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(71) Applicant: NINGDE AMPEREX TECHNOLOGY LIMITED [CN/CN]; No. 1, XinGang Road, ZhangWan Town, JiaoCheng District, Ningde, Fujian 352100 (CN).

(72) Inventors: WANG, Bin; No. 1, XinGang Road, ZhangWan Town, JiaoCheng District, Ningde, Fujian 352100 (CN). WEN, Qian; No. 1, XinGang Road, ZhangWan Town, JiaoCheng District, Ningde, Fujian 352100 (CN). ZHANG, Yibo; No. 1, XinGang Road, ZhangWan Town, JiaoCheng District, Ningde, Fujian 352100 (CN). HU, Qiaoshu; No. 1, XinGang Road, ZhangWan Town, JiaoCheng District, Ningde, Fujian 352100 (CN).

(74) Agent: LEE AND LI - LEAVEN IPR AGENCY LTD.; Unit 2202, Tower A, Beijing Marriott Center, No. 7, Jian Guo Men South Avenue, Dongcheng District, Beijing 100005 (CN).

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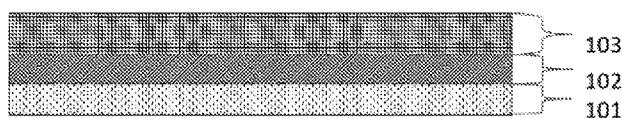


FIG. 1A

(57) Abstract: An anode, an electrochemical device and an electronic device comprising the same are provided. Embodiments provided an anode comprising: a current collector (101), a first anode structure layer (102) and a second anode structure layer (103). The first anode structure layer (102) comprises a first framework material and the second anode structure layer (103) comprises a second framework material, wherein the first anode structure layer (102) is disposed between the current collector (101) and the second anode structure layer (103), and the first framework material has a higher oxidation-reduction potential for lithium ion or electronic conductivity than the second framework material. When the anode with double-layer structure provided is charged, the space utilization ratio of the anode can be enhanced, the rate capability of the electrochemical device can be enhanced, the formation of lithium dendrites may be inhibited, and the volume change amount of the anode can be reduced, thereby enhancing the safety performance and cycle performance of the electrochemical device.



**ANODE, AND ELECTROCHEMICAL DEVICE AND  
ELECTRONIC DEVICE COMPRISING SAME  
CROSS REFERENCE TO RELATED APPLICATIONS**

The present application claims the benefit of priority from the China  
5 Patent Application No. 201910227266.2, filed on 25 March 2019, the  
disclosure of which is hereby incorporated by reference in its entirety.

**BACKGROUND**

**1. Field of the Invention**

The present application relates to the field of energy storage  
10 technologies, and in particular, to an anode and an electrochemical device  
comprising the same.

**2. Description of the Related Art**

Electrochemical devices (for example, lithium-ion batteries) have  
entered our daily lives with advancements in technology and environmental  
15 protection requirements. In order to meet performance requirements of the  
electronic device with high energy consumption for the electrochemical  
device, the energy density of the electrochemical device is ever increasing,  
and the attendant safety risk is becoming ever more prominent. Therefore,  
it is particularly important to investigate electrochemical devices with good  
20 safety performance.

In order to enhance the energy density and operating voltage of  
lithium-ion batteries, one of the feasible research solutions is using lithium  
metal as the anode. However, the use of lithium metal as the anode may  
cause various problems during the cycle of charging and discharging, such  
25 as side reaction with the electrolytic solution, formation of lithium  
dendrites, and increase in the volume change rate of the anode, thereby  
deteriorating the safety and cycling performances of the lithium-ion battery.  
Therefore, it is still necessary to further improve the structure of the anode  
to obtain an anode with high ionic conductivity and good structural

stability.

## SUMMARY

In view of the problems in the prior art, an objective of the present application is to provide an anode, and an electrochemical device and an electronic device comprising the same in an attempt to solve at least one of the problems existing in the related art at least to some extent.

Some embodiments of the present application provide an anode, including: a current collector, a first anode structure layer and a second anode structure layer. The first anode structure layer comprises a first framework material and the second anode structure layer comprises a second framework material, wherein the first anode structure layer is arranged between the current collector and the second anode structure layer, and the first framework material has a higher oxidation-reduction potential for lithium ion or electronic conductivity than the second framework material.

According to some embodiments, the first framework material has an oxidation-reduction potential for lithium ion of about -50 mV to about 250 mV, and the second framework material has an oxidation-reduction potential for lithium ion of about -100 mV to about 200 mV.

According to some embodiments, the first framework material has an electronic conductivity of about  $1 \times 10^{-2}$  S/m to about  $6.30 \times 10^7$  S/m, and the second framework material has an electronic conductivity of about  $1 \times 10^{-25}$  S/m to about  $5.95 \times 10^7$  S/m.

According to some embodiments, the anode further includes at least one third anode structure layer, the third anode structure layer comprising a third framework material, wherein the second anode structure layer is arranged between the first anode structure layer and the third anode structure layer, and the second framework material has a higher lithium ion oxidation-reduction potential or electronic conductivity than the third framework material.

According to some embodiments, the anode includes a plurality of the third anode structure layers, wherein the third framework material comprised in any one of the plurality of the third anode structure layers has a higher lithium ion oxidation-reduction potential or electronic conductivity than the third framework material comprised in the other third anode structure layers farther from the current collector.

According to some embodiments, the first framework material, the second framework material and the third framework material are each independently selected from the group consisting of a high molecular polymer, a carbon-based material, a metal material, a solid electrolyte material, a composite material and combinations thereof.

According to some embodiments, the high molecular polymer is selected from the group consisting of polyethylene oxide, polyimide, polyacrylic acid, polyethylene, polypropylene, polyacrylonitrile, polystyrene, polyvinyl fluoride, polyetheretherketone, polyester, polyvinylidene chloride, polytetrafluoroethylene, polyethylene terephthalate, derivatives thereof, and combinations thereof.

According to some embodiments, the carbon-based material is selected from the group consisting of porous carbon, carbon nanotubes, carbon fibers, graphene, hollow carbon spheres and combinations thereof.

According to some embodiments, the metal material is selected from the group consisting of copper, silver, gold, nickel and alloys thereof.

According to some embodiments, the solid electrolyte material is selected from the group consisting of lithium phosphate ( $\text{Li}_3\text{PO}_4$ ), lithium titanium phosphate ( $\text{Li}_x\text{Ti}_y(\text{PO}_4)_3$ , wherein  $0 < x < 2$  and  $0 < y < 3$ ), lithium aluminum titanium phosphate ( $\text{Li}_x\text{Al}_y\text{Ti}_z(\text{PO}_4)_3$ , wherein  $0 < x < 2$ ,  $0 < y < 1$ , and  $0 < z < 3$ ),  $\text{Li}_{1+x+y}(\text{Al}, \text{Ga})_x(\text{Ti}, \text{Ge})_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ , wherein  $0 \leq x \leq 1$  and  $0 \leq y \leq 1$ , lithium lanthanum titanate ( $\text{Li}_x\text{La}_y\text{TiO}_3$ , wherein  $0 < x < 2$  and  $0 < y < 3$ ), lithium germanium thiophosphate ( $\text{Li}_x\text{Ge}_y\text{P}_z\text{S}_w$ , wherein  $0 < x < 4$ ,  $0 < y < 1$ ,  $0 < z < 1$ , and  $0 < w < 5$ ), lithium nitride ( $\text{Li}_x\text{N}_y$ , wherein  $0 < x < 4$ ,

0<y<2), SiS<sub>2</sub> glass (Li<sub>x</sub>Si<sub>y</sub>S<sub>z</sub>, wherein 0≤x<3, 0<y<2, and 0<z<4), P<sub>2</sub>S<sub>5</sub> glass (Li<sub>x</sub>P<sub>y</sub>S<sub>z</sub>, wherein 0≤x<3, 0<y<3, and 0<z<7), Li<sub>2</sub>O, LiF, LiOH, Li<sub>2</sub>CO<sub>3</sub>, LiAlO<sub>2</sub>, Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-GeO<sub>2</sub> ceramic, garnet ceramic (Li<sub>3+x</sub>La<sub>3</sub>M<sub>2</sub>O<sub>12</sub>, wherein 0≤x≤5, and M is Te, Nb or Zr) and combinations thereof.

According to some embodiments, the composite material comprises a framework material selected from the group consisting of a high molecular polymer, a carbon-based material, a metal material, a solid electrolyte material and combinations thereof, and the inner and outer surfaces of the framework material are covered by another material selected from the group consisting of a high molecular polymer, a carbon-based material, a metal material, a solid electrolyte material, an insulating material and combinations thereof, wherein the insulating material is selected from the group consisting of HfO<sub>2</sub>, SrTiO<sub>3</sub>, SnO<sub>2</sub>, CeO<sub>2</sub>, MgO, NiO, CaO, BaO, ZnO, ZrO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub> and combinations thereof.

According to some embodiments, the first anode structure layer has a porosity of about 30% to about 98%, and the second anode structure layer has a porosity of about 30% to about 98%.

According to some embodiments, the first anode structure layer and the second anode structure layer have a thickness of about 0.1 μm to about 1 mm, and the anode has a total thickness of about 0.1 μm to about 2 mm.

