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(56) Documents Cited:
CN 115893471 A
JP S5410937
Journal of Electronic Materials, vol. 50, Zhang Hongmei et al., "Silver-Modified Carbon Fluoride as the Cathode Material for Pouch-Type Primary Lithium Batteries", p. 4075-4082.

(58) Field of Search:
INT CL **C01B, C01G, H01M**

(54) Title of the Invention: **Method for compounding carbon fluoride with silver oxide by plasma induction, and use of primary lithium battery**
Abstract Title: **A method for modifying carbon fluoride with silver oxide**

(57) A method for modifying carbon fluoride is disclosed which comprises mixing silver oxide and a carbon fluoride powder in absolute ethanol to form a mixture; placing the mixture in a ball mill tank, and conducting ball milling to obtain a mixed slurry; drying the mixed slurry in an oven to obtain a silver oxide-doped carbon fluoride material; and the silver oxide-doped carbon fluoride material in a cavity of a tubular furnace of a plasma-enhanced chemical vapour deposition (PECVD) device; vacuumizing the cavity; and conducting plasma induction to obtain a carbon fluoride-based cathode material modified. The vacuum is 10-30 Pa; the plasma excitation power is 50 -150 W.

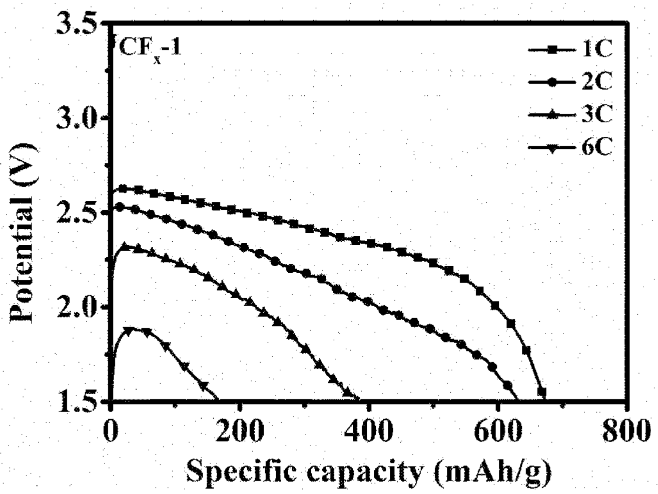

FIG. 2

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

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DRAWINGS

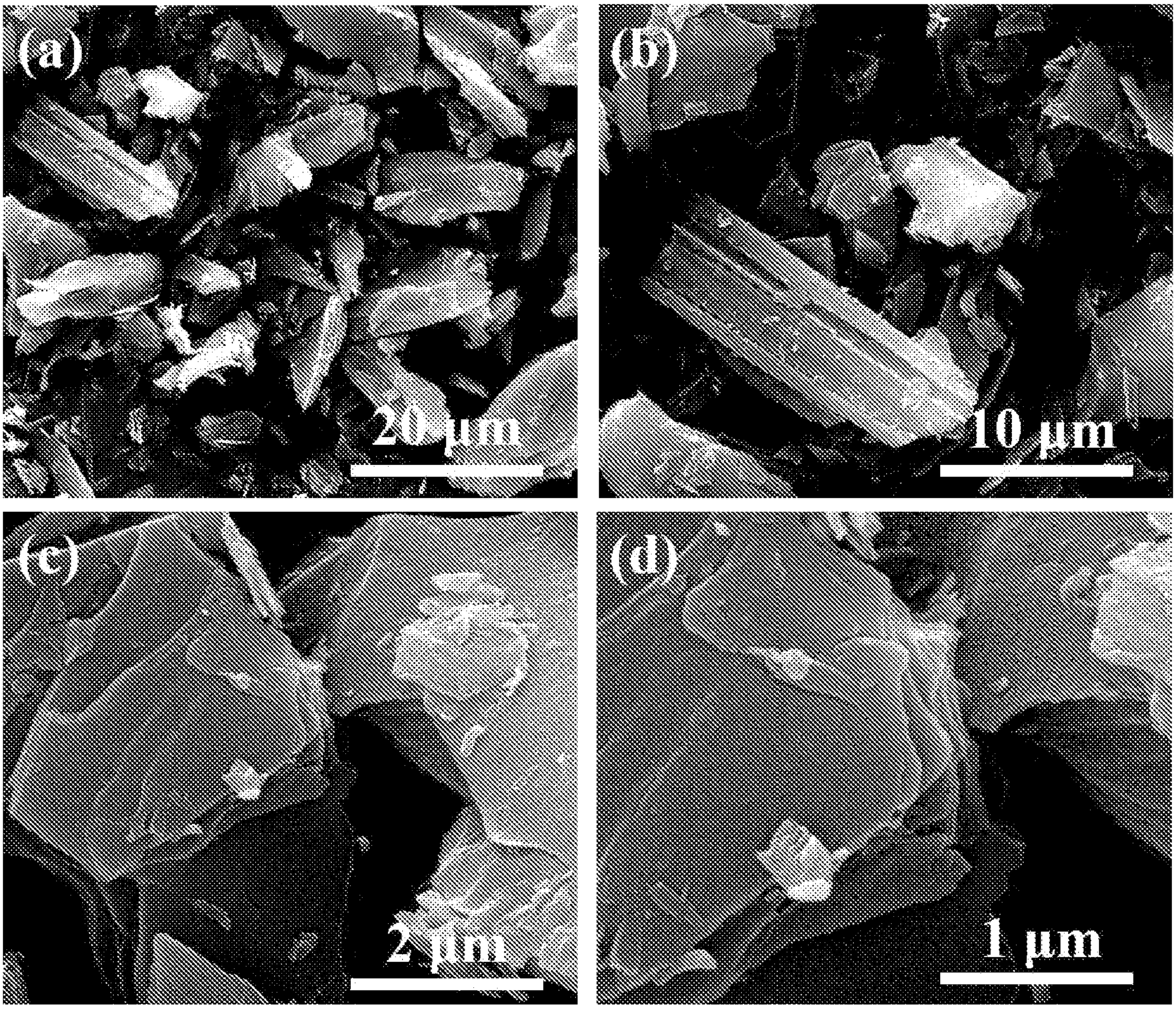
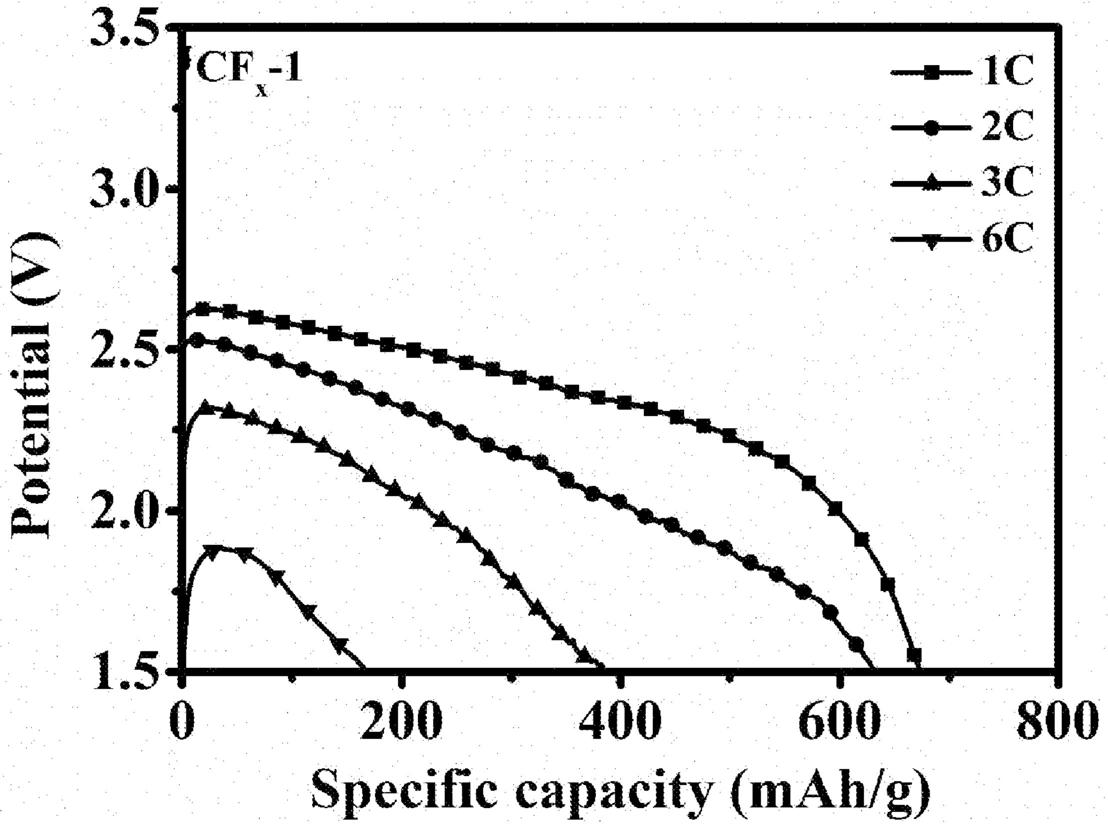


