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# Influence of $Y^{3+}$ doping on structure and electrochemical performance of layered $Li_{1.05}V_3O_8$

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**Abstract:** $LiOH·H_2O$, $V_2O_5$ and $Y(NO_3)_3$ were used as raw materials to synthesize the precursors containing Li, V and Y by liquid-state reaction, then the cathode materials $Li_{1.05}Y_xV_{3-x}O_8$ ($x$=0, 0.002 5, 0.005, 0.01, 0.02, 0.1, 0.2) for lithium-ion battery were obtained by calcining the precursors. The influence of $Y^{3+}$ doping on structure, conductivity and electrochemical performance of $Li_{1.05}V_3O_8$ were investigated by using XRD, cyclic voltammograms, AC impedance, etc. The results show that $Li_{1.05}Y_xV_{3-x}O_8$ with different doping amounts have well-developed crystal structure of layered $Li_{1.05}V_3O_8$ and lengthened interlayer distance of (100) crystal plane. $Y^{3+}$ can insert into crystal lattice completely when the doping amount is small and the impurity phase of $YVO_4$ is found when $x \geqslant 0.1$. There is no change in the process of $Li^+$ insertion-deinsertion with $Y^{3+}$ doping. The conductivity is clearly improved due to small amount of $Y^{3+}$ doping and it tends to increase first and then decrease with increasing doping amount. The initial discharge capacity and plateau potential are both enhanced with proper amount of $Y^{3+}$ doping. When $x$ is 0.005, the first specific discharge capacity reaches 288.9 mA·h/g, 4.60 % larger than that of undoped sample (276.2 mA·h/g). When $x \leqslant 0.1$, the average discharge plateau potentials are enhanced by about 0.15 V, which makes for higher energy density.

**Key words:** lithium-ion battery; cathode material; $Li_{1.05}Y_xV_{3-x}O_8$; doping; cyclic voltammogram; conductivity

## 1 Introduction

$Li_{1+x}V_3O_8$, as a promising cathode material for lithium-ion battery, was researched popularly for it has advantages such as low cost, high specific capacity, long cycle life and stability in air[1−3]. At present, its multi-plateau, low discharge voltage and unideal general electrochemical performance are the main problems which can't meet practical use. People have done a lot of work on improving synthesis method and optimizing techniques[4−7]. But studies on doping are relatively less and the results are not satisfactory. An early investigation on the substitution of $V^{5+}$ with larger alliovalent cations $Mo^{6+}$ and $Cr^{6+}$ by solid-reaction method indicated that doping leads electrochemical performance to be worse[8]. Another report[9] about mechanically doping $Mo^{6+}$ showed the initial discharge capacity approached to theoretical values (270 mA·h/g). But there was no study on cycle performance. Co-doped $Li_{1+x}V_3O_8$[10], synthesized by sol-gel method combined with spray-drying method, has good capacity retention that is 96.7% after 20 cycles but low initial discharge capacity of 212 mA·h/g. The initial discharge capacity of $Ag^+$-$LiV_3O_8$ synthesized by $V_2O_5$ wet sol[11] is only 196 mA·h/g and it remains at 180 mA·h/g after 250 cycles. Therefore, it is very important to look for proper doping chemical element and method in order to improve electrochemical performance of $Li_{1+x}V_3O_8$.

In this paper, $LiOH·H_2O$, $V_2O_5$ and $Y(NO_3)_3$ were used as raw materials to synthesize precursor by a liquid-state reaction method, then $Li_{1.05}Y_xV_{3-x}O_8$ as cathode material for lithium-ion battery was obtained by calcining the precursors. The influence of $Y^{3+}$ doping on structure, conductivity and electrochemical performance of $Li_{1.05}V_3O_8$ was researched by XRD, cyclic voltammograms, AC impedance and so on.

## 2 Experimental

### 2.1 Preparation of materials

$Li_{1.05}Y_xV_{3-x}O_8$ ($x$=0, 0.002 5, 0.005, 0.01, 0.02, 0.1,

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0.2) were prepared with stoichiometrical amounts of $LiOH{\cdot}H_2O$, $V_2O_5$ and $Y(NO_3)_3$. First, LiOH was dissolved in de-ionized water, then $V_2O_5$ and $Y(NO_3)_3$ were added slowly into LiOH solution with stirring at high speed. At last, $NH_4OH$ was dropped until pH reached 8.5. The solution was stirred for 30 min. The liquid mixture was then baked in 90 ℃ bath for 4 h and then was put in vacuum at 120 ℃ for 2 h to evaporate additional water. The remaining powders just were the precursor needed. The precursor was ground and pressed into blocks, calcined at 480 ℃ for 10 h by auto-controlled temperature program in the air with heating rate of 3 ℃/min and cooling rate of 1 ℃/min. The resulting material was sieved by a 500-mesh sieve.

