ELSEVIER Science Press
Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 26(2016) 2687−2692
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Influence of synthesis temperature on electrochemical performance of polyoxomolybdate as cathode material of lithium ion battery

Wen-liang LI[1,2], Er-fu NI[2], Xin-hai LI[1], Hua-jun GUO[1]

1. School of Metallurgy and Environment, Central South University, Changsha 410083, China;
2. Highpower International Inc., Shenzhen 518111, China

Received 31 May 2016; accepted 25 September 2016

Abstract: In order to improve the electrochemical performance of polyoxomolybdate $Na_3[AlMo_6O_{24}H_6]$(NAM) as the cathode material of lithium ion battery, the NAM materials with small particle size were synthesized by elevating the synthesis temperature in the solution. The as-prepared NAM materials were investigated by FT-IR, XRD, SEM and EIS. Their discharge−charge and cycle performance were also tested. The results show that the particle size decreases to less than 10 μm at the temperature of higher than 40 °C. When synthesized at 80 °C, the NAM with the smallest particle size (~3 μm) exhibits the best electrochemical performance such as high initial discharge capacity of 409 mA·h/g and coulombic efficiency of 95% in the first cycle at 0.04*C*.

Key words: polyoxomolybdate; lithium ion battery; cathode material; high capacity

---

1 Introduction

The worldwide demand for energy storage devices has increased rapidly year by year. Lithium ion battery (LIB) as one of the most suitable energy storage systems has been intensively investigated since 1990s, because of their higher energy density and more stable cycle performance compared with those of lead-acid batteries and nickel-metal hydride battery [1−3]. LIB is attractive power sources for a variety of applications, such as portable electronic devices, transportation vehicles, and stationary storage of renewable energy sources like solar and wind. In current LIB technology, it is generally acknowledged that the cell voltages and capacities are mainly determined by the cathode material which is also the limiting factor for lithium ion transfer [4]. The conventional cathode materials mainly focus on the transition metal intercalation oxides, such as the layered compounds $LiMO_2$ (M=Co, Ni, Mn, etc.), spinel compounds LiM_2O_4 (M=Mn, etc.), and olivine compounds $LiMPO_4$ (M=Fe, Mn, Ni, Co, etc.) [5−22]. However, the achievable specific capacities of the conventional cathode materials are usually lower than 200 mA·h/g, which are insufficient for meeting the increasing energy demand for large-scale applications, such as hybrid electric vehicles and electric vehicles.

Polyoxometalates (POM) have been recently studied as the cathode/anode materials of lithium ion battery [23−34]. Different form the conventional cathode materials, lithium ion can react with the molecular cluster ion units that are independent from the recoverability of crystal structure. Furthermore, multiple electron redox can proceed by the transition metal with high valence number like vanadium and molybdenum in the molecular unit, so high capacity with deep discharge in the wide voltage window could be obtained in POM. Nanosize polyoxovanadates $K_7[NiV_{13}O_{38}]$ and $K_7[MnV_{13}O_{38}]$ have been prepared by re-crystallization in the solution containing organic solvent acetone, the nanosize particles showed improved electrochemical performance [24,30]. The polyoxomolybadate $(NH_4)_6[NiMo_9O_{32}]$ re-crystallized in nanosize porous Ketjen Black (KB) exhibited high rate performance at the improved current density [32]. However, the cycle performance of POM was degraded when decreased the particle size to nanoscale. It is suggested that the poor cycle performance of the nanosize particle should be due to the increased catalysis of POM to the electrolyte oxidation decomposition. The as-prepared Anderson type polyoxomolybadate $Na_3[AlMo_6O_{24}H_6]$ (NAM) usually shows large particle size, which greatly suppresses the

---

Corresponding author: Er-fu NI; Tel: +86-755-89686522; E-mail: nierfu0733@163.com
DOI: 10.1016/S1003-6326(16)64396-0

electrochemical performance, and there is no report that how to decrease the particle size of the as-prepared NAM in the synthesis process. In this work, the influence of synthesis temperature on the particle size of the NAM was studied, and the electrochemical performance of the NAM was investigated.

