

Much improved capacity and cycling performance of LiVMoO_6 cathode for lithium ion batteries

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Received 23 October 2006; received in revised form 22 February 2007; accepted 24 February 2007

Available online 28 February 2007

Abstract

Spherical LiVMoO_6 nanocrystals as cathode for lithium ion batteries were synthesized using a solvothermal reaction method. Powder XRD data indicate that a single phase LiVMoO_6 with brannerite-type structure is obtained at 550°C by the thermal treatment of the precursor for 6 h. SEM image shows that the particles are composed of loosely stacked spheres with a uniform particle size about 40 nm. The electrode properties of LiVMoO_6 have also been studied by galvanostatic cycling and ac impedance spectroscopy. LiVMoO_6 nanospheres delivered 172 mAh g^{-1} capacity in the initial discharge process with a reversible capacity retention of 94.4% after 100 cycles in the range of 3.6–1.80 V versus metallic Li at a current density of 100 mA g^{-1} . The microstructure developed in the electrodes give evidence that the particle size and morphological properties play an important role in the much improved capacity and cycling stability at large currents than ordinary samples.

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Keywords: LiVMoO_6 ; Nanomaterials; Electrochemical performance; Cathode; Lithium ion batteries

1. Introduction

Since the commercialization of the lithium ion batteries by Sony Energetic, much efforts have been focused on the development of LiNiO_2 , $\text{Li}(\text{Ni}, \text{Co})\text{O}_2$, and LiMn_2O_4 as alternatives to the expensive and toxic cathode material LiCoO_2 [1]. Nevertheless, no practical materials mentioned above that satisfy the requirements of the lithium secondary batteries as well LiCoO_2 have yet been identified. In this regard, many scientists are searching for new cathode materials, such as those containing vanadium and iron, to enlarge the application in electric vehicles and hybrid electric vehicles, where low-price, long calendar life and high rate capability are expected [2,3].

Vanadium-based composite oxides have been paid special attention as possible cathode materials for rechargeable lithium batteries in recent years [4–9]. Among them, brannerite-type LiVMoO_6 has been reported both as cathode and anode materials because of their open structure and interesting characteristics

from a standpoint of the variety of oxidation states [9–15]. Michael et al. [9] show low discharge capacity in the range of 3.0–4.5 V suggesting the presence of non-stoichiometric compounds with the presence of V^{4+} or Mo^{5+} ions differed substantially from monophasic LiVMoO_6 . The long life cycling instability of brannerite cathode materials upon lithium insertion has been discussed by Cushing et al. [10]. However, the structural arrangement of VO_6 octahedra play an important role in their ability to intercalate Li ions and gives a poor cycle performance for the deformation of structure [11–12]. A significant capacity fade during cycles shows the instability and the attempt to prepare LiVMoO_6 materials using different methods showed a limited success to improve the poor stability as well as reversible capacity at large currents [13].

It is known that the manipulation of materials in nanoscale is a feasible means for optimizing electrode properties to achieve significantly enhanced capacity and fast insertion/extraction kinetics, which offer promises to the application of lithium ion batteries in high-power devices [16]. In this paper, we introduced a novel route to synthesize spherical LiVMoO_6 nanocrystals using a solvothermal reaction method. The electrode properties of LiVMoO_6 as cathode for lithium ion batteries have been much improved with significant enhanced capacity as well as

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cycling stability at larger currents than those reported previously in literatures [9–13].

2. Experimental

2.1. Materials preparation

A mixture of $\text{LiOH} \cdot \text{H}_2\text{O}$, NH_4VO_3 and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in a 1:1:1 molar ratio of Li:V:Mo was used as the starting materials. A proper amount of absolute alcohol was added to the mixture to get a dense solution and the solution was stirred by a motor in whole process. Subsequently, small volume of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (38 wt.%) solution were dropped into salt solution to make a partial reduction reaction of V and Mo. The slurry was transferred into a container and sealed in an autoclave with a solvothermal process. After dried under vacuum at 80°C , a gray precursor was obtained. The precursor was then treated at 550°C in air for 6 h to give yellow LiVMoO_6 powders. Traditional solid-state reaction method [10] and sol-gel method [9] were also used to prepare the LiVMoO_6 bulk sample and micron powders as a contrast.

