

Amorphous FeVO₄ as high-capacity cathode precursor for lithium second battery

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Abstract. Various vanadates have been investigated to accelerate the development of advanced technologies, especially in the area of electronics. Amorphous FeVO₄ was synthesized by the liquid phase precipitation method. This precursor was firstly discharged and then charged as cathode material of lithium second battery, in which the valence of two kinds of metals can be changed. Thermal analysis (TG-DTA), powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) have been used for their characterization. The result revealed the existence of two pairs of redox couples, Fe³⁺/Fe²⁺ and V⁵⁺/V⁴⁺. The electrochemical investigation has shown that at higher potentials amorphous FeVO₄ can react with 1, 1.5 and 2 mol Li, respectively.

Keywords: vanadates, amorphous, lithium second battery.

1. Introduction

Globally, driven by the social and economic progress, the newly sustainable, clean, and high-performance energy storage and conversion devices have been highly required [1]. The civilization has been wrapped by a huge number of smart electronics gadgets, especially built with different types of sensors and communication devices, which need a reliable, portable and durable energy storage device [2]. The main classes of electrochemical energy storages are batteries, fuel cells and electrochemical capacitors etc.

Among a variety of energy storage devices, Lithium ion batteries (LIBs), as a renewable power source, have been considered as one of the most important energy storage devices due to their high energy densities, environmental friendly technology, and long cycle and have occupied vast majority of portable electronics market in the last two decades [3]. To meet the recent demand for minimizing the size of portable electronics and electrifying transportation, it is urgent to develop efficient electrode materials for LIBs having a high reversible lithium (Li) capacity, an excellent rate capability, and cycling stability [4].

In a recent past, acceleration in the development of advanced technologies in the area of electronics, various vanadates have been investigated in many fields of application, which can be used as anode material, luminescence material, photocatalyst for degradation of organic pollutants and so on [5]. Many vanadates materials are vital components from an industrial viewpoint and have been proved to be promising due to their low cost, high chemical stability and excellent electrocatalytic properties [6].

As anode material, when discharged to voltage of lower than 0.2 V, FeVO₄ can uptake 7 Li. M. Hayashibara et al. [7] studied the chemical lithiation characteristics of crystalline FeVO₄. Either amorphous or crystallized FeVO₄ displayed reversible capacities of 900 mAhg⁻¹, however they both displayed poor capacity retention. It is found that at lower potentials crystal structure of FeVO₄ collapsed and Fe was evident [8].

In this paper we wanted to prepare an amorphous precursor. The precursor was firstly discharged and then charged as cathode material of lithium second battery, in which the valence of two kinds of metals can be changed. FeVO₄ as the cathode precursor has seldom been reported. In the range from 3.6 V to 2.0 V vs. Li⁺/Li, the initial discharge capacity of crystalline FeVO₄ was

about 70 mAhg^{-1} [9]. Crystalline FeVO_4 will undergo structural amorphization, so the initially amorphous FeVO_4 cathode is expected to overcome the irreversible structural change and have better capacity retention than crystalline FeVO_4 . On the other hand, if vanadium in $(\text{VO}_4)^{3-}$ polyanion were electrochemically active, there would be more than one lithium intercalation which was favored for high capacity cathode. M. Sugawara used amorphous FeVO_4 as a positive active material and the discharge capacity of the amorphous FeVO_4 maintained over 200 mAhg^{-1} after 50 cycles [10]. They thought the good cycling behavior of amorphous cathode might be attributed to the isotropic, flexible and low-density structures which suppress the deterioration of the cathode during charge-discharge cycles. Herein we prepared amorphous FeVO_4 by the soft chemistry method and investigated the electrochemical properties of the amorphous FeVO_4 at higher potentials.

