

ELECTROLYTE AND VANADIUM REDOX FLOW BATTERY

[0001] This application claims priority to the Chinese Patent Application No. 202211446542.2 filed with the China Patent Office on November 21, 2022,
5 entitled “Electrolyte Solutions and All-Vanadium Redox Flow Batteries”, the entire content of which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] The present disclosure relates to a technical field of electrolyte
10 solution preparation, and specifically relates to an electrolyte solution and an all-vanadium redox flow battery.

BACKGROUND

[0003] The all-vanadium redox flow battery is a redox flow battery in which vanadium ions of different valences are used as positive and negative active
15 substances, and the active substances are dissolved in the supporting electrolyte and present in a liquid circulating flow state. As one of the new energy storage batteries, the all-vanadium redox flow battery has the characteristics of large capacity, high safety, long life, and resource saving, and can be widely used in renewable energy power generation, grid peak shaving, smart micro-grid, backup
20 power, and other fields. The electrolyte solution is the storage carrier of electrical energy in the all-vanadium redox flow battery system, and its performance directly affects the electrode life, energy density and efficiency, system cost and other indicators of the system, and is related to the reliability of the battery system.

[0004] The long-term stable operation of the all-vanadium redox flow
25 battery system depends on two factors: the stability of the battery material and the stability of the electrolyte solution. Frequent high-SOC operation (overcharging)

of the battery will cause the system electrode material to oxidize and lose conductivity; high SOC electrolytes are prone to crystallization or precipitation at high temperatures; for electrolytes containing high-concentration HCl systems, a large amount of Cl_2 evolution causes serious corrosion of battery-related materials and increasing system environmental risks. Therefore, reasonable control of chlorine gas generation during battery operation is an urgent problem to be solved.

TECHNICAL PROBLEM

[0005] This present disclosure provides an electrolyte solution that controls the amount of chlorine gas evolution by adjusting the concentration of chlorine ions in the electrolyte solution to solve the problem of excess chlorine gas evolution. Another object of the present disclosure is to provide an all-vanadium redox flow battery containing the above electrolyte solution.

TECHNICAL SOLUTIONS

[0006] In a first aspect, embodiments of the present disclosure provide an electrolyte solution, the electrolyte solution includes: a positive electrolyte solution and a negative electrolyte solution, the positive electrolyte solution and negative electrolyte solution include chloride ions, sulfate ions and vanadium ions; both the positive electrolyte solution and the negative electrolyte solution satisfy:

[0007] $3.0 \leq [c(\text{Cl}^-) + c(\text{SO}_4^{2-})] / c(\text{V}^{n+}) \leq 3.6;$

[0008] the $c(\text{Cl}^-)$ represents a concentration of the chloride ions, the $c(\text{SO}_4^{2-})$ represents a concentration of the sulfate ions, and the $c(\text{V}^{n+})$ represents a concentration of the vanadium ions.

[0009] In some embodiments,

[0010] the $c(\text{Cl}^-)$ satisfies: $1.5 \text{ mol/L} \leq c(\text{Cl}^-) \leq 6.5 \text{ mol/L}$; and/or

- [0011] the $c(\text{SO}_4^{2-})$ satisfies: $0.5 \text{ mol/L} \leq c(\text{SO}_4^{2-}) \leq 5.5 \text{ mol/L}$; and/or
- [0012] the $c(\text{V}^{n+})$ satisfies: $1.6 \text{ mol/L} \leq c(\text{V}^{n+}) \leq 2.65 \text{ mol/L}$.
- [0013] In some embodiments, the $c(\text{Cl}^-)$ and the $c(\text{SO}_4^{2-})$ further satisfy:
- [0014] $0.4 \leq c(\text{Cl}^-)/c(\text{SO}_4^{2-}) \leq 3.1$.
- 5 [0015] In some embodiments, the $c(\text{Cl}^-)$ and the $c(\text{V}^{n+})$ further satisfy:
- [0016] $0.5 \leq c(\text{Cl}^-)/c(\text{V}^{n+}) \leq 3.0$.
- [0017] In some embodiments, the positive electrolyte solution further includes phosphate ions, and the positive electrolyte solution further satisfies:
- [0018] $2.9 \leq [c(\text{Cl}^-) + c(\text{SO}_4^{2-}) + c(\text{PO}_4^{3-})]/c(\text{V}^{n+}) \leq 3.7$;
- 10 [0019] the $c(\text{PO}_4^{3-})$ represents a concentration of the phosphate ions.
- [0020] In some embodiments, the $c(\text{PO}_4^{3-})$ further satisfies:
- [0021] $0.01 \text{ mol/L} \leq c(\text{PO}_4^{3-}) \leq 0.15 \text{ mol/L}$; and/or
- [0022] $0.02 \leq c(\text{PO}_4^{3-})/c(\text{V}^{n+}) \leq 0.06$; and/or
- [0023] $[c(\text{Cl}^-) + c(\text{SO}_4^{2-}) + c(\text{PO}_4^{3-}) - 0.8 \times c(\text{V}^{n+})] \geq 4.2 \text{ mol/L}$;
- 15 [0024] $0.8 \times c(\text{V}^{n+})$ represents an average molar concentration of acid group ions bound by the vanadium ions in the positive electrolyte solution.
- [0025] In some embodiments, the negative electrolyte solution further includes phosphite ions, and the negative electrolyte solution further satisfies:
- [0026] $2.9 \leq [c(\text{Cl}^-) + c(\text{SO}_4^{2-}) + c(\text{PO}_3^{3-})]/c(\text{V}^{n+}) \leq 3.7$;
- 20 [0027] the $c(\text{PO}_3^{3-})$ represents the concentration of the phosphite ions.
- [0028] In some embodiments, the $c(\text{PO}_3^{3-})$ further satisfies:
- [0029] $0.01 \text{ mol/L} \leq c(\text{PO}_3^{3-}) \leq 0.15 \text{ mol/L}$; and/or
- [0030] $0.03 \leq c(\text{PO}_3^{3-})/c(\text{V}^{n+}) \leq 0.1$; and/or
- [0031] $[c(\text{Cl}^-) + c(\text{SO}_4^{2-}) + c(\text{PO}_3^{3-}) - 1.5 \times c(\text{V}^{n+})] \leq 4.5 \text{ mol/L}$;
- 25 [0032] $1.5 \times c(\text{V}^{n+})$ represents an average molar concentration of acid

group ions bound by the vanadium ions in the negative electrolyte solution.

[0033] In some embodiments, the positive electrolyte solution and the negative electrolyte solution further include an additive, and the positive electrolyte solution and the negative electrolyte solution further satisfy:

5 [0034] $2.9 \leq [c(\text{Cl}^-) + c(\text{SO}_4^{2-}) + c(\text{A})] / c(\text{V}^{n+}) \leq 3.7$;

[0035] the $c(\text{A})$ represents a concentration of the additive.