### 2.2 Characteristic measurements

The prepared material was characterized by X-ray diffraction (XRD, Japan Rigaku D/max-RB) using monochromatic Cu $K_\alpha$ radiation source at 40 kV, 100 mA, with a scan rate of 10(°)/min and step length of 0.02°. The morphology was investigated by scan electron microscopy (SEM, JSM-5800).

### 2.3 Electrochemical measurements

Cyclic voltammogram tests were carried out with CHI660a electrochemical workstation. A powder microelectrode[12] was used as working electrode, the lithium metal was used as reference and counter electrode. The scanning rate was 1 mV/s and the scanning voltage range was 1.65−4.1 V.

Ion conductivity tests were carried out with 1255 Frequency Response Analyser and 1286 Electrochemical Interface. The samples were directly pressed into slice with diameter of 7 mm and Pt was used as current collectors. The AC impedance experiment was performed in frequency range of $1-10^7$ Hz and the voltage was 10 mV.

Galvanostatic charge-discharge tests were carried out with LAND-2001A systems. Positive electrode was prepared by pressing the mixture of $Li_{1.05}Y_xV_{3-x}O_8$, acetylene black and polyvinylidene(PVDF) in a mass ratio of 80:15:5 onto a aluminum foil, which was dried under vacuum at 110 ℃ for at least 2 h before use. Lithium metal served as negative electrode and Celgard2400 as membrane. The electrolyte was 1 mol/L $LiPF_6$ in a 1:1(volume ratio) mixture of ethylene carbonate(EC) and diethyl carbonate(DEC). The cells were assembled in an argon-filled dry box. The current is 30 mA/g and cutoff voltage is from 1.8 to 4.0 V (vs $Li/Li^+$).

## 3 Results and discussion

### 3.1 Influence of $Y^{3+}$ doping on structure of $Li_{1.05}V_3O_8$

The XRD patterns of $Li_{1.05}Y_xV_{3-x}O_8$ ($x$=0, 0.005, 0.01, 0.1, 0.2) are shown in Fig.1. All samples with different amounts of $Y^{3+}$ doping have very strong diffraction peaks and well-developed crystal structure of layered $Li_{1.05}V_3O_8$. But the impurity phase of $YVO_4$ is found when $x \geqslant 0.1$. The radius of the sixth coordinate $V^{5+}$ in the layered $LiV_3O_8$ is 0.054 nm while that of the sixth coordinate $Y^{3+}$ is 0.090 nm, which is consistent with the necessity of radius to form an incomplete isomorphous solid solution. It is accorded with the results of XRD tests. Based on this, it can be concluded that only when the doping amount is small, can $Y^{3+}$ substitute $V^{5+}$ totally and locate in the crystal lattice sites of $V^{5+}$. $Li_{1.05}Y_xV_{3-x}O_8$ isomorphous solid solution is formed.

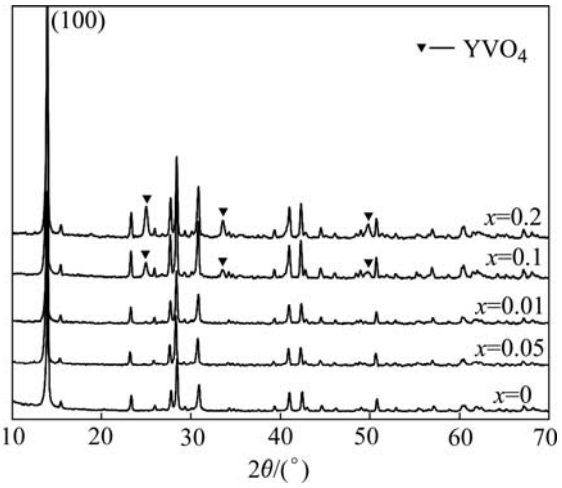


**Fig.1** XRD patterns of $Li_{1.05}Y_xV_{3-x}O_8$

Fig.2 illustrates the influence of $Y^{3+}$ doping amount on interlayer distance of (100) crystal plane. The $d_{100}$ values increase with $Y^{3+}$ doping, which makes it easier for $Li^+$ to insert and deinsert. There is a peak of $d_{100}$ when $x$ is 0.005. From this point $d_{100}$ decreases smoothly