In some embodiments, the present application provides an electrochemical device, including: a cathode, a separator and the anode in the above embodiments.

In some embodiments, the present application provides an electronic device, comprising the electrochemical device in the above embodiments.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

The following will briefly illustrate the accompanying drawings necessary to describe the embodiments of the present application or the

prior art so as to facilitate the description of the embodiments of the present application. The accompanying drawings described below are only part of the embodiments of the present application.

FIG. 1A is a side view showing the structure of a single-sided anode according to some embodiments of the present application.

FIG. 1B is a side view showing the structure of a double-sided anode according to some embodiments of the present application.

FIG. 1C is a side view showing the structure of a multilayer structure anode according to some embodiments of the present application.

FIG. 2 is a schematic diagram of a preparation method of an anode according to some embodiments of the present application.

FIG. 3 is a side view showing the structure of an electrode assembly according to some embodiments of the present application.

## DETAILED DESCRIPTION OF EMBODIMENTS

In order to make the objects, technical solutions and advantages of the present application more clear, the technical solutions of the present application will be clearly and completely described in the following with reference to the embodiments of the present application. It is apparent that the described embodiments are a part of the embodiments of the present application, rather than all of the embodiments. All other embodiments obtained by those skilled in the art based on the technical solutions and embodiments provided by the present application and without the creative work are all within the scope of the present application.

In this specification, unless otherwise specified or limited, the relative terms such as "central", "longitudinal", "lateral", "front", "rear", "right", "left", "internal", "external", "lower", "higher", "horizontal", "vertical", "higher than", "lower than", "above", "below", "top" and "bottom", and their derivatives (e.g. "horizontally", "downward", "upward") should be interpreted as referring to the directions described in the discussion or in

the drawings. These relative terms are used for convenience only in the description and are not required to construct or operate the present application in a particular direction.

Further, for convenience of description, "first", "second", "third" and the like may be used herein to distinguish different components of one drawing or series of drawings. "First", "second", "third" and the like are not intended to describe the corresponding components.

In addition, amounts, ratios and other numerical values are sometimes presented herein in a range format. It should be understood that such range formats are for convenience and brevity, and should be interpreted with flexibility, and include not only those numerical values that are specifically designated as range limitations, but also include all individual numerical values or sub-ranges that are within the range, as each value and sub-range is specified explicitly.

In the detailed description and the claims of the present application, the terms "substantially", "generally", "essentially" and "about" are used to describe and explain small variations. When being used in combination with an event or circumstance, the term may refer to an example in which the event or circumstance occurs precisely, and an example in which the event or circumstance occurs approximately. For example, when being used in combination with a value, the term may refer to a variation range of less than or equal to  $\pm 10\%$  of the value, for example, less than or equal to  $\pm 5\%$ , less than or equal to  $\pm 4\%$ , less than or equal to  $\pm 3\%$ , less than or equal to  $\pm 2\%$ , less than or equal to  $\pm 1\%$ , less than or equal to  $\pm 0.5\%$ , less than or equal to  $\pm 0.1\%$ , or less than or equal to  $\pm 0.05\%$ . In addition, amounts, ratios and other numerical values are sometimes presented herein in a range format. It should be appreciated that such range formats are for convenience and conciseness, and should be flexibly understood as comprising not only values explicitly specified to range constraints, but also all individual values or sub-ranges within the ranges, like explicitly specifying each value and each sub-range.

In the detailed description and claims of the present application, the term "framework material" is defined as a material having a three-dimensional structure and having pores in the interior of the three-dimensional structure, which may be a conventional choice in the art.

5 In an electrochemical device (for example, a lithium-ion battery), lithium metal used as an anode of the electrochemical device can increase the energy density of the battery and the operating voltage of the battery. However, with the charge and discharge cycle of the electrochemical device, the use of lithium metal as the anode may cause various problems  
10 including: side reaction with the electrolytic solution, formation of lithium dendrites, and increase in the volume change rate of the anode. Among the problems, the increase in the volume change rate of the anode in may cause the interfacial area between the anode and other adjacent structures to be easily peeled off, so that the impedance is drastically increased, and in  
15 severe cases, the deformation of the electrochemical device may also occur.

The present application provides an anode having a multilayer structure. The anode has two or more layers. By using different material compositions and framework material structure designs for each layer, the layer closer to the current collector has a higher lithium ion oxidation-  
20 reduction potential or electronic conductivity.

The structure of the anode of the embodiments of the present application and the advantageous effects of the structure will be described below with reference to FIGS. 1A-1C.

The anode of the present application may be a single-sided structure or  
25 a double-sided structure. FIG. 1A is a side view showing the structure of a single-sided anode according to some embodiments of the present application.

As shown in FIG. 1A, the anode of the present application includes: a current collector 101, a first anode structure layer 102 and a second anode structure layer 103, wherein the first anode structure layer 102 is arranged  
30

between the current collector 101 and the second anode structure layer 103. The first anode structure layer 102 comprises a first framework material, the second anode structure layer 103 comprises a second framework material, and the first framework material has a higher lithium ion oxidation-reduction potential or electronic conductivity than the second framework material. The pores existing in the first framework material and the second framework material reserve a space for deposition of lithium metal, and therefore, the volume change rate of the anode during the charge and discharge cycle is reduced, thereby improving problems of interface peeling, cell deformation and the like.

Further, by designing the first framework material to have a higher lithium ion oxidation-reduction potential or electronic conductivity than the second framework material, the lithium metal can be preferentially deposited in the first anode structure layer 102 adjacent to the current collector 101, thereby preventing the lithium metal from being preferentially deposited in the second anode structure layer 103 away from the current collector 101 and blocking the lower portion thereof, causing the lithium metal to fail to fill the entire anode, and further reducing the rate of the anode in volume change during the charge and discharge cycle. The anode of the present application can significantly enhance space utilization ratio and optimize the rate capability of the electrochemical device. In addition, the structure of the anode may also homogenize and densify lithium metal deposition, thereby reducing side reactions between the lithium metal and the electrolyte and formation of lithium dendrites, and improving the energy density and cycle life of the lithium metal battery.

In some embodiments, the first framework material has a lithium ion oxidation-reduction potential of about -50 mV to about 250 mV, and the second framework material has a lithium ion oxidation-reduction potential of about -100 mV to about 200 mV.

In some embodiments, the first framework material has an electronic conductivity of about  $1 \times 10^{-2}$  S/m to about  $6.30 \times 10^7$  S/m, and the second framework material has an electronic conductivity of about  $1 \times 10^{-25}$  S/m to

about  $5.95 \times 10^7$  S/m.

In some embodiments, the first anode structure layer 102 and the second anode structure layer 103 each have a porosity of about 30% to about 98%. If the porosity of each of the first anode structure layer 102 and the second anode structure layer 103 is too low, the volumetric energy density of the electrochemical device thereof will be too low. If the porosity is too high, the anode will have an unstable structure and be easy to collapse during the preparation process or the cycle process.

In some embodiments, the first anode structure layer 102 and the second anode structure layer 103 have a thickness of about 0.1  $\mu\text{m}$  to about 1 mm, and the anode has a total thickness of about 0.1  $\mu\text{m}$  to about 2 mm.

FIG. 1B is a side view showing the structure of a double-sided anode according to some embodiments of the present application.

As shown in FIG. 1B, the first anode structure layer 102 and the second anode structure layer 103 are arranged on both side surfaces of the current collector 101, wherein the first anode structure layer 102 is located between the current collector 101 and the second anode structure layer 103.

FIG. 1C is a side view showing the structure of a multilayer structure anode according to some embodiments of the present application.

In some embodiments, the anode of the present application further includes at least one third anode structure layer 104. As shown in FIG. 1C, the third anode structure layer 104 comprises a third framework material, wherein the second anode structure layer 103 is arranged between the first anode structure layer 102 and the third anode structure layer 104, and the second framework material has a higher lithium ion oxidation-reduction potential or electronic conductivity than the third framework material.

In some embodiments, the third anode structure layer 104 has a thickness of about 0.1  $\mu\text{m}$  to about 1 mm.

It should be understood that although FIG. 1C only illustrates the single-layer third anode structure layer 103, FIG. 1C is merely an exemplary embodiment illustrating the multilayer structure of the anode of the present application. Those skilled in the art can adjust the number of layers of the anode structure layer in the anode according to the specific needs of the present disclosure without being limited thereto.

In some embodiments, the anode of the present application may further comprises a plurality of the third anode structure layers 104, wherein the third framework material comprised in any one of the plurality of the third anode structure layers 104 has a higher lithium ion oxidation-reduction potential or electronic conductivity than the third framework material comprised in the other third anode structure layers farther from the current collector. For example, the difference of the oxidation-reduction potential of the anode structure layer in the anode closer to the current collector minus the oxidation-reduction potential of the farther anode structure layer is greater than 0 mV, or the anode structure layer in the anode closer to the current collector has a higher electronic conductivity. The inside of the anode using the multilayer structure of the present application may be completely filled with lithium metal, thereby avoiding waste of space, further maximizing the energy density of the anode, and enhancing the energy density of the anode by 10% or more.

In some embodiments, the first anode structure layer 102, the second anode structure layer 103 and the third anode structure layer 104 have a pore size of about 0.1 mm to about 10 mm and a pore density of about 5 ppi to about 30 ppi.