[0036] In some embodiments, the additive satisfies at least one of the following features:

[0037] (a) the concentration of the additive $c(\text{A})$ satisfies:
10 $0.02 \text{ mol/L} \leq c(\text{A}) \leq 0.2 \text{ mol/L}$;

[0038] (b) the additive is one or more additives containing $-\text{OH}$, $-\text{COOH}$ or $-\text{NH}_2$ functional group.

[0039] In some embodiments, the temperature stability range of the electrolyte solution is $-30 \sim 60^\circ\text{C}$.

15 [0040] In some embodiments, the chloride ions are provided by an acid or salt containing the chloride ions; the sulfate ions are provided by an acid or salt containing the sulfate; the vanadium ions are provided by a vanadate.

[0041] In a second aspect, embodiments of the present disclosure also provide an all-vanadium redox flow battery containing the above electrolyte
20 solution.

BENEFICIAL EFFECTS

[0042] Compared with the prior art, the electrolyte solution of this disclosure includes: a positive electrolyte solution and a negative electrolyte, the positive electrolyte solution and negative electrolyte solution include chloride
25 ions, sulfate ions and vanadium ions; both the positive electrolyte solution and negative electrolyte solution satisfy: $2.9 \leq [c(\text{Cl}^-) + c(\text{SO}_4^{2-})] / c(\text{V}^{n+}) \leq 3.6$; $c(\text{Cl}^-)$

represents the concentration of chloride ions, $c(\text{SO}_4^{2-})$ represents the concentration of sulfate ions, $c(\text{V}^{n+})$ represents the concentration of vanadium ions. When Cl^- , SO_4^{2-} and V^{n+} in the electrolyte solution meet the appropriate concentration relationship, the Cl_2 production rate can be greatly reduced, reducing the corrosion of battery materials. At the same time, a small amount of Cl_2 evolved can compensate for the oxidation of the battery electrode carbon felt, and the electrode The carbon felt protects and reduces the risk level of chlorine-containing electrolytes operation environmental.

BRIEF DESCRIPTION OF THE DRAWINGS

[0043] FIG. 1 is a flow chart of the preparation process of the all-vanadium redox flow battery electrolyte solution provided by some embodiments of the present disclosure;

[0044] FIG. 2 shows the electrode corrosion situation after using the electrolyte solution provided in Example 1;

[0045] FIG. 3 shows the electrode corrosion situation after using the electrolyte solution provided in Comparative Example 1.

DETAILED DESCRIPTION

[0046] The present disclosure provides an electrolyte solution and all-vanadium redox flow battery. In order to make the purpose, technical solutions and effects of the present disclosure clear and definite, the present disclosure will be further described in detail below with reference to the accompanying drawings and examples. It should be understood that the specific embodiments described herein are only used to explain the present disclosure and are not used to limit the present disclosure.

[0047] The applicant found that due to the high temperature (the temperature inside the container in tropical areas will exceed 50 degrees Celsius), in order to avoid easy precipitation of V_2O_5 by the positive electrolyte solution at high temperatures, the temperature range of stable use of the electrolyte solution

is narrowed, and the battery system is equipped with auxiliary equipment for refrigeration, heating, and ventilation, which will consume power and reduce the overall efficiency of the battery system. Therefore, expanding the temperature range of safe use of the electrolyte solution can effectively reduce the cost of auxiliary equipment and its power consumption, and improve the overall efficiency while reducing the cost of the battery system. Moreover, once the heat exchange equipment fails, the high and low temperature resistance of the electrolyte solution itself is particularly important for the overall stability of the battery system. The higher the concentration of vanadium ions in the electrolyte, the higher the energy density of the corresponding system and the higher the cost performance, but the narrower the safe temperature range, the higher the risk of 5-valent vanadium precipitation at high temperatures. The temperature stable range of the traditional pure sulfuric acid system electrolyte solution is smaller, while the energy density of the mixed acid system electrolyte solution of sulfuric acid and hydrochloric acid is greatly improved, but it will produce harmful chlorine gas during battery operation. In addition, the low pressure in the plateau area causes the evolved Cl_2 to be difficult to dissolve back into the electrolyte solution. The highly volatile HCl in the solution is continuously circulated to the magnetic pump, resulting in the aggravation of gas binding, and shutdown of the pump leads to the lack of reactants in the battery and overcharging and burning. The evolution rate of Cl_2 is accelerated due to high Cl^- concentration, and the pressure of the tank increases the risk of Cl_2 escaping from the system. How to reduce the amount of Cl_2 evolved while maintaining its high temperature performance is an urgent problem to be solved for mixed acid electrolytes. At the same time, its excessively high HCl concentration leads to serious low-temperature precipitation problems of the negative electrode trivalent solution (it is very easy to produce VCl_3 crystallization), blocking pipelines and causing the system to fail to operate, which affects the further industrialization of this technology. Therefore, for all-vanadium redox flow battery electrolyte, its

reasonable control of Cl_2 evolution has become an urgent problem to be solved.

[0048] Based on the above problems, embodiments of the present disclosure provide an electrolyte solution for an all-vanadium redox flow battery. The electrolyte solution includes: a positive electrolyte solution and a negative electrolyte, the positive electrolyte solution and negative electrolyte solution include chloride ions, sulfate ions and vanadium ions; both the positive electrolyte solution and negative electrolyte solution satisfy:

$$[0049] \quad 2.9 \leq [c(\text{Cl}^-) + c(\text{SO}_4^{2-})] / c(\text{V}^{n+}) \leq 3.6;$$

[0050] $c(\text{Cl}^-)$ represents a concentration of chloride ions, $c(\text{SO}_4^{2-})$ represents a concentration of sulfate ions, and $c(\text{V}^{n+})$ represents a concentration of vanadium ions.

[0051] In some embodiments, $c(\text{Cl}^-)$ satisfies: $1.5 \text{ mol/L} \leq c(\text{Cl}^-) \leq 6.5 \text{ mol/L}$; the value of $c(\text{Cl}^-)$ can be any one or the range between any two of 1.5 mol/L, 2.0 mol/L, 2.5 mol/L, 3.0 mol/L, 3.5 mol/L, 4.0 mol/L, 4.5 mol/L, 5.5 mol/L, 6.0 mol/L and 6.5 mol/L. It is noted that the specific value of $c(\text{Cl}^-)$ is only given as an example, provided that any value or the range between any two values within the range of 1.5~6.5 mol/L is within the protection scope of this disclosure.

[0052] In some embodiments, $c(\text{Cl}^-)$ further satisfies: $2.5 \text{ mol/L} \leq c(\text{Cl}^-) \leq 5.5 \text{ mol/L}$; $c(\text{Cl}^-)$ further satisfies: $3.0 \text{ mol/L} \leq c(\text{Cl}^-) \leq 5.0 \text{ mol/L}$; $c(\text{Cl}^-)$ most preferably satisfies: $3.5 \text{ mol/L} \leq c(\text{Cl}^-) \leq 4.5 \text{ mol/L}$.

