

19



LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie

11

N° de publication :

LU506510

12

BREVET D'INVENTION

B1

21

N° de dépôt: LU506510

51

Int. Cl.:

B01J 37/08, B01J 23/70, H01M 12/08

22

Date de dépôt: 05/03/2024

30

Priorité:

72

Inventeur(s):

LI Xuelian – China

43

Date de mise à disposition du public: 05/09/2024

74

Mandataire(s):

BIOPATENTS IP CONSULTANCY –
5691NW Son (Netherlands)

47

Date de délivrance: 05/09/2024

73

Titulaire(s):

TAIYUAN UNIVERSITY OF TECHNOLOGY –
030024 Taiyuan, Shanxi (China)

54

HIGH-PERFORMANCE CATALYST FOR CARBON DIOXIDE CATALYTICALLY-REDUCING BATTERIES AND PREPARATION METHOD THEREOF.

57

The present invention relates to the technical field of preparing catalysts and discloses a high-performance catalyst adapted to carbon dioxide catalytically-reducing batteries and a preparation method thereof. The method includes the steps of S1 accurately weighing out zinc nitrate hexahydrate, cobalt nitrate hexahydrate and 2-methylimidazole by corresponding weights through an electronic balance, respectively, then pouring them into anhydrous methanol sequentially and mixing them fully; and S2 adding a 2-methylimidazole solution dropwise to a solution in which zinc nitrate hexahydrate and cobalt nitrate hexahydrate have dissolved and stirring it by a magnetic stirrer to obtain a purple solution. In the present invention, a silicon-coated catalyst is prepared through a special process, so as to improve the stability and electrocatalytic activity of the catalyst, and then improve the battery performance and enhance the reduction effect of the catalyst to carbon dioxide. Moreover, the silicon-coated catalyst has excellent stability, thus the silicon layer can protect the core part of the catalyst from the impact of the external environment, ensure that the catalyst has high activity even used for a long time, and guarantee the catalyst stability. The silicon layer acting as a buffer layer, can also catalyse the in-situ growth of CNT during the carbonization process, so as to construct a hybrid dimension heterostructure that integrates two-dimensional Co-N-C nanosheets and one-dimensional CNT, and build a cross-interconnected three-dimensional network channel, and provide sufficient space for accommodating discharge products, ensuring the reversible decomposition of products arising from electrochemical reduction of carbon dioxide, and

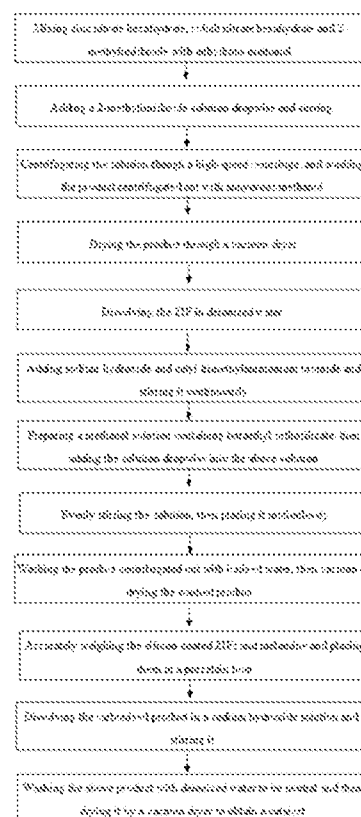


Fig. 1

guaranteeing the catalyst high-efficiency and stable operation.

FIELD OF THE INVENTION

5 The present invention relates to the technical field of preparing catalysts, in particular to a high - performance catalyst adapted to carbon dioxide catalytically-reducing batteries and a preparation method thereof.

BACKGROUND OF THE INVENTION

10 After 1973, among numerous energy storage systems, lithium-ion batteries have represented one of typical applications of clean energy but in recent years, but with rapid development of electric equipment, their development is limited by their inherent energy density, which can no longer meet the energy consumption requirements of equipment in future.

15 Compared with traditional ion batteries, M-CO₂ batteries have higher specific capacity and energy density, and the discharge products of M-CO₂ batteries are more stable than those of metal-oxygen batteries. Moreover, M-CO₂ batteries can realize the conversion of chemical energy to green electricity by way of combining with CO₂ catalytic conversion and energy conversion and storage technology, acting as a significant technical means to effectively abate CO₂ emission in the short term.

20 In the CO₂ battery, Li having high reactivity, high energy density and high theoretical equilibrium potential, is considered to be a promising candidate material for the anode, which needs water-and-oxygen-free conditions, but in the battery an organic electrolyte is mostly applied, and a reactant CO₂ is soluble in an organic ester/ether solvent, in addition, the cathode has to provide porous channels for the diffusion of metal ions, electrolytes and carbon dioxide, 25 provide sufficient storage space for solid-state discharge products, and provide a site for the formation and decomposition of catalysed discharge products. Moreover, the oxidation-reduction reaction process of the Li-CO₂ battery involves a transfer process of charges across a gas-liquid-solid-solid phase interface, and the insulating discharge product Li₂CO₃ produced during the discharge process will accumulate on the cathode, thus its accumulation state and degradation 30 rate will directly influence the reversibility of the reaction and the cycling performance of the battery. As a result, problems such as weak reaction impetus, severe polarization, poor reversibility, and capacity fading during cycling will occur to the battery.

Therefore, it is necessary to develop a high - performance catalyst adapted to carbon dioxide catalytically-reducing batteries and a preparation method thereof.

35

SUMMARY OF THE INVENTION

In view of the deficiencies of the prior art, the invention provides a high - performance catalyst adapted to carbon dioxide catalytically-reducing batteries and a preparation method thereof, so

as to solve the problems such as weak reaction impetus, severe polarization, poor reversibility, and capacity fading during cycling occurring to the Li-CO₂ battery, of which the oxidation-reduction reaction process involves a transfer process of charges across a gas-liquid-solid-solid phase interface, wherein the insulating discharge product Li₂CO₃ produced during the discharge process will accumulate on the cathode, and its accumulation state and degradation rate will directly influence the reversibility of the reaction and the cycling performance of the battery.

In order to achieve the above object, the technical scheme adopted in the present invention is as follows: a high - performance catalyst adapted to carbon dioxide catalytically-reducing batteries consisting of 0.25 g ~ 1.05 g of cobalt nitrate hexahydrate, 0.25 g ~ 0.80 g of zinc nitrate hexahydrate, 2.30 g ~ 2.35 g of 2-methylimidazole, 20 g ~ 100 g of anhydrous methanol, 100 g ~ 150 g of deionized water, 0.01 g ~ 0.06 g of sodium hydroxide, 0.10 g ~ 0.15 g of cetyl trimethylammonium bromide, 0.1 g ~ 0.6 g of tetraethyl orthosilicate, and 1.5 g ~ 2.5 g of melamine by weight.

