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DESCRIPTION WO2023173559A1

¹⁰ A sulfonic acid group functionalized siloxane for zinc-based flow battery and a preparation method thereof
Technical Field

[0001]

¹⁵ The invention belongs to the technical field of battery electrode material preparation, and relates to a sulfonic acid group functionalized siloxane for zinc-based liquid flow battery and a preparation method thereof. Using sulfonated siloxane/zinc composite foil for the negative electrode of zinc-based flow batteries can solve the serious side reactions such as zinc dendrite growth, accumulation, hydrogen evolution and dead zinc that exist in the current zinc-based flow batteries during charging and discharging, promote the practical application of zinc-based flow batteries with high coulombic efficiency and stable performance for distributed energy storage systems, and demonstrate the huge potential of zinc-based flow batteries in the field of energy storage.

²² Background Art

[0002]

²⁶ With the continuous consumption of non-renewable energy such as fossil energy, social environment and energy issues are becoming increasingly prominent, and the proportion of renewable energy such as solar energy and wind energy in the energy structure is increasing. However, these renewable energy sources inevitably have the problem of intermittent and unstable supply. Therefore, to achieve a continuous supply of renewable energy, mature and stable electrochemical energy storage technology is necessary.

[0003]

³⁴ Among the many existing electrochemical energy storage technologies, flow batteries (FBs) are considered to be the most promising grid-level energy storage technology due to their extremely high safety, charge and discharge efficiency, and flexibility.

³⁷ Compared with other technologies, the power density and energy density of flow batteries can be designed

independently, and the electrolyte inside them is usually an inorganic aqueous solution. The electrolyte usually circulates separately on the anode side and the cathode side. The anode and cathode are separated by an ion-conductive membrane. It has the advantages of low cost and high safety, and is very suitable for large-scale energy storage device applications. Among the many systems of flow batteries, zinc-based flow batteries (ZFBs) such as zinc-bromine flow batteries and zinc-iron flow batteries have been widely studied as early as 1970, and there are already many demonstration application projects.

[0004]

48 Although zinc-based flow battery technology has become relatively mature after decades of development, common problems in the charging and discharging process have always hindered the further development of ZFBs.

51 Like lithium-ion batteries, the negative electrode of zinc-based flow batteries is very prone to zinc dendrite growth and deposition on the electrode and membrane during the charging and discharging process. As the flow battery operates, the growing zinc dendrites will continue to grow and may eventually pierce the separator, causing the battery to short-circuit and fail. At the same time, the zinc deposited on the membrane will continue to accumulate, causing a sharp increase in the internal resistance of the battery and increasing unnecessary energy loss. Therefore, the design of new electrode materials that induce uniform zinc deposition is particularly important, which directly determines whether the contradiction between zinc dendrite growth and accumulation can be effectively resolved.

[0005]

62 Currently, there is no research work on silicene materials for zinc anodes in zinc-based flow batteries.

63 Siloxene is a new type of two-dimensional material. Our research found that the Si_6 ring in the corrugated two-dimensional skeleton of siloxene contains a large number of Si-O-Si and -OH zinc-philic groups. Siloxene can not only act as a reservoir to capture Zn^{2+} or $\text{Zn}(\text{OH})_4^{2-}$ inside the anode, inhibiting dendrites while reducing the loss of active substances, but also the large number of oxygen-containing groups and defect sites on the surface of siloxene make it easy to be further modified by functional groups, such as sulfonic acid groups, further enhancing the ability of siloxene to induce and anchor Zn^{2+} , promoting the uniform deposition of Zn^{2+} , enhancing the ability to modify the electrode/electrolyte interface, reducing the occurrence of hydrogen evolution and side reactions, and improving the stability of the electrode.

[0006]

75 Based on the above research background, the present invention efficiently prepares sulfonic acid group-functionalized grafted siloxane nanosheets. The preparation method is simple to operate, the cost of raw materials is low, the raw materials used are environmentally friendly, and it is suitable for large-scale commercial preparation.