FIG. 1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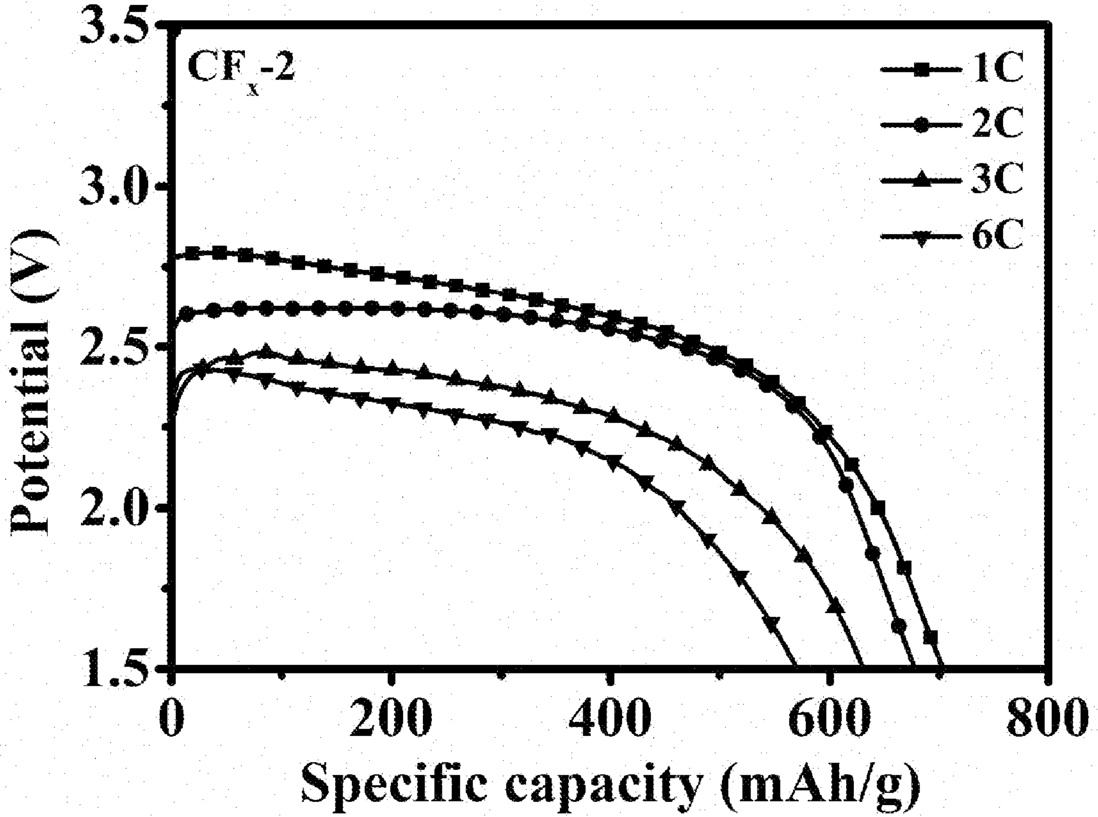
2C
3C
6C
3.5
3.0
2.5
2.0
1.5
Potential (V)
0
200
400
600
800
Specific capacity (mAh/g)

FIG. 2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6C
3.5
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Potential (V)
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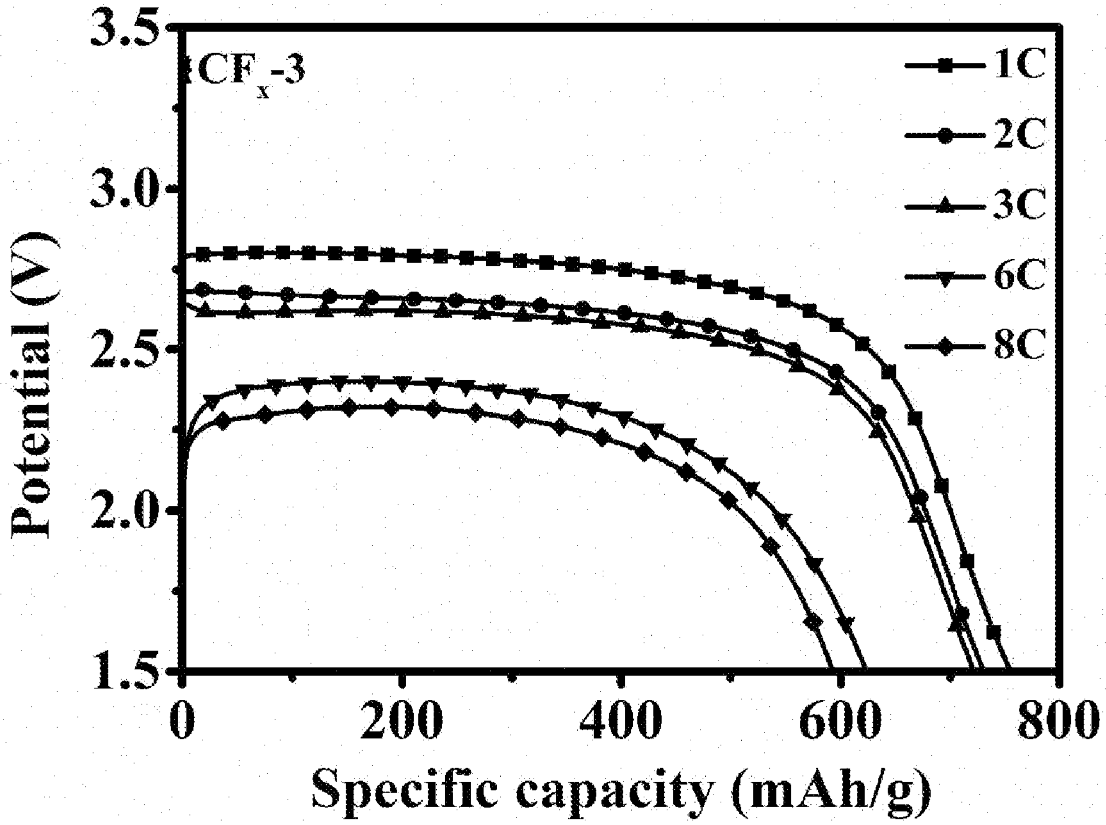
600
800
Specific capacity (mAh/g)

