

Short communication

Synthesis and electrochemical properties of $\text{LiY}_{0.1}\text{V}_3\text{O}_8$

C.Q. Feng^{a,b}, L.F. Huang^a, Z.P. Guo^{b,c,*}, J.Z. Wang^{b,c}, H.K. Liu^{b,c}

^a Faculty of Chemistry and Material Sciences, Hubei University, Wuhan 430062, China

^b Institute for Superconducting and Electronic Materials, University of Wollongong, NSW 2522, Australia

^c ARC Centre of Excellence for Electromaterials Science, University of Wollongong, NSW 2522, Australia

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Abstract

$\text{LiY}_{0.1}\text{V}_3\text{O}_8$ compound was successfully prepared by using a simple, rapid and easily scaled up method, i.e. the rheological phase reaction method. The microstructural characteristics of $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ materials were examined by X-ray diffraction and scanning electron microscopy (SEM). Compared with LiV_3O_8 compound, the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ shows expanded crystal lattices, and the expansion is more significant along the *c*-axis. The electrochemical properties of the as-synthesized $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ compounds were investigated. It was found that the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ electrodes exhibited better reversibility and higher capacities than LiV_3O_8 electrodes. The reasons for the improved electrochemical performance of the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ electrodes are also discussed.

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1. Introduction

LiV_3O_8 has been extensively studied because of its possible application as a cathode material in rechargeable lithium batteries, due to its attractive electrochemical properties, such as high specific energy and good cycle stability as lithium ion battery cathode [1–4]. This compound was traditionally prepared by a high temperature solid-state reaction method, in which Li_2CO_3 reacted with V_2O_5 at 650–680 °C [4,5]. At such high reaction temperatures, the lithium source would evaporate, so accurate element ratios were difficult to control. Another defect of this synthetic method is that the LiV_3O_8 product showed low capacity as a cathode, such as 180 mAh g^{-1} in the range of 1.8–4.0 V. Many improved methods have been proposed, but liquid reaction was one of the methods that attracted our interest [6–9]. The liquid reaction method did not need a high reaction temperature, and the expected product could deliver higher capacity as a cathode. However, these liquid reaction synthesis methods need a long reaction time and some additional processes, such as application of the sol–gel process, stirring and heating. It takes a long time for these liquid reactions to synthesize the expected

compounds. In addition, the cycling stability of cathodes made from as-prepared materials was not good. These prevented its application in lithium ion batteries.

This paper reports on $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ compounds prepared by a new synthetic method (the rheological phase reaction method) and contains the first investigation of the electrochemical properties of the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$. The results provide both a theoretical basis and an experimental foundation for application of this kind of compound as lithium ion battery cathode material.

2. Experimental

2.1. Synthesis and characterization of $\text{LiY}_{0.1}\text{V}_3\text{O}_8$

The starting materials were analytically pure LiOH , V_2O_5 , Y_2O_3 and citric acid. The LiOH , Y_2O_3 , V_2O_5 and citric acid were mechanically mixed in the molar ratio of 1:0.05:1.5:4.8 in an agate mortar. After the mixture was ground homogeneously, an appropriate amount of water was added to the powder to obtain a rheological phase state mixture. The mixture was then heated at 90 °C for 12 h, and a gray-green precursor was obtained. After that, the precursor was sintered at 480 °C for 12 h to form the expected product. LiV_3O_8 particles were synthesized by the same method but in the absence of Y_2O_3 .

The precursor was tested by thermogravimetric analysis (TGA) to discover its pattern of decomposition. TGA profiles

* Corresponding author at: Institute for Superconducting and Electronic Materials, University of Wollongong, NSW 2522, Australia. Tel.: +61 2 4221 5727; fax: +61 2 4221 5731.

E-mail address: zguo@uow.edu.au (Z.P. Guo).

were measured on a Pekin TGA-7 instrument with a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$ in air atmosphere. The structure of the expected products was examined by X-ray diffractometry (XRD) with the X-ray diffraction carried out on a Philips 1730 diffractometer with Cu $K\alpha$ radiation. The morphology of the samples was observed using a JEOL JSM 6460A scanning electron microscope (SEM).

