



Theoretical calculation and experimental verification of $Zn_3V_3O_8$ as an insertion type anode for LIBs



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ABSTRACT

The charge/discharge mechanism and electrochemical performance of $Zn_3V_3O_8$ as anode for Li-ion batteries are systematically studied. Theoretical calculation predicts that $Zn_3V_3O_8$ can act as a host for Li storage, and a possible diffusion way of Li-ions within the crystal structure is calculated via first principle methods. Experimentally, $Zn_3V_3O_8$ nanosheets with porous architecture are fabricated via a facile hydrothermal pretreatment and subsequent sintering. The $Zn_3V_3O_8$ shows superior electrochemical performance with graphite electric additive, exhibiting discharge/charge capacity of 541/537 mAh g^{-1} after 200 cycles at a specific current of 120 mA g^{-1} . The Li-storage mechanism is also studied via ex-situ XRD, and the maintenance of main diffraction peaks during lithiation/delithiation process suggests a possible intercalation/extraction mechanism of the $Zn_3V_3O_8$.

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1. Introduction

While the energy density of Li-ion batteries (LIBs) has doubled since the first commercialization in 1990s, numerous approaches are still being explored for further improvement. Despite significant performance improvement promoted by the development of binder, conductive additive and electrolyte, electrode materials have always been playing a crucial role to boost the performance of LIBs [1]. According to the charge/discharge mechanisms, electrode materials can be divided into three categories: (1) the insertion type material, typically as graphite [2]; (2) the conversional type material, mainly referring to transition metal oxides [3]; (3) alloy type material, such as Si [4]. Unfortunately, the practical applications of conversional and alloy type materials in LIBs are badly restricted by their severe volume expansion, which results in unexpected capacity attenuation. In contrast, insertion type materials,

such as graphite and $Li_4Ti_5O_{12}$, have been successfully commercialized in LIBs owing to their high reversibility in lithiation/delithiation as well as high stability in cycling. To advance the performance of LIBs, further exploration on new insertion type material is still highly anticipated, while, regrettably, little progress has been achieved up to now.

Metal vanadates have proven effective in constructing kinetically favourable Li-ions channels as anodes or cathodes for LIBs, with the reduction/oxidation of vanadium element keeping electric neutrality during the intercalation/extraction of Li-ions into/from these channels [5–8]. Here in this paper, we demonstrate theoretically and verify from experimental results that $Zn_3V_3O_8$ can be used as an insertion type anode for LIBs. The possible intercalation sites and diffusion ways of lithium ions within the $Zn_3V_3O_8$ crystal structure were firstly calculated via first-principle method. Furthermore, the insertion/extraction mechanism was also proved via ex-situ XRD measurement.

2. Experimental section and theoretical calculation

2.1. Fabrication procedure

The chemicals were analytical grade and Graphite was natural

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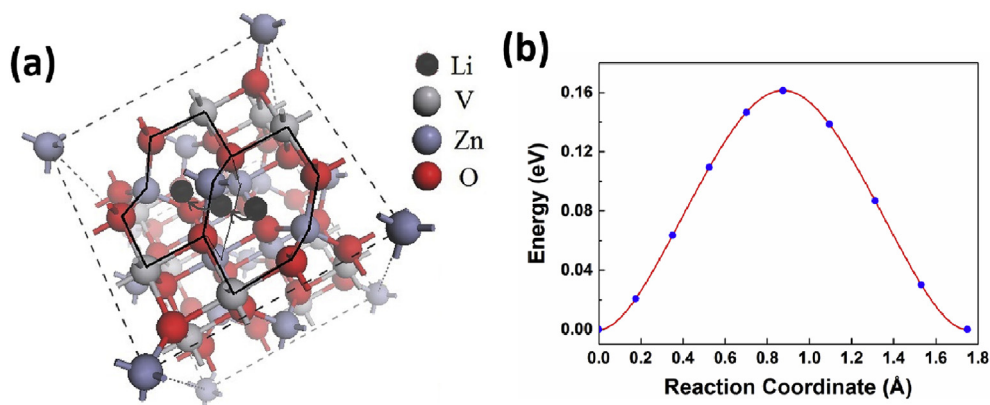


Fig. 1. (a) The crystal structure of $Zn_3V_3O_8$. The thicker solid line indicates the V-O-Zn eight-membered ring and the thin line is corresponding to the V-O-Zn five-membered ring. (b) The minimum energy curve of the Li atom diffusion path between the center of the eight-membered rings. The middle state is the Li atom occupies the center of the five (six)-membered ring.

with purity of 99.8%, both were purchased from Alfa Aesar. In a typical procedure, 4 mmol $C_4H_6O_4Zn \cdot 4H_2O$, 2 mmol V_2O_5 and 5 mmol $C_6H_{12}N_4$ were dissolved in 40 ml distilled water and stirred for 30 min until a homogeneous yellowy suspension was formed. Then it was transferred into a 50 ml teflonlined autoclave, sealed and heated at 160 °C for 24 h. Finally, the reaction products were dried and sintered in N_2 atmosphere at 600 °C for 5 h. Before electrode preparation, $Zn_3V_3O_8$ and graphite with weight ratio of 1:1 were manually rubbed for 30 min.

