EFFECT OF B₂O₃ ADDITION ON THE ELECTROCHEMICAL PERFORMANCE OF LiVMoO₆ CATHODE MATERIAL

Margarita Milanova, Reni Iordanova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,
G. Bonchev, str. bld. 11, 1113 Sofia, Bulgaria
E-mail: margi71@abv.bg

ABSTRACT

In this paper, we report for the preparation of LiVMoO₆ cathode material with and without B₂O₃ addition (B-LVM and LVM) by melt quenching method followed by heat treatment at 580°C. XRD, Raman and SEM investigations were performed to examine the phase formation, local structure and morphology of the obtained products. The results indicate that B₂O₃ acts as a sintering agent. The synthesized B-LVM material is comprised of clusters of agglomerated tightly packed small particles. The electrochemical performance of B-LVM and LVM as cathodes in lithium ion batteries was examined. The specific capacity estimated of the B₂O₃ – added LiVMoO₆ approaches 300 mAh g⁻¹ which is larger than the specific capacity reported so far in the literature for this material. Although that the addition of the B₂O₃ enhances the capacity does not improve the cycling stability of the LiVMoO₆.

Keywords: boron oxide, LiVMoO₆, lithium batteries.

INTRODUCTION

It is generally believed that the capacity of the cathode materials is one of the major factors of the performance of Lithium-ion batteries (LIBs) [1, 2]. Recently a great number of vanadates containing transition metal ions, [3, 4] have been extensively studied as a possible electrode active materials in lithium batteries. Among them, the Brannerite-type LiVMoO₆ have attracted special attention both as cathode and anode material because of its open structure and interesting characteristic from a stand point of the variety of oxidation state [5 - 13]. Despite the high specific capacity (250 mAh g⁻¹ between 1.5 and 3.5 V), LiVMoO₆ suffers from fundamental problems including low initial Coulombic efficiency and a long life cycling instability. A significant capacity fade during the cycles shows that irreversible structural and morphological changes take place in the electrode material upon lithium insertion [7, 8, 14].

There are several papers reporting that the introduction of a boron oxide to layered lithium transitional metal oxide leads to increase their conductivity and structural stability. [15 - 20]. This improvement is associated with the expansion of the interlayer distances with boron doping, leading to a much easier lithium ion intercalation/deintercalation [15, 20]. The strong B-O bonds can enhance the structural stability of the cathode [17, 19]. As a well-known sintering agent, the addition of B₂O₃ to the cathode will improve its density and structural integrity [16].

In the present work, we have investigated the effect of B₂O₃ addition on the structure and electrochemical performance of LiVMoO₆ cathode material.

EXPERIMENTAL

The homogenized batch of the Li₂CO₃, V₂O₅, MoO₃ and H₃BO₃ with appropriate composition for the 90LiVMoO₆:10B₂O₃ molar ratio was melted in alumina crucible for 20 min at 800°C in air atmosphere. According to the electron microprobe analysis (EMRA), performed in our previous studies, the amount of Al₂O₃ dissolved into the glasses obtained by melting in alumina crucibles is at about 8 - 10 mol % [21]. Amorphous
sample was obtained by quenching of the melt between two stainless steel plates. The quenched sample was heat treated 5 h at 500°C and 10 h at 580°C in order to obtain well crystallized materials, denoted here as B-LVM. For the sake of comparison LiVMoO₆ denoted here as LVM without B addition was prepared, using the same procedure. The obtained materials were characterized by X-ray diffraction (XRD), differential thermal analysis (DTA), Raman spectroscopy, and scanning electron microscopy (SEM). X-ray diffraction measurements were conducted using CuKα radiation in a laboratory X-ray diffractometer (Ultima IV, Rigaku Corp.). The thermal parameters of the B-LVM amorphous sample obtained were determined using differential thermal analysis (DTA) (Thermo Plus TG8110, Rigaku). Raman measurement of B-LVM and LVM were performed in the range 200 - 1200 cm⁻¹ on a micro-Raman system from Jobin-Yvon Horiba (LABRAM HR-800) spectrometer with green laser (wavelength: 532 nm). The morphology and microstructure of B-LVM and LVM were investigated by scanning electron microscope (JEOL, JSM-5300).

