Novel Cathode Materials $\text{Li}_x\text{Na}_{2-x}\text{V}_2\text{O}_6$ ($x = 2, 1.4, 1, 0$) for High-Performance Lithium-Ion Batteries

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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. $\text{Li}_x\text{Na}_{2-x}\text{V}_2\text{O}_6$ ($x = 2, 1.4, 1, 0$) 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 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, 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.

Keywords:

Lithium ion battery, cathode, sodium, doping, lithium vanadium oxide

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 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, $\text{V}^{5+}/\text{V}^{4+}$ and $\text{V}^{4+}/\text{V}^{3+}$ 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 $\text{V}^{5+}/\text{V}^{4+}$ 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 environmental friendly. Wang synthesized the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 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 $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, 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

$\text{Li}_x\text{Na}_{2-x}\text{V}_2\text{O}_6$ ($x = 2, 1.4, 1, 0$) compounds were prepared via a resorcinol-formalin assisted sol-gel method. Firstly, $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ 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 $\text{Li}_x\text{Na}_{2-x}\text{V}_2\text{O}_6$ ($x = 2, 1.4, 1, 0$). As a result, the LiVO_3 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, 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 $\text{Li}_x\text{Na}_{2-x}\text{V}_2\text{O}_6$ 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% $\text{Li}_x\text{Na}_{2-x}\text{V}_2\text{O}_6$ 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 sheets 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 to 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 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, 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.

Figure 1 Structure views of LiVO_3 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, LiNaV_2O_6 , and NaVO_3 .

Fig. 2 shows the XRD patterns of the as-prepared compounds LiVO_3 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, 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 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, 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: C2/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 ($2\theta=18.6^\circ$) 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 achieve better electrochemical performance. Therefore, rational performances of the $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$ and LiNaV_2O_6 compounds could be expected.

Figure 2 XRD patterns of the LiVO_3 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, LiNaV_2O_6 and NaVO_3 .

Table 1 Rietveld refined cell parameters of the LiVO_3 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, LiNaV_2O_6 and NaVO_3 .

Sample	a , nm	b , nm	c , nm	V , nm^3
x=0	10.158	8.4175	5.8853	473.4
x=1.4	10.146	8.869	5.854	495.9
x=1	10.187	9.074	5.84	507.3
x=2	10.552	9.468	5.879	558

Fig. 3 shows the SEM images of the LiVO_3 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, LiNaV_2O_6 and NaVO_3 compounds. The particle size of LiVO_3 without Na doping was $\sim 1.5 \mu\text{m}$. With the increase in Na doping amount, the particle size slightly reduced and consisted of submicron-size grains. However, when Na completely substituted Li to form NaVO_3 , the particle size increased up to several micrometers. Generally, small particle size can provide a short diffusion pathway for lithium ion insertion-extraction from the host materials [21, 22]. Thus the sample with an appropriate amount of Na-doping may contribute to good electrochemical performance.

Figure 3 SEM images of the (a) LiVO_3 , (b) $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, (c) LiNaV_2O_6 and (d) NaVO_3 .

Cyclic Voltammetry testing of the cathode materials was conducted to understand the effect of Na-doping on electrochemical behavior of LiVO_3 . Fig. 4 shows the CV curves of the first three cycles in the voltage range 1.0-3.5 V. Fig. 4a,b,c showed similar CV shape, indicating that appropriate Na-incorporation into LiVO_3 did not change the electrochemical behavior. The CV curves of LiVO_3 in Fig. 4a showed a main oxidation peak at 2.7 V, corresponding to the oxidation reaction of the $\text{V}^{4+}/\text{V}^{5+}$

