



Regular article

A novel NiCoMnO₄ anode material: Construction of nanosheet architecture and superior electrochemical performances



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ABSTRACT

Novel NiCoMnO₄ nanosheets have been designed and fabricated via a facile hydrothermal derived process. The microstructure results reveal that the as-prepared material has a typical spinel structure and possesses a nanosheet morphology. Due to the unique chemical composition and nanostructure, the NiCoMnO₄ nanosheets exhibit a very high reversible capacity of 1329.3 mAh g⁻¹ at 200 mA g⁻¹ after 100 cycles and show excellent rate performance of 501.6 mAh g⁻¹ even at 5000 mA g⁻¹ when used as anode material for lithium-ion batteries (LIBs).

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In order to reduce the rapid depletion of fossil-fuel and environmental pollution these years, much effort has been devoted to searching for renewable energy to replace traditional fossil fuels [1,2]. Lithium-ion battery (LIB) is regarded as an ideal substitute, which can be applied to various portable electronic devices and hybrid electric vehicles (HEVs) due to its high energy densities, long cycle life, no memory effect, environment friendliness and safety [3–5]. However, the commercial anode material graphite cannot meet the demand of applications in high energy and high power devices owing to its low theoretical specific capacity (only 372 mAh g⁻¹) and poor rate capability [6,7].

As one of the typical binary transition metal oxides, NiCo₂O₄ has higher specific capacity of ~890 mAh g⁻¹ (twice higher than that of graphite) and higher electronic conductivity (higher than that of single transition metal oxides), which has been hot explored as one potential anode material for LIBs [8,9]. However, the toxicity and high cost of cobalt retard the commercial application of NiCo₂O₄. Besides, volume effect during charge/discharge process damages the cycle stability, and this is a common problem for transition metal oxides. To overcome these shortcomings and provide guidance to explore novel transition metal oxides system, we designed a novel anode material NiCoMnO₄ and constructed a unique nanosheet architecture via a facile hydrothermal process in this work. Firstly, substitution of Co by nontoxic and

cheap Mn can effectively reduce the toxicity and cost of NiCo₂O₄. Secondly, electrochemical active Mn also can ensure that there is almost no sacrifice of specific capacity. Finally, unique nanosheets can supply enough free interspace to effectively alleviate volume variation [10, 11]. The electrochemical performance results show that the NiCoMnO₄ nanosheets can be evaluated as a novel anode material for LIBs, and they exhibit high specific capacity, superior cycling stability and excellent rate capability. To the best of our knowledge, the present work is the first report in LIBs.

For the preparation of NiCoMnO₄ nanosheets, 2 mmol each of Ni(CH₃COO)₂·4H₂O, Co(CH₃COO)₂·4H₂O and Mn(CH₃COO)₂·4H₂O were dissolved in 18 mL deionized water with constant stirring. Then, a mixed solution of 12 mL KOH (2 mol L⁻¹) and 1.5 mL H₂O₂ (30 wt%) was dropped slowly into the above solution under vigorous stirring. The mixture was stirred for another 0.5 h and then transferred to a 50 mL Teflon-lined autoclave followed by heating to 180 °C for 24 h. After cooling down to room temperature, the precipitate was washed for several times and then dried. Finally, the as-prepared black precursor was calcined at 450 °C for 2 h in air to obtain NiCoMnO₄ nanosheets.