2.2. Structural, componential and morphological characterization

The structure and morphology of the products were characterized by X-Ray powder diffraction (Rigaku Ultima IV Cu $K\alpha$ radiation $\lambda = 1.5406 \text{ \AA}$), X-Ray Photoelectron spectroscopy (XPS, Escalab MKII, Mg $K\alpha$ $h\nu = 1253.6 \text{ eV}$), field-emission scanning electron microscopy (FE-SEM JSM 7500F, JEOL), and transmission electron microscopy (JEOL, JEM-2100F).

2.3. Electrochemical characterization

To prepare the anode electrode, $Zn_3V_3O_8/G$ (80 wt%), acetylene black (10 wt%), and polyvinylidene fluoride (PVDF, 0.02 $g\ ml^{-1}$, 10 wt%) were mixed and coated on copper foil and cut into disc electrodes with a diameter of 14 mm. Coin-type cells (2025) with a structure of Li/membrane/anode electrode were assembled in an argon-filled glove box (Mbraun, Unilab, German). The electrolyte is composed of 1 M $LiPF_6$ dissolved in ethylene carbonate (EC), dimethyl carbonate (DMC) with volume ratio 1:1. The membrane is Celgard 2400 microporous polypropylene. The cells were tested in voltage region 0.02–3 V with a multichannel battery test system (LAND CT2001A). When calculating the specific capacity of an electrode, the weight of both $Zn_3V_3O_8$ and G was considered. The cyclic voltammetry (CV) measurement was carried out on a CHI660C electrochemical workstation at a scan rate of 0.2 $mV\ s^{-1}$. Electrochemical impedance spectroscopy (EIS) measurement was performed on CHI660C electrochemical workstation under open circuit conditions over a frequency region from 0.01 Hz to 100 kHz. The cells were disassembled and the electrodes were washed via

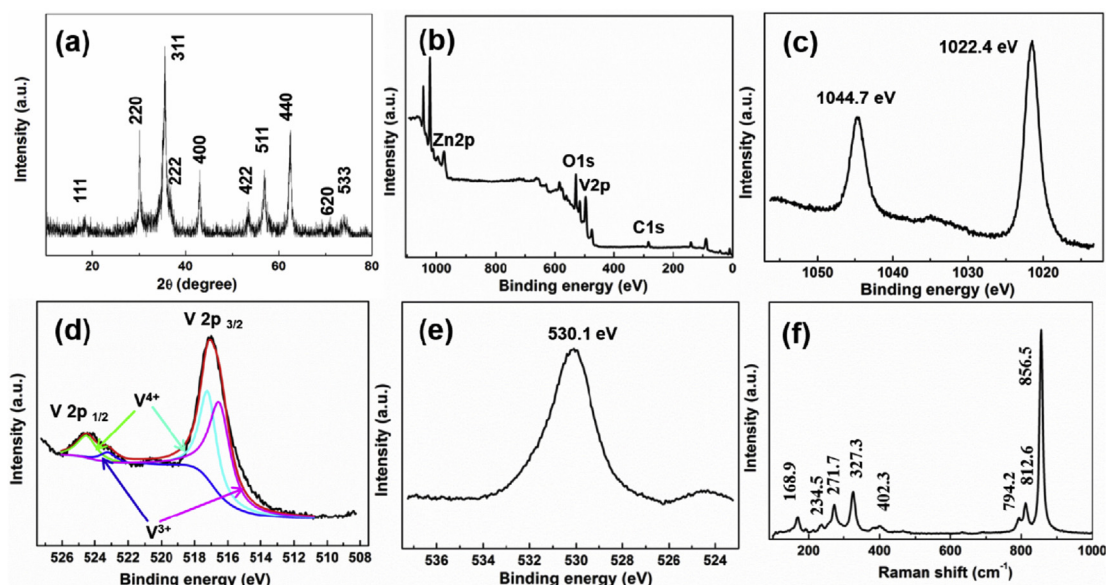


Fig. 2. (a) XRD pattern, (b)–(e) XPS spectra and (f) Raman spectrum of the $Zn_3V_3O_8$. (b) The survey spectrum; High resolution spectrum of (c) Zn 2p, (d) V 2p and (e) O 1s.

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