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Inventeur(s):
WU Guojiang – China

43

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Mandataire(s):
Patent42 SA – 4081 Esch-sur-Alzette (Luxembourg)

47

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Titulaire(s):
KAILI UNIVERSITY – Kaili Economic Development
Zone (China)

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A method for preparing an anode for aqueous zinc-ion batteries, as well as its products and applications.

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The present invention relates to the field of battery technology, specifically to a method for preparing an anode for aqueous zinc-ion batteries, as well as the product and its applications. The preparation method for the aqueous zinc-ion battery anode includes the following steps: Carbonization of corn starch: corn starch is carbonized to obtain biomass carbon. Mixing and sintering: the biomass carbon is mixed and ground with potassium hydroxide, followed by sintering to produce a solid. Acid treatment: dilute hydrochloric acid is added dropwise to the solid until the pH is neutral, followed by filtration, washing, and drying to obtain porous activated carbon. Mixing with polymer: the porous activated carbon is mixed uniformly with polyvinylidene fluoride (PVDF) and N-methyl-2-pyrrolidone (NMP) to create a homogeneous mixture. Coating on zinc foil: the mixture is then coated onto the surface of zinc foil and dried to yield the aqueous zinc-ion battery anode.

DESCRIPTION

A METHOD FOR PREPARING AN ANODE FOR AQUEOUS ZINC-ION BATTERIES, AS WELL AS ITS PRODUCTS AND APPLICATIONS

TECHNICAL FIELD

The present invention relates to the field of battery technology, specifically to a method for preparing an anode for aqueous zinc-ion batteries, as well as its products and applications.

BACKGROUND

Aqueous zinc-ion batteries (AZIBs) have garnered significant research interest due to their inherent safety, low cost, and high theoretical capacity (5855 mAh/cm³). As energy storage devices for large battery systems, they serve as excellent alternatives to lithium-ion batteries. However, issues such as uncontrolled dendrite growth, side reactions, and hydrogen evolution reactions lead to deterioration of the zinc electrode interface, resulting in poor coulombic efficiency, short cycle life, and even short-circuit failures, which hinder further development. Many strategies have been employed to address these problems, including artificial SEI interfaces, electrolyte optimization, and electrode design. Among these, constructing a refined artificial interface on the zinc anode is an effective method to suppress zinc dendrite growth and alleviate electrolyte corrosion.

Currently, various interfacial layers have been explored, including inorganic compounds (CaCO₃, TiO₂, ZrO₂, Al₂O₃, ZnF₂), carbon materials (carbon nanotubes, carbon black, and graphene), and polymers (polyamide and MOF). Carbon materials, in particular, are ideal for SEI due to their high corrosion resistance and stability in aqueous electrolytes.

Conductive and porous carbon coatings, owing to their large specific surface area, not only facilitate uniform electric field distribution at the interface but also guide zinc to preferentially deposit in the porous carbon gaps rather than grow vertically into dendrites.

Some related studies have reported that using graphene as a zinc coating can yield dendrite-free zinc anodes. Epitaxial graphene can induce zinc ions to preferentially grow along the (002) crystal plane, effectively suppressing dendrite growth. Similarly, zinc electrodes coated with carbon nanotubes can also effectively limit zinc dendrites, as the presence of carbon nanotubes helps to homogenize the electric field on the zinc anode surface. Batteries demonstrate good performance during repeated cycling without significant polarization.

Considering the high costs associated with graphene and carbon nanotubes, there is a need to propose a more economical biomass carbon coating for zinc-ion batteries to enhance their cycle life and capacity.

SUMMARY

Based on the above content, the present invention provides a method for preparing an anode for aqueous zinc-ion batteries, along with its products and applications. This invention uses corn flour as a raw material to obtain biomass carbon (BC), which is further processed to create porous activated carbon (PAC). By coating PAC onto the surface of zinc foil, a BC/Zn anode (the anode for the aqueous zinc-ion battery) is prepared to enhance the cycle life and capacity of the aqueous zinc-ion battery.

To achieve the aforementioned objectives, the present invention proposes the following solutions:

Technical Solution 1: A method for preparing an anode for an aqueous zinc-ion battery, comprising the following steps:

1. Carbonizing corn flour to obtain biomass carbon;
2. Mixing the biomass carbon with potassium hydroxide, grinding, and then sintering to obtain a solid;
3. Dripping dilute hydrochloric acid into the solid until the pH is neutral, followed by filtering, washing, and drying to obtain porous activated carbon;
4. Mixing the porous activated carbon with polyvinylidene fluoride and N-methylpyrrolidone to obtain a uniform mixture;
5. Coating the mixture onto the surface of zinc foil and drying to obtain the anode for the aqueous zinc-ion battery.

