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AQUEOUS BATTERY

Abstract

To suppress the electrolysis of an aqueous electrolyte solution on a negative electrode surface when an aqueous potassium ion battery is being charged/discharged. SOLUTION: An aqueous electrolyte solution comprises potassium pyrophosphate which is dissolved at a concentration of 2 mol or more per one kg of water. It is assumed as to the aqueous electrolyte solution that a pyrophosphate ion is decomposed on a negative electrode surface and then a coating is formed on a high-work function portion of the negative electrode surface when a battery is being charged/discharged. As a result, the direct contact of the aqueous electrolyte solution and the negative electrode surface is suppressed and when the battery is being charged/discharged, the electrolysis of the aqueous electrolyte solution on the negative electrode surface is suppressed. SELECTED DRAWING: FIG. 3

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Background/Summary

TECHNICAL FIELD

[0001] The present application discloses an aqueous battery.

BACKGROUND ART

[0002] PTL 1 discloses an aqueous electrolyte solution used in an aqueous battery, which includes water and potassium pyrophosphate dissolved at a concentration of 2 mol or more per 1 kg of the water. When the aqueous battery is formed using the aqueous electrolyte solution disclosed in PTL 1, decomposition of the aqueous electrolyte solution on the surface of a negative electrode is easily suppressed even when the aqueous battery is charged and discharged because of wide potential window on the reduction side of the aqueous electrolyte solution. In PTL 1, a Ti foil and an Au foil are used as electrode current collectors when the aqueous electrolyte solution is evaluated.

CITATION LIST

Patent Literature

[0003] [PTL 1] JP 2019-220294 A

SUMMARY

Technical Problem

[0004] Conventional aqueous batteries have room for improvement with respect to measures against corrosion of the current collector. For example, in aqueous batteries, when a current collector containing Al is used, Al is easily eluted from the current collector into the aqueous electrolyte solution when the battery is charged and discharged. When a current collector containing Al is used in aqueous batteries, new technology is required to suppress elution of Al from the current collector into the aqueous electrolyte solution.

Solution to Problem

[0005] The present application discloses, as aforementioned solution to problem, a plurality of aspects below.

<Aspect 1>

[0006] An aqueous battery including a positive electrode, an aqueous electrolyte solution and a negative electrode, wherein [0007] one or both of the positive electrode and the negative electrode has/have a current collector containing Al, [0008] the current collector is in contact with the aqueous electrolyte solution, [0009] the aqueous electrolyte solution contains water and potassium polyphosphate dissolved in the water, [0010] at least one of proton, hydroxide ion and polyphosphate ion contained in the aqueous electrolyte solution behaves as a carrier ion, and [0011] the aqueous electrolyte solution has no freezing point at -40°C . or higher.

<Aspect 2>

[0012] The aqueous battery according to aspect 1, wherein [0013] the aqueous electrolyte solution does not involve salt precipitation when cooling from 0°C . to -40°C .

<Aspect 3>

[0014] The aqueous battery according to aspect 1 or 2, wherein [0015] at least the positive electrode has the current collector.

<Aspect 4>

[0016] The aqueous battery according to any one of aspects 1 to 3, wherein [0017] the aqueous electrolyte solution contains water and potassium polyphosphate dissolved at a concentration of 4 mol or more and 7 mol or less per 1 kg of the water.

<Aspect 5>

[0018] The aqueous battery according to any one of aspects 1 to 4, wherein [0019] the aqueous electrolyte solution has a viscosity of 40 mPa·s or more and 350 mPa·s or less at 20° C.
<Aspect 6>

[0020] The aqueous battery according to any one of aspects 1 to 5, having a bipolar structure, wherein [0021] a positive electrode active material layer is formed on one side of the current collector and a negative electrode active material layer is formed on the other side of the current collector.

EFFECTS

[0022] According to the aqueous battery of the present disclosure, it is easy to suppress elution of Al from a current collector into an aqueous electrolyte solution.

Description

BRIEF DESCRIPTION OF DRAWINGS

[0023] FIG. 1 schematically shows an example of a structure of an aqueous battery.

[0024] FIG. 2 schematically shows an example of a structure of an aqueous battery.

[0025] FIG. 3 shows a time-potential curve when a 0.5 m aqueous electrolyte solution is used in an electrochemical cell of Example and a constant current on the oxidation side is applied.

[0026] FIG. 4 shows a time-potential curve when a 5 m aqueous electrolyte solution is used in electrochemical cells of Examples and a constant current on the oxidation side is applied.

[0027] FIG. 5 shows a time-potential curve when a 1 m aqueous electrolyte solution is used in electrochemical cells of Examples and a constant current on the reduction side is applied.

[0028] FIG. 6 shows a time-potential curve when a 5 m aqueous electrolyte solution is used in electrochemical cells of Examples and a constant current on the reduction side is applied.

[0029] FIG. 7A shows a charge-discharge curve of a cell for evaluation when using an Al foil as a current collector.

[0030] FIG. 7B shows a charge-discharge curve of a cell for evaluation when using a Ti foil as a current collector.

[0031] FIG. 8A is a graph showing the relationship between the concentration and the crystallization peak temperature (freezing point) of an aqueous electrolyte solution.

[0032] FIG. 8B is a graph showing the relationship between the concentration and the crystallization peak intensity of an aqueous electrolyte solution.

[0033] FIG. 9 is a graph showing the relationship between the concentration and the glass transition temperature of an aqueous electrolyte solution.

[0034] FIG. 10 is a graph showing the relationship between the concentration and the viscosity of an aqueous electrolyte solution.

DESCRIPTION OF EMBODIMENTS

1. Aqueous Battery

[0035] The aqueous battery according to the embodiment will be described below with reference to the drawings, but the technology of the present disclosure is not limited to the following embodiments. FIG. 1 schematically shows an example of a structure of an aqueous battery 100 according to the embodiment. As shown in FIG. 1, the aqueous battery 100 includes a positive electrode 10, an aqueous electrolyte solution 20 and a negative electrode 30. One or both of the positive electrode 10 and the negative electrode 30 has/have a current collector containing Al. The current collector is in contact with the aqueous electrolyte solution 20. The aqueous electrolyte solution 20 contains water and potassium polyphosphate dissolved in the water. In the aqueous battery 100, at least one of proton, hydroxide ion and polyphosphate ion contained in the aqueous electrolyte solution 20 behaves as a carrier ion. The aqueous electrolyte solution 20 has no freezing point at -40° C. or higher.

1.1 Positive Electrode

[0036] It is possible to use, as the positive electrode **10**, any known positive electrode for an aqueous battery. As shown in FIG. 1, the positive electrode **10** may include a positive electrode active material layer **11** and a positive electrode current collector **12**.

1.1.1 Positive Electrode Active Material Layer

[0037] The positive electrode active material layer **11** contains a positive electrode active material. The positive electrode active material layer **11** is impregnated with the aqueous electrolyte solution **20**. The positive electrode active material layer **11** may contain, in addition to the positive electrode active material, a conductive aid and/or a binder. The positive electrode active material layer **11** may also contain various other additives. The content of each component in the positive electrode active material layer **11** may be appropriately determined according to the objective battery performance. For example, the content of the positive electrode active material may be 40% by mass or more, 50% by mass or more, 60% by mass or more, or 70% or more, and may be 100% or less or 90% by mass or less, based on 100% by mass of the entire positive electrode active material layer **11** (total solid content). The shape of the positive electrode active material layer **11** is not particularly limited, and the positive electrode active material layer may be, for example, a sheet-shaped positive electrode active material layer having an approximately flat surface. The thickness of the positive electrode active material layer **11** is not particularly limited, and may be, for example, 0.1 μm or more, 1 μm or more, or 10 μm or more, and may be 2 mm or less, 1 mm or less, or 500 μm or less.