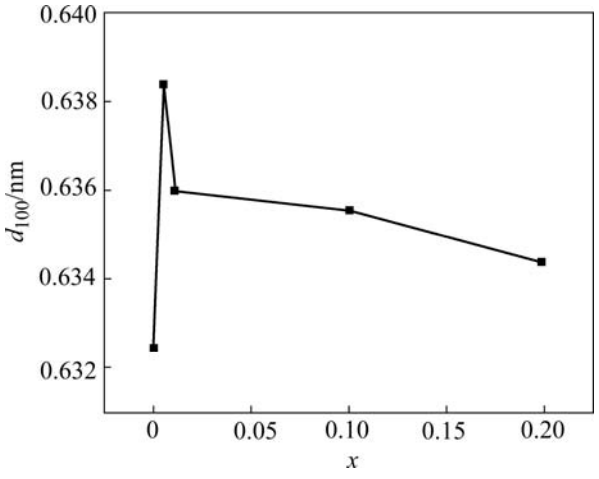


**Fig.2** Influence of $Y^{3+}$ doping amount on $d_{100}$

with increasing doping amount.

### 3.2 Influence of $Y^{3+}$ doping on morphology of $Li_{1.05}V_3O_8$

Fig.3 gives the SEM photographs of $Li_{1.05}Y_xV_{3-x}O_8$ ($x$=0, 0.005, 0.01, 0.02). As seen from Fig.3, the morphologies of $Y^{3+}$-doped samples become irregular and their particle sizes also become larger with increasing the doping amount of $Y^{3+}$.

### 3.2 Influence of $Y^{3+}$ doping on $Li^+$ insertion-deinsertion

The cyclic voltammogram curves of $Li_{1.05}Y_xV_{3-x}O_8$ ($x$=0, 0.005, 0.02, 0.2) in the first cycle are shown in Fig.4. As a whole, the cyclic voltammogram curves of $Y^{3+}$-doped samples are similar to those of undoped ones, that is, they all have two reduction peaks and one oxidation peak, which indicates that $Y^{3+}$ doping does not change the process of $Li^+$ insertion-deinsertion. The little difference of shapes and positions of redox peaks between $Y^{3+}$-doped and undoped samples may be caused by varied crystal field due to $Y^{3+}$ doping, which leads to various $Li^+$ deinsertion energy in each crystal site.

### 3.4 Influence of $Y^{3+}$ doping on ion conductivity

In order to deeply study the influence of $Y^{3+}$ doping on ion conductivity of the layered $Li_{1.05}V_3O_8$, AC impedance experiment was carried out. The AC impedance diagram and corresponding equivalent circuit are given respectively in Fig.5 and Fig.6. The conductivity can be calculated according to the results of AC impedance test and equation $\sigma=l/RS$[13], where $l$, S and $R$ are thickness, area and total resistance ($R$ is the sum of $R_b$ and $R_{gb}$), respectively. The calculated results are shown in Fig.7. A small amount of $Y^{3+}$ doping improves the conductivity and it tends to increase first and then decrease with increasing the amount of $Y^{3+}$ doping. When $x$ is 0.005, the ion conductivity of sample has an optimum value, which is 2.13 times that of undoped sample. The ion conductivity has a direct proportion to $Li^+$ diffusion coefficient, so higher conductivity is helpful to $Li^+$ insertion-deinsertion.

