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Research Article

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Manufacturing practice of different shape of presoma Co_3O_4

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ABSTRACT

For obtaining different shape of presoma Co_3O_4 of positive pole material of Lithium-ion battery, such as sphere, polyhedron, octahedron Co_3O_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 ℃), while it was cooled in the furnace to 285 ℃, 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 Co_3O_4 could be obtained; When nitrogen: air=50%:50%, the oxygen content of the baked atmosphere was 10.5%, good octahedron -shape Co_3O_4 could be acquired, and the octahedron Co_3O_4 grew at the style of corkscrew spin.

Keywords: Shape;presoma;Co_3O_4; Sphere; Polyhedron; Octahedron

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INTRODUCTION

Co_3O_4 is an important raw material of positive pole material of Lithium-ion battery[1]. In the famous world products, the shape of Co_3O_4 is either sphere, or octahedron (such as Umico Company)[2].So it is important to realize the different shapes of Co_3O_4[3]. The article introduces how to produce different shapes of Co_3O_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 Co_3O_4

Shape of Co_3O_4 while Not Inputting Nitrogen

Covering and Uncovering Effects on The Shape of Co_3O_4

Experiments showed, the product Co_3O_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%.

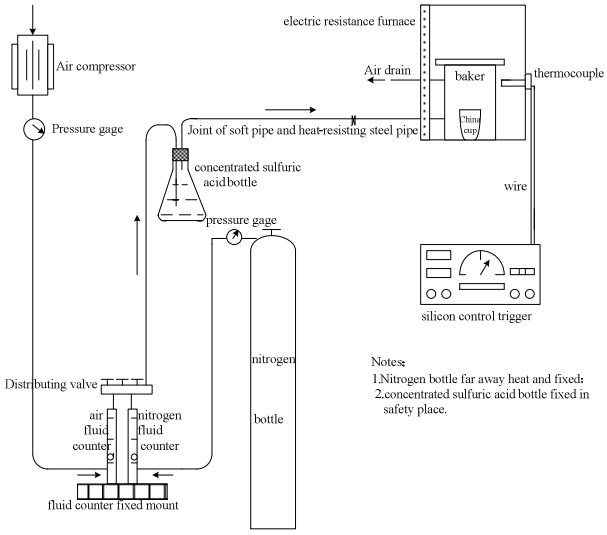


Fig1 Experiment Set

Plan 1:Increasing temperature 2h,keeping temperature 5h(it was adjusted at 850 ℃),while it was cooled in the furnace to 285 ℃,then it was cooled in the opening air, SEM as Fig2,product's diameter distribution was as Fig 3, X diffraction graph was as Fig 4.

Fig2 Co_3O_4 SEM graph while uncovered

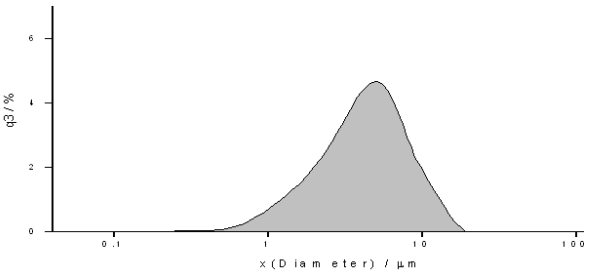


Fig3 Particle diameter distribution graph

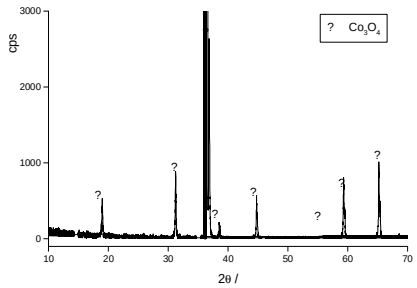


Fig 4 X diffraction graph

Analyzing Fig 2, Fig 3, Fig 4, and the result could be known. The crystal shape of Co_3O_4 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 Co_3O_4

Plan 2:Increasing temperature 1h,keeping temperature 2h(the temperature was adjusted at 500 ℃),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 ℃),then cooled with stove. The SEM was as Fig 5.