[0053] In some embodiments, $c(\text{SO}_4^{2-})$ satisfies: $0.5 \text{ mol/L} \leq c(\text{SO}_4^{2-}) \leq 5.5 \text{ mol/L}$; the value of $c(\text{SO}_4^{2-})$ can be any one or the range between any two of 0.5 mol/L, 1.0 mol/L, 1.5 mol/L, 2.0 mol/L, 2.5 mol/L, 3.0 mol/L, 3.5 mol/L, 4.0 mol/L, 4.5 mol/L, 5.0 mol/L and 5.5 mol/L. It is noted that the specific value of $c(\text{SO}_4^{2-})$ is only given as an example, provided that any value or the range

between any two values in the range of 0.5~5.5 mol/L is within the protection scope of this disclosure.

[0054] In some embodiments, $c(\text{SO}_4^{2-})$ further satisfies: 1.5 mol/L $\leq c(\text{SO}_4^{2-}) \leq 4.5$ mol/L; $c(\text{SO}_4^{2-})$ further satisfies: 1.5 mol/L $\leq c(\text{SO}_4^{2-}) \leq 3.5$ mol/L; $c(\text{SO}_4^{2-})$ most preferably satisfies: 1.5 mol/L $\leq c(\text{SO}_4^{2-}) \leq 2.5$ mol/L.

[0055] In some embodiments, $c(\text{V}^{n+})$ satisfies: 1.6 mol/L $\leq c(\text{V}^{n+}) \leq 2.65$ mol/L; the value of $c(\text{V}^{n+})$ can be any one or the range between any two of 1.6 mol/L, 1.7 mol/L, 1.8 mol/L, 1.9 mol/L, 2.0 mol/L, 2.1 mol/L, 2.2 mol/L, 2.3 mol/L, 2.4 mol/L, 2.5 mol/L, 2.6 mol/L. It is noted that the specific value of $c(\text{V}^{n+})$ is only given as an example, provided that any value or the range between any two values within the range of 1.6~2.65 mol/L is within the protection scope of this disclosure.

[0056] In some embodiments, under high SOC conditions, the VO_2^+ content is greater than 90%, and high-concentration VO_2^+ will react with Cl^- at a certain rate to generate Cl_2 . The reaction formula is: $2\text{VO}_2^+ + 2\text{Cl}^- + 4\text{H}^+ \rightarrow \text{Cl}_2 + 2\text{VO}^{2+} + 2\text{H}_2\text{O}$. It can be seen that chlorine gas will be produced under high SOC, and Cl^- can improve the stability of VO_2^+ at high temperatures. However, after the range of $2.9 \leq [c(\text{Cl}^-) + c(\text{SO}_4^{2-})]/c(\text{V}^{n+}) \leq 3.6$ is limited, the generation amount of Cl_2 can be controlled within a certain range. At the same time, a certain amount of chlorine gas evolved can compensate for the oxidation of the battery electrode carbon felt and avoid the oxidation of the carbon felt electrode due to insufficient substrate VO_2^+ from overcharging. Based on the above principle, the battery charging open circuit voltage OCV can be expanded from 1.50V to 1.54V, and the system discharge energy density can be increased by more than 20%. In addition, under the controlled Cl^- concentration of 1.5~6.5

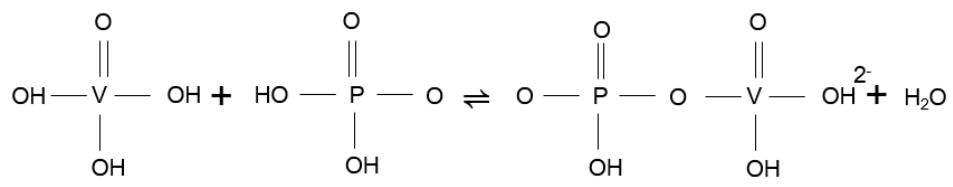
mol/L, it will also avoid environmental dangers caused by gas binding of the circulation pump and increase in system pressure due to high-rate evolution of Cl_2 .

[0057] In some embodiments, $c(\text{Cl}^-)$ and $c(\text{SO}_4^{2-})$ further satisfy:
 5 $0.4 \leq c(\text{Cl}^-)/c(\text{SO}_4^{2-}) \leq 3.1$. It is noted that as long as the range of $c(\text{Cl}^-)/c(\text{SO}_4^{2-})$ is any value in the range of $0.4 \sim 3.1$ or a range between any two values, it is within the protection scope of this disclosure. For the electrolyte, Cl^- and SO_4^{2-} are symbols of the mixed acid system, and the ratio between the two determines the stability of the electrolyte solution. When Cl^- and SO_4^{2-} coexist and reach the
 10 above ratio, on the one hand, HCl saturated vapor pressure can be reduced; on the other hand, since SO_4^{2-} and Cl^- can bind with V^{n+} to form two salts with different spatial structures, it can alleviate the decrease in electrolyte solution stability caused by the structure of a single acid group bound with vanadium ions at high temperatures when it reaches the upper limit of solubility.

[0058] In some embodiments, $c(\text{Cl}^-)$ and $c(\text{V}^{n+})$ further satisfy:
 15 $0.5 \leq c(\text{Cl}^-)/c(\text{V}^{n+}) \leq 3.0$. It is noted that as long as the range of $c(\text{Cl}^-)/c(\text{V}^{n+})$ is any value in the range of $0.5 \sim 3.0$ or a range between any two values, it is within the protection scope of this disclosure. For the electrolyte, the proportional relationship between $c(\text{Cl}^-)$ and $c(\text{V}^{n+})$ can further reflect the situation of chlorine
 20 precipitation. This is because under the appropriate ratio of Cl^- and V^{n+} , after the Cl^- bound by V^{n+} is removed in the solution, there is still free H^+ to maintain the conductivity and solubility of the solution, so as to further maintain the battery efficiency and high-temperature stability of the battery. When the ratio of Cl^- and V^{n+} is within the above range, it can be ensured that Cl^- has strong complexing
 25 ability, and there is still residual Cl^- to provide H^+ and evolve a certain amount of

chlorine gas, and the electrode is protected by a certain amount of chlorine gas evolved.