A preparation method of the high - performance catalyst adapted to carbon dioxide catalytically-reducing batteries, comprising the steps of

- S1. accurately weighing out zinc nitrate hexahydrate, cobalt nitrate hexahydrate and 2-methylimidazole by corresponding weights through an electronic balance, respectively, then pouring them into anhydrous methanol sequentially and mixing them fully;
- S2. adding a 2-methylimidazole solution dropwise to a solution in which zinc nitrate hexahydrate and cobalt nitrate hexahydrate have dissolved and stirring it through a magnetic stirrer to obtain a purple solution;
- S3. centrifugating the purple solution through a high - speed centrifuge, and washing the product centrifugated out with anhydrous methanol;
- S4. drying the washed product through a vacuum dryer to obtain a purple product ZIF;
- S5. weighing out ZIF through a precision electronic balance, and dissolving the ZIF in deionized water;
- S6. adding sodium hydroxide and cetyl trimethylammonium bromide to the solution sequentially, and stirring it continuously;
- S7. preparing a methanol solution containing tetraethyl orthosilicate by way of mixing them evenly, then adding the solution dropwise into the above solution;
- S8. evenly stirring the above solution by a magnetic stirrer at room temperature, then placing it motionlessly, next removing the supernatant in the solution by means of centrifugation;
- S9. washing the product centrifugated out with ionized water, then vacuum-drying the washed product through a vacuum dryer to obtain silicon-coated ZIFs;
- S10. accurately weighing the silicon-coated ZIFs and melamine through a precision electronic balance and placing them in a porcelain boat, next moving it to a tube furnace to carbonize them under protection of a hydrogen argon gas mixture, so as to obtain a Co-N-C@CNT catalyst;

S11. dissolving the carbonized Co-N-C@Si in a sodium hydroxide solution and stirring it through a heat-collecting thermostatic magnetic stirrer; and

S12. washing the above product with deionized water to be neutral and then drying it by a vacuum dryer to obtain a Co-N-C@CNT catalyst.

5 Step 1. firstly, accurately weighing out zinc nitrate hexahydrate, cobalt nitrate hexahydrate and 2-methylimidazole by corresponding weights through an electronic balance, respectively, so as to ensure an accurate formulation during this process, secondly, pouring the raw materials into anhydrous methanol sequentially and mixing them fully, so as to enable them to be fully dissolved and evenly mixed;

10 Step 2. adding a 2-methylimidazole solution dropwise to a solution containing zinc nitrate hexahydrate and cobalt nitrate hexahydrate and enabling this process to slowly progress, so as to ensure that the chemical reactions occurring in the solution can be carried out sufficiently;

Step 3. enabling a purple solution to be centrifugated through a high - speed centrifuge, so as to separate solid particles from the solution, and enabling the solid product centrifugated out to be washed with anhydrous methanol, so as to remove the impurities in the solution and obtain a pure product;

Step 4. removing the moisture in the product and obtain a dried product ZIF by way of vacuum drying, and enabling the drying temperature and time to be strictly controlled, so as to ensure the quality and stability of the product;

20 Step 5. accurately weighing out the ZIF through a precision electronic balance and dissolving it in deionized water, so as to ensure that the ZIF is fully dissolved in preparation for the subsequent steps;

Step 6. adding sodium hydroxide and cetyl trimethylammonium bromide into the above solution sequentially meanwhile stirring them continuously, so as to adjust the pH and the surface activity of the solution, and continuing stirring, so as to ensure fully-mixing;

Step 7. preparing a methanol solution containing tetraethyl orthosilicate and adding it dropwise to the above solution, so as to ensure that the solution can be evenly mixed;

Step 8. evenly stirring the above solution at room temperature, then placing it motionlessly, next removing the supernatant in the solution by means of centrifugation to obtain a purer product;

30 Step 9. washing the product centrifugated out with ionized water to remove impurities, then vacuum-drying the washed product to obtain silicon-coated ZIFs; and

Step 10. accurately weighing out silicon-coated ZIFs and melamine through a precision electronic balance and placing them in a porcelain boat, next moving it to a tube furnace to carbonize them, so as to obtain a Co-N-C@CNT catalyst.

35 Preferably, in S2, the magnetic stirrer stirs the solution at a stirring speed of 100 rpm - 1000 rpm at 2030°C for 2h - 4h.

Preferably, in S4, the vacuum dryer dries the washed product at 70°C - 90°C for 11 - 13 h.

Preferably, in S8, the magnetic stirrer stirs the solution at a stirring speed of 100 rpm - 1000 rpm at 20°C - 30°C for 20 min - 40 min, and the solution is placed motionlessly for 1 h - 3 h. LU506510

Preferably, in S9, the vacuum dryer dries the washed product at 70°C - 90°C for 11 - 13 h.

Preferably, in S10, the carbonization progresses by way of raising temperature to 340°C - 360°C at a rate of 5°C/min, then keeping constant temperature for 1 h - 3 h, next raising temperature to 750°C - 850°C at a rate of 2°C/min, then performing carbonization at constant temperature for 1 h - 3 h, finally lowering temperature to room temperature at 20°C - 30°C in the tube furnace, to obtain a Co-N-C@CNT catalyst.

Preferably, in S11, the heat-collecting thermostatic magnetic stirrer stirs the solution at a stirring speed of 200 rpm - 300 rpm at 40°C - 60°C for 11 h - 13 h.

Preferably, in S12, the vacuum dryer dries the washed product at 70°C - 90°C for 11 - 13 h.

Preferably, the model number of the heat-collecting thermostatic magnetic stirrer is DF-101S.

A magnetic stirrer is used to enable zinc nitrate hexahydrate and cobalt nitrate hexahydrate to fully react with 2-methylimidazole by way of controlling its stirring time, stirring temperature, and stirring speed, so as to form the homogeneous purple solution. A vacuum dryer is used to enable moisture to be absolutely removed from the product by way of controlling temperature and drying time, ensuring the dryness and stability of the product. The magnetic stirrer helps to ensure homogeneous mixing and precipitation separation of the above solution. A heat-collecting thermostatic magnetic stirrer is used to enable the carbonized products to be fully dispersed and mixed in the solution by way of controlling its stirring time, stirring temperature, and stirring speed.

The high-performance catalyst adapted to carbon dioxide catalytically-reducing batteries and the preparation method thereof provided by the present invention have the following beneficial effect.