FIG. 3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3C
6C
8C
Potential (V)
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2.5
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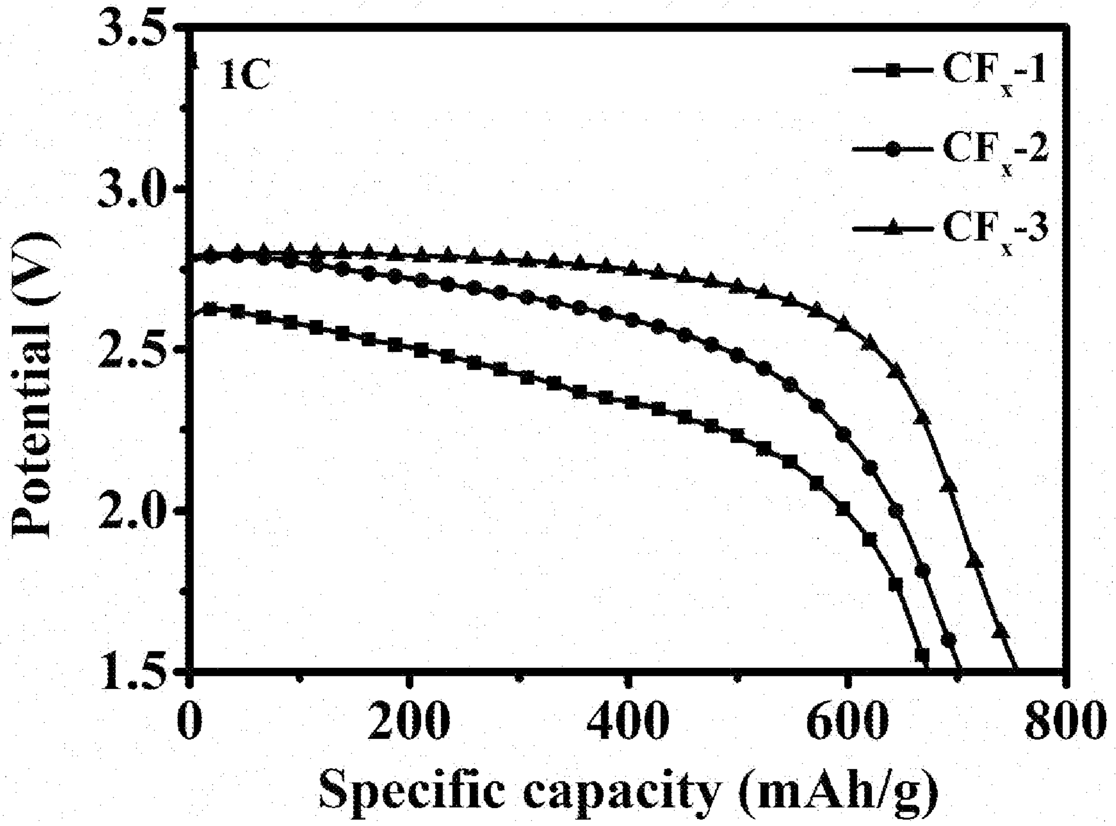
1.5
0
200
400
600
800
Specific capacity (mAh/g)

FIG. 4


1C
CF$_x$-1
CF$_x$-2
CF$_x$-3
Potential (V)
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3.0
2.5
2.0
1.5
0
200
400
600
800
Specific capacity (mAh/g)

