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Systematic comparison of hollow and solid $Co_3V_2O_8$ micro-pencils as advanced anode materials for lithium ion batteries

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ABSTRACT

Cobalt vanadates have been demonstrated as superior anode candidates for lithium ion batteries (LIBs) owing to their unique advantages, such as superb specific capacity, low operating potential, and excellent cycling stability. Among the cobalt vanadates, $Co_3V_2O_8$ manifests tremendous potential of commercialization because of their controllable particle size and morphology. In this study, we readily synthesized both hollow and solid $Co_3V_2O_8$ micro-pencils and thoroughly compared their electrochemical properties. Employed as anode for LIBs, the hollow $Co_3V_2O_8$ exhibited much higher initial specific capacity than the solid ones (~1200 $mAhg^{-1}$ vs. ~680 $mAhg^{-1}$). When tested at 1000 mAg^{-1}, the hollow $Co_3V_2O_8$ displayed superior reversible capacity over the solid ones (~650 $mAhg^{-1}$ vs. ~450 $mAhg^{-1}$ after 300 cycles), benefiting from the hollow architecture. Moreover, the hollow micro-pencils showed better rate performance, with outstanding stability and capacity loss when higher current density was applied. The comparative study demonstrated the hollow $Co_3V_2O_8$ is more efficient than the solid ones for LIB anodes. Based on the comparison on pure micro-pencils, further approach (e.g. graphene coating) can be exploited for superior performance towards ultimate application in lithium-ion batteries.

1. Introduction

Nowadays, rechargeable lithium-ion batteries (LIBs) have assumed an increasingly crucial role in industrial and domestic applications, due to their high energy densities, excellent cycle life, no memory effect and environmental benignity [1–4]. Unfortunately, graphite, the current commercial anode in LIBs, has a low theoretical specific capacity (372 $mAhg^{-1}$), limiting their high-power application such as electric vehicles, which elicits relentless pursuit of novel anode materials [5–7]. As a promising alternative, transition metal oxides (TMOs) have attracted much attention owing to their high specific capacities (600–1000 $mAhg^{-1}$) and earth-abundant sources [8–18]. Among TMOs, mixed metal oxides possess excellent reversible capacity, and decent mechanical stability, closely related to the mixed valence of metal cations, interfacial effects, and the synergic effects of the multiple metal species [19–21]. Specifically, several families of metal vanadate materials, which derive outstanding electrochemical properties from multiple valence states of V (+2, +3, +4, +5) and complex chemical reaction process, have been frequently reported as anodes for LIBs: Metal = Co [20,22–35], Cu [36,37], Zn [38–41], Mn [42–44], Ni [45,46], and Li [47–51]. These materials reach a perfect balance between lithium storage capability and capacity retention in the cycling process. On the one hand, vanadates have demonstrated much higher specific capacity than graphite. On the other hand, unlike silicon and alloy anode, whose accommodation of so much lithium is accompanied by enormous volume changes (>300%) in the host metal, vanadates have milder lattice stress and the consequential crumbling [47,52–54].

Amid the abovementioned metal vanadates, cobalt vanadates have a relatively high capacity and better cycling performance, captivating lots of researchers in the past three years. In terms of pure $Co_3V_2O_8$, some unique morphologies had been acquired. Wu and co-workers successfully obtained $Co_3V_2O_8$ hollow hexagonal prismatic micro-pencils [30]. Yang and co-workers fabricated

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multilayered $Co_3V_2O_8$ nanosheets capable of maintaining a specific capacity of 1114 $mAhg^{-1}$ over 100 cycles at 1000 mAg^{-1} [24]. Xiang et al. synthesized $Co_3V_2O_8$ hollow nanofibers delivering a high specific capacity of 900 $mAhg^{-1}$ at 5 Ag^{-1} and long cycling stability up to 2000 cycles [31]. Luo et al. produced $Co_3V_2O_8$ interconnected hollow microsphere achieving 320 $mAhg^{-1}$ even at 20 Ag^{-1} [33].

However, when developed innovative method and acquired materials of superb electrochemical performance, some interesting areas of binary cobalt vanadates still remain vague: for example, few work shed light on the exact influence of specific $Co_3V_2O_8$ unit particle morphology. Zhang et al. have compared the capacity of $Co_3V_2O_8$ micro-pencils of different size and inner structure [20], but so far, the impact of hollow and solid structure on materials still lacks exploration. Wu et al. demonstrated the excellent electrochemical properties of hollow hexagonal prismatic pencils, and revealed the growth mechanism of solid and hollow structures explicitly, yet the solid $Co_3V_2O_8$ was overlooked.

Simultaneously, most researchers wholeheartedly sought to reduce the particle size, enhance the porosity and create more void for higher capacity. It is acknowledged that hollow structures can contribute to high surface area, abundant void space, and short ion/electron transport distance. However, according to several earlier investigations, porous or hollow structure may hamper the electrochemical behavior of anode materials in some aspects [55,56]. Therefore, considering the drawback of former work on $Co_3V_2O_8$ micro-pencils and the mania towards hollow/mesoporous characteristic, the comparison of solid and hollow structures is necessary for pure $Co_3V_2O_8$. Furthermore, the intrinsic scanty electric conductivity, the poor cycling stability because of the remarkable volume fluctuation (though milder than silicon and alloy anode) and the reduced crystallinity of the active materials still hinder the vanadate-based anode from practical applications in next-generation LIBs [25,32], awaiting better fabricating approach.