[0059] In some embodiments, the positive electrolyte solution further includes phosphate ions, and the positive electrolyte solution further satisfies:
 5 $2.9 \leq [c(\text{Cl}^-) + c(\text{SO}_4^{2-}) + c(\text{PO}_4^{3-})] / c(\text{V}^{n+}) \leq 3.7$; $c(\text{PO}_4^{3-})$ represents the concentration of the phosphate ions. When Cl^- , SO_4^{2-} , PO_4^{3-} and V^{n+} in the electrolyte solution meet the above range, the electrolyte solution can protect the electrode performance, and the phosphate ions further improve the stability to V^{n+} , so as to greatly reduce the evolution rate of the chlorine gas. The stabilizing effect of
 10 phosphate ions on V^{n+} is due to its binding with $[\text{VO}_2(\text{H}_2\text{O})_3]^+$, which inhibits the deprotonation process of vanadium ions at high temperatures. The complexation reaction is:



[0060] At the same time, at high temperatures, the HCl-containing
 15 electrolyte solution Cl^- and VO_2^+ generate soluble VO_2Cl to avoid the generation of insoluble V_2O_5 . Under the control of the positive electrode relationship formula $2.9 \leq [c(\text{Cl}^-) + c(\text{SO}_4^{2-}) + c(\text{PO}_4^{3-})] / c(\text{V}^{n+}) \leq 3.7$, low-concentration free HCl further reduces the Cl_2 production rate, which greatly reduces the corrosion resistance requirements of battery materials. At the same time, it reduces the risk level of the
 20 operation environment of the HCl-containing electrolyte, and the tolerance of HCl-containing batteries to plateau areas can be further improved.

[0061] In some embodiments, $c(\text{PO}_4^{3-})$ further satisfies: $0.01 \text{ mol/L} \leq c(\text{PO}_4^{3-}) \leq 0.15 \text{ mol/L}$; the value of $c(\text{PO}_4^{3-})$ can be any one or the range

between any two of 0.01 mol/L, 0.02 mol/L, 0.03 mol/L, 0.04 mol/L, 0.05 mol/L, 0.06 mol/L, 0.07 mol/L, 0.08 mol/L, 0.09 mol/L, 0.10 mol/L, 0.11 mol/L, 0.12 mol/L, 0.13 mol/L, 0.14 mol/L and 0.15 mol/L. It is noted that the specific value of $c(\text{PO}_4^{3-})$ is only given as an example, provided that any value or the range
 5 between any two values within the range of 0.01~0.15 mol/L is within the protection scope of this disclosure.

[0062] In some embodiments, $c(\text{PO}_4^{3-})$ further satisfies: $0.02 \leq c(\text{PO}_4^{3-})/c(\text{V}^{n+}) \leq 0.06$. By limiting the proportional relationship between PO_4^{3-} and V^{n+} , excessive generation of insoluble VOPO_4 precipitation can be avoided, while too
 10 low PO_4^{3-} cannot form an effective spatial configuration and results in no protective effect.

[0063] In some embodiments, $c(\text{PO}_4^{3-})$ further satisfies:

[0064] $[c(\text{Cl}^-) + c(\text{SO}_4^{2-}) + c(\text{PO}_4^{3-}) - 0.8 \times c(\text{V}^{n+})] \geq 4.2 \text{ mol/L}$; $0.8 \times c(\text{V}^{n+})$ represents the average molar concentration of acid group ions bound by vanadium
 15 ions in the positive electrolyte solution. When the above range is met, it can be ensured that after the total acid groups are bound by vanadium ions, there will still be a controllable concentration of free acid to provide H^+ to ensure the high temperature solubility, stability and conductivity of the solution.

[0065] In some embodiments, the negative electrolyte solution further
 20 includes phosphite ions, and the negative electrolyte solution further satisfies: $2.9 \leq [c(\text{Cl}^-) + c(\text{SO}_4^{2-}) + c(\text{PO}_3^{3-})]/c(\text{V}^{n+}) \leq 3.7$; $c(\text{PO}_3^{3-})$ represents the concentration of the phosphite ions. Since an excessively high H^+ concentration in the solution will increase the risk of V^{3+} precipitation, when the negative electrode solution satisfies the above formula, the H^+ provided by the free acid groups must meet
 25 this value range. At the same time, phosphite ions can stabilize trivalent vanadium

ions at low temperatures in the negative electrode of the electrolyte, and in the reducing environment of the negative electrode, phosphorous acid can exist stably without being oxidized.

[0066] In some embodiments, $c(\text{PO}_3^{3-})$ further satisfies: 0.01
 5 $\text{mol/L} \leq c(\text{PO}_3^{3-}) \leq 0.15 \text{ mol/L}$; the value of $c(\text{PO}_3^{3-})$ can be any one or the range between any two of 0.01 mol/L, 0.02 mol/L, 0.03 mol/L, 0.04 mol/L, 0.05 mol/L, 0.06 mol/L, 0.07 mol/L, 0.08 mol/L, 0.09 mol/L, 0.10 mol/L, 0.11 mol/L, 0.12 mol/L, 0.13 mol/L, 0.14 mol/L and 0.15 mol/L. It is noted that the specific value of $c(\text{PO}_3^{3-})$ is only given as an example, provided that any value or the range
 10 between any two values within the range of 0.01~0.15 mol/L is within the protection scope of this disclosure.

[0067] In some embodiments, $c(\text{PO}_3^{3-})$ further satisfies: $0.03 \leq c(\text{PO}_3^{3-})/c(\text{V}^{n+}) \leq 0.1$; when $c(\text{PO}_3^{3-})$ and $c(\text{V}^{n+})$ meet the above range, the low-temperature stabilization effect of phosphite ions can be further improved to
 15 prevent excessive PO_3^{3-} concentration from increasing the viscosity of the negative electrode solution and reducing the conductivity of the solution and increasing the electrochemical reaction resistance of the battery.

[0068] In some embodiments, $c(\text{PO}_3^{3-})$ further satisfies:

[0069] $[c(\text{Cl}^-) + c(\text{SO}_4^{2-}) + c(\text{PO}_3^{3-}) - 1.5 \times c(\text{V}^{n+})] \leq 4.5 \text{ mol/L}$; $1.5 \times c(\text{V}^{n+})$
 20 represents the average molar concentration of acid group ions bound by vanadium ions in the negative electrolyte solution. If the above range is satisfied, after the total acid groups in the solution are bound by vanadium ions, the H^+ precipitated by the remaining free acid groups is not enough to affect the stability of the vanadium ions.

25 [0070] In some embodiments, the positive electrolyte solution and

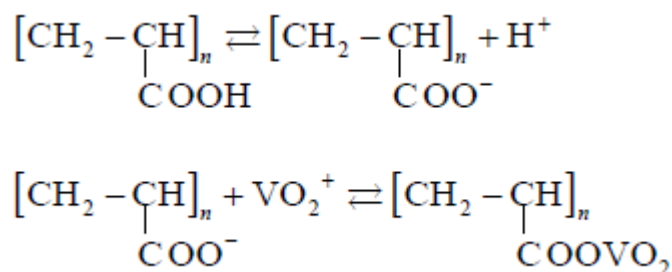
negative electrolyte solution further include an additive, and the positive electrolyte solution and negative electrolyte solution further satisfy: $2.9 \leq [c(\text{Cl}^-) + c(\text{SO}_4^{2-}) + c(\text{A})] / c(\text{V}^{n+}) \leq 3.7$; $c(\text{A})$ represents a concentration of the additive.