2.2. Physical characterization

XRD data were collected on a Bruker AXS D8 diffractometer using $\text{Cu K}\alpha$ 1 radiation ($1.54056 \text{ \AA}$) in the 2θ range of 10 – 120° with a step-scan mode and 0.01° step were normalized to a constant acquisition time of 4 s. The thermal stability of the precursor was examined by means of TG and DTA with a Netzsch STA 449 thermal analysis system at a heating rate of $5^\circ\text{C}/\text{min}$ from 20 to 800°C in a flow of air. XPS measurements were performed on a KRATOS XSAM800 photoelectron spectrometer with an exciting source of $\text{Mg K}\alpha = 1253.6 \text{ eV}$. The microstructure of LiVMoO_6 powders and electrode were observed by a scanning electron microscope (FEI QUANTA 200).

2.3. Charge/discharge testing

The galvanostatic cycling tests were carried out using the coin-type cell (size: 2016), which consisted of a working electrode and a lithium foil counter electrode separated by a Celgard 2400 microporous membrane. Electrodes was prepared by mixing LiVMoO_6 powders with 10% acetylene black and 5% PTFE, compressing the mixture onto a nickel gauze current collector. A 1 mol/L solution of LiClO_4 dissolved in EC/DEC (1:1, volume) was used as the electrolyte. The cells were assembled in an Argon-filled glove box (Mikrouna Super 1220/750) and cycled between 1.80 and 3.60 V versus metallic lithium. ac impedance measurements were performed on CHI660A by applying an ac voltage of 5 mV amplitude in the frequency range 1–10 MHz.

3. Results and discussion

Fig. 1 shows the TG–DTA curves of the precursor grown by the wet chemical technique. There is a successive loss before 198°C , attributed to the general behavior of the precursor synthesized by wet chemical route for removing of absorbed small molecule substances, e.g., alcohol, ammonia and water with about 22 wt.% loss. The stage between 205 and 294°C was complicated and it could be presumed that sharp endothermic peak at ca. 284°C in the DTA curves is the combination of violent decomposition and oxidation process of low-valence vanadium and molybdenum oxides to form a homogeneous LiVMoO_6 phase. Subsequent endothermic peak appears about 448°C corresponds to a crystallization of LiVMoO_6 [13] and a well-brannerite phase was obtained at 550°C . The endothermic peak at ca. 650°C is attributed to the thermal decomposition of LiVMoO_6 [13,15].

Fig. 2 illustrates the refined powder XRD patterns of the as-prepared LiVMoO_6 sample. The WinPLOTR program

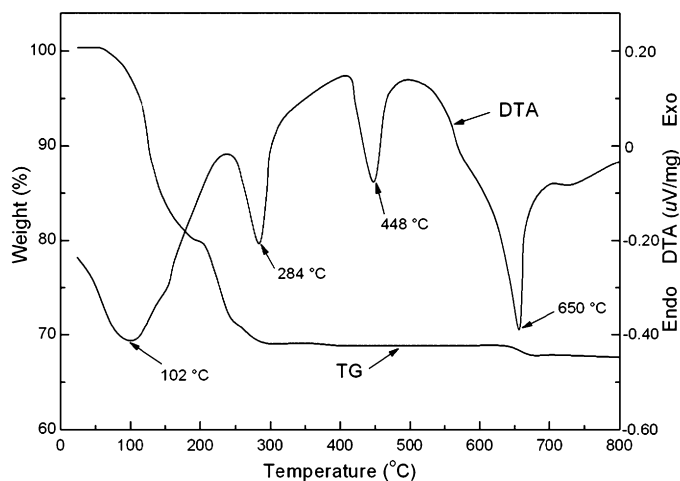


Fig. 1. TG and DTA curves of the precursor.