2. Experimental section

2.1. Preparation

The starting materials were ammonium metavanadate (NH_4VO_3) and iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$). The reaction consisted of mixing the stoichiometric amount of the two solutions and controlling the pH. The precipitate was separated by the centrifugation, washed with water and ethanol and then dried at $50 \text{ }^\circ\text{C}$ overnight. The precursor precipitate was finally calcined at different temperatures for 15 h to get the samples.

2.2. Characterization

Thermal stability was analysed by TG-DTA experiments using a NETZSCH STA 449C apparatus. The precursor precipitate with weight of 12.171 mg was heated in air at a rate of 5 K/min . The power XRD was performed on a RIGAKU D/max-RB diffractometer using $\text{Cu K}\alpha$ radiation. XPS data were obtained using an ESCALab 250 electron spectrometer from Thermo Scientific Corporation with monochromatic $150 \text{ W AlK}\alpha$ radiation. The base pressure was about $6.5 \times 10^{-10} \text{ mbar}$. The binding energies were referenced to the C1s line at 284.8 eV from alkyl or adventitious carbon.

2.3. Electrochemical properties

The electrochemical properties of the FeVO_4 were evaluated by using lithium metal as the anode. A slurry of active material (70wt%) with acetylene black (10wt%) and polyvinylidene fluoride (20wt%) was coated on Al foil to prepare the cathode. One mole LiPF_6 in a 1:1 mixture with ethylene carbonate and dimethyl carbonate was used as the electrolyte.

3. Results and discussion

Fig. 1 shows the TG-DTA curve of the precursor $\text{FeVO}_4 \cdot n\text{H}_2\text{O}$. Five distinct thermal phenomena appear on the DTA curve. The first endothermic peak is located at $97 \text{ }^\circ\text{C}$, corresponding to a 12 % loss of water. There are three exothermic effects appeared at $250 \text{ }^\circ\text{C}$, $331 \text{ }^\circ\text{C}$ and $456 \text{ }^\circ\text{C}$. M. Touboul et al. have investigated the DTA curve of $\text{FeVO}_4 \cdot 3\text{H}_2\text{O}$. Their results showed the exothermal effect between $230 \text{ }^\circ\text{C}$ and $260 \text{ }^\circ\text{C}$ corresponded to the decomposition of NH_4NO_3 . The exothermic phenomena occurred at $330 \text{ }^\circ\text{C}$ and $456 \text{ }^\circ\text{C}$ were attributed to a modification of the amorphous phase and the crystallization of the compound, respectively. And an endothermic peak appeared at $605 \text{ }^\circ\text{C}$, which was different with M. Touboul's work.

Fig. 2 shows the XRD pattern of the compounds annealed at different temperature. The compounds obtained at $50 \text{ }^\circ\text{C}$ and $300 \text{ }^\circ\text{C}$ were both amorphous. The compound annealed at $700 \text{ }^\circ\text{C}$ was crystalline and was identified as the triclinic FeVO_4 (JCPDS 38-1372). We studied

the electrochemical performance of the amorphous FeVO_4 obtained at 300 °C as cathode precursor.

The voltage-capacity curves and cycle behavior of the amorphous FeVO_4 were shown in Fig. 3. As a cathode precursor the amorphous FeVO_4 were first discharged and then charged to 4.2 V. By controlling the depth of discharge (DOD), the lithium uptake was calculated by the discharge capacity. The discharge capacity were settled as 157, 235 and 314 mAhg^{-1} , corresponding to 1, 1.5, 2 lithium uptake, respectively. The first two charge-discharge curves at the current of 10 mA g^{-1} were given in Fig. 3(a), (b) and (c). The slopes of three charge and discharge profiles were slightly steep. And their medium voltage was about 2.7 V, 2.3 V and 2.0 V. The cycle behaviors of the amorphous FeVO_4 were shown in Fig. 3(d), (e) and (f). So the amorphous FeVO_4 can react reversibly with 1, 1.5, 2 lithium ions, resulting in capacities as large as 157 mAhg^{-1} , 235 mAhg^{-1} and 314 mAhg^{-1} , respectively. Although their medium voltage was all below 3 V, the energy density of the amorphous FeVO_4 reached about 424, 540 and 628 Whkg^{-1} , respectively. So the amorphous FeVO_4 could be considered as a potential cathode precursor for lithium second battery.

