Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 27(2017) 377−381
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Synthesis and characterization of ε-$VOPO_4$ nanosheets for secondary lithium-ion battery cathode

Ze-hua CHEN[1], Yi-zhu MA[2], Peng-cheng MA[1], Jian-liang CAO[1], Yan WANG[1], Guang SUN[1],
Xiao-dong WANG[1], Hari BALA[1], Chuan-xiang ZHANG[1], Zhan-ying ZHANG[1]

1. College of Chemistry and Chemical Engineering, Henan Polytechnic University, Jiaozuo 454000, China;
2. National Center for Quality National Center for Quality Supervision and Inspection of
Building Decoration Materials, Zhengzhou 450004, China

Received 24 August 2015; accepted 8 December 2015

Abstract: Vanadium (III) phosphate monoclinic $VPO_4 \cdot H_2O$ was synthesized hydrothermally. The ε-$VOPO_4$ nanosheets, formed by the oxidative de-intercalation of protons from monoclinic $VPO_4 \cdot H_2O$, can reversibly react with more than 1 mol lithium atoms in two steps. Crystal XRD analysis revealed that the structure of the ε-$VOPO_4$ nanosheets is monoclinic with lattice parameters of α=7.2588(4) Å, b=6.8633(2) Å and c=7.2667(4) Å. The results show that the ε-$VOPO_4$ nanosheets have a thickness of 200 nm and uniform crystallinity. Electrochemical characterization of the ε-$VOPO_4$ monoclinic nanosheets reveals that they have good electrochemical properties at high current density, and deliver high initial capacity of 230.3 mA·h/g at a current density of 0.09 mA/cm^2. Following the first charge cycle, reversible electrochemical lithium extraction/insertion at current density of 0.6 mA/cm^2 affords a capacity retention rate of 73.6% (2.0−4.3 V window) that is stable for at least 1000 cycles.

Key words: lithium-ion battery; nanosheet; vanadium phosphate; cathode material; synthesis; characterization

---

1 Introduction

During the past decade, the energy shortage and the environment pollution have become serious due to the development of economy and the increase of the population. As a result, the intermittence of the renewable energies such as wind, wave and solar outputs, better energy storage and assistance systems have been the main focuses. However, these renewable energies are dependent on time and season [1]. Undoubtedly, energy storage systems should be developed and used to the reality, which is of vital importance to the social development in the future. Among various storage technologies, the development of battery systems with high energy density as well as long-term cycling stability is a crucial step on the path toward broad implementation of hybrid or electric cars and is a key element for broad adoption of renewable energy technologies [2−4].

Nowadays, lithium-ion batteries have been widely used in many fields as power suppliers for mobile equipment. Most of the present lithium batteries used in electronic devices or hybrid electric vehicles employ transition metal oxides such as $LiCoO_2$, $LiMn_2O_4$ or mixed metal analogs such as Li(Ni,Mn,Co)O_2, olivine $LiFePO_4$ as the active cathode materials [5−8]. The present commercial cathode material, $LiCoO_2$, possesses some problems in large-scale utilization, due to its high cost and low safety [9−11]. The oxide-based materials ($LiCoO_2$, $LiNiO_2$), the spinel $LiMn_2O_4$, and all their substituted variations have been extensively studied as positive electrode materials [12−17]. Vanadium phosphates have been extensively studied because of their importance in selective catalysis of hydrocarbon oxidation reactions. Vanadium phosphates are also attractive due to their higher free energy of reaction, and the greater possible change of oxidation state.

Seven phases of VPO_4 were synthesized and their lithium intercalation properties were investigated as

---

Foundation item: Projects (51172065, 51404097, 51504083, U1404613) supported by the National Natural Science Foundation of China; Project (16A150009) supported by the Key Scientific Research Project for Higher Education of Henan Province, China; Project (16A150009) supported by the Natural Science Foundation of Henan Province (General Program), China; Project (166115) supported by the Postdoctoral Science Foundation of Henan Province, China

Corresponding author: Ze-hua CHEN; Tel: +86-18839155118; E-mail: chen1861@hpu.edu.cn