[0038] Any substance capable of functioning as the positive electrode active material of the aqueous battery in which at least one of proton, hydroxide ion and polyphosphate ion is used as a carrier ion can be used as the positive electrode active material. The positive electrode active material has a higher charge-discharge potential than that of the below-mentioned negative electrode active material, and can be appropriately selected in consideration of the potential window of the below-mentioned aqueous electrolyte solution **20**. The positive electrode active material may be various hydroxides or oxides such as $\text{Ni}(\text{OH})_{2.2}$ which is a layered nickel hydroxide compound (for example, JP 2023-154313 A), $\text{A}_{x/2}\text{K}_{y/2}\text{Ni}_{1-z}\text{M}_z\text{O}_{2+\delta}$ (where A is at least one of Li, Na, Rb, Cs, Mg, Ca, Sr, Ba and Sc, M is at least one of transition metal group elements, 2A group elements, 3A group elements, 2B group elements and 3B group elements, relationships $0 \leq x < 0.5$, $0 < y \leq 0.5$, $0 \leq z \leq 0.5$, $0 < n \leq 2$ and $(\alpha \cdot x) + y \leq 0.5$ are satisfied, and α is the valence of the cation of A, for example, JP 2023-132287 A), manganese spinel (for example, $\text{LiMn}_{0.2}\text{O}_{0.4}$), and nickel-manganese-cobalt containing composite oxide (NMC). The positive electrode active material may also be oxides and polyanions containing alkali metal elements. More specifically, the positive electrode active material may be a composite oxide of alkali metal elements and transition metal. Such composite oxide may be at least one selected from alkali metal cobalt composite oxides ($\text{AmCoO}_{0.2}$, etc., “Am” is alkali metal element, the same shall apply hereinafter), alkali metal nickel composite oxides ($\text{AmNiO}_{0.2}$, etc.), alkali metal nickel titanium composite oxides ($\text{AmNi}_{0.1/2}\text{Ti}_{0.1/2}\text{O}_{0.2}$, etc.), alkali metal nickel manganese composite oxides ($\text{AmNi}_{0.1/2}\text{Mn}_{0.1/2}\text{O}_{0.2}$, $\text{AmNi}_{0.1/3}\text{Mn}_{0.2/3}\text{O}_{0.2}$, etc.), alkali metal manganese composite oxides ($\text{AmMnO}_{0.2}$, $\text{AmMn}_{0.2}\text{O}_{0.4}$, etc.), alkali metal iron manganese composite oxides ($\text{Am}_{0.2/3}\text{Fe}_{0.1/3}\text{Mn}_{0.2/3}\text{O}_{0.2}$, etc.), alkali metal nickel cobalt manganese composite oxides ($\text{AmNi}_{0.1/3}\text{Co}_{0.1/3}\text{Mn}_{0.1/3}\text{O}_{0.2}$, etc.), alkali metal iron composite oxides ($\text{AmFeO}_{0.2}$, etc.), alkali metal chromium composite oxide ($\text{AmCrO}_{0.2}$, etc.), alkali metal iron phosphate compounds ($\text{AmFePO}_{0.4}$, etc.), alkali metal manganese phosphate compounds ($\text{AmMnPO}_{0.4}$, etc.) and alkali metal cobalt phosphate compounds ($\text{AmCoPO}_{0.4}$). Alternatively, the positive electrode active material may be an organic active material such as Prussian blue. Alternatively, the positive electrode active material may be at least one selected from alkali metal titanium composite oxides, $\text{TiO}_{0.2}$ and sulfur(S) which show a noble charge-

discharge potential compared to the below-mentioned negative electrode active material. The positive electrode active material may be those which insert and deinsert a carrier ion by intercalation, or those which insert and deinsert a carrier ion by a conversion reaction or an alloying reaction. Only one positive electrode active material may be used alone, or two or more thereof may be used in combination.

[0039] The shape of the positive electrode active material may be any shape capable of functioning as the positive electrode active material of the battery. For example, the positive electrode active material may be in the form of particles. The positive electrode active material may be a solid material, a hollow material, a material with voids, or a porous material. The positive electrode active material may be a primary particle, or a secondary particle obtained by agglomeration of a plurality of primary particles. The mean particle diameter D50 of the positive electrode active material may be, for example, 1 nm or more, 5 nm or more, or 10 nm or more, and may be 500 μm or less, 100 μm or less, 50 μm or less, or 30 μm or less. The mean particle diameter D50 in the present application is the particle diameter (median diameter) at 50% of the integrated value in the volume-based particle diameter distribution determined by the laser diffraction and scattering method.

[0040] Examples of the conductive aid which can be included in the positive electrode active material layer **11** include carbon materials such as vapor-phase-grown carbon fiber (VGCF), acetylene black (AB), Ketjen black (KB), carbon nanotube (CNT) and carbon nanofiber (CNF); and metal materials such as nickel, titanium, aluminum, stainless steel and the like which are slightly insoluble (poorly soluble) in an electrolyte solution. The conductive aid may be, for example, in the form of particles or fibers, and the size thereof is not particularly limited. Only one conductive aid may be used alone, or two or more thereof may be used in combination.

[0041] Examples of the binder which can be included in the positive electrode active material layer **11** include butadiene rubber (BR)-based binders, butylene rubber (IIR)-based binders, acrylate-butadiene rubber (ABR)-based binders, styrene-butadiene rubber (SBR)-based binders, polyvinylidene fluoride (PVdF)-based binders, polytetrafluoroethylene (PTFE)-based binders, polyimide (PI)-based binders and the like. Only one binder may be used alone, or two or more thereof may be used in combination.

1.1.2 Positive Electrode Current Collector

[0042] As shown in FIG. **1**, the positive electrode **10** may include a positive electrode current collector **12** in contact with the positive electrode active material layer **11**. The positive electrode current collector **12** is in contact with an aqueous electrolyte solution **20**. It is possible to use, as the positive electrode current collector **12**, any material capable of functioning as the positive electrode current collector of the aqueous battery. When the below-mentioned negative electrode current collector **32** contains Al, the positive electrode current collector **12** may contain Al or may not contain Al. When the below-mentioned negative electrode current collector **32** does not contain Al, the positive electrode current collector **12** contains Al. As mentioned below, elution of Al from the current collector into the aqueous electrolyte solution particularly easily occurs on the positive electrode side which becomes the oxidation potential. According to the aqueous battery **100** of the present disclosure, even if the positive electrode collector **12** contains Al, it is possible to suppress elution of Al from the positive electrode collector **12** into the aqueous electrolyte solution **20**. Namely, in the aqueous battery **100**, at least the positive electrode **10** may have a current collector containing Al.

[0043] When the positive electrode current collector **12** contains Al, the entire positive electrode current collector **12** may be composed of Al, or at least a portion of the surface thereof may be composed of Al. For example, the positive electrode current collector **12** may be made of an Al foil, or the surface of a metal foil or some base material may be coated with Al. The positive electrode current collector **12** may be those in which Al is present on at least a portion of the surface in contact with the aqueous electrolyte solution **20**, or Al may be present over the entire surface in

contact with the aqueous electrolyte solution **20**.

[0044] The positive electrode current collector **12** may be in the form of foil, plate, mesh, perforated metal and foam. The positive electrode current collector **12** may be formed of a metal foil or a metal mesh. In particular, the metal foil is excellent in ease of handling or the like. The positive electrode current collector **12** may be composed of a plurality of foils. The metal material constituting the positive electrode current collector **12** include those containing at least one element selected from the group consisting of Cu, Ni, Al, V, Au, Pt, Mg, Fe, Ti, Pb, Co, Cr, Zn, Ge, In, Sn and Zr. In particular, the positive electrode current collector **12** preferably contains Al, as mentioned above. The positive electrode current collector **12** may be those in which the above metal is plated or vapor-deposited on a metal foil or a base material. When the positive electrode current collector **12** is composed of a plurality of metal foils, the positive electrode current collector may have some layer between the plurality of metal foils. The thickness of the positive electrode current collector **12** is not particularly limited, and may be, for example, 0.1 μm or more, or 1 μm or more, and may be 1 mm or less, or 100 μm or less.

1.2 Aqueous Electrolyte Solution

[0045] The aqueous electrolyte solution **20** contains water and potassium polyphosphate dissolved in the water. The aqueous electrolyte solution **20** may be in contact with the above-mentioned positive electrode collector **12** and may be contained in the above-mentioned positive electrode active material layer **11**, and may be in contact with the below-mentioned negative electrode collector **32** and may be contained in the below-mentioned negative electrode active material layer **31**, and the aqueous electrolyte solution may be held by the separator **40** between the positive electrode **10** and the negative electrode **30**.

1.2.1 Solvent

[0046] The aqueous electrolyte solution **20** contains water as a solvent. The solvent contains water as a main component. Namely, water accounts for 50 mol % or more and 100 mol % or less of the total amount of solvent constituting the aqueous electrolyte solution (100 mol %). Water may account for 70 mol % or more, 90 mol % or more, or 95 mol % or more of the total amount of the solvent. Meanwhile, the upper limit of the proportion of water in the solvent is not particularly limited. The solvent may be composed only of water (100 mol % water).

[0047] The solvent may contain, in addition to water, solvents other than water as long as the above problems can be solved, for example, from the viewpoint of forming solid electrolyte interphase (SEI) on the surface of the active material. Examples of solvents other than water include one or more organic solvents selected from ethers, carbonates, nitriles, alcohols, ketones, amines, amides, sulfur compounds and hydrocarbons. The solvents other than water may account for 50 mol % or less, 30 mol % or less, 10 mol % or less, or 5 mol % or less of the total amount of solvents constituting the electrolyte solution (100 mol %).

1.2.2 Electrolyte

[0048] An electrolyte is dissolved in the aqueous electrolyte solution **20**, and the electrolyte may dissociate into cations and anions in the aqueous electrolyte solution **20**. In the aqueous electrolyte solution **20**, cations and anions may form aggregates (associations) in close proximity to each other.