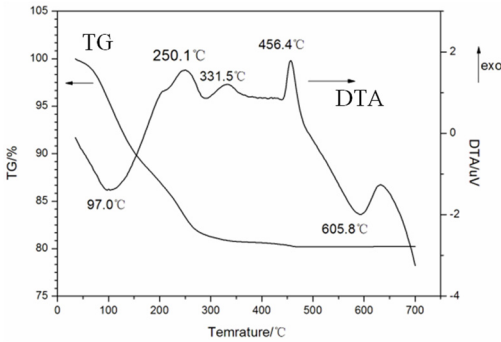


Fig. 1. TG and DTA curves of the precursor $\text{FeVO}_4 \cdot n\text{H}_2\text{O}$

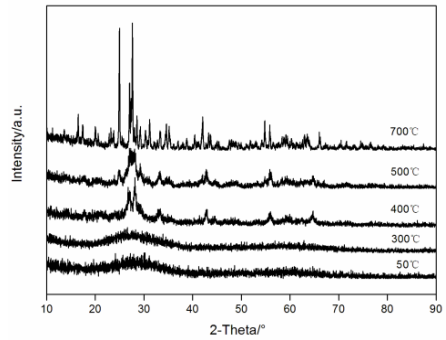
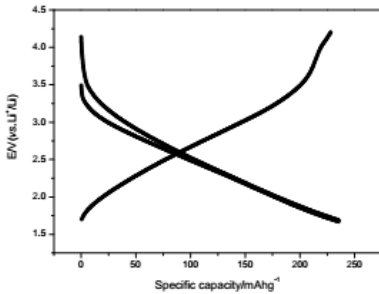
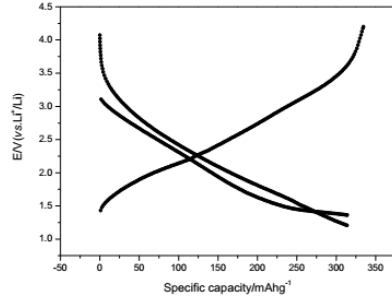


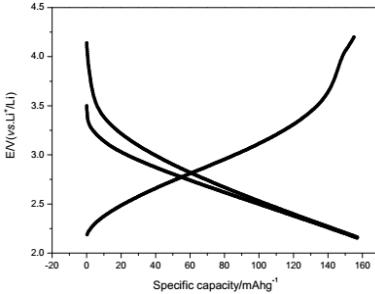
Fig. 2. The XRD pattern of the samples annealed at different temperature



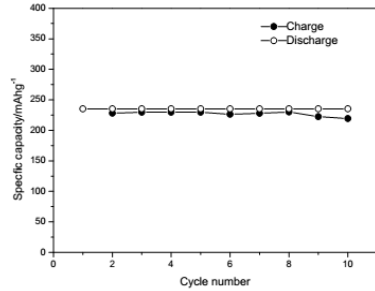
a) Charge/discharge curves for capacity-controlled discharge with 1 lithium embedded



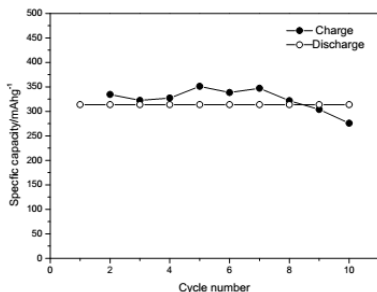
b) Charge/discharge curves for capacity-controlled discharge with 1.5 lithium embedded