The layered $Li_{1.05}V_3O_8$ is a mixed conductor of electron and ion. In this study, $Y_2O_3$ was added as an acceptor. Some $Y^{3+}$ insert into crystal structure and substitute $V^{5+}$ to form solid solution. The defect reaction is

$$Y_2O_3 + O_2 = 2Y_v'' + 4h^{\bullet\bullet} + 5O_o^{\times} \quad (1)$$

Additional $Li^+$ plays the role to maintain electricity neutral in crystal. While the quantity of $Li^+$ is not enough to balance electrovalance, the oxide ion vacancy will be produced. The defect reaction is

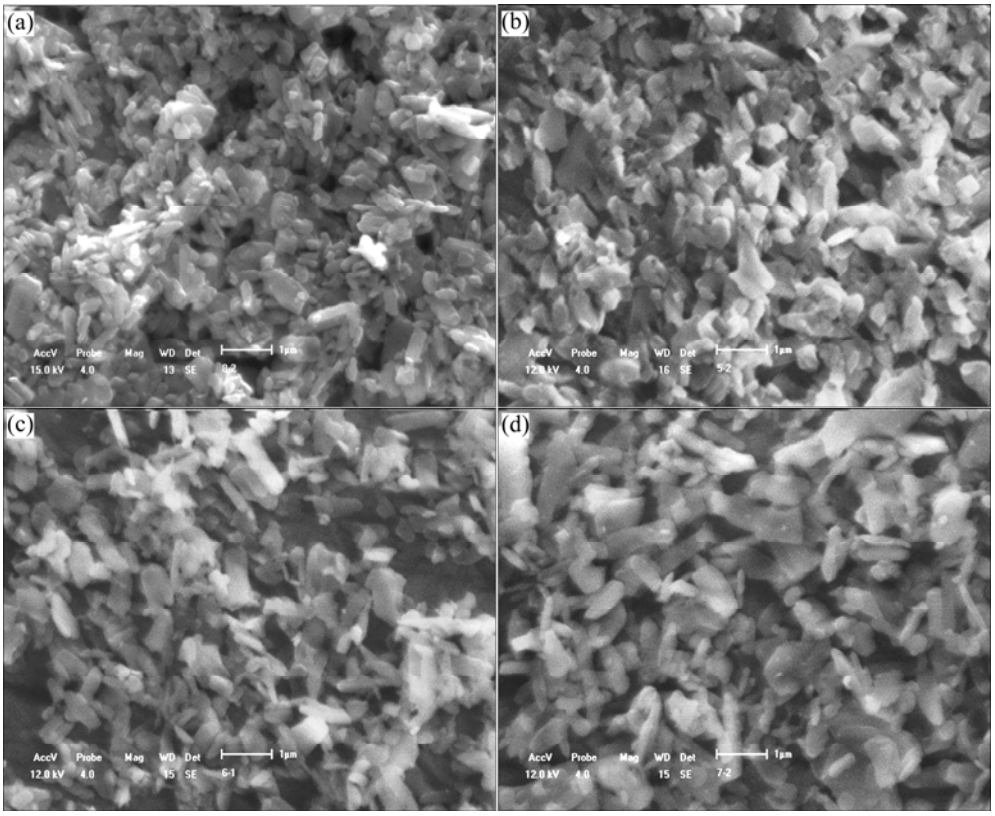