1.2.2.1 Potassium Polyphosphate

[0049] The aqueous electrolyte solution **20** contains potassium polyphosphate dissolved in the water. The term “potassium polyphosphate” refers to a salt in which at least part of the hydrogen of polyphosphoric is replaced by potassium. In other words, the concept of “potassium polyphosphate” includes potassium hydrogen polyphosphate. Specific examples of potassium polyphosphate include potassium pyrophosphate ($\text{K}_{4-x}\text{H}_x\text{P}_2\text{O}_7$), potassium tripolyphosphate ($\text{K}_{5-x}\text{H}_x\text{P}_3\text{O}_{10}$), potassium tetrapolyphosphate ($\text{K}_{6-x}\text{H}_x\text{P}_4\text{O}_{13}$), potassium heptapolyphosphate ($\text{K}_{7-x}\text{H}_x\text{P}_7\text{O}_{16}$) and the like. In particular, when potassium pyrophosphate ($\text{K}_{4-x}\text{H}_x\text{P}_2\text{O}_7$) is

used as the potassium polyphosphate, higher performance is easily ensured. In the aqueous electrolyte solution **20**, “potassium polyphosphate dissolved in water” can dissociate into potassium ions and anions. In the aqueous electrolyte solution **20**, potassium ions may completely dissociate from anions, or may form aggregates (associations) in close proximity to anions. For example, when the aqueous electrolyte solution **20** contains potassium pyrophosphate dissolved in water, “potassium pyrophosphate dissolved in water” in the aqueous electrolyte solution **20** may be present as ions such as K^{+} , $P_2O_7^{4-}$, $KP_2O_7^{3-}$, $K_2P_2O_7^{2-}$, and $K_3P_2O_7^{-}$, or aggregates (associations) of these ion, and may be present as $HP_2O_7^{3-}$, $H_2P_2O_7^{2-}$ and $H_3P_2O_7^{-}$ by drawing H^{+} from H_2O , or may present as $HKP_2O_7^{-}$, $HKP_2O_7^{2-}$ and $H_2KP_2O_7^{-}$ by the association of H^{+} and K^{+} . In the aqueous electrolyte solution **20**, “concentration of potassium polyphosphate dissolved in water” is specified by converting ions, aggregates (associations), etc. contained in aqueous electrolyte solution **20** into potassium polyphosphate.

[0050] In the aqueous battery **100** of the present disclosure, the components and concentration in the aqueous electrolyte solution **20** are determined so that “aqueous electrolyte solution **20** does not have a freezing point at $-40^{\circ}C$. or higher”. According to the inventors' new knowledge, in order to achieve the conditions that “aqueous electrolyte solution **20** does not have a freezing point at $-40^{\circ}C$. or higher”, the concentration of potassium polyphosphate in the aqueous electrolyte solution **20** should be higher than ever before. According to the inventors' new knowledge, when the freezing point is adjusted by dissolving only potassium polyphosphate in water in the aqueous electrolyte solution, the freezing point of the aqueous electrolyte solution decreases as the concentration of potassium polyphosphate in water increases, and when the concentration of potassium polyphosphate in the aqueous electrolyte solution exceeds a certain level, the freezing point substantially disappears. Namely, when the concentration of potassium polyphosphate in the aqueous electrolyte solution is a certain level or more, the aqueous electrolyte solution does not have a freezing point at $-60^{\circ}C$. or higher. For example, when the aqueous electrolyte solution **20** contains the water and potassium polyphosphate dissolved at a concentration of 4 mol or more per 1 kg of the water, the freezing point of the aqueous electrolyte solution **20** disappears and thus the aqueous electrolyte solution **20** does not have a freezing point at $-40^{\circ}C$. or higher. However, when other components are dissolved in the aqueous electrolyte solution **20** together with potassium polyphosphate in water, the minimum concentration of potassium polyphosphate at which the freezing point of the aqueous electrolyte solution disappears may be less than 4 mol/kg. In this respect, the concentration of potassium polyphosphate per 1 kg of water in the aqueous electrolyte solution **20** may be, for example, 2.5 mol or more, 3.0 mol or more, 3.5 mol or more, or 4.0 mol or more.

[0051] As mentioned above, in order to achieve the conditions that “aqueous electrolyte solution **20** does not have a freezing point at $-40^{\circ}C$. or higher”, it is effective to adjust the concentration of potassium polyphosphate in the aqueous electrolyte solution **20** to a higher concentration than ever before, and specifically, the conditions are easily satisfied when the aqueous electrolyte solution **20** contains the water and potassium polyphosphate dissolved at a concentration of 4 mol or more per 1 kg of the water. The upper limit of the concentration of potassium pyrophosphate in the aqueous electrolyte solution **20** is not particularly limited, and if the concentration is excessively high, the viscosity of the aqueous electrolyte solution **20** may increase excessively and the ionic conductivity or the like of the aqueous electrolyte solution **20** may deteriorate. In consideration of achieving the conditions that “aqueous electrolyte solution **20** does not have a freezing point at $-40^{\circ}C$. or higher” and of keeping the viscosity of the aqueous electrolyte solution **20** within an appropriate range, the aqueous electrolyte solution **20** may contain the water and potassium polyphosphate dissolved at a concentration of 4 mol or more and 7 mol or less per 1 kg of the water. The concentration may be 6 mol or less.

[0052] The aqueous electrolyte solution **20** may contain potassium ions as cations. In the aqueous electrolyte solution **20**, it is not necessary for the entire potassium ions contained in the aqueous electrolyte solution **20** to be converted as “dissolved potassium polyphosphate”. Namely, the aqueous electrolyte solution **20** may contain more potassium ions than the concentration which can be converted as potassium polyphosphate. For example, if potassium ion sources other than potassium polyphosphate (for example, KOH, CH₃COOK, K₃PO₄, etc.) are added and dissolved in water together with potassium polyphosphate when producing the aqueous electrolyte solution **20**, the aqueous electrolyte solution **20** will contain more potassium ions than the concentration which can be converted as potassium polyphosphate. The aqueous electrolyte solution **20** may contain other cations as long as the above problems can be solved. For example, alkali metal ions other than potassium ions, alkaline earth metal ions, transition metal ions and the like may be contained.

[0053] The aqueous electrolyte solution **20** may contain, as anions, polyphosphate ions (it may be present in a state of being linked to various cations as mentioned above). For example, when containing polyphosphate ions as anions, the pyrophosphate ions may form aggregates (associations) with potassium ions such as P₂O₇⁴⁻, as well as KP₂O₇³⁻, K₂P₂O₇²⁻ and K₃P₂O₇⁻, and may be present as HP₂P₂O₇³⁻, H₂P₂P₂O₇²⁻ and H₃P₂P₂O₇⁻ by drawing H⁺ from H₂O, or may be present as HKP₂P₂O₇⁻, HKP₂P₂O₇²⁻ and H₂KP₂P₂O₇⁻ by the association of H⁺ and K⁺. In the aqueous electrolyte solution **20**, it is not necessary for the entire polyphosphate ions contained in the aqueous electrolyte solution **20** to be converted as “dissolved potassium polyphosphate”. Namely, the aqueous electrolyte solution **20** may contain more polyphosphate ions than the concentration which can be converted as potassium polyphosphate. For example, if polyphosphate ion sources other than potassium polyphosphate (for example, polyphosphate such as H₄P₂O₇) are added and dissolved in water together with potassium polyphosphate when producing an aqueous electrolyte solution **20**, the aqueous electrolyte solution **20** will contain more polyphosphate ions than the concentration which can be converted as potassium polyphosphate. The aqueous electrolyte solution **20** may contain other anions as long as the above problems can be solved. For example, anions derived from other electrolytes mentioned below may be contained.

1.2.2.2 Other Components Containable in Aqueous Electrolyte Solution

[0054] The aqueous electrolyte solution **20** may contain other electrolytes. For example, the aqueous electrolyte solution may contain at least one selected from KPF₆, KBF₄, K₂SO₄, KNO₃, CH₃COOK, (CF₃SO₂)₂NK, KCF₃SO₃, (FSO₂)₂NK, K₂HPO₄, KH₂PO₄, KPO₃ and the like. Other electrolytes may account for 50 mol % or less, 30 mol % or less, or 10 mol % or less of the total amount of electrolytes dissolved in the electrolyte solution (100 mol %).

[0055] The aqueous electrolyte solution **20** may contain, in addition to the above-mentioned electrolytes, an acid, a hydroxide and the like to adjust the pH of the aqueous electrolyte solution **20**. Various additives may be contained.

1.2.3 Freezing Point

[0056] As mentioned above, the aqueous electrolyte solution **20** does not have a freezing point at -40° C. or higher. Here, the presence or absence of “freezing point” of the aqueous electrolyte solution **20** is confirmed by differential scanning calorimetry (DSC). Note that the DSC sweep rate is set at 5° C./min for both descending temperature and ascending temperature, and the sweep range is set as follows: temperature descending to -120° C. from room temperature, followed by temperature ascending to 40° C. The atmosphere in DSC is an atmosphere of inert gas such as Ar, and the pressure is equal to the atmospheric pressure. However, since a sealed aluminum container is used for the evaluation, the atmosphere inside the container is the sealed atmosphere under

atmospheric pressure. If the crystallization peak temperature (freezing point temperature) is not confirmed at -40°C . or higher when the aqueous electrolyte solution is measured under the above conditions, the aqueous electrolyte solution is considered to have “no freezing point at -40°C . or higher”. The aqueous electrolyte solution **20** may have no freezing point at -60°C . or higher, may have no freezing point at -80°C . or higher, no freezing point at -100°C . or higher, or no freezing point at -120°C . or higher. In the aqueous battery **100** of the present disclosure, in order to achieve the conditions that “aqueous electrolyte solution **20** does not have a freezing point at -40°C . or higher”, it is effective to make the polyphosphoric acid concentration in the aqueous electrolyte solution **20** higher (for example, high concentration of 4 mol or more per 1 kg of water), as mentioned above. When the aqueous electrolyte solution **20** does not have a freezing point at -40°C ., it becomes difficult for Al contained in the current collector to elute into the aqueous electrolyte solution **20**, as mentioned below. When the aqueous electrolyte solution **20** does not have a freezing point at -40°C ., it is also possible to use the aqueous battery **100** even at extremely low temperature. Namely, the aqueous battery **100** of the present disclosure operates properly even in cold district.

