Superior electrochemical performance of Li3VO4/N-doped C as anode for Li-ion batteries

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<th>Journal:</th>
<th>Journal of Materials Chemistry A</th>
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<tr>
<td>Manuscript ID</td>
<td>TA-COM-06-2015-004402.R1</td>
</tr>
<tr>
<td>Article Type</td>
<td>Communication</td>
</tr>
<tr>
<td>Date Submitted</td>
<td>30-Jul-2015</td>
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</tbody>
</table>
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High performance Li$_3$VO$_4$/N-doped C anode was successfully prepared, which delivers initial discharge/charge capacity of 600/472 mAh g$^{-1}$ at 150 mA g$^{-1}$, maintaining of 462/460 mAh g$^{-1}$ after 100 cycles. It shows no capacity attenuation over 2200 cycles at 2000 mA g$^{-1}$, delivering discharge/charge capacity of 267/264 mAh g$^{-1}$.

Lithium vanadate, Li$_3$VO$_4$ shows safer discharge plateau than graphite and lower voltage plateau and higher capacity than Li$_4$Ti$_5$O$_{12}$, which is demonstrated to be a promising anode for Li-ion batteries. However, the electronic conductivity of Li$_3$VO$_4$ is low compared to its ionic conductivity, which may cause a large polarization in charge/discharge process. As results, on the one hand, the lithiation degree of Li$_3$VO$_4$ attenuates distinctly along with the increasing of particle size. On the other hand, the specific capacity of Li$_3$VO$_4$ decreases sharply along with the increasing of specific current, showing unsatisfied rate performance. Previous research has demonstrated that improving the electronic conductivity of Li$_3$VO$_4$ can distinctly enhance its electrochemical performance. Attempts on combining Li$_3$VO$_4$ with carbonaceous materials such as graphene, carbon nanotubes, amorphous carbon and natural graphite as well as depositing Li$_3$VO$_4$ on Ni foam have been tried to improve the electrochemical performance of Li$_3$VO$_4$, which have gained impressive results.\(^{5-7}\)

Recently, it has been reported that N-doped carbon (N-C) supported materials can further improve the cycle performance and rate capability owing to the improved electronic conductivity, ion permeability of the carbon layer, charge transfer at the interface and stability of the SEI films. For example, N-C coated Fe$_3$O$_4$ delivers capacity retention of 99% after 100 cycles at 500 mA g$^{-1}$ and subsequent 100 cycles at 1000 mA g$^{-1}$, which exhibits specific capacity of 982 mAh g$^{-1}$ after 100 cycles at 500 mA g$^{-1}$, Li$_4$Ti$_5$O$_{12}$ coated with N-C shows 124 mAh g$^{-1}$ after 2200 cycles at 2C.\(^{10}\) It is thus reasonable to believe that combining Li$_3$VO$_4$ with N-C can further improve its electrochemical performance. However, research on Li$_3$VO$_4$/N-C has not been reported by now.

In our previous study, we fabricated Li$_3$VO$_4$ via a solution based method.\(^{11}\) It was found that the intermedial solution phase can improve the homogeneity of the final products, which will be beneficial for symmetrical N-C combination at nanoscale. Here in this paper, we report the preparation of Li$_3$VO$_4$/N-C via introducing hexamethylenetetramine in the intermedial solution, which can act as both carbon source and N-doping agent.\(^{12}\) In the subsequent sintering process, the generation of Li$_3$VO$_4$ and the formation of N-C occur simultaneously, resulting in the formation of Li$_3$VO$_4$/N-C composite architecture. On the one hand, the N-C layer can distinctly improve the electronic conductivity of the composite, and the N-C layer can prevent the growth of Li$_3$VO$_4$ particles, maintaining high electrochemical activity. On the other hand, good contact between Li$_3$VO$_4$ and N-C layer can improve the structure stability of the Li$_3$VO$_4$/N-C electrode in cycling. As results, the as-prepared Li$_3$VO$_4$/N-C shows superior electrochemical performance as anode for Li-ion batteries.
pyrrolic N, respectively, and the peak near 399.1 eV can ascribe to C-N or C≡N.\textsuperscript{9,15,18} According to the XRD, Raman and XPS results, it can be confirmed that Li\textsubscript{3}VO\textsubscript{4}/N-C composite architecture is successfully prepared.