2 Experimental

The synthesis method of NAM was reported in Ref. [35]. The detailed synthesis procedure is as follows. Firstly, 7.498 g $AlCl_3·6H_2O$ was dissolved in 125 mL distilled water, then 17.5 g $Na_2MoO_4·2H_2O$ was added to the solution. The pH of the solution was adjusted to 1.8 by dropwise addition of 36% HCl. The solution was stabilized at pH 1.8 for 10 min, then evaporated at 60, 70, 80, 90 °C, respectively. The crystals were precipitated out and were filtered, and then washed with ethanol−water mixture solution. All of the as-prepared samples were dried at 120 °C for 1 h before electrode preparation. The sample at 40 °C was also synthesized by the reported method for control [30].

Fourier transform infrared (FT-IR) spectra were collected with a spectrometer (Bruker, Alpha) in the range of 400−1200 cm^{-1}. The crystal structure of as-prepared NAM was characterized by a powder X-ray diffractometer (XRD) (Bruker, AXS GMBH) with Cu K_α (40 kV, 40 mA) radiation. The diffraction data were recorded from 10° to 90° in 2θ. The morphologies were observed by field emission scanning electron microscope (FESEM, Nova NanoSEM 450). The particle size distribution was recorded by the particle size analyzer (Malvern Mastersizer 2000). The cathodes were prepared by mixing NAM, carbon ECP 600JD, and polytetrafluoroethylene (PTFE) in a mass ratio of 32:64:4. The electrochemical performance of cathodes was tested at 25 °C by using CR−2032 coin cells, which were assembled in an argon filled glovebox using metallic lithium as anode, and 1 mol/L $LiPF_6$ in a mixed solvent of ethylene carbonate and diethyl carbonate at a volume ratio of 3:7 as electrolyte. Cycle performance was tested on a NEWARE CT−4008 equipment between 1.5 and 4.2 V (vs Li/Li^+) at 0.04*C* (1*C*=455 mA/g). Electrochemical impedance spectra (EIS) were performed with a CHI660C (Shanghai Chenhua) impedance analyzer in the frequency range of 10^5−10^{-2} Hz with an amplitude of 10 mV.

3 Results and discussion

3.1 FT-IR and XRD analysis

To investigate the stability of the molecular cluster ion $[AlMo_6O_{24}H_6]^{3-}$ synthesized at higher temperatures, FT-IR spectra were recorded, as shown in Fig. 1. It is clearly shown that the similar characteristic absorption peaks of the molecular cluster ion are observed at the wavenumber of 400−1000 cm^{-1}. This means that the molecular cluster ion was stable when synthesized at higher temperatures than 40 °C. It can be seen that the vibrational frequencies at 947 and 920 cm^{-1} with strong intensities are assigned to the symmetric and asymmetric stretching of Mo—O bonds, and the other vibrations of 574, 530 and 447 cm^{-1} are attributed to the asymmetric stretching Al—O band and the bending of O—Al—O, Mo—O—Mo bonds. Figure 2 shows the XRD patterns of the as-prepared NAM at the temperatures of 60, 70, 80 and 90 °C, respectively. It can be seen that the crystal structures are consistent with the NAM in ICSD No. 281185. However, the intensity ratios of the as-prepared NAM do not match well with the ICSD pattern, which should be caused by the difference in the orientation of powders, because the conditions for the crystal growth in this work are different from that of the previously reported one [34].