1.2.4 Other Properties

[0057] As long as the aqueous electrolyte solution **20** contains the solvents and electrolytes mentioned above and meets the requirements for the freezing point mentioned above, there is no particular limitation on other properties. An example of other properties of the aqueous electrolyte solution **20** will be described below.

1.2.4.1 Presence or Absence of Precipitation of Salt

[0058] It is preferable that the aqueous electrolyte solution **20** does not involve salt precipitation when cooling from 0°C . to -40°C . Thus, when the aqueous electrolyte solution **20** does not involve salt precipitation due to temperature change, it becomes possible to perform stable ionic conduction even at low temperature. For example, the aqueous battery **100** can be used even at extremely low temperature in cold district. The aqueous electrolyte solution **20** includes water and potassium polyphosphate dissolved in the water, as mentioned above. According to the inventors' new knowledge, the saturation solubility of potassium polyphosphate in water has low temperature dependence and scarcely changes at low temperature of 0°C . or lower. In this respect, even if potassium polyphosphate is dissolved in the aqueous electrolyte solution **20** at 0°C . at high concentration (for example, high concentration of 4 mol or more per 1 kg of water) and the aqueous electrolyte solution **20** is cooled from 0°C . to -40°C ., precipitation of potassium polyphosphate does not substantially occur in the aqueous electrolyte solution **20**.

1.2.4.2 Viscosity

[0059] If the viscosity of the aqueous electrolyte solution **20** is too high, the ionic conductivity of aqueous electrolyte solution **20** may deteriorate. Meanwhile, if potassium polyphosphate is dissolved at high concentration in the aqueous electrolyte solution **20**, the aqueous electrolyte solution **20** may have a certain level of the viscosity. From the above point of view, the aqueous electrolyte solution **20** may have a viscosity of 40 mPa·s or more and 350 mPa·s or less at 20°C . The viscosity may be 300 mPa·s or less, 250 mPa·s or less, or 200 mPa·s or less.

1.2.4.3 pH

[0060] The pH of the aqueous electrolyte solution **20** is not particularly limited. However, if the pH is too high, the potential window on the oxidation side of the aqueous electrolyte solution may be narrow. In this respect, the pH of the aqueous electrolyte solution may be 4 or more and 13 or less. The pH may be 5 or more, 6 or more, or 7 or more, and may be 12 or less.

1.3 Negative Electrode

[0061] It is possible to use, as the negative electrode **30**, any known negative electrode for an aqueous battery. As shown in FIG. 1, the negative electrode **30** may include a negative electrode active material layer **31** and a negative electrode current collector **32**.

1.3.1 Negative Electrode Active Material Layer

[0062] The negative electrode active material layer **31** contains a negative electrode active material. The negative electrode active material layer **31** is impregnated with the aqueous electrolyte solution **20**. The negative electrode active material layer **31** may contain, in addition to the negative electrode active material, a conductive aid and/or a binder. The negative electrode active material layer **31** may also contain various other additives. The content of each component in the negative electrode active material layer **31** may be appropriately determined according to the objective battery performance. For example, the content of the negative electrode active material may be 40% by mass or more, 50% by mass or more, 60% by mass or more, or 70% or more, and may be 100% or less, or 90% by mass or less, based on 100% by mass of the entire negative electrode active material layer **31** (entire solid content). The shape of the negative electrode active material layer **31** is not particularly limited, and may be, for example, a sheet-shaped negative electrode active material layer having an approximately flat surface. The thickness of the negative electrode active material layer **31** is not particularly limited, and may be, for example, 0.1 μm or more, 1 μm or more, or 10 μm or more, and may be 2 mm or less, 1 mm or less, or 500 μm or less.

[0063] It is possible to use, as the negative electrode active material, any substance capable of functioning as the negative electrode active material of the aqueous battery in which at least one of proton, hydroxide ion and polyphosphate ion is used as a carrier ion. The negative electrode active material has a lower charge-discharge potential than that of the above-mentioned positive electrode active material, and can be appropriately selected in consideration of the potential window of the above-mentioned aqueous electrolyte solution **20**. For example, the negative electrode active material is potassium-transition metal composite oxide; titanium oxide; metal sulfides such as Mo.sub.6S.sub.8 ; elemental sulfur; $\text{KTi.sub.2(PO.sub.4).sub.3}$; NASICON-type compounds; and WO.sub.3 . Alternatively, the negative electrode active material may be a hydrogen storage alloy. Alternatively, the negative electrode active material may be an inorganic compound having a crystal structure that belongs to space group **123**. The inorganic compound having a crystal structure that belongs to space group **123** may contain, for example, element A, element M and O, wherein the element A is at least one of Bi and La, and wherein M is at least one of Bi, Mn, Fe, Co and Ni, and both of element A and element M may be Bi. The negative electrode active material may be those which insert and deinsert a carrier ion by intercalation, or which insert and deinsert a carrier ion by a conversion reaction or an alloying reaction. Only one negative electrode active material may be used alone, or two or more thereof may be used in combination.

[0064] The shape of the negative electrode active material may be any shape capable of functioning as the negative electrode active material of the battery. For example, the negative electrode active material may be in the form of particles. The negative electrode active material may be a solid material, a hollow material, a material with voids, or a porous material. The negative electrode active material may be a primary particle, or a secondary particle obtained by agglomeration of a plurality of primary particles. The mean particle diameter D50 of the negative electrode active material may be, for example, 1 nm or more, 5 nm or more, or 10 nm or more, and may be 500 μm or less, 100 μm or less, 50 μm or less, or 30 μm or less.

[0065] Examples of the conductive aid which can be contained in the negative electrode active material layer **31** include carbon materials such as vapor-phase-grown carbon fiber (VGCF), acetylene black (AB), Ketjen black (KB), carbon nanotube (CNT) and carbon nanofiber (CNF); and metal materials such as nickel, titanium, aluminum, stainless steel and the like which are slightly insoluble (poorly soluble) in an electrolyte solution. The conductive aid may be, for example, in the form of particles or fibers, and the size thereof is not particularly limited. Only one conductive aid may be used alone, or two or more thereof may be used in combination.

[0066] Examples of the binder which can be contained in the negative electrode active material layer **31** include butadiene rubber (BR)-based binders, butylene rubber (IIR)-based binders, acrylate-butadiene rubber (ABR)-based binders, styrene-butadiene rubber (SBR)-based binders,

polyvinylidene fluoride (PVdF)-based binders, polytetrafluoroethylene (PTFE)-based binders, polyimide (PI)-based binders and the like. Only one binder may be used alone, or two or more thereof may be used in combination.

1.3.2 Negative Electrode Current Collector

[0067] As shown in FIG. 1, the negative electrode **30** may include a negative electrode current collector **32** in contact with the negative electrode active material layer **31**. The negative electrode current collector **32** is in contact with an aqueous electrolyte solution **20**. It is possible to use, as the negative electrode current collector **32**, any material capable of functioning as the negative electrode current collector of the aqueous battery. When the above-mentioned positive electrode current collector **12** contains Al, the negative electrode current collector **32** may contain Al or may not contain Al. When the above-mentioned positive electrode current collector **12** does not contain Al, the negative electrode current collector **32** contains Al.

[0068] When the negative electrode current collector **32** contains Al, the entire negative electrode current collector **32** may be composed of Al, or at least a portion of the surface thereof may be composed of Al. For example, the negative electrode current collector **32** may be made of an Al foil, or the surface of a metal foil or some base material may be coated with Al. The negative electrode current collector **32** may be those in which Al is present on at least a portion of the surface in contact with the aqueous electrolyte solution **20**, or Al may be present over the entire surface in contact with the aqueous electrolyte solution **20**.