FIG. 5

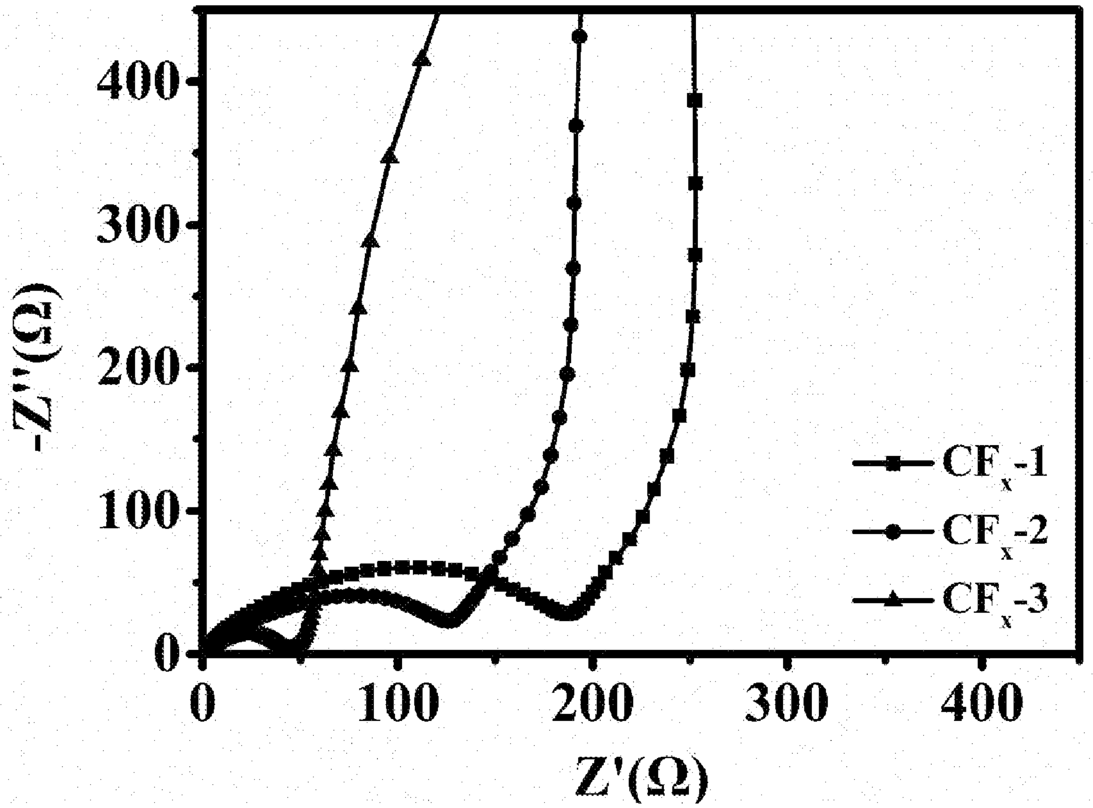

FIG. 6

METHOD FOR COMPOUNDING CARBON FLUORIDE WITH SILVER OXIDE BY PLASMA INDUCTION, AND USE OF PRIMARY LITHIUM BATTERY

TECHNICAL FIELD

[0001] The present disclosure belongs to the technical field of cathode materials for lithium batteries, and specifically relates to a method for modifying a carbon fluoride material by combining ball milling, silver oxide doping, oxidation, and air plasma induction, and the use of a modified carbon fluoride material as a cathode material of a lithium primary battery in preparing a primary lithium/carbon fluoride battery.

BACKGROUND

[0002] As a cathode material for primary lithium batteries, carbon fluoride materials have large specific energy, high operating voltage, wide operating temperature range, and small self-discharge, making them widely used in energy, military, medical and other fields. However, due to poor electrical conductivity, carbon fluoride materials have poor discharge performance at high rates, and have problems such as voltage delay and low discharge platform, making the fluoride-carbon-lithium batteries unable to meet the high-rate discharge requirements. Therefore, it has always been the research difficulties of carbon fluoride materials in improving the electrochemical performance of primary lithium/carbon fluoride battery systems and enabling carbon fluoride materials to achieve high energy density and well discharge performance under high current output. At present, given the research difficulties of carbon fluoride materials, most of the methods are adopted to avoid disadvantages in electrochemical performance of the carbon fluoride materials, such as mixing other cathode materials, metal oxides and their composites to modify cathode materials, carbon coating, or coating with other conductive materials. For example, Chinese patent 202110553040.9 disclosed a method for preparing a cathode active material composited with carbon fluoride. In this method, carbon fluoride and Ketjen black are mixed by ball milling to obtain a carbon fluoride-based composite active cathode material, which improves the initial voltage hysteresis of lithium fluoride batteries. However, in this method, an excessively high proportion of Ketjen black mixed with the cathode material may reduce the specific capacity of carbon fluoride, making it difficult to maintain the high specific capacity of the lithium/fluoride carbon battery itself. As another example, Chinese patent 202110722710.5 disclosed a method for modifying a fluoride carbon-based cathode material with chromium oxide or composites thereof. In the method, $Cr_2O_5@C$ or Cr_8O_{21} is uniformly mixed with the fluoride carbon material by high-energy ball milling, and then calcined at high temperature to obtain a carbon fluoride material with a small amount of uniformly-coated $Cr_2O_5@C$ or Cr_8O_{21} on the surface. The method improves the rate performance of the lithium/carbon fluoride battery and reduces the temperature rise during discharge of the lithium/carbon fluoride battery. However, the method sacrifices a small amount of capacity of the carbon fluoride material, with still serious voltage hysteresis after improvement and still low voltage platform after enhancement. Therefore, it is extremely important to develop a carbon fluoride-based cathode material, which can ensure that the specific capacity of the carbon fluoride material is not damaged, and can meet the high-rate discharge requirements, improve the voltage delay, and increase the voltage platform.

SUMMARY

[0003] Given defects in the background, an objective of the present disclosure is to provide a method for modifying carbon fluoride by combining silver oxide doping and an air plasma induction technology. In the present disclosure, the idea of modification mainly includes four aspects: silver oxide and a carbon fluoride material are ball-milled to reduce a particle size; free ions in an air plasma bombard the silver oxide to reduce silver oxide to achieve partial silver doping; in addition to oxygen-containing groups in the air plasma, the reduction of silver oxide causes a large number of oxygen-containing groups in the free ions, such that a surface of the carbon fluoride material is slightly oxidized; and air plasma induction further modulates an F/C value and a C-F bond type of the carbon fluoride material. The carbon fluoride modified by this combined technology is used as a cathode material, and a lithium/carbon fluoride battery is obtained with high rate performance, excellent specific capacity, desirable energy density, and high voltage platform, as well as a significantly improved voltage hysteresis effect.

[0004] To achieve the above objective, the present disclosure adopts the following technical solutions.

[0005] The present disclosure provides a method for modifying carbon fluoride by combining silver oxide doping and an air plasma induction technology, including the following steps:

[0006] step 1, mixing silver oxide and a carbon fluoride powder according to a mass ratio of (0.1-0.9):1 in absolute ethanol to form a mixture;

[0007] step 2, placing the mixture in a ball mill tank, adding 5 mm zirconia balls, 8 mm zirconia balls, and 10 mm zirconia balls at a mass ratio of 5:3:2, and conducting ball milling at 200 r/min to 400 r/min for 0.5 h to 4 h to obtain a mixed slurry;

[0008] step 3, drying the mixed slurry in an oven at 40°C to 60°C for 6 h to 12 h, and sieving with a 200-mesh sieve to obtain a silver oxide-doped carbon fluoride material; and

[0009] step 4, placing 0.1 g to 100 g of the silver oxide-doped carbon fluoride material in a cavity of a tubular furnace of plasma-enhanced chemical vapor deposition (PECVD) equipment;

vacuumizing the cavity with a vacuum pump under an air atmosphere to maintain a vacuum degree in the cavity at 10 Pa to 30 Pa for 10 min to 30 min; and conducting plasma induction with a plasma excitation source at an excitation power of 50 W to 150 W for 1 min to 120 min to obtain a carbon fluoride-based cathode material modified by combining the silver oxide doping and the air plasma induction technology.