79 It effectively solved the problem of zinc dendrite growth and accumulation in zinc-based flow batteries, and achieved long-term safe and stable operation of zinc-based flow batteries. It is of great significance to the

practical application of zinc-based flow batteries with high coulombic efficiency and stable performance for distributed energy storage systems.

[0007]

⁸⁸ Summary of the invention

[0008]

⁹² The purpose of the present invention is to provide a sulfonic acid group functionalized siloxane for zinc-based liquid flow batteries and a preparation method thereof in the technical field of battery electrode material preparation. The method adopted has the advantages of low cost and high efficiency.

⁹⁵ The prepared sulfonated siloxane nanomaterials have a high functional group grafting rate and good stability, which greatly inhibits zinc dendrites, hydrogen evolution and passivation side reactions, effectively solving the problems currently faced by zinc-based liquid flow batteries.

[0009]

¹⁰¹ To achieve the above purpose, the technical solution adopted by the present invention is:

[0010]

¹⁰⁵ A sulfonic acid group functionalized siloxene is firstly prepared by using calcium disilicide (CaSi_2) having a silicon and calcium layered structure as a silicon source, and then decalcifying and exfoliating CaSi_2 by selecting an efficient and suitable topological reaction solvent and an oxidant such as hydrochloric acid, phosphoric acid and boric acid to obtain siloxene nanosheets.

¹⁰⁹ Then, a functional group grafting agent rich in sulfonic acid groups, such as sulfanilic acid and poly (4-styrene sulfonic acid), is selected to effectively graft the siloxene nanosheets through a wet chemical reaction, thereby obtaining sulfonic acid group functionalized siloxane nanosheets.

¹¹² This nanosheet material can be used in zinc-based liquid flow batteries to solve the problems of zinc dendrite growth and accumulation in zinc-based liquid flow batteries.

[0011]

¹¹⁷ Specifically, a method for preparing sulfonic acid group functionalized siloxane comprises the following steps:

[0012]

¹²¹ (1) Using calcium disilicide (CaSi_2) as the silicide raw material, the silicide raw material and the monobasic or polybasic acid oxidant are fully mixed, and the mixed solution is cooled to a low temperature of -10 to -20 ° C in an ethanol bath;

[0013]

¹²⁸ (2) subjecting the low-temperature mixed solution obtained in step (1) to a full reaction under ultrasonic conditions, wherein the reaction solution is maintained at the low temperature and a constant temperature during the reaction process;

[0014]

¹³⁴ (3) The reaction solution obtained in step (2) is collected by vacuum filtration, and the collected wet powder is added to the sulfonic acid grafting agent solution, and then ultrasonically assisted dispersion is performed to allow the mixture to react fully, and finally the reaction solution is removed by centrifugation, and the precipitate is collected and freeze-dried to obtain the sulfonic acid group-modified siloxane nanosheet powder.

[0015]

¹⁴² In the above technical solution, further, in the step (1), the monobasic or polybasic acid oxidant is at least one of hydrochloric acid, phosphoric acid, and boric acid;

[0016]

¹⁴⁷ Furthermore, in step (1), the molar ratio of the monoacid oxidant to calcium disilicide is 2:1 to 3:1; the molar ratio of the polyacid oxidant to calcium disilicide is 1.5:1 to 2.5:1;

[0017]

¹⁵² During the reaction in step (1) and step (2), the temperature of the reaction solution is always maintained at -10 to -20 ° C; at this temperature, the reaction process can be promoted to proceed gently and orderly, so that the silicon layer in the calcium disilicide can be fully stripped off, and the uncontrollable stripping of the siloxane nanosheets caused by the reaction temperature being too high is avoided, resulting in insufficient stripping, thereby causing the coulomb efficiency of the zinc negative electrode of the zinc-based liquid flow battery to become unstable.

[0018]

¹⁶¹ In the step (2), the ultrasonic working power range of the calcium silicide topological chemical stripping process is 300-600 watts (W); the ultrasonic working time is 48-72 hours;

[0019]

¹⁶⁶ The sulfonic acid grafting agent used in step (3) is at least one of sulfanilic acid, poly (4-styrene sulfonic acid), or corresponding salts;

[0020]

¹⁷¹ The mass ratio of calcium disilicide and sulfonic acid grafting agent used in step (3) is 1:0.1 to 1:1.