[0069] The negative electrode current collector **32** may be in the form of foil, plate, mesh, perforated metal and foam. The negative electrode current collector **32** may be formed of a metal foil or a metal mesh. In particular, the metal foil is excellent in ease of handling or the like. The negative electrode current collector **32** may be composed of a plurality of foils. The metal material constituting the negative electrode current collector **32** include those containing at least one element selected from the group consisting of Cu, Ni, Al, V, Au, Pt, Mg, Fe, Ti, Pb, Co, Cr, Zn, Ge, In, Sn and Zr. In particular, the negative electrode current collector **32** may contain at least one selected from the group consisting of Al, Ti, Pb, Zn, Sn, Mg, Zr, and In, and may contain Al as mentioned above. All of Al, Ti, Pb, Zn, Sn, Mg, Zr and In have low work function, and even if the negative electrode current collector **32** comes into contact with the aqueous electrolyte solution **20** on the reduction potential, it is considered to be difficult for the aqueous electrolyte solution **20** to undergo electrolysis. The negative electrode current collector **32** may be those in which the above metal is plated or vapor-deposited on a metal foil or a base material. When the negative electrode current collector **32** is composed of a plurality of metal foils, the negative electrode current collector may have some layer between the plurality of metal foils. The thickness of the negative electrode current collector **32** is not particularly limited, and may be, for example, 0.1 μm or more, or 1 μm or more, and may be 1 mm or less, or 100 μm or less.

1.4 Other Structures

[0070] The aqueous battery **100** may be a secondary battery. The aqueous battery **100** may be an aqueous battery (aqueous proton battery) in which proton is used as a carrier ion, an aqueous battery (aqueous hydroxide ion battery) in which hydroxide ion is used as a carrier ion, or an aqueous battery (aqueous polyphosphoric anion battery) in which polyphosphoric anion is used as a carrier ion. It is considered that when the aqueous battery **100** is an aqueous battery in which one or both of at least proton and hydroxide ion is/are present as a carrier ion, especially, an aqueous battery in which at least proton is used as a carrier ion, high capacity can be easily obtained. The aqueous battery **100** may have, in addition to the above basic structure, for example, the following other structures.

1.4.1 Separator

[0071] As mentioned above, in the aqueous battery **100**, a separator **40** may be present between the positive electrode **10** and the negative electrode **30**. The separator **40**, which may be used, is a separator used in a conventional aqueous electrolyte solution battery (nickel-metal hydride battery,

zinc air battery, etc.). For example, the separator is a separator including, as a base material, a nonwoven fabric made of a material such as cellulose, or a separator including, as a base material, a film made of a resin such as polypropylene. The thickness of the separator **40** is not particularly limited, and may be, for example, 5 μm or more and 1 mm or less.

1.4.2 Bipolar Structure

[0072] As mentioned above, in the aqueous battery **100**, both the positive electrode current collector **12** and the negative electrode current collector **32** may contain Al. In this respect, in the aqueous battery **100**, a current collector containing Al may be used as a bipolar current collector which serves as both the positive electrode current collector **12** and the negative electrode current collector **32**. Namely, the positive electrode **10** and the negative electrode **30** may share one current collector. FIG. 2 shows an example of a bipolar structure. As shown in FIG. 2, the aqueous battery **100** may have a bipolar structure, and a positive electrode active material layer **11** may be formed on one side of an Al-containing current collector **50** (bipolar current collector which functions as both the positive electrode collector **12** and negative electrode collector **32**) and a negative electrode active material layer **31** may be formed on the other side of the current collector **50**. In this case, the Al-containing current collector **50** may not have liquid permeability, that is, the aqueous electrolyte solution **20** may not permeate from the positive electrode active material layer **11** to the negative electrode active material layer **31** via the current collector **50** and vice versa.

1.4.3 Terminal or the Like

[0073] The aqueous battery **100** may include, in addition to the above structure, a terminal, a battery case and the like. Other structures are obvious to those skilled in the art who refer to the present application, and are therefore explanation will be omitted here.

1.5 Method for Producing Aqueous Battery

[0074] The aqueous battery **100** of the present disclosure can be produced, for example, as follows.

1.5.1 Method for Producing Aqueous Electrolyte Solution

[0075] The aqueous electrolyte solution **20** can be produced, for example, by mixing water with potassium polyphosphate. Alternatively, the aqueous electrolyte solution can also be produced by mixing water with a potassium ion source and a polyphosphate ion source. The mixing method is not particularly limited, and any known mixing method can be used. By simply filling a container with water and potassium polyphosphate, followed by standing, they are mixed with each other to finally obtain an aqueous electrolyte solution **20**.

1.5.2 Production of Positive Electrode

[0076] The positive electrode **10** is produced, for example, as follows. A positive electrode active material and etc. constituting the positive electrode active material layer **11** is dispersed in a solvent to obtain a positive electrode mixture paste (slurry). The solvent used in this case is not particularly limited, and water and various organic solvents can be used. Using a doctor blade or the like, the positive electrode mixture paste (slurry) is applied on the surface of the positive electrode current collector **12**, and then dried to form a positive electrode active material layer **11** on the surface of the positive electrode current collector **12**, thus obtaining a positive electrode **10**. It is possible to use, as the coating method, an electrostatic coating method, a dip coating method, a spray coating method and the like, including a doctor blade method.

1.5.3 Production of Negative Electrode

[0077] The negative electrode **30** is produced, for example, as follows. A negative electrode active material and etc. constituting the negative electrode active material layer **31** are dispersed in a solvent to obtain an negative electrode mixture paste (slurry). The solvent used in this case is not particularly limited, and water and various organic solvents can be used. Using a doctor blade or the like, the negative electrode mixture paste (slurry) is applied on the surface of the negative electrode current collector **32**, and then dried to form a negative electrode active material layer **31** on the surface of the negative electrode current collector **32**, thus obtaining a negative electrode **30**. It is possible to use, as the coating method, an electrostatic coating method, a dip coating method, a

spray coating method and the like, including a doctor blade method.

1.5.4 Housing or the Like in Battery Case

[0078] The aqueous electrolyte solution **20**, the positive electrode **10** and the negative electrode **30** are housed in a battery case to obtain an aqueous battery **100**. For example, a separator **40** is sandwiched between the positive electrode **10** and negative electrode **30** to obtain a laminate including the positive electrode collector **12**, the positive electrode active material layer **11**, the separator **40**, the negative electrode active material layer **31** and the negative electrode collector **32** in this order. Other members such as terminal are attached to the laminate as necessary. The laminate is housed in a battery case and the battery case is filled with the aqueous electrolyte solution **20**, and the laminate and the electrolyte solution are sealed in the battery case so that the laminate is immersed in the aqueous electrolyte solution **20** to obtain an aqueous battery **100**.

1.6 Function and Effect in Aqueous Battery

[0079] According to the aqueous battery **100** of the present disclosure, it is possible to suppress elution of Al from the electrode collector into the aqueous electrolyte solution **20** by the following function and effect.

1.6.1 Function and Effect when Al is Contained in Positive Electrode Current Collector

[0080] During charging and discharging of the battery, the potential of the positive electrode becomes the potential on the oxidation side. Therefore, Al contained in the positive electrode current collector emits electrons, leading to an easily dissolvable state. Specifically, Al contained in the positive electrode current collector dissolves into the aqueous electrolyte solution while coordinating with anions and water molecules contained in the aqueous electrolyte solution.

[0081] In the aqueous battery **100** of the present disclosure, as mentioned above, the aqueous electrolyte solution **20** does not have a freezing point at -40°C . or higher. Namely, in the aqueous electrolyte solution **20**, H_2O molecules cannot form a network of crystallization with each other, leading to fewer freezable H_2O molecules and fewer free hydroxide ions.

Therefore, it is difficult for Al eluted from the current collector into the aqueous electrolyte solution **20** to diffuse through H_2O and OH^- , and Al eluted into the aqueous electrolyte solution **20** tends to stay in the vicinity of the current collector. Meanwhile, as mentioned above, potassium polyphosphate is dissolved in the aqueous electrolyte solution **20**, that is, anions derived from potassium polyphosphate such as polyphosphate ions can be present in the aqueous electrolyte solution **20**. Therefore, in the aqueous battery **100** of the present disclosure, during charging and discharging of the battery, Al contained in the positive electrode current collector **12** is easily coordinated with anions derived from potassium polyphosphate and eluted. Here, for example, aluminum pyrophosphate has extremely low solubility in the aqueous electrolyte solution **20**. Therefore, Al coordinated with anions derived from potassium polyphosphate is quickly precipitated as a solid. In other words, an insoluble or poor soluble Al compound is precipitated near the surface of the positive electrode collector **12**, and the Al compound adheres to the surface of the positive electrode collector **12** to form a protective film (passive film) on the surface. As a result, in the aqueous battery **100** of the present disclosure, it is possible to suppress elution of Al from the positive electrode collector **12** into the aqueous electrolyte solution **20** by the protective film.

1.6.2 Function and Effect when Al is Contained in Negative Electrode Current Collector

[0082] During charging and discharging of the battery, the potential of the negative electrode becomes the potential on the reduction side. Therefore, electrolysis of the aqueous electrolyte solution in contact with the negative electrode causes generation of hydroxide ions, and the pH of the aqueous electrolyte solution in the vicinity of the negative electrode tends to increase. When the pH of the aqueous electrolyte solution near the negative electrode increases, the solubility of Al in the aqueous electrolyte solution increases, and the Al contained in the negative electrode current collector is easily eluted into the aqueous electrolyte solution.