[0010] In step 1, a total mass of the carbon fluoride powder and the silver oxide that form the mixture and a mass of the absolute ethanol have a ratio of (3-5):1.

[0011] In step 2, a total mass of the carbon fluoride powder and the silver oxide in the mixture placed in the ball mill tank and a mass of the zirconia balls have a ratio of 1:(1-2).

[0012] In step 2, the ball milling is conducted for 30 min and then stopped for 10 min.

[0013] The present disclosure further provides use of the carbon fluoride modified by combining silver oxide doping and an air plasma induction technology as a cathode material of a primary lithium/carbon fluoride battery, where the primary lithium/carbon fluoride battery includes a carbon fluoride-based cathode material, a lithium metal anode, an electrolyte, and a diaphragm.

[0014] Further, the carbon fluoride-based cathode material is formed by coating a mixed slurry of the carbon fluoride modified by combining silver oxide doping and an air plasma induction technology, SP, and polyvinylidene fluoride (PVDF) on an aluminum foil current collector.

[0015] Compared with the prior art, the present disclosure has the following beneficial effects.

[0016] The present disclosure provides a method for modifying carbon fluoride by combining silver oxide doping and an air plasma induction technology, and a preparation method of a primary lithium battery. In the present disclosure, ball milling of silver oxide and a carbon fluoride material can reduce particle size and enhance the rate performance of the primary lithium/carbon fluoride battery. In addition, the free ions in the air plasma bombard the silver oxide to reduce the silver oxide to achieve partial silver doping, such that the silver can be used as a conductive network during the discharge of the primary lithium/carbon fluoride battery. This can improve the poor discharge performance and voltage hysteresis at high rates, and maintain a high-discharge voltage platform for primary lithium fluoride batteries. In addition to oxygen-containing groups in the air plasma, silver oxide reduction makes a large number of oxygen-containing groups in the free ions, such that the surface of the carbon fluoride material is slightly oxidized. Air plasma induction further regulates the F/C value and C-F bond type of the carbon fluoride material, such that the primary lithium/carbon fluoride battery can provide more capacity. Therefore, the carbon fluoride modified by combining the silver oxide doping and the air plasma induction technology has high rate performance, excellent specific capacity, desirable energy density, and high voltage platform, laying an important foundation for the promotion and application of the lithium/carbon fluoride battery.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] FIG. 1 shows SEM images of a carbon fluoride composite CF_x-3 (silver oxide: CF_x=0.9:1) modified by combining silver oxide doping and an air plasma technology obtained in Example 2 at different magnifications;

[0018] FIG. 2 shows discharge curves of a primary lithium/carbon fluoride battery assembled with an original carbon fluoride material at different discharge rates, where CF_x-1 is the original carbon fluoride material;

[0019] FIG. 3 shows discharge curves of a primary lithium/carbon fluoride battery assembled with a carbon fluoride composite CF_x-2 (silver oxide: CF_x=0.1:1) obtained by ball milling silver oxide and air plasma treatment in Example 1 at different discharge rates, where CF_x-2 is the carbon fluoride material modified by combining silver oxide doping and an air plasma technology obtained in Example 1;

[0020] FIG. 4 shows discharge curves of a primary lithium/carbon fluoride battery assembled with the carbon fluoride composite CF_x-3 (silver oxide: CF_x=0.9:1) modified by combining silver oxide doping and an air plasma technology obtained in Example 2 at different discharge rates, where CF_x-3 is the carbon fluoride material modified by combining silver oxide doping and an air plasma technology obtained in Example 2; and

[0021] FIG. 5 shows EIS curves of the primary lithium/carbon fluoride batteries assembled with the original carbon fluoride material CF_x-1, the carbon fluoride material CF_x-2 obtained in Example 1, and the carbon fluoride material CF_x-3 obtained in Example 2; where CF_x-1 is the original carbon fluoride material, CF_x-2 is the carbon fluoride material obtained by ball milling and air plasma treatment in Example 1, and CF_x-3 is the carbon fluoride material modified by combining silver oxide doping and an air plasma technology obtained in Example 2.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0022] The technical solutions of the present disclosure will be further described below through specific examples.

[0023] **Example 1**

[0024] A method for modifying carbon fluoride by combining silver oxide doping and an air plasma induction technology included the following steps:

[0025] step 1, silver oxide and a carbon fluoride powder were mixed according to a mass ratio of 0.1:1 in absolute ethanol to form a mixture;

[0026] step 2, the mixture was placed in a ball mill tank, 5 mm zirconia balls, 8 mm zirconia balls, and 10 mm zirconia balls were added at a mass ratio of 5:3:2, and ball milling was conducted at 400 r/min for 2 h to obtain a mixed slurry;

[0027] step 3, the mixed slurry was dried in an oven at 40°C for 12 h, and sieved with a 200-mesh sieve to obtain a silver oxide-doped carbon fluoride material; and

[0028] step 4, 0.5g of the silver oxide-doped carbon fluoride material was placed in a cavity of a tubular furnace of PECVD equipment; the cavity was vacuumized with a vacuum pump under an air atmosphere to maintain a vacuum degree in the cavity at 10 Pa for 10 min; and plasma induction was conducted with a plasma excitation source at an excitation power of 50 W for 10 min to obtain a carbon fluoride material after ball milling and air plasma treatment, marked as CF_x-2.

