



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



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Abstract: In order to improve the electrochemical performance of polyoxomolybdate $\text{Na}_3[\text{AlMo}_6\text{O}_{24}\text{H}_6]$ (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 ($\sim 3 \mu\text{m}$) exhibits the best electrochemical performance such as high initial discharge capacity of 409 $\text{mA}\cdot\text{h/g}$ and coulombic efficiency of 95% in the first cycle at 0.04C.

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 ($M=\text{Co}$, Ni , Mn , etc.), spinel compounds LiM_2O_4 ($M=\text{Mn}$, etc.), and olivine compounds LiMPO_4 ($M=\text{Fe}$, Mn , Ni , Co , etc.) [5–22]. However, the achievable specific capacities of the conventional cathode materials are usually lower than 200 $\text{mA}\cdot\text{h/g}$, 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 from 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 $\text{K}_7[\text{NiV}_{13}\text{O}_{38}]$ and $\text{K}_7[\text{MnV}_{13}\text{O}_{38}]$ have been prepared by re-crystallization in the solution containing organic solvent acetone, the nanosize particles showed improved electrochemical performance [24,30]. The polyoxomolybdate $(\text{NH}_4)_6[\text{NiMo}_9\text{O}_{32}]$ 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 polyoxomolybdate $\text{Na}_3[\text{AlMo}_6\text{O}_{24}\text{H}_6]$ (NAM) usually shows large particle size, which greatly suppresses the

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 $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 125 mL distilled water, then 17.5 g $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ 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 0.04C ($1C=455 \text{ mA/g}$). 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 $[\text{AlMo}_6\text{O}_{24}\text{H}_6]^{3-}$ 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].

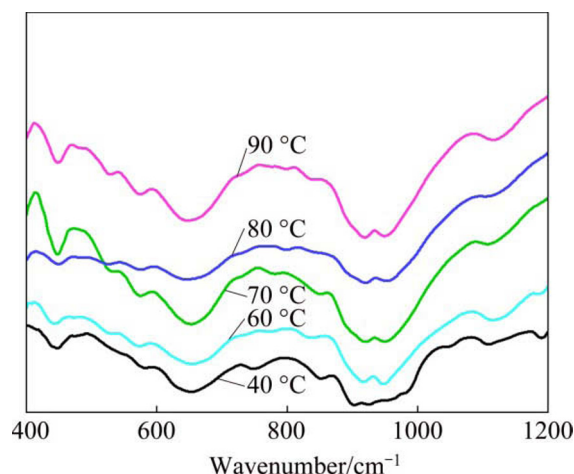


Fig. 1 FT-IR spectra of NAM synthesized at different temperatures

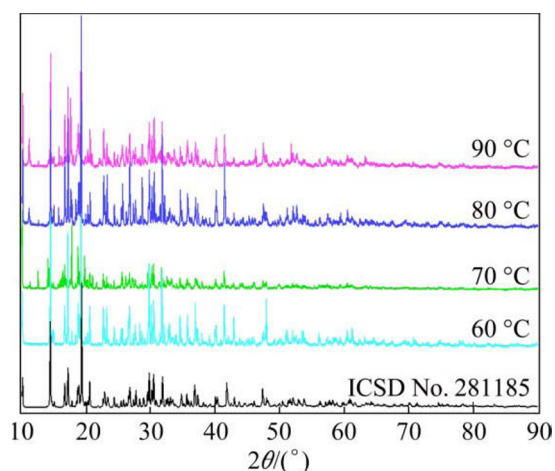


Fig. 2 XRD patterns of NAM synthesized at different temperatures

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