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Study on the effect of temperature on the cathode material Li_2CoSiO_4 charge-discharge property

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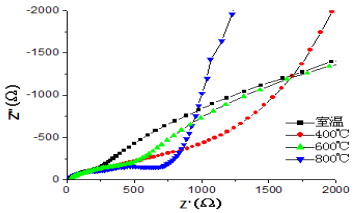
Abstract: In this paper, Li_2CoSiO_4 with a space group of Pmn21 that was synthesized by hydrothermal route at 160 ℃. A series of Li_2CoSiO_4 with different structures produced after the as-prepared sample calcined at different temperatures (400, 600 and 800 ℃). Based on the results from electrochemical impedance spectroscopy, as it is well known that Li_2CoSiO_4 obtained at 800 ℃ shows the best dynamic properties among four samples. Furthermore, the reversible discharge capacity of 201.5 mAh/g can be delivered in this compound, which is higher than that released by other samples. Therefore, Li_2CoSiO_4 prepared at 800 ℃ is a potential cathode candidate for lithium-ion batteries.



Keywords: Hydrothermal method; Li_2CoSiO_4; Heat-treatment; Electrochemical analysis; Charge discharge efficiency

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1. Introduction

Elements of human society to maintain operation of the framework is the material, energy and information-driven interaction. Survival and development of energy and solidarity of human society, and the common goals and aspirations of all human beings is the sustainable development [1-2]. To improve the energy to the structure of human, and at the same time developing new clean energy, in order to achieve sustainable development [3]. Many countries introduced many policies to encourage people to find new energy sources to develop gradually replace depleting polluting natural energy resources, such as solar, wind, hydro, and geothermal, nuclear power, there is now a very popular car in hybrid, while the hybrid is the most critical battery power and endurance. Recently the major car manufacturers are increasing their efforts to study chemical batteries.

A power supply device is the use of chemical change, the other energy into electrical energy [4]. Common battery leads acid batteries, zinc-manganese batteries and so on. Compared to other battery, the lithium battery function is especially significant. Lithium increasingly appeared in the eyes of the people, in terms of life (cell phones, electric cars, etc.), or from work (such as the IT industry, etc.), or other aspects of aerospace can see its shadow [5]. Lithium has become the world's largest battery hot commodity development: safety, high energy, high voltage and stable discharge performance, and environmental pollution is its series of advantages.

Li_2CoSiO_4 current research results also very little, when used as an electrode material. In some cases, there is still a lot less than the actual capacity of the theoretical, cycle performance is no lack of imagination, such as the superior [6-8]. Heat through the material, study materials, phase change law, which developed some of the decisions with the battery charge and discharge capacity of the size of the relevant material factors help make some relevant research Li_2CoSiO_4 materials.

2. Method

2.1. Experiment procedure

In this paper, the experimental hydrothermal synthesis method to synthesize preparation Li_2CoSiO_4, specific experimental procedure is as follows:

(1) Take 25ml of distilled water, and then the nano-SiO2 and stoichiometry of LiOH • H2O (99%) was added to the distilled water, stir to dissolve after 20 hours, while the other will CoC2O4 • 2H2O was added to 20 ml of dissolved in distilled water.

(2) After CoC2O4 completely uniformly dissolved in 20ml of distilled water, the solution was slowly added to dissolve the SiO2 and a solution of LiOH.

(3) The homogeneous mixed solution was stirred for half an hour, and then this mixed solution was placed in 100 ml reaction vessel. The first reaction vessel with argon gas drain, after about 0.5 h after completion of the exhaust gas, and then put into the reactor at a reaction oven 160 ℃ three days.

(4) Completion of the reaction, after the product was cooled with water and ethanol, centrifuged and

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washed, to obtain the pure Li2CoSiO4 material.

(5) Then Li2CoSiO4 material into A, B, C, D four groups temperature of the heat treatment. Wherein group A is not heated; group B over 40 minutes from room temperature to 400 ℃, and then remained stable under the conditions of 400 ℃ of two hours; group C for 60 minutes from room temperature to 600 ℃, and then under the conditions of 600 ℃ in stably maintaining two hours; D group with 80 minutes from room temperature to 800 ℃, and then remained stable under the conditions of 800 ℃ of two hours (the heating process is carried out at a high temperature vacuum furnace carbon tube). Finally, samples of the above components are sufficiently cool to room temperature.