[0021]

¹⁷⁵ The solvent of the sulfonic acid grafting agent solution in step (3) is at least one of anhydrous ethanol, methanol, ether and acetone;

[0022]

¹⁸⁰ The concentration of the sulfonic acid grafting agent solution in step (3) is 0.1 to 1 mol L⁻¹;

[0023]

¹⁸⁴ The power of ultrasonic dispersion in step (3) is 200-300 watts (W), and the ultrasonic time is 12-24 hours;

[0024]

¹⁸⁸ In the step (3), the sample is pre-frozen before freeze-drying by freezing with liquid nitrogen. Pre-freezing can fully freeze the sample to prevent agglomeration during the freeze-drying process;

[0025]

¹⁹³ A zinc-based liquid flow battery negative electrode material is prepared by mixing the sulfonic acid group-modified siloxane nanosheets obtained in the step (3) with a PVDF solution in a certain proportion to obtain a slurry; then coating the mixed slurry on the surface of a zinc foil, preferably air-drying the coated zinc foil to obtain a sulfonated siloxane-coated zinc negative electrode for use as a zinc-based liquid flow battery negative electrode.

[0026]

²⁰¹ In the above scheme, the mass ratio of sulfonic acid group-modified siloxane and PVDF is 1:1 to 5:1;

[0027]

²⁰⁵ The concentration of the PVDF solution is 20 mg ml⁻¹ to 80 mg ml⁻¹;

[0028]

²⁰⁹ The solvent of the PVDF solution is at least one of DMF and NMP;

[0029]

- 213 The present invention prepares siloxane and studies the surface functionalization modification technology through topological chemistry and wet chemical methods, and can control the preparation of high-quality and uniform thickness sulfonic acid group-functionalized siloxane for the zinc negative electrode of zinc-based liquid flow batteries, further enhance the ability of siloxane to induce and anchor Zn^{2+} , and promote the uniform deposition performance of Zn^{2+} .
- 218 The present invention is the first to modify sulfonic acid groups on the surface of siloxane by topological chemistry and wet chemistry methods, and utilize the synergistic effect of siloxane and its surface functionalized sulfonic acid groups on Zn^{2+} to induce efficient and uniform deposition of Zn^{2+} , thereby improving the coulombic efficiency and cycle stability of zinc-based liquid flow batteries.
- 223 The implementation of the present invention aims to achieve efficient utilization of zinc metal negative electrodes in zinc-based liquid flow batteries and provide new ideas and methods for the modification of zinc-based liquid flow batteries.

[0030]

- 229 The advantages of this method are:

[0031]

- 233 The growth and preparation operation is simple, fast and low-cost, and does not require expensive material growth equipment; this method can effectively peel off CaSi_2 and efficiently graft, and the yield of sulfonated siloxane nanosheet material preparation is high; the prepared sulfonated siloxane has high stability and can be strongly and evenly coated on the surface of the negative electrode of the zinc-based liquid flow battery, and will not fall off or peel off after multiple cycles; the sulfonated siloxane coating of the negative electrode greatly inhibits the inevitable dendrite growth and accumulation problems of zinc-based liquid flow batteries, demonstrating the feasibility of high-performance zinc-based liquid flow batteries.

240 BRIEF DESCRIPTION OF THE DRAWINGS

[0032]

- 244 FIG1 is a scanning electron microscope (SEM) image of the silicon source (CaSi_2) used in Example 1;

[0033]

- 249 FIG2 is a sulfonic acid group functionalized siloxane solution prepared in Example 1;

[0034]

²⁵² FIG3 is a scanning electron microscope (SEM) image of the sulfonic acid group functionalized siloxane prepared in Example 1;

[0035]

²⁵⁸ FIG4 is a transmission electron microscope (TEM) image of the sulfonic acid group functionalized siloxane prepared in Example 1;

[0036]

²⁶³ FIG5 is an EDS spectrum analysis image of the sulfonic acid group functionalized siloxane prepared in Example 1;

[0037]

²⁶⁸ FIG6 is a transmission electron microscope (TEM) image of the sulfonic acid group functionalized siloxane prepared in Example 2;

[0038]

²⁷³ FIG7 is a scanning electron microscope (SEM) image of the sulfonic acid group functionalized siloxane prepared in Example 4;

[0039]

²⁷⁸ FIG8 is a performance test of the coulombic efficiency of a battery of a sulfonic acid group functionalized siloxane coated Zn electrode in Example 4.