[17] was used for the peak position calculation and the automatic indexation was carried out with the DICVOL04 program [18] against the first 21 experimental diffraction peaks. A monocline solution was found with unit-cell parameters of $a = 9.34669(4) \text{ \AA}$, $b = 3.53278(5) \text{ \AA}$ and $c = 6.63548(3) \text{ \AA}$, $\beta = 111.640(4)^\circ$ with the following figures of merit: $M_{20} = 134.6$, $F_{20} = 116.7$. Model-based refinements of all profile and structural parameters yield to the following reliability factors: $R_{\text{obs}} = 4.79\%$, $R_p = 5.65\%$, $R_{\text{wp}} = 8.37\%$ with all the isotropic atomic displacement parameters defined. The best solution was suggested with unit-cell parameters, $C2/m$ space group, $a = 9.25460(2) \text{ \AA}$, $b = 3.64843(5) \text{ \AA}$, $c = 6.63568(3) \text{ \AA}$, $\beta = 110.155(6)^\circ$, $V = 210.229(13) \text{ \AA}^3$, $Z = 2$. The major indexation was also listed in Fig. 2.

Fig. 3 displays the XPS spectra of V 2p doublet and Mo 3d doublet for the precursor and LiVMoO_6 nanospheres. In the designed route of partial reduction, self-assembly and re-oxidation, V(+5) and Mo(+6) in the starting materials were firstly reduced by $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ to low valence. The spectral lines in Fig. 3A at 516.4 and 517.1 eV are attributed to the core $2p_{3/2}$

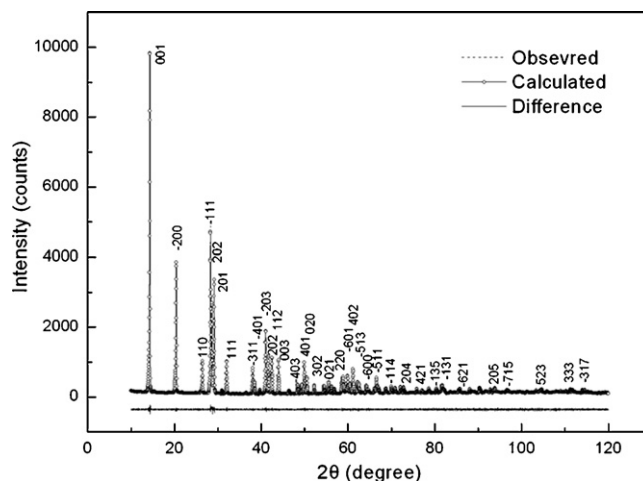


Fig. 2. Refined powder XRD patterns of the as-synthesized spherical LiVMoO_6 nanocrystals.

