

An Aqueous Electrolyte Solution

FIELD OF THE INVENTION

[0001] The present invention related to secondary batteries, especially those employing aqueous electrolyte. The application cites various publications, the entire contents of which are incorporated herein by reference into this application.

BACKGROUND OF THE INVENTION

[0002] Large-scale energy storage technology is the foundation of new energy promotion and energy innovation. It plays an important role in the optimization of the national energy structure and the stable operation of the power grid. Electrochemical battery has been extensively investigated in the field of energy storage due to their high conversion efficiency, flexible assembly, and freedom from geographical constraints. The application has gradually begun to be commercialized from demonstration. Large scale commercialization of energy storage requires products of "low cost, long life, high safety, and easy recovery". Therefore, it is particularly necessary to accelerate the breakthrough of current products and explore new technologies. The lithium-ion battery (LIB) based on organic electrolytes has been widely used in mobile electronic devices and electric vehicles. But LIB fundamentally does not maintain high cycle life in high temperature applications, and its risk of thermal runaway requires complex system with high cost and operation expense to ensure the safety, especially in large-scale integrated energy storage system (MWh-level and above). Energy storage batteries using aqueous electrolytes generally have a high safety factor. For example, lead-acid batteries have a history of 150 years, but environmental pollution and short life span limits the large-scale application. In recent years, energy storage batteries based on aqueous electrolytes (with neutral pH) have attracted wide attention from researchers. One of the main features is that the electrolyte system is neutral, which is intrinsically safe and environmentally friendly.

[0003] Aqueous batteries have certain advantages such as low cost, high safety factor, friendly environmental, and ease of manufacturing. However, there are still some challenges. Among others, its electrochemical stability window is relatively narrow due

to electrolysis of water. This problem hinders the further development of water-based batteries.

[0004] At present, there are several methods to broaden the electrochemical stability window (alternatively, electrochemical window) of water-based batteries. First, a high-concentration of organic salt electrolyte is used, i.e., adding a large amount of organic salt (mass fraction greater than 50%) into the aqueous solution ¹. The electrochemical stability window of the liquid is widened to 3.0 V, but the addition of a large amount of organic salt leads to high viscosity of the electrolyte and high cost of organic salt. Second, a dual-pH electrolyte is used ². This method uses an ion exchange membrane to separate the positive and negative electrolytes. The pH difference between the cathode and anode sides induces the expansion of the electrochemical stability window. However, the high cost of ion exchange membranes and the complex battery structure hinder the commercialization. Another method is the use of polar protic solvent hybrid electrolyte ³. Small molecule compounds, interacting with water molecules to regulate the hydrogen bond network, thereby broadens the electrochemical stability window of the electrolyte. This method, however, is not effective when the amount of organic matter (for example organic solvent) in electrolyte solution is low, e.g., the volume fraction is less than 30%. Furthermore, a large amount of organic matter will reduce the safety. Use of gel-sol electrolyte is another method. As gel polymer has abundant functional groups, such as COO-, C-O, O-C-O, which can form hydrogen bonds with water molecules, thereby decreasing the amount of free water. This method, however, has no obvious effect on the expansion of the electrochemical stability window ⁴.

[0005] It is well acknowledged that multiple characteristics of aqueous battery be critically balanced. For instance, it is highly challenging to obtain an aqueous electrolyte solution with a wide electrochemical stability window while keeping the cost low. Therefore, a new type of aqueous electrolyte suitable for industrial production is highly needed. The present invention discloses an aqueous electrolyte solution comprising a hybrid surfactant which contains an ionic Gemini surfactant and a non-ionic surfactant. The hybrid surfactant constructs a multi-component/multi-scale

interface on the surface of the electrode to broaden the electrochemical stability window of the electrolyte.

SUMMARY OF THE INVENTION

[0006] The present invention discloses an aqueous battery comprising an aqueous electrolyte solution comprising a predetermined amount of both an ionic Gemini surfactant and a non-ionic surfactant. The aqueous electrolyte solution is featured for its controlled viscosity and conductivity. The corresponding aqueous battery exhibits a broader electrochemical window, increased specific capacity, and improved cycling performance.