Technical Solution 2: An aqueous zinc-ion battery anode prepared according to the method described above.

Technical Solution 3: An aqueous zinc-ion battery, including a cathode, an anode, and an electrolyte, with the above-mentioned aqueous zinc-ion battery anode serving as the anode.

Technical Effects: The invention innovatively introduces a biomass carbon coating. The biomass carbon (BC) is derived from corn flour (CF) and offers advantages such as low cost, large specific surface area, good conductivity, and excellent chemical stability. Additionally, the porous structure of biomass carbon helps construct a continuous conductive network with sufficient void space to accommodate zinc ion deposition. The cycle life of the BC/Zn electrode in symmetric cells is significantly extended (up to 200 hours). After 100 cycles, at a current density of 0.5 A/g, the capacity retention of the full battery improves from 44% to 69%.

DETAILED DESCRIPTION OF THE INVENTION

Now, various exemplary embodiments of the present invention are described in detail. This detailed description should not be considered as limiting the present invention, but should be understood as a more detailed description of certain aspects, features and embodiments of the present invention.

It should be understood that the terms described in the present invention are only for describing specific embodiments and are not used to limit the present invention. In addition, for the numerical range in the present invention, it should be understood that each intermediate value between the upper and lower limits of the range is also specifically disclosed. The intermediate value in any stated value or stated range, and each smaller range between any other stated value or intermediate value in the stated range are also included in the present invention. The upper and lower limits of these smaller ranges may be independently included or excluded in the range.

Unless otherwise specified, all technical and scientific terms used herein have the same meanings as commonly understood by those skilled in the art in the field to which the present invention relates. Although the present invention describes only preferred methods and materials, any methods and materials similar or equivalent to those described herein may also be used in the implementation or testing of the present invention. All documents mentioned in this specification are incorporated by reference to disclose and describe the methods and/or materials related to the documents. In the event of a conflict with any incorporated document, the content of this specification shall prevail.

It is obvious to those skilled in the art that various modifications and changes may be made to the specific embodiments of the present invention description without departing from the scope or spirit of the present invention. Other embodiments obtained from the present invention description are obvious to the technician. The present invention description and examples are only exemplary.

The terms "including", "comprising", "having", "containing", etc. used in this article are open-ended terms, which means including but not limited to.

The "room temperature" described in the present invention, unless otherwise specified, means 20-30°C.

The first aspect of the invention provides a preparation method for an aqueous zinc-ion battery anode, including the following steps:

Carbonizing corn flour to obtain biomass carbon;

Mixing and grinding the biomass carbon with potassium hydroxide, followed by sintering to obtain a solid;

Dropping dilute hydrochloric acid into the solid until the pH reaches neutral, then filtering, washing, and drying to obtain porous activated carbon;

Mixing the porous activated carbon uniformly with polyvinylidene fluoride (PVDF) and N-methylpyrrolidone (NMP) to obtain a mixture;

Coating the mixture onto the surface of zinc foil and drying to obtain the aqueous zinc-ion battery anode.

In a preferred embodiment of the invention, the carbonization specifically involves heating from room temperature to 500°C at a rate of 5°C/min and maintaining that temperature for 1 hour. In another preferred embodiment, the mass ratio of biomass carbon to potassium hydroxide is 1:3.

In a further preferred embodiment, the sintering specifically involves heating from room temperature to 800°C at a rate of 5°C/min and holding that temperature for 1 hour. In another preferred embodiment, the mass ratio of porous activated carbon to PVDF is 9:1. NMP serves as a dispersant in this invention, and there are no specific limitations on the amount of NMP used, as long as it disperses the porous activated carbon evenly with the PVDF.

The second aspect of the invention provides the aqueous zinc-ion battery anode prepared according to the aforementioned preparation method.

The third aspect of the invention provides an aqueous zinc-ion battery, which includes a cathode, an anode, and an electrolyte, with the aforementioned aqueous zinc-ion battery anode serving as the anode.

In a preferred embodiment of the invention, the cathode is MnO_2 ; the electrolyte is a mixed aqueous solution of 2M ZnSO_4 and 0.1M MnSO_4 .