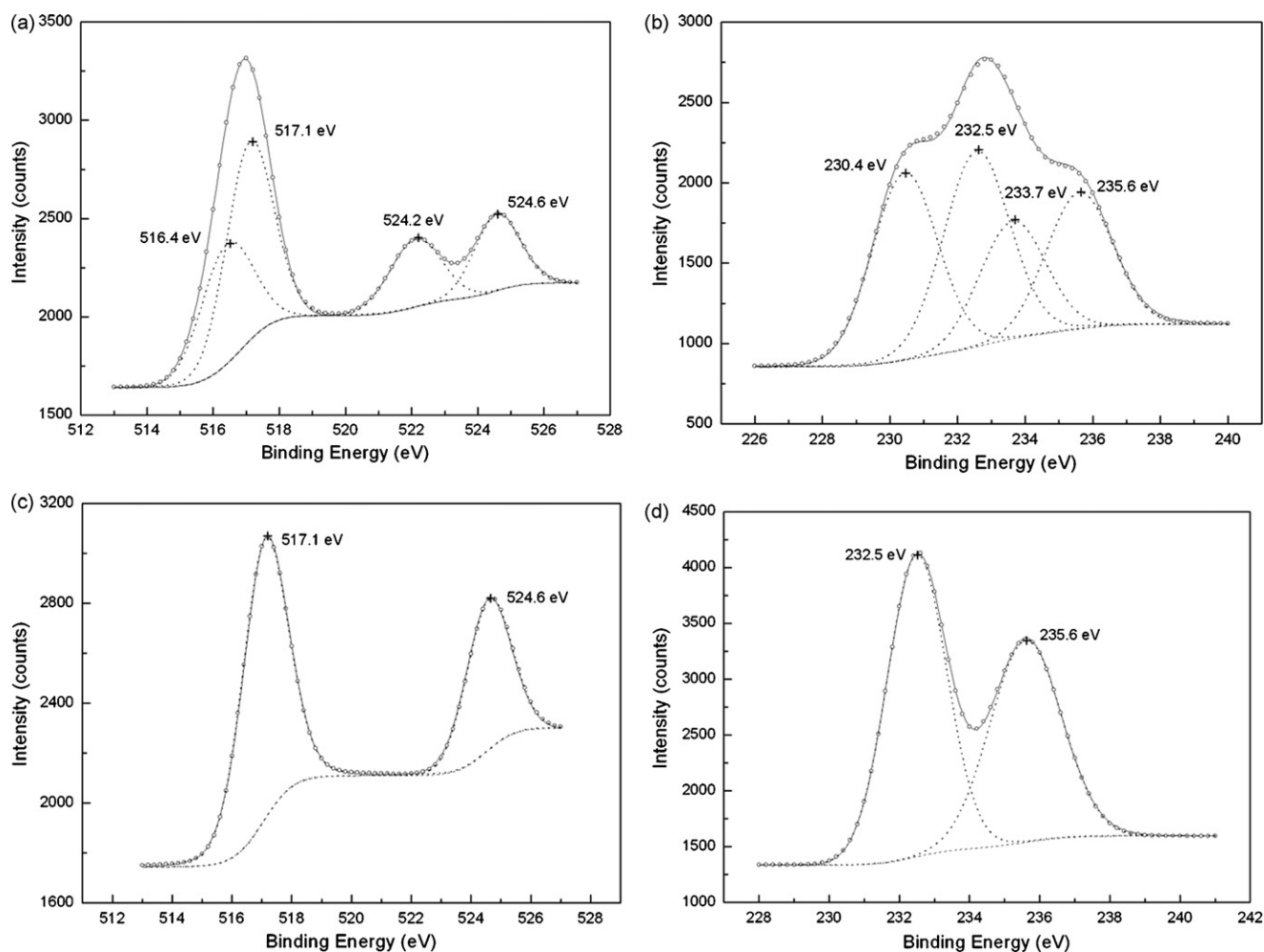


Fig. 3. XPS spectra of V 2p doublet and Mo 3d doublet: (A) V 2p doublet in the precursor; (B) Mo 3d doublet in the precursor; (C) V 2p doublet in LiVMoO₆ nanospheres; (D) Mo 3d doublet in LiVMoO₆ nanospheres.

peaks for V(+4) and V(+5) [19], respectively. The presence of the lines at 230.4 and 233.7 eV in Fig. 3B correspond to 3d_{3/2} and 3d_{5/2} peaks of Mo(+5), indicating a partial reduction of Mo(+6) [20]. Subsequent oxidation of the precursor in the air gave a single phase LiVMoO₆ confirmed by XRD data, which is consistent with the characteristic shape of V(+5) and Mo(+6) as shown in Fig. 3C and D.