redox couple, together with some other small oxidation peaks, implying a complex multi-phase transition mechanism during lithium deintercalation and intercalation process [23]. During the reversed scan, there were three reduction peaks at 1.5, 2.5 and 2.8 V for LiVO_3 . For $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$ and LiNaV_2O_6 , similar redox peaks were presented, but the peak potential slightly shifted due to the difference in crystalline. These results suggested that the Na-doping could suppress the phase transition of LiVO_3 during Li-ion insertion and extraction processes. Meanwhile, the first cycle was slightly different from the subsequent cycles, which was likely caused by some structural modifications during the first charge-discharge operations [11, 24]. However, the CV curve of NaVO_3 in Fig. 4d showed significant difference, and no sharp redox peaks were noticeable. This was explained that the over-doping of Na destroyed the main structure and changed the electrochemical behavior of the LiVO_3 .

Figure 4 Cyclic voltammograms of the (a) LiVO_3 , (b) $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, (c) LiNaV_2O_6 and (d) NaVO_3 at a scan rate of 0.1 mV s^{-1} .

The charge/discharge capacities of the electrodes were then evaluated. Fig. 5 shows the discharge capacities of the LiVO_3 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, LiNaV_2O_6 and NaVO_3 electrodes at 0.5 C as a function of cycle number. The discharge capacities of all the four cathodes gradually decayed over cycling. When $x=2$, the LiVO_3 electrode delivered a specific capacity of 319 mAh g^{-1} at the first cycle reducing to 163 mAh g^{-1} after 100 cycles, retaining 51% of its initial value. When $x=0$, the NaVO_3 electrode delivered an initial discharge capacity of 288 mAh g^{-1} and faded to 160 mAh g^{-1} after 100 cycles. The poor capacity retention was ascribed to the over doping of Na and relatively large particle size. When $x=1.4$ and 1, the $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$ and LiNaV_2O_6 electrodes delivered higher capacities of 199 mAh g^{-1} and 193 mAh g^{-1} after 100 cycles respectively. Someone may doubt that the difference in capacity was contributed by the various surface areas. Therefore, BET surface areas of the four samples were estimated by N_2 adsorption-desorption. The adsorption-desorption isotherm curves were overlapped, and the N_2 adsorption-desorption isotherm of the LiNaV_2O_6 is given in Fig. S1. The surface areas were very close in the range of $8.92\text{-}12.72 \text{ m}^2 \text{ g}^{-1}$, and no significant difference in the specific surface area was observed. The values of specific capacity didn't follow the sequence of the BET surface area. It is reasonable to deduce that the best battery performance of the LiNaV_2O_6 is mainly ascribed to the Na doping, which could be explained that an appropriate amount of Na-doping improved the cycling performance due to the pillar effect of sodium ions and larger space for the movement of lithium ions [25].

Figure 5 Cycling performances of the LiVO_3 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, LiNaV_2O_6 and NaVO_3 electrodes.

TEM and high resolution TEM (HRTEM) images taken from the LiNaV_2O_6 cathodes before and after cycling are shown in Figure 6. Fig. 6a showed the LiNaV_2O_6 with a particle size less than $1\ \mu\text{m}$, which was consistent with the SEM result. The HRTEM of LiNaV_2O_6 in Fig. 6b showed a legible lattice fringe with a basal distance of $0.31\ \text{nm}$, corresponding to the (-530) lattice spacing of monoclinic LiNaV_2O_6 . After cycling, the LiNaV_2O_6 displayed similar particle size and still retained its original morphology without any structure collapse shown in Fig. 6c, and the lattice fringe with a spacing of $0.24\ \text{nm}$ was still visible but did not belong to any planes of LiNaV_2O_6 , demonstrating the monoclinic LiNaV_2O_6 was transformed into a new phase (supposed to be $\text{Li}_{1+x}\text{NaV}_2\text{O}_6$) after cycling.

Figure 6 TEM and HRTEM images of LiNaV_2O_6 cathodes before (a,b) and after 100 cycles (c, d).

