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Research Article

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Preparation method for manufacturing Co_3O_4

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ABSTRACT

For getting good physical and chemical properties of Co_3O_4, some preparation methods should be adopted, such as technology process, purifying method, depositing way, washing method, drying temperature and time, baking temperature and time, baking atmosphere, etc. Only are these works prepared well, the satisfied precursor and the product Co_3O_4 could be obtained.

Keywords: Technology process; Reacting method; Drying and baking condition.

INTRODUCTION

In the traditional manufacturing process,the usual manufactured Co_3O_4 technology is not very strictly.And the product which is manufactured according to traditional technology process can’ t satisfy the physical and chemical index requirements of high quality and properties of Li ion battery raw material,To the update in China,the highest quality grade of Co_3O_4 in the world hasn’t appeared,so for obtaining the raw material Co_3O_4 which is needed for producing lithium cobalt oxide[1,2],we begin to research according to the imported material Co_3O_4（Umicore corporation producing）.Its’ cobalt and impurity content have no specific from Chinese product obviously,but it have many obvious differences from Chinese products in some areas such as crystal shape,particle size distribution, apparent density(or tap density),Umicore’s product SEM is shown as Fig1,the particle size distribution is shown as Fig2,X ray diffraction pattern is shown as Fig3.

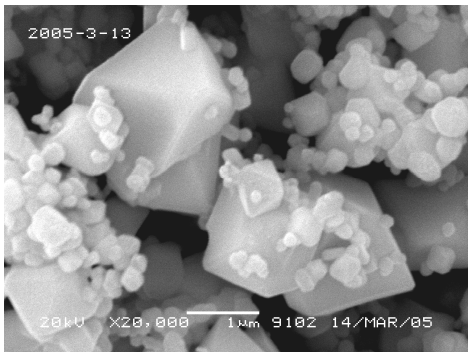

Fig1 Umicore’s product SEM

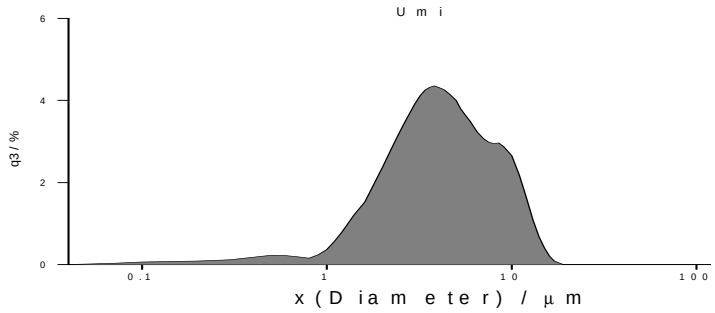

Fig2 Umicore cooperation products' particle size distribution

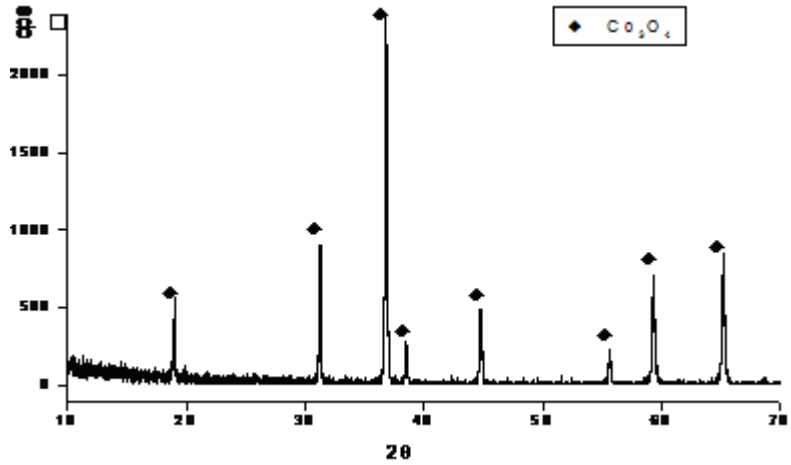

Fig3 Umicore cooperation products'X ray diffraction pattern

EXPERIMENTAL SECTION

Main raw materials and equipments

Main raw materials: Na_2CO_3,H_2O_2,NaOH,$CoCl_2$•$6H_2O$,purified water;

Baking volume：Designed by own,it is shown as Fig 4.