Fig. 4 shows the SEM images of obtained LiVMoO₆ powders and the electrode. The particles in Fig. 4A were well spherical with uniform diameter size about 40 nm, which are loosely stacked with a porous state, providing high specific surface area. It is different with coarse-grained powders synthesized via high-temperature reactions [10–12] and sol–gel method [9] with a reaction time of no less than 24 h. That is, less energy is cost during the preparation process of power storage materials. Moreover, the physical features of this material are apparently controllable depending on the N₂H₄·H₂O solution used, which play a crucial role in the process of partial reduction, self-assembly and re-oxidation. This new adaptable structure prompted us to construct different morphologies in which sizes and chemical environments could be varied [21]. An example of the microstructure developed in the electrodes

after 100 cycles are shown in Fig. 4B. The grain size and spherical morphology were retained, which helps to get proper particle size as stable cathode materials for high rate current rechargeable lithium batteries despite the presence of small amount of Li₂MoO₄ [13] phase with spherical particles about 220 nm.

The typical discharge–charge profiles of LiVMoO₆ nanospheres are presented in Fig. 5A with a constant current density of 100 mA g^{−1}. There is a potential plateau at 2.25 V in the activated process by initially discharging to 1.8 V and a gradually vanishing plateau at about 2.4 V in the following cycles, which is lower than the reported results [9–13]. The charge plateaus at about 2.7, 3.4 and 3.7 V correspond to Mo⁴⁺/Mo⁵⁺, Mo⁴⁺/Mo⁵⁺ and V⁴⁺/V⁵⁺ pairs, respectively. In order to evaluate the relationship of electrochemical properties and physical characteristics, ac impedance was performed on LiVMoO₆ materials prepared from different methods. Fig. 5B shows impedance spectra of three LiVMoO₆ samples in the end of the initial charge cycle, nanospheres via the wet chemical technique, micron powders by sol–gel method [9] and bulk sample from traditional solid-state reaction [10], respectively. The semicircle observed in the middle frequency region can be attributed to the impedance of charge transfer reaction (*R*_{ct})

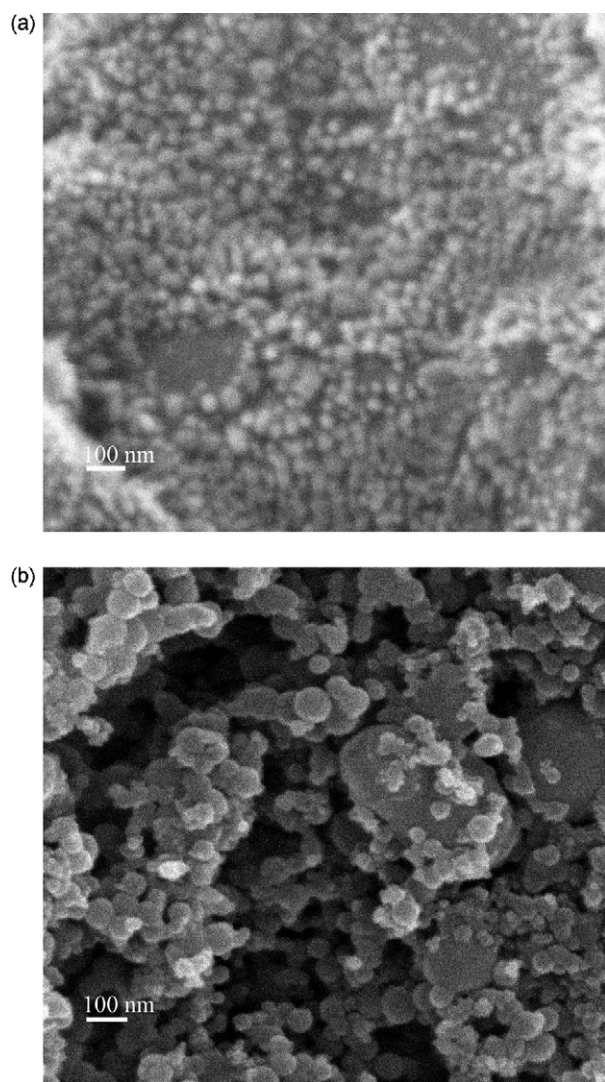


Fig. 4. Particle sizes and morphological features: (A) SEM image of LiVMoO_6 nanospheres; (B) SEM image of LiVMoO_6 electrode after 100 cycles.