[0040]

²⁸³ FIG9 is a transmission electron microscope (TEM) image of the mixed slurry of sulfonic acid group functionalized siloxane nanosheets and PVDF prepared in Example 1;

[0041]

²⁸⁸ FIG10 is a transmission electron microscope (TEM) image of the mixed slurry of sulfonic acid group functionalized siloxane nanosheets and PVDF prepared in Example 5;

[0042]

²⁹³ FIG11 is a comparison of the battery coulombic efficiency performance test of the sulfonic acid group

functionalized siloxane coated Zn electrode and the uncoated commercial Zn electrode in Example 1.

[0043]

299 FIG12 is a battery coulombic efficiency performance test of the sulfonic acid group functionalized siloxane coated Zn electrode under high current density and long cycle conditions in Example 1.

301 DETAILED DESCRIPTION

[0044]

305 In order to make the objectives, technical solutions and advantages of the present invention more clearly understood, the present invention is further described in detail below in conjunction with the accompanying drawings and embodiments.

308 It should be understood that the specific embodiments described herein are only used to explain the present invention, and are not used to limit the present invention.

310 In addition, the technical features involved in the various embodiments of the present invention described below can be combined with each other as long as they do not conflict with each other.

[0045]

315 Embodiment 1:

[0046]

319 (1) Weigh 2 g of CaSi_2 as the silicide raw material powder and place it in a 500 ml orange-cap bottle.

[0047]

324 (2) Take 100 ml of concentrated hydrochloric acid (mass fraction 36%-38%) and add it to the orange-capped bottle in (1) to obtain a green turbid solution, and place the solution in a -10°C ethanol bath to precool to -10°C .

[0048]

330 (3) The turbid solution in (2) that had been precooled to -10°C was subjected to an ultrasonicator-assisted reaction with an ultrasonic power of 300 W and a reaction time of 48 h, during which the temperature of the reaction solution was maintained at -10°C .

[0049]

336 (4) The turbid solution in (3) is vacuum filtered to collect the gray wet powder to obtain siloxane nanosheets

with good morphology.

[0050]

³⁴² (5) A sulfanilic acid solution with a concentration of 0.5 mol L⁻¹ was prepared in anhydrous ethanol solvent.

[0051]

³⁴⁷ (6) The wet powder collected in (4) was added to 30 ml of the ethanol solution of sulfonic acid amine prepared in (5), and dispersed with ultrasound assistance at an ultrasound power of 300 W and an ultrasound time of 12 h.

[0052]

³⁵³ (7) The mixed solution prepared in (6) was centrifuged at a speed of 12000 rpm and a centrifugation time of 30 min.

[0053]

³⁵⁸ (8) Collect the centrifugal precipitate in (7), add 100 ml of anhydrous ethanol, and perform ultrasonic cleaning at a power of 300 W for 1 h.

[0054]

³⁶³ (9) The mixed solution in (8) was centrifuged at a speed of 12000 rpm and a centrifugation time of 30 min.

[0055]

³⁶⁷ (10) Collect the centrifugal precipitate in (9) and freeze it by pouring 50 ml of liquid nitrogen.

[0056]

³⁷¹ (11) The frozen product in (10) was placed in a freeze dryer, the temperature of the freezer was set at -50 ° C, and freeze-dried for 24 h to obtain a sulfonic acid group-functionalized siloxane sample.

[0057]

³⁷⁶ (12) Weigh 80 mg of the sulfonic acid group functionalized siloxane sample in (11), add 1 ml of 20 mg ml⁻¹ PVDF NMP solution, and mix under magnetic stirring conditions at a magnetic stirring speed of 1500 rpm for 12 h to obtain a slurry of sulfonic acid group functionalized siloxane.