Fig. 7a shows the rate performance of the LiVO_3 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, LiNaV_2O_6 , and NaVO_3 electrodes tested in a mode that all cells were charged at 0.1 C to 4.0 V and discharged at various rates (C/3, C/2, 1 C, 2 C, 4 C, 6 C, 8 C and 10 C) to 1.0 V, and the cells ran for 10 cycles at each rate. The LiVO_3 electrode at C/3 delivered the highest capacity of 317 mAh g^{-1} , but reduced sharply with the increase in current density, and only delivered a discharge capacity of 76 mAh g^{-1} at a high current density of 10 C. When the current density was reversed back to C/3, the discharge capacity was only 179 mAh g^{-1} . The NaVO_3 electrode delivered the lowest discharge capacity at almost all the C rates with a capacity of 74 mAh g^{-1} at 10 C, which was ascribed to its relatively high crystallization and large particle size. On the other hand, the Na-doping electrodes of $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$ and LiNaV_2O_6 delivered high discharge capacities of 306 mAh g^{-1} and 295 mAh g^{-1} at C/3 respectively. When the current

density raised up to 10 C, they still delivered capacities of 106 mAh g⁻¹ and 117 mAh g⁻¹ respectively, which were much higher than ~ 74 mAh g⁻¹ for LiVO₃ and NaVO₃ electrodes. Moreover, when the current density returned to C/3, the discharge capacities were recovered to 238 mAh g⁻¹ and 235 mAh g⁻¹ respectively, revealing good electrochemical reversibility of the Na-doped electrodes. It could be explained that Na⁺ ions functioned as pillars in the layer structures, providing larger space for the movement of lithium ions, thus leading to an increased Li⁺ ions diffusion coefficient and an improved rate performance. To further demonstrate rate performance of the four electrodes, the capacity retention at various C rates was analyzed and showed in Fig. 7b. Again the Na-doping electrodes showed better capacity retention than LiVO₃ or NaVO₃ electrodes, and the LiNaV₂O₆ electrodes displayed the highest capacity retention, which was in good agreement with previous results. Therefore, the LiNaV₂O₆ was considered as the optimized Na-doping compound for LIB cathode application. The discharge/discharge curves of the LiNaV₂O₆ cathode at various rates are shown in Fig. 7c. It's observed all the charge/discharge curves remained similar shape at all the C rates. The several charge/discharge plateaus in the voltage profiles at low C rates corresponded to the Li ions intercalation/deintercalation in the layered materials, which was in good agreement with the CV curves in Fig. 4c. As the C rate increased, the major voltage platforms declined because of the further electrochemical polarization and Ohmic polarization at large current rates [26]. Moreover, the average operation voltage was still maintained at over 1.8 V even at 10 C.

Figure 7 (a) Cycling performance and (b) capacity retention at various C rates of the LiVO_3 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, LiNaV_2O_6 and NaVO_3 electrodes, and (c) charge/discharge curves at various C rates of the LiNaV_2O_6 electrodes.

The lithium storage performance of LiNaV_2O_6 cathode was compared with other vanadium oxide based cathode materials from the recent literature in Table S1. As observed, the stable capacities of the LiNaV_2O_6 cathode at both low rate and high rate were on the top level among the values reported in literature. The enhanced electrochemical performance of the LiNaV_2O_6 electrode was explained by the following reasons: firstly, the Na-doping led to the increase in interlayer spacing of LiNaV_2O_6 , which resulted in much easier lithium ion intercalation/deintercalation and better rate capability, secondly, the appropriate amount of Na-doping led to the decrease in particle size, which increased the exposed surface area of electrode to electrolyte and boosted the specific capacity, thirdly, the submicron-sized cross section features might inhibit vanadium dissolution from the lattice over cycling, which guaranteed the structural stability of the LiNaV_2O_6 .

