A Co-Solvent Electrolyte for Prussian Blue Analogue Material

TECHNICAL FIELD

[0001] The present invention relates to a co-solvent electrolyte system used for Prussian blue analogues.

BACKGROUND OF THE INVENTION

[0002] Prussian blue is a transition metal ion ferrocyanide compound. Due to its open framework structure and adjustable component composition, Prussian blue and its derivatives have great application potential in the field of electrochemical energy storage.

[0003] Prussian blue materials are usually prepared in aqueous solution, lattice vacancies may be occupied by water molecules, and the presence of interstitial water and $M(CN)_6$ vacancies is inevitable during the preparation of Prussian blue materials. In organic electrolyte systems, interstitial water can precipitate during the charging and discharging process, causing the deterioration of organic solvents, and even inducing safety hazards: (1) Due to its strong moisture absorption and high specific surface area, a large amount of moisture in the environment will be adsorbed during the preparation process of slurry and electrode. During the charging and discharging process of organic sodium ion batteries, water molecules may be electrolyzed into hydrogen gas, making the sodium ion batteries unable to perform normal charging and discharging due to gas expansion. (2) Water molecules may also have side reactions with the electrolyte. On one hand, the generated side reaction products may deposit onto the surface of the positive and negative electrodes, resulting in difficulties in sodium ion deinterlacing, lower capacity and poor cycle performance. On the other hand, the production of side reaction products such as HF may corrode the passivation films on the surface of the positive and negative electrode plates, cause reaction of the positive and negative electrode active materials with the electrolyte to form new

passivation films, which will result in the continuous consumption of sodium ions, capacity decrease, and cycle performance deterioration of sodium ion batteries.

[0004] In aqueous electrolytes, the cathode electrode is very prone to oxygen evolution reactions. Once active oxygen is precipitated, the Prussian blue cathode electrode material will be oxidized, and induce its cycle performance decrease. In addition, oxygen molecules precipitated during the cycle will react with inserted Na+, consuming charging capacity (Na - (insertion) + ½ H_2O + ¼ $O_2 \rightarrow Na^+ + OH^-$).

SUMMARY OF THE INVENTION

[0005] Combining the characteristics of Prussian blue material itself, the present invention patent proposes a co-solvent electrolyte system for Prussian blue analogues, using a mixed system of co-solvent and deionized water. The co-solvent solution can reduce the occurrence of side reactions in aqueous electrolytes, while the addition of deionized water plays a positive role in improving the conductivity of the overall electrolyte, with the following advantages:

1. Greatly prolong the electrode life;
2. Effectively broaden the electrochemical window of battery operation and limit the occurrence of water electrolysis side reactions during battery operation;
3. The battery can operate over a wide temperature range (capacity retention rate at – 30℃ is greater than 70%); and
4. Electrolyte has intrinsic safety characteristics and low cost.

DESCRIPTION OF THE DRAWINGS

[0006] FIG 1. Capacity retention of Prussian blue analogues / sodium titanium phosphate cell.

[0007] FIG 2. Charge and discharge curve at different temperatures.

DETAILED DESCRIPTION OF THE INVENTION

[0008] The present invention relates to a co-solvent electrolyte applied to Prussian blue analogues. The electrolyte solvent consists of a co-solvent solution and deionized water, with a mass ratio of 5-98%. The types of cosolvent are polyethylene glycol, sodium polyacrylate, glycerol, agar, carrageenan, gelatin, ethanol, sodium alginate, vinyl carbonate, diethyl carbonate, dimethyl carbonate, sulfolane, trimethyl phosphate, dimethyl sulfone, diethylene glycol dimethyl ether, methyl ethyl carbonate, propylene carbonate, methylcellulose, and one or more of carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl methyl fiber, acrylic acid, maleic acid or maleic anhydride, N, N-methylene-bis-acrylamide methacrylate, butyl diacrylate, or diallyl phthalate. Depending on the design requirement of viscosity and conductivity, the co-solvent solution can be mixed in different proportions.

[0009] The electrolyte salt described in the present invention is one or more of sodium perchlorate, sodium sulfate, sodium formate, sodium acetate, sodium nitrate, sodium chloride, sodium carbonate, sodium bromide, sodium acetate, sodium iodide, and sodium oxalate. Features and advantages of this invention are:

1. Compared with pure organic electrolytes, the interstitial water in the preparation process of Prussian blue analog materials and the water adsorbed during the electrode sheet preparation process no longer cause side reactions and are no longer fatal defects of batteries;

2. Compared to pure water electrolytes, the content of deionized water can be adjusted according to the actual use of electrochemical windows, thereby reducing the occurrence of hydrogen evolution and oxygen evolution side reactions. At the same time, the probability of oxygen evolution side reactions is reduced, which is conducive to ensuring

the stability of Prussian Blue materials;

3. The co-solvent electrode liquid can alleviate the side reactions and capacity degradation problems of Prussian blue materials in organic electrolytes and pure hydroelectric media, and extend the electrode life;

4. Effectively broaden the electrochemical window of battery operation and limit the occurrence of water electrolysis side reactions during battery operation;

5. Due to the low freezing point of co-solvent solution, the low-temperature performance of the electrolyte can be guaranteed. The battery can operate in a wide temperature range (capacity retention rate at - 30 ℃ is greater than 70%); and

6. Electrolyte has intrinsic safety characteristics and low cost.

[0010] References or published articles are cited in this patent application. The cited literature and published articles together serve as reference data for this application to more fully describe the latest level in the field related to the invention. It should also be noted that during the entire application process, the transitional terms "including", "comprising", or "characterized by" are synonymous, inclusive, or open-ended, and do not exclude additional, unlisted elements or method steps.