2.2. Electrochemical measurements

Electrochemical measurements of the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ and the LiV_3O_8 were accomplished by assembling CR2032 coin cells. The cathode was prepared by mixing active materials with 10 wt% carbon black and 5 wt% PVDF (polyvinylidene fluoride) solution. The active materials and carbon black powders were first added to a solution of PVDF in *N*-methyl-2-pyrrolidinone (NMP) to make a slurry with appropriate viscosity. The slurry was then spread on aluminum foil to form the electrode. After the electrode was dried at $100\text{ }^{\circ}\text{C}$ for 2 h in vacuum, it was compressed at a rate of about 150 kg cm^{-2} . Coin cells were assembled in an argon filled glove box, where the counter electrode was Li metal and the electrolyte was 1 M LiPF_6 dissolved in a 50/50 vol% mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). These cells were cycled between 1.5 and 3.85 V at a constant current density of 40 mA g^{-1} at room temperature to measure the electrochemical response.

3. Results and discussion

3.1. The formation process of $\text{LiY}_{0.1}\text{V}_3\text{O}_8$

A gray-green powder precursor was obtained after heating the rheological phase state mixture at $90\text{ }^{\circ}\text{C}$ for 12 h. According to Tsaramyrsi's report [10], V_2O_5 could act as an oxidant in an acidic system and combine with citric acid to form a $[(\text{VO}_2)\text{C}_6\text{H}_7\text{O}_7]^{2-}$ complex.

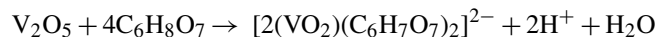


Fig. 1 shows the TGA curve of the precursor. It can be seen that the weight loss process can be divided into three stages. The first weight loss begins at room temperature and ends at $180\text{ }^{\circ}\text{C}$ with a weight loss of 15%, which mainly corresponds to the loss

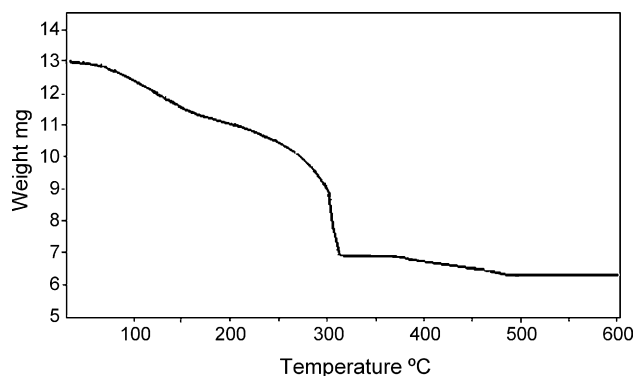


Fig. 1. TGA curve of the precursor powders.

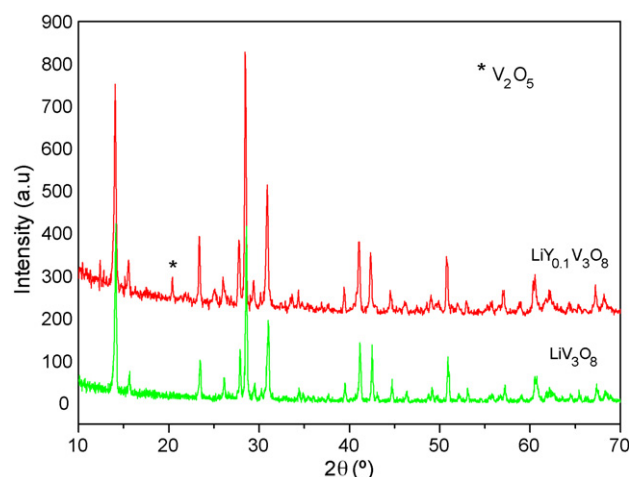


Fig. 2. XRD patterns of the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ and LiV_3O_8 compounds.

of water and the excess of free citric acid which has not combined with V_2O_5 . The second weight loss occurs in the temperature range of $180\text{--}325\text{ }^{\circ}\text{C}$ and is attributed to the decomposition of the complexes into intermediates, which is associated with a weight loss of 34.6%. The third weight loss happens in the temperature range of $325\text{--}480\text{ }^{\circ}\text{C}$ and is caused by the full decomposition of the intermediates and the formation of $\text{LiY}_{0.1}\text{V}_3\text{O}_8$. The weight loss stops at $480\text{ }^{\circ}\text{C}$, and weight remains stable up to $600\text{ }^{\circ}\text{C}$, indicating that the expected compound could be obtained by heating the precursor at $480\text{ }^{\circ}\text{C}$.