To further illustrate the difference in electrochemical behavior of the LiVO_3 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, LiNaV_2O_6 and NaVO_3 electrodes, electrochemical impedance

spectroscopy (EIS) was carried out. Fig. 8a shows the Nyquist plots of the LiVO_3 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, LiNaV_2O_6 and NaVO_3 electrodes, and all the Nyquist plots displayed similar profiles, consisting of an approximate semicircle in the high frequency region and an inclined straight line in low frequency range. The diameter of the semicircle represents charge transfer resistance (R_{ct}), and the sloping line in the low frequency region represents lithium-ion diffusion process (Warburg impedance) within the electrode [26, 27]. The charge transfer resistance listed in Table 2 displayed that R_{ct} decreased with the increase in Na-doping, and the LiNaV_2O_6 electrode showed the smallest resistance. The decrease in R_{ct} could be explained that the doping of Na in LiVO_3 created an additional electron hopping paths, which contributed to better charge transfer ability and electrical conductivity, then relieved the Ohmic polarization and electrochemical polarization resulting in smaller charge transfer resistance.

In order to further explain the effect of Na-doping, the diffusion coefficient of lithium ion was calculated via the following equation using the data from the Nyquist plots in the low-frequency region [17, 28].

$$D_{\text{Li}} = \frac{R^2 T^2}{2A^2 n^4 F^4 C_{\text{Li}}^2 \sigma^2} \quad (1)$$

where R is the gas constant, T is the absolute temperature, A is the surface area of the cathode, n is the number of electron per molecule during oxidation, F is the Faraday constant, C_{Li} is the concentration of lithium ion, and σ is the Warburg factor which is related to relationship between Z' and w . Fig. 8b shows the plot of Z' as a function of $w^{-1/2}$, and the Warburg factor σ was obtained from the slope of the fitted linear line. According to Equation (1), lithium ion diffusion coefficient values within

the LiVO_3 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, LiNaV_2O_6 and NaVO_3 electrodes were estimated and listed in Table 2. The results showed that the diffusion coefficient of Li ion was significantly increased by an appropriate amount of Na-doping, and the LiNaV_2O_6 electrode possessed the largest Li diffusion coefficient.

Figure 8 (a) Nyquist plots of the LiVO_3 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, LiNaV_2O_6 and NaVO_3 electrodes, and (b) plots of Z' as a function of $\omega^{-1/2}$ using the data in the low-frequency region for the LiVO_3 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, LiNaV_2O_6 and NaVO_3 electrodes.

Table 2 Charge transfer resistances and lithium ion diffusion coefficients of the four electrodes obtained by EIS.

Electrode	LiVO_3	$\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$	LiNaV_2O_6	NaVO_3
R_{ct} (Ω)	312	91	87	256
D_{Li} ($\text{cm}^2 \text{s}^{-1}$)	2.16×10^{-14}	1.26×10^{-13}	1.34×10^{-13}	2.7×10^{-14}

4. Conclusions

$\text{Li}_x\text{Na}_{2-x}\text{V}_2\text{O}_6$ ($x = 2, 1.4, 1, 0$) cathodes, namely LiVO_3 , $\text{Li}_{1.4}\text{Na}_{0.6}\text{V}_2\text{O}_6$, LiNaV_2O_6 and NaVO_3 were successfully prepared through a sol-gel method. SEM images showed that the particle size slightly changed when Na substituted Li in LiVO_3 , and XRD patterns confirmed the Na was successfully doped in the compound. CV, galvanostatic charge/discharge and EIS were used to study the effect of Na doping amount on the electrochemical performances. All the cathodes displayed similar lithium intercalation/deintercalation behavior, but the cycling and rate performances were strongly affected by the Na doping amount. The Na doped cathodes delivered higher capacities at all the C rates than the undoped or over doped cathodes. LiNaV_2O_6 ($x=1$) was considered as the optimized Na doping compound, as it delivered an improved capacity of 193 mAh g^{-1} at 0.5 C after 100 cycles, and had the smallest charge transfer resistance and the largest Li^+ diffusion coefficient.

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