Cycling performance of B-LVM and LVM was tested by construction of Li/B-LVM and Li/LVM cells employing liquid electrolyte. The composite cathode consisted of a mixture of active material (B-LVM and LVM, respectively) acetylene black and 8 wt % polyvinylidene fluoride (PVDF) dissolved in N-methylpyrrolidone (NMP) in 90:5:5 weight ratio. After mixing of the electrode materials, the slurries were painted on a stainless mesh (1 × 1 cm) as a current collector. Then, the electrodes were dried at 130°C for 3 h and pressed between stainless steel plates under 280 MPa. The prepared electrodes as a working electrodes and single lithium foil used as both the counter and reference electrode were put into the three-electrode - type electrochemical cells. The electrolyte used for analysis was 1M LiPF₆ dissolved in ethylene carbonate/diethyl carbonate (EC/DEC, 33/67). Cells were assembled in an argon-filled glove box. The prepared test cells were discharged and charged in the potential range from 1.8 to 3.7 V under a current density of 0.1 mA cm⁻² at room temperature in Ar atmosphere using a charge-discharge measuring device (BTS-2004; Nagano). Electrochemical impedance measurements of the test cells before and after discharge - charge measurements were performed using a charge-discharge measuring device (SI1260 Solartron) in the frequency range from 100 to 1 MHz.

RESULTS AND DISCUSSION

Phase characterization and microstructure investigation

X-ray amorphous sample was obtained by quenching of the melt with composition 90LiVMoO₆·10B₂O₃ (Fig. 1a). The as-quenched 90LiVMoO₆·10B₂O₃ sample was investigated by differential thermal analysis (DTA) in order to establish the temperature at which the crys-

![Fig. 1. XRD pattern (a) and DTA curve (b) of 90LiVMoO₆·10B₂O₃ sample obtained by melt quenching.](image-url)
tallization of LiVMoO$_6$ starts. The DTA curve (Fig. 1b) contains a hump at 215°C corresponding to the glass transition temperature ($T_g$), followed by an exothermic peak at 270°C, due to the crystallization ($T_x$) of LiVMoO$_6$ and an endothermic effect at 640°C, attributed to the thermal decomposition ($T_m$) of LiVMoO$_6$ [8, 10, 12]. Having in mind DTA data obtained, the quenched 90LiVMoO$_6$.10B$_2$O$_3$ sample was calcined for 5 hours at various temperatures in order to obtained well crystallized material (Fig. 2). As one can see the patterns obtained for the samples calcined for 5 hours at 270°C (Fig. 2a); 450°C (Fig. 2b) and 500°C (Fig. 2c), respectively show broad and poorly resolved diffraction peaks characteristic for the LiVMoO$_6$ phase. All the peaks are indexed assuming a C2/m symmetry that corresponds to the monoclinic citing of the brannerite structure [22]. The diffraction pattern of the B$_2$O$_3$-added LiVMoO$_6$ heat-treated for 5 h at 500°C and additionally for 10 h at 580°C (B-LVM) exhibits a well resolved peaks compared to those calcined at lower temperatures and for less time. Hence, despite that the crystallization starts around 270°C, well-crystallized LiVMoO$_6$ phase have been obtained at 580°C. Impurity peaks that could originate from the boron and lithium components were not observed in the XRD pattern. For the sake of comparison, pure LiVMoO$_6$ material was prepared in the same way (Fig. 2e). According to the XRD data, the diffraction lines in the XRD pattern of the boron added LiVMoO$_6$ (B-LVM) (Fig. 2d) are less intense as compared to the LiVMoO$_6$ without B$_2$O$_3$ (LVM) (Fig. 2e) which indicates poorer crystallinity and/or higher degree of aggregation of the particles. This suggestion is also confirmed by the Raman analysis. Fig. 3 compares Raman spectra of B-LVM and LVM obtained. Raman spectra of both samples contain the absorption bands typical for the various MeO$_6$ (Me = V, Mo, Li) octahedral units building the lattice [8, 23, 24]. Table 1 presents the detailed assignment of the Raman bands observed. As it is seen from the Fig. 3, Raman spectrum of the boron - added LiVMoO$_6$ (B-LVM) contains broader and less intense absorption bands than the bands in the spectrum of pristine LiVMoO$_6$ sample (LVM), evidencing its lower degree of crystallinity. As there is no noticeable shift in the bands position, it could be assumed that addition of the B$_2$O$_3$ does not influence the local structure of the LiVMoO$_6$. Probably no boron...
is incorporated within LiVMoO$_6$ during the synthesis and B$_2$O$_3$ has a sintering effect only. SEM investigations confirmed this suggestion. SEM images at different magnifications of LiVMoO$_6$ with and without B$_2$O$_3$ addition (B-LVM and LVM) obtained are shown on Fig. 4. a,b and c,d, respectively. As it is seen from the figure, B-LVM is characterized with a sintered microstructure and a higher degree of particles aggregation as compared with the pure LiVMoO$_6$. The SEM micrographs of the boron added LiVMoO$_6$ also show that the particles of B-LVM are smaller and have more irregular shape as compared with the particles of pure LiVMoO$_6$, which coincides well with the XRD data obtained.