and a Li ionic diffusion process in low frequency region. There is a noticeable decrease in the impedance of charge transfer reaction as well as Li^+ ion diffusion of LiVMoO_6 electrode materials (average particle size of 40 nm, 750 nm and 5 μm). Since lithium-insertion and extraction are in general limited by the rate of diffusion, the aforementioned features of smaller grain size can favour Li^+ ions mobility in the particles by shortening the ion diffusion pathway. That is, a large current capability of LiVMoO_6 nanospheres is offered.

Cycling performance of three LiVMoO_6 samples synthesized via different methods mentioned above is presented in Fig. 6. It is clearly that Li/LiVMoO_6 cells display significantly enhanced capacity and cycling performance while the decrease of particle sizes. In fact, the physical properties of LiVMoO_6 nanospheres in this work provide a full Li ionic diffusion and electron exchange. As mentioned above, one cannot expect the above features in compounds prepared via conventional reactions [9–12], such as nano-sized grains and porous state, which are very desirable for a material to be employed as electrode

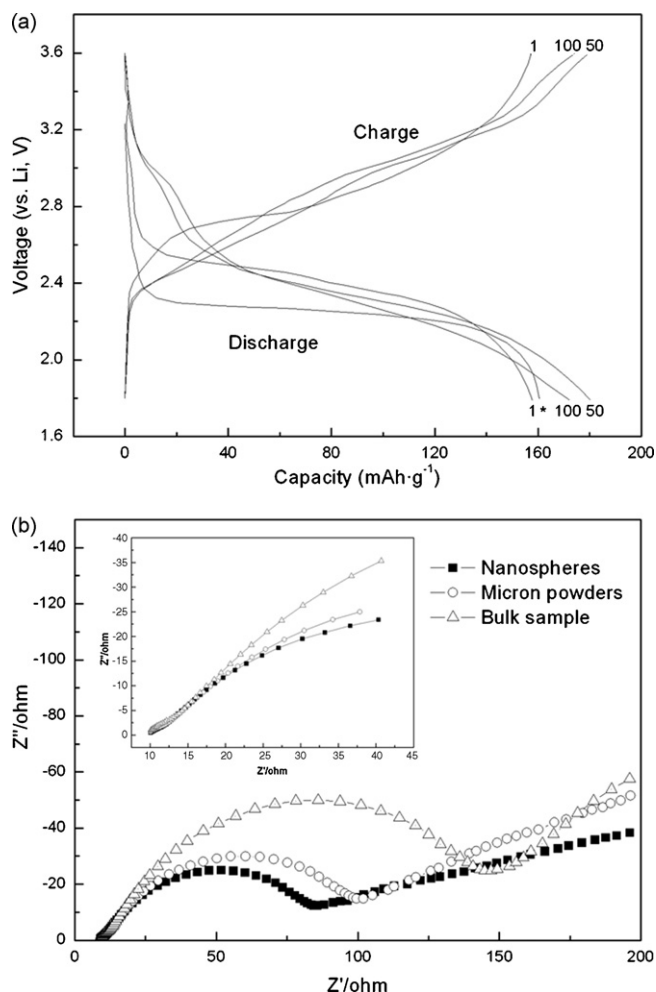


Fig. 5. Electrochemical performance of Li/LiVMoO_6 cells: (A) discharge and charge curves of the cell at a current rate of 100 mA g^{-1} for 1st cycle, 50th cycle and 100th cycle; (*) for the activated process by discharging to 1.8 V; (B) ac impedance spectra of LiVMoO_6 cells made by different methods charged to 3.8 V.