3.2. Crystal structure of $\text{LiY}_{0.1}\text{V}_3\text{O}_8$

Fig. 2 shows the X-ray patterns of $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ synthesized at $480\text{ }^{\circ}\text{C}$ for 12 h. The X-ray pattern of undoped LiV_3O_8 is also presented in Fig. 2 for comparison. All XRD peaks except for the marked peaks (attributed to the small amount of V_2O_5) correspond to the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ monoclinic structure with the space group $\text{P}2_1\text{m}^{-1}$. The lattice parameters of the materials were calculated from the XRD data. Compared with the LiV_3O_8 compound ($a = 0.6524\text{ nm}$, $b = 0.3715\text{ nm}$, $c = 1.1766\text{ nm}$), the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ shows an expanded crystal lattice ($a = 0.6552\text{ nm}$, $b = 0.3719\text{ nm}$, $c = 1.1825\text{ nm}$), and the expansion is more significant along the c -axis. The basic structure of LiV_3O_8 consists of VO_6 octahedrons and VO_5 trigonal bipyramids, with the lithium ions arranged between octahedral sites [11]. For the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ compound, the Y ions may also occupy the interlayer sites. Since the diameter of Y ions is much larger than that of Li ions, the interlayer distance undergoes an expansion with Y doping. This leads to a much easier lithium ions intercalation/detercalation process during the charge/discharge cycles, therefore, a much better electrochemical performance for the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ cathodes could be expected (as shown below).

SEM micrographs of the as-prepared LiV_3O_8 and $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ at $480\text{ }^{\circ}\text{C}$ are shown in Fig. 3. It can be seen that the LiV_3O_8 sample exhibits big crystals that are composed of some thin nanosheets, while the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ sample presents disordered and bar-like particles with a wide range of particle sizes. The largest one had its longest side as long as $5\text{ }\mu\text{m}$, and

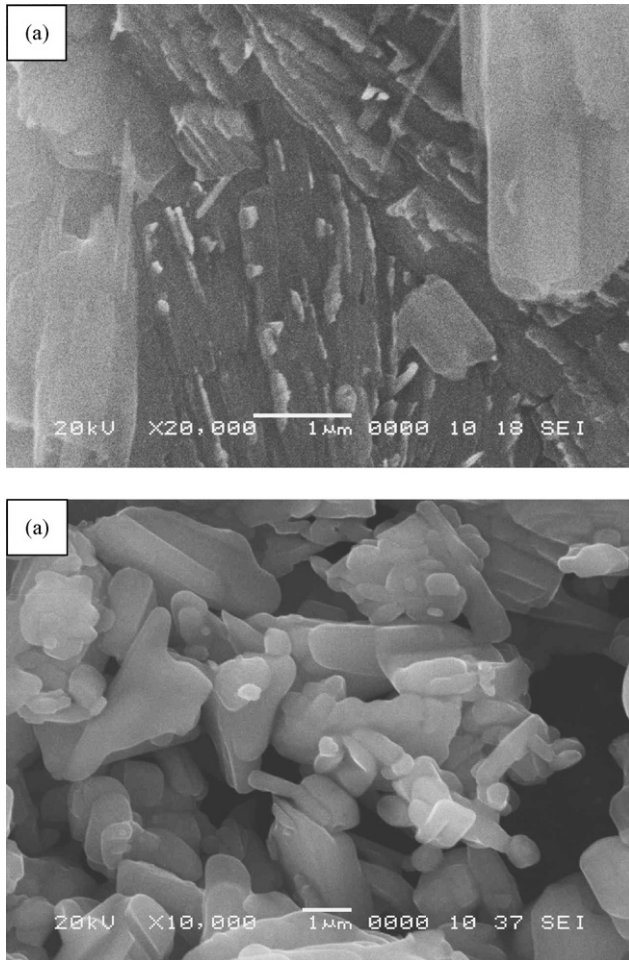


Fig. 3. SEM images of as-prepared (a) LiV_3O_8 and (b) $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ powders.

the smallest one had a longest side of less than $0.3 \mu\text{m}$. The different morphology of the crystals formed may be due to the ponderomotive forces that act at the interfaces and cavities to bring about a rapid growth of the grains and a systematic elimination of porosity [12]. During the formation of the layered metal oxides, the ponderomotive effect was responsible for the rapid growth along the layers. With Y doping, the growth along the layers may be disturbed to some extent, therefore, in contrast to the formation of the superposition structure of nanosheets, bar-like particles with smaller particle sizes were developed for the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ sample.