1. In the present invention, a silicon-coated catalyst is prepared through a special process, so as to improve the stability and electrocatalytic activity of the catalyst, and then improve the battery performance and enhance the reduction effect of the catalyst to carbon dioxide. Moreover, the silicon-coated catalyst has excellent stability, thus the silicon layer can protect the core part of the catalyst from the impact of the external environment, ensure that the catalyst has high activity even used for a long time, and guarantee the catalyst stability. The silicon layer acting as a buffer layer, can also catalyse the in-situ growth of CNT during the carbonization process, so as to construct a hybrid dimension heterostructure that integrates two-dimensional Co-N-C nanosheets and one-dimensional CNT, and build a cross-interconnected three-dimensional network channel, and provide sufficient space for accommodating discharge products, ensuring the reversible decomposition of products arising from electrochemical reduction of carbon dioxide, and guaranteeing the catalyst high-efficiency and stable operation.

2. A novel Co-N-C@CNT catalyst provided by the present invention exhibits excellent performance in terms of electrocatalytic activity and stability, and using the catalyst can achieve

high current density and low overpotential, and enhance the reduction efficiency of carbon dioxide. Moreover, in the process of electrochemical reaction, it can effectively lower the activation energy and promote the faster conversion of reactants into products, so it is very important to improve the reduction efficiency of carbon dioxide. Therefore, during the reduction process, the decrease in activation energy can accelerate the reaction rate and increase the yield of the product. The Co-N-C@CNT catalyst is coupled with a hybrid dimension heterostructure that integrates two-dimensional Co-N-C nanosheets and one-dimensional CNT, so as to build a cross-interconnected three-dimensional network channel, and provide sufficient space for accommodating discharge products, ensuring the reversible decomposition of products arising from electrochemical reduction of carbon dioxide, guaranteeing the catalyst high - efficiency and stable operation and raising the efficiency for electrochemically oxygenizing and decomposing the product.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a flow chart of the preparation method of the present invention;
Fig. 2 is a flow chart of the experimental process for the catalyst of the present invention;
Fig. 3 shows a GCD curve of the present invention.

DETAILED DESCRIPTION OF SOME EMBODIMENTS

The technical solutions in the embodiments of the present invention will be clearly and completely described as follows in combination with the drawings in the examples of the present invention, but obviously, the described examples are only a part of the embodiments of the present invention, rather than all the embodiments. Based on the examples of the present invention, all other examples obtained by a person skilled in the art without creative efforts shall fall within the protection scope of the present invention.

EXAMPLE 1

- S1. Use an electronic balance to weigh out 0.5 g of cobalt nitrate hexahydrate, 0.5 g of zinc nitrate hexahydrate and 2.33 g of 2-methylimidazole, respectively, and then pour them into 20 g of anhydrous methanol sequentially for mixing.
- S2. Add a 2-methylimidazole solution dropwise to a solution in which zinc nitrate hexahydrate and cobalt nitrate hexahydrate have dissolved, and then use a magnetic stirrer to stir it at a speed of 200 rpm at 20°C for 2 hours to obtain a purple solution.
- S3. Centrifugate the purple solution through a high - speed centrifuge, and then wash the product centrifugated out with anhydrous methanol.
- S4. Place the washed product in a vacuum dryer and dry it at 80°C for 12 hours to obtain a purple product ZIF.
- S5. Use a precision electronic balance to weigh out ZIF and dissolve it into deionized water.

- S6. Add 0.03 g of sodium hydroxide and 0.12 g of cetyltrimethylammonium bromide into the solution sequentially, and stir it.
- S7. Prepare a methanol solution containing 0.3 g of tetraethyl orthosilicate, add it dropwise into the above solution, and stir it evenly at 25°C, then place it motionlessly for 2 hours.
- 5 S8. Wash the product centrifugated out with ionized water, and dry it at 80°C for 12 hours in a vacuum dryer to obtain silicon-coated ZIFs.
- S9. Use a precision electronic balance to weigh out 0.5 g of silicon-coated ZIFs and 2 g of melamine, place them in a porcelain boat, and then move the porcelain boat into a tube furnace;
- 10 S10. Heat the porcelain boat under the protection of a hydrogen argon gas mixture, and raise temperature to 350°C at a rate of 5°C/min, then keep constant temperature for 1 hour, next raise temperature to 800°C at a rate of 2°C/min, keep constant temperature for 2 hours, finally cool it to 25°C to obtain a Co-N-C@CNT catalyst.
- S11. Dissolve the carbonized Co-N-C@Si in a sodium hydroxide solution, then use a heat-
15 collecting thermostatic magnetic stirrer to stir it at 50°C for 12 hours.
- S12. Wash the material with deionized water, and on the pH 7 occurring to the material, place the material in a vacuum dryer and dry it at 80°C for 12 hours to obtain a Co-N-C@CNT catalyst.

Conclusion: This example involves steps of mixing metal salts with the 2-methylimidazole
20 solution, filtering and washing the product, then drying it to obtain the silicon-coated ZIFs. Coating with silicon can improve the stability and durability of ZIFs materials, enhance their performance in catalysis and electrochemistry applications, and coating with silicon can increase the surface area of the material, provide more active sites, and improve reaction efficiency.

25 **EXAMPLE 2**

- S1. Use an electronic balance to weigh out 1.05 g of cobalt nitrate hexahydrate, 0.80 g of zinc nitrate hexahydrate and 2.35 g of 2-methylimidazole, respectively, and then pour them into 100 g of anhydrous methanol sequentially for mixing.
- S2. Add a 2-methylimidazole solution dropwise to a solution in which zinc nitrate hexahydrate
30 and cobalt nitrate hexahydrate have dissolved, and then use a magnetic stirrer to stir it at a speed of 1000 rpm at 30°C for 4 hours to obtain a purple solution.
- S3. Centrifugate the purple solution through a high - speed centrifuge, and then wash the product centrifugated out with anhydrous methanol.
- S4. Place the washed product in a vacuum dryer and dry it at 90°C for 13 hours to obtain a
35 purple product ZIF.
- S5. Use a precision electronic balance to weigh out ZIF and dissolve it into 150 g of deionized water.
- S6. Add 0.06 g of sodium hydroxide and 0.15 g of cetyltrimethylammonium bromide into the

solution sequentially, and stir it.

S7. Prepare a methanol solution containing 0.6 g of tetraethyl orthosilicate, add it dropwise into the above solution, and stir it evenly at 25°C, then place it motionlessly for 3 hours.