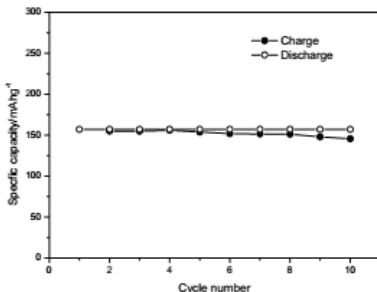
c) Charge/discharge curves for capacity-controlled discharge with 2 lithium embedded



d) Cycling properties of 1 lithium embedded controlled discharge



e) Cycling properties of 1.5 lithium embedded controlled discharge



f) Cycling properties of 2 lithium embedded controlled discharge

Fig. 3. Voltage-capacity profiles and cycle behavior of amorphous FeVO₄

The cyclic voltammetry (CV) curve of amorphous FeVO₄/Li cell in the range of 1.0-4.0 V at a rate of 0.25 mV/s was shown in Fig. 4. During the first cathodic scan (lithium intercalation) the voltammogram showed a broad peak around 2.6 V and an intense peak at 1.1 V. In the first anodic scan (lithium deintercalation) there were two broad peaks around 2.2 V and 3.2 V. In the 10th cycle, the two oxidation peaks (around 2.7 V, 3.4 V) and reduction peaks (around 2.0 V, 3.0 V) became lower and broaden. So the first cycle maybe an activated process. The CV featured two pairs of oxidation-reduction peaks, which was probably associated with both redox couples, Fe³⁺/Fe^x (x=+2, 0) and V⁵⁺/V^y (y=+4, +3).

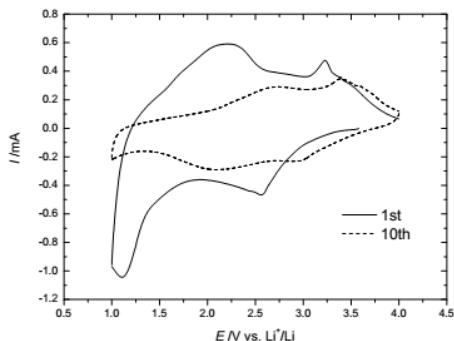


Fig. 4. Cyclic voltammetry of amorphous FeVO₄/Li cell for the 1st and 10th cycle (0.25 mV/s)

To provide evidence supporting our hypothesis about two redox couples, Fe³⁺/Fe^x (x = +2, 0) and V⁵⁺/V^y (y=+4,+3), the XPS investigation was performed. Fig. 5 represented the voltage-composition profiles of amorphous FeVO₄/Li cell in the first cycle. Different Li_xFeVO₄ (x = 0, 1, 2) compositions were labeled from A to E. The start point of the cell is A. Firstly the discharge process was A→B→C. And then the charge process was C→D→E. Fig. 6 showed the Fe 2p and V 2p XPS spectra of different Li_xFeVO₄ compositions during the first discharge-charge cycle. The binding energy fitting parameters and valence of Fe and V were reported in Table 1. The Fe 2p_{3/2} peak at 711.5eV and V 2p_{3/2} peak at 517.5eV could be assigned to Fe³⁺ and V⁵⁺ in the as-prepared amorphous FeVO₄ precursor (sample A). When discharged to uptake 1 Li (sample B), the binding energy of the Fe 2p_{3/2} peak could be fitted to those of Fe³⁺ (711.2eV) and Fe⁰ (705.7eV), the binding energy of the V 2p_{3/2} peak fitting to those of V⁵⁺ (517.1eV). After full discharge to uptake 2 Li (sample C) the valence of Fe and V was 0 (705.7eV) and +4 (516.1eV), respectively. Sample D had too small amount of Fe to have evident Fe 2p peaks and the peak of V 2p_{3/2} could be fitted to those of V⁵⁺ (517.1eV) and V⁴⁺ (516.4eV). After full charge to remove 2 Li (sample E), the peak of Fe 2p_{3/2} changed to the position of Fe²⁺ (710.9eV, 715.2eV). And the peak of V 2p_{3/2} shifted to higher binding energy and could be fitted to those of V⁵⁺ (517.1eV). The result was consistent with the CV feature and demonstrated the existence of both redox couples, Fe³⁺/Fe^x

($x = +2, 0$) and V^{5+}/V^y ($y = +4$), and the details are shown in Table 1.

