

The synthesis and electrochemical performance of LiV_3O_8 cathode with Lanthanum-doped

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Abstract. $\text{Li}_{1-x}\text{La}_x\text{V}_3\text{O}_8$ cathode materials has been synthesized by pechini sol-gel method. The electrochemical performances of $\text{Li}_{1-x}\text{La}_x\text{V}_3\text{O}_8$ ($x=0-0.05$) have been studied by X-ray diffraction (XRD), galvanostatic charge-discharge, and cyclic voltammetric (CV). The results showed that the optimal content of the La^{3+} doping in LiV_3O_8 was $x=0.01$, and the first discharge capacity of $\text{Li}_{0.99}\text{La}_{0.01}\text{V}_3\text{O}_8$ sample in the voltage range of 2.0-4.0V was 230mAhg^{-1} , which was much higher than that of LiV_3O_8 (200mAhg^{-1}). The $\text{Li}_{0.99}\text{La}_{0.01}\text{V}_3\text{O}_8$ cathode also showed higher discharge voltage plateau than LiV_3O_8 cathode from the CV curves.

Introduction

Layered trivanadate, LiV_3O_8 , has been widely studied as a cathode materials for lithium-ion batteries because of its attractive characteristics, such as high specific capacity, facile preparation, good rate capacity and low cost^[1-4]. However, for the successful application of LiV_3O_8 as a cathode in lithium ion batteries, the discharge capacity and cycle stability of LiV_3O_8 remain awaiting to be increased. Doping had been studied widely as an effective way to improve electrochemical performances of electrode materials for Li-ion battery. In spite of a number of experiments have been done on doped LiV_3O_8 , the results were far from being satisfactory^[5]. It is of great significance to look for proper doping elements and methods in order to improve electrochemical performance of LiV_3O_8 .

The radius of La^{3+} is 1.06 pm, by La^{3+} doping, La^{3+} may substitute Li^+ ion or V^{5+} which occupies the interlayer site of LiV_3O_8 structure. The interlayer distance will undergo an expansion with La doping, leading to a much easier lithium ion intercalation/deintercalation. The discharge capacity and cycle stability of LiV_3O_8 cathode will be expected to be enhanced by La doping.

In this paper, $\text{Li}_{1-x}\text{La}_x\text{V}_3\text{O}_8$ materials was synthesized by pechini sol-gel method of NH_4VO_3 , Li_2CO_3 , $\text{C}_6\text{H}_8\text{O}_6$ and PEG-2000. X-ray diffraction, scanning electron microscope, galvanostatic charge-discharge cycle test and cyclic voltammetry analysis are employed to investigate the structures and electrochemical performances of $\text{Li}_{1-x}\text{La}_x\text{V}_3\text{O}_8$ materials.

Experimental

All of the reagents were analytical grade and were used without further purification. Li_2CO_3 , $\text{La}(\text{NO}_3)_3$, NH_4VO_3 , $\text{C}_6\text{H}_8\text{O}_6$ and PEG-2000 were used as starting materials, they were dissolved in deionized water and mixed together under magnetic stirred in a molar ratio of Li: La: V: $\text{C}_6\text{H}_8\text{O}_6$: PEG= 1-x: x: 3: 3: 0.1 ($x=0, 0.01, 0.02, 0.05$). The solution was dried in air at 70°C until a black xerogel was obtained. Afterwards, the xerogel was calcined at 450°C in a muffle furnace oven for 10h to obtain the samples.

The phase composition and structures of the synthesized compounds were investigated by means of powder X-ray diffractometer (XRD-7000) using Cu K α radiation ($\lambda=0.15418$ nm) in the range of 10–70°.

Electrochemical experiments were carried out using a coin battery cell. A metallic lithium foil served as the anode electrode. The cathode electrode was fabricated by blending the $\text{Li}_{1-x}\text{La}_x\text{V}_3\text{O}_8$ active material (80 wt.%) with acetylene black (10 wt.%) and polyvinylidene fluoride (PVDF, 10 wt.%). The slurry was pasted on an Al foil and then dried in vacuum oven. The electrolyte was 1 mol·L⁻¹ LiPF₆ dissolved in EC and DMC (EC: DMC = 1:1, by v/v ratio). Galvanostatic charge-discharge cycling was performed on a Land-2001A battery tester (Wuhan, China). Cyclic voltammetry (CV) was collected between 4.0V and 2.0V on a ZAHNER®-IM6e electrochemical workstation using a sweeping rate of 100 μVs^{-1} .