S8. Wash the product centrifugated out with ionized water, and dry it at 90°C for 13 hours in a vacuum dryer to obtain silicon-coated ZIFs.

S9. Use a precision electronic balance to weigh out 0.6 g of silicon-coated ZIFs and 2.5 g of melamine, place them in a porcelain boat, and then move the porcelain boat into a tube furnace;

S10. Heat the porcelain boat under the protection of a hydrogen argon gas mixture, and raise temperature to 360°C at a rate of 5°C/min, then keep constant temperature for 3 hours, next raise temperature to 850°C at a rate of 2°C/min, keep constant temperature for 3 hours, finally cool it to 25°C to obtain a Co-N-C@CNT catalyst.

S11. Dissolve the carbonized Co-N-C@Si in a sodium hydroxide solution, then use a heat-collecting thermostatic magnetic stirrer to stir it at 60°C for 13 hours.

S12. Wash the material with deionized water, and on the pH 7 occurring to the material, place the material in a vacuum dryer and dry it at 90°C for 13 hours to obtain a Co-N-C@CNT catalyst.

Conclusion: This example involves the steps of mixing the silicon-coated ZIFs with melamine, performing a high - temperature carbonization treatment, and then washing and drying it to obtain a Co-N-C@CNT catalyst, which has excellent electrocatalytic properties and can be applied in energy conversion of CO₂ batteries. The preparation process of the catalyst enables high - efficient electrocatalytic activity and long-term stability through carbonization treatment and formation of metal-nitrogen coordination structures.\

EXAMPLE 3

S1. Use an electronic balance to weigh out 1 g of cobalt nitrate, 0.8g of zinc nitrate and 2 g of 2-methylimidazole, respectively, and then and pour them into 50 g of anhydrous methanol sequentially for mixing.

S2. Transfer the mixed solution to a closed container and place it motionlessly at 25°C for 24 hours to make the reaction fully carried out.

S3. Filter the reaction solution through a filter paper to separate a solid precipitate from the solution.

S4. Wash the solid precipitate with anhydrous methanol to remove impurities, and then place the washed product in a ventilation dryer and dry it at 25°C for 48 hours to obtain a purple product ZIF.

S5. Use a precision electronic balance to weigh out ZIF and dissolve it into 100 g of deionized water.

S6. Add 0.05 g of sodium hydroxide and 0.2 g of cetyltrimethylammonium bromide into the

solution sequentially, and stir it.

- S7. Prepare a methanol solution containing 0.5 g of ethyl tetraacetate, add it dropwise into the above solution, and stir it evenly at 25°C, then place it motionlessly for 4 hours.
- S8. Wash the product centrifugated out with ionized water, and dry it for 48 hours in a ventilation dryer to obtain silicon-coated ZIFs.
- S9. Use a precision electronic balance to weigh out 0.8g of silicon-coated ZIFs and 2.2 g of melamine, place them in a porcelain boat, and then move the porcelain boat into a tube furnace;
- S10. Heat the porcelain boat under the protection of a hydrogen argon gas mixture, and raise temperature to 380°C at a rate of 4°C/min, then keep constant temperature for 2 hours, next raise temperature to 820°C at a rate of 3°C/min, keep constant temperature for 3 hours, finally cool it to room temperature to obtain a Co-N-C@CNT catalyst.
- S11. Dissolve the carbonized Co-N-C@Si in a sodium hydroxide solution, then use a heat-collecting thermostatic magnetic stirrer to stir it at 70°C for 14 hours.
- S12. Wash the material with deionized water, and on the pH 7 occurring to the material, place the material in a ventilation dryer and dry it at room temperature for 48 hours to obtain a Co-N-C@CNT catalyst.

Conclusion: This example is a variant of Example 1, differing in the ratio of the metal salt to the 2-methylimidazole and varying in treatment time, so as to prepare a silicon-coated ZIFs material, which can be optimized in its composition and structure and improve in the performance of the catalyst by way of adjusting the ratio of the metal salt to the 2-methylimidazole and the melamine and the treatment time.

EXAMPLE 4

- S1. Use an electronic balance to weigh out 0.8 g of cobalt nitrate, 0.6 g of zinc nitrate and 1.5 g of 2-methylimidazole, respectively, and then and pour them into 30 g of anhydrous methanol sequentially for mixing.
- S2. Transfer the mixed solution to a closed container and place it motionlessly at 25°C for 6 hours to make the reaction fully carried out.
- S3. Filter the reaction solution through a filter paper to separate a solid precipitate from the solution.
- S4. Wash the solid precipitate with anhydrous methanol to remove impurities, and then place the washed product in a ventilation dryer and dry it at 25°C for 24 hours to obtain a purple product ZIF.
- S5. Use a precision electronic balance to weigh out ZIF and dissolve it into 80 g of deionized water.
- S6. Add 0.04g of sodium hydroxide and 0.1 g of cetyltrimethylammonium bromide into the solution sequentially, and stir it.

- S7. Prepare a methanol solution containing 0.4g of ethyl acetate, add it dropwise into the above solution, and stir it evenly at 25°C, then place it motionlessly for 3 hours.
- S8. Wash the product centrifugated out with ionized water, and dry it for 36 hours in a ventilation dryer to obtain silicon-coated ZIFs.
- 5 S9. Use a precision electronic balance to weigh out 0.6 g of silicon-coated ZIFs and 1.8g of melamine, place them in a porcelain boat, and then move the porcelain boat into a tube furnace;
- S10. Heat the porcelain boat under the protection of a hydrogen argon gas mixture, and raise temperature to 400°C at a rate of 3°C/min, then keep constant temperature for 2 hours, next
10 raise temperature to 850°C at a rate of 4°C/min, keep constant temperature for 4 hours, finally cool it to 25°C to obtain a Co-N-C@CNT catalyst.
- S11. Dissolve the carbonized Co-N-C@Si in a sodium hydroxide solution, then use a heat-collecting thermostatic magnetic stirrer to stir it at 80°C for 16 hours.
- S12. Wash the material with deionized water, and on the pH 7 occurring to the material, place
15 the material in a ventilation dryer and dry it at 25°C for 36 hours to obtain a Co-N-C@CNT catalyst.

Conclusion: This example is a variant of Example 2, differing in the ratio of the coated ZIFs to the melamine and varying in carbonization treatment time, so as to prepare a Co-N-C@CNT catalyst. This method helps to determine the optimal catalyst composition and treatment
20 conditions to obtain the best electrocatalytic performance.

