Rheological phase synthesis and electrochemical performances of $LiVMoO_6$ as a high-capacity anode material for lithium ion batteries

YONGGUANG LIANG, SHUIJIN YANG, ZONGHUI YI, MING LI, JUTANG SUN*, YUNHONG ZHOU
Department of Chemistry, Wuhan University, Wuhan, 430072, People's Republic of China
E-mail: jtsun@whu.edu.cn

Research for new anode materials has been stimulated by the development of lithium ion batteries since the introduction of carbon as a negative material in 1990 by Sony Energetics Inc. Some metal oxides and metal-based composite oxides [1, 2], nitrides [3, 4] and intermetallics [5, 6], which capacities are comparable or superior to those of graphitized carbon (theoretical maximum capacity of 372 mA hr g^{-1} [7, 8]), were considered as possible candidates for next generation of anode materials. Recently, several vanadium composite oxides exhibited their high-capacity and high-rate performance as negative electrode materials due to their open structure and interesting characteristics from a standpoint of the variety of oxidation states [9–12].

$LiMoVO_6$ crystallizes with the $ThTi_2O_6$ brannerite-type structure [13] and its electrochemical properties as a positive electrode material for lithium secondary batteries have been investigated [14–16]. But the performance of $LiMoVO_6$ as negative electrode material was seldom reported. In this work, brannerite-type $LiMoVO_6$ powder was obtained by rheological phase reaction method [17]. The result of electrochemical tests showed that the obtained $LiMoVO_6$ as a novel anode material was also feasible and demonstrated very high energy density.

The precursor was prepared by rheological phase reaction method. Analytical reagent grade chemicals, $LiOH{\cdot}H_2O$, NH_4VO_3 and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, were used as the starting materials and fully mixed by grinding in a 1:1:1 molar ratio. A proper amount of water was added to get a rheological body and the mixture was sealed in a closed container for 8 hr at 80 °C. After drying under vacuum at 80 °C for several hours, the precursor was pyrolyzed at 550 °C for 10 hr in air, and soft yellow powder $LiMoVO_6$ was obtained. Thermogravimetry and differential thermal analysis (TG/DTA) of the precursor were performed by the Netzsch STA 449 thermal analysis system at a heating rate of 10 °C/min in air. The X-ray diffraction (XRD) measurements of the sample were carried out by Shimadzu XRD-6000 diffractometer with CuKα_1 radiation ($\lambda = 1.54056$ Å). The particle sizes and morphological features were observed by a scanning electron microscope (Hitachi SEM X-650).

Electrochemical experiments were carried out in simulated cell system, using $LiVMoO_6$ as a working electrode and lithium as a counter electrode. The working electrode pellet (1 cm diameter circle) was prepared from obtained $LiVMoO_6$, carbon black and polytetrafluoroethylene (PTFE) in the weight proportion 80, 15, 5, respectively. The electrolyte used was 1 mol L^{-1} with $LiPF_6$ dissolved in a 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) by volume. A porous polypropylene film (Celegar 2300) was saturated in electrolyte to separate two electrodes. The cell was discharged and charged between 3.0 and 0.01 V vs. Li^+/Li at a constant current density of 100 mA g^{-1}.

The TG and DTA curves of the precursor are shown in Fig. 1. It indicates that the decomposition of the precursor proceeds as follows. The endothermic peaks on the DTA curve located at about 120 °C, 216 °C and 332 °C are due to the decomposition of ammonium molybdates [18]. The peak at about 454 °C and 494 °C in the DTA curves corresponds to the formation of $LiMoVO_6$ and its crystallization of the brannerite phase [16]. However, the sharp endothermic peak at 650 °C is attributed to the thermal decomposition of $LiMoVO_6$ [19].

The XRD pattern of prepared $LiMoVO_6$ is presented in Fig. 2, which exhibited typical characteristics of brannerite-type $LiMoVO_6$ with cell parameters $a = 9.3364(8)$ Å, $b = 3.6436(3)$ Å, $c = 6.6326(7)$ Å and $\beta = 111.622(9)^\circ$, which agrees with literature [13].

Fig. 3 exhibits scanning electron micrographs of the powders of $LiVMoO_6$. As seen from the morphology, the presence of loosely stacked grains agglomerated by particle (average size 700 nm) with a porous state is noteworthy, which average size is 4 μm estimated from SEM data. Nevertheless, one cannot expect the above features in similar compounds prepared via conventional solid-state reaction [14–16], such as submicronic grains and porous state, which are very desirable for a material to be employed as electrode-active material in rechargeable lithium-containing batteries.

Fig. 4 shows the charge and discharge curves of $LiMoVO_6$/Li test cell at a constant current density of 100 mA g^{-1} in first two cycles. The initial discharge

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* Author to whom all correspondence should be addressed.

