability (71.1% capacitance retention from 6–30 mA/cm²).
- The capacitance of the film could retained 77.7% after 2000 cycles.

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ABSTRACT

A room-temperature thermal substrate process, induction heating deposition was introduced to fabricate a layer of porous nickel-based compounds on nickel foam as supercapacitor electrode materials. The as-prepared film was composed of sheet-like NiO, Ni₂O₃, NiOOH and 3Ni(OH)₂·2H₂O (α -Ni(OH)₂). It possessed a hierarchical 3D-interconnected porous nanostructure with reasonable pore size distribution, among which nickel foam provided macropores, the produced 3D-interconnected sheet supplied mesopores ranging from 8 nm to 80 nm at a peak of 14 nm, while smaller mesopores with a size of about 2.5 nm were directly fomed on the sheet-like crystals. This unique pore nanostructure of the nickel (hydr)oxide compounds, despite its specific area of only 48 m² g⁻¹, could not only facilitate the diffusion of electrolyte into the electrode material surface, but also offer more active sites for the electrochemical redox reactions. Thus, the film delivered a very high areal capacitance of 4.5 and 3.2 F cm⁻² at 6 and 30 mA cm⁻² corresponding to 2250 and 1600 F g⁻¹ at 3 and 15 A g⁻¹, as well as an excellent rate capability (71.1% capacitance retention from 6 to 30 mA cm⁻²) and good cycling stability (77.7% capacitance retention after 2000 cycles).

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1. Introduction

With the decreasing availability of fossil fuels coupled with their resultant environmental issues, it attracts considerable attention for researchers worldwide to seize clean and sustainable energy sources and their storage technologies [1]. Supercapacitors (SCs), are considered to be a new class of energy storage devices because of their high power density, short charging time, long cycle life and high reliability [2]. Among different SC materials, nickel (hydr)

oxides are known to be attractive alternative candidates for SCs due to their high specific capacitance (3570 F g⁻¹ for α -Ni(OH)₂, 2584 F g⁻¹ for NiO and 2082 F g⁻¹ for β -Ni(OH)₂), low cost, environmental friendliness and well defined electrochemical redox activity, [2,3]. However, their actual specific capacitance reported for various nanostructures are still far below the theoretical values, likely because the pseudocapacitive effects are restricted only to a narrow region near their surface.

To overcome this issue, it is important to construct porous nanostructure electrode materials directly grown on a conductive collector [4]. Up to now, only a few film technologies have been employed to achieve nickel (hydr)oxide film as supercapacitive electrode materials, such as hydrothermal method [5], chemical bath

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deposition [6], electrochemical methods [7–10], electrochemical dealloying [11], atomic layer deposition [12]. Through these technologies, some progresses have been made to achieve the excellent electrochemical performance of nickel (hydr)oxide films on nickel foam. For examples, X.H Xiong et al. adopted hydrothermal technology to achieve ultrathin Ni(OH)₂ nanoflakes on nickel foam, which showed a specific capacitance of as high as 2342 F g⁻¹ and 1100 F g⁻¹ (3.74 F cm⁻² and 1.76 F cm⁻²) at 2 mA cm⁻² and 8 mA cm⁻² [13]. Li Y et al. prepared an interconnected nanosheet NiO film with mesopores by anodization in heating alkalia, which presented a specific capacitance of 4.74 and 3.50 F cm⁻² at 4 and 20 mA cm⁻², respectively [14]. Xiong XH et al. reported a three-dimensional ultrathin Ni(OH)₂ nanosheets on nickel foam in situ grown on nickel foam using hydrothermal method in a mixed solution of NaOH and (NH₄)₂S₂O₈, which produced a specific capacitance of 2384.5 F g⁻¹ at 2 mA cm⁻² (4.8 F cm⁻²) and ~1288 F g⁻¹ at 10.25 mA cm⁻² (2.64 F cm⁻²), respectively [15]. QF Zhou etc utilized a chemical method in NH₄NO₃ to get a in-situ Ni(OH)₂ on NF, exhibiting a specific capacitance of 6.4 and 1.62 F cm⁻² at 2.5 and 30 mA cm⁻² [16], respectively. In spite of the higher utilization efficiency of the nickel (hydr)oxide films at low current densities, the areal specific capacitance is still low especially at high rate capability. Moreover, the current methods still contained multiple steps or corrosive solvents, or they were operated at higher temperature. Thus, a better process should be developed to fabricate a nickel (hydr)oxide nanostructure film as high-performance SC electrode materials.

Herein, we, for the first time, introduced a room thermal substrate process, induction heating deposition (IHD) method [17], for fabrication of high-performance nickel (hydr)oxides on NF for SCs. The technology offers many advantages such as, room temperature thermal substrate process, the control of deposit grain size, surface morphology and film thickness, cost effectiveness, and ease of process, etc. Through this method, a 3D hierarchical porous structure of nickel (hydr)oxides with a rational pore size distribution have successfully deposited on NF, exhibiting excellent electrochemical performance especially at higher rate capability.