**Fig.3** SEM photographs of $Li_{1.05}Y_xV_{3-x}O_8$: (a) $x$=0; (b) $x$=0.005; (c) $x$=0.01; (d) $x$=0.02

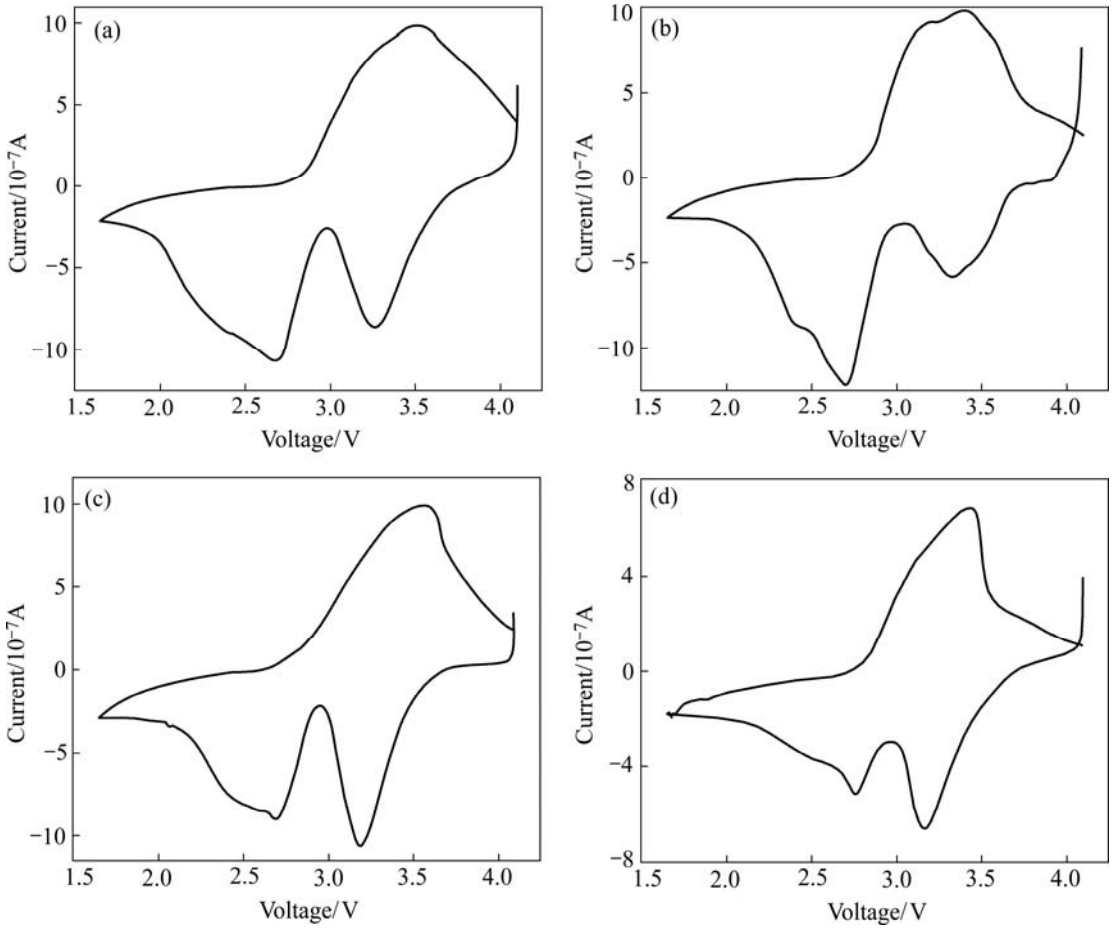


**Fig.4** Cyclic voltammograms of $Li_{1.05}Y_xV_{3-x}O_8$: (a) $x$=0; (b) $x$=0.005; (c) $x$=0.02; (d) $x$=0.2

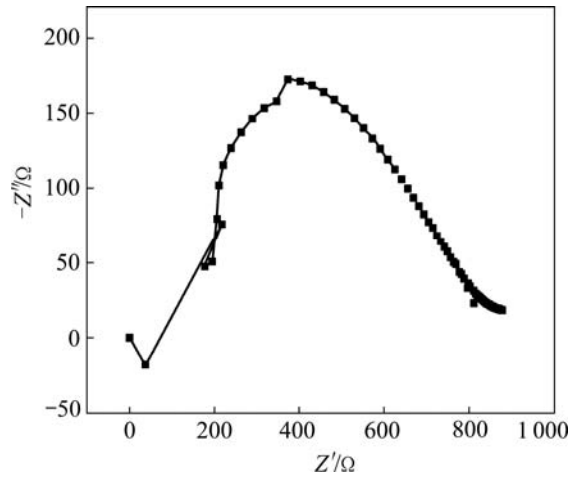


**Fig.5** Complex impedance diagram of $Li_{1.05}Y_{0.005}V_{2.995}O_8$

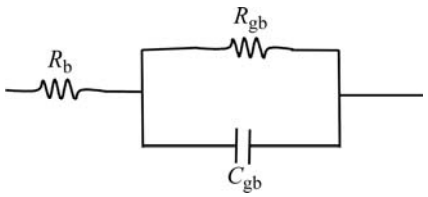


**Fig.6** Equivalent circuit ($R_b$ is total resistance of crystal particle; $R_{gb}$ is total resistance of crystal interface; $C_{gb}$ is total capacitance of crystal interface)