[0058]

³⁸³ (13) The sulfonic acid group functionalized siloxane slurry in (12) is coated on the surface of the zinc foil by flat coating, with a coating thickness of 10 μm and a coating speed of 10 cm min^{-1} .

[0059]

³⁸⁸ (14) The zinc foil coated with the slurry in (13) is dried in a forced air drying oven at a drying temperature of 60 ° C. for 12 h to obtain a zinc negative electrode coated with sulfonated siloxane, which is used as a negative electrode for a zinc-based liquid flow battery.

[0060]

³⁹⁴ Embodiment 2:

[0061]

³⁹⁸ The same steps as in Example 1 were used to prepare sulfonic acid group functionalized siloxane, except that 100 ml of concentrated hydrochloric acid in step (2) of Example 1 was replaced with 50 ml of phosphoric acid solution (85 wt.% in H_2O), and other reaction conditions remained unchanged.

[0062]

⁴⁰⁴ TEM characterization showed that the thickness of the silicene nanosheets was significantly higher than that of the silicene nanosheets prepared in Example 1, which indicates that phosphoric acid as a topological chemical solvent and oxidant for exfoliating CaSi_2 is less efficient than hydrochloric acid as a topological chemical solvent and oxidant for exfoliating CaSi_2 . However, it can also be seen from the TEM image that phosphoric acid also successfully exfoliated the layered dense structure of CaSi_2 into independent sheet-like silicene nanosheets, indicating that phosphoric acid is also a suitable topological chemical solvent and oxidant.

[0063]

⁴¹⁴ Embodiment 3:

[0064]

⁴¹⁸ The same steps as in Example 1 were taken to prepare sulfonic acid group functionalized siloxane, except that the 0.5 mol L^{-1} sulfonamide solution in step (5) of Example 1 was replaced with a 0.5 mol L^{-1} poly(4-styrenesulfonic acid) solution, and other reaction conditions remained unchanged.

[0065]

423 Embodiment 4:

[0066]

428 The same steps as in Example 1 were taken to prepare sulfonic acid group functionalized siloxane, except that the -10°C ethanol bath precooled to -10°C in step (2) of Example 1 was replaced by a 10°C water bath preheated to 10°C , and other reaction conditions were unchanged.

[0067]

434 SEM characterization showed that in this case, calcium disilicide was not fully stripped at a stripping temperature of 10°C . The reaction temperature was too high, resulting in uncontrollable stripping of the siloxane nanosheets and insufficient stripping.

437 After the sulfonic acid group modification, the insufficiently stripped siloxane nanosheets are coated on the surface of the zinc negative electrode, which will cause the coulombic efficiency of the zinc negative electrode of the zinc-based liquid flow battery to become unstable. As shown in Figure 8, the test current condition is 1mA cm^{-2} , the zinc plating capacity is 1mAh cm^{-2} , and the battery is cycled for about 100 times. The coulombic efficiency becomes unstable. It can be seen that in this case, the calcium disilicide is not fully stripped at the stripping temperature of 10°C , resulting in the sulfonic acid-modified siloxane nanosheets coated on the zinc surface unable to fully inhibit the growth of zinc dendrites, resulting in battery failure.

[0068]

448 Therefore, the exfoliation reaction of calcium disilicide must be maintained at a low temperature of -10°C to -20°C so that the reaction process can proceed gently and orderly, promoting the silicon layer in calcium disilicide to be fully exfoliated and obtaining uniform siloxane nanosheets, laying the foundation for subsequent sulfonic acid group modification.

[0069]

455 Embodiment 5:

[0070]

459 The same steps as in Example 1 were taken to prepare a zinc negative electrode coated with sulfonated siloxene, except that: in step (12) of Example 1, 80 mg of sulfonic acid group functionalized siloxene sample was weighed and 1 ml of 20 mg ml^{-1} PVDF NMP solution was added, and the other reaction conditions remained unchanged.

[0071]

⁴⁶⁵ TEM characterization showed that the nanosheets prepared in this example after the sulfonic acid group functionalized siloxane nanosheets and PVDF were mixed were thicker than the nanosheets prepared in Example 1 after the sulfonic acid group functionalized siloxane nanosheets and PVDF were mixed. This is because the proportion of PVDF was increased.