2. Materials and methods

The experiments of induction heating deposition were conducted using an ultrahigh frequency induction heating power supply made in Shenzhen Suanping Co.,Ltd. The experimental setup and procedure were the same as that of preparing hydroxyapatite coatings on carbon/carbon composites, which can be referred as the public paper [17]. The as-used experimental power and frequency was 1 KW and 378 KHz, respectively.

The solution of the deposition of nickel-based compounds was composed of 1 mmol of Ni(NO₃)₂·6H₂O (0.291 g), 4 mmol of urea (0.240 g), and 2 mmol of NH₄F (0.074 g) and 500 ml of deionized water, and nickel foam substrates with a size of 50 × 10 × 1 mm³ were cut from a large piece of NF. Before deposition, NF samples were carefully cleaned using a 0.5 M HCl solution for 30 min in order to remove their surface oxide film. Then, they were cleaned in deionized water, absolute ethanol, and acetone for 10 min in sequence in an ultrasonic bath. After drying, NF samples were rolled into the shape of circular ring, fastening in the middle of the induction coil. After the 4 h experiment, the samples were washed in an ultrasonic bath for 1 min in deionized water, and then dried in a lofter drier at 393 K. Finally, the NF samples was partly sealed by epoxy resin so as to expose an area of 10 × 10 mm² for next tests.

The surface morphology and microstructure of the samples were examined by a field-emission scanning electron microscope (FESEM, S-3400N, Tokyo, Japan) and a high-resolution transmission electron microscope (TEM, Zeiss LIBRA 200, Germany). The phases

and chemical compositions of the as-achieved samples were identified by an X-ray diffractometer and an X-ray photoelectron spectroscopy system (XPS; ULVAC-PHI 1800, Japan). The mass was weighted by a micro-balance with a resolution of 0.01 mg before and after the IDH process. The loading density of the film was about 2 mg/cm². The film sample (5 × 5 mm²) was pressed and then characterized by BET nitrogen sorption surface area measurements (Micromeritics ASAP 2020, America). Specific surface area of the product was calculated by the BET method, and pore sizes were calculated using BJH method.

The electrochemical performance of the as-prepared electrode was measured by cyclic voltammetry (CV), galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) tests with an electrochemical workstation (CHI660D, Chen Hua, Shang Hai, China). And, the cycle life of the sample was measured by a battery program-control test system (LAND BT2013A, Land, Wuhan,China). All the tests were conducted at room temperature in a three-electrode configuration with the as-prepared sample (10 × 10 mm²) as the working electrode, a platinum foil (10 × 20 mm²) as the counter electrode, a Hg/HgO (1.0 M KOH) electrode as the reference electrode, and 1.0 M KOH aqueous solution as the electrolyte, while EIS tests were performed by applying an AC voltage with an amplitude of 5 mV at the open circuit potential, and the frequency ranged from 0.01 Hz to 100 KHz.

3. Results and discussion

Fig. 1 gives the schematical illustration of the film formation process on nickel foam. First, a NF sample is fixed in a glass tube with a circulating solution containing nickel ions and some additives, and then put in an induction coil connected with an induction heating power supply. When the power supply is turned on, an electromagnetic wave would produced in the induction coil, and meantime induce NF to generate inductive current, resulting in the NF being heated and its temperature rising. Consequently, the Ni-containing solution on the surface of the NF will saturate and vaporize accompanying with lots of bubble formation, and subsequently nickel (hydr)oxide crystals will preferentially grow on the NF to form a film.

Fig. 2 shows the XRD patterns of NF and the as-prepared sample. Besides the nickel peaks, the other peaks were corresponded to the (101) and (202) crystal planes of Ni₂O₃ (PDF#14-0481), the (211) and (101) crystal planes of NiOOH (PDF#27-0956), the (200) and (220) crystal planes of NiO (PDF#02-1216) and the (110), (200), (103) and (300) crystal planes of 3Ni(OH)₂·2H₂O. (PDF#22-0444), which means the as-achieved film was composed of several nickel-based compounds. The presence of these compounds was also proved by XPS, as shown in Fig. 3. The survey scan in Fig. 3(a) displayed the presence of Ni and O from the as-achieved film, and C coming from the film surface contamination from air. The Ni2p_{2/3} peak was divided into four peaks through a Gaussian fitting method, as shown in Fig. 3(b), therinto the peaks at 853.8 eV and 857.3 eV were assigned to NiO and NiOOH, respectively, and, the adjacent two peaks at 855.6 eV and 855.8 eV were ascribed to Ni₂O₃, and 3Ni(OH)₂·2H₂O [18].

Fig. 4 shows the SEM morphologies of the as-prepared film. This film was clearly observed to contain many rugged particles, as shown in Fig. 4(a). In these particles, many nanosheet-like structures were interconnected one another, presenting a highly open and porous three-dimension (3D) nanosheet-like architecture (Fig. 4(b) and (c)). The 3D morphology might be responsible for periodic electromagnetic heating and resultant bubble evolution. These sheets were ultrasonically peeled off in 10% alcohol solution for further observation through TEM. A typical image of these sheets, shown in Fig. 4(d), revealed that they present an ultrathin structure with lots

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