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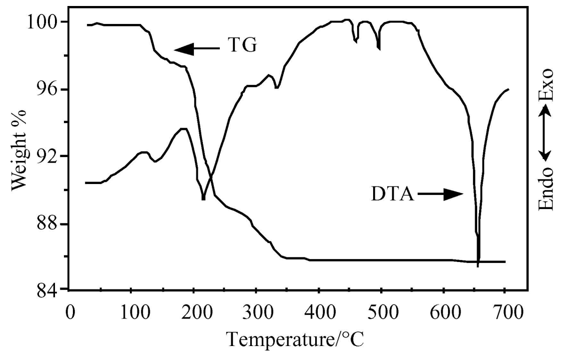

Figure 1 TG and DTA curves of the precursor.

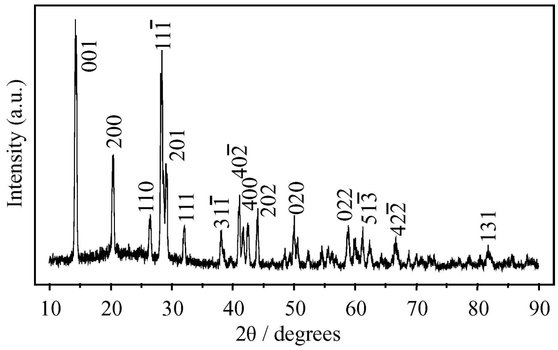

Figure 2 XRD patterns of brannerite-type $LiMoVO_6$.

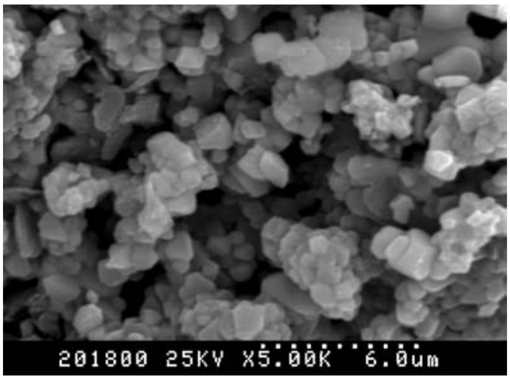

Figure 3 SEM image of $LiMoVO_6$.

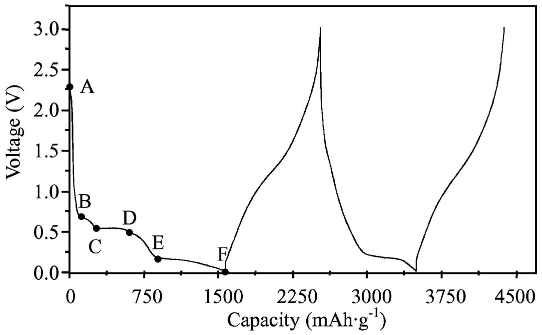

Figure 4 The charge and discharge curves of $LiMoVO_6$/Li test cell at a current density of 100 mA g^{-1}.

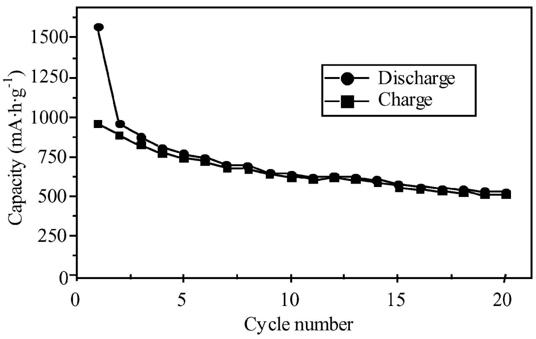

Figure 5 Cycle performance of $LiMoVO_6$ at current density of 100 mA g^{-1}.

capacity is 1572 mA hr g^{-1} with an high reversible capacity about 964 mA hr g^{-1}. The plateaus during the charge process emerge below 2.0 V, which is suitable for practical application.

As shown in Fig. 4, there are four potential plateaus located at 0.703 V (BC), 0.541 V (CD), 0.488 (DE) and 0.178 V (EF) in the first discharge process and the capacity of above four plateaus is 170 mA hr g^{-1}, 344 mA hr g^{-1}, 268 mA hr g^{-1} and 696 mA hr g^{-1}, respectively. In the following cycle, the plateau at 0.488 and 0.178 V still exist but others disappeared. The irreversible lithium-insertion reaction includes the process of AB, BC and CD with total capacity of 608 mA hr g^{-1} due to the formation of solid electrolyte interface (SEI) and the irreversible reaction of lithium with oxygen atoms in the active material in respect [11]. Later two plateaus (DE, EF) capacity is 964 mA hr g^{-1}, nearly equal to that of the first extraction reaction of lithium. The testing results agree well with the speculated results according to the variety of V and Mo oxidation states based on the mechanism described in literature [11].

The cycle performance of brannerite-type $LiMoVO_6$ within 20 cycles is shown in Fig. 5. The reversible capacity diminished rapidly in the first four cycles. In the following cycles, the process of charge and discharge become relatively stable and the efficiency of charge and discharge amounts to 97.0%. The charge capacity retention from the fifth to twentieth cycle is 66.7% with an average capacity fade of 2.08% per cycle.

From the results above, brannerite-type $LiMoVO_6$ demonstrates a large reversible capacity, low charge plateaus potential and relatively excellent cycleability as negative electrode material. The improvement of cycleability of $LiMoVO_6$ will help practical application as anode materials for lithium ion batteries in the future.

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