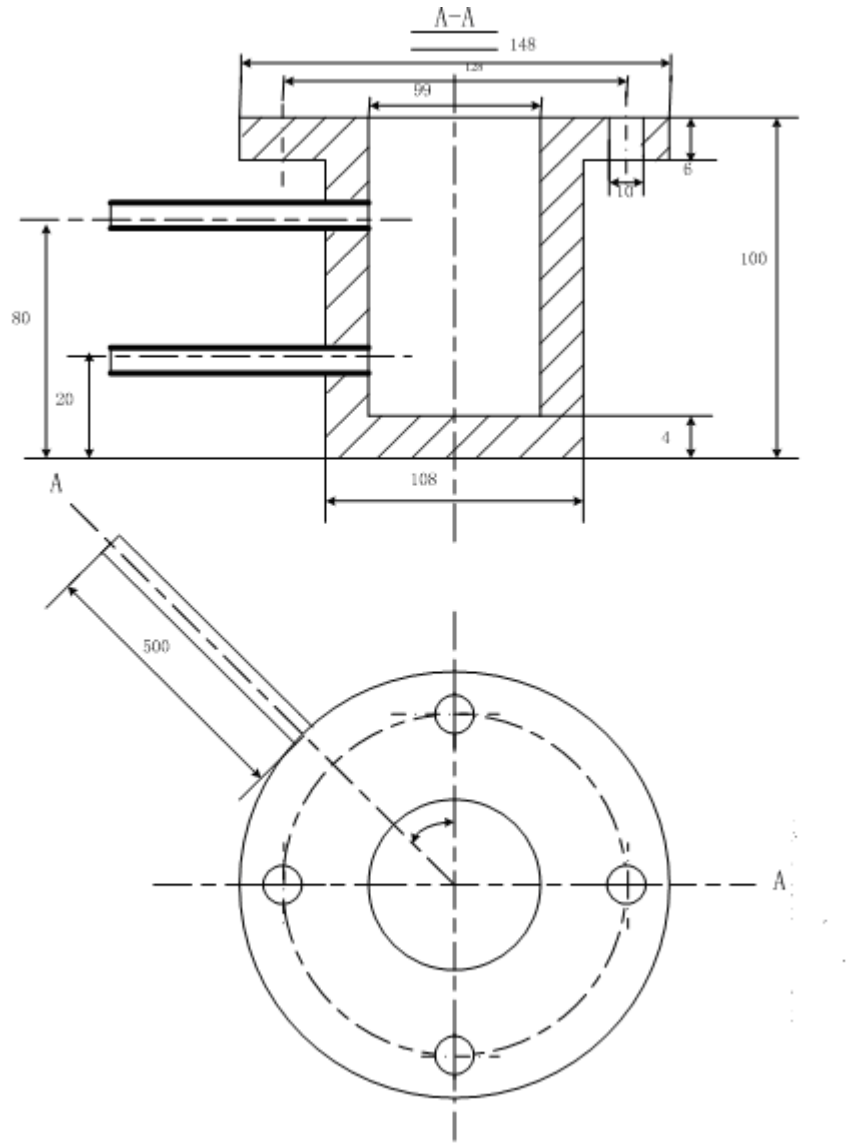

Fig4 Baking volume(heat resistant steel)

For obtaining high quality Co_3O_4, according to research experiment ,principle technology process adapted is shown as Fig 5.

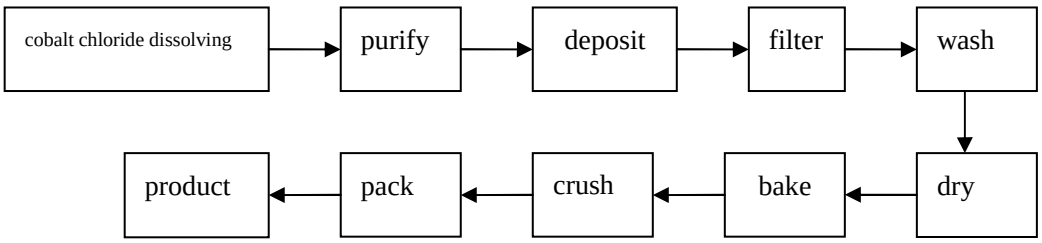

Fig5 Co_3O_4 manufactured technology process

In the above principle technology, procedures such as purifying, depositing,baking are all key points to ensure electron grade Co_3O_4 product quality(physical and chemical properties),they are also the researched focuses and puzzles needed to solve.Thus procedures of washing,filtering,crushing(screening) should be considered more from equipment and industrialization so as to ensure the technology flowing paths smoothly.

Basic chemical equation

According to above principle technology to manufacture electron grade Co_3O_4 product,the basic equations are as

bellow,from equation1~9[3,4].