[0011] The invention can be better understood by referring to the following embodiments. Those skilled in the art can understand that the following examples are only intended to illustrate the invention, not to limit the scope of the invention. The scope of the invention is defined by the scope of the claims.

Examples

[0012] **Example A.** The electrodes were prepared by coating method wherein Prussian blue analog was used as the cathode electrode active material, and sodium titanium phosphate as the anode electrode active material. Polyethylene glycol was used as the co-solvent solution, and sodium perchlorate was used as the electrolyte salt (1 mol/kg). The relationship between co-solvent content and electrochemical stability window is shown in Table 1.

Table 1

	Mass ratio of co-solvent solution	**Oxygen evolution potential (vs SHE)**	**Hydrogen evolution potential (vs SHE)**	**Electrochemical window**
Comparative	0	1.39	-1.10	2.49
Example 1	40%	1.57	-1.21	2.78
Example 2	60%	1.59	-1.25	2.84
Example 3	80%	1.65	-1.27	2.92
Example 4	90%	1.70	-1.32	3.02

[0013] As the content of co-solvent solution increases, the electrochemical stability window of the electrolyte widens, mainly due to the destruction of the hydrogen bond network in water by the co-solvents, strengthening the O-H bond of water molecules, thereby reducing the activity of water molecules.

[0014] **Example B.** Using the electrodes of Example A, different types of co-solvent solution and different mass ratios were used to prepare the electrolyte, in order to determine the viscosity, conductivity, and oxygen evolution potential of the electrolyte, as shown in Table 2.

Table 2

	co-solvent solution	Mass ratio of co-solvent solution	Electrolyte salt 1 mol/kg	Conductivity mS/cm	Oxygen evolution potential (vs SHE)
Example 5	Polyethylene glycol	80%	Sodium perchlorate	12.5	1.65
Example 6	Glycerol	20%	Sodium acetate	15.6	1.52
Example 7	Trimethyl phosphate	90%	Sodium perchlorate	22.8	1.42
Example 8	Vinyl carbonate	20%	sodium chloride	78.9	1.35
Example 9	Diethylene glycol dimethyl ether	80%	Sodium acetate	16.5	1.30
Example 10	Trimethyl phosphate, Sulfolane (Mass ratio 1:1)	50%	Sodium perchlorate	35.7	1.58

[0015] **Example C.** The electrodes were prepared by coating method wherein Prussian blue analog was used as the cathode electrode active material and sodium titanium phosphate as the anode electrode active material. Sodium perchlorate was used as the electrolyte salt (1 mol/kg), dissolved in deionized water (100%, comparative) or polyethylene glycol/deionized water (90/10, Example 4), and cycled at 5C. The capacity retention curve of the entire battery is shown in Figure 1.

[0016] **Example D.** Using the formula of co-solvent electrolyte in Example 4, the charge and discharge capacity of the battery was tested at room temperature of 25 ℃ and minus 30 ℃. The capacity retention rate of the battery at minus 30 ℃ can be as high as 70% (see Figure 2).

What is claimed is:

1. A battery comprising a co-solvent electrolyte and one or more electrodes made with a Prussian blue material, said co-solvent electrolyte comprising a co-solvent and deionized water, wherein the proportion of the co-solvent is 5-98% w/w.

2. The battery of claim 1, wherein said proportion of the co-solvent is 40-90% w/w.

3. The battery of claim 1, wherein the co-solvent is one or more of polyethylene glycol, sodium polyacrylate, glycerol, agar, carrageenan, gelatin, ethanol, sodium alginate, vinyl carbonate, diethyl carbonate, dimethyl carbonate, sulfolane, trimethyl phosphate, dimethyl sulfone, diethylene glycol dimethyl ether, methyl ethyl carbonate, propylene carbonate, methylcellulose, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl methyl fiber, acrylic acid, maleic acid, maleic anhydride, methacrylic acid, N, N-methylene-bis-acrylamide, butyl diacrylate, and diallyl phthalate, wherein the amount of co-solvent determines viscosity and conductivity.

4. The battery of claim 1, wherein the co-solvent electrolyte comprises an electrolyte salt selected from sodium perchlorate, sodium sulfate, sodium formate, sodium acetate, sodium nitrate, sodium chloride, sodium carbonate, sodium bromide, sodium acetate, sodium iodide, and sodium oxalate.

5. The battery of claim 4, wherein the concentration of the electrolyte salt is 0.1 to 2 mol/kg.

6. The battery of claim 1, wherein Prussian blue material serves as an anode active material.

7. The battery of claim 1, where sodium titanium phosphate serves as a cathode active material.