[0083] In contrast, in the aqueous battery **100** of the present disclosure, as mentioned above, the

aqueous electrolyte solution **20** does not have a freezing point at -40°C . or higher. Namely, in the aqueous electrolyte solution **20**, fewer freezable water is present, in other words, less electrolyzable water is present in the first place. Therefore, elution of Al contained in the negative electrode current collector **32** is difficult to progress. As mentioned above, potassium polyphosphate is dissolved in the aqueous electrolyte solution **20**, that is, anions derived from potassium polyphosphate, such as polyphosphate ions, can be present in the aqueous electrolyte solution **20**. Therefore, in the aqueous battery **100** of the present disclosure, even if Al contained in the negative electrode current collector **32** is eluted into the aqueous electrolyte solution **20** during charging and discharging of the battery, Al is quickly coordinated with anions derived from potassium polyphosphate and deposited as a solid which is an Al compound. In other words, an insoluble or poor soluble Al compound is precipitated near the surface of the negative electrode collector **32**, and the Al compound adheres to the surface of the negative electrode collector **32** to form a protective film (passive film) on the surface. As a result, in the aqueous battery **100** of the present disclosure, it is possible to further suppress elution of Al from the negative electrode collector **32** into the aqueous electrolyte solution **20** by the protective film.

1.6.3 Other Effects

[0084] In the aqueous electrolyte solution batteries, those containing Ti and Ni are used as current collectors to prevent corrosion of the current collector (for example, PTL 1). It has been considered difficult to adopt metals other than these because they elute at, for example, positive electrode potential. However, since Ti and Ni are expensive, an alternative technology using inexpensive metals is needed for the widespread use of the aqueous electrolyte solution batteries. In this respect, in the aqueous battery **100** of the present disclosure, those containing Al are used as current collectors to reduce the overall cost of the battery, while the above-mentioned aqueous electrolyte solution **20** is employed to suppress elution of Al from the current collector into the aqueous electrolyte solution.

2. Method for Suppressing Elution of Al from Current Collector of Aqueous Battery into Aqueous Electrolyte Solution

[0085] The technology of the present disclosure also has an aspect as a method for suppressing elution of Al from the current collector of the aqueous battery in which at least one of proton, hydroxide ion and polyphosphate ion is used as a carrier ion into the aqueous electrolyte solution. Namely, the method of the present disclosure is characterized by using a current collector containing Al and an aqueous electrolyte solution which satisfies the following requirements (1) and (2) in the aqueous battery in which at least one of proton, hydroxide ion and polyphosphate ion is used as a carrier ion. Details of the aqueous electrolyte solution and details of the battery structure are as mentioned above. [0086] (1) The aqueous electrolyte solution contains water and potassium pyrophosphate dissolved in the water. [0087] (2) The aqueous electrolyte solution does not have a freezing point of -40°C . or higher.

3. Vehicle Having Aqueous Battery

[0088] As mentioned above, according to the aqueous battery of the present disclosure, it is possible to suppress elution of Al from the current collector into the aqueous electrolyte solution. Namely, deterioration of the battery is easily suppressed. Such aqueous battery can be suitably used, for example, in at least one vehicle selected from hybrid electric vehicle (HEV), plug in hybrid electric vehicle (PHEV) and battery electric vehicle (BEV). Namely, the technology of the present disclosure also has an aspect as a vehicle having an aqueous battery, the aqueous battery including a positive electrode, an aqueous electrolyte solution and a negative electrode, wherein one or both of the positive electrode and the negative electrode has/have a current collector containing Al, the current collector is in contact with the aqueous electrolyte solution, the aqueous electrolyte solution contains water and potassium polyphosphate dissolved in the water, at least one of proton, hydroxide ion and polyphosphate ion contained in the aqueous electrolyte solution behaves as a carrier ion, and the aqueous electrolyte solution has no freezing point at -60°C . or

higher. Details of the aqueous electrolyte solution and details of the battery structure are as described above.

EXAMPLES

[0089] Hereinafter, the technology of the present disclosure will be described in more detail by way of Examples, but the technology of the present disclosure is not limited to the following Examples.

1. Fabrication of Aqueous Electrolyte Solution

[0090] K.sub.4P.sub.2O.sub.7 was dissolved in 1 kg of pure water at a predetermined concentration (0.5 to 5 mol) to obtain an aqueous electrolyte solution for evaluation.

2. Fabrication of Electrochemical Cell

[0091] In an electrochemical cell (VM4, manufactured by EC FRONTIER CO., LTD), an Al foil was used for a working electrode, Pt mesh was used for a counter electrode, Ag/AgCl was used for a reference electrode, and the above aqueous electrolyte solution was used as an electrolyte solution.

3. Evaluation Conditions

[0092] A constant current was applied to an electrochemical cell at 25° C. for 30 minutes under the following conditions (1-1) or (1-2). A constant electric potential was applied to the electrochemical cell at 25° C. for 30 minutes under the following conditions (2-1) or (2-2). Tests were carried out for each of current and potential on the oxidation side, and current and potential on the reduction side.

(Oxidation Side)

[0093] (1-1) Constant current: 0.1.fwdarw.0.1.fwdarw.0.2.fwdarw.0.3.fwdarw.0.5 mA/cm.sup.2, for 30 minutes each. [0094] (OCP for 30 minutes between evaluations)

[0095] (2-1) Constant voltage: 1.0.fwdarw.1.1.fwdarw.1.2.fwdarw.1.4.fwdarw.1.6 V (vs. Ag/AgCl), for 30 min each [0096] (OCP for 30 minutes between evaluations)

(Reduction side) [0097] (1-2) Constant current: -0.1.fwdarw.-0.1.fwdarw.-0.2.fwdarw.

-0.3.fwdarw.-0.5 mA/cm.sup.2, for 30 minutes each [0098] (OCP for 30 minutes between

evaluations) [0099] (2-2) Constant voltage: -1.3.fwdarw.-1.4.fwdarw.-1.5.fwdarw.-1.7.fwdarw.-1.9 V (vs. Ag/AgCl), for 30 min each [0100] (OCP of r30 min between evaluations)

4. Evaluation Results (in the Case of Constant Current)

4.1 Aforementioned Condition 1-1, in the Case of 0.5 m Electrolyte Solution

[0101] When an oxidation current was applied in an electrochemical cell using a 0.5 mol/kg K.sub.4P.sub.2O.sub.7 aqueous electrolyte solution, an Al foil of an electrode (positive electrode) on the oxidation side disappeared and the electrolyte solution was transformed into a white gel. A potential-pH diagram shows that a standard electrode potential of Al in the aqueous electrolyte solution at pH 11 is about -2.3 V (vs. SHE), so that there is a possibility that Al is eluted (corroded) just by immersing the Al foil in the aqueous electrolyte solution, and it is considered that elution is accelerated by application of a small oxidation current. In fact, as a result of application of the oxidation current using the Al foil, the evaluation surface in contact with the electrolyte solution disappeared completely, which indicates that the protective layer of Al by its original oxide film did not function at all and elution progressed. Main cause of the white gel-like appearance of the electrolyte solution after the evaluation is that eluted Al ions interacted with P.sub.2O.sub.7 ions in the electrolyte solution to precipitate as Al.sub.4(P.sub.2O.sub.7).sub.3. This suggested that when Al ions interact with P.sub.2O.sub.7 ions, a compound with very low solubility is produced and precipitated as a solid. FIG. 3 shows a time-potential curve when a 0.5 m aqueous electrolyte solution is used and a constant current on the oxidation side is applied.

4.2 Aforementioned Condition 1-1, in the Case of 5 m Electrolyte Solution

[0102] When an oxidation current was applied in an electrochemical cell using a 5 mol/kg K.sub.4P.sub.2O.sub.7 aqueous electrolyte solution, the potential continued to increase with time and reached the cut voltage of the device, causing the evaluation to be interrupted. It is considered that the overvoltage increased due to the passivation of the Al foil surface and gradual

electrochemical insulation of the solid-liquid interface. Looking at the Al foil after evaluation, the evaluated surface retained its metallic luster and the aqueous electrolyte solution showed no change at all from the initial state, thus confirming that the state was very different from that in the case of the 0.5 m electrolyte solution. As mentioned above, it has been confirmed that when Al and P.sub.2O.sub.7 ions interact with each other, solid precipitates with very low solubility are generated. In this respect, in the dilute solution such as the above 0.5 m electrolyte solution, it is considered that the dissolved Al ions are once dissolved and diffused using H.sub.2O and OH.sup.- as ligands, and then gradually solidified by interacting with P.sub.2O.sub.7 ions, leading to precipitation of solids in the aqueous electrolyte solution. As a result, the solids are deposited and precipitated in the aqueous electrolyte solution, and elution of Al into the electrolyte solution have progressed. In contrast, in the case of the 5 m electrolyte solution, the concentration of P.sub.2O.sub.7 ions in the electrolyte solution was very high, and the discoloration of a pH test paper immersed in the electrolyte solution after the below-mentioned evaluation on the reduction side was also slow. Therefore, it is considered that the diffusion action via H.sub.2O and OH.sup.- is scarcely exerted, and Al ions eluted from the Al foil promptly interact with P.sub.2O.sub.7 ions before diffusing far away. Therefore, it is considered that the solid is precipitated near the surface of the Al foil, and the solid adheres to the surface of the Al foil to form a passive film (protective film) such as $\text{Al.sub.4(P.sub.2O.sub.7).sub.3}$, leading to suppression of continuous elution of Al. FIG. 4 shows a time-potential curve when a 5 m aqueous electrolyte solution was used and a constant current on the oxidation side was applied.