According to the embodiments of the present application, the current collector 101 may be any anode current collector commonly used in the art, including, but not limited to, tin foil, copper foil, lithium foil and lithium-clad copper foil.

According to the embodiments of the present application, the first framework material, the second framework material and the third

framework material are each independently selected from the group consisting of a high molecular polymer, a carbon-based material, a metal material, a solid electrolyte material, a composite material and combinations thereof.

5 In some embodiments, the high molecular polymer is selected from the group consisting of polyethylene oxide, polyimide, polyacrylic acid, polyethylene, polypropylene, polyacrylonitrile, polystyrene, polyvinyl fluoride, polyetheretherketone, polyester, polyvinylidene chloride, polytetrafluoroethylene, polyethylene terephthalate, derivatives thereof,  
10 and combinations thereof;

In some embodiments, the carbon-based material is selected from the group consisting of porous carbon, carbon nanotubes, carbon fibers, graphene, hollow carbon spheres and combinations thereof;

15 In some embodiments, the metal material is selected from the group consisting of copper, silver, gold, nickel and alloys thereof.

In some embodiments, the solid electrolyte material is selected from the group consisting of lithium phosphate ( $\text{Li}_3\text{PO}_4$ ), lithium titanium phosphate ( $\text{Li}_x\text{Ti}_y(\text{PO}_4)_3$ , wherein  $0 < x < 2$  and  $0 < y < 3$ ), lithium aluminum titanium phosphate ( $\text{Li}_x\text{Al}_y\text{Ti}_z(\text{PO}_4)_3$ , wherein  $0 < x < 2$ ,  $0 < y < 1$ , and  $0 < z < 3$ ),  
20  $\text{Li}_{1+x+y}(\text{Al}, \text{Ga})_x(\text{Ti}, \text{Ge})_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ , wherein  $0 \leq x \leq 1$  and  $0 \leq y \leq 1$ , lithium lanthanum titanate ( $\text{Li}_x\text{La}_y\text{TiO}_3$ , wherein  $0 < x < 2$  and  $0 < y < 3$ ), lithium germanium thiophosphate ( $\text{Li}_x\text{Ge}_y\text{P}_z\text{S}_w$ , wherein  $0 < x < 4$ ,  $0 < y < 1$ ,  $0 < z < 1$ , and  $0 < w < 5$ ), lithium nitride ( $\text{Li}_x\text{N}_y$ , wherein  $0 < x < 4$ ,  $0 < y < 2$ ),  $\text{SiS}_2$  glass ( $\text{Li}_x\text{Si}_y\text{S}_z$ , wherein  $0 \leq x < 3$ ,  $0 < y < 2$ , and  $0 < z < 4$ ),  $\text{P}_2\text{S}_5$  glass ( $\text{Li}_x\text{P}_y\text{S}_z$ ,  
25 wherein  $0 \leq x < 3$ ,  $0 < y < 3$ , and  $0 < z < 7$ ),  $\text{Li}_2\text{O}$ ,  $\text{LiF}$ ,  $\text{LiOH}$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{LiAlO}_2$ ,  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5-\text{TiO}_2-\text{GeO}_2$  ceramic, garnet ceramic ( $\text{Li}_{3+x}\text{La}_3\text{M}_2\text{O}_{12}$ , wherein  $0 \leq x \leq 5$ , and M is Te, Nb or Zr) and combinations thereof.

30 In some embodiments, the composite material comprises a framework material selected from the group consisting of a high molecular polymer, a

carbon-based material, a metal material, a solid electrolyte material and combinations thereof, and the inner and outer surfaces of the framework material are covered by another material selected from the group consisting of a high molecular polymer, a carbon-based material, a metal material, a solid electrolyte material, an insulating material and combinations thereof, wherein the insulating material is selected from the group consisting of  $\text{HfO}_2$ ,  $\text{SrTiO}_3$ ,  $\text{SnO}_2$ ,  $\text{CeO}_2$ ,  $\text{MgO}$ ,  $\text{NiO}$ ,  $\text{CaO}$ ,  $\text{BaO}$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$  and combinations thereof.

In some embodiments, the preparation method of the composite material may be a preparation method commonly used in the art, including, but not limited to, atomic layer deposition (ALD) and electrochemical deposition.

The preparation method of an anode provided by the present application will be described below with reference to FIG. 2.

As shown in FIG. 2, the preparation method of the anode includes: the first anode structure layer 102 and the second anode structure layer 103 are sequentially stacked to form a multilayer structure and placed on the surface of the current collector 101, and the multilayer structure is pressed against the current collector 101 by using a roller 201 by means of rolling.

It should be understood that the preparation method of the anode of the present application may be a conventional electrode plate preparation method in the art. Those skilled in the art, through the content of the specification or the claims, may select any preparation method in the art according to specific needs without being limited thereto.

Some embodiments of the present application provide an electrochemical device, including a cathode, a separator and the anode of the above embodiments. In some embodiments, the electrochemical device is a lithium-ion battery, and a lithium-ion battery will be used as an example below to illustrate the composition and preparation method of the electrochemical device of the present application.

According to some embodiments of the present application, the cathode comprises a cathode current collector and a cathode active material layer on a surface thereof, wherein the cathode active material layer comprises a cathode active material and a conductive agent. In some  
 5 embodiments, the cathode current collector includes, but not limited to, aluminum foil or nickel foil.

In some embodiments, examples of the cathode active material may include at least one of lithium cobaltate, lithium iron phosphate, lithium manganese iron phosphate, sodium iron phosphate, lithium vanadium  
 10 phosphate, sodium vanadium phosphate, oxylithium vanadium phosphate, oxysodium vanadium phosphate, lithium vanadate, lithium manganate, lithium nickelate, lithium nickel cobalt manganese oxide, lithium-rich manganese-based material, lithium nickel cobalt aluminum oxide and lithium titanate.

In the above cathode active material, the chemical formula of the lithium cobaltate may be  $\text{Li}_a\text{Co}_b\text{M}_{1c}\text{O}_{2-d}$ , wherein  $\text{M}_1$  is at least one of nickel (Ni), manganese (Mn), magnesium (Mg), aluminum (Al), boron (B), titanium (Ti), vanadium (V), chromium (Cr), iron (Fe), copper (Cu), zinc (Zn), molybdenum (Mo), tin (Sn), calcium (Ca), strontium (Sr), tungsten  
 15 (W), yttrium (Y), lanthanum (La), zirconium (Zr) and silicon (Si), and the values of a, b, c and d are respectively in the following ranges:  $0.8 \leq a \leq 1.2$ ,  $0.8 \leq b \leq 1$ ,  $0 \leq c \leq 0.2$ , and  $-0.1 \leq d \leq 0.2$ ;

In the above cathode active material, the chemical formula of the lithium nickelate may be  $\text{Li}_e\text{Ni}_f\text{M}_{2g}\text{O}_{2-h}$ , wherein  $\text{M}_2$  is at least one of cobalt (Co), manganese (Mn), magnesium (Mg), aluminum (Al), boron (B),  
 25 titanium (Ti), vanadium (V), chromium (Cr), iron (Fe), copper (Cu), zinc (Zn), molybdenum (Mo), tin (Sn), calcium (Ca), strontium (Sr), tungsten (W), zirconium (Zr) and silicon (Si), and the values of e, f, g and h are respectively in the following ranges:  $0.8 \leq e \leq 1.2$ ,  $0.3 \leq f \leq 0.98$ ,  $0.02 \leq g \leq 0.7$ , and  $-0.1 \leq h \leq 0.2$ ;

In the above cathode active material, the chemical formula of the

lithium manganate may be  $\text{Li}_i\text{Mn}_{2-j}\text{M}_3\text{O}_{4-k}$ , wherein  $\text{M}_3$  is at least one of cobalt (Co), nickel (Ni), magnesium (Mg), aluminum (Al), boron (B), titanium (Ti), vanadium (V), chromium (Cr), iron (Fe), copper (Cu), zinc (Zn), molybdenum (Mo), tin (Sn), calcium (Ca), strontium (Sr) and tungsten (W), and the values of  $i$ ,  $j$  and  $k$  are respectively in the following ranges:  $0.8 \leq i \leq 1.2$ ,  $0 \leq j < 1.0$  and  $-0.2 \leq k \leq 0.2$ .

In the above cathode active material, the chemical formula of the lithium nickel cobalt manganese oxide may be  $\text{LiNi}_l\text{Co}_m\text{Mn}_n\text{O}_2$ , wherein the values of  $l$ ,  $m$  and  $n$  are respectively in the following ranges:  $0 < l < 1.0$ ,  $0 < m < 1.0$  and  $0 < n < 1.0$ , and  $l+m+n=1$ .

In some embodiments, the conductive agent includes at least one of conductive carbon black, carbon fibers, acetylene black, Ketjen black, graphene and carbon nanotubes. It will be understood by those skilled in the art that various cathodes widely used in the lithium-ion batteries are suitable for use in the present application without being limited thereto.

The separator in some embodiments of the present application includes, but not limited to, at least one selected from the group consisting of polyethylene, polypropylene, polyethylene terephthalate, polyimide and aramid. For example, the polyethylene includes at least one component selected from the group consisting of high-density polyethylene, low-density polyethylene and ultra-high molecular weight polyethylene. In particular, the polyethylene and polypropylene, which have a good effect on preventing short circuits, can improve the stability of the battery by the shutdown effect. Those skilled in the art will appreciate that various separators widely used in the lithium-ion batteries are suitable for use in the present application.