BRIEF DESCRIPTION OF THE FIGURES

[0007] Fig. 1A shows electrochemical stability window in normal electrolyte (-1.3-1.1V), and Fig. 1B shows electrochemical stability window in electrolyte with the hybrid surfactant (-1.4-1.3V).

[0008] Fig. 2A shows specific capacity and cycling performance in control electrolyte, and Fig. 2B shows specific capacity and cycling performance in electrolyte with hybrid surfactant.

DETAILED DESCRIPTION OF THE INVENTION

[0009] Conventional surfactant, e.g., 1,3-propanedisulfonic acid disodium (PDDS), is known as an additive to widen the electrolyte window of aqueous electrolyte ⁵. However, the addition of surfactant leads to some side effects. For example, the increased viscosity deteriorates the ion mobility in the electrolyte, preventing its application in aqueous battery, particularly large-scale production. The invention found that a desirable viscosity of a normal electrolyte solution is no more than 5.0 mPa·s while the expected conductivity is no less than 45.0 mS/cm. The electrolyte solution with 10wt% of glycerin (a conventional surfactant) has a viscosity of 10.2 mPa·s and a conductivity of 23.5mS/cm. The viscosity is much higher than that of an electrolyte without surfactant. For example, a solution of sodium sulfate at a concentration of 1.0

molar/L has a viscosity of 2.8 mPa/s. The existence of glycerin also significantly decreases the conductivity.

[0010] The present invention utilized a hybrid surfactant comprising both an ionic Gemini surfactant and a non-ionic surfactant in aqueous electrolyte with controlled viscosity and conductivity. The ionic Gemini surfactant contains at least two ions and at least two hydrophobic chains in each molecule. In one embodiment, the ionic Gemini surfactant contains a spacer between two ions or between an ion and the hydrophobic chains. In one embodiment, the spacer can be short or long, flexible or rigid. The hydrophobic chains may be same or different. In one embodiment, some of the hydrophobic chains can be shorter or longer than others. In one embodiment, the ions therein may be cationic or anionic. On one hand, ionic Gemini surfactant is featured for its strong surface adsorption. The arrangement of ionic Gemini surfactant molecules is closer than that of ordinary surfactants, thereby weakening the electrostatic repulsion between the hydrophilic groups and the repulsive force of the hydration layer, so that it exhibits a higher surface adsorption capacity. On another hand, the ionic Gemini surfactant is featured for its low critical micelle concentration (CMC). In general, its CMC is only 1/10 to 1/100 of traditional surfactants. Also, it exhibits solubilizing effects and cost advantage.

[0011] However, because this ionic Gemini surfactant has a certain length of connection group, when the hydrophilic group is adsorbed on the surface of the electrode, it cannot form a dense cover. Therefore, ionic Gemini surfactant alone plays no or very limited roles in limiting the direct contact between water molecules and the active material of electrode. The present invention creatively uses a non-ionic surfactant with short chains in connection with the ionic surfactant, wherein the non-ionic surfactant can fill the gaps of ionic Gemini surfactants adsorbed on the electrode. On one hand, the interface comprising both surfactants adsorbed on the electrodes is densely packed to block the direct contact more effectively between water molecules and electrode, thus expanding the electrochemical window. On the other hand, the ions

of the electrolyte can still pass the interface and electrochemically react with the active material.

[0012] This hybrid surfactant can construct a multi-component/multi-scale interface on the surface of the battery active material. The interface blocks the direct contact between water molecules and the active material. At the same time, the ionic metal ions in the electrolyte can easily pass through the interface and electrochemically react with the active material.

[0013] The present invention provides an aqueous electrolyte with a wide electrochemical stability window and a preparation method thereof.