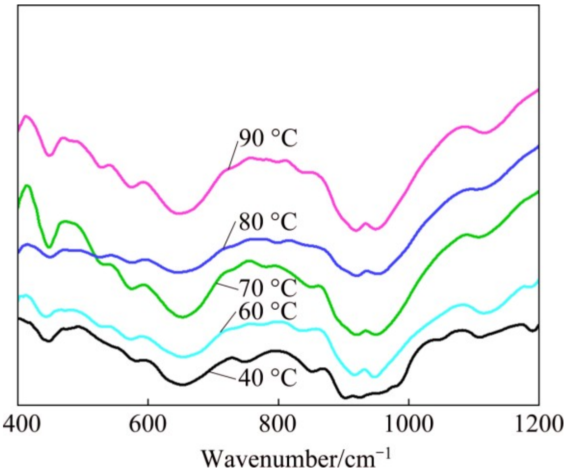

Fig. 1 FT-IR spectra of NAM synthesized at different temperatures

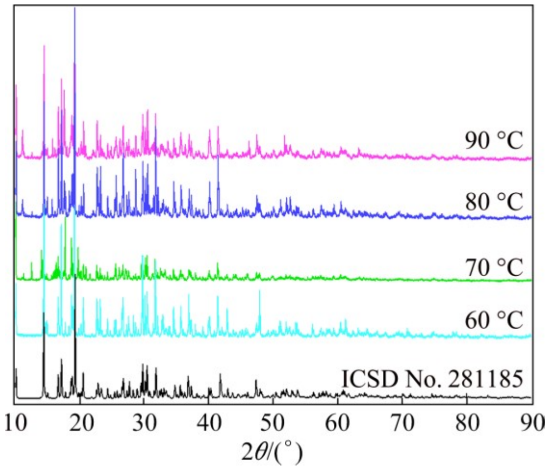

Fig. 2 XRD patterns of NAM synthesized at different temperatures

3.2 Morphologies and particle size distribution

Figure 3 shows the morphologies of the NAM synthesized at different temperatures. It can be seen that the crystals synthesized at the temperatures higher than 40 °C have irregular morphologies, which are similar to the crystals synthesized at 40 °C. The particle size distribution is shown in Fig. 4. It is clearly shown that the particle size is greatly decreased at the elevated temperatures. The particle sizes (D_{50}) are 50.90, 8.23, 6.05, 3.04 and 7.28 μm at the temperatures of 40, 60, 70, 80 and 90 °C, respectively. As we all know, low temperature leads to slow nucleation rate and large particle size. With the increase of synthesis temperature, nucleation rates speeded up and a large amount of crystal nucleus were formed quickly without enough time to grow up; therefore, the particle size of NAM decreased at the elevated synthesis temperature. However, when the synthesis temperature further increased to 90 °C, the agglomeration of small crystal nucleus resulted in the increase of the particle size. This means that the synthesis temperature of 80 °C is the optimum temperature for obtaining the smallest particle. It is well known that the small size particle is helpful to shortening lithium ion diffusion path and improving electrochemical performance.

3.3 Electrochemical performance

Figure 5(a) shows the first discharge−charge performance of NAM synthesized at different temperatures. It can be seen that NAM synthesized at 80 °C showed the largest capacity. Initial discharge capacities of 370.1, 389.4, 393.3, 409.1 and 397.2 mA·h/g were obtained at the temperatures of 40, 60, 70, 80 and 90 °C, respectively. It should be noted