2.2. Experiment Materials

Table 2-1 experimental drug specifications and production units

Reactant	Chemical formula	Purity	Manufacturer
Ethanol	C2H6O	AR	Sinopharm Chemical Reagent Co., Ltd.
Lithium hydroxide	Cu(OH)2	AR	Sinopharm Chemical Reagent Co., Ltd.
Acetone	C3H6O	AR	Sinopharm Chemical Reagent Co., Ltd.
1 micron silica	1μm SiO2	AR	Sinopharm Chemical Reagent Co., Ltd.
Manganese oxalate	MnC2O4	AR	Sinopharm Chemical Reagent Co., Ltd.
Distilled water	H2O	AR	Sinopharm Chemical Reagent Co., Ltd.

2.3. Experiment instruments

Table 2-2 laboratory equipment specifications and production units

Instrument Specifications	Manufacturer
85-1C magnetic stirrer	Shanghai Mei Ying Pu Instruments Inc.
DF-101C type collector-type thermostat heating magnetic stirrer	British Yu Gongyi City to China Instrument
2XZ type rotary vane vacuum pump	Zhejiang Huangyan refinement pump plant
DZF vacuum oven	Shanghai Jing Hong Experimental Equipment Co., Ltd.
RS-30A ultrasonic cleaning machine	Ningbo Rongshun Technology Instrument
Unilab type of inert gas glove box	German company Braun
DHG-9053A type	Instrument Manufacturing Co., Ltd. Shanghai Hui Tai
DHG Series electric oven thermostat blast	Shanghai Hua Lian Medical Devices Co., Ltd.
High-temperature vacuum furnace carbon tube	Furnace Co., Ltd. Shanghai Chen Hua

Note：In addition, this experiment also used agate mortar, glass dryer, AB204-N electronic balance equipment, analog battery manufacturer custom.

2.4. Battery assembly and testing laboratories

Battery Cathode: the binder PVDF (polyvinylidene fluoride, polyvinylidene fluoride), a conductive agent, acetylene black, active samples were 1: 1: 4 weight ratio combination, after uniformly coating the above composition of the 0.02 mm aluminum foil, the positive electrode sheet that is sufficiently dried after the battery.

Electrolyte: 1:1:1 the volume ratio of 1 mol / L LiPF6 / EC + DMC + EMC as a battery electrolyte.

Diaphragm: porous polypropylene film as a battery separator.

Battery negative: lithium battery anode piece.

Test: charging and discharging cycle, the voltage adjustment range is 2.0 ~ 4.8 V, a magnification of C / 16 (about 10 mA/g).

3. Results and discussion

3.1. After heat treatment at different temperatures Li2CoSiO4 charge and discharge characteristics of the cathode material

We can see from the four charge-discharge characteristics of the graph, with the increasing charge capacity. The battery voltage is constantly increasing, and when the capacity to reach a particular point, the voltage generally tends to balance, this time we can know that the battery charge for the first time is over, this feature also used when the battery discharged.

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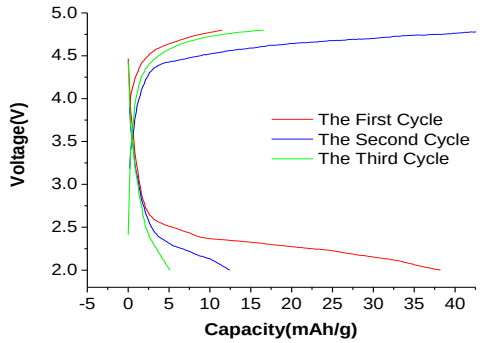

Figure 1. The first three charge and discharge at room temperature Li_2CoSiO_4 battery cathode material assembled curve.

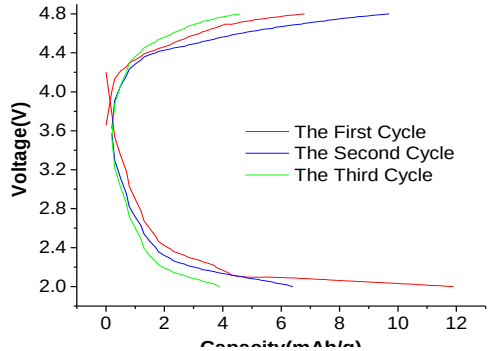

Figure 2. 400 ℃ heat treatment prior todischarge Li2CoSiO4 three battery cathode material assembled curve.