EXAMPLE 5

- S1. Use an electronic balance to weigh out 1.2 g of cobalt nitrate, 0.9g of zinc nitrate and 2.5 g of 2-methylimidazole, respectively, and then and pour them into 40 g of anhydrous methanol
25 sequentially for mixing.
- S2. Transfer the mixed solution to a closed container and place it motionlessly at 25°C for 8 hours to make the reaction fully carried out.
- S3. Filter the reaction solution through a filter paper to separate a solid precipitate from the solution.
- 30 S4. Wash the solid precipitate with anhydrous methanol to remove impurities, and then place the washed product in a ventilation dryer and dry it at 25°C for 36 hours to obtain a purple product ZIF.
- S5. Use a precision electronic balance to weigh out ZIF and dissolve it into 120 g of deionized water.
- 35 S6. Add 0.06 g of sodium hydroxide and 0.15 g of cetyltrimethylammonium bromide into the solution sequentially, and stir it.
- S7. Prepare a methanol solution containing 0.8g of ethyl acetate, add it dropwise into the above solution, and stir it evenly at 25°C, then place it motionlessly for 4 hours.

S8. Wash the product centrifugated out with ionized water, and dry it for 48 hours in a ventilation dryer to obtain silicon-coated ZIFs.

S9. Use a precision electronic balance to weigh out 0.9g of silicon-coated ZIFs and 2.8g of melamine, place them in a porcelain boat, and then move the porcelain boat into a tube furnace;

S10. Heat the porcelain boat under the protection of a hydrogen argon gas mixture, and raise temperature to 420°C at a rate of 4°C/min, then keep constant temperature for 3 hours, next raise temperature to 880°C at a rate of 5°C/min, keep constant temperature for 5 hours, finally cool it to 25°C to obtain a Co-N-C@CNT catalyst.

S11. Dissolve the carbonized Co-N-C@Si in a sodium hydroxide solution, then use a heat-collecting thermostatic magnetic stirrer to stir it at 100°C for 18 hours.

S12. Wash the material with deionized water, and on the pH 7 occurring to the material, place the material in a vacuum dryer and dry it at 80°C for 12 hours to obtain a Co-N-C@CNT catalyst.

Conclusion: This example is a variant of Example 1, differing in the ratio of the metal salt to the 2-methylimidazole and varying in treatment time, so as to prepare a silicon-coated ZIFs material, so it is possible to search the influence of material ratio and treatment conditions on material properties.

TEST EXPERIMENT:

Objective: To evaluate the performance of the prepared silicon-coated ZIFs and Co-N-C@CNT catalyst in a carbon dioxide reducing battery.

Steps:

- Prepare an anode and cathode of a carbon dioxide reducing battery, and assemble them as a battery;
- Place the battery in an electrochemical test system at a constant temperature and constant voltage, and set temperature and pressure conditions;
- Perform cyclic voltammetry tests to record the changes of current density with potential and evaluate the electrocatalytic activity of the catalyst;
- Perform a potentiostatic test to record the changes of current density over time and evaluate the stability of the catalyst; and
- Record experimental data, and perform data analysis to compare the catalyst with the material formulation in performance difference.

COMPARATIVE EXPERIMENT 1: Comparison of catalyst carriers

Object: Silicone-coated ZIFs and non-coated ZIFs

Parameters: catalyst carrier type, current density, potential, temperature

Experimental Data Table 1:

LU506510

Condition	Catalyst carrier type	current density (mA/cm ²)	potential (V)	temperature (°C)
Example1	Silicone-coated ZIFs	5.2	-0.8	50
Example 3	non-coated ZIF	4.7	-0.7	50
Comparative Experiment 1	Silicone-coated ZIFs	6.3	-0.7	55
Comparative Experiment 2	non-coated ZIF	5.8	-0.6	55

COMPARATIVE EXPERIMENT 2: Comparison of catalysts

Object: Silicon-coated ZIFs materials and Co-N-C@CNT catalysts

5

Parameters: catalyst type, current density, potential, temperature

Experimental Data Table 2:

Condition	Catalyst type	current density (mA/cm ²)	potential (V)	temperature (°C)
Example1	Silicone-coated ZIFs	5.2	-0.8	50
Example 2	Co-N-C	8.7	-0.9	50
Comparative Experiment 1	Silicone-coated ZIFs	6.3	-0.7	55
Comparative Experiment 2	Co-N-C	7.8	-0.8	55

COMPARATIVE EXPERIMENT 3: Comparison of catalyst precursors

10

Object: Co-N-C@CNT catalyst for catalyst precursors

Parameters: catalyst precursor type, current density, potential, temperature

Experimental Data Table 3:

Condition	Catalyst precursor type	current density (mA/cm ²)	potential (V)	temperature (°C)
Example1	Precursor 1	8.7	-0.9	50
Example 4	Precursor 2	9.5	-1.0	50
Comparative Experiment 1	Precursor 1	9.0	-0.8	55
Comparative Experiment 2	Precursor 2	9.8	-0.9	55

15

Conclusions:

1. Coating with silicon can improve the stability and electrocatalytic activity of the catalyst, achieve higher current density and lower overpotential, and the preparation method of the high - performance catalyst adapted to carbon dioxide catalytically-reducing batteries can enhance the reduction effect of the catalyst on carbon dioxide and improve the performance of the battery.
2. The catalyst has excellent electrocatalytic activity and stability, which can achieve high current density and low overpotential, and the method of preparing the Co-N-C@CNT catalyst can improve the surface structure and active site of the catalyst, and enhance the reduction efficiency of carbon dioxide.
3. The silicon-coated ZIFs can provide higher catalytic activity and stability, and the Co-N-C@CNT catalyst significantly influences on improvement of catalyst performance.
4. As shown in Fig.3, the initial discharge and charge capacities of Co-N-C-800 are 6.93 mAh/cm² and 3.04 mAh/cm², respectively, which are much higher than those of Co-N-C-700 and Co-N-C-900, and achieve strong energy conversion capacity during the reaction of CO₂RR and CO₂ER. This phenomenon arises from a cause that the defect sites and active sites of Co-N-C-700 and Co-N-C-900 are blocked by particulate impurities, while Co-N-C-800 smooth in surface has a wide specific surface area to carry the products and retains the active sites to degrade the products during charging. This proves that the combination of a porous structure with Co-N_x active sites plays an important role in deep charge and discharge.

Despite having shown and described the examples of the present invention, it is understandable for a person skilled in the art to make a variety of changes, modifications, substitutions and variants on these examples without departing from the principle and essence of the invention, and the protection scope of the present invention is defined by the attached claims and their equivalents.