[0014] In one embodiment, the electrolyte solution contains both an ionic Gemini surfactant and a non-ionic surfactant. The ionic Gemini surfactant can be cationic surfactants, anionic surfactants, or zwitterionic surfactants. In one embodiment, the cation in the ionic Gemini surfactants include without limitation primary, secondary, or tertiary amines. In one embodiment, the anion in the ionic Gemini surfactants includes without limitation carboxylate, sulfate, sulfonate, phosphate, and their derivatives.

[0015] In one embodiment, the ionic Gemini surfactant can be an oligomeric surfactant, or is selected from ethylene bis(hexadecamidopropyl dimethyl ammonium bromide) (molecular weight: 869.0), sodium dilauroyl ethylenediamine dipropionate (molecular weight: 612), ethylene bis[(Dodecyldimethyl) chloride/ammonium bromide] (molecular weight: 569), and octyl polyoxyethylene tetradecyl ammonium chloride (molecular weight: 485 - 2,000).

[0016] In one embodiment, the non-ionic surfactant includes but is not limited to ethoxylate, fatty acid ester of polyhydroxy compound, fatty acid ester of glycerol, glycerol monostearate, glycerol monolaurate, fatty acid ester of sorbitol, alkyl polyglucoside and their derivatives. The non-ionic surfactant may be selected from tridecyl alcohol polyoxyethylene ether (molecular weight: 583), tripentaerythritol (molecular weight: 372), dodecyl phenyl polyoxyethylene(12) ether (molecular weight: 790), and sorbitan monolaurate(molecular weight: 346).

[0017] In one embodiment, the aqueous electrolyte comprises 0.001-0.100 mol/L of ionic Gemini surfactant and 0.01-0.1mol/L of non-ionic surfactant. In one embodiment, the concentration (mol/L) ratio of non-ionic surfactant to ionic Gemini surfactant is in a range of 10-100. In one embodiment, the concentration (mol/L) ratio of non-ionic surfactant to ionic Gemini surfactant is in a range of 10-50. In one embodiment, the concentration (mol/L) ratio of non-ionic surfactant to ionic Gemini surfactant is in a range of 10-20.

[0018] In one embodiment, the electrolyte solution comprises metal ions such as lithium, sodium, potassium, zinc, calcium, magnesium at a concentration ranging from 0.01-5.0mol/L. In one embodiment, the electrolyte solution comprises anions selected from chloride, sulfate, sulfonate, nitrate, sulfite, hypochlorite and phosphate at a concentration ranging from 0.01-5.0mol/L.

[0019] The aqueous electrolyte solution of the present invention is prepared as follows. A predetermined amount of ionic Gemini surfactant and the non-ionic surfactant are dissolved in water by stirring or ultrasonic, obtaining a surfactant solution. The temperature is controlled between 25-50°C. One or more inorganic electrolyte salts are added into the surfactant solution, followed by adjusting pH to 6.0 – 8.0 using an acid or basic solution. The predetermined amount is to ensure the viscosity and conductivity of the final electrolyte solution within the desirable range, i.e., a viscosity of no more than 5.0 mPa.S and a conductivity of no less than 45.0 mS/cm. In case a “predetermined amount” does not lead to the desirable viscosity and conductivity, it should be recalculated and adjusted. The amount of the hybrid surfactant, their ratio and the pH value of the electrolyte solution are key factors in controlling and adjusting the viscosity and conductivity.

[0020] In one embodiment, the present invention provides an aqueous electrolyte solution with an improved electrochemical stability window for electrochemical device. In one embodiment, the aqueous electrolyte solution comprises contains a hybrid surfactant comprising an ionic Gemini surfactant and a non-ionic surfactant, wherein the aqueous electrolyte solution has a viscosity of no more than 5.0 mPa/s.

[0021] In one embodiment, the aqueous electrolyte solution has a conductivity of no less than 45 mS/cm.

[0022] In one embodiment, the ionic Gemini surfactant contains two or more ions in each molecule.

[0023] In one embodiment, the ionic Gemini surfactant is an anionic or cation surfactant.