According to some embodiments of the present application, the above lithium-ion battery further includes an electrolyte, the electrolyte may be one of a gel electrolyte or an electrolytic solution, and the electrolytic solution includes a lithium salt and a non-aqueous solvent.

In some embodiments, the lithium salt is selected from one or more of  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiB}(\text{C}_6\text{H}_5)_4$ ,  $\text{LiCH}_3\text{SO}_3$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ ,  $\text{LiC}(\text{SO}_2\text{CF}_3)_3$ ,  $\text{LiSiF}_6$ ,  $\text{LiBOB}$  and lithium difluoroborate. For example, the lithium salt is  $\text{LiPF}_6$  because  $\text{LiPF}_6$  can give a high ionic conductivity and improve the cycle performance.

In some embodiments, the non-aqueous solvent may be a carbonate compound, a carboxylate compound, an ether compound, other organic solvents or a combination thereof.

In some embodiments, the carbonate compound may be a chain carbonate compound, a cyclic carbonate compound, a fluorocarbonate compound or a combination thereof.

In some embodiments, examples of the chain carbonate compound are diethyl carbonate, dimethyl carbonate, dipropyl carbonate, methyl propyl carbonate, ethyl propyl carbonate, ethyl methyl carbonate and combinations thereof. Examples of the cyclic carbonate compound are ethylene carbonate, propylene carbonate, butylene carbonate, vinyl ethylene carbonate, propyl propionate and combinations thereof. Examples of the fluorocarbonate compound are fluoroethylene carbonate, 1,2-difluoroethylene carbonate, 1,1-difluoroethylene carbonate, 1,1,2-trifluoroethylene carbonate, 1,1,2,2-tetrafluoroethylene carbonate, 1-fluoro-2-methylethylene carbonate, 1-fluoro-1-methylethylene carbonate, 1,2-difluoro-1-methylethylene carbonate, 1,1,2-trifluoro-2-methylethylene carbonate, trifluoromethylethylene carbonate and combinations thereof.

In some embodiments, examples of the carboxylate compound are methyl acetate, ethyl acetate, n-propyl acetate, t-butyl acetate, methyl propionate, ethyl propionate,  $\gamma$ -butyrolactone, decalactone, valerolactone, mevalonolactone, caprolactone, methyl formate and combinations thereof.

In some embodiments, examples of the ether compound are dibutyl ether, tetraethylene glycol dimethyl ether, diglyme, 1,2-dimethoxyethane, 1,2-diethoxyethane, ethoxymethoxyethane, 2-methyltetrahydrofuran,

tetrahydrofuran and combinations thereof.

In some embodiments, examples of other organic solvents are dimethyl sulfoxide, 1,2-dioxolane, sulfolane, methyl sulfolane, 1,3-dimethyl-2-imidazolidinone, N-methyl-2-pyrrolidone, formamide,  
5 dimethylformamide, acetonitrile, trimethyl phosphate, triethyl phosphate, trioctyl phosphate, phosphate and combinations thereof.

The structure and preparation method of the electrode assembly in some embodiments of the present application are described below in conjunction with FIG. 3. FIG. 3 is a side view showing the structure of an  
10 electrode assembly according to some embodiments of the present application. As shown in FIG. 3, the electrode assembly comprises two sets of current collectors 101, first anode structure layers 102, second anode structure layers 103, separators 303, cathode active material layers 302 and cathode current collectors 301 sequentially arranged in opposite.

Some embodiments of the present application provide a preparation  
15 method of a lithium-ion battery, including: the cathode, the separator and the anode of the present application are sequentially wound or stacked into an electrode assembly, and then loaded into, for example, an aluminum plastic film, the electrolytic solution is injected, and formation and  
20 packaging are performed to prepare the lithium-ion battery.

Those skilled in the art will appreciate that the structure of the electrode assembly described above and the preparation method of the lithium-ion battery are merely exemplary embodiments. Other methods  
25 commonly used in the art can be employed as a preparation method of a lithium-ion battery without departing from the disclosure of the present application.

Those skilled in the art will appreciate that while the above is illustrated with a lithium-ion battery, the electrochemical device of the present application further includes any other suitable electrochemical  
30 device. The electrochemical device in the embodiments of the present

application includes any device that generates an electrochemical reaction without departing from the disclosure of the present application, and the specific examples of the device include all kinds of primary batteries, secondary batteries, solar cells or capacitors. In particular, the electrochemical device is a lithium secondary battery, including a lithium metal secondary battery, a lithium ion secondary battery, a lithium polymer secondary battery, or a lithium ion polymer secondary battery.

The use of the electrochemical device of the present application is not particularly limited and can be used for any use known in the prior art. According to some embodiments of the present application, the electronic device comprising the electrochemical device of the present application includes, but not limited to, a notebook computer, a pen input computer, a mobile computer, an e-book player, a portable phone, a portable fax machine, a portable copy machine, a portable printer, stereo headphones, a video recorder, a liquid crystal display television, a portable cleaner, a portable CD player, a mini disk, a transceiver, an electronic notebook, a calculator, a memory card, portable recorder, a radio, a backup power, a motor, a car, a motorcycle, a power bicycles, a bicycle, a lighting fixture, a toy, a game console, a clock, an electric tool, a flash lamp, a camera, a large household battery and a lithium-ion capacitor.

The technical solution of the present invention will be further described below in conjunction with the comparative examples and specific embodiments, but not limited thereto. It will be understood by those skilled in the art that the preparation methods described in the present application are merely exemplary embodiments, and any modification or equivalent of the technical solutions of the present invention without departing from the scope of the technical solutions of the present invention shall be included in the protection scope of the present invention.

## PREFERRED EMBODIMENT OF THE PRESENT INVENTION

### Preparation of cathode

By using aluminum foil as a cathode current collector, a layer of lithium cobaltate slurry (positive electrode material layer) was uniformly coated on both surfaces of the cathode current collector, the lithium cobaltate slurry being composed of 90 wt% of lithium cobaltate, 1.5 wt% of polyvinylidene fluoride (PVDF) and 8.5 wt% of conductive carbon black (Super P), then the cathode current collector coated with the lithium cobaltate slurry was baked at 90 °C for 1 h, and was subjected to cutting and slitting to prepare the cathode (size 38 mm × 58 mm).

#### **Preparation of electrolytic solution**

In an argon atmosphere environment with a water content of less than 10 ppm, lithium hexafluorophosphate and a non-aqueous organic solvent (ethylene carbonate: ethyl methyl carbonate: diethyl carbonate = 30:50:20, mass ratio) were uniformly mixed according to a fixed ratio to form the electrolytic solution having a lithium salt concentration of 1.15 M.

#### **Preparation of lithium-ion battery**

By using polyethylene having a thickness of 15 μm as the separator, the anode, the separator and the above-mentioned double-coated cathode of the embodiments and comparative examples were stacked and fixed in the order of FIG. 3 of the present application to form an electrode assembly. The electrode assembly was loaded in an aluminum foil packaging bag, and the electrolytic solution was injected into the electrode assembly, and subjected to vacuum encapsulation, standing, formation, shaping and the like, thereby completing the preparation of the lithium-ion batteries of the following embodiments and comparative examples.

After completing the preparation of the anode and lithium-ion battery of the following embodiments and comparative examples (i.e., fresh anode and lithium-ion battery), the thickness, width and length were recorded to determine the size of the anode and the lithium-ion battery. The anode volume change test was then performed on the fresh lithium-ion battery.

#### **Anode volume change test**

The lithium-ion battery to be tested was allowed to stand in a  $25\pm 3^{\circ}\text{C}$  environment for 30 minutes, and charged at a constant current of 0.05 C to a voltage of 4.40 V, and then the electrochemical device was discharged at a rate of 0.05 C to 3.00 V. The fully discharged lithium-ion battery was slowly charged to a rated voltage in a constant current manner to be fully charged and the charge amount of the battery was recorded to calculate the lithium metal deposited on the anode to be tested. The lithium-ion battery in which a fixed amount of lithium metal had been deposited was then disassembled and the anode of the battery was taken out. The anode was cut to expose the cross section, and the cross section was polished by using an ion cutter (Leica, EM TIC 3X). Finally, the thickness increment of the anode structure layer in the anode was measured by an electron microscope.

Lithium metal deposition amount ( $\text{mAh}/\text{cm}^2$ ) = full charge amount of lithium-ion battery ( $\text{mAh}$ ) / single-sided area of current collector ( $\text{cm}^2$ ) and thickness increment of anode structure layer (%) = thickness increment of anode structure layer / total thickness of fresh anode structure layer.

### Preparation of anode

#### Example 1

Copper foam (first framework material) having a thickness of 100  $\mu\text{m}$  was used as the first anode structure layer, wherein the copper foam had a lithium ion oxidation-reduction potential and an electronic conductivity of -45 mV and  $5.96\times 10^7$  S/m respectively, and the first anode structure layer had a porosity of 50% to 90%, a pore size of 0.1 mm to 10 mm and a pore density of 5 ppi to 30 ppi.