3.3. Electrochemical characterization of the as-prepared $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ compound

To get a rough estimation of the electrochemical behavior of the compounds, cyclic voltammetric experiments were initially conducted at a scan rate of 0.1 mV s^{-1} . Cyclic voltammograms of $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ and LiV_3O_8 electrodes in lithium ion cells, in which lithium foil was used as the counter electrode and reference electrode, are shown in Fig. 4. There are a few pairs of cathodic/anodic peaks with two main pairs that can be observed. These peaks originate from the phase transitions between $\text{Li}_{1+x}\text{Y}_{0.1}\text{V}_3\text{O}_8$ with different x values ($0 < x < 4$).

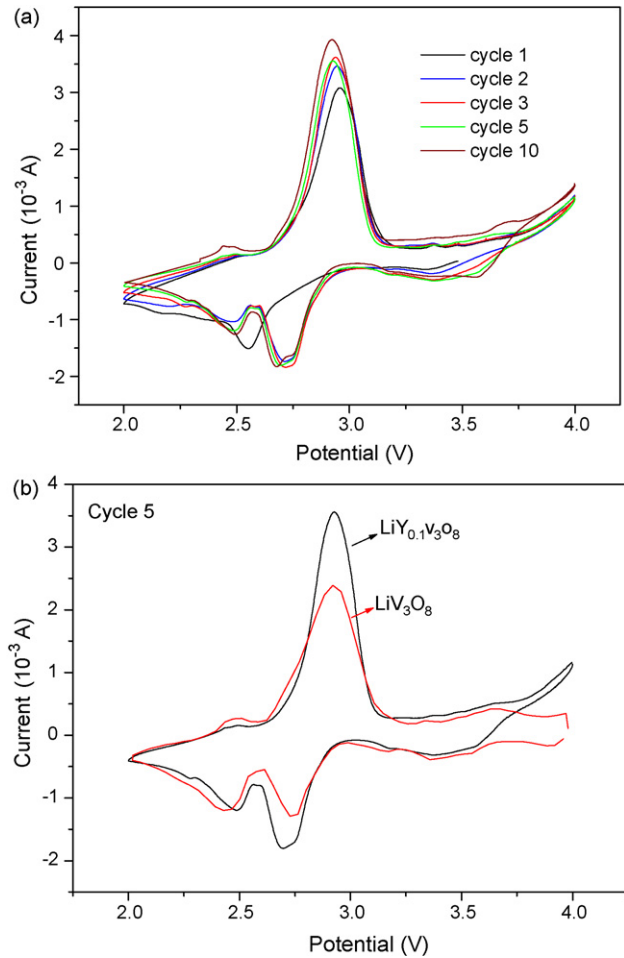


Fig. 4. Cyclic voltammograms of (a) the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ and (b) $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ and LiV_3O_8 electrodes for cycle 5.

Fig. 4(a) shows the CV curves of $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ cathode. It can be seen that the intensity of peaks increases with cycling, indicating good cycling stability of the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ cathode. Fig. 4(b) compares the 5th CV curve of $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ cathode with that of LiV_3O_8 electrode. The profiles of CV curves for both electrodes are similar. The peak intensity for $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ electrode is much higher than for LiV_3O_8 electrode, suggesting higher capacity and faster kinetics for Li^+ intercalation/deintercalation in the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ electrode.

Fig. 5 compares the charge/discharge curves of the 2nd, the 5th and the 10th cycles for the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ and LiV_3O_8 electrodes. Cells were charged/discharged at a current rate of 40 mA g^{-1} . There are several plateaus in the voltage profiles for the lithium intercalation and deintercalation of $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ electrode (Fig. 5(a)), which are quite similar to those of the LiV_3O_8 electrodes (Fig. 5(b)). These voltage plateaus correspond to the cathodic/anodic peaks in the CV curves.