4.3 Aforementioned Condition 1-2, in the Case of 1 m Electrolyte Solution

[0103] In an ordinary aqueous electrolyte solution, when a reducing current flows, hydrogen gas is generated and the pH of the electrolyte increases, as shown in the following formula. Therefore, when an Al foil made of amphoteric metal is used in the electrode (negative electrode) on the reduction side, as the electrolyte solution becomes a strong base with an increase in pH, Al is eluted from the Al foil into the electrolyte solution and thus the Al foil eventually disappears. In fact, when a reducing current was applied in an electrochemical cell using a 1 mol/kg $\text{K.sub.4P.sub.2O.sub.7}$ aqueous electrolyte solution, the Al foil on the reducing electrode (negative electrode) disappeared and the electrolyte solution was transformed into a white gel-like state. This is considered to be due to elution of Al from the Al foil into the electrolyte solution and precipitation of $\text{Al.sub.4(P.sub.2O.sub.7).sub.3}$ in the electrolyte solution, similar to the case where the oxidation current is applied in the 0.5 m electrolyte solution. FIG. 5 shows a time-potential curve when a 1 m aqueous electrolyte solution was used and a constant current on the reduction side was applied.



4.4 Aforementioned Condition 1-2, in the Case of 5 m Electrolyte Solution

[0104] In the 5 mol/kg $\text{K.sub.4P.sub.2O.sub.7}$ aqueous electrolyte solution, Al was not eluted after application of the electric current and retained its original shape, and no change was observed in the electrolyte solution. When a pH test paper was immersed in the electrolyte solution after evaluation, the color did not change immediately after immersion, but gradually changed to purple after a few minutes, indicating pH 14. This suggests that when the electrolyte of the aqueous electrolyte solution is mainly composed of $\text{K.sub.4P.sub.2O.sub.7}$, the electrolyte solution differs from ordinary aqueous solutions in elementary properties, and the diffusion of H.sub.2O and OH.sup.- in the solution is very slow, and that Al foil is not eluted even in the presence of such a strong base because a passive film such as $\text{Al.sub.4(P.sub.2O.sub.7).sub.3}$ was formed on the surface of the Al foil, similar to the evaluation results on the oxidation side mentioned above. FIG. 6 shows a time-potential curve when a 5 m aqueous electrolyte solution is used and a constant current is applied on the reduction side.

4.5 Supplementation

-1.56 -1.60 -1.63 -1.60 -1.58 -0.24 2.19 4.36 5.50 6.31 7.42 Ni -0.27 -1.23 -1.25 -1.31 -1.35
-1.40 -0.25 0.96 0.97 1.04 1.09 1.16 Sn -0.97 -1.80 -1.83 -1.87 -1.90 -1.97 -0.97 -0.92 -0.91
— — — Cu -0.39 -1.48 -1.49 -1.52 -1.52 -1.53 -0.37 -0.25 -0.25 -0.21 -0.19 -0.15 Zn -1.38
-1.74 -1.75 -1.79 -1.82 -1.85 -1.36 -1.29 -1.30 -1.29 -1.28 -1.26 Pt -0.22 -1.20 -1.22 -1.29
-1.35 -1.41 -0.20 1.41 1.43 1.53 1.60 1.69 W -0.48 -1.40 -1.41 -1.45 -1.46 -1.48 -0.50 -0.24
-0.23 -0.19 -0.17 -0.13

[0109] As is apparent from the results shown in Table 1, only the Ti foil showed a sharp increase in electrode resistance due to passivation, similar to the Al foil. A Ni foil and a Pt foil are known to be stable in aqueous solution systems with a pH higher than acidic, even when they are at oxidation side potential, and shows an ordinary current-potential relationship. In contrast, for a Sn foil, a Cu foil, a Zn foil and a W foil, which are known to be unstable at the oxidizing potential, unlike an Al foil, elution of metal ions continued to progress even in a 5 mol/kg K₂P₂O₇ aqueous electrolyte solution. This revealed that if the solubility of the eluted metal ion and the P₂O₇ compound coordinated thereto is not low, the elution reaction cannot be stopped because a passive film is not formed by the adhesion and deposition of the compound. Namely, the elution suppression effect of the metallic foil by the passivation film can be said to be significantly exhibited when a metallic foil containing Al is used.

7. Evaluation Assuming Aqueous Battery

[0110] A 5 mol/kg K₂P₂O₇ aqueous solution was prepared as the aqueous electrolyte solution. An Al foil or a Ti foil was prepared as a current collector, Ni(OH)₂ as a positive electrode active material, acetylene black (AB) as a conductive aid, and SBR and CMC as binders were mixed with each other in a mass ratio of Ni(OH)₂:AB:SBR:CMC=77:20:2.5:0.5 to fabricate a positive electrode active material mixture. Using a doctor blade, the positive electrode active material mixture was uniformly applied to the surface of the Al foil or Ti foil and then dried to obtain a positive electrode for evaluation. Namely, the positive electrode is that in which a positive electrode active material layer containing a positive electrode active material is formed on the surface of the Al foil or Ti foil as a positive electrode current collector. La₂Ni₇ as a negative electrode active material, acetylene black (AB) as a conductive aid, and SBR and CMC as binders were mixed with each other in a mass ratio of

La₂Ni₇:AB:SBR:CMC=77:20:2.5:0.5 to fabricate a negative electrode active material mixture. Using a doctor blade, the negative electrode active material mixture was uniformly applied to the surface of the Al foil or Ti foil and then dried to obtain a negative electrode for evaluation. Namely, the negative electrode is that in which a negative electrode active material layer containing a negative electrode active material is formed on the surface of the Al foil or Ti foil as a negative electrode current collector. Using the above aqueous electrolyte solution, positive electrode and negative electrode, an evaluation cell (SB9, manufactured by EC FRONTIER CO., LTD) was formed. Charge-discharge tests were performed on each of the formed evaluation cells to obtain charge-discharge curves. The results are shown in FIG. 7A and FIG. 7B. FIG. 7A shows the results when Al foil was used as a current collector, and FIG. 7B shows the results when Ti foil was used as a current collector. In FIG. 7A and FIG. 7B, the solid line is the charge curve and the dashed line is the discharge curve. As is clear from the results shown in FIG. 7A and FIG. 7B, charging and discharging were possible for both evaluation cells. This revealed that sufficient conductivity is ensured between the active material and the Al foil when charging/discharging is performed after coating and forming the electrode, and that passive film is difficult to form between the solid and the solid, such as between the active material and the Al foil. Namely, in the aqueous battery, it is considered that the adverse effect due to formation of the passive film is not substantially exerted. Although the above example shows an aqueous battery in which the carrier ion is a proton, the carrier ion in an aqueous battery may be proton, hydroxide ion, polyphosphate ion, or a combination of these ions.

8. Summary

[0111] As is apparent from above results, when an aqueous electrolyte solution containing K.sub.2P.sub.2O.sub.7 is used as the electrolyte, it is possible to perform charging and discharge of the active material while suppressing elution of Al foil at the oxidation and reduction potentials if the concentration of K.sub.2P.sub.2O.sub.7 is as high as 4 mol/kg or more. Namely, it is possible for an aqueous battery including a positive electrode, an aqueous electrolyte solution and a negative electrode, wherein one or both of the positive and negative electrodes has/have a current collector containing Al, the current collector is in contact with the aqueous electrolyte solution, and the aqueous electrolyte solution contains water and potassium pyrophosphate dissolved at a concentration of 4 mol/kg or more per 1 kg of the water, at least one of proton, hydroxide ion and polyphosphate ion contained in the aqueous electrolyte solution behaves as a carrier ion, to suppress elution of Al from the current collector into the aqueous electrolyte solution.

9. Further Examination of Aqueous Electrolyte Solution

[0112] In the above, an examination was made of the case where only K.sub.2P.sub.2O.sub.7 is dissolved in pure water as an electrolyte in an aqueous electrolyte solution. As a result, it has been found that when the concentration of K.sub.2P.sub.2O.sub.7 is 4 mol/kg or more, elution of Al at the oxidation and reduction potentials is suppressed by the formation of a passive film on the surface of the Al foil. However, this concentration of “4 mol/kg” is not necessarily the minimum concentration required to suppress elution of Al. For example, if other electrolytes or some additives are dissolved together with K.sub.2P.sub.2O.sub.7 in the aqueous electrolyte solution, there is a possibility that elution of the Al foil at the oxidation and reduction potentials can be suppressed even if the concentration of K.sub.2P.sub.2O.sub.7 is less than 4 mol/kg. Namely, if two conditions below can be satisfied, elution of Al at the oxidation potential and reduction potential is considered to be suppressed even if the concentration of K.sub.2P.sub.2O.sub.7 in the aqueous electrolyte solution is less than 4 mol/kg: [0113] (1) Al ions eluted from the Al foil into the aqueous electrolyte solution interact with anions (for example, P.sub.2O.sub.7 ions) derived from K.sub.2P.sub.2O.sub.7 and are precipitated as an insoluble compound, and [0114] (2) The insoluble compound is precipitated in the vicinity of the Al foil and adheres to the surface of the Al foil to form a passive film (the eluted Al does not diffuse far from the Al foil via H.sub.2O and OH.sup.-).