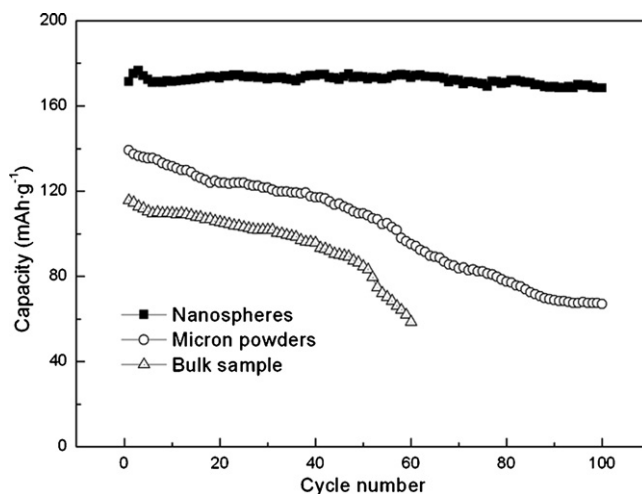


Fig. 6. Cycling performance of different Li/LiVMoO_6 cells made by different methods at a current rate of 100 mA g^{-1} .

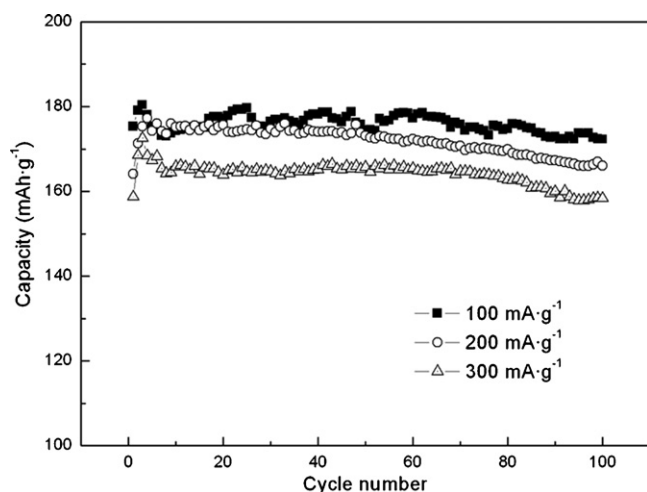


Fig. 7. Cycling performance of Li/LiVMoO₆ cell at different current rates.

material in rechargeable lithium-containing batteries. On contrast, to larger particles of coarse-grained LiVMoO₆ powders, the rate of ionic diffusion through the particle is slow relative to the effective current density (the rate of charge transfer at the surface). This would result in a radial lithium concentration gradient with the particle.

Fig. 7 shows the cycling behaviors of LiVMoO₆ nanospheres at different current rates. The discharge capacity ascends slightly in the first three cycles, following a gradually vanishing, then keep stable. The activated LiVMoO₆ displays excellent cycling stability at large currents with discharge capacity of 172, 166 and 158 mAh g⁻¹ after 100 cycles between 3.6 and 1.80 V at a current density of 100, 200 and 300 mA g⁻¹, respectively. Average coulombic efficiency at different current rate is no less than 96.0% from the first cycle to the 100th. Li-ion diffusion became easier for full Li-intercalating as well as better capacity utilization due to smaller average grain size and the increasing exposed surface area. Clearly, there is a correlation between the cycling performance of the LiVMoO₆ powders and their morphological properties.

4. Conclusions

Spherical LiVMoO₆ nanocrystals have been prepared by a novel wet chemical technique using solvothermal reaction method. The electrode properties of obtained LiVMoO₆ material imply there is a correlation between their excellent cycling per-

formance at large current and the nature of nanostructures. The manipulation of materials in nanometer scale is useful for optimizing LiVMoO₆ electrode properties for rechargeable lithium batteries.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (No. 20771087).

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