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Novel cathode materials $Li_xNa_{2-x}V_2O_6$ (x = 2, 1.4, 1, 0) for high-performance lithium-ion batteries

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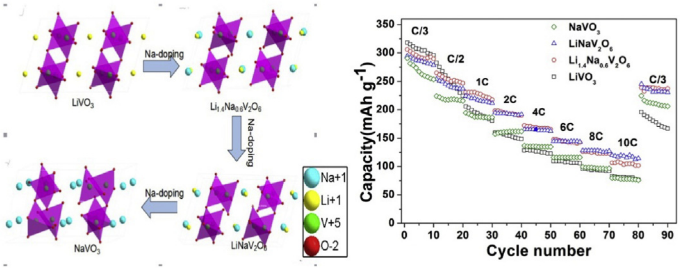
HIGHLIGHTS

- $Li_xNa_{2-x}V_2O_6$ (x = 2, 1.4, 1, 0) is prepared for high performance Li-ion batteries.
- The amount of Na-doping strongly affects the Li-ion battery performance.
- The $LiNaV_2O_6$ cathode displays the best cycling and rate performances.
- Na doping offers good intercalation channels and increases diffusion coefficient.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, sodium doped $LiVO_3$ cathode is proposed to achieve enhanced cycling performance for lithium ion battery (LIB) application. $Li_xNa_{2-x}V_2O_6$ (x = 2, 1.4, 1, 0) compounds have been prepared and characterized, and X-ray diffraction patterns confirmed the successful Na doping with various amounts in the $LiVO_3$. The electrochemical performances of the various Na doped compounds $LiVO_3$, $Li_{1.4}Na_{0.6}V_2O_6$, $LiNaV_2O_6$, and $NaVO_3$ are evaluated by cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy. The results reveal that Na-doping amount strongly affects the electrochemical performance, and $LiNaV_2O_6$ (x = 1) is considered as the optimized Na doped compound for LIB cathodes. The $LiNaV_2O_6$ cathode displays enhanced cycling and rate performances as a specific capacity of 193 mAh g^{-1} at 0.5 C after 100 cycles is delivered. The enhanced performance is explained that the doping of Na can provide good channels and increase Li^+ diffusion coefficient for lithium ion intercalation/deintercalation.

1. Introduction

Rechargeable lithium ion batteries (LIBs) have received considerable attentions in recent years for their wide applications ranging from small portable electronics to electric vehicles and potentially stationary large-scale energy storage systems [1–3]. However, the high cost and low capacity of the currently commercial cathode materials such as $LiCoO_2$ and $LiFePO_4$ will definitely limit the further application of lithium-ion batteries in the future, especially in large-scale energy storage systems. Therefore, it is very urgent to explore new cathode materials with higher capacity and power density for LIBs, such as Li-rich layered composites, vanadium oxides, metal fluorides, etc [4,5].

Vanadium oxides and their derivatives have been considered as

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one of the most promising candidates due to their excellent performances, such as high specific energy, rate capability, as well as low cost and abundant resource of vanadium in the earth [6,7]. Among Li-V-O family compounds, LiV_2O_5 has been explored very early, and LiV_3O_8 as an insertion material has also received considerable attentions [8,9]. Both the layered oxides involve two consecutive redox couples, V^{5+}/V^{4+} and V^{4+}/V^{3+} during lithium intercalation-deintercalation process, leading to the structure transition and capacity loss. Therefore, these materials exhibit unsatisfactory performances. Meanwhile, a new vanadate $LiVO_3$ involving only one redox couple V^{5+}/V^{4+} has shown the advantage of keeping structural reversibility and integration. Moreover, $LiVO_3$ exhibits a higher specific capacity because Li-rich rock phase can deintercalate up to one lithium cation per formula [10,11]. Unfortunately, the long cycling performance of $LiVO_3$ cathode is not satisfied [12], because the dissolution of vanadium and the structural transformation to the rock salt structure during cycling induce capacity fading of the electrode materials. Herein, great efforts are needed to improve cycling life of $LiVO_3$ for its wide application as a cathode material in lithium ion batteries.

Cycling stability is strongly related to morphology and structure of the electrode materials, and there are various approaches to enhance cycling performance of electrodes, which involves different methods to prepare the cathode materials with modified morphology or structure [13,14]. Among those methods, doping has been proved to be an essential approach to solve the capacity fading problem. A variety of cations including B, K, Si, Ni, Mn, Mo, has been doped into cathode materials to enhance the battery performances [15]. For instance, B-LiV_3O_8 prepared through an aqueous reaction process exhibited an initial specific discharge capacity of 269.4 mAh g^{-1}, remaining 232.5 mAh g^{-1} after 100 cycles at a current density of 150 mA g^{-1} in the voltage range of 1.8–4.0 V, and displayed much better performance than the un-doped LiV_3O_8 [16]. Additionally, Na is also a promising dopant candidate because Na element is cheap, abundant and environmentally friendly. Wang synthesized the $LiNi_{0.5}Mn_{1.5}O_4$ with 5% of Na dopant, and revealed that the doped cathode material delivered a much higher specific capacity than that without Na-doping, the discharge capacity remained 82% of reversible capacity after 400 cycles, demonstrating much better cycling stability [17]. Moreover, Na-doping could improve the kinetic performance of $LiFePO_4$ because it resulted in lower electrode polarization and higher lithium-ion diffusion coefficient [18]. However, to the best of our knowledge, so far there is no study on Na-doped $LiVO_3$ cathode material for enhanced lithium ion battery performances.