DOI: 10.1016/S1003-6326(17)60042-6

cathode materials [15,17−19]. Several vanadyl phosphates $VOPO_4$ were investigated as cathode materials [20,21]. Till now, the polymorphs have not satisfactory electrochemical performance, and more efforts are needed to make use of the high operating voltage and reasonable theoretical capacity of $VOPO_4$. The ε-$VOPO_4$ compound has particularly interesting properties, such as an approximately 4 V flat discharge potential, which is about 0.5 V higher than that of $LiFePO_4$, and higher electronic conductivity, leading to the possibility of attaining higher power systems and theoretical energy density compared with $LiFePO_4$ [8]. This material adopts a stable 3D tunneling structure with the theoretical specific capacity of ~168 mA·h/g (α-$LiVOPO_4$). Compared with $LiFePO_4$, ε-$VOPO_4$ has a much higher conductivity (1×10^{-6} S/cm vs 1×10^{-10} S/cm of $LiFePO_4$) [22,23]. Furthermore, similar to $LiFePO_4$, the rate capability of $VOPO_4$ can be improved by decreasing the particle size [19]. For ε-$VOPO_4$, we might intercalate two lithium ions into the structure, which may deliver larger capacity if both lithium ions participate in electrochemistry. Overall, all these advantages make ε-$VOPO_4$ a great candidate for next generation of high energy density lithium-ion batteries. Although various preparation methods have been reported for ε-$VOPO_4$, there is a possibility that ε-$VOPO_4$ with larger capacity and better cycle stability can be obtained by changing the preparation method and crystal structure size. In Ref. [21], we reported the electrochemical behavior of the β-$VOPO_4$/ε-$VOPO_4$ composite and nanostrucutral ε-$VOPO_4$ formed from the monoclinic and tetragonal forms of $VPO_4\cdot H_2O$. In this study, ε-$VOPO_4$ nanosheets were synthesized and their electrochemical performances as the cathode materials were investigated.

2 Experimental

The ε-$VOPO_4$ was prepared using the method as described by SONG et al [24]. The monoclinic $VPO_4\cdot H_2O$ precursor was synthesized in the aqueous solution, the reactants were 16.7 mL standardized H_3PO_4 solution (2.39 mol/L), 1.60 g VCl_3, and 20 mL deionized water, with the pH adjusted by triethylmethylammonium hydroxide (20% in water) to 3 under stirring for 7 d. The monoclinic $VPO_4\cdot H_2O$ precursors were obtained in corresponding solutions in 125 mL PTFE-lined Parr autoclaves at 180 °C for 3 d, then ramp-cooled to room temperature at 0.5 °C/min. The ε-$VOPO_4$ from the monoclinic phase was obtained by heating the precursor in oxygen at 500 °C for 3 h.

The electrochemical properties of these samples were evaluated in 2325-type coin cells. The cathodes were prepared by grinding 80% (mass fraction) active material with 10% (mass fraction) conductive carbon and 10% (mass fraction) PVDF binder in a mortar and pestle. NMP (1-methyl-2-pyrrolidinone, Aldrich) was added to create a paste, which was laminated onto aluminum foil and vacuum dried at 90 °C before use. The electrolyte was 1 mol/L $LiPF_6$ (lithium hexafluorophosphate) dissolved in a solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) (LP30 from EM Industries) with a volume ratio of 1:1; a Celgard 2400 separator (Hoechst Celanese) was used. The coin cells were assembled in a glove box filled with pure helium. A Macpile potentiostat was used to cycle the cells at 0.09 mA/cm^2 between 2 and 4.3 V at room temperature.

3 Results and discussion

The diffraction data were collected for the prepared material over a 12 h period on a Scintag XDS 2000 powder diffractometer using Cu K_α radiation (λ= 1.5418 Å) operating in a θ−θ geometry between 2θ values of 15° and 75° with a step size of 0.02° and a collection time of 8 s per point. The XRD pattern of the prepared material is shown in Fig. 1, which agrees with those previously reported [20,24]. The XRD pattern can be indexed as a monoclinic structure with a space group *Cc*. Rietveld refinement was carried out using GSAS + EXPGUI [25]. Cell parameters were refined to a=7.2588(4) Å; b=6.8633(2) Å; c=7.2667(4) Å; β=115.391(3) Å; V=328.26(2) Å^3 (space group *Cc*). The XRD data revealed that the sample was a single-phase material. The two main diffraction peaks were observed at 26° and 29°. This agreed with our previous report [20].

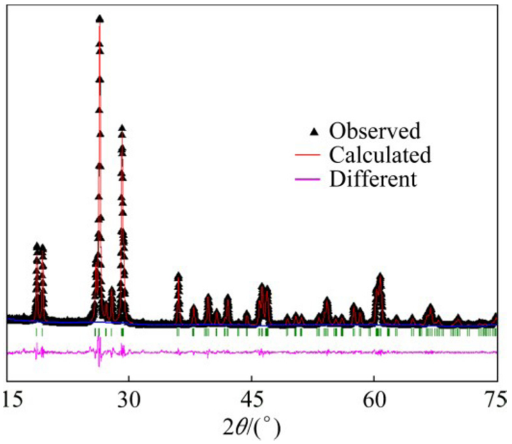

Fig. 1 XRD pattern and Rietveld refinement of ε-$VOPO_4$ nanosheets

The ε-$VOPO_4$ nanosheets have been derived from monoclinic $VPO_4\cdot H_2O$. The crystal structure of ε-$VOPO_4$ consists of corner sharing VO_6 octahedra and PO_4 tetrahedra [26], as shown in Fig. 2. The easy inversion of vanadyl bonds offers a mechanism which allows the $VOPO_4$ host lattice to fine-adjust for the accommodation