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Highly mesoporous $LaNiO_3/NiO$ composite with high specific surface area as a battery-type electrode

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ABSTRACT

This study reports the fabrication and characterization of mesoporous $LaNiO_3/NiO$ composite with a very high specific surface area for a battery-type electrode. The mesoporous $LaNiO_3/NiO$ composite was synthesized via a sol–gel method by using silica gel as a template, the colloidal silica gel was obtained by the hydrolysis and polymerization of tetraethoxysilane in the presence of La and Ni salts. We investigated the structure and the electrochemical properties of mesoporous $LaNiO_3/NiO$ composite in detail. The mesoporous composite sample showed a specific surface area of $372\ m^2\ g^{-1}$ with 92.7% mesoporous area and displayed remarkable electrochemical performance as a battery-type electrode material for supercapacitor. The specific capacity values were found to be $237.2\ mAh\ g^{-1}$ at a current density of $1\ A\ g^{-1}$ and $128.6\ mAh\ g^{-1}$ at a high current density of $20\ A\ g^{-1}$ in 1 M KOH aqueous electrolyte. More importantly, this mesoporous composite also showed an excellent cycling performance with the retention of 92.6% specific capacitance after 60,000 charging and discharging cycles.

1. Introduction

Electrochemical capacitors (ECs), known as supercapacitors, have been widely investigated due to their unique advantages such as high power density, fast charging, excellent cycling stability, etc. Therefore, they are promising candidates for next-generation power devices [1–4]. ECs are generally divided into electrochemical double layer capacitors (EDLCs) and pseudocapacitors, and their storage principles of electrical energy are achieved by separation of charges in a Helmholtz double layer and by reversible Faradaic redox reactions with charge-transfer [5]. Currently, carbonaceous materials with high surface area, such as activated carbon, graphene and carbon nanotubes, have been demonstrated to be effective electrode materials for supercapacitors operated in both aqueous electrolyte and organic electrolyte [6–9]. However, these electrode materials might not provide sufficient energy and power densities for future market applications of energy storage or conversion systems compared with the battery-type capacitive metal oxides [10].

A number of transition metal oxides, such as ruthenium oxide [11], manganese dioxide [12], nickel oxides [13], cobalt oxide [14] and vanadium oxide [15] have been confirmed to be excellent electrode materials for supercapacitors owing to their outstanding structural flexibility and the high specific capacitances or capacities. Nickel oxide (NiO) with a theoretical specific capacity of $358\ mAh\ g^{-1}$ is considered as a promising electrode material for pesudocapacitor due to its excellent electrochemical performance, easy availability and low cost [16]. Nanostructured nickel oxides of porous nanocrystals [17], ordered mesoporous structures [18], ultrafine quantum dots [19], and nanowires [20] have been synthesized as advanced electrode materials for use in supercapacitors, improvement in their electrochemical properties.

The actual mechanism of stored electrical energy in a supercapacitor is mainly accompanied by an electron charge-transfer between electrolyte and electrode, which is accomplished through electrosorption, redox reactions and intercalation processes [21]. The amount of electrical charge stored in a capacitor is proportional to the specific surface area, transfer rate of electrolyte in the pores, and charge-transfer rate. An efficient way to increase the specific capacitance is to improve the structural performance of electrode materials with high electrical conductivity and low total internal resistance through high surface area and unique mesoporous structures for fast ion transfer for electrosorption and redox reactions [4,22].

Intrinsically, pure nickel oxide is an insulator, and its electrical conductivity is around $10^{-4}\ s\ cm^{-1}$ [23], which increases both the sheet resistance and the charge transfer resistance of the electrodes, leading to a small part of their theoretical capacitance and a poor rate

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capability [24]. To solve the above problem, various hybrid structures, such as modification with conductive carbon-based materials [25–28] and metal oxides directly deposited on highly conductive nanostructures [29,30] have been suggested to improve the ion and electron transport in the electrodes. However, high cost and complicated synthetic routes of the above materials limit the potential use of NiO-based electrodes in supercapacitors.

For a supercapacitor electrode, a long cycle life is a critical factor for evaluating the possibility of practical application of an electrode in a device [31,32]. An electrochemical capacitor, whose electrodes are constructed of carbon-based materials, can have a long-term stability of over 100,000 cycles because it is a typical electrical double layer (EDL)-type supercapacitor [33,34]. However, when transition metal oxides are used in the case of battery-type electrode materials for hybrid supercapacitors, most of them can only be used for a relatively short cycle life. For example, $NiCo_2O_4$ nanosheet/graphene retained 94% after 14,000 cycles [35], $NiCo_2S_4@MnO_2$ retained 82% after 2000 cycles [36], $MnCo_2O_4$ hollow microspheres retained 93.6% after 2000 cycles [37] and $NiCo_2O_4$ thin films retained 96.5% after 10,000 cycles [38] of their capacity. The charge storage capability of transition metal oxides is based on the redox reactions at the interface between electrode materials and electrolyte solutions, leading to the degraded microstructures of the electrode materials.

Binary metal oxide of $LaNiO_3$ (LNO) is a perovskite-type metal oxide with the lattice parameter of 0.384 nm for pseudocubic structure, and exhibits a good metallic behavior with a resistivity of ~10^{-5} mΩ cm at room temperature [39]. Metallic LNO films are considered as promising alternatives for the platinum electrode as bottom electrodes for the integration of ferroelectric films on silicon wafer to match the structure of ferroelectric oxides and improve the leakage current characteristics [40]. In the present work, considering the characteristics of oxide such as variable valency of nickel element and good compatibility with NiO, LNO is composited with NiO to fabricate a highly mesoporous structure with high specific surface area as electrode materials of supercapacitors. The results presented here with the as-prepared mesoporous $LaNiO_3$/NiO composite showed improved electrical conductivity, a high specific capacitance and ultra-long cycle life.