Then we have the first three charge-discharge curves to compare various temperature treated after Li2CoSiO4 assembled battery cathode materials, we can clearly see, the assembly room cathode material than the first charge capacity of the battery is 11.5 mAh/g, the initial discharge capacity 38.2 mAh/g, the second charge capacity ratio is 45.5 mAh/g, the discharge capacity was 12.4 mAh/g, the third charge specific capacity is 16.6 mAh/g, the discharge capacity is 5.1 mAh/g; 400 ℃ treatment after assembling the battery cathode material than the first charge capacity is 6.8 mAh/g, the initial discharge capacity is 11.9 mAh/g, a second charge over capacity 9.7 mAh/g, the discharge capacity is 6.4 mAh /g, the third charging more than the capacity of 4.6 mAh/g, the discharge capacity is 3.9 mAh/g; 600 ℃ treatment for the first time after charging the battery cathode material assembled specific capacity is 38.7 mAh /g, the initial discharge capacity was 22.9 mAh/g, the second charging more than the capacity of 23.8 mAh/g, the discharge capacity is 0.9 mAh/g, the third charge specific capacity is 2.1 mAh/g, the discharge capacity is 0.6 mAh/g; 800 ℃ treatment for the first time after charging the battery cathode material assembled specific capacity is 264.6 mAh/g, the initial discharge capacity of 114.4 mAh/g, the second charge capacity ratio is 318.6 mAh/g, the discharge capacity is 201.5 mAh/g, the third charge specific capacity is 126.1 mAh/g , discharge capacity is 100.5 mAh/g. From this point we can see, the electrochemical properties of the material treated at 800 ℃ is better than the material temperature after other treatment.

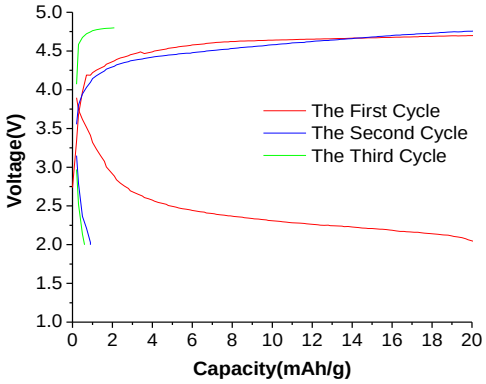

Figure 3. 600 ℃ heat treatment prior todischarge Li2CoSiO4 three battery cathode material assembled curve.

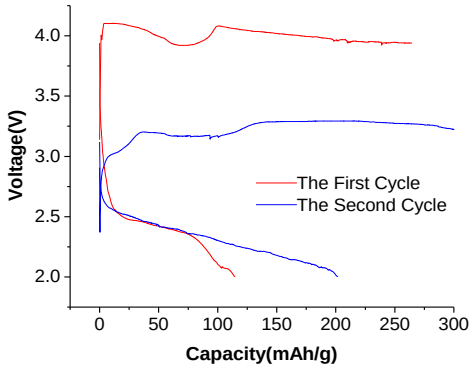

Figure 4. 800 ℃ heat treatment priorto discharge Li2CoSiO4 secondary battery cathode material assembled curve.

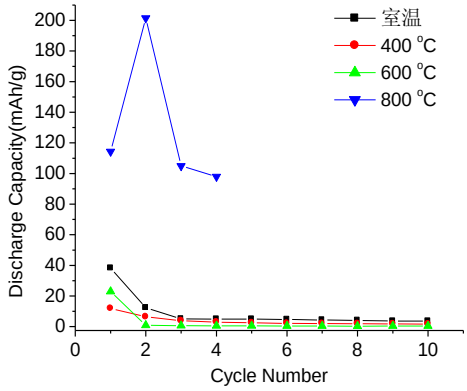

Figure 5. Different temperatures of Li2CoSiO4 assembled battery cathode material than the capacity chart

From Figure 5 we can conclude that the heat treatment at 800 ℃ Li2CoSiO4 cathode material

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under the same conditions with a maximum discharge capacity, the electrochemical characteristics superior Li2CoSiO4 cathode material temperature treatment after the other three.