Result and Discussion

Fig. 1 shows the X-ray diffraction patterns of the results materials of $\text{Li}_{1-x}\text{La}_x\text{V}_3\text{O}_8$ ($x=0, 0.01, 0.02, 0.05$). All samples have strong and sharp diffraction peaks and can be indexed into monoclinic LiV_3O_8 with space group of P21/m (JCPDS #72-1193). No peaks from other phase have been detected until the content of $\text{La}^{3+} \geq 0.02$, indicating the largest content of the La^{3+} doping in LiV_3O_8 is $x=0.01$. With the doping levels increased further, the intensities of diffraction peaks of LaVO_4 and some impurities enlarged gradually. The radiuses of La^{3+} is much larger than that of the sixth coordinate V^{5+} in the layered LiV_3O_8 which led to it difficult to form a complete isomorphous solid solution of $\text{Li}_{1-x}\text{La}_x\text{V}_3\text{O}_8$.

The lattice parameters, volume and crystal size of the unit cell were calculated and summarized in Table 1. When the La^{3+} doping increased to 0.01, the value of lattice parameters, volume and the crystal size were all enlarged. The expansion of the lattice crystal could provide more lattice space for lithium intercalation and deintercalation. During the deintercalation process, the lattice would be also prevented from shrinking by the doped La^{3+} due to the large volume of the crystals. When the doping amount was larger than 0.02, the structure of the formed LiV_3O_8 has been different, thus, the unfavourable results appeared.

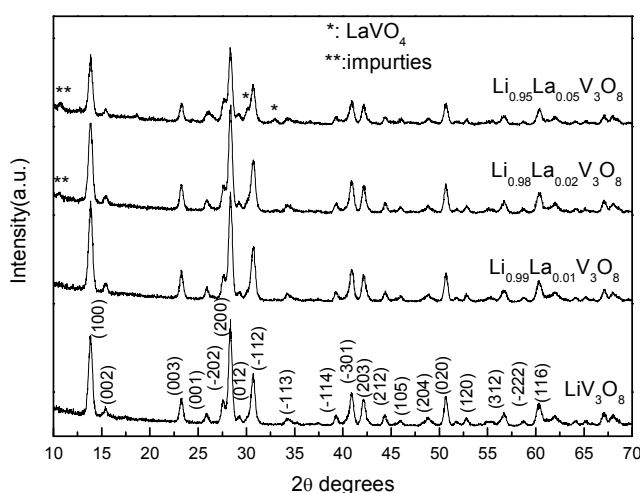


Fig. 1 X-ray diffraction patterns of $\text{Li}_{1-x}\text{La}_x\text{V}_3\text{O}_8$ ($x=0, 0.01, 0.02, 0.05$) by pechini sol-gel technique at 450°C

Table 1 Lattice parameters, unit cell volume and crystal size of $\text{Li}_{1-x}\text{La}_x\text{V}_3\text{O}_8$ ($x=0, 0.01, 0.02, 0.05$) cathode materials

compounds	a/Å	b/Å	c/Å	V/nm ³	Xs/Å
LiV_3O_8	6.66	3.60	12.03	275.49	182
$\text{Li}_{0.99}\text{La}_{0.01}\text{V}_3\text{O}_8$	6.67	3.60	12.05	275.63	183
$\text{Li}_{0.98}\text{La}_{0.02}\text{V}_3\text{O}_8$	6.67	3.60	12.02	275.56	181
$\text{Li}_{0.95}\text{La}_{0.05}\text{V}_3\text{O}_8$	6.67	3.60	12.03	274.70	180

Fig. 2(a) indicates initial discharge curves of $\text{Li}_{1-x}\text{La}_x\text{V}_3\text{O}_8$ ($x=0, 0.01, 0.02, 0.05$) cathode materials with a current density of about 28mA g^{-1} ($C/10$) in the voltage range of 2.0-4.0V. As shown in Fig.2, the discharge capacity of $\text{Li}_{0.99}\text{La}_{0.01}\text{V}_3\text{O}_8$ sample (230mAh g^{-1}) is much higher than that of LiV_3O_8 (200mAh g^{-1}), which is well consistent with the previous XRD analysis. It is also found that the discharge capacity gradually decreases with increasing amount of La and the observed values are 185mAh g^{-1} and 175mAh g^{-1} . This may be due to the formation of increasing quantities of the other phases (LaVO_4 and some impurities) with increasing La content in the composites, which effectively reduces the amount of active LiV_3O_8 and results in a decrease in the discharge capacity.

Fig. 2(b) shows the electrochemical cycling performance of $\text{Li}_{1-x}\text{La}_x\text{V}_3\text{O}_8$ ($x=0, 0.01, 0.02, 0.05$) cathode materials. After 10 cycles, the discharge capacities of $\text{Li}_{0.99}\text{La}_{0.01}\text{V}_3\text{O}_8$ were 160mAh g^{-1} corresponding to a capacity retention of about 70%, which was higher than that of LiV_3O_8 (~64%). It is interesting to note that although the capacity of $\text{Li}_{0.95}\text{La}_{0.05}\text{V}_3\text{O}_8$ is only 175mAh g^{-1} in the first cycle, it retains 95% of the capacity after 10 cycles (167mAh g^{-1}). The observed remarkable capacity retention for La doped LiV_3O_8 might be due to the LaVO_4 samples appeared prevented the Li^+ ions deintercalation from the structure and enhanced the stabilization of the layered structure of LiV_3O_8 .