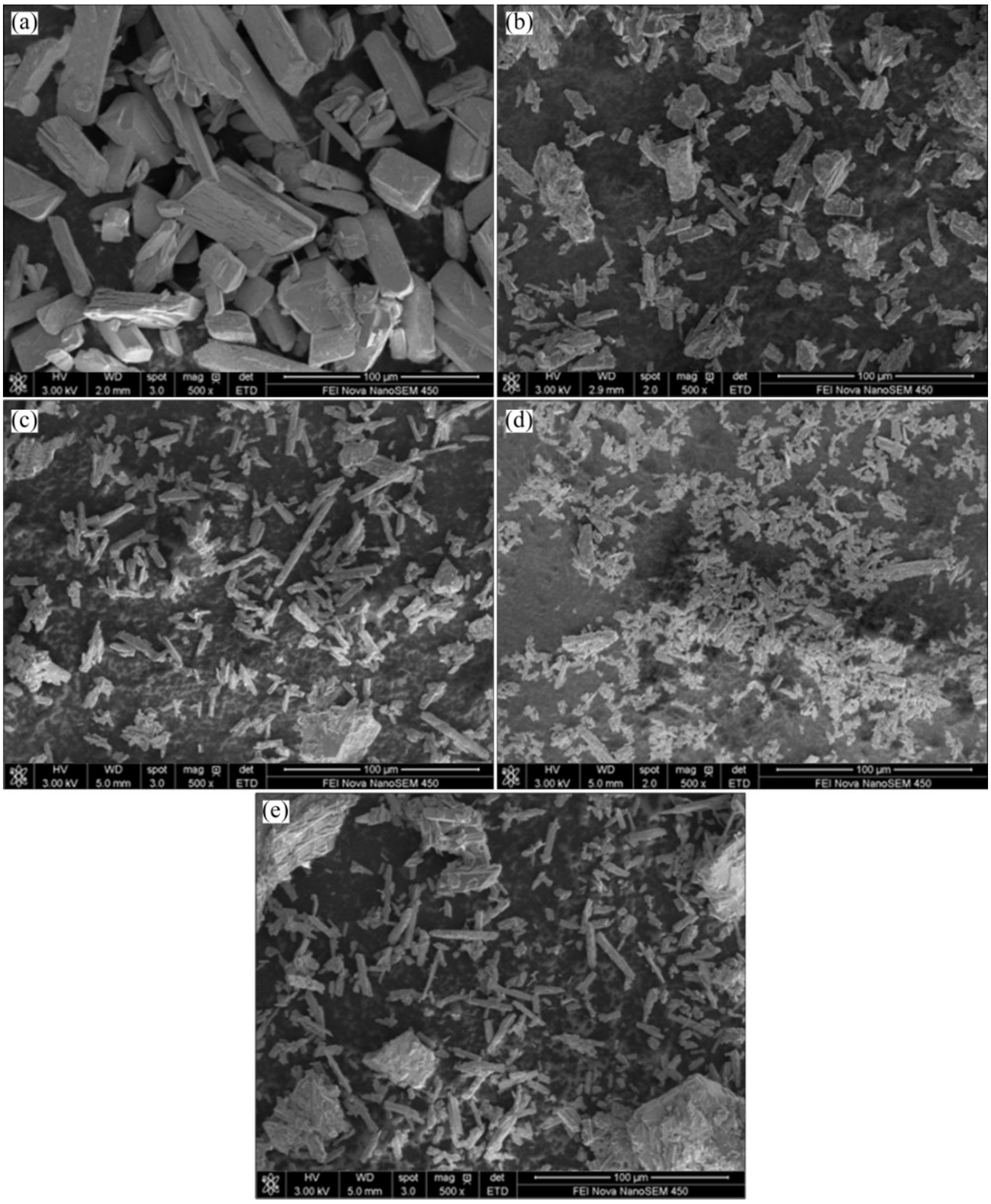

Fig. 3 SEM images of NAM synthesized at different temperatures: (a) 40 °C; (b) 60 °C; (c) 70 °C; (d) 80 °C; (e) 90 °C