A polyimide layer having a thickness of 100  $\mu\text{m}$  and a porosity of 60% was prepared by an electrospinning technique, which includes the following steps: 15 wt% of polyimide powder (CP-0650, DuPont) was dissolved in an N-methylpyrrolidone (NMP) solution, and stirred at a speed of 750 rpm for 12 hours in a  $60^{\circ}\text{C}$  oil bath to form a homogeneous solution. Then, the solution was placed in a glass syringe with a stainless steel

needle and connected to a voltage source (ES30P-5 W, Gamma High Voltage Research). A voltage of 15 kV was applied to the needle to form the polyimide layer, wherein the needle was at a distance of 15 cm from the substrate, the syringe was pushed at a rate of 10 mL/min, and a reverse  
5 voltage of 1 kV was applied to the substrate to increase the uniformity of electrospinning. A copper metal layer having a thickness of 10 nm was coated on the fiber surface of the polyimide layer by atomic layer deposition to form a composite material (second framework material), that is, a copper-clad polyimide layer having a thickness of 100  $\mu\text{m}$ , and the  
10 copper-clad polyimide layer was used as the second anode structure layer, wherein the copper-clad polyimide layer had a lithium ion oxidation-reduction potential and an electronic conductivity of -45 mV and  $4.5 \times 10^6$  S/m respectively.

Double-sided lithium-clad copper foil was used as a current collector,  
15 wherein the copper layer in the current collector had a thickness of 12  $\mu\text{m}$  and the lithium coating had a single-sided thickness of 50  $\mu\text{m}$ , and the current collector was die-cut to a size of 40 mm  $\times$  60 mm. Then, the first anode structure layer and the second anode structure layer were sequentially arranged and combined with the current collector by rolling,  
20 wherein a roller having a weight of 1 kg and a width of 10 cm was used and the rolling speed was 1 cm/s, thereby obtaining the anode.

### Example 2

The preparation method is the same as in Example 1. The difference is that in Example 2, by using copper foam having a thickness of 100  $\mu\text{m}$  as a  
25 substrate, a silver metal layer having a thickness of 1  $\mu\text{m}$  was coated on the copper fiber surface by electrochemical deposition such that the surface in a three-dimensional structure was coated by silver to form a composite material (first framework material), that is, a silver-clad copper foam layer having a thickness of 100  $\mu\text{m}$ , and the silver-clad copper foam layer was  
30 used as the first anode structure layer, wherein the silver-clad copper foam layer had a lithium ion oxidation-reduction potential and an electronic conductivity of 5 mV and  $6.1 \times 10^7$  S/m respectively, and the first anode

structure layer had a porosity of 50% to 90%, a pore size of 0.1 mm to 10 mm and a pore density of 5 ppi to 30 ppi.

#### Example 3

5 The preparation method is the same as in Example 2. The difference is that in Example 3, a silver-clad copper foam layer having a thickness of 150  $\mu\text{m}$  was used as the first anode structure layer.

#### Example 4

10 The preparation method is the same as in Example 2. The difference is that in Example 4, a copper-clad polyimide layer having a thickness of 150  $\mu\text{m}$  was used as the second anode structure layer.

#### Example 5

The preparation method is the same as in Example 2. The difference is that in Example 5, a silver-clad copper foam layer having a thickness of 250  $\mu\text{m}$  was used as the first anode structure layer.

#### 15 Example 6

The preparation method is the same as in Example 2. The difference is that in Example 6, a silver-clad copper foam layer having a thickness of 400  $\mu\text{m}$  was used as the first anode structure layer.

#### Example 7

20 The preparation method is the same as in Example 1. The difference is that in Example 7, by using a carbon cloth (Shanghai Hesen Electric) having a thickness of 150  $\mu\text{m}$  as a substrate, a silver metal layer having a thickness of 1  $\mu\text{m}$  was coated on the fiber surface by electrochemical deposition such that the surface in a three-dimensional structure was coated  
25 by silver to form a composite material (first framework material), that is, a silver-clad carbon layer having a thickness of 150  $\mu\text{m}$ , and the silver-clad carbon layer was used as the anode structure layer, wherein the silver-clad carbon layer had a lithium ion oxidation-reduction potential and an

electronic conductivity of 5 mV and  $9 \times 10^6$  S/m respectively.

#### Example 8

The preparation method is the same as in Example 2. The difference is that in Example 8, copper foam (second framework material) having a  
5 thickness of 100  $\mu\text{m}$  was used as the second anode structure layer.

#### Example 9

The preparation method is the same as in Example 7. The difference is that in Example 9, copper foam (second framework material) having a  
thickness of 100  $\mu\text{m}$  was used as the second anode structure layer.

#### 10 Example 10

The preparation method is the same as in Example 7. The difference is that in Example 10, a carbon cloth (Shanghai Hesen Electric) having a  
thickness of 150  $\mu\text{m}$  was used as the second anode structure layer, wherein  
the carbon cloth had a lithium ion oxidation-reduction potential and an  
15 electronic conductivity of -20 mV and  $1.3 \times 10^3$  S/m respectively.

#### Example 11

The preparation method is the same as in Example 2. The difference is that in Example 11, a carbon cloth (Shanghai Hesen Electric) having a  
thickness of 150  $\mu\text{m}$  was used as the second anode structure layer, wherein  
20 the carbon cloth had a lithium ion oxidation-reduction potential and an  
electronic conductivity of -20 mV and  $1.3 \times 10^3$  S/m respectively.

#### Example 12

The preparation method is the same as in Example 11. The difference is that in Example 12, a silver-clad copper foam layer having a thickness of  
25 200  $\mu\text{m}$  was used as the first anode structure layer.

#### Example 13

The preparation method is the same as in Example 11. The difference is that in Example 13, a silver-clad copper foam layer having a thickness of 300  $\mu\text{m}$  was used as the first anode structure layer.

#### Comparative Example 1

5 A polyimide layer having a thickness of 200  $\mu\text{m}$  and a porosity of 60% was prepared by an electrospinning technique, which includes the following steps: 15 wt% of polyimide powder (CP-0650, DuPont) was dissolved in an N-methylpyrrolidone (NMP) solution, and stirred at a speed of 750 rpm for 12 hours in a 60°C oil bath to form a homogeneous solution.  
10 Then, the solution was placed in a glass syringe with a stainless steel needle and connected to a voltage source (ES30P-5 W, Gamma High Voltage Research). A voltage of 15 kV was applied to the needle to form the polyimide layer, wherein the needle was at a distance of 15 cm from the substrate, the syringe was pushed at a rate of 10 mL/min, and a reverse  
15 voltage of 1 kV was applied to the substrate to increase the uniformity of electrospinning. A copper metal layer having a thickness of 10 nm was coated on the fiber surface of the polyimide layer by atomic layer deposition to form a composite material (single-layer framework material), that is, a copper-clad polyimide layer having a thickness of 200  $\mu\text{m}$ , and  
20 the copper-clad polyimide layer was used as the single-layer anode structure layer.

Double-sided lithium-clad copper foil was used as a current collector, wherein the copper layer in the current collector had a thickness of 12  $\mu\text{m}$  and the lithium coating had a single-sided thickness of 50  $\mu\text{m}$ , and the  
25 current collector was die-cut to a size of 40 mm×60 mm. Then, the single-layer anode structure layer was combined with the current collector by rolling, wherein a roller having a weight of 1 kg and a width of 10 cm was used and the rolling speed was 1 cm/s, thereby obtaining the anode.

#### Comparative Example 2

30 The preparation method is the same as in Comparative Example 1. The

difference is that in Comparative Example 2, copper foam (single-layer framework material) having a thickness of 200  $\mu\text{m}$  was used as the single-layer electrode structure layer.

#### Comparative Example 3

- 5        The preparation method is the same as in Comparative Example 1. The difference is that in Comparative Example 3, carbon cloth (Shanghai Hesun Electric) (single-layer framework material) having a thickness of 300  $\mu\text{m}$  was used as the single-layer electrode structure layer.

#### Comparative Example 4

- 10       The preparation method is the same as in Comparative Example 1. The difference is that in Comparative Example 4, by using copper foam having a thickness of 200  $\mu\text{m}$  as a substrate, a silver metal layer having a thickness of 1  $\mu\text{m}$  was coated on the copper fiber surface by electrochemical deposition such that the surface in a three-dimensional structure was coated  
15       by silver to form a composite material (single-layer framework material), that is, a silver-clad copper foam layer having a thickness of 200  $\mu\text{m}$ , and the silver-clad copper foam layer was used as the single-layer anode structure layer.

#### Comparative Example 5

- 20       Double-sided lithium-clad copper foil was directly used as an anode, wherein the copper layer in the anode had a thickness of 12  $\mu\text{m}$  and the lithium coating had a single-sided thickness of 50  $\mu\text{m}$ , and the anode had a size of 40 mm×60 mm.

#### Comparative Example 6

- 25       The preparation method is the same as in Example 1. The difference is that in Comparative Example 6, by using copper foam having a thickness of 100  $\mu\text{m}$  as a substrate, a silver metal layer having a thickness of 1  $\mu\text{m}$  was coated on the copper fiber surface by electrochemical deposition such that the surface in a three-dimensional structure was coated by silver to

form a composite material (second framework material), that is, a silver-clad copper foam layer having a thickness of 100  $\mu\text{m}$ , and the silver-clad copper foam layer was used as the second anode structure layer.