**Electrochemical characterization**

The electrochemical charge/discharge measurements of B$_2$O$_3$-added LiVMoO$_6$ (B-LVM) and pristine LiVMoO$_6$ (LVM) obtained were carried out using Li
metal as a counter electrode between 2.0 and 3.5 V under a current density of 0.05 mA cm$^{-2}$ at 25°C. The discharge-charge curves of the test cells for 10 cycles are shown in Fig. 5. As it is seen from the figure, B-LVM shows significantly higher first discharge capacity approaching 300 mAh g$^{-1}$, as compared with the LVM, delivering a first discharge capacity at about 150 mAh g$^{-1}$ when cycled from 2 to 3.5 V against Li metal. The specific capacity of boron-added LiVMoO$_6$ (B-LVM) estimated is larger than the specific capacity reported so far in the literature for this material (250 mAh g$^{-1}$) [8]. One possible reason for the enhanced capacity of B-LVM may be the smaller particles of boron-added LiVMoO$_6$. Since electrochemical lithium intercalation and deintercalation are generally limited by the rate of diffusion, the smaller grain size can favor the lithium-ion mobility in the particles by reducing the ion-diffusion pathway [12, 25]. However, the capacity drops sharply by more than 95% after the first cycle, which indicates instability of the both crystalline phases investigated.

The electrochemical data show that the addition of the B$_2$O$_3$ enhances the capacity but does not improve the cycling stability of the LiVMoO$_6$.

In order to understand the cycling behavior of the Li/B-LVM and Li/LVM cells, ac impedance measurements were carried out. Fig. 6 compares the impedance spectra of test cells before and after discharge-charge for 10 cycles. The impedance spectrum of both B-LVM and LVM electrodes are very similar in shape and contain three semicircles of different sizes. The high-frequency diffusion, the smaller grain size can favor the lithium-ion mobility in the particles by reducing the ion-diffusion pathway [12, 25]. However, the capacity drops sharply by more than 95% after the first cycle, which indicates instability of the both crystalline phases investigated.