Table 1. The binding energy fitting parameters and valence of different sample

Sample	Fe $2p_{3/2}$ /eV	Valence of Fe	V $2p_{3/2}$ /eV	Valence of V
A	711.5	+3	517.5	+5
B	711.2, 705.7	+3,0	517.1	+5
C	705.7	0	516.1	+4
D	—	—	517.1, 516.4	+5, +4
E	710.9, 715.2	+2	517.1	+5

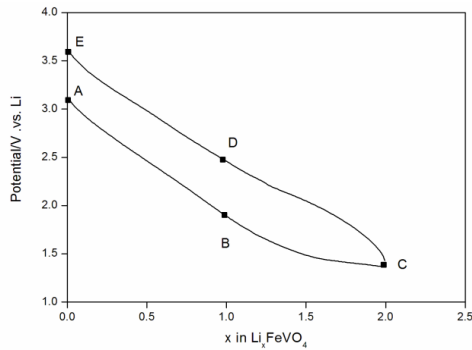


Fig. 5. Discharge-charge profile of amorphous FeVO_4/Li cell. A: discharge initially, B: discharge until 1 lithium is embed, C: discharge until 2 lithium are embed, D: charges until 1 lithium is taken off, E: charges until 2 lithium are taken off

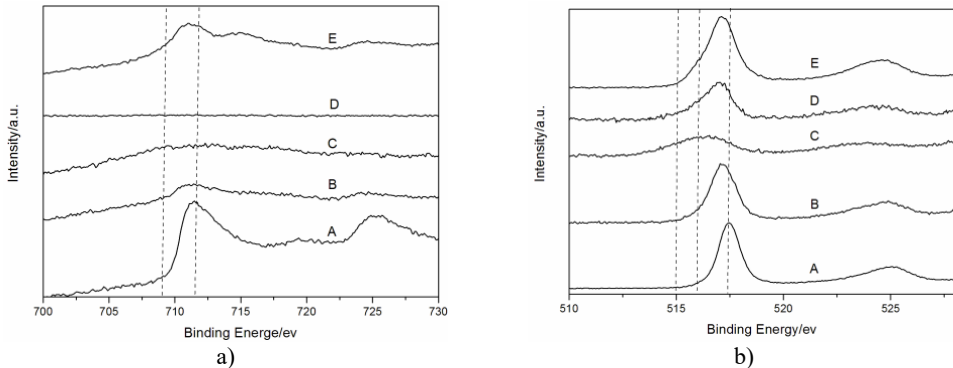


Fig. 6. The XPS spectra of different Li_xFeVO_4 compositions: a) Fe 2p and b) V 2p

4. Conclusions

In this paper we focus on the reverse lithium embedding of ferovanadate and try to verify whether double valence transformation occurs during the reaction of ferovanadate with lithium. The chemical composition of the amorphous form was first confirmed by precipitating the amorphous form by the liquid phase method. Charge and discharge experiments demonstrated that amorphous ferovanadate can react with 1, 1.5 and 2 lithium at higher potentials with discharge capacities of 157, 235 and 314 mAh g^{-1} , respectively, and can remain largely stable after 10 weeks of cycling. The capacity and energy density of the amorphous FeVO_4/Li cell can reach 314 mAhg^{-1} and 618 WhKg^{-1} , respectively. The existence of two pairs of redox couples in amorphous FeVO_4 , $\text{Fe}^{3+}/\text{Fe}^x$ ($x = +2, 0$) and V^{5+}/V^y ($y = +4$), was demonstrated by CV and XPS measurement. Therefore, the amorphous FeVO_4 could be considered as potential cathode precursor for lithium second battery.

Acknowledgements

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