[0029] Example 2

[0030] A method for modifying carbon fluoride by combining silver oxide doping and an air plasma induction technology included the following steps:

[0031] step 1, silver oxide and a carbon fluoride powder were mixed according to a mass ratio of 0.9:1 in absolute ethanol to form a mixture;

[0032] step 2, the mixture was placed in a ball mill tank, 5 mm zirconia balls, 8 mm zirconia balls, and 10 mm zirconia balls were added at a mass ratio of 5:3:2, and ball milling was conducted at 400 r/min for 4 h to obtain a mixed slurry;

[0033] step 3, the mixed slurry was dried in an oven at 60°C for 12 h, and sieved with a 200-mesh sieve to obtain a silver oxide-doped carbon fluoride material; and

[0034] step 4, 10 g of the silver oxide-doped carbon fluoride material was placed in a cavity of a tubular furnace of a PECVD equipment; the cavity was vacuumized with a vacuum pump under an air atmosphere to maintain a vacuum degree in the cavity at 30 Pa for 30 min; and plasma induction was conducted with a plasma excitation source at an excitation power of 200 W for 30 min to obtain a carbon fluoride material modified by combining silver oxide doping and an air plasma technology, marked as CF_x-3.

[0035] Example 3

[0036] A method for modifying carbon fluoride by combining silver oxide doping and an air plasma induction technology included the following steps:

[0037] step 1, silver oxide and a carbon fluoride powder were mixed according to a mass ratio of 0.5:1 in absolute ethanol to form a mixture;

[0038] step 2, the mixture was placed in a ball mill tank, 5 mm zirconia balls, 8 mm zirconia balls, and 10 mm zirconia balls were added at a mass ratio of 5:3:2, and ball milling was conducted at 300 r/min for 1 h to obtain a mixed slurry;

[0039] step 3, the mixed slurry was dried in an oven at 50°C for 6 h, and sieved with a 200-

mesh sieve to obtain a silver oxide-doped carbon fluoride material; and

[0040] step 4, 50g of the silver oxide-doped carbon fluoride material was placed in a cavity of a tubular furnace of a PECVD equipment; the cavity was vacuumized with a vacuum pump under an air atmosphere to maintain a vacuum degree in the cavity at 20 Pa for 20 min; and plasma induction was conducted with a plasma excitation source at an excitation power of 200 W for 20 min to obtain a carbon fluoride material modified by combining silver oxide doping and an air plasma technology.

[0041] **Example 4**

[0042] A method for modifying carbon fluoride by combining silver oxide doping and an air plasma induction technology included the following steps:

[0043] step 1, silver oxide and a carbon fluoride powder were mixed according to a mass ratio of 0.7:1 in absolute ethanol to form a mixture;

[0044] step 2, the mixture was placed in a ball mill tank, 5 mm zirconia balls, 8 mm zirconia balls, and 10 mm zirconia balls were added at a mass ratio of 5:3:2, and ball milling was conducted at 250 r/min for 2 h to obtain a mixed slurry;

[0045] step 3, the mixed slurry was dried in an oven at 60°C for 12 h, and sieved with a 200-mesh sieve to obtain a silver oxide-doped carbon fluoride material; and

[0046] step 4, 100 g of the silver oxide-doped carbon fluoride material was placed in a cavity of a tubular furnace of a PECVD equipment; the cavity was vacuumized with a vacuum pump under an air atmosphere to maintain a vacuum degree in the cavity at 10 Pa to 30 Pa for 30 min; and plasma induction was conducted with a plasma excitation source at an excitation power of 100 W for 20 min to obtain a carbon fluoride material modified by combining silver oxide doping and an air plasma technology.

[0047] Assembly of a battery:

[0048] The original carbon fluoride material and the carbon fluoride material modified by combining silver oxide doping and an air plasma technology obtained by Examples 1 to 4, SP, and a binder PVDF were prepared in a mass ratio of 8:1:1 to obtain a slurry separately; the slurry was evenly coated on an aluminum foil current collector, and vacuum-dried at 80°C for 12 h to obtain a cathode sheet. In a glove box, metal lithium was used as an anode, and the electrode sheet prepared from carbon fluoride was used as a cathode. A button battery was assembled in the glove box, and then allowed to stand for 24 h for the test. The original carbon fluoride material was marked as CF_x-1, the carbon fluoride material obtained in Example 1 was marked as CF_x-2, and the carbon fluoride material obtained in Example 2 was marked as CF_x-3.

[0049] FIG. 1 showed SEM images of the carbon fluoride material CF_x-3 obtained in Example 2 under different magnifications; it was seen that the carbon fluoride material was block-layered with a smooth surface. After being modified by combining silver oxide doping and air plasma technology, the carbon fluoride material produced many exfoliated lamellar carbon fluoride structures.

[0050] FIG. 2 showed discharge curves of a primary lithium/carbon fluoride battery assembled with an original carbon fluoride material CF_x-1 at different discharge rates; it was seen that as the discharge rate increased, the specific capacity decreased. At a high discharge rate of 6 C, its specific capacity was less than 200 mAh g^{-1}. Moreover, the primary lithium/carbon fluoride battery assembled with the original carbon fluoride material CF_x-1 had an unstable voltage plateau, poor rate performance, and inability to discharge at a high rate. Under a discharge rate of 1 C, the cut-off voltage was 1.5 V, and the specific capacity was 673.54 mAh·g^{-1}.