In this work, for the first time Na is introduced into $LiVO_3$ compound with various doping content to form $Li_{1.4}Na_{0.6}V_2O_6$, $LiNaV_2O_6$, and $NaVO_3$ compounds, and it is found that the Na doping can provide good channels for lithium ion intercalation/deintercalation in the cathode materials, resulting in enhanced battery performances. Meanwhile, over-doping may destroy the main structure, leading to poor stability. The $LiNaV_2O_6$ is the optimal Na-doping compound showing the best cycling stability and rate performance.

2. Experimental section

2.1. Materials preparation

$Li_xNa_{2-x}V_2O_6$ (x = 2, 1.4, 1, 0) compounds were prepared via a resorcinol-formalin assisted sol-gel method. Firstly, $CH_3COOLi\cdot 2H_2O$ and CH_3COONa with various stoichiometric amounts were mixed and dissolved in ethanol at 60 °C. Secondly, 0.006 mol of NH_4VO_3 and 2 g of oxalic acid were added into the solution and stirred. After the compounds were completely dissolved, 0.72 g of resorcinol and 0.8 mL of formalin were added into the mixed solution. Then, the solution was dried in the air at 50 °C to evaporate the ethanol and then was heated to 80 °C for 24 h in an oven for thermal polymerization. The precursor was ground into fine powders, and calcined at 400 °C for 10 h in air to obtain the doped $Li_xNa_{2-x}V_2O_6$ (x = 2, 1.4, 1, 0). As a result, the $LiVO_3$, $Li_{1.4}Na_{0.6}V_2O_6$, $LiNaV_2O_6$ and $NaVO_3$ products were prepared.

2.2. Morphology and structure characterizations

X-ray diffraction (XRD, Bruker AXS, D8 Advance) was carried out to characterize the $Li_xNa_{2-x}V_2O_6$ samples. Scanning electron microscopy (SEM, Histachi S-4800) and transmission electron microscopy (TEM, JEM-2100F) were used to characterize the morphologies of the samples.

2.3. Electrochemical testing

The electrodes were prepared by mixing 80 wt% $Li_xNa_{2-x}V_2O_6$ powder, 10 wt% Super P and 10 wt% polyvinylidene fluoride (PVDF) together and dispersing in *N*-methyl-2-pyrrolidone (NMP) to form homogeneous slurry, and then the slurry was coated onto aluminum foil to form the electrodes. The slurry coated electrodes were dried under vacuum at 80 °C overnight and gently calendered. 2016-type coin cells were assembled in an argon-filled glove box using Li metal sheet as the counter electrode and microporous membrane (Celgard 2400) as the separator. The electrolyte was 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethylene methyl carbonate (EMC) (1:1:1 by weight). Galvanostatic charging and discharging in the voltage range of 1.5 V–4.0 V were tested at room temperature using LAND battery testing system. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted in an IM 6e Zahner potentiostat. EIS was performed in the frequency range of 100 kHz to 0.01 Hz with potential amplitude of 10 mV.

3. Results and discussion

Fig. 1 shows the structure views of $LiVO_3$, $Li_{1.4}Na_{0.6}V_2O_6$, $LiNaV_2O_6$ and $NaVO_3$. All compounds have the unidimensional structure characteristics, and in such a structure, lithium cations have high mobility resulting in high possibility of structural rearrangements.

Fig. 2 shows the XRD patterns of the as-prepared compounds $LiVO_3$, $Li_{1.4}Na_{0.6}V_2O_6$, $LiNaV_2O_6$, and $NaVO_3$. The Na-doped samples (x = 1.4, 1, 0) displayed similar XRD patterns to the $LiVO_3$ (x = 2) sample which was identical to the standard $LiVO_3$ structure (JCPDS No: 33-0835). Table 1 lists the Rietveld refined cell parameters of the $LiVO_3$, $Li_{1.4}Na_{0.6}V_2O_6$, $LiNaV_2O_6$ and $NaVO_3$ obtained by analyzing the XRD data with jade 6.0 software. All the compounds have monoclinic structure with the space group: *C*2/*c*, and no extra reflection was observed. In this work, it can be seen that the main diffraction peaks moved to smaller angle with the increase in Na doping amount, this was because that Na was inserted into the internal lattice to expand the interlayer spacing. The substitutions of Na^+ with much larger ionic radius of 1.02 Å for Li^+ (0.76 Å) in the cathode materials resulted in the expansion of the interplanar distance of crystal plane, providing a good channel for the Li^+ intercalation/deintercalation [19,20]. Additionally, when increasing the amount of Na doping, the main peak ($2\theta = 18.6°$) intensity became weak, indicating low crystallization, and these materials formed solid solutions. In $NaVO_3$, the amount of doping atom exceeded the limit of the solid solution, which might destroy the main structure. As we know, the diffusion paths of Li^+ in the materials with lower crystallization become shorter, which tended to