Manufacturing practice of different shape of presoma \( \text{Co}_3\text{O}_4 \)

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ABSTRACT

For obtaining different shape of presoma \( \text{Co}_3\text{O}_4 \) of positive pole material of Lithium-ion battery, such as sphere, polyhedron, octahedron \( \text{Co}_3\text{O}_4 \), they could all be obtained in different atmosphere and different heat treatment system. The atmosphere included covering and uncovering, and the inputting of different nitrogen ratio. The heat treatment system included constant and changeable. The result showed, plan 1: Increasing temperature 2h, keeping temperature 5h(it was adjusted at 850 \( \text{°C} \)), while it was cooled in the furnace to 285 \( \text{°C} \), then it was cooled in the opening air, good sphere shape presoma could be gotten; While nitrogen: air=25%:75%, the oxygen content of the baked atmosphere was 15.75%, good polyhedron-shape \( \text{Co}_3\text{O}_4 \) could be obtained; When nitrogen: air=50%:50%, the oxygen content of the baked atmosphere was 10.5 %, good octahedron -shape \( \text{Co}_3\text{O}_4 \) could be acquired, and the octahedron \( \text{Co}_3\text{O}_4 \) grew at the style of corkscrew spin.

Keywords: Shape; presoma; \( \text{Co}_3\text{O}_4 \); Sphere; Polyhedron; Octahedron

INTRODUCTION

\( \text{Co}_3\text{O}_4 \) is an important raw material of positive pole material of Lithium-ion battery\(^1\). In the famous world products, the shape of \( \text{Co}_3\text{O}_4 \) is either sphere, or octahedron (such as Umico Company)\(^2\). So it is important to realize the different shapes of \( \text{Co}_3\text{O}_4 \)\(^3\). The article introduces how to produce different shapes of \( \text{Co}_3\text{O}_4 \) in different atmosphere, in shapes of sphere, polyhedron, and octahedron.

EXPERIMENTAL SECTION

SET

In the baking process, air flow was controlled through air fluid counter, nitrogen flow was controlled by nitrogen fluid counter, after the two kinds gas entered into distributing valve, they were mixed evenly, moisture and impurity were moved by concentrated sulfuric acid, then they went into heating baker. Baker was placed in electric resistance furnace, platinum-rhodium-platinum thermocouple could induce and transmit, silicon control trigger, temperature controller of electric resistance furnace could control time and temperature. The experiment set is as Fig1.

AFFECTS ON DIFFERENT ATMOSPHERE ON SHAPE OF \( \text{Co}_3\text{O}_4 \)

Shape of \( \text{Co}_3\text{O}_4 \) while Not Inputting Nitrogen

Covering and Uncovering Effects on The Shape of \( \text{Co}_3\text{O}_4 \)

Experiments showed, the product \( \text{Co}_3\text{O}_4 \) had obvious difference whether china cup was covered or uncovered, because the oxygen content was very lower while it was covered. When it was uncovered, the reaction happened in the air, with the oxygen content of the baking atmosphere at 21%.
Plan 1: Increasing temperature 2h, keeping temperature 5h (it was adjusted at 850 °C), while it was cooled in the furnace to 285 °C, then it was cooled in the opening air, SEM as Fig 2. Product’s diameter distribution was as Fig 3. X diffraction graph was as Fig 4.

Analyzing Fig 2, Fig 3, Fig 4, and the result could be known. The crystal shape of Co₃O₄ was sphere by this plan. The particle diameter distribution was even, and a single peak had appeared.

**Effects of different baking stages on the shape of Co₃O₄**

Plan 2: Increasing temperature 1h, keeping temperature 2h (the temperature was adjusted at 500 °C), then cooled in the stove; then putting the baked powder into the stove, increasing temperature 2h, keeping the temperature 5h (the temperature was adjusted at 850 °C), then cooled with stove. The SEM was as Fig 5.
The sample that was baked in the covered china cup, for obtaining octahedron $\text{Co}_3\text{O}_4$, the oxygen content should be controlled. The different step baked crystal had better shaped crystal, more octahedron $\text{Co}_3\text{O}_4$ and the particle distribution was even. From the theory, plan 2 was actually making presoma baked into $\text{Co}_3\text{O}_4$ in first step, it was the second step to bake sample in higher temperature for obtaining octahedron shape $\text{Co}_3\text{O}_4$.

### $\text{Co}_3\text{O}_4$ Shape while Nitrogen Being Inputted

When the stove atmosphere was weakly oxidizing atmosphere, the cleavage product was $\text{CoO}$, when the oxidizing atmosphere was stronger, the cleavage product was $\text{Co}_3\text{O}_4$ or $\text{Co}_2\text{O}_3$, so the main factors affecting the shape of cobaltous oxide were the stove atmosphere and temperature. From analyzing thermodynamics, $\text{CoO}$ could be oxidized into $\text{Co}_3\text{O}_4$ or $\text{Co}_2\text{O}_3$ during the temperature $400\sim900\,^\circ\text{C}$ in the air. When the oxygen content of the atmosphere couldn’t be controlled, the ideal octahedron or polyhedron shape might be obtained difficulty. The oxygen content of the atmosphere could be controlled through inputting nitrogen accurately, so as to get change from quantity to quality.

The baking system was constant: Increasing temperature 1h, then keeping temperature at $500\,^\circ\text{C}$ 1h, and increasing the temperature to $850\,^\circ\text{C}$ using 40min, keeping the temperature time 5h, while it was cooled in the stove till $100\,^\circ\text{C}$, it was put out at last.