[0072]

⁴⁷³ Embodiment 6:

[0073]

⁴⁷⁷ Transmission electron microscopy (TEM) characterization and analysis

[0074]

⁴⁸¹ Transmission electron microscopy was used to determine the high-resolution morphology of sulfonic acid group-functionalized siloxane.

⁴⁸³ FIG4 is a TEM image of the sample of Example 1, which shows that the prepared sulfonated siloxane has a smooth and uniform two-dimensional structure with a lateral size of several microns.

⁴⁸⁵ In addition, TEM images showed that the sheet-like sulfonated siloxane had high transparency, indicating that the thickness of its nanosheets was very thin.

[0075]

⁴⁹⁰ Embodiment 7:

[0076]

⁴⁹⁴ Energy Dispersive Spectrometer (EDS) Characterization and Analysis

[0077]

⁴⁹⁸ EDS was used to determine whether the sulfonic acid groups were successfully modified in the siloxane structure.

⁵⁰⁰ Figure 5 is an EDS image of the sample in Example 1, which reveals that the characteristic atomic signal of the sulfonic acid group, sulfur (S) atoms, exists in the entire sulfonated siloxene nanosheet. Since the newly formed layered silicon nanosheet has high activity, the sulfonic acid group can be quickly modified on the surface of the siloxene nanosheet, proving that the siloxene has been successfully modified with sulfonic acid to obtain sulfonic acid group-functionalized siloxene.

[0078]

507 Embodiment 8:

[0079]

512 Sulfonic acid functionalized siloxane for battery performance testing in zinc-based flow batteries

[0080]

516 Figure 11 is a battery coulombic efficiency performance test comparison between the sulfonic acid group functionalized siloxane coated Zn electrode and the uncoated commercial Zn electrode in Example 1. The test current condition is 1 mA cm^{-2} , the zinc plating capacity is 1 mAh cm^{-2} , and the average coulombic efficiency of the sulfonic acid group functionalized siloxane coated Zn electrode reaches more than 99.2%. There is no short circuit phenomenon after 200 cycles. The uncoated commercial Zn electrode has a short circuit phenomenon after about 40 cycles. This is because the surface of the Zn electrode lacks the protection of the sulfonic acid group functionalized siloxane, and the zinc dendrites grow rapidly and pierce the diaphragm, causing the battery to fail.

524 At the same time, we tested the zinc plating/zinc stripping performance of the sulfonic acid group functionalized siloxane coated Zn electrode in Example 1 under high current and long cycle conditions, as shown in Figure 12, to further reveal the performance of sulfonic acid group functionalized siloxane in regulating Zn^{2+} deposition and inhibiting zinc dendrites.

528 As shown in Figure 12, the test current condition is 5 mA cm^{-2} , the zinc plating capacity is 1 mAh cm^{-2} , the average coulombic efficiency of the sulfonic acid group functionalized siloxane coated Zn electrode reaches more than 99.5%, and there is no short circuit phenomenon after 1600 cycles. This reveals that the sulfonic acid group functionalized siloxane of the zinc negative electrode of the zinc-based liquid flow battery improves the ability of the negative electrode interface to induce and anchor Zn^{2+} , and promotes the uniform deposition performance of Zn^{2+} . This shows that the sulfonic acid group functionalized siloxane composite zinc electrode can effectively solve a series of serious problems such as zinc dendrite growth and high zinc deposition overpotential during charging and discharging of zinc-based liquid flow batteries, and promotes the practical application of zinc-based liquid flow batteries with high coulombic efficiency and stable performance for distributed energy storage systems.

[0081]

541 In summary, the topological chemical method proposed in the present invention realizes the regulated preparation of sulfonic acid group-functionalized siloxane nanosheets.

543 Zinc-based liquid flow batteries that use sulfonic acid group-functionalized siloxane to coat the negative electrode have greatly suppressed the growth and accumulation of zinc dendrites, demonstrated excellent performance in long-term stable energy storage, and promoted the commercial application of zinc-based liquid flow batteries.