[0024] In one embodiment, the non-ionic surfactant is ethoxylate, fatty acid ester of polyhydroxy compounds, fatty acid ester of glycerol, glycerol monostearate, glycerol monolaurate, fatty acid ester of sorbitol, alkyl polyglucoside or their derivatives.

[0025] In one embodiment, the ionic Gemini surfactant has a concentration of 0.001-0.1mol/L in said aqueous electrolyte solution.

[0026] In one embodiment, the non-ionic surfactant has a concentration of 0.01-0.1mol/L in said aqueous electrolyte solution.

[0027] In one embodiment, the molar ratio of non-ionic surfactant to the ionic Gemini surfactant ranges from 10 to 100.

[0028] In one embodiment, the electrochemical device is an aqueous ionic battery.

[0029] In one embodiment, the present invention provides an electrochemical device comprising an anode, a cathode and the aqueous electrolyte solution placed between the anode and cathode, wherein the ionic Gemini surfactant and non-ionic surfactant constructs an interface on the surface of the active material of the anode and cathode, wherein the interface blocks direct contact between water molecules and the active material, by which electrolysis of water molecules is restricted or inhibited, and allows passage of ions in the electrolyte solution through the interface and electrochemical reaction with the active material.

[0030] In one embodiment, the aqueous electrolyte solution has an electrochemical stability window of 2.6 – 2.7 V.

[0031] In one embodiment, the electrochemical device has a specific capacity of higher than that without the ionic Gemini surfactant and non-ionic surfactant.

[0032] In one embodiment, the specific capacity of electrochemical device is 10%-40% higher than that without the ionic Gemini surfactant and non-ionic surfactant at a rate ranging from 0.1C to 1.0C.

[0033] In one embodiment, the present invention also provides a method of preparing the aqueous electrolyte solution, wherein the method comprises:

- 1) dissolving a predetermined amount of an ionic Gemini surfactant and a non-ionic surfactant in water at a controlled temperature by mechanical stirring or ultrasonic mixing, resulting in a surfactant solution; and
- 2) adding one or more inorganic electrolyte salts into the surfactant solution, followed by adjusting pH value to 6.0 – 8.0, thereby obtaining the aqueous solution of claim 2 with a viscosity of no more than 5.0 mPa.S and a conductivity of no less than 45.0 mS/cm.

[0034] In one embodiment, the controlled temperature ranges from 25°C and 50°C.

[0035] In one embodiment, the one or more inorganic electrolyte salts comprise a cation selected from the group consisting of lithium, sodium, potassium, zinc, calcium, and magnesium.

[0036] In one embodiment, the one or more inorganic electrolyte salts comprise an anion selected from the group consisting of chloride, sulfate, sulfonate, and phosphates.

[0037] In one embodiment, the cation has a concentration ranging from 0.01 mol/L to 5 mol/L in said aqueous electrolyte solution.

Examples

[0038] The invention will be better understood by reference to the Experimental Details which follow, but those skilled in the art will readily appreciate that the specific experiments detailed are only illustrative and are not meant to limit the invention as described herein, which is defined by the claims which follow thereafter.

[0039] Throughout this application, various references or publications are cited. Disclosures of these references or publications in their entireties are hereby incorporated by reference into this application in order to more fully describe the state

of the art to which this invention pertains. It is to be noted that the transitional term “comprising”, which is synonymous with “including”, “containing” or “characterized by”, is inclusive or open-ended and does not exclude additional, un-recited elements or method steps.

Example 1

[0040] In this example, ethylene bis (hexadecamidopropyl dimethyl ammonium bromide) ($C_{44}H_{92}O_2N_4Br_2$, molecular weight: 869.0, Zhengzhou YiHeFine Chemicals Co., Ltd.) and tridecyl alcohol polyoxyethylene ether (molecular weight: 583, Shanghai Macklin Biochemical Co., Ltd.) are used as the ionic Gemini surfactant and non-ionic surfactant, respectively. Table 1 shows the influence of different concentration and processing pH on the viscosity of electrolyte (sample 1 is used in Example 2). The high viscosity deteriorates the ion mobility in the electrolyte and rate capability.