CLAIMS

1. A high - performance catalyst adapted to carbon dioxide catalytically-reducing batteries consisting of 0.25 g ~ 1.05 g of cobalt nitrate hexahydrate, 0.25 g ~ 0.80 g of zinc nitrate hexahydrate, 2.30 g ~ 2.35 g of 2-methylimidazole, 20 g ~ 100 g of anhydrous methanol, 100 g ~ 150 g of deionized water, 0.01 g ~ 0.06 g of sodium hydroxide, 0.10 g ~ 0.15 g of cetyl trimethylammonium bromide, 0.1 g ~ 0.6 g of tetraethyl orthosilicate, and 1.5 g ~ 2.5 g of melamine by weight.
2. A preparation method of the high - performance catalyst adapted to carbon dioxide catalytically-reducing batteries as claimed in claim 1, comprising the steps of
 - S1. accurately weighing out zinc nitrate hexahydrate, cobalt nitrate hexahydrate and 2-methylimidazole by corresponding weights through an electronic balance, respectively, then pouring them into anhydrous methanol sequentially and mixing them fully;
 - S2. adding a 2-methylimidazole solution dropwise to a solution in which zinc nitrate hexahydrate and cobalt nitrate hexahydrate have dissolved and stirring it through a magnetic stirrer to obtain a purple solution;
 - S3. centrifugating the purple solution through a high - speed centrifuge, and washing the product centrifugated out with anhydrous methanol;
 - S4. drying the washed product through a vacuum dryer to obtain a purple product ZIF;
 - S5. weighing out ZIF through a precision electronic balance, and dissolving the ZIF in deionized water;
 - S6. adding sodium hydroxide and cetyl trimethylammonium bromide to the solution sequentially, and stirring it continuously;
 - S7. preparing a methanol solution containing tetraethyl orthosilicate by way of mixing them evenly, then adding the solution dropwise into the above solution;
 - S8. evenly stirring the above solution by a magnetic stirrer at room temperature, then placing it motionlessly, next removing the supernatant in the solution by means of centrifugation;
 - S9. washing the product centrifugated out with ionized water, then vacuum-drying the washed product through a vacuum dryer to obtain silicon-coated ZIFs;
 - S10. accurately weighing the silicon-coated ZIFs and melamine through a precision electronic balance and placing them in a porcelain boat, next moving it to a tube furnace to carbonize them under protection of a hydrogen argon gas mixture, so as to obtain a Co-N-C@CNT catalyst;
 - S11. dissolving the carbonized Co-N-C@Si in a sodium hydroxide solution and stirring it through a heat-collecting thermostatic magnetic stirrer; and
 - S12. washing the above product with deionized water to be neutral and then drying it by a vacuum dryer to obtain a Co-N-C@CNT catalyst.

3. The preparation method according to claim 2, wherein in S2, the magnetic stirrer stirs the solution at a stirring speed of 100 rpm - 1000 rpm at 20°C - 30°C for 2h - 4h.
4. The preparation method according to claim 2, wherein in S4, the vacuum dryer dries the washed product at 70°C - 90°C for 11 - 13 h.
5. The preparation method according to claim 2, wherein in S8, the magnetic stirrer stirs the solution at a stirring speed of 100 rpm - 1000 rpm at 20°C - 30°C for 20 min - 40 min, and the solution is placed motionlessly for 1 h - 3 h.
6. The preparation method according to claim 2, wherein in S9, the vacuum dryer dries the washed product at 70°C - 90°C for 11 - 13 h.
7. The preparation method according to claim 2, wherein in S10, the carbonization progresses by way of raising temperature to 340°C - 360°C at a rate of 5°C/min, then keeping constant temperature for 1 h - 3 h, next raising temperature to 750°C - 850°C at a rate of 2°C/min, then performing carbonization at constant temperature for 1 h - 3 h, finally lowering temperature to room temperature at 20°C - 30°C in the tube furnace, to obtain a Co-N-C@CNT catalyst.
8. The preparation method according to claim 2, wherein in S11, the heat-collecting thermostatic magnetic stirrer stirs the solution at a stirring speed of 200 rpm - 300 rpm at 40°C - 60°C for 11 h - 13 h.
9. The preparation method according to claim 2, wherein in S12, the vacuum dryer dries the washed product at 70°C - 90°C for 11 - 13 h.
10. The preparation method according to claim 8, wherein the model number of the heat-collecting thermostatic magnetic stirrer is DF-101S.

1. Ein Hochleistungskatalysator, der für Kohlendioxid katalytisch reduzierende Batterien geeignet ist, bestehend aus 0,25 g ~ 1,05 g Kobaltnitrat-hexahydrat, 0,25 g ~ 0,80 g Zinknitrat-hexahydrat, 2,30 g ~ 2. 35 g 2-Methylimidazol, 20 g - 100 g wasserfreies Methanol, 100 g - 150 g entionisiertes Wasser, 0,01 g - 0,06 g Natriumhydroxid, 0,10 g - 0,15 g Cetyltrimethylammoniumbromid, 0,1 g - 0,6 g Tetraethylorthosilikat und 1,5 g - 2,5 g Melamin nach Gewicht.
2. Verfahren zur Herstellung des Hochleistungskatalysators, der für Kohlendioxid katalytisch reduzierende Batterien nach Anspruch 1 geeignet ist, umfassend die folgenden Schritte
 - S1. mit Hilfe einer elektronischen Waage genaues Abwiegen der entsprechenden Gewichte von Zinknitrat-hexahydrat, Kobaltnitrat-hexahydrat und 2-Methylimidazol, dann nacheinander Einfüllen in wasserfreies Methanol und vollständiges Mischen;
 - S2. tropfenweise Zugabe einer 2-Methylimidazol-Lösung zu einer Lösung, in der sich Zinknitrat-hexahydrat und Kobaltnitrat-hexahydrat gelöst haben, und Rühren mit einem Magnetrührer, um eine violett-farbige Lösung zu erhalten;
 - S3. Zentrifugieren der violett-farbenen Lösung durch eine Hochgeschwindigkeits-zentrifuge und Waschen des abzentrifugierten Produkts mit wasserfreiem Methanol;
 - S4. Trocknen des gewaschenen Produkts durch einen Vakuum-trockner, um ein violett-farbiges Produkt ZIF zu erhalten;
 - S5. Abwiegen des ZIF mit einer elektronischen Präzisionswaage und Auflösen des ZIF in entionisiertem Wasser;
 - S6. nacheinander Zugabe von Natriumhydroxid und Cetyltrimethylammoniumbromid zu der Lösung und kontinuierliches Rühren;
 - S7. Herstellen einer Methanol-lösung, die Tetraethylorthosilikat enthält, durch gleichmäßiges Mischen und anschließende tropfenweise Zugabe der Lösung in die obige Lösung;
 - S8. gleichmäßiges Umrühren der obigen Lösung mit einem Magnetrührer bei Raumtemperatur, dann unbewegliches Abstellen und anschließendes Entfernen des Überstands in der Lösung durch Zentrifugieren;
 - S9. Waschen des heraus-zentrifugierten Produkts mit ionisiertem Wasser, dann Vakuum-trocknen des gewaschenen Produkts durch einen Vakuum-trockner, um silikonbeschichtete ZIFs zu erhalten;
 - S10. genaues Abwiegen der siliziumbeschichteten ZIFs und des Melamins mit Hilfe einer elektronischen Präzisionswaage und Einbringen in ein Porzellanschiffchen, anschließend Einbringen in einen Roh-rofen, um sie unter dem Schutz einer Wasserstoff-Argon-Gasmischung zu verkohlen, um einen Co-N-C@CNT-Katalysator zu erhalten;
 - S11. Auflösen des karbonisierten Co-N-C@Si in einer Natriumhydroxid-lösung und Rühren