[0115] The present inventors have investigated the difference between the physical properties of the aqueous electrolyte solution in which elution of Al can be suppressed by satisfying conditions (1) and (2) and the physical properties of the aqueous electrolyte solution in which Al elution cannot be suppressed because conditions (1) and (2) are not satisfied through various tests.

9.1 Fabrication of Aqueous Electrolyte Solution

[0116] K.sub.4P.sub.2O.sub.7 was dissolved in 1 kg of pure water to a predetermined concentration (0.5 to 7 mol) to obtain an aqueous electrolyte solution for evaluation.

9.2 Confirmation by DSC

[0117] The peak crystallization temperature (freezing point temperature) and glass transition temperature of each aqueous electrolyte solution were confirmed by differential scanning calorimetry (DSC). Note that the DSC sweep rate was set at 5° C./min for both descending temperature and ascending temperature, and the sweep range was set as follows: temperature descending to -120° C. from room temperature, followed by temperature ascending to 40° C. The atmosphere in DSC was an atmosphere of inert gas such as Ar, and the pressure was equal to the atmospheric pressure. However, since a sealed aluminum container was used for the evaluation, the atmosphere inside the container was the sealed atmosphere under atmospheric pressure. FIG. 8A shows the relationship between the concentration and the crystallization peak temperature (freezing point) of an aqueous electrolyte solution. FIG. 8B shows the relationship between the concentration and the crystallization peak intensity of an aqueous electrolyte solution. FIG. 9 shows the relationship between the concentration and the glass transition temperature of an aqueous electrolyte solution.

[0118] As is apparent from the results shown in FIG. 8A and FIG. 8B, when the concentration of

K.sub.4P.sub.2O.sub.7 in the aqueous electrolyte solution is 4 mol/kg or more, there is no crystallization peak in DSC, that is, the aqueous electrolyte solution has no freezing point at -40° C. or higher. As is apparent from the results shown in FIG. 9, the glass transition temperature changes specifically when the concentration of K.sub.4P.sub.2O.sub.7 in the aqueous electrolyte solution is around 4 mol/kg.

[0119] These results suggest that when the concentration of K.sub.4P.sub.2O.sub.7 in the aqueous electrolyte solution is 4 mol/kg or more, the solution structure (clusters, networks, etc.) is significantly changed due to the disappearance of interactions between H.sub.2O molecules. For example, it is thought that H.sub.2O molecules are surrounded by ions and aggregates (associations) derived from K.sub.4P.sub.2O.sub.7, and the network derived from K.sub.4P.sub.2O.sub.7 becomes stronger, and H.sub.2O molecules can no longer form a crystallization network with each other.

[0120] In other words, if “aqueous electrolyte solution in which K.sub.4P.sub.2O.sub.7 is dissolved and does not have a freezing point at -40° C. or higher”, it can be said that the dissolved Al can react with anions derived from K.sub.4P.sub.2O.sub.7, and the network of H.sub.2O molecules and OH.sup.- required for the eluted Al to diffuse in the solution is absent, and that the above two conditions, that is: [0121] (1) Al ions eluted from the Al foil into the aqueous electrolyte solution interact with anions (for example, P.sub.2O.sub.7 ions) derived from K.sub.4P.sub.2O.sub.7 and are deposited as an insoluble compound; and [0122] (2) The insoluble compound precipitates in the vicinity of the Al foil and adheres to the surface of the Al foil to form a passive film (the eluted Al does not diffuse far from the Al foil via H.sub.2O and OH.sup.-)

can be satisfied. For example, even if the concentration of K.sub.4P.sub.2O.sub.7 in the aqueous electrolyte solution is less than 4 mol/kg, the above conditions (1) and (2) can be satisfied by dissolving other electrolytes and additives so that “the aqueous electrolyte solution has no freezing point at -40° C. or higher”, (1) and (2) above are considered to be satisfied.

9.3 Presence or Absence of Salt Precipitation after Cooling

[0123] Each aqueous electrolyte solution was cooled from 0° C. to -40° C., and the presence of salt precipitation was checked by DSC. As a result, no peaks originating from salt precipitation were observed in any of the aqueous electrolyte solution concentrations.

[0124] Among conventional highly concentrated aqueous electrolyte solutions, there are those in which the amount of dissolvable electrolyte varies greatly depending on temperature, and salts are easily precipitated by temperature changes. For example, a highly concentrated lithium imide salt solution known as an aqueous electrolyte solution for aqueous lithium ion batteries, and a highly concentrated sodium imide salt solution known as an aqueous electrolyte solution for aqueous sodium ion batteries, precipitate salt when the temperature drops from room temperature by several degrees, and there is concern that the precipitated salt may inhibit battery reaction. In contrast, the aqueous electrolyte solution for aqueous batteries in this example can be used in various environments as a stable electrolyte that does not freeze at extremely low temperatures and does not cause salt precipitation, as mentioned above.

9.4 Confirmation of Viscosity

[0125] The viscosity of each aqueous electrolyte solution at 20° C. was confirmed. The viscosity was measured using a laboratory vibration viscometer (MODEL VM-10A-L, VM-10A-M, SEKONIC). FIG. 10 shows the relationship between the concentration and viscosity of the aqueous electrolyte solution. As shown in FIG. 10, viscosity increases rapidly when the concentration of K.sub.4P.sub.2O.sub.7 in the aqueous electrolyte solution is 4 mol/kg or more. For example, from the viewpoint of suppressing deterioration of the ionic conductivity, the smaller the viscosity of the aqueous electrolyte solution, the better. For example, if the concentration of K.sub.4P.sub.2O.sub.7 is 7 mol/kg or less, the viscosity does not increase excessively and is suitable.

10. Supplementation

[0126] In the above example, the case in which potassium pyrophosphate is dissolved as potassium

polyphosphate in an aqueous electrolyte solution was illustrated. However, potassium polyphosphate dissolved in the aqueous electrolyte solution is not limited to potassium pyrophosphate. The present inventor has confirmed that even when potassium polyphosphate other than potassium pyrophosphate (e.g., potassium tripolyphosphate) is dissolved in the aqueous electrolyte solution instead of or together with potassium pyrophosphate, the above effect of passivation of the Al foil surface is obtained and the same effect as above is exerted.

11. Conclusion

[0127] From the above results, it can be said that when an aqueous battery in which at least one of proton, hydroxide ion and polyphosphate ion is used as a carrier ion is formed, it is possible to suppress elution of Al from the current collector containing Al into the aqueous electrolyte solution at the oxidation potential and reduction potential if the aqueous electrolyte solution meets the following requirements (A) and (B). [0128] (A) The aqueous electrolyte solution contains water and potassium polyphosphate dissolved in the water. [0129] (B) The aqueous electrolyte solution does not have a freezing point -40°C . or higher.

REFERENCE SIGNS LIST

[0130] **10**: Positive electrode [0131] **11**: Positive electrode active material layer [0132] **12**: Positive electrode current collector [0133] **20**: Aqueous electrolyte solution [0134] **30**: Negative electrode [0135] **31**: Negative electrode active material layer [0136] **32**: Negative electrode current collector [0137] **40**: Separator [0138] **100**: Aqueous battery

Claims

1. An aqueous battery comprising a positive electrode, an aqueous electrolyte solution and a negative electrode, wherein one or both of the positive electrode and the negative electrode has/have a current collector containing Al, the current collector is in contact with the aqueous electrolyte solution, the aqueous electrolyte solution contains water and potassium polyphosphate dissolved in the water, at least one of proton, hydroxide ion and polyphosphate ion contained in the aqueous electrolyte solution behaves as a carrier ion, and the aqueous electrolyte solution has no freezing point at -40°C . or higher.
 2. The aqueous battery according to claim 1, wherein the aqueous electrolyte solution does not involve salt precipitation when cooling from 0°C . to -40°C .
 3. The aqueous battery according to claim 1, wherein at least the positive electrode has the current collector.
 4. The aqueous battery according to claim 1, wherein the aqueous electrolyte solution contains water and potassium polyphosphate dissolved at a concentration of 4 mol or more and 7 mol or less per 1 kg of the water.
 5. The aqueous battery according to claim 1, wherein the aqueous electrolyte solution has a viscosity of 40 mPa.Math.s or more and 350 mPa.Math.s or less at 20°C .
 6. The aqueous battery according to claim 1, having a bipolar structure, wherein a positive electrode active material layer is formed on one side of the current collector and a negative electrode active material layer is formed on the other side of the current collector.
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