The technical solutions described in this invention are conventional in the field unless otherwise specified, and the reagents or raw materials used are commercially sourced or publicly available unless otherwise noted.

The following is a detailed explanation of the technical solutions provided by this invention in conjunction with the implementation examples, but they should not be understood as limiting the scope of protection of the invention.

Example 1

Step 1: Preparation and characterization of the BC/Zn anode

Corn flour was placed in a tubular furnace and heated from room temperature to 500°C at a rate of 5°C/min, maintaining that temperature for 1 hour for carbonization. It was then naturally cooled to room temperature to obtain biomass carbon (BC). The BC was mixed and ground with potassium hydroxide in a mass ratio of 1:3. The resulting powdered mixture was sintered in a tubular furnace, specifically heated from room temperature to 800°C at a rate of 5°C/min and held at that temperature for 1 hour before naturally cooling to room temperature.

The sintered solid was taken out, and dilute hydrochloric acid was added until the pH reached 7, followed by filtration and thorough washing. Finally, it was dried in an oven at 80°C to obtain porous activated carbon (PAC).

PAC and polyvinylidene fluoride (PVDF) were mixed in a mass ratio of 9:1, with N-methylpyrrolidone (NMP) used as a dispersant to obtain a uniform mixture. The mixture was coated onto zinc foil. Finally, it was placed in an oven and dried at 80°C for 5 hours to obtain the BC/Zn anode.

Step 2: Preparation of MnO₂ Cathode

Add 0.608 g of KMnO₄ to 70 mL of deionized water and add 1.27 mL of hydrochloric acid, stirring for 30 minutes. Then transfer the solution to a 100 mL Teflon-lined autoclave and maintain it at 140°C for 12 hours. Finally, wash the resulting sample with deionized water until neutral, and dry it at 80°C in an air atmosphere to obtain the MnO₂ cathode.

Step 3: Manufacturing of the Full Cell

The CR2032 coin cell was assembled using the prepared MnO₂ cathode and BC/Zn anode, with the electrolyte being a mixed aqueous solution of 2M ZnSO₄ and 0.1M MnSO₄.

Characterization and electrochemical measurements were conducted on the samples prepared in Example 1, with the testing methods as follows: Scanning electron microscopy (SEM, GeminiSEM 500) was used to obtain the sample morphology; X-ray diffraction (XRD, Cu K α , 1.5418 Å) was performed for sample characterization; current discharge (GCD) was measured using a Neware testing system (0.8-1.8 V); electrochemical impedance spectroscopy (EIS) was measured using CHI660e (0.01 Hz-100 kHz). The test results are as follows:

In Example 1, the MnO₂ cathode was prepared using a hydrothermal method. The XRD spectrum of the synthesized MnO₂ cathode shows that all diffraction peaks correspond to α -MnO₂ (JCPDS: 44-0141), and no characteristic peaks of other impurities were observed. This indicates that the purity of the MnO₂ cathode prepared in this invention is high.

Evaluation of the Cycle Stability of the BC/Zn Anode Prepared in Example 1

The symmetric coin cell consists of two identical zinc (or BC/Zn) electrodes and an electrolyte (2 M ZnSO_4 aqueous solution). At a current density of 1 mA/cm^2 , the polarization voltage of the $\text{Zn}||\text{Zn}$ symmetric cell remained within 0.06 V for 40 hours. After 40 hours, the polarization voltage gradually increased with the cycling time. In contrast, the $\text{BC/Zn}||\text{BC/Zn}$ composite symmetric cell maintained a polarization voltage above 0.06 V and operated for 200 hours at the same current density. The differences between the two symmetric zinc-ion batteries are closely related to the influence of the current collector on the zinc micro-morphology. The performance of the BC/Zn anode prepared in this invention exceeds that of most reported SEI materials. Biomass carbon is abundant and low-cost, making it a material with great potential as a zinc anode SEI material.

This invention studies the cycle stability of a zinc-manganese zinc full battery based on two types of zinc anodes. The results show that the initial discharge capacities of the $\text{BC/Zn}||\text{MnO}_2$ battery and the $\text{Zn}||\text{MnO}_2$ battery are 269.5 mAh/g and 264.5 mAh/g, respectively, at a current density of 0.5 A/g. After 100 cycles, the capacity of the $\text{BC/Zn}||\text{MnO}_2$ battery is 186 mAh/g, while the capacity of the $\text{Zn}||\text{MnO}_2$ battery is only 116.7 mAh/g. The main reason for this is that the porous carbon covering the anode provides a stable deposition site for zinc, and due to the high specific surface area of zinc, the interfacial electric field is distributed evenly. Therefore, during the charging and discharging process, the deposition and stripping of zinc ions in the battery exhibit higher stability, thereby enhancing the stability of the zinc-ion battery.