[0071] In some embodiments, for the electrolyte solution system
 5 containing Cl^- , if the concentration of Cl^- in the system is too high, a large amount of Cl_2 will be generated, and the additive cannot be added in the presence of the high concentration of Cl_2 because the additive is easily oxidized and decomposed, but the low-rate production of Cl_2 in this disclosure allows the additive to be added safely and exist stably. At the same time, the generation of Cl_2 of the electrolyte
 10 solution containing Cl^- in the positive electrode compensates to protect the positive carbon felt electrode from oxidation. High charging capacity will bring the risk of high-temperature precipitation caused by the increase in positive SOC, and the addition of the additive can maintain stability and further avoid the danger caused by increasing the open circuit voltage.

[0072] In some embodiments, the additive satisfies: the concentration of additive $c(\text{A})$ satisfies: $0.02 \text{ mol/L} \leq c(\text{A}) \leq 0.2 \text{ mol/L}$; the value of $c(\text{A})$ can be any one or a range between any two of 0.02 mol/L, 0.05 mol/L, 0.1 mol/L, 0.15 mol/L and 0.2 mol/L. It is noted that the specific value of $c(\text{A})$ is only given as an
 20 example, provided that any value or the range between any two values within the range of 0.02~0.2 mol/L is within the protection scope of this disclosure.

[0073] In some embodiments, the additive is one or more of additives containing -OH, -COOH or - NH_2 functional group. When the Cl^- concentration is in the range of 1.5~6.5 mol/L, the addition of the additive can effectively maintain high-temperature stability, and the temperature range is wider, and the battery
 25 operating temperature window can reach $-15^\circ\text{C} \sim 60^\circ\text{C}$. This is because -COOH

or -NH₂ group can be adsorbed on the surface of vanadium ions or bound by vanadium ions, forming a structure with a three-dimensional effect, which enhances the repulsive force between vanadium hydrated ions and makes them more dispersed, thereby preventing vanadium ions from colliding with each other, inhibiting the generation of precipitation, and improving the stability of the electrolyte solution. The thermal stabilization mechanism is as follows:



[0074] The increase in the effective hydroxyl functional group -OH can provide more active sites for electron transfer, so that the hydroxyl compound can effectively improve the electrochemical activity of the electrolyte solution. In addition, the additive can improve the reversibility of the VO²⁺/VO₂⁺ electrode process. -COOH or -NH₂ can improve the electron mass transfer process in the VO²⁺/VO₂⁺ electrode process, improve the electrochemical activity, increase the utilization rate of the electrolyte, and improve the battery efficiency and overall performance.

[0075] In some embodiments, the additive may include any one or a combination of more of glycerol, succinic acid, aminomethanesulfonic acid, methanesulfonic acid, glutamic acid, oxalic acid, etc.

[0076] In some embodiments, the temperature stability range of the electrolyte solution is -30~60°C. The temperature stability range of the electrolyte solution is determined by the Cl⁻ concentration. When the Cl⁻ concentration is in

the range of 1.5~6.5 mol/L, the temperature stability range of the electrolyte solution is widened to -30~60°C, which can greatly save investment in thermal management equipment, and reduce auxiliary power consumption and improve energy efficiency of the battery system. The preferred temperature stability range of the electrolyte solution is -15 ~ 60°C; the negative electrolyte solution (trivalent solution) is stable for at least 7 days at an ambient temperature of -15°C; the positive electrolyte solution (5-valent solution) is stable for at least 10 days at an ambient temperature of 60°C.

[0077] In some embodiments, the chloride ions are provided by a chloride ion-containing acid or salt; the sulfate ions are provided by a sulfate-containing acid or salt; the vanadium ions are provided by a vanadate.

[0078] In some embodiments, the chloride ions are provided by hydrochloric acid, the sulfate ions are provided by sulfuric acid, and the vanadium ions are provided by multi-stage purified ammonium vanadate.

[0079] All-vanadium redox flow battery

[0080] The all-vanadium redox flow energy storage battery includes a battery stack and an electrolyte solution storage tank. The battery stack and the liquid storage tank are connected by a liquid inlet pipeline and a liquid outlet pipeline. The liquid inlet pipeline is equipped with a circulation pump.

[0081] The battery stack consists of an ion diaphragm, guide plates, carbon felt electrodes, flow channel frames and fastening end plates in series.

[0082] The diaphragm of the battery:

[0083] Theoretically, only H^+ is allowed to pass through, and the cross-mixing of vanadium ions in different valence states in the positive and negative electrolytes is inhibited. Therefore, a cation exchange membrane with good

conductivity and selective permeability is preferred, and a perfluorosulfonic acid ion exchange membrane can also be used. Improving the hydrophilicity, selective permeability and service life of the ion exchange membrane is one of the ways to improve the efficiency of the vanadium battery.

5 [0084] Other battery materials:

[0085] To achieve large-capacity energy storage in an all-vanadium redox flow battery, several single cells must be connected in series or parallel. In this way, except for the terminal electrodes, basically all electrodes must be made into bipolar electrodes. Due to the strong oxidizing properties of VO_2^+ and the
10 strong acidic property of the electrolyte solution containing sulfuric acid and hydrochloric acid, electrode materials for the vanadium battery must be resistant to strong oxidation and strong acidity, at the same time, they must have low resistance, good conductivity, high mechanical strength, good electrochemical property and other characteristics. The vanadium battery electrode materials are
15 mainly carbon, such as graphite, carbon cloth, carbon felt, etc.; bipolar plates are mostly made of composite materials, such as conductive polymers, polymer composites, etc.

[0086] After the materials of each part of the battery stack are assembled in sequence, they are connected to the corresponding inlets and outlets
20 of the positive and negative electrolyte solution storage tanks, and the all-vanadium redox flow battery is assembled.

[0087] Example 1

[0088] Referring to FIG. 1, taking the multi-stage purified ammonium vanadate $(\text{NH}_4)_x(\text{VO}_3)_y$ as an example, it is calcined at 750°C for 5 hours to
25 obtain high-purity vanadium pentoxide (V_2O_5), reducing gas (NH_4 or H_2) is

continuously introduced, and it is calcined for 10 hours to obtain vanadium tetroxide (V_2O_4) or vanadium trioxide (V_2O_3). These two oxides are mixed in a ratio of 1:1 (trivalent and tetravalent oxides account for 50% each), sulfuric acid and hydrochloric acid are added to make a mixed acid electrolyte solution for the
 5 positive and negative electrodes of the all-vanadium redox flow battery.