Table 1 Viscosity of electrolyte solution tested by rotational viscometer.

Sample	ionic Gemini surfactant	Concentration mol/L	non-ionic surfactant	Concentration mol/L	Ratio	pH of electrolyte	Viscosity mPa/s	Conductivity mS/cm
0 ^a	0	0	0	0	n/a		2.8	62.6
1	Ethylene bis (hexadecamidopropyl dimethyl ammonium bromide)	0.001	tridecyl alcohol polyoxyethylene ether	0.02	20	6.5	4.2	58.0
2	Ethylene bis (hexadecamidopropyl dimethyl ammonium	0.001	tridecyl alcohol polyoxyethylene ether	0.02	20	9	15.9	39.5

	bromide)							
3	Ethylene bis (hexadecami dopropyl dimethyl ammonium bromide)	0.001	tridecyl alcohol polyoxye thylene ether	0.05	50	6	28.0	18.9

a: sample 0 refers to an electrolyte solution with 1.0 mol/L Na₂SO₄.

Example 2

[0041] Ethylene bis (hexadecamidopropyl dimethyl ammonium bromide) (C₄₄H₉₂O₂N₄Br₂, molecular weight: 869.0, Zhengzhou YiHe Fine Chemicals Co., Ltd.) and tridecyl alcohol polyoxyethylene ether (molecular weight: 583, Shanghai Macklin Biochemical Co., Ltd.) are used as the ionic Gemini surfactant and non-ionic surfactant, respectively. Sodium sulfate is used as the electrolyte salt. A predetermined amount of ethylene bis(hexadecamidopropyl dimethyl ammonium bromide) and tridecyl alcohol polyoxyethylene ether are dispersed into deionized water, thereby obtaining a surfactant solution with 0.001mol/L and 0.02mol/L of the ionic Gemini surfactant and non-ionic surfactant, respectively.

[0042] An inorganic electrolyte salt, sodium sulfate, is added to the surfactant solution, resulting in a 1.0M sodium sulfate electrolyte solution. The initial pH is 6.0 and is adjusted to 6.5 using a base, e.g., sodium hydroxide.

[0043] A 1.0M sodium sulfate solution without any surfactants is used as control electrolyte solution for comparison.

[0044] Test I: the hydrogen and oxygen evolution potential were tested in different electrolyte solutions (i.e., the electrolyte solution with the hybrid surfactant and the control electrolyte solution), Ag/KCl/AgCl, Ti, Pt are used as reference electrode, work electrode and counter electrode, respectively.

[0045] Test II: sodium titanium phosphate and manganese oxide are used as anode and cathode electrodes, respectively. Ti foil is as the current collector. The specific capacity and cycle performance of the batteries were tested, the test voltage range is 1.0-2.0V

[0046] According to the test results (Fig. 1), the aqueous electrolyte solution with hybrid oligomeric surfactant has a wider electrochemical window. The hydrogen evolution potential is reduced from -1.3V to -1.4V, while the oxygen evolution potential is increased from 1.1V to 1.3V. The electrochemical stability window is increased from 2.4 V to 2.7V.

[0047] The full battery using electrolyte with the hybrid surfactant has a specific capacity of 110mAh/g and 95mAh/g at a rate of 0.1C and 0.2C, respectively, which is much higher than that with the control electrolyte, i.e., 100mAh/g and 70mAh/g at a rate of 0.1C and 0.2C, respectively. The specific capacity is increased by 10% and 35% at a rate of 0.1C and 0.2C, respectively.

[0048] The cycling performance are showed in Figs. 2A and 2B. After 100 cycles, the capacity of the battery with control electrolyte is decreased from 72.0 to 54.9 mAh/g, resulting in a retention rate of 76.3%. As for the battery with the hybrid surfactant in the electrolyte solution, the capacity decreases from 95.0 to 85.4 mAh/g after 100 cycles, leading to an improved retention rate of 89.9%.