To further investigate the reasons for the differences in electrochemical stability between the two sets of batteries, a series of experimental studies were conducted, including photography, XRD, SEM, and EIS measurements.

Before and after 100 charge-discharge cycles, the initial zinc foil surface was flat and smooth, while after 100 cycles, distinct zinc dendrites and corrosion appeared on the zinc foil surface, with dendrites adhering to and penetrating the separator. Without modifying the porous carbon layer, the nucleation of dendrites on the zinc foil surface further attracts zinc deposition on the dendrites, leading to the accumulation and growth of dendrites. In contrast, the BC/Zn surface showed no significant changes before and after 100 cycles.

After 100 cycles, no dendrites were observed on the surfaces of the BC/Zn and the separator, indicating that the biomass carbon coating suppresses dendrite formation. This is attributed to its high surface area, which adsorbs and directs zinc to fill the gaps between carbon particles rather than promote vertical growth of dendrites. Scanning electron microscopy (SEM) results further confirmed the morphological changes on the surfaces of the Zn and BC/Zn electrodes. The original zinc foil surface was flat and smooth. After 100 cycles, many thick and large blocky products appeared on the zinc foil electrode, responding well to zinc dendrites. In contrast, the BC/Zn electrode remained non-dendritic after cycling. After applying the biomass carbon layer, the surface of BC/Zn became rougher with numerous voids, providing ample space for zinc deposition and release throughout the entire lifecycle. Notably, compared to before cycling, many ultrathin nanosheets grew on the PAC layer's surface as byproducts during the discharge process. To clarify these byproducts, the XRD results of the Zn and BC/Zn anodes after cycling were studied. After 100 cycles, several new peaks were also observed, which were identified by XRD analysis as $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$.

EIS measurements were performed on the Zn batteries before and after 100 cycles. The results indicated that the charge transfer resistance (R_{ct}) increased for both types of batteries after 100 cycles due to the appearance of byproducts ($\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$) on the electrode surface, which increased R_{ct} .

Additionally, comparing the R_{ct} of the two full cells after cycling, the R_{ct} of the $Zn||MnO_2$ battery rose from $9.3\ \Omega$ before cycling to $51.4\ \Omega$ after 100 cycles. Such a significant increase likely resulted from the extensive formation of dendrites on the Zn anode, which interfered with charge transfer at the interface. Encouragingly, the R_{ct} of the $BC/Zn||MnO_2$ battery only increased from $4.8\ \Omega$ to $10.8\ \Omega$. Based on the SEM analysis, this result can be attributed to the BC coating on the dendrites, which, due to its larger surface area for adsorption and guiding zinc, is more effective in filling the gaps between carbon particles rather than promoting vertical dendrite growth.

From the above analysis, the rapid capacity loss of the $Zn||MnO_2$ battery with the untreated anode is attributed to zinc dendrites and corrosion on the anode surface. For the $BC/Zn||MnO_2$ battery with the biomass carbon coating, the surface change of the anode was minimal, indicating that the biomass carbon coating effectively limits dendrite formation. Therefore, the stability of the battery is significantly improved.

In summary, without the modification of a biomass carbon layer, the nucleation of dendrites on the zinc foil surface further attracts zinc deposition on the dendrites, leading to dendrite accumulation and growth. The porous structure of biomass carbon not only helps build a continuous conductive network with sufficient void space to promote uniform distribution of the interfacial electric field, but its large surface area facilitates preferential filling of the gaps between carbon particles by zinc, rather than vertical dendrite growth. Simple surface treatment of zinc using the biomass carbon coating significantly enhances the uniformity of the Zn^{2+} deposition/dissolution process, improving the cycling life of AZIBs by approximately five times. In the electrochemical performance tests of the battery, the $BC/Zn||MnO_2$ composite battery exhibited higher capacity and stability than the $Zn||MnO_2$ battery. This strategy should be advantageous for the practical production of highly stable AZIBs.