In order to understand the cycling behavior of the Li/B-LVM and Li/LVM cells, ac impedance measurements were carried out. Fig. 6 compares the impedance spectra of test cells before and after discharge-charge for 10 cycles. The impedance spectrum of both B-LVM and LVM electrodes are very similar in shape and contain three semicircles of different sizes. The high-frequency
smaller semicircle can be attributed to the resistance of the passive film on the cathode \[17, 26, 27\]. The formation of the passive film on the cathode is caused by the high potential between the cathode and the electrolyte interfaces at the fully charged state. During cycling, this potential causes the electrolyte decomposition on the cathode \[26\]. The larger low frequency semicircle can be attributed to the charge transfer resistance across the interface between the liquid electrolyte and B-LVM and LVM, respectively \[17, 27\]. The third, smaller semicircle in the low frequency region can be assigned as the ionic diffusion of the electrolyte \[28\]. The ac impedance spectra of the both Li/B-LVM and Li/LVM tested cells are characterized with an incomplete semicircle with a large diameter corresponding to a capacitive behavior (blocking electrode effect) \[22\]. This result shows that obtained materials suffered from the structural instability leading to the sharp decreasing of the specific capacity. Further studies over the factors affecting the electrochemical behavior of B\(_2\)O\(_3\)-added LiVMoO\(_6\) as positive electrode active material in lithium-ion batteries are needed.

CONCLUSIONS

Crystalline LiVMoO\(_6\) with addition of 10 mol % B\(_2\)O\(_3\) was synthesized by melt quenching method followed by heat treatment in order to increase the degree of crystallinity of the material. The obtained B\(_2\)O\(_3\)-added LiVMoO\(_6\) (B-LVM) was compared by pristine LiVMoO\(_6\) (LVM), prepared in the same way. It was found that the B\(_2\)O\(_3\) added has a sintering effect only and does not change the layered structure of LiVMoO\(_6\). The cycling discharge-charge behavior of the B-LVM as positive electrode in test cells employing liquid electrolyte evidenced that the addition of the B\(_2\)O\(_3\) significantly enhances the specific capacity but does not improve the cycling stability of the LiVMoO\(_6\).

Acknowledgements

The experiments were performed with equipment included in the National Infrastructure N1 SEVE supported by the Ministry of Education and Science under grant agreement № DO1-160/28.08.18. Some of this work was done while the author M. Milanova was visiting the Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University under financial support by The Matsumae International Foundation (MIF) in the framework of the Matsumae International Fellowship Program April-September 2014.

REFERENCES

2. R. Yu, X. Wang, D. Wang, L. Ge, H. Shu, X. Yang, Self-assembly synthesis and electrochemical performance of Li\(_{1.5}\)Mn\(_{0.75}\)Ni\(_{0.15}\)Co\(_{0.10}\)O\(_{2+δ}\) microspheres with multilayer shells, J. Mater. Chem. A, 3, 2015, 3120-3129.
6. C. Julien, 4-Volt cathode materials for rechargeable lithium batteries wet chemistry synthesis, structure and electrochemistry, Ionics 6, 2000, 30-46.
10. Y. Liang, S. Yang, Z. Yi, M. Li, J. Sun, Y. Zhou, Rheological phase synthesis and electrochemical performances of LiVMoO\(_6\) as a high-capacity anode material for lithium ion batteries, J. Mater. Sci., 40, 2005, 5553-5555.
12. L. Zhou, Y. Liang, L. Hu, X. Han, Z. Yi, J. Sun, S. Yang, Much improved capacity and cycling perfor-
mance of LiVMoO$_6$ cathode for lithium ion batteries, J. Alloys Comp., 457, 2008, 389-393.


16. S. Jouanneau, W. Bahmet, K.W. Eberman, L.J. Krause, J.R. Dah, Effect of Sintering Agent, B$_2$O$_3$,on Li[Ni$_{0.5}$Co$_{0.5}$Mn$_{0.5}$]O$_2$, Materials, J. Electrochem. Soc., 151, A1789-A1796.


20. Y.Feng, Y. Li, F. Hou, Boron doped lithium trivanadium date as a cathode material for an enhanced rechargeable lithium ion batteries, J. Power Sources, 187, 2009, 224-228.


22. R. Run, A. Wadsley, The crystal structure of ThTi$_2$O$_6$ (brannerite), Acta Cryst., 21, 1966, 974-978.


26. J. Li, E. Murphy, J. Winnick, P.A. Kohl, Studies on the cycle life of commercial lithium ion batteries during rapid charge-discharge cycling, J. Power Sources, 102, 2001, 294-301.