[1]Purification（Purifying Fe,Ca,Cu,Pb）

$2Fe^{2+}+ H_2O_2 ==2Fe^{3+}+ 2OH^-$ Formula（1）

$Fe^{3+}+3OH^- == Fe(OH)_3\downarrow$ Formula（2）

$Ca^{2+}+2F^- == CaF_2\downarrow$ Formula（3）

$Cu^{2+}+S^{2-}==CuS\downarrow$ Formula（4）

$Pb^{2+}+S^{2-}==PbS\downarrow$ Formula（5）

[2]Deposition（sodium carbonate as precipitant）

$2\ Co^{2+}+2CO_3^{2-}+H_2O==Co_2(OH)_2CO_3\downarrow+ CO_2\uparrow$ Formula（6）

$Co^{2+}+CO_3^{2-}==CoCO_3\downarrow$ Formula（7）

[3]Baking

$3Co_2(OH)_2CO_3+ O_2==2Co_3O_4+3H_2O\uparrow+ 3CO_2\uparrow$ Formula（8）

$6CoCO_3+ O_2==2Co_3O_4+6CO_2\uparrow$ Formula（9）

RESULTS AND DISCUSSION

Purifying method

In the bought cobalt chloride solution($CoCl_2$),clarifier is added,the concrete ways are adopted according to raw materials' different impurities.

Method to remove Fe:Using H_2O_2 as oxidant, NaOH is used to adjust pH value, $Fe(OH)_3$ is removed to dislodge Fe,the pH value is about 2.2 when $Fe(OH)_3$ begins to deposit.

Methods to remove Ca: fluoride such as NH_4F,NaF is used to deposit CaF_2 so as to remove Ca.

Methods to remove Cu,Pb:sulfide such as H_2S,$(NH_4)_2S$ is used to deposit CuS, PbS so as to remove Cu,Pb.

Sulfur ion can react with metal ion to deposit,the reacting equation is: $M^{2+}+S^{2-}==MS\downarrow$

The deposition forming mainly is determined by the metal kind and solution pH value,different ion will be deposited in different pH value.solution pH value could be adjusted to less than 0.85,the impurity such as Hg,Ag,Cu,Sn,Bi,Pb,Cd,Zn could be removed to less than 10^{-4}mol/L so as to separate with cobalt.In the practice, Zn is very difficult to remove from cobalt solution by the method of sulfide,the extraction method should be adopted.

Methods to remove Ni:reagent diacetyldioxime is used.

Depositing method

Feeding velocity,feeding method,stiring method,reation temperature and time are included.The main purpose is to provide demanded precursor of purity,impurity content,crystal style and particle size.It's one of the key technology,also is the complex technology part which has many affected factors.

There are such reactor added methods:
1)Adding Na_2CO_3 solution into $CoCl_2$ solution while stirring;
2) Adding $CoCl_2$ solution into Na_2CO_3 solution while stirring;
3) $CoCl_2$ solution and Na_2CO_3 solution added at the same time.

According to relative references,the priority plan will be adopted: Adding Na_2CO_3 solution into $CoCl_2$ solution slowly,the adding velocity is about 10~14ml/min.

Stirring method:mechanical agitation is used,the stirring velocity is 210r/min.
Reacting temperature：50～60℃.
Reacting time：0.5～1h.

Washing method
For it's small experiment,the vacuum filtration is used for washing,the conductivity of washed water is measured after each washing,when the conductivity is basically stable,the washing should be finished.According to the higher demanded quality of purity for product,the washed water should be selected as purified water(exchange water, infiltration water),etc.

Drying temperature and time
The drying temperature is 100℃,drying time is over 8 hours.Dried precursor is crushed as the next experiment object.

Baking temperature and time
Dried precursor should be baked between 750～900℃ temperature degree.If the temperature is lower,the crystal won't grow completely,it's also difficult to obtain octahedron shape crystal;otherwise,if the temperature is higher,the crystal will melt or produce chemical transformation.

Backing time is between 2~10h.

Baking method have one time baking or two times baking.

Baking atmosphere
Dried precursor is put into the baking china,it has two methods which is covered or uncovered;If the precursor is put in the closed volume,the oxygen content could be adjusted through adding nitrogen.

CONCLUSION

1) The purifying method include removing Fe, Ca, Cu,Pb, Ni,etc.
2) The reactor added method is adding Na_2CO_3 solution into $CoCl_2$ solution slowly.
3) The washed water should be selected as purified water(exchange water, infiltration water),etc.
4) The drying temperature is 100℃,drying time is over 8 hours.
5) The baking temperature is between 750～900℃ degree.Backing time is between 2~10h.

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