The embodiments described above are only descriptions of the preferred modes of the present invention, and are not intended to limit the scope of the present invention. Without departing from the design spirit of the present invention, various modifications and improvements made to the technical solutions of the present invention by ordinary technicians in this field should all fall within the protection scope determined by the claims of the present invention.

CLAIMS

1. A method for preparing an anode for an aqueous zinc-ion battery, characterized by the following steps:

carbonizing corn starch to obtain biomass carbon;

mixing and grinding the biomass carbon with potassium hydroxide, followed by sintering to produce a solid;

adding dilute hydrochloric acid dropwise to the solid until the pH is neutral, followed by filtration, washing, and drying to obtain porous activated carbon;

mixing the porous activated carbon uniformly with polyvinylidene fluoride (PVDF) and N-methyl-2-pyrrolidone (NMP) to form a mixture;

coating the mixture onto the surface of zinc foil and drying to obtain the aqueous zinc-ion battery anode.

2. The method for preparing the aqueous zinc-ion battery anode according to claim 1, characterized in that the carbonization specifically involves heating from room temperature to 500°C at a rate of 5°C/min and holding for 1 hour.

3. The method for preparing the aqueous zinc-ion battery anode according to claim 1, characterized in that the mass ratio of biomass carbon to potassium hydroxide is 1:3.

4. The method for preparing the aqueous zinc-ion battery anode according to claim 1, characterized in that the sintering specifically involves heating from room temperature to 800°C at a rate of 5°C/min and maintaining temperature for 1 hour.

5. The method for preparing the aqueous zinc-ion battery anode according to claim 1, characterized in that the mass ratio of porous activated carbon to polyvinylidene fluoride is 9:1.

6. The aqueous zinc-ion battery anode obtained from the method described in claim 1.

7. An aqueous zinc-ion battery, including a cathode, anode, and electrolyte, characterized in that the anode is the aqueous zinc-ion battery anode described in claim 6.

8. The aqueous zinc-ion battery according to claim 7, characterized in that the cathode is MnO_2 and the electrolyte is a mixed aqueous solution of 2M ZnSO_4 and 0.1M MnSO_4 .

REVENDEICATIONS

1. Procédé de préparation d'une anode pour une batterie zinc-ion aqueuse, caractérisé par les étapes suivantes :

carbonisation de l'amidon de maïs pour obtenir du carbone de biomasse ;

mélange et broyage du carbone de biomasse avec de l'hydroxyde de potassium, suivi d'un frittage pour produire un solide ;

ajout goutte à goutte d'acide chlorhydrique dilué au solide jusqu'à ce que le pH soit neutre, suivi d'une filtration, d'un lavage et d'un séchage pour obtenir du charbon actif poreux ;

mélange uniforme du charbon actif poreux avec du polyfluorure de vinylidène (PVDF) et de la N-méthyl-2-pyrrolidone (NMP) pour former un mélange ;

application du mélange sur la surface d'une feuille de zinc et séchage pour obtenir l'anode de batterie zinc-ion aqueuse.

2. Procédé de préparation de l'anode aqueuse de batterie zinc-ion selon la revendication 1, caractérisé en ce que la carbonisation implique spécifiquement un chauffage de la température ambiante à 500°C à une vitesse de 5°C/min et un maintien pendant 1 heure.

3. Procédé de préparation de l'anode aqueuse de batterie zinc-ion selon la revendication 1, caractérisé en ce que le rapport massique du carbone de biomasse à l'hydroxyde de potassium est de 1:3.

4. Procédé de préparation de l'anode aqueuse de batterie zinc-ion selon la revendication 1, caractérisé en ce que le frittage implique spécifiquement un chauffage de la température ambiante à 800°C à une vitesse de 5°C/min et un maintien de la température pendant 1 heure.

5. Procédé de préparation de l'anode de batterie zinc-ion aqueuse selon la revendication 1, caractérisé en ce que le rapport massique du charbon actif poreux au polyfluorure de vinylidène est de 9:1. LU508430

6. Anode de batterie zinc-ion aqueuse obtenue à partir du procédé décrit dans la revendication 1.

7. Batterie zinc-ion aqueuse, comprenant une cathode, une anode et un électrolyte, caractérisée en ce que l'anode est l'anode de batterie zinc-ion aqueuse décrite dans la revendication 6.

8. Batterie zinc-ion aqueuse selon la revendication 7, caractérisée en ce que la cathode est du MnO_2 et l'électrolyte est une solution aqueuse mixte de 2M ZnSO_4 et 0,1M MnSO_4 .