The experimental parameters and measurement results of Examples 1-13 and Comparative Examples 1-6 described above are shown in Table 1 below.

Table 1

| Sample                | First Anode structure Layer/Single-Layer Anode structure Layer |                                                |                               |                             | Second Anode structure Layer |                                                |                               |                             | Total Thickness of Anode structure Layer ( $\mu\text{m}$ ) | Lithium Metal Deposition Amount ( $\text{mAh}/\text{cm}^2$ ) | Total Thickness Increment of Anode structure Layer ( $\mu\text{m}$ ) | Thickness Increment (%) |
|-----------------------|----------------------------------------------------------------|------------------------------------------------|-------------------------------|-----------------------------|------------------------------|------------------------------------------------|-------------------------------|-----------------------------|------------------------------------------------------------|--------------------------------------------------------------|----------------------------------------------------------------------|-------------------------|
|                       | First Framework Material/Single-Layer Framework Material       | Lithium Ion Oxidation-reduction potential (mV) | Electronic Conductivity (S/m) | Thickness ( $\mu\text{m}$ ) | Second Framework Material    | Lithium Ion Oxidation-reduction potential (mV) | Electronic Conductivity (S/m) | Thickness ( $\mu\text{m}$ ) |                                                            |                                                              |                                                                      |                         |
| Comparative Example 1 | Copper-clad polyimide                                          | -45                                            | $4.5 \times 10^6$             | 200                         | N/A                          | N/A                                            | N/A                           | N/A                         | 200                                                        | 23                                                           | 51                                                                   | 25.5%                   |
| Comparative Example 2 | Copper foam                                                    | -45                                            | $5.96 \times 10^7$            | 200                         | N/A                          | N/A                                            | N/A                           | N/A                         | 200                                                        | 23                                                           | 71                                                                   | 35.5%                   |
| Comparative Example 3 | Carbon cloth                                                   | -20                                            | $1.3 \times 10^3$             | 300                         | N/A                          | N/A                                            | N/A                           | N/A                         | 300                                                        | 35                                                           | 77                                                                   | 25.7%                   |
| Comparative Example 4 | Silver-clad copper foam                                        | 5                                              | $6.1 \times 10^7$             | 200                         | N/A                          | N/A                                            | N/A                           | N/A                         | 200                                                        | 23                                                           | 44                                                                   | 22.0%                   |
| Comparative Example 5 | N/A                                                            | N/A                                            | N/A                           | N/A                         | N/A                          | N/A                                            | N/A                           | N/A                         | 0                                                          | 23                                                           | 297                                                                  | N/A                     |
| Comparative Example 6 | Copper foam                                                    | -45                                            | $5.96 \times 10^7$            | 100                         | Silver-clad copper foam      | 5                                              | $6.1 \times 10^7$             | 100                         | 200                                                        | 23                                                           | 72                                                                   | 36.0%                   |
| Example 1             | Copper foam                                                    | -45                                            | $5.96 \times 10^7$            | 100                         | Copper-clad polyimide        | -45                                            | $4.5 \times 10^6$             | 100                         | 200                                                        | 23                                                           | 16                                                                   | 8.0%                    |
| Example 2             | Silver-clad copper foam                                        | 5                                              | $6.1 \times 10^7$             | 100                         | Copper-clad polyimide        | -45                                            | $4.5 \times 10^6$             | 100                         | 200                                                        | 23                                                           | 11                                                                   | 5.5%                    |
| Example 3             | Silver-clad copper foam                                        | 5                                              | $6.1 \times 10^7$             | 150                         | Copper-clad polyimide        | -45                                            | $4.5 \times 10^6$             | 100                         | 250                                                        | 29                                                           | 19                                                                   | 7.6%                    |
| Example 4             | Silver-clad copper foam                                        | 5                                              | $6.1 \times 10^7$             | 100                         | Copper-clad polyimide        | -45                                            | $4.5 \times 10^6$             | 150                         | 250                                                        | 29                                                           | 18                                                                   | 7.2%                    |
| Example 5             | Silver-clad copper foam                                        | 5                                              | $6.1 \times 10^7$             | 250                         | Copper-clad polyimide        | -45                                            | $4.5 \times 10^6$             | 100                         | 350                                                        | 41                                                           | 29                                                                   | 8.3%                    |
| Example 6             | Silver-clad copper foam                                        | 5                                              | $6.1 \times 10^7$             | 400                         | Copper-clad polyimide        | -45                                            | $4.5 \times 10^6$             | 100                         | 500                                                        | 58                                                           | 64                                                                   | 12.8%                   |
| Example 7             | Silver-clad carbon cloth                                       | 5                                              | $9 \times 10^6$               | 150                         | Copper-clad polyimide        | -45                                            | $4.5 \times 10^6$             | 100                         | 250                                                        | 29                                                           | 21                                                                   | 8.4%                    |
| Example 8             | Silver-clad copper foam                                        | 5                                              | $6.1 \times 10^7$             | 100                         | Copper foam                  | -45                                            | $5.96 \times 10^7$            | 100                         | 200                                                        | 23                                                           | 18                                                                   | 9.0%                    |
| Example 9             | Silver-clad carbon cloth                                       | 5                                              | $9 \times 10^6$               | 150                         | Copper foam                  | -45                                            | $5.96 \times 10^7$            | 100                         | 250                                                        | 29                                                           | 23                                                                   | 9.2%                    |
| Example 10            | Silver-clad carbon cloth                                       | 5                                              | $9 \times 10^6$               | 150                         | Carbon cloth                 | -20                                            | $1.3 \times 10^3$             | 150                         | 300                                                        | 35                                                           | 29                                                                   | 9.7%                    |
| Example 11            | Silver-clad copper foam                                        | 5                                              | $6.1 \times 10^7$             | 100                         | Carbon cloth                 | -20                                            | $1.3 \times 10^3$             | 150                         | 250                                                        | 29                                                           | 20                                                                   | 8.0%                    |

|            |                         |   |                   |     |              |     |                   |     |     |    |    |       |
|------------|-------------------------|---|-------------------|-----|--------------|-----|-------------------|-----|-----|----|----|-------|
| Example 12 | Silver-clad copper foam | 5 | $6.1 \times 10^7$ | 200 | Carbon cloth | -20 | $1.3 \times 10^3$ | 150 | 350 | 41 | 28 | 8.0%  |
| Example 13 | Silver-clad copper foam | 5 | $6.1 \times 10^7$ | 300 | Carbon cloth | -20 | $1.3 \times 10^3$ | 150 | 450 | 52 | 52 | 11.6% |

As shown in Table 1, the anodes of Examples 1-13 of the present application can effectively reduce the thickness increment of the anode to 12.8% or less of the total thickness of the anode structure layer as compared with Comparative Examples 1-6. Comparing Comparative Examples 1, 2 and 4 with Examples 1, 2 and 8, it can be seen that in the case of the same total thickness of 200  $\mu\text{m}$ , the anode in the double-layer structure of the present application can effectively reduce the lithium metal deposition formed on the anode structure layer, and the total thickness increment can be greatly reduced from the range of 44  $\mu\text{m}$  to 71  $\mu\text{m}$  to the range of 11  $\mu\text{m}$  to 18  $\mu\text{m}$ . At the same time, comparing Example 3 and Example 4, it can be seen that the thickness variations of the first anode structure layer and the second anode structure layer in the thickness range of the first anode structure layer and the second anode structure layer provided by the present application can all effectively reduce the volume change rate of the anode.

In addition, comparing Comparative Example 1 with Example 1, it can be seen that when the first framework material (silver-clad copper foam layer) of the first anode structure layer (closer to the current collector) in the structure of the anode according to the embodiment of the present application has a higher electronic conductivity than the second framework material (copper foam) of the second anode structure layer, the volume change rate of the anode can be effectively reduced.

Finally, comparing Example 8 with Comparative Example 6, it can be seen that when the first framework material (silver-clad copper foam layer) of the first anode structure layer (closer to the current collector) in the structure of the anode according to the embodiment of the present application has a higher lithium ion oxidation-reduction potential than the second framework material (copper foam) of the second anode structure layer, the volume change rate of the anode can be effectively reduced. In contrast, when the first framework material (copper foam) of the first

anode structure layer (closer to the current collector) has a lower lithium ion oxidation-reduction potential than the second framework material (silver-clad copper foam layer) of the second anode structure layer, the thickness increment percentage of the anode will be significantly increased from 9.0% to 36.0%.

Through the description of the above embodiments and comparative examples of the present application, it should be understood that the present application provides a novel anode, and an electrochemical device and an electronic device comprising the same. By adopting a double-layer or multilayer anode structure layer design, the space utilization ratio of the anode can be effectively enhanced, the formation of lithium dendrites may be inhibited, and the volume change amount of the anode can be reduced.

References throughout the specification of the present application to "embodiments", "partial embodiments," "an embodiment," "another example", "examples", "specific examples" or "partial examples" mean that at least one embodiment or example in the embodiments of the present application comprises specific features, structures, materials or characteristics described in the embodiment or example. Therefore, descriptions appearing throughout the specification, such as "in some embodiments", "in the embodiments", "in an embodiment", "in another example", "in an example", "in a particular example" or "examples", are not necessarily referring to the same embodiments or examples in the embodiments of the present application. Furthermore, the specific features, structures, materials or characteristics in the descriptions can be combined in any suitable manner in one or more embodiments or examples.

