



Nickel and nitrogen co-doped tin dioxide nano-composite as a potential anode material for lithium-ion batteries



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ABSTRACT

As a promising high capacity anode material for lithium-ion batteries (LIBs), tin dioxide (SnO₂) has attracted considerable interest in recent studies. In this paper, nickel-doped tin dioxide (Ni/SnO₂), nickel and nitrogen co-doped tin dioxide (Ni-N/SnO₂) are prepared to modify the electrochemical properties of as-prepared SnO₂. Samples of pure SnO₂, Ni/SnO₂ and Ni-N/SnO₂ are characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) and high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray analysis (EDAX), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and Brunauer–Emmett–Teller (BET). It is found that doping and co-doping process does not affect the phase structure of pristine SnO₂. However, it obviously influences the morphology, specific surface area, and electrochemical properties of SnO₂. Galvanostatic cycling indicates that the Ni-N/SnO₂ nano-composite still remains a high charge capacity of 631 mAh g⁻¹ after 50 cycles. Rate performance evaluation shows that a capacity of 621 mAh g⁻¹ can still be delivered when the current returns back to 0.1 C after 50 cycles at different current densities. Cyclic voltammetry (CV) analysis proves that Ni and N co-doping accelerates the electrode reaction. The results of electrochemical impedance spectroscopy (EIS) demonstrate the low charge-transfer resistance for Ni-N/SnO₂, and the following quantitative calculation further confirms the highest electric conductivity and ionic conductivity of Ni-N/SnO₂ compared with those of pure SnO₂ and Ni/SnO₂. This explains the superior capacity retention and rate performance of co-doped material.

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1. Introduction

Lithium-ion batteries (LIBs) have been extensively used in portable electronics and are further expected to be applied in hybrid electric vehicles (HEVs), electric vehicles (EVs), and energy storage for utility grids [1–4]. Although successful commercialization of LIBs has significantly accelerated technological advancements, it still remains a challenge to develop new materials with high capacity, long life-span, good rate capability, and environmental benignity [5–7]. In the past several decades, great effort has been paid to achieve these objectives. Noticeably, tin dioxide (SnO₂) has been widely investigated due to its high theoretical specific capacity of 1494 mAh g⁻¹ (SnO₂ + 8.8 Li⁺ + 8.8 e⁻ ↔ 2Li₂O + Li_{4.4}Sn), which has been regarded as one of the most promising candidates to replace the commercialized graphitic carbon (with theoretical capacity of 372 mAh g⁻¹) [8–16].

Unfortunately, the practical application of SnO₂ to LIBs is severely hindered by its rapid capacity decay, which can be ascribed to pulverization, particle aggregation, and unstable solid electrolyte interphase (SEI) film formation and decomposition, with all of these originating from the huge volume change upon alloying and dealloying process and low conductivity [17–19]. Several strategies have been put forward to enhance the cyclability of tin-based electrode materials by using composites with hollow structures, fabricating intermetallic compounds and active composites, and selecting an optimized binder [20,21]. However, these approaches still face challenges to obtain both excellent cyclability and desirable voltage plateaus since SnO₂ nanoparticles are prone to aggregate with large volume expansion during cycling [22]. Therefore, rational design to protect SnO₂ nanoparticles from agglomeration and suppress the absolute volume change during cycling is expected to provide high-performance electrodes.

Recently, Ni has been successfully doped into the lattice of SnO₂ [23–27], and it is found that the doped samples exhibit volume buffering effect [24,25] and increased electronic conductivity