Fig. 1 (a) XRD pattern, (b) Raman spectrum and (c)-(f) XPS spectra of the Li\textsubscript{3}VO\textsubscript{4}/N-C. (c) The survey spectrum; High resolution spectrum of (d) V2p, (e) C1s and (f) N1s.

Fig. 2 (a) SEM, (b) TEM image, (c) SAED pattern and (d) HRTEM image of the Li\textsubscript{3}VO\textsubscript{4}/N-C.
Fig. 2(a) is a low magnification SEM image of the as-prepared products, which exhibits a large number of nanoparticles with mean size about 300 nm. Meanwhile, EDS elemental mapping demonstrates clearly the presence of V, O, C and N element in the products (see ESI, Fig. s1), suggesting the successful preparation of Li$_3$VO$_4$/N-C. For further studying the microstructure of the Li$_3$VO$_4$/N-C, a TEM image is characterized and shown in Fig. 2(b). As seen, these nanoparticles are composed of a large number of small particles with mean size about 40 nm. Fig. 2(c) is a SAED pattern of the Li$_3$VO$_4$/N-C, which exhibits irregular diffraction spots, suggesting the polycrystalline characteristics of Li$_3$VO$_4$. Meanwhile, weak diffraction rings can be attributed to amorphous C. The microstructure of the Li$_3$VO$_4$/N-C was also testified by HRTEM image. As shown in Fig. 2(d), the interplanar spacing for the nanoparticle is 0.413 and 0.206 nm, which corresponds to the (110) and (220) face of orthorhombic Li$_3$VO$_4$, respectively. The amorphous layer with a thickness about 8 nm can ascribe to C in the Li$_3$VO$_4$/N-C.

Galvanostatic charge/discharge cycling was carried out in the potential window of 0.02~3.0 V versus Li. Fig. 3(a) shows the capacity retention and the initial three and 100th charge/discharge voltage profiles of the Li$_3$VO$_4$/N-C electrode at a specific current of 150 mA g$^{-1}$. As seen, the initial discharge curve differs slightly from the subsequent ones, showing two sloping potential regions (1.5~0.8 and 0.8~0.02 V), which correspond to the insertion of lithium ions into Li$_3$VO$_4$/N-C and the formation of solid electrolyte interface (SEI). The subsequent discharge curves show similar profiles with two sloping potential regions (1.5~0.4 and 0.4~0.02 V), accompanied by capacity attenuation. All the charge curves exhibit similar profile with a sloping potential region from 0.8 to 2.5 V, corresponding to the extraction of lithium ions from Li$_3$VO$_4$. The initial discharge capacity is 600 mAh g$^{-1}$, which is bigger than the charge capacity (472 mAh g$^{-1}$) owing to the formation of SEI. Remarkably, the Li$_3$VO$_4$/N-C shows superior cycle performance, which delivers discharge and charge capacities of 462 and 460 mAh g$^{-1}$ after 100 cycles. The electrochemical performance of the Li$_3$VO$_4$/N-C shows distinct improvement compared with those reported in
literature (capacity comparison see ESI, tab. s1†).

The high specific capacity of the Li$_3$VO$_4$/N-C is relevant to its specific architecture. In the Li$_2$VO$_4$/N-C, the small size of Li$_2$VO$_4$ is a guarantee of short diffusion pathway of lithium ions, and the N-C layer can provide high electron transfer efficiency (EIS spectra and the fitted electrochemical kinetic parameters of pristine Li$_2$VO$_4$ and the Li$_2$VO$_4$/N-C see ESI, Fig. s2 and tab. s2), which result in enhanced electrochemical reaction kinetics, improving the lithiation degree of the Li$_2$VO$_4$/N-C. Meanwhile, the good contact between Li$_2$VO$_4$ and N-C layer can provide stable charge transfer process in cycling (EIS spectra and the fitted electrochemical kinetic parameters of the Li$_2$VO$_4$/N-C in cycling see ESI, Fig. s3 and tab. s3), resulting in excellent cycle stability.\(^5\) The effect of N-C on the electrochemical performance of Li$_2$VO$_4$/N-C electrodes was also evaluated. The presence of N-C can improve the specific capacity of the electrode,\(^6\) and an appropriate amount of hexamethylenetetramine is beneficial to obtain the highest specific capacity (cycle performance of pristine and Li$_2$VO$_4$/N-C obtained with different amount of hexamethylenetetramine see ESI, Fig. s4). The cyclic voltammetric (CV) curves of the Li$_2$VO$_4$/N-C electrode were tested over a voltage region from 0 to 3.0 V at a scan rate of 0.2 mV s\(^{-1}\). As shown in Fig. 3(b), the profiles of CV curves for the 2nd and 3rd cycle are similar, whereas an obvious difference between the first and the subsequent two cycles is found. In the 1st cathodic scan, three obvious reduction peaks at around 0.71, 0.52 and 0.35 V are observed, which correspond to the insertion of lithium ions into Li$_2$VO$_4$ and the formation of SEI.\(^3,6,7,11\)