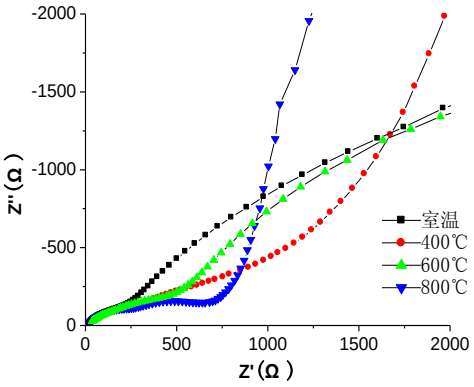

Figure 6. 4V voltage AC impedance underdifferent temperatures after four and a halfhours after charging heat Li2CoSiO4 assembledbattery cathode materials analysis map

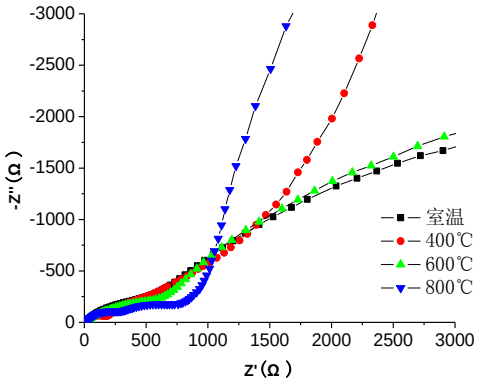

Figure 7. 4.5 V voltage after charging down after half an hour to four different temperature heat treatment Li2CoSiO4 battery cathode material assembled AC impedance spectra analysis

3.2. After heat treatment at different temperatures AC impedance Li2CoSiO4 assembled battery cathode materials analysis

The four different heat treatment temperatures after Li2CoSiO4 battery cathode materials were assembled in front of the cycle after cycle, as well as after charging at 4 V, 4.5 V, 4.8 V AC impedance conditions for a half-hour analysis, the following Fidgure6, 7, 8, 9, 10.

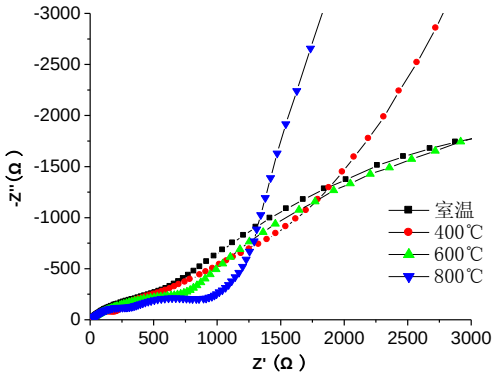

Figure 8. 4.8V voltage AC impedance under different temperatures after four and a half hours after charging heat Li2CoSiO4 assembled battery cathode materials analysis map

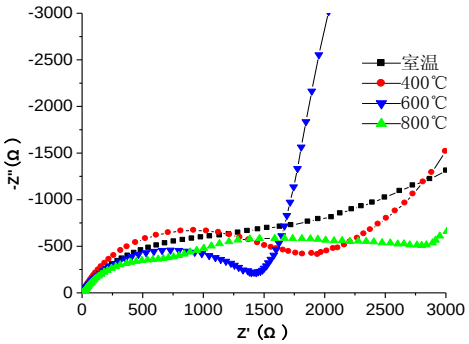

Figure 9. Four different temperatures before and after heat treatment cycle Li2CoSiO4 battery cathode material assembled AC impedance spectra analysis

AC impedance spectroscopy of technical analysis is the lithium ions between the transition metal oxides and carbon materials deintercalation process [8]. We know that, the deintercalation of lithium ions consists of three parts: a low frequency region, intermediate frequency region and high frequency region. Where in the low frequency region: region hatched and solid state diffusion of lithium ions related to the slope of the large impedance large, and vice versa called Warburg impedance. IF areas: Area semicircle and charge transfer in the battery, whereas the size of the semicircle being is a reflection of the size of its impedance, which comes mainly from the impedance of the electrolyte impedance surface. High-frequency areas: Area radius semicircle represents the impedance of the size, the size of the radius (size impedance) with lithium ions through the membrane of SEI diffusion migration related. The impedance calls the migration resistance [9-10].