durch einen wärmeaufnehmenden thermostatischen Magnetprüher; und

LU506510

S12. Waschen des obigen Produkts mit entionisiertem Wasser, bis es neutral ist, und anschließendes Trocknen in einem Vakuumtrockner, um einen Co-N-C@CNT-Katalysator zu erhalten.

- 5 3. Verfahren zur Herstellung nach Anspruch 2, wobei in S2 der Magnetprüher die Lösung mit einer Rührgeschwindigkeit von 100 U/min - 1000 U/min bei 20°C - 30°C für 2h - 4h rührt.
- 10 4. Verfahren zur Herstellung nach Anspruch 2, wobei in S4 der Vakuumtrockner das gewaschene Produkt bei 70°C - 90°C für 11 - 13 h trocknet.
- 15 5. Verfahren zur Herstellung nach Anspruch 2, dadurch gekennzeichnet, dass in S8 der Magnetprüher die Lösung mit einer Rührgeschwindigkeit von 100 U/min - 1000 U/min bei 20°C - 30°C für 20 min - 40 min rührt und die Lösung für 1 h - 3 h bewegungslos gestellt wird.
- 20 6. Verfahren zur Herstellung nach Anspruch 2, dadurch gekennzeichnet, dass in S9 der Vakuumtrockner das gewaschene Produkt bei 70°C - 90°C für 11 - 13 h trocknet.
- 25 7. Verfahren zur Herstellung nach Anspruch 2, wobei in S10 die Karbonisierung erfolgt durch Erhöhen der Temperatur auf 340°C - 360°C mit einer Rate von 5°C/min, dann Halten der konstanten Temperatur für 1 h - 3 h, nächstes Erhöhen der Temperatur auf 750°C - 850°C mit einer Rate von 2°C/min, dann Durchführen der Karbonisierung bei konstanter Temperatur für 1 h - 3 h, schließlich Absenken der Temperatur auf Raumtemperatur bei 20°C - 30°C im Rohrfen, um einen Co-N-C@CNT-Katalysator zu erhalten.
- 30 8. Verfahren zur Herstellung nach Anspruch 2, wobei in S11 der wärmeaufnehmende thermostatische Magnetprüher die Lösung mit einer Rührgeschwindigkeit von 200 U/min - 300 U/min bei 40°C - 60°C für 11 h - 13 h rührt.
9. Verfahren zur Herstellung nach Anspruch 2, wobei in S12 der Vakuumtrockner das gewaschene Produkt bei 70°C - 90°C für 11 - 13 h trocknet.
10. Verfahren zur Herstellung nach Anspruch 8, wobei die Modellnummer des wärmesammelnden thermostatischen Magnetprühers DF-101S ist.

