Preparation of Octahedral Mn$_3$O$_4$ by Liquid Phase Method

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Abstract. Octahedral manganese trioxide was prepared from manganese sulfate solution with air as oxidant and compound additive as pH regulator. The results showed that the product had high crystallinity, stable baseline and significant diffraction peak. The micro morphology was formed by stacking regular octahedral structure, the particle size was uniform, and it was about 200nm, the pores were rich, the specific surface area was 6.5 m$^2$/g, and the tap density was 2.11g/cm$^3$. All performance indexes of the product met the excellent standard of soft ferrite manganese trioxide (GBT21836-2008).

Keywords: Manganese sulfate, Air, pH regulator, Octahedral Mn$_3$O$_4$

1. Introduction

With the rapid development of lithium battery industry, the demand for manganese oxide was increasing, and more stringent requirements were put forward for its product performance [1-4]. The traditional cathode material of lithium manganate (LiMn$_2$O$_4$) battery was mainly prepared by high temperature solid state method with MnO$_2$ as manganese source. The battery material prepared by this method had low capacity, poor high-temperature performance and poor economic benefits, which could not meet the demand of lithium battery industry for high-quality manganese oxide [5-7]. In recent years, octahedral manganese trioxide had been widely used in lithium battery industry [8]. Studies by many scholars had shown that compared with manganese dioxide as manganese source, LiMn$_2$O$_4$ synthesized by octahedral manganese trioxide had better electrochemical properties, which could significantly improve the specific capacity and stable rate performance of battery materials [9-12]. In addition, both octahedral manganese trioxide and lithium manganate had spinel structure. The internal structure would not change dramatically when preparing lithium manganate with octahedral manganese trioxide as manganese source, and the material structure would be more stable. Therefore, the preparation of lithium manganate by octahedral manganese trioxide instead of manganese dioxide would be a new trend in the development of battery industry [13-14].

A preparation method of octahedral manganese trioxide without introducing other impurities was proposed in this paper. Octahedral manganese trioxide was prepared by adjusting the pH of the solution with compound additives and oxidizing manganese sulfate solution in situ with air. The products were analyzed by XRD and SEM, which would lay a foundation for the subsequent study of electrochemical properties.
2 Experiment

2.1. Reagents and Equipments
Manganese sulfate and absolute ethanol were analytical pure reagents produced by Sinopharm Chemical Reagent Co., Ltd. The compound additive was self-made by the research team, and the main elements are C, H, O, Mn and N. The equipment used included CR-P600 piston air compressor, HH-2J digital display constant temperature water bath, electronic universal stove, P4Z vacuum suction pump, DHG-101-4B constant temperature blast drying oven, JJ-1 precision booster electric mixer, SZ-93A automatic double pure water distiller, etc.

2.2. Experimental Process
1L manganese sulfate monohydrate solution with Mn$^{2+}$ of 20g/L was prepared and poured into the reactor. Then air was introduced, and the flow rate of air was 3L/min. The compound additive was added into the reactor and adjusted the pH of the solution to 9. The reactor was put into a water bath with a constant temperature of 80℃ for reaction. After 5 hours of reaction, the solution was took out for filtration. The obtained filter residue was manganese trioxide. It would be washed with deionized water for several times, and then dried in a constant temperature drying oven at 100℃ 12 hours. Finally, the samples were took out and bagged for subsequent analysis.

2.3. Performance Characterization
The phase identification was carried out by D8ADVANCE X-ray powder diffractometer of Brooke company in Germany. The morphology and energy spectrum was done using Su8020 field emission scanning electron microscope of Hitachi. The specific surface area was measured by ASAP2460 automatic specific surface area analyzer of American Mike company.

3. Results and Discussion

3.1. Phase Analysis
The XRD pattern of octahedral manganese trioxide prepared was shown in figure 1.

![Figure 1. XRD pattern of octahedral manganous oxide.](image)

It can be seen from figure 1 that the phase composition of the product was Mn$_3$O$_4$. It had significant diffraction peak, stable baseline, good crystallinity, no other impurity diffraction peak. The precipitation efficiency of Mn$^{2+}$ was more than 97.25% and the purity of manganese trioxide was high.
Therefore, octahedral manganese trioxide with high purity could be prepared by using air as oxidant and compound additive as pH regulator.

3.2. Micro Morphology Analysis
The micro morphology of octahedral manganese trioxide was shown in figure 2.

![SEM spectra of octahedral manganous oxide.](image)

Figure 2. SEM spectra of octahedral manganous oxide.

It could be seen from Fig. 2 that the micro morphology of manganous oxide prepared with air as oxidant and compound additive as pH regulator was a regular octahedral structure, the particles were stacked with each other, evenly distributed. The particle size was uniform, about 200nm, and the pores were rich. At the same time, the specific surface area of the product was 6.5m²/g and the tap density was 2.11g/cm³, which would have good electrochemical potential.

3.3. Energy Spectrum Analysis
The element proportion of octahedral manganese trioxide and EDS energy spectrum were shown in table 1 and figure 3.

Table 1. Main elements in the product.

| O(%)  | Mn(%) | Mn/O |
|-------|-------|------|
| 45.10 | 53.51 | 1.18 |
It could be seen from table 1 that the oxidation degree of manganese sulfate could be expressed by calculating the percentage of manganese and oxygen in manganese trioxide. The smaller the ratio of manganese and oxygen percentage was, the higher the oxidation degree of manganese was. The manganese oxygen ratio of manganese trioxide prepared with air as oxidant and compound additive as pH regulator was 1.18, so the oxidation degree was better.

It could be seen from figure 3 that octahedral manganese trioxide was prepared with air as oxidant and compound additive as pH regulator. The main constituent elements were Mn and O, and contained a small amount of C and N. A small amount of C element was caused by the filter paper adhered when manganese trioxide was taken from the filter cake. The N element was entrained by additive. In addition, the EDS spectrum showed that there were no other impurity diffraction peaks and the impurity content was less, so the purity of manganese trioxide was high.

4. Conclusion
Manganese trioxide was prepared by in-situ oxidation from manganese sulfate solution with air as oxidant and compound additive as pH regulator. The phase, morphology, energy spectrum and specific surface area of manganese trioxide were analyzed. The prepared manganous oxide had octahedral structure. The phase composition of the product was Mn$_3$O$_4$, with significant diffraction peak, stable
baseline, good crystallinity and no other impurity diffraction peak. The particles were evenly distributed, about 200nm, with abundant pores. The specific surface area of the product was 6.5m$^2$/g, the tap density was 2.11g/cm$^3$, the manganese oxygen ratio was 1.18, and the oxidation degree was good. Using it as manganese source, lithium manganate with excellent electrochemical properties was expected to be prepared.

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