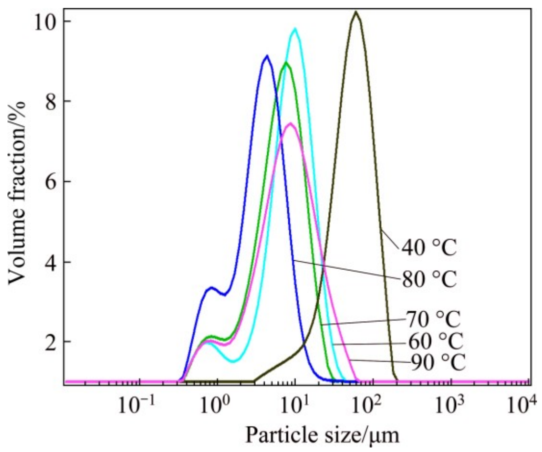

Fig. 4 Particle size distributions of NAM synthesized at different temperatures

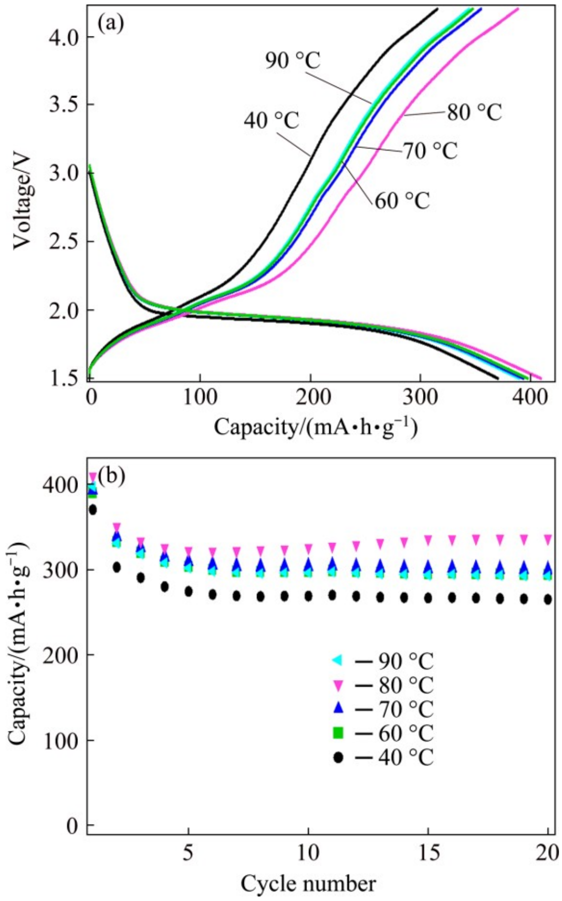

Fig. 5 First discharge−charge curves (a) and cycle performance (b) of NAM at 0.04*C*

that NAM synthesized at 40 °C showed the largest irreversible capacity in the following charge process, which induced the low coulombic efficiency of 85.2% during the first cycle. On the other hand, NAM synthesized at temperatures of 60, 70, 80 and 90 °C showed higher coulombic efficiencies of 88.4%, 90.2%, 94.9%, and 87.5%, respectively. The cycle performance of NAM is shown in Fig. 5(b). The NAM with small particle size showed higher discharge capacity compared with the NAM synthesized at the low temperature of 40 °C. Capacity retention of 82.1% was obtained after 20 cycles for the NAM synthesized at 80 °C. These results demonstrate that the elevated synthesis temperature is beneficial for decreasing the particle size of as-prepared NAM, and furthermore, the smallest particle size could be obtained at 80 °C, which showed higher capacity.

To analyze the effect of particle size on the cycle performance of NAM, EIS measurements were investigated for the samples synthesized at different temperatures after the first cycle, the respective Nyquist plots are shown in Fig. 6. It is clearly shown that all of the Nyquist plots consist of one semicircle in the high-frequency region and a linear part in the low-frequency region. The semicircles in the high-frequency region would be attributed to the resistances of the charge-transfer for the cathode material. The slope lines in the low-frequency region are related to the solid-state diffusion of lithium ions in the cathode. The equivalent circuit proposed to fit the Nyquist plots is shown in the inset of Fig. 6, where R_s is the electrolyte resistance; R_{ct} is the charge-transfer resistance; CPE_{ct} and Z_w are the constant phase element and Warburg impedance, respectively. The R_{ct} values are 170, 140, 136, 88 and 130 Ω at the temperatures of 40, 60, 70, 80 and 90 °C, respectively. The results of EIS indicate that the improved electrochemical performance of NAM should be ascribed to the decrease of particle size, which further improves the electric conductivity of electrode, facilitating the lithium ion diffusion in the electrode.