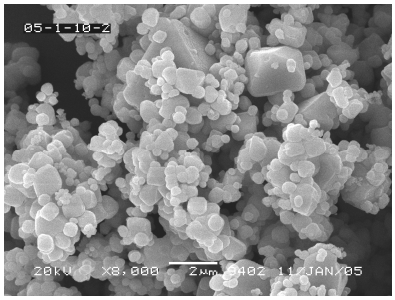


Fig 5 Different steps baked Co_3O_4 SEM

The sample that was baked in the covered china cup,for obtaining octahedron Co_3O_4, the oxygen content should be controlled. The different step baked crystal had better shaped crystal, more octahedron Co_3O_4 and the particle distribution was even. From the theory, plan 2 was actually making presoma baked into Co_3O_4 in first step, it was the second step to bake sample in higher temperature for obtaining octahedron shape Co_3O_4.

Co_3O_4 Shape while Nitrogen Being Inputted

When the stove atmosphere was weakly oxidizing atmosphere, the cleavage product was CoO, when the oxidizing atmosphere was stronger, the cleavage product was Co_3O_4 or Co_2O_3,so the main factors affecting the shape of cobaltous oxide were the stove atmosphere and temperature. From analyzing thermodynamics, CoO could be oxidized into Co_3O_4 or Co_2O_3 during the temperature 400~900℃ in the air. When the oxygen content of the atmosphere couldn't be controlled, the ideal octahedron or polyhedron shape might be obtained difficultly. 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℃1h,and increasing the temperature to 850℃ using 40min,keeping the temperature time 5h, while it was cooled in the stove till 100℃, it was put out at last.

Effects of Varying Nitrogen Ratio on Shape of Co_3O_4

For observing the ratio of nitrogen and air that was the oxygen content affection on shape of Co_3O_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.

Tab1 Relation of crystal shape and oxygen content

No	Oxygen content of baked atmosphere,%	Shape of Co_3O_4	Related testing figure	Inputting air time period
1	5.25	Irregular polyhedron	Fig 6	Inputting gas at the beginning of keeping temperature at 500℃,stopping gas at the end of keeping temperature at 880℃
2	10.5	Thick and big octahedron	Fig 7	
3	15.75	regular polyhedron	Fig 8	
4	21	Irregular crystal style	abandoning	