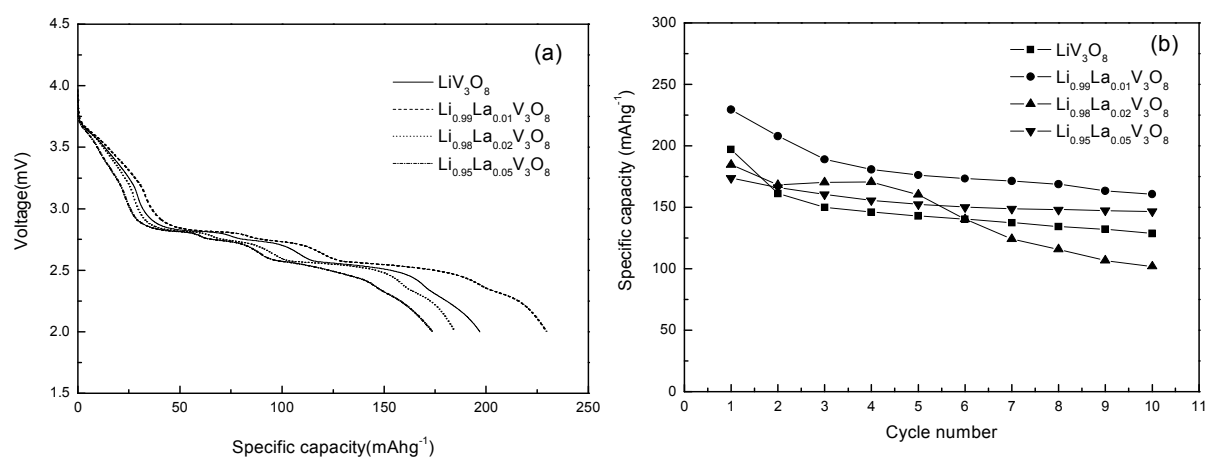


Fig. 2 (a) First discharge curves of samples synthesized at different content of La^{3+} in LiV_3O_8 .
(b) Variation of discharge capacity with cycle number of samples.

In Fig.3, cyclic voltammetric experiments were carried out to further understand the electrochemical behavior of $\text{Li}_{0.99}\text{La}_{0.01}\text{V}_3\text{O}_8$ and LiV_3O_8 at a sweeping rate of $100\ \mu\text{Vs}^{-1}$ in the potential range from 4.0 to 2.0V. There are three main oxidation peaks at 2.80V, 2.73V and 2.54V, and two main reduction peaks at 2.83V and 2.75V in the curve for LiV_3O_8 sample, which are ascribed to lithium intercalation/ deintercalation processes. It can be observed that, from the curve for $\text{Li}_{0.99}\text{La}_{0.01}\text{V}_3\text{O}_8$ samples, the $\text{Li}_{0.99}\text{La}_{0.01}\text{V}_3\text{O}_8$ cathode shows higher discharge voltage plateau (2.85V and 2.80V) than LiV_3O_8 cathode, indicating its better performance as cathode material in lithium ion batteries.

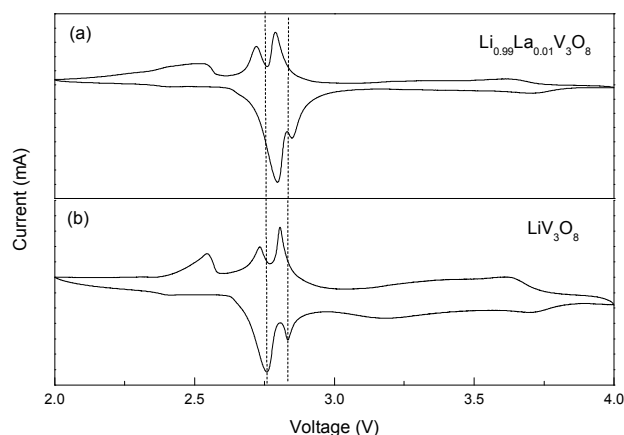


Fig. 3 The CV curves of (a) $\text{Li}_{0.99}\text{La}_{0.01}\text{V}_3\text{O}_8$ and LiV_3O_8 samples at a scan rate of $100\mu\text{Vs}^{-1}$ in the potential range from 2.0 to 4.0V.

Summary

In summary, the different content of La^{3+} was doped into LiV_3O_8 by a pechini sol-gel method. The as-prepared materials were well characterized. The $\text{Li}_{0.99}\text{La}_{0.01}\text{V}_3\text{O}_8$ cathode shows higher discharge capacity and higher voltage plateau than these of LiV_3O_8 . The reason for the good electrochemical performance is that the La^{3+} expands the lattice crystal and provide more lattice space for lithium intercalation and deintercalation.

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