Herein, we successfully synthesized $Co_3V_2O_8$ hollow micro-pencils (HMPs) and $Co_3V_2O_8$ solid micro-pencils (SMPs) through a facile hydrothermal method, followed by systematic and thorough comparison. The HMPs exhibited an excellent lithium storage capacity (1200 $mAhg^{-1}$ at 1000 mAg^{-1}) and good cycling retention (650 $mAhg^{-1}$ after 300 cycles), while the SMPs showed comparatively poor electrochemical performance (only ~680 $mAhg^{-1}$ at first cycle and ~450 $mAhg^{-1}$ remained after 300 cycles). The electrochemical properties and cycling process of the prepared HMPs and SMPs were exhaustively studied, with explanations from the alteration of the anode materials. The XRD patterns demonstrated the identical crystal formation of both $Co_3V_2O_8$ samples. The SEM images unveiled the details of solid and hollow structures, which were confirmed by the Brunauer-Emmett-Teller (BET) and Langmuir surface area measurement. The electrochemical impedance spectroscopy (EIS) was first applied on the hollow micro-pencils. Simultaneously, the whole life of the $Co_3V_2O_8$ micro-pencils was qualitatively summarized and analyzed, helping to explain the difference between HMPs and SMPs. In a nutshell, $Co_3V_2O_8$ micro-pencil has a considerable potential to be mass-manufactured in industry in light of its independent and controllable particle unit, thus we hope our study can enlighten the further research in $Co_3V_2O_8$, which is the likely candidate for the next-generation anode material in LIBs.

2. Experiment section

2.1. Sample preparation

2.1.1. All the chemicals were analytical grade

SMPs: First, 1.1687 g (0.01 mol) of NH_4VO_3 was dissolved into 200 ml deionized water at 80 °C, awaiting its color turned to transparent pale green under vigorous stirring for several minutes. Then, 0.24 g (0.006 mol) of NaOH was added into the former solution, which should change to be transparent and colorless after a while. Later, 0.475 g (0.002 mol) of $CoCl_2 \cdot 6H_2O$ was dissolved into the mixed solution. Stirring for 5 min, the reddish brown precursor suspension was transferred into a tightly sealed 200 ml Teflon-lined autoclave, maintained at 180 °C for 12 h. After cooling to ambient temperature naturally, the products were washed 5 times using deionized water and 2 times with absolute ethanol. Subsequently, the product was dried at 80 °C for 12 h, followed by annealing in air atmosphere at 500 °C for 4 h.

HMPs: All the conditions were kept identical except the dosage of alkaline (0.01 mol $LiOH \cdot H_2O$), the reaction temperature (200 °C) and the reaction time (16 h) in the hydrothermal procedure.

2.2. Materials characterization

XRD analysis of both the prepared samples were performed on a Bruker-D8 Advanced X-ray Diffractometer (Cu Kαradiation: $\lambda = 1.5406$ Å) at a scanning speed of 2 deg min^{-1}. The circumstantial morphologies of the materials, interior and exterior, were detected by field-emission scanning microscope (FE-SEM, JSM-5900LV, JEOL). The transmission electron microscope (TEM) was conducted on JEM2100 (JEOL, Japan). To obtain the specific surface areas of two products, Brunauer-Emmett-Teller (BET) and Langmuir surface area measurements were conducted on a JWGB BK100C surface analyzer at 77 K.

2.3. Electrochemical measurement

The electrochemical characterization was implemented on 2032 type coin cells consisting of two electrodes ($Co_3V_2O_8$ as working electrode and Li metal as counter electrode) and the separator (Celgard 2350 microporous membrane). The cells were assembled in an Ar-filled glovebox with both the oxygen and the moisture content below 1 ppm. The ultimate anode was prepared by a 2-h coating procedure, in which 70 wt% former synthesized $Co_3V_2O_8$, 20 wt% conducting acetylene black, and 10 wt% Carboxyl Methyl Cellulose (CMC) were sufficiently mixed. Then, the slurry was pasted uniformly onto a clean copper foil and dried at 80 °C for 12 h in vacuum oven. Finally, the film was punched to be an electrode in a diameter of 15 mm. The loading density of the active material was ~1.5 mg cm^{-2}, which is similar with those in previous studies of cobalt vanadates electrodes [22–24]. The electrolyte exploited was 1 M $LiPF_6$ in ethyl carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (volume ratio 1:1:1). The half-cells were tested at a voltage range of 0.01–3.0 V (vs. Li^+/Li) at room temperature, using a CT2001A LAND Cell test system, where galvanostatic charge-discharge cycling performance simultaneously derived from. Cyclic voltammetry (CV) testing was carried out between 0.01 and 3 V (vs. Li/Li^+) at a scan rate of 0.2 mVs^{-1}. Electrochemical impedance spectroscopy (EIS) was completed on a CHI660C electrochemical workstation (Shanghai Chenhua instrument company, China).

3. Results and discussion

3.1. Structure and morphology

Both the products were characterized by X-ray diffraction (XRD), which unveiled the composition and the crystal structure of $Co_3V_2O_8$ micro-pencils. The XRD patterns of HMPs and SMPs in Fig. 1(a) show that the main diffraction peaks of both the obtained $Co_3V_2O_8$ micro-pencils can be perfectly matched to the cubic