Remarkably, the reduction peak near 0.35 V was not observed for most Li$_2$VO$_4$, whereas a weak reduction peak of Li$_2$VO$_4$/N-C near 0.35 V accompanies by distinct improvement of capacity.\(^3,7,11,23\)

Thus it can be deduced that the observation of clear reduction peak near 0.35 V is relevant to the enhanced lithiation of the Li$_3$VO$_4$/N-C. The reduction peaks shift to 0.48 and 0.76 V in the 2nd cathodic scan and 0.54 and 0.84 V in the 3rd cycle, which can ascribe to the activation of the Li$_2$VO$_4$/N-C electrode, being similar to that reported in literature.\(^3,6,7,11\) The profiles for the initial three anodic scan are similar, showing an oxidation peak near 1.37 V, which is attributed to the delithiation process that can be described as: Li$_{3-x}$VO$_4$$→$ Li$_x$VO$_4$ + xe\(^{-}\) (x≤3).\(^3,6,7,11,22\) Fig. 3(c) shows the discharge and charge curves of the Li$_2$VO$_4$/N-C electrode at various specific currents from 100 to 2000 mA g\(^{-1}\). Along with the increasing of specific currents, the discharge and charge capacities decrease owing to the enhanced polarization.\(^1,2,11\) The 10th discharge capacity is 485, 454, 396, 339, 301 and 274 mA h g\(^{-1}\) at specific currents of 100, 200, 500, 1000, 1500 and 2000 mA g\(^{-1}\), respectively. After that, the 10th discharge capacity can restore to 488 mA h g\(^{-1}\) when reverting the specific current to 100 mA g\(^{-1}\), suggesting good recover ability.

The rate performance of the Li$_2$VO$_4$/N-C shows discharge and charge capacities of 357 and 264 mA h g\(^{-1}\) in the initial cycle at a specific current of 2000 mA g\(^{-1}\), which maintain of 267 and 264 mA h g\(^{-1}\) after 2200 cycles, showing no capacity attenuation in cycling. The superior electrochemical performance, the facile fabrication method, and the low cost endow the Li$_3$VO$_4$/N-C with practical application in Li-ion batteries.

In summary, Li$_2$VO$_4$/N-doped C was successfully prepared via a facile way, which shows superior electrochemical performance as anode for Li-ion batteries owing to the enhanced lithiation degree, electronic conductivity and structure stability. The reversible capacity of the Li$_2$VO$_4$/N-C can research 460 mA h g\(^{-1}\) after 100 cycles at a specific current of 150 mA g\(^{-1}\), and 264 mA h g\(^{-1}\) after 2200 cycles at a specific current of 2000 mA g\(^{-1}\). Meanwhile, the facile fabrication method reported here is facile and low cost, which is beneficial for the practical application of the Li$_2$VO$_4$/N-C in Li-ion batteries.

Acknowledgement

We gratefully acknowledge the financial support from Natural Science Foundation of China (NSFC, 51302152, 51272128, and 51302153). Moreover, the authors are grateful to Dr. Jianlin Li at Three Gorges University for his kind support to our research.

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\(^{c}\) Electronic Supplementary Information (ESI) available: [details of any supplementary information should be included here]. See DOI: 10.1039/b000000x/