References

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What is claimed is:

1. An aqueous electrolyte solution for electrochemical device, comprising an ionic Gemini surfactant and a non-ionic surfactant, wherein the aqueous electrolyte solution has a viscosity of no more than 5.0 mPa/s and the aqueous electrolyte solution has an improved electrochemical stability window in comparison with that without the ionic Gemini surfactant and the non-ionic surfactant.
2. The aqueous electrolyte solution of claim 1, wherein the aqueous electrolyte solution has a conductivity of no less than 45 mS/cm.
3. The aqueous electrolyte solution of claim 1, wherein the ionic Gemini surfactant contains two or more ions in each molecule.
4. The aqueous electrolyte solution of claim 1, wherein the ionic Gemini surfactant is an anionic or cation surfactant.
5. The aqueous electrolyte solution of claim 1, wherein the non-ionic surfactant is ethoxylate, fatty acid ester of polyhydroxy compounds, fatty acid ester of glycerol, glycerol monostearate, glycerol monolaurate, fatty acid ester of sorbitol, alkyl polyglucoside or their derivatives.
6. The aqueous electrolyte solution of claim 1, wherein the ionic Gemini surfactant has a concentration of 0.001-0.1mol/L in said aqueous electrolyte solution.
7. The aqueous electrolyte solution claim 1, wherein the non-ionic surfactant has a concentration of 0.01-0.1mol/L in said aqueous electrolyte solution.
8. The aqueous electrolyte solution of claim 1, wherein the molar ratio of non-ionic surfactant to the ionic Gemini surfactant ranges from 10 to 100.
9. The aqueous electrolyte solution of claim 1, wherein the electrochemical device is an aqueous ionic battery.
10. An electrochemical device comprising an anode, a cathode and the aqueous electrolyte solution of claim 1 placed between the anode and cathode, wherein the ionic Gemini surfactant and non-ionic surfactant constructs an interface on the surface of the active material of the anode and cathode, wherein the interface blocks direct contact between water molecules and the active material, by which

electrolysis of water molecules is restricted or inhibited, and allows passage of ions in the electrolyte solution through the interface and electrochemical reaction with the active material.

11. The electrochemical device of claim 10, wherein the aqueous electrolyte solution has an electrochemical stability window of 2.6 – 2.7 V.
12. The electrochemical device of claim 10, wherein the electrochemical device has a specific capacity of higher than that without the ionic Gemini surfactant and non-ionic surfactant.
13. The electrochemical device of claim 11, wherein the specific capacity of electrochemical device is 10%-40% higher than that without the ionic Gemini surfactant and non-ionic surfactant at a rate ranging from 0.1C to 1.0C.
14. A method for preparing the aqueous electrolyte solution of claim 2, comprising:
 - 3) dissolving a predetermined amount of an ionic Gemini surfactant and a non-ionic surfactant in water at a controlled temperature by mechanical stirring or ultrasonic mixing, resulting in a surfactant solution; and
 - 4) adding one or more inorganic electrolyte salts into the surfactant solution, followed by adjusting pH value to 6.0 – 8.0, thereby obtaining the aqueous solution of claim 2 with a viscosity is no more than 5.0 mPa.S and a conductivity of no less than 45.0 mS/cm.
15. The method of claim 14, wherein the controlled temperature ranges from 25°C and 50°C.
16. The method of claim 14, wherein said one or more inorganic electrolyte salts comprise a cation selected from the group consisting of lithium, sodium, potassium, zinc, calcium, and magnesium.
17. The method of claim 14, wherein said one or more inorganic electrolyte salts comprise an anion selected from the group consisting of chloride, sulfate, sulfonate, nitrate, sulfite, hypochlorite and phosphate.
18. The method of claim 16, wherein the cation has a concentration ranging from 0.01 mol/L to 5 mol/L in said aqueous electrolyte solution.