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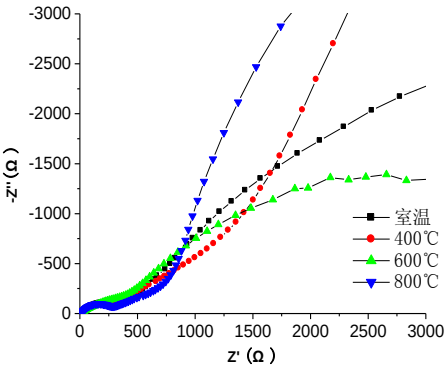

Figure 10. After four different temperature heat treatment cycle Li2CoSiO4 battery cathodematerial assembled AC impedance spectra analysis

In Figure 6 to Figure 10 is the temperature of the heat treatment after four Li2CoSiO4 assembled battery cathode materials were charged in 4 V, 4.5 V, 4.8 V voltage before and after half an hour, and after four different temperature heat treatment cycle cathode material assembled Li2CoSiO4 battery AC impedance spectra analysis. Where in the abscissa Z 'represents the real part of the impedance, the ordinate Z' 'represents the imaginary part of the impedance. You can see from the above comparison of spectra, in addition to mapping the cycle before, the other spectrum semicircle radius temperature 800 ℃ after treatment Li2CoSiO4 minimum battery cathode material assembled, that the impedance minimum, it can be concluded that the lithium ion deintercalation process, electrochemical impedance after heat treatment temperature 800 ℃ smallest, most suitable as a lithium-ion battery cathode materials[11].

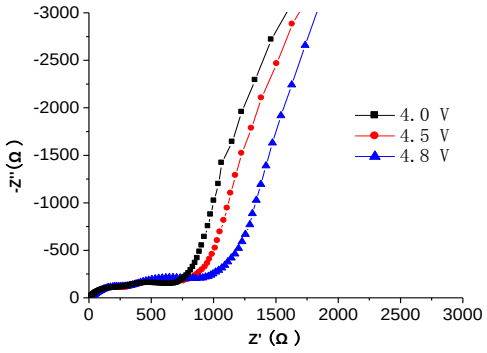

Figure 11. After charging at 4.0 V, 4.5 V, 4.8 V condition for half an hour, after the heat treatment temperature of 800 ℃ Li2CoSiO4 A impedance analysis of battery cathode materials assembled map

Figure 11 shows that between 4.0 ~ 4.8V, rising as the charging voltage, the impedance of the battery is also increased, which can be drawn, at a lower voltage (4.0 V) charge can be made after the heat treatment temperature of 800 ℃ Li2CoSiO4 cathode material assembled battery internal resistance is smaller, and the material delithiation to 4.8 V, lithium extrusion becomes more difficult, resulting in deterioration of performance of the electrode kinetics[12-13].

From Figure 12, we can see that for after the heat treatment temperature of 800 ℃ Li2CoSiO4 cathode materials, semi-circular loop prior to the high-frequency region of the radius is much larger than the cycle, it can be concluded that the internal resistance of the battery decreases circulationa.

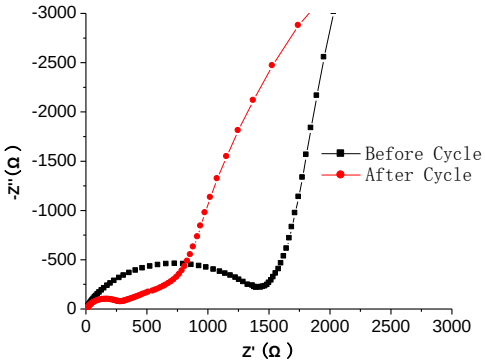

Figure 12. After the temperature of 800 ℃ before and after heat treatment cycle Li2CoSiO4 battery cathode material assembled AC impedance spectra analysis

4. Summary

Four temperature treated Li2CoSiO4 material, the charge-discharge experiments testing, Li2CoSiO4 material temperature of 800 ℃ after treatment has a discharge capacity is significantly higher than other types of materials; the AC impedance spectra of the test and analysis, and 800 resistance Li2CoSiO4 material ℃ temperature after the heat treatment to be significantly lower than other types of materials, and the temperature of 800 ℃ after Li2CoSiO4 material after heat treatment of the assembled battery when the charging at 4.0 V, with a minimum of electrochemical impedance.

With the increase of test temperature, changes the structure and properties of materials are not very regular, electrochemical performance only after the heat treatment temperature of 800 ℃ best. While on the road for the preparation of new lithium-ion batteries need to cross a very big obstacle, but the electrochemical properties of temperature change material structure of the lithium-ion battery materials research further impetus.

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