[0089] The obtained mixed acid electrolyte solution includes a positive electrolyte solution and a negative electrolyte, and the positive electrolyte solution is controlled to contain 1.9 mol SO_4^{2-} , 3.9 mol Cl^- and 2.0 mol V^{n+} ; the negative electrolyte solution is controlled to contain 1.9 mol SO_4^{2-} , 3.9 mol Cl^- and 2.0 mol
 10 V^{n+} .

[0090] Example 2

[0091] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive electrolyte solution contains 1.9 mol SO_4^{2-} , 4.1 mol Cl^- and 2.0 mol V^{n+} ; the
 15 negative electrolyte solution contains 1.9 mol SO_4^{2-} , 4.1 mol Cl^- and 2.0 mol V^{n+} .

[0092] Example 3

[0093] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive electrolyte solution contains 1.9 mol SO_4^{2-} , 4.3 mol Cl^- and 2.0 mol V^{n+} ; the
 20 negative electrolyte solution contains 1.9 mol SO_4^{2-} , 4.3 mol Cl^- and 2.0 mol V^{n+} .

[0094] Example 4

[0095] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive electrolyte solution contains 1.9 mol SO_4^{2-} , 4.5 mol Cl^- and 2.0 mol V^{n+} ; the
 25 negative electrolyte solution contains 1.9 mol SO_4^{2-} , 4.5 mol Cl^- and 2.0 mol V^{n+} .

[0096] Example 5

[0097] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive electrolyte solution contains 1.9 mol SO_4^{2-} , 4.7 mol Cl^- and 2.0 mol V^{n+} ; the
5 negative electrolyte solution contains 1.9 mol SO_4^{2-} , 4.7 mol Cl^- and 2.0 mol V^{n+} .

[0098] Example 6

[0099] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive electrolyte solution contains 1.9 mol SO_4^{2-} , 4.9 mol Cl^- and 2.0 mol V^{n+} ; the
10 negative electrolyte solution contains 1.9 mol SO_4^{2-} , 4.9 mol Cl^- and 2.0 mol V^{n+} .

[0100] Example 7

[0101] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive electrolyte solution contains 1.9 mol SO_4^{2-} , 5.1 mol Cl^- and 2.0 mol V^{n+} ; the
15 negative electrolyte solution contains 1.9 mol SO_4^{2-} , 5.1 mol Cl^- and 2.0 mol V^{n+} .

[0102] Example 8

[0103] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive electrolyte solution contains 1.9 mol SO_4^{2-} , 5.3 mol Cl^- and 2.0 mol V^{n+} ; the
20 negative electrolyte solution contains 5.3 mol SO_4^{2-} , 4.7 mol Cl^- and 2.0 mol V^{n+} .

[0104] Example 9

[0105] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive electrolyte solution is controlled to contain 1.3 mol SO_4^{2-} , 4.0 mol Cl^- and 1.8 mol
25 V^{n+} ; the negative electrolyte solution contains 1.3 mol SO_4^{2-} , 4.0 mol Cl^- and 1.8

mol V^{n+} .

[0106] Example 10

[0107] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive
5 electrolyte solution contains 1.8 mol SO_4^{2-} , 4.0 mol Cl^- and 1.8 mol V^{n+} ; the negative electrolyte solution contains 1.8 mol SO_4^{2-} , 4.0 mol Cl^- and 2.0 mol V^{n+} .

[0108] Example 11

[0109] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive
10 electrolyte solution contains 2.1 mol SO_4^{2-} , 4.0 mol Cl^- and 1.8 mol V^{n+} ; the negative electrolyte solution contains 2.1 mol SO_4^{2-} , 4.0 mol Cl^- and 2.0 mol V^{n+} .

[0110] Example 12

[0111] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive
15 electrolyte solution contains 2.4 mol SO_4^{2-} , 4.0 mol Cl^- and 1.8 mol V^{n+} ; the negative electrolyte solution contains 2.4 mol SO_4^{2-} , 4.0 mol Cl^- and 2.0 mol V^{n+} .

[0112] Example 13

[0113] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive
20 electrolyte solution contains 2.2 mol SO_4^{2-} , 4.5 mol Cl^- and 1.87 mol V^{n+} ; the negative electrolyte solution contains 2.2 mol SO_4^{2-} , 4.5 mol Cl^- and 1.87 mol V^{n+} .

[0114] Example 14

[0115] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive
25 electrolyte solution contains 2.2 mol SO_4^{2-} , 4.5 mol Cl^- and 1.95 mol V^{n+} ; the

negative electrolyte solution contains 2.2mol SO_4^{2-} , 4.5mol Cl^- and 1.95mol V^{n+} .

[0116] Example 15

[0117] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive
5 electrolyte solution contains 2.2 mol SO_4^{2-} , 4.5 mol Cl^- and 2.05 mol V^{n+} ; the negative electrolyte solution contains 2.2 mol SO_4^{2-} , 4.5 mol Cl^- and 2.05 mol V^{n+} .

[0118] Example 16

[0119] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive
10 electrolyte solution contains 2.2 mol SO_4^{2-} , 4.5 mol Cl^- and 2.20 mol V^{n+} ; the negative electrolyte solution contains 2.2 mol SO_4^{2-} , 4.5 mol Cl^- and 2.20 mol V^{n+} .

[0120] Example 17

[0121] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive
15 electrolyte solution contains 2.2 mol SO_4^{2-} , 4.5 mol Cl^- and 2.30 mol V^{n+} ; the negative electrolyte solution contains 2.2 mol SO_4^{2-} , 4.5 mol Cl^- and 2.30 mol V^{n+} .

[0122] Example 18

[0123] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive
20 electrolyte solution contains 3.2 mol SO_4^{2-} , 1.5 mol Cl^- and 1.6 mol V^{n+} ; the negative electrolyte solution contains 3.2 mol SO_4^{2-} , 1.5 mol Cl^- and 1.6 mol V^{n+} .

[0124] Example 19

[0125] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive
25 electrolyte solution contains 2.5 mol SO_4^{2-} , 6.5 mol Cl^- and 2.6 mol V^{n+} ; the

negative electrolyte solution contains 2.5 mol SO_4^{2-} , 6.5 mol Cl^- and 2.6 mol V^{n+} .

[0126] Example 20

[0127] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive
5 electrolyte solution contains 2.2 mol SO_4^{2-} , 2.5 mol Cl^- and 1.60 mol V^{n+} ; the negative electrolyte solution contains 2.2 mol SO_4^{2-} , 2.5 mol Cl^- and 2.20 mol V^{n+} .

[0128] Example 21

[0129] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive
10 electrolyte solution contains 4.0 mol SO_4^{2-} , 4.5 mol Cl^- and 2.65 mol V^{n+} ; the negative electrolyte solution contains 4.0 mol SO_4^{2-} , 4.5 mol Cl^- and 2.65 mol V^{n+} .