2. Experimental section

A sol–gel route was employed in our experiments using tetraethyl orthosilicate (TEOS), nickel acetate and lanthanum acetate as the starting materials. Initially, 50 ml precursor solution was prepared from TEOS/ethanol/deionized water/2 M ammonia water in a volume ratio of 1:4:1:0.16 at room temperature under constant stirring. After 15 min of stirring, 5 ml of 1 M nickel acetate and 5 ml of 0.5 M lanthanum acetate aqueous solutions as well as an additional 0.2 ml of 2 M ammonia water were added and mixed with the above TEOS solution under continuous stirring for 20 min. The homogenized precursor solution was sealed and allowed to gel at 50 °C for 24 h. After removing solvent at 80 °C under vacuum atmosphere, the dried gel was heated from room temperature to 600 °C (or 650 °C) with a heating rate of 2 °C min^{-1} and maintained at 600 °C (or 650 °C) for 20 min. The calcined powders were then immersed in 100 ml of 2 M NaOH aqueous solution and stirred for 24 h at 80 °C to remove silica template and any other soluble inorganic salts. After rinsing with deionized water and absolute ethanol repeatedly, the powders were dried at 100 °C under vacuum for 4 h. Variation of residual mass ratio with rinsing time was shown in Fig. S1 (Supplementary Material).

Using a rotating target X-ray diffractometer, Ni-filtered CuK_α radiation was employed to determine the crystallinity of the powders by X-ray diffraction (Philips Xpert X–ray diffractometer). The morphology was analyzed by field emission scanning electron microscope (FESEM, Inspect F, FEI Co., U.S.) and high resolution transmission electron microscope (HRTEM; Libra 200FE, Germany). The specific surface area was estimated with the aid of the adsorption isotherms of N_2 molecules at 77 K using a Nova 2000e (Quantachrome Instrument, US) surface area analyzer, and the surface area was calculated using a BET plot method. The pore size distribution was calculated from the Barrett–Joyner–Halenda (BJH) method.

Electrochemical studies were carried out in 1 M KOH solution by measurement of cyclic voltammetry (CV) and AC impedance spectroscopy in an electrochemical workstation (CHI660D) with a three-electrode cell using an Hg/HgO reference electrode and a Pt coated titanium counter electrode. The working electrode was prepared by mixing 80 wt% of the active material, 10 wt% of conducting agent (carbon black), and 10 wt% of binder (polyvinylidene difluoride), and N-methyl-2-pyrrolidone (NMP), the latter was used as a solvent. The obtained paste was pressed onto carbon cloth current collectors (1.0×1.0 cm^2) and dried in a vacuum oven at 60 °C for 24 h. Approximately 0.8 mg of active material was coated on current collector in a working electrode. The galvanostatic charge–discharge (GCD) tests were performed by using a CT2001A rapid sampling battery testing system (LAND, China) at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of composite lanthanum and nickel oxide powders with an atom ratio of La: Ni=1:2 after heat treatment at 600 and 650 °C. All the diffraction peaks can be perfectly indexed to the cubic perovskite-type $LaNiO_3$ (JCPDS, card no 34–1181) and the cubic crystalline structure of NiO (JCPDS, card no 47–1049). No other peaks attributable to La_2O_3 or other phases can be observed (Fig. 1) although other materials with different atom ratios of La:Ni showed other phases as can be seen in Fig. S2 (See Supplementary Material). However, there may be amorphous or poorly crystalline lanthanum hydroxides and carbonates in the samples which were not detected by XRD but could be detected by Raman or IR spectroscopy [41]. By increasing the annealing temperature from 600 to 650 °C, the relative intensities of the peaks become slightly stronger, and there is almost no change in the calculated full width at half-maximum (FWHM) height, which suggests that increasing temperature is slightly beneficial to the degree of crystallinity with little or no effect on grain size. This result is unlike the previously reported results [42], which showed an increase in grain size. The possible reason for lack of grain growth here is the presence of abundant amorphous silica which prevented the grain growth of both LNO and NiO under our experimental conditions.

Fig. 2 shows a typical FESEM micrograph of mesoporous $LaNiO_3$/NiO composite annealed at 650 °C. It can be seen that mesoporous

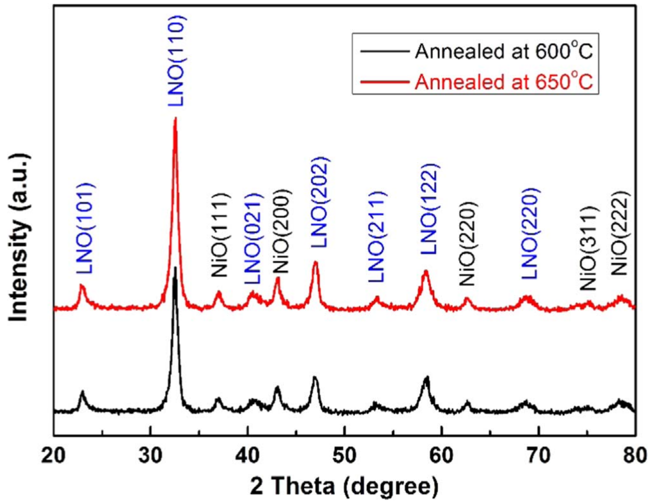

Fig. 1. XRD patterns of composite lanthanum and nickel oxides annealed at 600 or 650 °C.