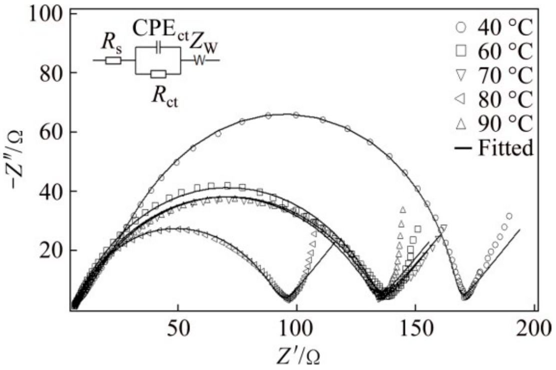

Fig. 6 Nyquist plots of NAM after one cycle at 0.04*C* (Inset: equivalent circuit proposed to fit Nyquist plots)

To further confirm that the downsized particle could significantly improve the electric conductivity, resulting in the improvement of electrochemical performance, the rate capabilities at higher rates were investigated, as shown in Fig. 7. It can be seen that the downsized particle showed much higher capacity than the large size particle. The discharge capacity of 270 mA·h/g can be obtained for NAM synthesized at 80 °C and 1*C*, which is about twice that of the NAM synthesized at 40 °C.

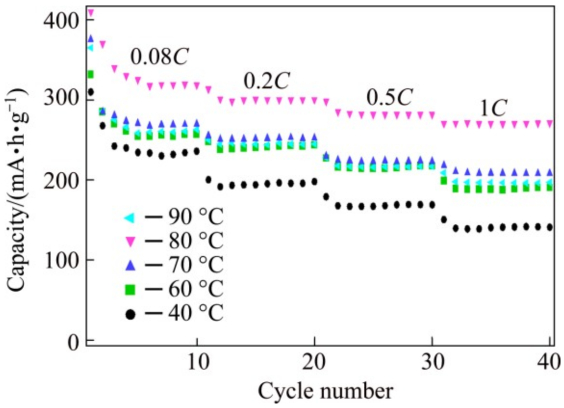

Fig. 7 Rate capabilities of NAM cycled at varied rates

4 Conclusions

Polyoxomolybdate materials with small particle size were synthesized by improving the synthesis temperature in the solution. The crystal structure of as-prepared NAM does not change at different synthesis temperatures. With the increase of the synthesis temperature, the particle size of as-prepared NAM decreases. When synthesized at the temperature of 80 °C, the NAM with the smallest particle exhibits the best electrochemical performance, which is promising to be a kind of new cathode materials for lithium ion battery.

References

[1] AIFANTIS K E, HACKNEY S A, KUMAR R V. High energy density lithium batteries:Materials,engineering, applications [M]. Germany: Wiley-VCH, 2010.

[2] LINDEN D,REDDY T B. Handbook of batteries [M]. 3rd ed. New York: McGraw-Hill, 2001.

[3] ABRAHAM K M, SCHALKWIJK W A V, HASSOUN J. Lithium batteries: Advanced technologies and applications [M]. New Jersey: John Wiley & Sons, Inc, 2013.

[4] XU B, QIAN D N, WANG Z Y, MENG S Y. Recent progress in cathode materials research for advanced lithium ion batteries [J]. Mater Sci Eng R, 2012, 73: 51−65.

[5] AURBACH D. Review of selected electrode–solution interactions which determine theperformance of Li and Li ion batteries [J]. J Power Sources, 2000, 89: 206−218.

[6] CABANA J, MONCONDUIT L, LARCHER D, PALACÍN M R. Beyond intercalation-based Li-ion batteries: The state of the art and challenges of electrode materials reacting through conversion reactions [J]. Adv Mater, 2010, 22: E170−E192.

[7] ELLIS B L, LEE K T, NAZAR L F. Positive electrode materials for Li-ion and Li-batteries [J]. Chem Mater, 2010, 22: 691−714.

[8] SONG Hai-shen, CAO Zheng, ZHANG Zhi-an, LAI Yan-qing, LIU Ye-xiang. Effect of vinylene carbonate as electrolyte additive on cycling performance of LiFePO$_4$/graphite cell at elevated temperature [J]. Transactions of Nonferrous Metals Society of China, 2014, 24(3): 723−728.

[9] GOODENOUGH J B, PARK K S. The Li-ion rechargeable battery: A perspective [J]. J Am Chem Soc, 2013, 135: 1167−1176.

[10] MELOT B C, TARASCON J M. Design and preparation of materials for advanced electrochemical storage [J]. Acc Chem Res, 2013, 46: 1226−1238.