[0130] Example 22

[0131] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, and PO_4^{3-} is added to
15 the positive electrolyte, so that the positive electrolyte solution contains 1.9 mol SO_4^{2-} , 3.9 mol Cl^- , 0.04 mol PO_4^{3-} and 2.0mol V^{n+} ; the negative electrolyte solution is controlled to contain 1.9 mol SO_4^{2-} , 3.9 mol Cl^- and 2.0 mol V^{n+} .

[0132] Example 23

[0133] The specific preparation method is the same as that in Example
20 1, except that the preset ion concentration ratio is different, and PO_4^{3-} is added to the positive electrolyte, so that the positive electrolyte solution contains 1.9 mol SO_4^{2-} , 3.9 mol Cl^- , 0.08 mol PO_4^{3-} and 2.0mol V^{n+} ; the negative electrolyte solution is controlled to contain 1.9 mol SO_4^{2-} , 3.9 mol Cl^- and 2.0 mol V^{n+} .

[0134] Example 24

25 [0135] The specific preparation method is the same as that in Example

1, except that the preset ion concentration ratio is different, and PO_4^{3-} is added to the positive electrolyte, so that the positive electrolyte solution contains 1.9 mol SO_4^{2-} , 5.3 mol Cl^- , 0.12 mol PO_4^{3-} and 2.0 mol V^{n+} ; the negative electrolyte solution is controlled to contain 1.9 mol SO_4^{2-} , 3.9 mol Cl^- and 2.0 mol V^{n+} .

5 [0136] Example 25

 [0137] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, and PO_3^{3-} is added to the negative electrolyte, so that the positive electrolyte solution contains 1.9 mol SO_4^{2-} , 3.9 mol Cl^- , and 2.0 mol V^{n+} ; the negative electrolyte solution is controlled to contain 1.9 mol SO_4^{2-} , 3.9 mol Cl^- , 0.06 mol PO_3^{3-} and 2.0 mol V^{n+} .

 [0138] Example 26

 [0139] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, and PO_3^{3-} is added to the negative electrolyte, so that the positive electrolyte solution contains 1.9 mol SO_4^{2-} , 3.9 mol Cl^- , and 2.0 mol V^{n+} ; the negative electrolyte solution is controlled to contain 1.9 mol SO_4^{2-} , 3.9 mol Cl^- , 0.13 mol PO_3^{3-} and 2.0 mol V^{n+} .

 [0140] Example 27

 [0141] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, and PO_3^{3-} is added to the negative electrolyte, so that the positive electrolyte solution contains 1.9 mol SO_4^{2-} , 5.3 mol Cl^- , and 2.0 mol V^{n+} ; the negative electrolyte solution is controlled to contain 1.9 mol SO_4^{2-} , 5.3 mol Cl^- , 0.2 mol PO_3^{3-} and 2.0 mol V^{n+} .

 [0142] Example 28

 [0143] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, and the additive

glycerol is added to the electrolyte, so that the positive electrolyte solution contains 1.9 mol SO_4^{2-} , 3.9 mol Cl^- , 2.0 mol V^{n+} and 0.02 mol glycerol; the negative electrolyte solution is controlled to contain 1.9 mol SO_4^{2-} , 3.9 mol Cl^- , and 2.0 mol V^{n+} .

5 [0144] Example 29

 [0145] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, and the additive succinic acid is added to the electrolyte, so that the positive electrolyte solution contains 1.9 mol SO_4^{2-} , 5.3 mol Cl^- , 2.0 mol V^{n+} and 0.2 mol succinic acid; the
10 negative electrolyte solution is controlled to contain 1.9 mol SO_4^{2-} , 5.3 mol Cl^- , 2.0 mol V^{n+} and 0.02 mol succinic acid.

 [0146] Example 30

 [0147] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive
15 electrolyte solution contains 2.0 mol SO_4^{2-} , 4.6 mol Cl^- and 2.25 mol V^{n+} ; the negative electrolyte solution contains 2.11 mol SO_4^{2-} , 4.33 mol Cl^- and 1.8 mol V^{n+} .

 [0148] Comparative example 1

 [0149] The specific preparation method is the same as that in Example
20 1, except that no chlorine is added, so that the positive electrolyte solution contains 1.9 mol SO_4^{2-} and 2.0 mol V^{n+} ; the negative electrolyte solution is controlled to contain 1.9 mol SO_4^{2-} and 2.0 mol V^{n+} .

 [0150] Comparative example 2

 [0151] The specific preparation method is the same as that in Example
25 1, except that the preset ion concentration ratio is different, so that the positive

electrolyte solution contains 1.9 mol SO_4^{2-} , 2.5 mol Cl^- and 2.0 mol V^{n+} ; the negative electrolyte solution is controlled to contain 1.9 mol SO_4^{2-} , 2.5 mol Cl^- and 2.0 mol V^{n+} .

[0152] Comparative example 3

5 [0153] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive electrolyte solution contains 1.9 mol SO_4^{2-} , 6.5 mol Cl^- and 2.0 mol V^{n+} ; the negative electrolyte solution is controlled to contain 1.9 mol SO_4^{2-} , 6.5 mol Cl^- and 2.0 mol V^{n+} .

10 [0154] Comparative example 4

[0155] The specific preparation method is the same as that in Example 1, except that the preset ion concentration ratio is different, so that the positive electrolyte solution contains 0.488 mol SO_4^{2-} , 6.898 mol Cl^- and 2.56 mol V^{n+} ; the negative electrolyte solution contains 0.615 mol SO_4^{2-} , 7.655 mol Cl^- and 1.941
15 mol V^{n+} .

[0156] The performance of the electrolytes of Examples 1-31 and Comparative examples 1-4 is tested or the electrolytes are prepared into all-vanadium redox flow batteries and the performance of the batteries is tested. See Tables 1 to 3 for specific test data.

20 [0157] The tests of all-vanadium redox flow batteries include the followings.

[0158] Battery efficiency test: A 5W single battery is used, and a mode of constant current charging + constant voltage charging + constant current discharging is used. The current density of the constant current charging is 110
25 mA/cm^2 , the cut-off voltage is 1.6 V, and then constant voltage charging is

performed at a voltage of 1.6 V, until the open circuit voltage of the battery is 1.54 V. Finally, the constant current discharging is performed at a constant current of 110 mA/cm² to a cut-off voltage of 1 V.

[0159] EE=discharging Wh/charging Wh×100%; CE=discharging
5 Ah/charging Ah×100%.

[0160] Cl₂ evolution rate test: for a single battery with different active materials ratios, NaOH solution is used to collect the gas in the upper layer of the positive electrolyte solution after two charging and discharging cycles, then ion chromatography is used to test the Cl⁻ concentration in the NaOH collection
10 solution, and the Cl₂ production rate in a unit time is obtained.