The crystal structure of the as-obtained material was investigated by a Rigaku miniflex X-ray diffraction (XRD). The element composition was investigated by X-ray photoelectron spectra (XPS, Escalab 250Xi). The morphology of the sample was observed on a field-emission scanning electron microscope (FESEM, Hitachi S4800). Transmission electron microscope (TEM), selected-area electron diffraction (SAED) and high resolution transmission electron microscope (HRTEM) images were acquired on a FEI Tecnai G2. The specific surface area and pore

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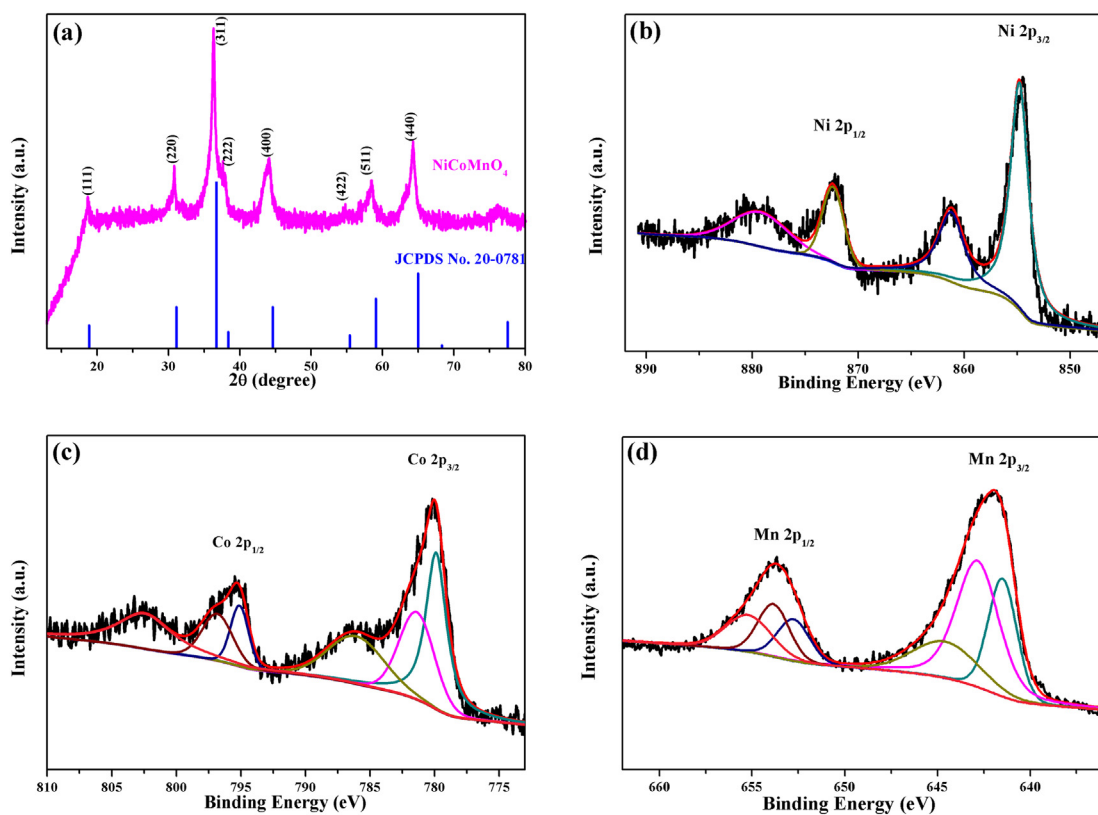


Fig. 1. (a) XRD pattern of NiCoMnO₄ nanosheets, XPS spectra of (b) Ni 2p, (c) Co 2p, (d) Mn 2p.

size distribution were performed through N₂ adsorption-desorption isotherms using a Micromeritics ASAP 2460 system.

The electrochemical performances of NiCoMnO₄ nanosheets were evaluated by using CR2025 coin cells. The work electrode consisted of 70 wt% NiCoMnO₄, 20 wt% Super P Li, 10 wt% polyvinylidene fluoride (PVDF) and Cu foil as the collector. The lithium metal was used as the counter electrode and the electrolyte was 1 mol L⁻¹ LiPF₆ in ethylene carbonate/dimethyl carbonate (EC:DMC = 1:1, v/v). Galvanostatic charge-discharge tests were carried out on a battery testing system (LAND CT2001A) between 0.01 and 3.0 V at different current densities. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were investigated on an electrochemical workstation (Autolab, PGSTAT302N). The CV curves (CVs) were tested in the voltage of 0.01–3.0 V at a scan rate of 0.1 mV s⁻¹, while the EIS were measured in the frequency range from 100 kHz to 0.01 Hz.