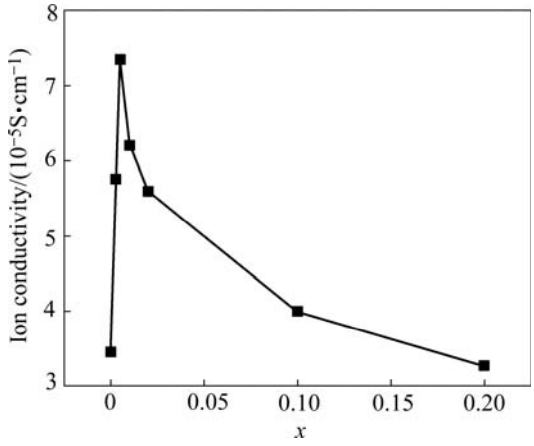


**Fig.7** Influence of $Y^{3+}$-doped amount on ion conductivity

$$Y_2O_3 = 2Y_v'' + 3O_o^{\times} + 2V_o^{\bullet\bullet} \quad (2)$$

Based on this, it can be concluded that $Y^{3+}$ doping introduces electron holes into crystal, which is one reason leading to increased conductivity. The reduced hindrance of $Li^+$ insertion-deinsertion due to increased $d_{100}$ is maybe another reason.

In case of increasing defect concentration in actual crystal, the electrostatic attractive power between positive and negative charges will cause complex defect

reactions to happen, which results in ion conductivity decreasing; on the other hand, the occurrence of second phase $YVO_4$ is a hindrance to improve conductivity, too. Therefore, the ion conductivity does not simply increase with increasing $Y^{3+}$ doping. The ideal ion conductivity can be obtained only by a proper amount of doping.

### 3.5 Influence of $Y^{3+}$ doping on electrochemical performance

The relationship between initial discharge capacity and $Y^{3+}$ doping amount is presented in Fig.8. It can be concluded that the initial discharge capacity can be improved by a proper amount of $Y^{3+}$ doping. When $x$ is 0.005, the first specific discharge capacity reaches 288.9 mA·h/g, which is 4.60% larger than that of undoped one (276.2 mA·h/g). Under this condition the mole number of inserted $Li^+$ is larger than that of $V^{5+}$, so $V^{4+}/V^{3+}$ transition must happen to accept additional electron, which indicates that $Li^+$ insertion is limited only by vacancy number that can be taken up by $Li^+$, not by electron number that can be accepted by $V^{5+}$. This consists with the view in Ref.[14]. With continuously increasing $Y^+$ doping amount, the initial discharge capacity drops sharply and it is only 234.1 mA·h/g when $x$ is 0.2.

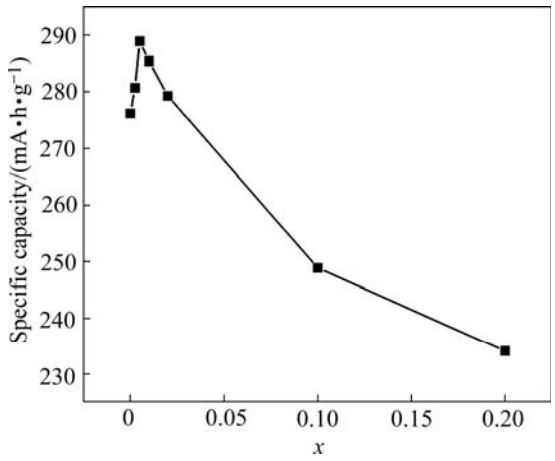


**Fig.8** Relationship between initial discharge capacity and $Y^{3+}$ doping amount

Fig.9 demonstrates the initial discharge curves of $Li_{1.05}Y_xV_{3-x}O_8$ with different $Y^{3+}$ doping amounts. As shown in Fig.9, the discharge voltage of samples is increased with $Y^{3+}$ doping increasing, and this effect is more notable within small doping range. When $x \leqslant 0.1$, the average discharge plateau potentials are enhanced by about 0.15 V. Higher discharge voltage leads energy density to be higher.