[0051] FIG. 3 showed discharge curves of a primary lithium/carbon fluoride battery assembled with the carbon fluoride composite CF_x-2 obtained by ball milling silver oxide and air plasma treatment in Example 1 at different discharge rates; it was seen from the comparison that the unstable voltage platform of the original carbon fluoride material CF_x-1 had been significantly improved after ball milling and air plasma treatment. After ball milling and air plasma treatment, the primary lithium/carbon fluoride battery assembled with the carbon fluoride material CF_x-2 had a cut-off voltage of 1.5 V at a discharge rate of 1 C, and a specific capacity increased to 703.38 mAh g^{-1}. Under a maximum discharge rate of 6 C, the cut-off voltage was 1.5 V, and the specific capacity was increased to 569.74 mAh·g^{-1}.

[0052] FIG. 4 showed discharge curves of a primary lithium/carbon fluoride battery assembled with the carbon fluoride composite CF_x-3 modified by combining silver oxide doping and an air plasma technology obtained in Example 2 at different discharge rates; by comparing with FIG. 2 and FIG. 3, it was seen that the discharge curve of the primary lithium/carbon fluoride battery assembled with the CFx-3 that was further doped with silver oxide had a significantly more stable and higher a voltage platform. Under a discharge rate of 1 C, the cut-off voltage was 1.5 V, the voltage platform increased to 2.74 V, and the specific capacity increased to 755.51 mAh·g^{-1}. Under a high discharge rate of 8 C, the cut-off voltage was 1.5 V, the voltage platform reached 2.27 V, and the specific capacity was increased to 592.14 mAh·g^{-1}.

[0053] FIG. 5 showed EIS curves of the primary lithium/carbon fluoride batteries assembled with the original carbon fluoride material CF_x-1, the carbon fluoride material CF_x-2 obtained in Example 1, and the carbon fluoride material CF_x-3 obtained in Example 2; the charge transfer resistance R_{ct} corresponded to the semicircle in the EIS curve, and the slope of the straight line in the EIS curve represented the diffusion resistance of Li^+. After analysis, the carbon fluoride material CF_x-1 had R_{ct} of 185.50 Ω; after subsequent treatment with AgO and air plasma, the carbon fluoride material CF_x-2 had R_{ct} reduced to 126.00 Ω; after combined modification of silver oxide doping and air plasma technology, the carbon fluoride material CF_x-3 had R_{ct} reduced to 44.49 Ω. The analysis results confirmed that not only the air plasma induction modification was beneficial to reduce R_{ct}, but also the silver oxide doping could further reduce R_{ct}. The lower R_{ct} was more conducive to charge transfer and ion transport, such that the cathode material of the primary lithium/carbon fluoride battery prepared by CF_x-3 had an improved performance.

WHAT IS CLAIMED IS:

1. A method for modifying carbon fluoride by combining silver oxide doping and an air plasma induction technology, comprising the following steps:

step 1, mixing silver oxide and a carbon fluoride powder according to a mass ratio of (0.1-0.9):1 in absolute ethanol to form a mixture;

step 2, placing the mixture in a ball mill tank, adding 5 mm zirconia balls, 8 mm zirconia balls, and 10 mm zirconia balls at a mass ratio of 5:3:2, and conducting ball milling at 200 r/min to 400 r/min for 0.5 h to 4 h to obtain a mixed slurry;

step 3, drying the mixed slurry in an oven at 40°C to 60°C for 6 h to 12 h, and sieving with a 200-mesh sieve to obtain a silver oxide-doped carbon fluoride material; and

step 4, placing 0.1 g to 100 g of the silver oxide-doped carbon fluoride material in a cavity of a tubular furnace of a plasma-enhanced chemical vapor deposition (PECVD) equipment; vacuumizing the cavity with a vacuum pump under an air atmosphere to maintain a vacuum degree in the cavity at 10 Pa to 30 Pa for 10 min to 30 min; and conducting plasma induction with a plasma excitation source at an excitation power of 50 W to 150 W for 1 min to 120 min to obtain a carbon fluoride-based cathode material modified by combining the silver oxide doping and the air plasma induction technology.

2. Use of the carbon fluoride-based material modified by combining the silver oxide doping and the air plasma induction technology prepared by the preparation method according to claim 1 as a cathode material of a primary lithium/carbon fluoride battery.

Application No:	GB2217501.2	**Examiner:**	Nicholas Mole
Claims searched:	1-2	**Date of search:**	27 June 2023

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
A,&	-	CN 115893471 A (UNIV CHINA ELECTRONIC SCI & TECHNOLOGY) see abstracts
A	-	JP S5410937 A (SEIKO INSTR & ELECTRONICS) see abstracts
A	-	Journal of Electronic Materials, vol. 50, Zhang Hongmei et al., "Silver-Modified Carbon Fluoride as the Cathode Material for Pouch-Type Primary Lithium Batteries", p. 4075-4082. see examples

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^X :

Worldwide search of patent documents classified in the following areas of the IPC

C01B; C01G; H01M

The following online and other databases have been used in the preparation of this search report

WPI, EPODOC, Patent Fulltext, INSPEC, XPESP, XSPRNG

International Classification:

Subclass	Subgroup	Valid From
C01B	0032/10	01/01/2017
H01M	0004/583	01/01/2010