The above description summarizes the features of several embodiments, which enables those of ordinary skill in the art to understand the various aspects of the present application. Those of ordinary skill in the art can readily take the present application as a basis for designing or modifying other compositions to achieve the same objectives and/or the same advantages as the embodiments herein. It is also to be understood by those of ordinary skill in the art that these equal examples do not depart

from the spirit and scope of the present application, and it is possible to make various changes, substitutions and modifications to the present application without departing from the spirit and scope of the present application. Although the methods disclosed herein have been described  
5 with reference to the specific operations that are performed in a specific order, it should be understood that these operations can be combined, subdivided, or reordered to form an equivalent method without departing from the teachings of the present application. Therefore, unless otherwise specifically indicated herein, the order and grouping of operations shall not  
10 be construed as any limitation on the present application.

**What is claimed is:**

1. An anode, comprising:  
a current collector;  
a first anode structure layer, the first anode structure layer  
5 comprising a first framework material; and  
a second anode structure layer, the second anode structure layer  
comprising a second framework material, wherein the first anode structure  
layer is arranged between the current collector and the second anode  
structure layer, and the first framework material has a higher oxidation-  
10 reduction potential for lithium ion or electronic conductivity than the  
second framework material.
2. The anode according to claim 1, wherein the first framework  
material has a lithium ion oxidation-reduction potential of about -50 mV to  
about 250 mV, and the second framework material has a lithium ion  
15 oxidation-reduction potential of about -100 mV to about 200 mV.
3. The anode according to claim 1, wherein the first framework  
material has an electronic conductivity of about  $1 \times 10^{-2}$  S/m to about  
 $6.30 \times 10^7$  S/m, and the second framework material has an electronic  
conductivity of about  $1 \times 10^{-25}$  S/m to about  $5.95 \times 10^7$  S/m.
- 20 4. The anode according to claim 1, further comprising at least  
one third anode structure layer, the third anode structure layer comprising a  
third framework material, wherein the second anode structure layer is  
arranged between the first anode structure layer and the third anode  
structure layer, and the second framework material has a higher lithium ion  
25 oxidation-reduction potential or electronic conductivity than the third  
framework material.
5. The anode according to claim 4, comprising a plurality of the  
third anode structure layers, wherein the third framework material  
comprises in any one of the plurality of the third anode structure layers has

a higher lithium ion oxidation-reduction potential or electronic conductivity than the third framework material comprised in the other third anode structure layers farther from the current collector.

6. The anode according to claim 4, wherein the first framework material, the second framework material and the third framework material are each independently selected from the group consisting of a high molecular polymer, a carbon-based material, a metal material, a solid electrolyte material, a composite material and combinations thereof.

7. The anode according to claim 6, wherein the high molecular polymer is selected from the group consisting of polyethylene oxide, polyimide, polyacrylic acid, polyethylene, polypropylene, polyacrylonitrile, polystyrene, polyvinyl fluoride, polyetheretherketone, polyester, polyvinylidene chloride, polytetrafluoroethylene, polyethylene terephthalate, derivatives thereof, and combinations thereof;

the carbon-based material is selected from the group consisting of porous carbon, carbon nanotubes, carbon fibers, graphene, hollow carbon spheres and combinations thereof;

the metal material is selected from the group consisting of copper, silver, gold, nickel and alloys thereof; and

the solid electrolyte material is selected from the group consisting of lithium phosphate ( $\text{Li}_3\text{PO}_4$ ), lithium titanium phosphate ( $\text{Li}_x\text{Ti}_y(\text{PO}_4)_3$ , wherein  $0 < x < 2$  and  $0 < y < 3$ ), lithium aluminum titanium phosphate ( $\text{Li}_x\text{Al}_y\text{Ti}_z(\text{PO}_4)_3$ , wherein  $0 < x < 2$ ,  $0 < y < 1$ , and  $0 < z < 3$ ),  $\text{Li}_{1+x+y}(\text{Al}, \text{Ga})_x(\text{Ti}, \text{Ge})_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ , wherein  $0 \leq x \leq 1$  and  $0 \leq y \leq 1$ , lithium lanthanum titanate ( $\text{Li}_x\text{La}_y\text{TiO}_3$ , wherein  $0 < x < 2$  and  $0 < y < 3$ ), lithium germanium thiophosphate ( $\text{Li}_x\text{Ge}_y\text{P}_z\text{S}_w$ , wherein  $0 < x < 4$ ,  $0 < y < 1$ ,  $0 < z < 1$ , and  $0 < w < 5$ ), lithium nitride ( $\text{Li}_x\text{N}_y$ , wherein  $0 < x < 4$ ,  $0 < y < 2$ ),  $\text{SiS}_2$  glass ( $\text{Li}_x\text{Si}_y\text{S}_z$ , wherein  $0 \leq x < 3$ ,  $0 < y < 2$ , and  $0 < z < 4$ ),  $\text{P}_2\text{S}_5$  glass ( $\text{Li}_x\text{P}_y\text{S}_z$ , wherein  $0 \leq x < 3$ ,  $0 < y < 3$ , and  $0 < z < 7$ ),  $\text{Li}_2\text{O}$ ,  $\text{LiF}$ ,  $\text{LiOH}$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{LiAlO}_2$ ,  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5-\text{TiO}_2-\text{GeO}_2$  ceramic, garnet ceramic ( $\text{Li}_{3+x}\text{La}_3\text{M}_2\text{O}_{12}$ , wherein

$0 \leq x \leq 5$ , and M is Te, Nb or Zr) and combinations thereof.

8. The anode according to claim 6, wherein the composite material comprises a framework material selected from the group consisting of a high molecular polymer, a carbon-based material, a metal material, a solid electrolyte material and combinations thereof, and the inner and outer surfaces of the framework material are covered by another material selected from the group consisting of a high molecular polymer, a carbon-based material, a metal material, a solid electrolyte material, an insulating material and combinations thereof, wherein the insulating material is selected from the group consisting of  $\text{HfO}_2$ ,  $\text{SrTiO}_3$ ,  $\text{SnO}_2$ ,  $\text{CeO}_2$ ,  $\text{MgO}$ ,  $\text{NiO}$ ,  $\text{CaO}$ ,  $\text{BaO}$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$  and combinations thereof.

9. The anode according to claim 1, wherein the first anode structure layer has a porosity of about 30% to about 98%, and the second anode structure layer has a porosity of about 30% to about 98%.

10. The anode according to claim 1, wherein the first anode structure layer and the second anode structure layer have a thickness of about  $0.1 \mu\text{m}$  to about 1 mm, and the anode has a total thickness of about  $0.1 \mu\text{m}$  to about 2 mm.

11. An electrochemical device, comprising:

a cathode;

a separator; and

an anode, wherein the anode comprises:

a current collector;

a first anode structure layer, the first anode structure layer comprising a first framework material; and

a second anode structure layer, the second anode structure layer comprising a second framework material, wherein the first anode structure layer is arranged between the current collector and the

second anode structure layer, and the first framework material has a higher oxidation-reduction potential for lithium ion or electronic conductivity than the second framework material.

12. The electrochemical device according to claim 11, wherein the first framework material has a lithium ion oxidation-reduction potential of about -50 mV to about 250 mV, and the second framework material has a lithium ion oxidation-reduction potential of about -100 mV to about 200 mV.

13. The electrochemical device according to claim 11, wherein the first framework material has an electronic conductivity of about  $1 \times 10^{-2}$  S/m to about  $6.30 \times 10^7$  S/m, and the second framework material has an electronic conductivity of about  $1 \times 10^{-25}$  S/m to about  $5.95 \times 10^7$  S/m.

14. The electrochemical device according to claim 11, further comprising at least one third anode structure layer, the third anode structure layer comprising a third framework material, wherein the second anode structure layer is arranged between the first anode structure layer and the third anode structure layer, and the second framework material has a higher lithium ion oxidation-reduction potential or electronic conductivity than the third framework material.

15. The electrochemical device according to claim 14, comprising a plurality of the third anode structure layers, wherein the third framework material comprises in any one of the plurality of the third anode structure layers has a higher lithium ion oxidation-reduction potential or electronic conductivity than the third framework material comprised in the other third anode structure layers farther from the current collector.

16. An electronic device, comprising an electrochemical device, wherein the electrochemical device comprises:

a cathode;

a separator; and

an anode, wherein the anode comprises:

a current collector;

a first anode structure layer, the first anode structure layer comprising a first framework material; and

5 a second anode structure layer, the second anode structure layer comprising a second framework material, wherein the first anode structure layer is arranged between the current collector and the second anode structure layer, and the first framework material has a higher oxidation-reduction potential for lithium ion or electronic conductivity than the  
10 second framework material.

17. The electronic device according to claim 16, wherein the first framework material has a lithium ion oxidation-reduction potential of about -50 mV to about 250 mV, and the second framework material has a lithium ion oxidation-reduction potential of about -100 mV to about 200 mV.