The cyclic performances of $Li_{1.05}Y_xV_{3-x}O_8$ ($x$=0, 0.005, 0.01, 0.02, 0.1) are presented in Fig.10. When $x \leqslant$ 0.01, samples have good cyclic performance compared with the undoped ones. Whereas, with increasing the doping amount to $x$=0.02, the cyclic performance falls slightly and it is deteriorated with continuous increasing doping amount. The reasons may be that: when the amount of $Y^{3+}$doping is small, $Y^{3+}$ can insert into crystal lattice and remain unreactive in the charge-discharge process, so it has a good effect on crystal structure. At the same time, the value of $\Delta G_f^{\Theta}$ (−1813.9 kJ/mol) of $Y_2O_3$ is less than that of $V_2O_5$ (−1 395. 6 kJ/mol), which can deduce that the bond energy of Y—O is much

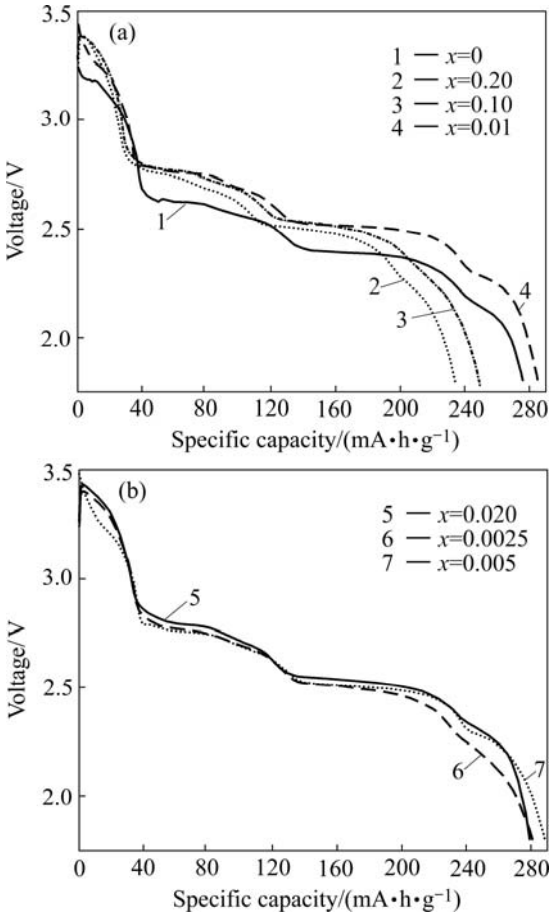


**Fig.9** Initial discharge curves of $Li_{1.05}Y_xV_{3-x}O_8$

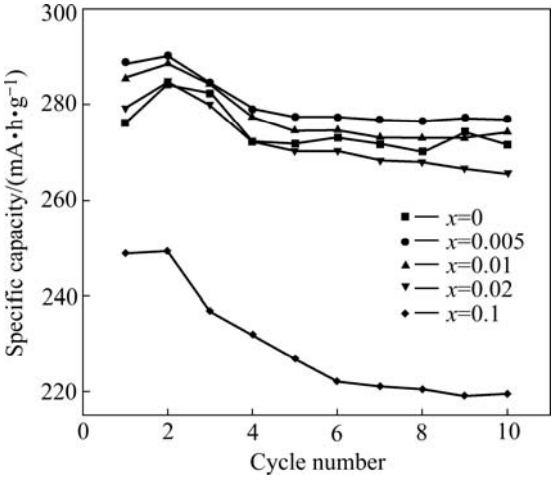


**Fig.10** Cyclic performance of $Li_{1.05}Y_xV_{3-x}O_8$

stronger than that of V—O, making crystal structure more stable, too. But on the contrary, due to the increased doping amount, the occurrence of second phase $YVO_4$ (tetragonal system) obstructs $Li^+$ insertion-deinsertion.

## 4 Conclusions

1) The materials with $Y^{3+}$ doping have well-developed crystal structure of layered $Li_{1.05}V_3O_8$ and lengthened interlayer distance of (100) crystal plane. $Y^{3+}$ can insert into crystal lattice completely when the doping amount is small and the impurity phase of $YVO_4$ is found when $x \geqslant 0.1$.

2) There is no change in the process of $Li^+$ insertion-deinsertion when $Y^{3+}$ is doped.

3) A small amount of $Y^{3+}$ doping can improve conductivity and it tends to increase first and then decrease with increasing amount.

4) The proper amount of $Y^{3+}$ doping can increase the initial discharge capacity. When $x$ is 0.005, the first specific discharge capacity reaches 288.9 mA·h/g, which is 4.60% larger than that of undoped sample (276.2 mA·h/g). When $x \leqslant 0.01$, the materials have good cyclic performance.

5) $Y^{3+}$ doping results in the plateau potential enhanced. When $x \leqslant 0.1$, the average discharge plateau potentials are enhanced by about 0.15 V, which leads energy density to be higher.

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