[11] WHITTINGHAM M S. Lithium batteries and cathode materials [J]. Chem Rev, 2004, 104: 4271−4301.

[12] AURBACH D, GAMOLSKY K, MARKOVSKY B, SALITRA G, GOFER Y, HEIDER U, OESTEN R, SCHMIDT M. Study of surface phenomena related to electrochemical lithium intercalation into Li$_x$MO$_y$host materials (M=Ni, Mn) [J]. J Electrochem Soc, 2000, 147(4): 1322−1331.

[13] LEVI M D, SALITRA G, MARKOVSKY B, TELLER H, AURBACH D, HEIDER U, HEIDERB L. Solid-state electrochemical kinetics of Li-ion intercalation into Li$_{1-x}$CoO$_2$: Simultaneous application of electroanalytical techniques SSCV, PITT, and EIS [J]. J Electrochem Soc, 1999, 164(4): 1279−1289.

[14] LI Z, DU F, BIE X F, ZHANG D, CAI Y M, CUI X R, WANG C Z. Electrochemical kinetics of the Li[Li$_{0.23}$Co$_{0.3}$Mn$_{0.47}$]O$_2$ cathode material studied by GITT and EIS [J]. J Phys Chem C, 2010, 114: 22751−22757.

[15] MIZUSHIMA K, JONES P C, WISEMAN P J, GOODENOUGH J B. Li$_x$CoO$_2$ (0<x<1): A new cathode material for batteries of high energy density [J]. Mater Res Bull, 1980, 15: 783−789.

[16] OHZUKU T, UEDA A. Solid-state redox reactions of LiCoO$_2$(R3m) for 4 volt secondary lithium cells [J]. J Electrochem Soc, 1994, 141: 2972−2977.

[17] REIMERS J N, DAHN J R. Electrochemical and in situ X-ray diffraction studies of lithium intercalation in Li$_x$CoO$_2$ [J]. J Electrochem Soc, 1992, 139: 2091−2097.

[18] SCHMIDTJ P, CHROBAK T, ENDER M, IllIG J, KLOTZ D, IVERS-TIFFÉE E. Studies on LiFePO$_4$ as cathode material using impedance spectroscopy [J]. J Power Sources, 2010, 196: 5342−5348.

[19] AMATUCCI G G, PEREIRA N, ZHENG T, TARASCON J M. Failure mechanism and improvement of the elevated temperature cycling of LiMn$_2$O$_4$ compounds through the use of the LiAl$_x$Mn$_{2-x}$O$_{4-z}$F$_z$ solid solution [J]. J Electrochem Soc A, 2001, 148: 171−182.

[20] ARREBOLA J C, CABALLERO A, HERNÁN L, MORALES J. Expanding the rate capabilities of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinel by exploiting the synergistic effect between nano and microparticles [J]. Electrochem Solid-State Lett A, 2005, 8(12): 641−645.

[21] JANG D H, SHIN Y J, OH S M, Dissolution of spinel oxides and capacily losses in 4 V Li/Li$_x$Mn$_2$O$_4$ cells [J]. J Electrochem Soc, 1996, 143: 2204−2211.

[22] THACKERAY M M, SHAO-HORN Y, KAHAIAN A J, KEPLER K D, SKINNER E, VAUGHEY J T, HACKNEY S A. Structural fatigue in spinel electrodes in high voltage (4 V) Li/Li$_x$Mn$_2$O$_4$ cells [J]. Electrochem Solid-State Lett, 1998, 1: 7−9.

[23] UEMATSU S, QUAN Z, SUGANUMA Y, SONOYAMA N. Reversible lithium charge–discharge property of bi-capped Keggin-type polyoxovanadates [J]. J Power Sources, 2012, 217: 13−20.

[24] NI E F, UEMATSU S, QUAN Z, SONOYAMA N. Improved electrochemical property of nanoparticle polyoxovanadate K$_7$NiV$_{13}$O$_{38}$ as cathode material for lithium battery [J]. J Nanopart Res, 2013, 15(16): 1−10.