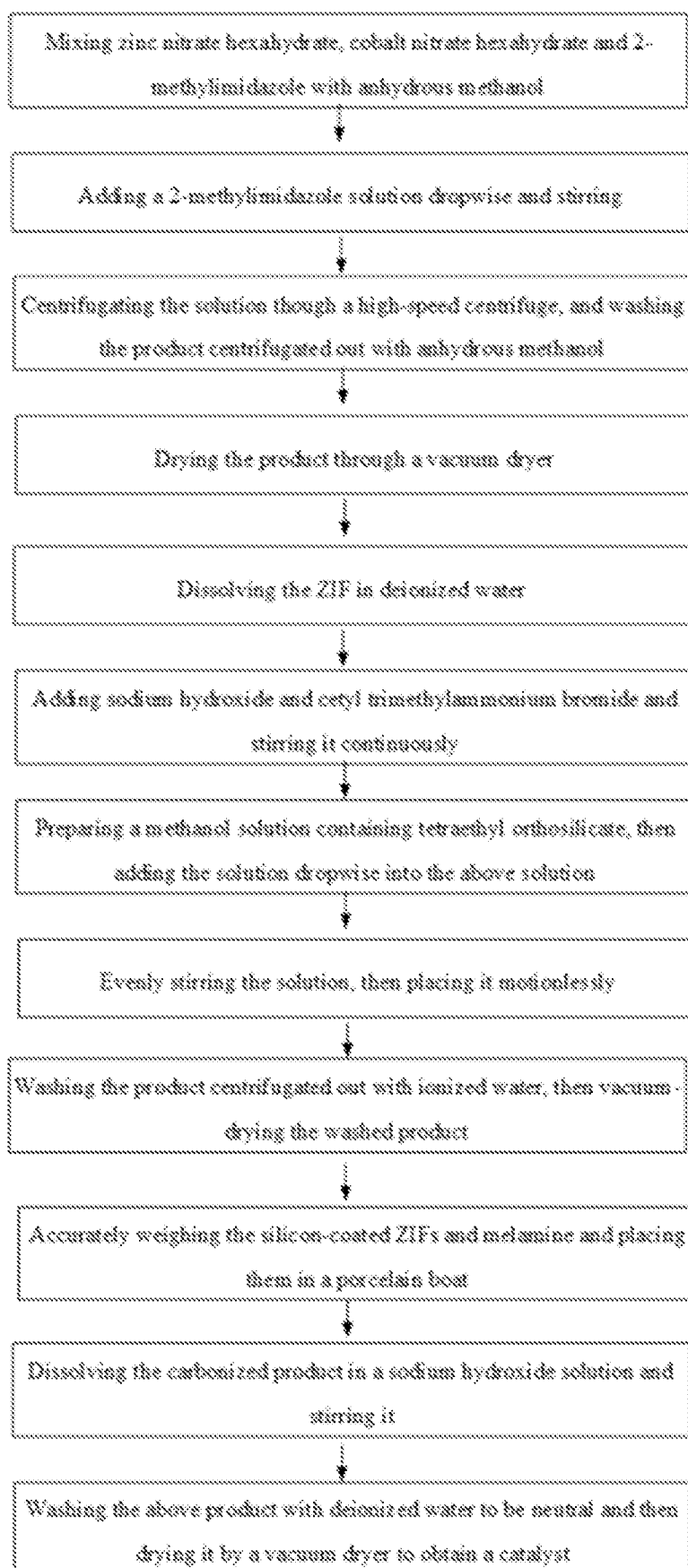


Fig. 1

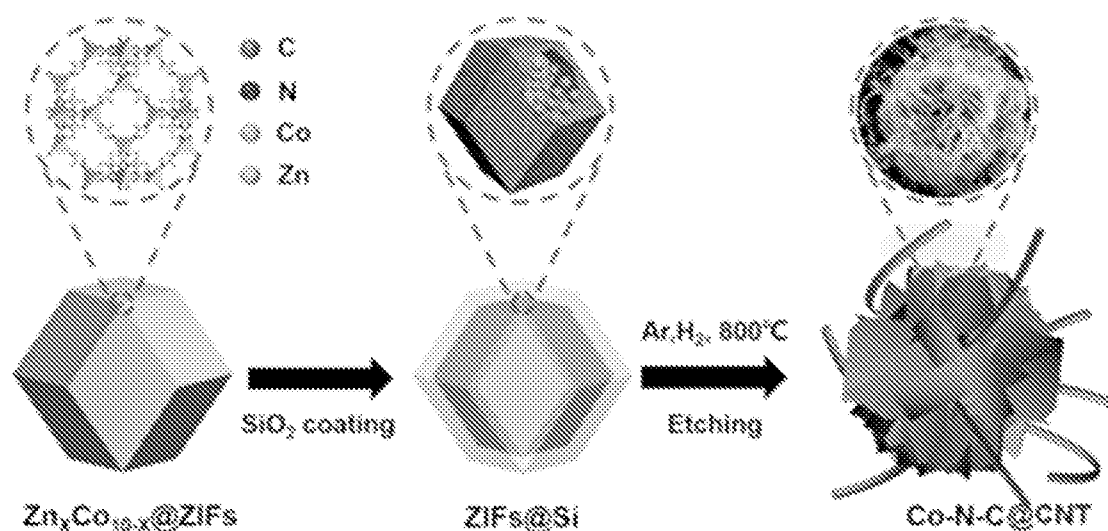


Fig. 2

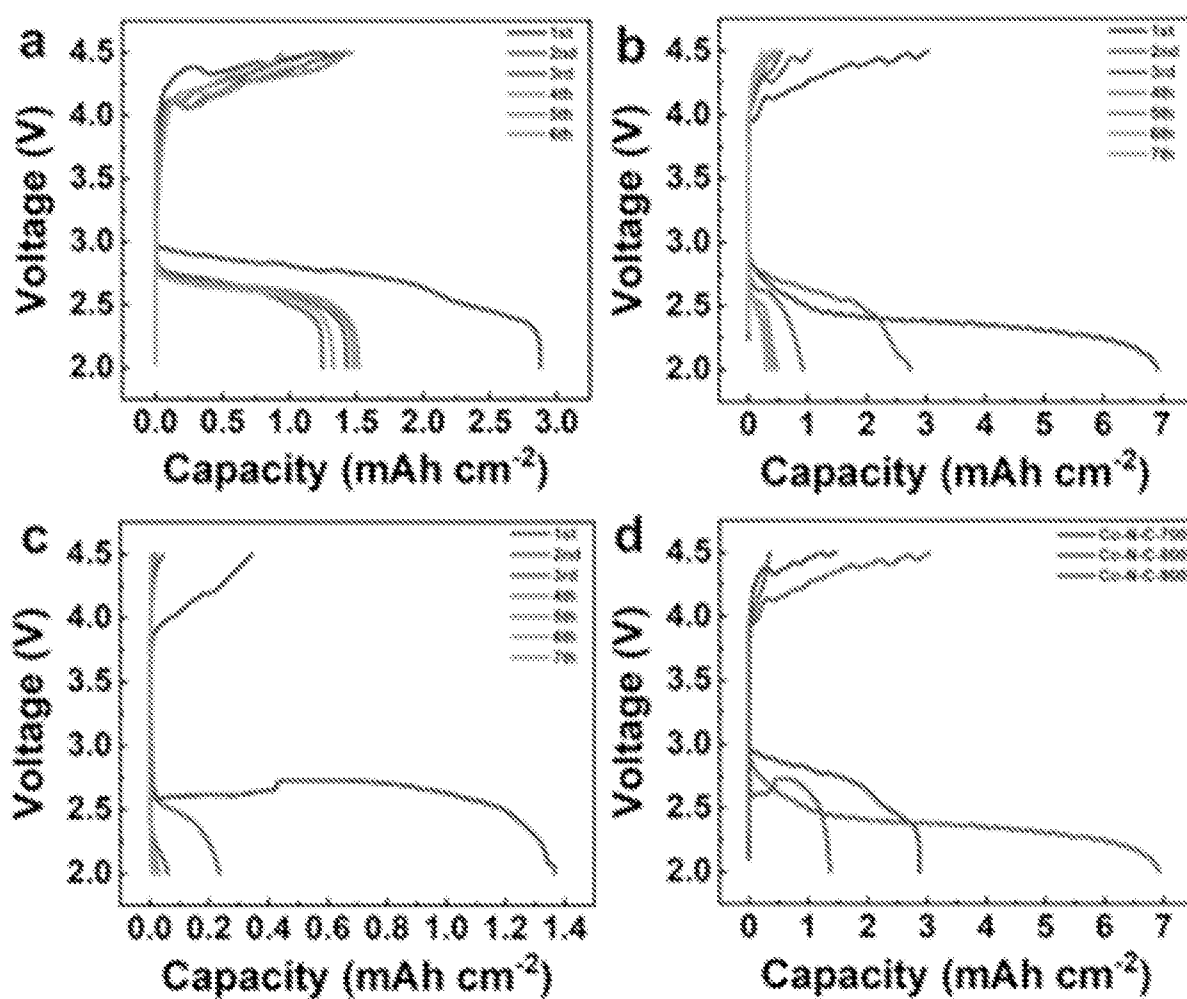


Fig. 3