Fig. 1a shows the XRD pattern of the NiCoMnO₄ nanosheets. All of the diffraction peaks are in agreement with NiCo₂O₄ (JCPDS card no. 20-0781) and no impurity peak is identified, which reveals that the substitution of Co by Mn does not change its spinel structure.

The fitted XPS spectra of Ni 2p, Co 2p and Mn 2p in NiCoMnO₄ nanosheets are shown in Fig. 1b, c and d, respectively. Four peaks are observed in Ni 2p spectrum. Two strong peaks of Ni 2p_{3/2} (854.7 eV) and Ni 2p_{1/2} (872.5 eV) as well as the corresponding two satellite peaks can be attributed to Ni²⁺ [12]. In the Co 2p spectrum, the fitting peaks at 779.7 and 795.0 eV are ascribed to Co³⁺, while the peaks at 781.5 and 796.7 eV are indexed to Co²⁺ [13,14]. Meanwhile, the Mn 2p spectrum is best fitted considering two spin-orbit doublets characteristic of Mn³⁺ and Mn⁴⁺, together with two satellites. The peaks at 641.4–641.6 eV and 642.8–643.5 eV are ascribed to Mn³⁺ and Mn⁴⁺, respectively [15]. Accordingly, these XPS results suggest that the chemical compositions of Ni, Co and Mn in the NiCoMnO₄ nanosheets are Ni²⁺,

Co²⁺/Co³⁺ and Mn³⁺/Mn⁴⁺, respectively, which agree well with the reported results [12,16,17].

The morphologies of the as-obtained NiCoMnO₄ sample at different magnifications are shown in Fig. 2a, b and c. It can be found that the sample possesses a sheet-like 2D structure. The sheets are uniform and freestanding, and the average diameter of the sheets is about 800 nm. Careful observation, the thickness of the ultrathin sheets can be estimated to be around 10 nm. Those indicate that the sample possesses a nanosheet structure. The SAED pattern of NiCoMnO₄ nanosheets is presented in Fig. 2d, which indicates the single-crystalline nature of the sample. In addition, the HRTEM images of NiCoMnO₄ in Fig. 2e and f reveal two sets of lattice spacing of 0.25 and 0.29 nm, corresponding to the (311) and (220) planes of NiCoMnO₄, respectively. These HRTEM results further confirm that the NiCoMnO₄ nanosheets possess a spinel structure, which is in accordance with the XRD results.

Fig. 3a shows the CVs of NiCoMnO₄ nanosheets. In the first cycle, three reduction peaks can be found. The first one at about 1.13 V can be attributed to the destruction of the crystal structure of the NiCoMnO₄ nanosheets [2]. The sharp peak at 0.75 V can be assigned to the reduction of NiCoMnO₄ to metallic Ni⁰, Co⁰ and Mn⁰, and accompanied by the formation of Li₂O. The last unnoticeable peak appeared at ~0.66 V can be attributed to the formation of the solid electrolyte interface (SEI) film [2,8]. The two broad oxidation peaks centered at 1.58 and 1.99 V are according to the oxidation reaction of Ni⁰, Mn⁰ and Co⁰ to Ni²⁺, Mn²⁺ and the mix valence of Co²⁺ and Co³⁺. In the subsequent cycles, the reduction peaks broaden and shift to higher voltage, due to the irreversible reaction of NiCoMnO₄ and irreversible capacity of SEI film. From the second cycle, the CVs nearly overlap, indicating good electrochemical reversibility. In order to further shed light on the mechanism of NiCoMnO₄ as anode material, XRD test of NiCoMnO₄ electrode at the charge state after the initial cycle were carried out and the result

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