[25] CHEN W, HUANG L J, HU J, LI T F, JIA F F, SONG Y F. Connecting carbon nanotubes to polyoxometalate clusters for engineering high-performance anode materials [J]. Phys Chem Chem Phys, 2014, 16: 19668−19673.

[26] KUME K, KAWASAKI N, WANG H, YAMADA T, YOSHIKAWA H, AWAGA K. Enhanced capacitor effects in polyoxometalate/graphene nanohybrid materials: A synergetic approach to high performance energy storage [J]. J Mater Chem A, 2014, 2: 3801−3807.

[27] NAUMAAN R, KHAN N, MAHMOOD N, LV C, SIMA G, ZHANG J, HAO J, HOU Y, WEI Y. Pristine organo-imido polyoxometalates as an anode for lithium ion batteries [J]. RSC Adv, 2014, 4: 7374−7379.

[28] NI E F, KUME T, UEMATSU S, QUAN Z, SONOYAMA N. Effect of annealing treatment on the electrochemical properties of polyoxomolybdate $K_4[SiMo_{12}O_{40}]$ as cathode material of lithium battery [J]. Electrochemistry, 2014, 82: 14−18.

[29] NI E F, UEMATSU S, SONOYAMA N. Anderson type polyoxomolybdate as cathode material of lithium ion battery and its reaction mechanism [J]. J Power Sources, 2014, 267: 673−681.

[30] NI E F, UEMATSU S, SONOYAMA N. Lithium intercalation into the polyoxovanadate $K_7MnV_{13}O_{38}$ as cathode material of lithium ion battery [J]. Solid State Ionics, 2014, 268: 222−225.

[31] WANG H, YAMADA T, HAMANAKA S, YOSHIKAWA H, AWAGA K. Cathode composition eependence of battery performance of polyoxometalate (POM) molecular cluster batteries [J]. Chem Lett, 2014, 43: 1067−1069.

[32] NI E F, UEMATSU S, TSUKADA T, SONOYAMA N. Lithium intercalation into polyoxomolybdate $(NH_4)_6[NiMo_9O_{32}]$ as the cathode material of lithium battery [J]. Solid State Ionics, 2016, 285: 83−90.

[33] SONOYAMA N, SUGANUMA Y, KUME T, QUAN Z. Lithium intercalation reaction into the Keggin type polyoxomolybdates [J]. J Power Sources, 2011, 196(16): 6822−6827.

[34] LI Wen-liang, NI Er-fu, LI Xin-hai, GUO Hua-jun. Polyoxovanadate $(NH_4)_7[MnV_{13}O_{38}]$ as cathode material for lithium ion battery and improved electrochemical performance [J]. Transactions of Nonferrous Metals Society of China, 2016, 26(9): 2372−2379.

[35] MANIKUMARI S, SHIVAIAH V, DAS S K. Identification of a near-linear supramolecular water dimer, $(H_2O)_2$, in the channel of an inorganic framework material [J]. Inorg Chem, 2002, 41: 6953−6955.

反应合成温度对锂离子电池正极材料聚氧钼酸盐电化学性能的影响

李文良 [1,2]，倪尔福 [2]，李新海 [1]，郭华军 [1]

1. 中南大学 冶金与环境学院，长沙 410083；
2. 豪鹏国际集团，深圳 518111

摘　要：为了改善聚氧钼酸盐 $Na_3[AlMo_6O_{24}H_6]$(NAM)作为锂离子电池正极材料的电化学性能，通过升高反应溶液的温度，得到了小粒径的 NAM 材料，并对其进行了红外光谱、XRD、扫描电镜、EIS 等分析和充放电性能测试。结果表明，当反应温度高于 40 °C 时，粒径降低到 10 μm 以下。当合成温度达到 80 °C 时，NAM 的粒径最小(~3 μm)，且其电化学性能最佳，在首次循环过程中，0.04*C* 下的首次放电容量高达 409 mA·h/g，库伦效率达 95%。

关键词：聚氧钼酸盐；锂离子电池；正极材料；高容量

(Edited by Xiang-qun LI)