### Effects of Varying Nitrogen Ratio on Shape of $\text{Co}_3\text{O}_4$

For observing the ratio of nitrogen and air that was the oxygen content affection on shape of $\text{Co}_3\text{O}_4$ in baked atmosphere, four groups were designed in the experiments of different nitrogen ratio to air, the SEM graphs were obtained, the better of particle diameter distribution and X diffraction also were gotten.

The four group ratios of nitrogen to oxygen were as follows:
1) Nitrogen: air$=75\%:25\%$, that is the oxygen content of baked atmosphere was $5.25\%$;
2) Nitrogen: air$=50\%:50\%$, that is the oxygen content of baked atmosphere was $10.5\%$;
3) Nitrogen: air$=25\%:75\%$, that is the oxygen content of baked atmosphere was $15.75\%$;
4) No nitrogen that is the oxygen content was $21\%$, the baked atmosphere was air.

The concrete results were as Tab 1 and related Figures.

### Tab 1 Relation of crystal shape and oxygen content

<table>
<thead>
<tr>
<th>No</th>
<th>Oxygen content of baked atmosphere,%</th>
<th>Shape of $\text{Co}_3\text{O}_4$</th>
<th>Related testing figure</th>
<th>Inputting air time period</th>
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</thead>
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<tr>
<td>1</td>
<td>5.25</td>
<td>Irregular polyhedron</td>
<td>Fig 6</td>
<td>Inputting gas at the beginning of keeping temperature at $500,^\circ\text{C}$. Stopping gas at the end of keeping temperature at $880,^\circ\text{C}$</td>
</tr>
<tr>
<td>2</td>
<td>10.5</td>
<td>Thick and big octahedron</td>
<td>Fig 7</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>15.75</td>
<td>Regular polyhedron</td>
<td>Fig 8</td>
<td></td>
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<tr>
<td>4</td>
<td>21</td>
<td>Irregular crystal style</td>
<td>abandoning</td>
<td></td>
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</table>
Fig6 Scanning electron microscope pictures (SEM)

Fig7 Scanning electron microscope picture (SEM)

Fig8 Scanning electron microscope pictures (SEM)

Fig9 Particle diameter distribution graph

Fig10 X diffraction chart

Fig9 and Fig10 were particle diameter distribution graph and X diffraction chart of Fig8, obviously, the polyhedron crystal style of plan (No3) was regular and evenly, the particle diameter distribution was reasonable, it was the ideal plan to manufacture polyhedron Co$_3$O$_4$.

Affection on Co$_3$O$_4$ Shape in Different Nitrogen Ratio

From the analysis of stable ratio of nitrogen and air in four groups’ experiments, Tab1’s No1, 2, 3 group’s shape of Co$_3$O$_4$ would have value to manufacture octahedron and polyhedron, especially in group 2, 3, from the result of experiment, the group 3’s polyhedron crystal was reasonable in practice, which says that the polyhedron Co$_3$O$_4$ experiment was successful. The next step was how to obtain stable and lots of octahedron Co$_3$O$_4$, so the following plans were designed:
1) Inputting air when the temperature was beginning at 500℃, air: nitrogen flow was 3:1, nitrogen flow was 0.1L/min, and air flow was 0.3L/min. When the keeping temperature was end at 500℃, air: nitrogen flow was 1:1, flows were both 0.1L/min, the inputting air and nitrogen were end until the keeping temperature at 850℃ was end.

2) Inputting air when the temperature was beginning at 500℃, air: nitrogen flow was 3:1, nitrogen flow was 0.1L/min, and air flow was 0.3L/min. When the keeping temperature was beginning at 850℃, air: nitrogen flow was 1:1, flows were both 0.1L/min, the inputting air and nitrogen were end until the keeping temperature at 850℃ was end, shown as Fig11.

3) Inputting air when the temperature was beginning at 500℃, air: nitrogen flow was 1:1, air and nitrogen flows were both 0.1L/min. When the keeping temperature was end at 500℃, air: nitrogen flow was 3:1, nitrogen flow was 0.1L/min, air flow was 0.3L/min., the inputting air and nitrogen were end until the keeping temperature at 850℃ was end, shown as Fig14.

4) Inputting air when the temperature was beginning at 500℃, air: nitrogen flow was 1:1, air and nitrogen flows were both 0.1L/min. When the keeping temperature was end at 500℃, air: nitrogen flow was 3:1, nitrogen flow was 0.1L/min, and air flow was 0.3L/min, the inputting air and nitrogen were end until the keeping temperature at 850℃ was end.

Fig11  Scanning electron microscope pictures (SEM)

Fig12 and Fig13 were particle diameter distribution graph and X diffraction chart of Fig11, obviously, the octahedron crystal style of plan (No 2) was regular and evenly, the particle diameter distribution was reasonable, it was the ideal plan to manufacture octahedron Co₃O₄.

Fig12  X diffraction graph

Fig13 Particle diameter distribution graph

Obviously, from Fig 14, octahedron Co₃O₄ grew at the style of corkscrew spin.

Fig14 Scanning electron microscope picture (SEM)
CONCLUSION

Baking temperature of product Co$_3$O$_4$ is between 835~890 ℃, for getting the wonderful crystal style, the baking temperature is 850 ℃, baking time is about 5~10 h.

If the baking time was constant, shape of crystal Co$_3$O$_4$ related to the baking temperature and baking atmosphere. While the baking temperature was at 850 ℃, the stove was air, the qualified sphere shape could be obtained; While the nitrogen was input and the oxide density was 15.75%, the even polyhedron particle of crystal Co$_3$O$_4$ could be obtained; While the nitrogen was input and the oxide density was 10.5%, the even octahedron particle of crystal Co$_3$O$_4$ could be obtained. So through above different method, the stove atmosphere ratio air to nitrogen was changed, the different crystal style would be gotten.

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REFERENCES