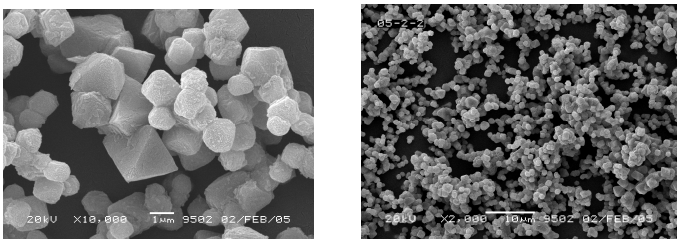


Fig6 Scanning electron microscope pictures (SEM）

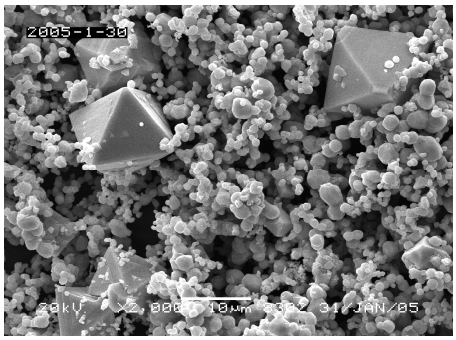


Fig7 Scanning electron microscope picture (SEM）

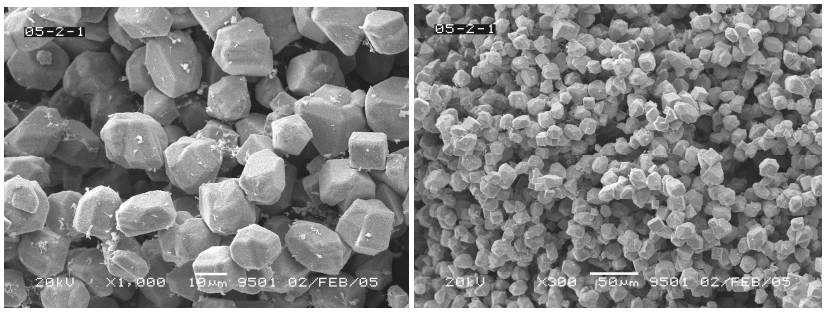


Fig8 Scanning electron microscope pictures (SEM）

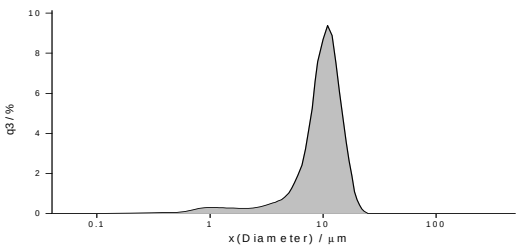


Fig9 Particle diameter distribution graph

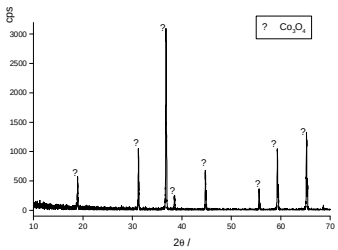


Fig10 X diffraction chart

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_3O_4.

Affection on Co_3O_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_3O_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_3O_4 experiment was successful. The next step was how to obtain stable and lots of octahedron Co_3O_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.

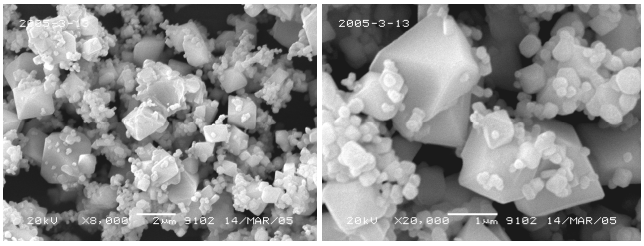
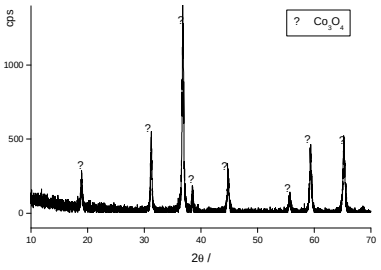


Fig11 Scanning electron microscope pictures (SEM）

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 Co_3O_4.



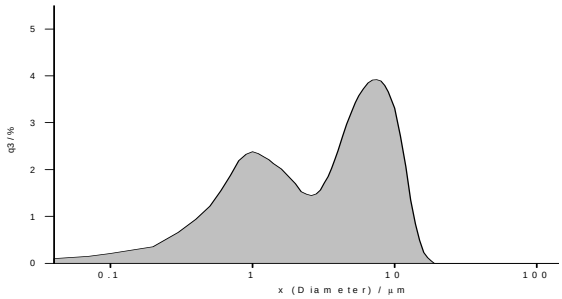


Fig12 X diffraction graph **Fig13 Particle diameter distribution graph**

Obviously, from Fig 14, octahedron Co_3O_4 grew at the style of corkscrew spin.

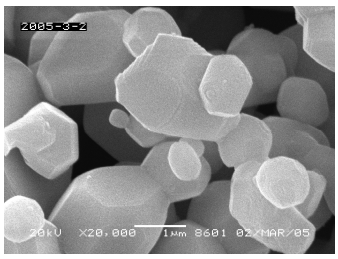


Fig14 Scanning electron microscope picture (SEM）

CONCLUSION

Baking temperature of product Co_3O_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_3O_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_3O_4 could be obtained; While the nitrogen was input and the oxide density was 10.5%,the even octahedron particle of crystal Co_3O_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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