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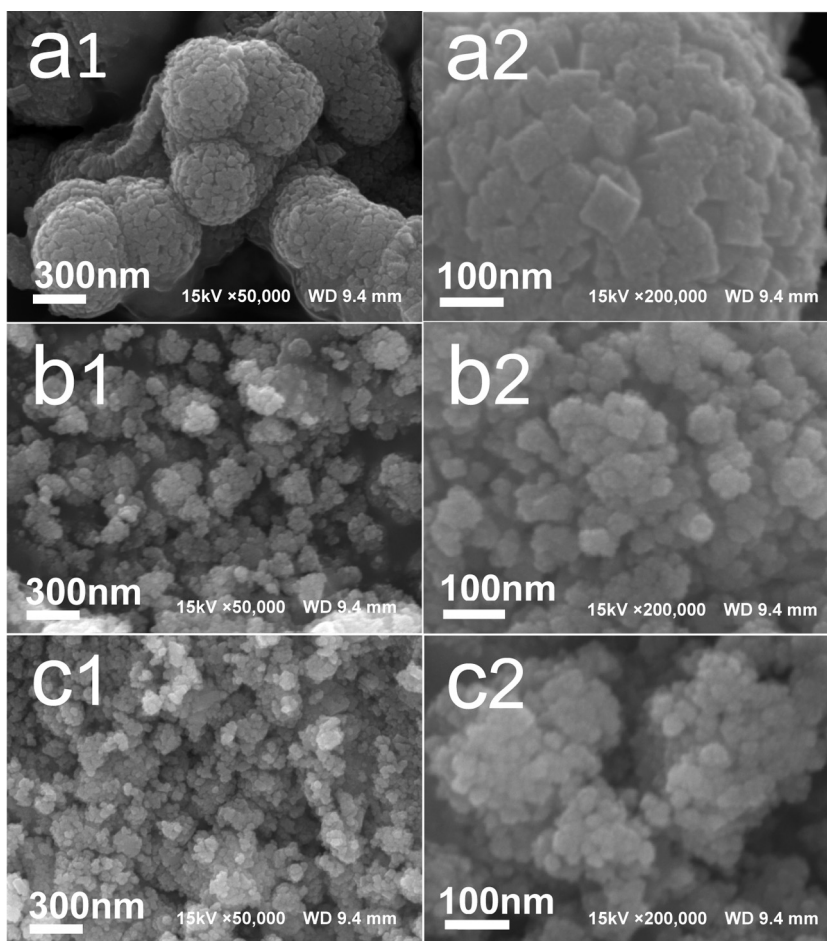


Fig. 1. Surface morphologies of SnO_2 (a1,a2), Ni/SnO_2 (b1,b2) and Ni-N/SnO_2 (c1,c2).

[26,27]. As the optimal capacity retention among the previous Ni doped SnO_2 reports, it only exhibits a specific capacity of about 260 mAh g^{-1} after 50 cycles [24], much lower than its theoretical value (781 mAh g^{-1}). Additionally, it has been well established that N-doped SnO_2 exhibits desirable enhanced electrical and optical properties, which could be attributed to the greatly increased conductivity [28–30].

In this work, a hydrothermal method is applied to prepare SnO_2 and Ni/SnO_2 . As a feature of this work, the Ni doped product is further thermal-treated under N_2 atmosphere to obtain Ni and N co-doped SnO_2 (Ni-N/SnO_2), which has not been reported in previous literatures. The physical and electrochemical properties of the as-prepared samples are extensively characterized and compared. It is found that the Ni and N co-doped material exhibits significantly improved electrochemical properties. Further, the improvement mechanism of Ni and N co-doping is also intensively explored.

2. Experimental

2.1. Material synthesis

The synthesis of Ni/SnO_2 was performed in a solvent of water starting from $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and NaOH . Typically, 40 mL of SnCl_4 (8 mmol) and NiCl_2 (0.48 mmol) was added to 40 mL of NaOH (56 mmol) with vigorous stirring. Next, the obtained solution was transferred into a 100 mL Teflon-lined autoclave and maintained at 180°C for 12 h. Afterwards, the flaxen precipitate was

collected, repeatedly washed with deionized water and ethanol to remove impurities, and isolated by vacuum filtration. The pure SnO_2 was obtained through the same route only with the absence of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. To prepare Ni and N co-doped SnO_2 , the obtained Ni/SnO_2 was dried in a vacuum oven at 70°C , and further sintered at 550°C for 18 h in nitrogen.

2.2. Physical characterizations

X-ray diffraction (XRD) patterns were recorded on a DX-2500 diffractometer (Fangyuan, Dandong) with $\text{Cu K}\alpha$ radiation of $\lambda = 0.154145 \text{ nm}$. The Raman spectra were collected on a laser Raman Spectrometer (RM-1000, Renishaw) with 633 nm He-Ne laser. Morphological characterizations were carried out on field-emission scanning electron microscopy (FESEM) (JEOL JSM 7001F). Energy Dispersive X-ray analysis (EDAX) was applied to determine the element composition and distribution together with FESEM. The image of high resolution transmission electron microscopy (HRTEM) was collected on Philips CM200 equipment to investigate the sample microstructure. Nitrogen adsorption measurements were performed on a Micromeritics ASAP 2020 adsorption analyzer. Specific surface areas were calculated by the Brunauer-Emmert-Teller (BET) method. Pore volumes and sizes were estimated from pore size distribution curves from the adsorption isotherms using the Barrett-Joyner-Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Electron Corporation spectrometer with an $\text{Al K}\alpha$ (1486.6 eV) radiation.

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