The corresponding charge/discharge capacities as a function of cycle number are shown in Fig. 6. It was found that the capacities of $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ electrode are higher than those of LiV_3O_8 electrode, and the capacity retention at room temperature is higher (0.48% capacity loss/cycle) for $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ electrode compared to LiV_3O_8 electrode (1.46% capacity loss/cycle). The

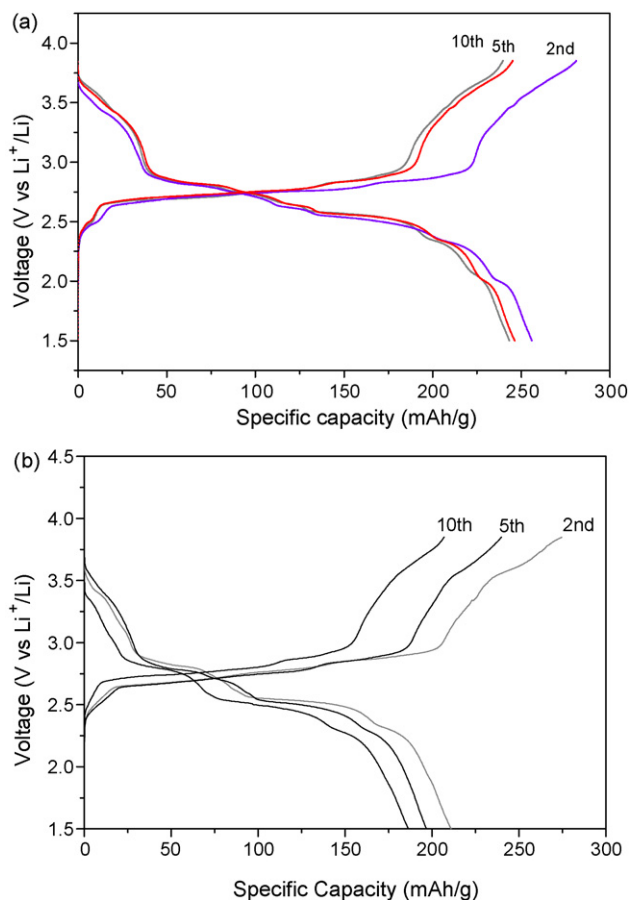


Fig. 5. The 2nd, 5th and 10th charge/discharge curves of (a) the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ and (b) the LiV_3O_8 cathodes.

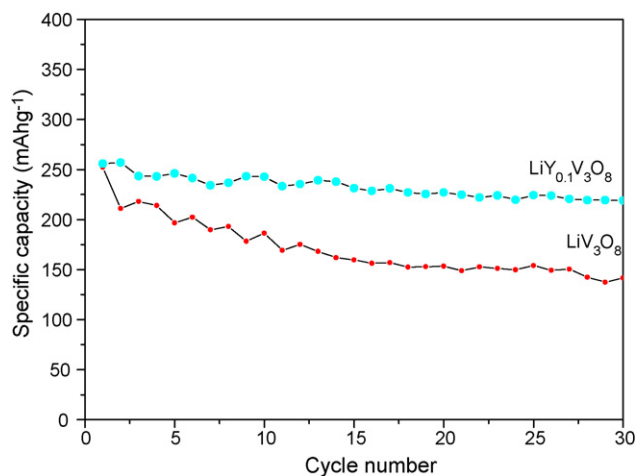


Fig. 6. Capacity as a function of cycle number for the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ and LiV_3O_8 electrodes.

discharge capacity for $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ electrode after 30 cycles is 85.5% of the first discharge capacity, while the capacity retention

for LiV_3O_8 electrode is only 55.9% after 30 charge/discharge cycles.

The possible reasons for the enhanced electrochemical character of the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ electrodes may be: (1) the doped Y ions occupy the interlayer sites between V_3O_8^- layers, leading to an increase in the interlayer distance as the diameter of the Y ions is much larger than that of the Li ions. This may result in a much easier lithium ion intercalation/detercalation process in $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ electrodes during the charge/discharge cycles, and thus a much better electrochemical performance for the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ cathodes could be achieved; (2) Y doping leads to morphology change of $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ samples compared to the bare LiV_3O_8 materials, this may induce an increase in reactive surface area of materials, thus improve the specific capacity of the electrodes.

4. Conclusions

In this study, a novel method (the rheological reaction method) was employed to synthesize $\text{LiY}_{0.1}\text{V}_3\text{O}_8$. Electrochemical measurements showed that the as-prepared $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ electrodes could be charged and discharged reversibly with a higher capacity and superior cycling reversibility than LiV_3O_8 electrodes. The lattice parameters and morphology change caused by Y doping, facilitate lithium ion intercalation/detercalation in the $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ electrodes, thus improve the electrochemical reactivity of the electrodes. Therefore, the as-prepared $\text{LiY}_{0.1}\text{V}_3\text{O}_8$ compound is a promising cathode material for application in rechargeable lithium ion batteries.

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