15 18. The electronic device according to claim 16, wherein the first framework material has an electronic conductivity of about  $1 \times 10^{-2}$  S/m to about  $6.30 \times 10^7$  S/m, and the second framework material has an electronic conductivity of about  $1 \times 10^{-25}$  S/m to about  $5.95 \times 10^7$  S/m.

19. The electronic device according to claim 16, further  
20 comprising at least one third anode structure layer, the third anode structure layer comprising a third framework material, wherein the second anode structure layer is arranged between the first anode structure layer and the third anode structure layer, and the second framework material has a higher lithium ion oxidation-reduction potential or electronic conductivity than the  
25 third framework material.

20. The electronic device according to claim 19, comprising a plurality of the third anode structure layers, wherein the third framework material comprises in any one of the plurality of the third anode structure layers has a higher lithium ion oxidation-reduction potential or electronic  
30 conductivity than the third framework material comprised in the other third

anode structure layers farther from the current collector.

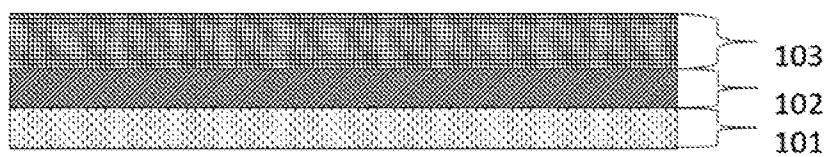


FIG. 1A

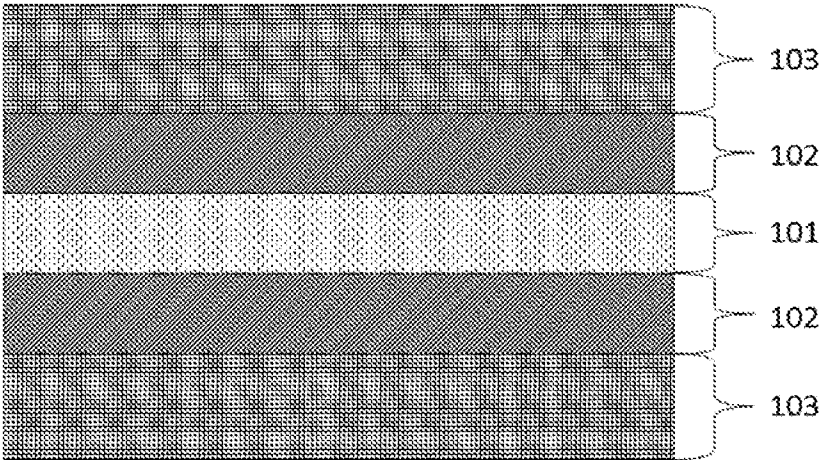


FIG. 1B

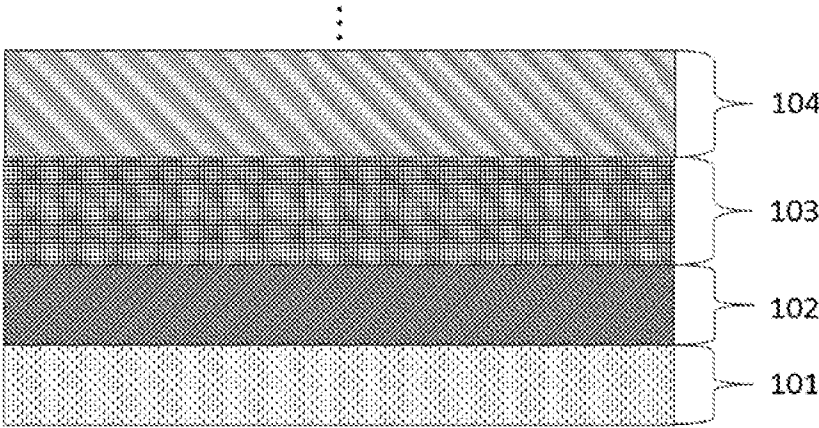


FIG. 1C

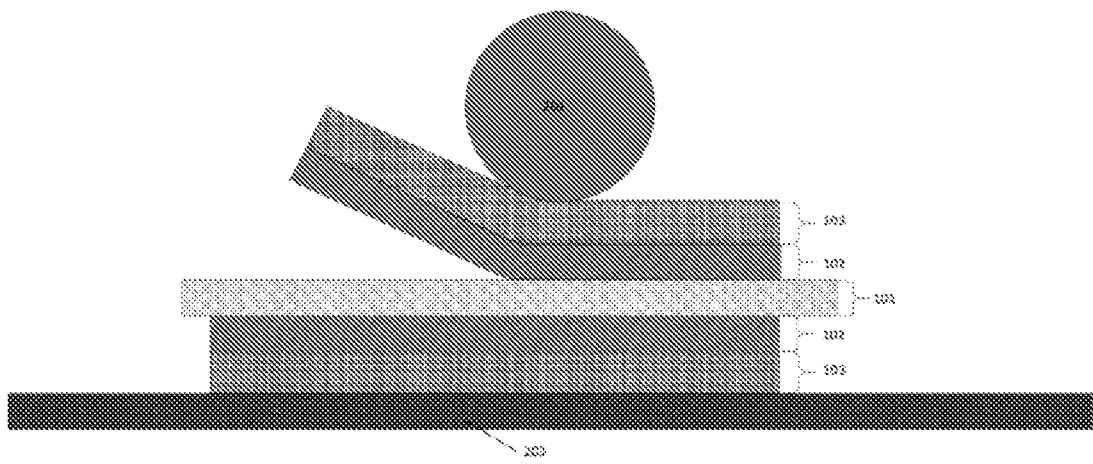


FIG. 2

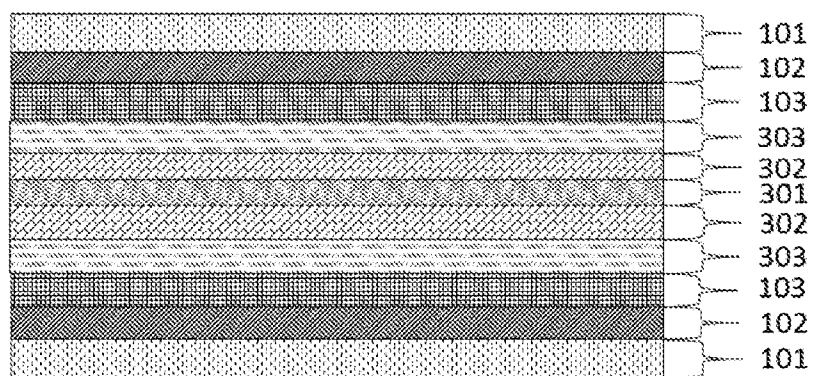


FIG. 3

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2019/122694

**A. CLASSIFICATION OF SUBJECT MATTER**

H01M 4/66(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNPAT,CNKI,WPLEPODOC,GOOGLE:battery, anode, negative, electrode, layer, framework, support, net, porous, reduction potential, electronic conductivity, lithium dendrite, protect

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                 | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------------------------------------|-----------------------|
| PX        | CN 109994739 A (NINGDE AMPEREX TECHNOLOGY LTD.) 09 July 2019 (2019-07-09)<br>description, paragraphs [0004]-[0019] | 1-20                  |
| X         | CN 106207191 A (UNIV. TSINGHUA) 07 December 2016 (2016-12-07)<br>description, paragraphs [0006]-[0021], [0032]     | 1-3, 9-13, 16-18      |
| A         | CN 108448063 A (UNIV. SOOCHOW) 24 August 2018 (2018-08-24)<br>full text                                            | 1-20                  |
| A         | CN 108539252 A (GU, T.) 14 September 2018 (2018-09-14)<br>full text                                                | 1-20                  |
| A         | CN 105845891 A (UNIV. TSINGHUA) 10 August 2016 (2016-08-10)<br>full text                                           | 1-20                  |
| A         | WO 2018164640 A1 (UNIV. NANYANG TECHNOLOGICAL) 13 September 2018<br>(2018-09-13)<br>full text                      | 1-20                  |



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

19 February 2020

Date of mailing of the international search report

06 March 2020

Name and mailing address of the ISA/CN

National Intellectual Property Administration, PRC  
6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing  
100088  
China

Authorized officer

JIAN, Ji

Facsimile No. (86-10)62019451

Telephone No. 86-(10)-53961479

**INTERNATIONAL SEARCH REPORT**  
**Information on patent family members**

International application No.

**PCT/CN2019/122694**

| Patent document<br>cited in search report |            |    | Publication date<br>(day/month/year) | Patent family member(s) |           |   | Publication date<br>(day/month/year) |
|-------------------------------------------|------------|----|--------------------------------------|-------------------------|-----------|---|--------------------------------------|
| CN                                        | 109994739  | A  | 09 July 2019                         | None                    |           |   |                                      |
| CN                                        | 106207191  | A  | 07 December 2016                     | CN                      | 106207191 | B | 22 February 2019                     |
| CN                                        | 108448063  | A  | 24 August 2018                       | None                    |           |   |                                      |
| CN                                        | 108539252  | A  | 14 September 2018                    | None                    |           |   |                                      |
| CN                                        | 105845891  | A  | 10 August 2016                       | CN                      | 105845891 | B | 18 June 2019                         |
| WO                                        | 2018164640 | A1 | 13 September 2018                    | None                    |           |   |                                      |