[0161] Accelerated test of electrode corrosion: a 5W single battery is used, and a mode of constant current charging + constant voltage charging + constant current discharging is used. The current density of the constant current charging is 110 mA/cm², the cut-off voltage is 1.8 V, and then constant voltage
15 charging is performed at a voltage of 1.8 V, until the open circuit voltage of the battery is 1.7 V. Finally, the constant current discharging is performed at a constant current of 110 mA/cm² to a cut-off voltage of 1 V.

[0162] After 50 cycles of charging and discharging, an AC impedance instrument was used to test the resistance change of the battery at the end of the
20 discharging and the battery was opened to observe the corrosion of the electrodes.

[0163] Table 1

	$\frac{[c(\text{Cl}^-) + c(\text{SO}_4^{2-})]}{c(\text{V}^{n+})}$	$\frac{c(\text{Cl}^-)}{c(\text{SO}_4^{2-})}$	$\frac{c(\text{Cl}^-)}{c(\text{V}^{n+})}$	$\frac{[c(\text{Cl}^-) + c(\text{SO}_4^{2-}) + c(\text{PO}_4^{3-})]}{c(\text{V}^{n+})}$	$\frac{[c(\text{Cl}^-) + c(\text{SO}_4^{2-}) + c(\text{PO}_3^{3-})]}{c(\text{V}^{n+})}$	$\frac{[c(\text{Cl}^-) + c(\text{SO}_4^{2-}) + c(\text{A})]}{c(\text{V}^{n+})}$
Example 1	2.9	2.05	1.95	/	/	/
Example 2	3	2.15	2.05	/	/	/
Example 3	3.1	2.26	2.15	/	/	/
Example 4	3.2	2.36	2.25	/	/	/
Example 5	3.3	2.47	2.35	/	/	/
Example 6	3.4	2.57	2.45	/	/	/
Example 7	3.5	2.68	2.55	/	/	/
Example 8	3.6	2.78	2.65	/	/	/
Example 9	2.94	3.07	2.22	/	/	/
Example 10	3.22	2.22	2.22	/	/	/
Example 11	3.38	1.90	2.22	/	/	/
Example 12	3.55	1.66	2.22	/	/	/
Example	3.58	2.04	2.40	/	/	/

13						
Example 14	3.43	2.04	2.30	/	/	/
Example 15	3.26	2.04	2.19	/	/	/
Example 16	3.04	2.04	2.04	/	/	/
Example 17	2.91	2.04	1.95	/	/	/
Example 18	2.93	0.46	0.93	/	/	/
Example 19	3.46	2.6	2.5	/	/	/
Example 20	2.93	1.13	1.56	/	/	/
Example 21	3.20	1.12	1.69	/	/	/
Example 22	/	2.05	1.95	2.92	/	/
Example 23	/	2.05	1.95	2.94	/	/
Example 24	/	2.78	2.65	3.66	/	/
Example 25	/	2.05	1.95	/	2.93	/

Example 26	/	2.05	1.95	/	2.96	/
Example 27	/	2.78	2.65	/	3.7	/
Example 28	/	2.05	1.95	/	/	2.91
Example 29	/	2.78	2.65	/	/	3.7
Example 30	2.93/ 3.58	2.3/2.1	2.1/2.4	/	/	/
Comparati ve example 1	0.95	/	/	/	/	/
Comparati ve example 2	2.2	1.31	1.25	/	/	/
Comparati ve example 3	4.15	3.61	3.25	/	/	/
Comparati ve example 4	2.88/ 4.26	14.1/12.4	2.6/3.9	/	/	/

	Battery internal resistance change/m Ω	Results of accelerate d test of electrode corrosion	Cl ₂ productio n rate mg/L/day	Energy efficienc y EE/%	Energy density/Wh/ L
Example 1	80	Slight	0.15	81.9	22.1
Example 2	109	Slight	0.24	82.2	24.8
Example 3	43	No corrosion	0.65	84.2	25.3
Example 4	38	No corrosion	0.93	85.5	27.1
Example 5	42.5	No corrosion	1.2	86.1	28.2
Example 6	53	No corrosion	1.15	86.6	28.7
Example 7	37	No corrosion	1.45	85.9	28.3
Example 8	39	No corrosion	1.95	86.3	28.1
Example 9	78	Slight corrosion	1.1	84.3	25.4
Example 10	36	No corrosion	0.98	86.5	28.7
Example 11	48	No corrosion	1.3	86.8	28.4
Example 12	58	No corrosion	1.28	85.8	28.1
Example 13	39	No corrosion	1.16	86.6	28.5
Example 14	45	No corrosion	1.08	87.1	29.5
Example 15	43	No corrosion	0.95	87.0	29.8
Example 16	43	No corrosion	0.87	86.1	29.9
Example 17	46	No corrosion	0.77	85.3	28.9
Example 18	102	Slight corrosion	0.13	87.6	20.8

Example 19	44	No corrosion	3.65	86.2	28.6
Example 20	93	Slight corrosion	0.08	83.8	27.4
Example 21	55	No corrosion	0.89	85.5	30.6
Example 22	32	No corrosion	1.34	86.9	29.5
Example 23	49	No corrosion	1.13	86.2	29.0
Example 24	40	No corrosion	3.73	86.8	28.8
Example 25	32	No corrosion	1.77	86.8	27.9
Example 26	31	No corrosion	1.52	85.8	29.6
Example 27	42	No corrosion	2.59	87.2	30.6
Example 28	39	No corrosion	0.99	86	28.3
Example 29	51	No corrosion	2.37	86.6	29.2
Example 30	39	No corrosion	1.2	86.31	29.38
Comparative example 1	898	Serious corrosion	0	78.9	21.3
Comparative example 2	1136	Serious corrosion	0	80.6	25.0
Comparative example 3	44	No corrosion	2.66	86.8	29.6
Comparative example 4	38	No corrosion	3.2	84.54	26.88

[0165] Table 3

	Positive	Negative electrode	Current density/mA/	Voltage range/V	Cutoff OCV/V	CE/%
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	electro de volume /mL	volume/ mL	cm ²			
Examp le 30	100	100	110	1~1.6	1.55	96.76
Compa rative examp le 4	100	100	110	1~1.6	1.55	96.25
	EE/%	VE/%	Energy density/Wh/ L	Energy attenuati on rate/%	Electroly te solution utilizatio n rate/%	
Examp le 30	86.31	89.2	29.38	5.68	89.16	
Compa rative examp le 4	84.54	87.83	26.88	8.7	88.86	

[0166] Referring to Table 1 and Table 2, it can be seen that for Examples 1-8 and Comparative Examples 1-3, when the concentrations of vanadium ions and sulfate ions remain unchanged, the production amount of Cl₂ gradually increases with the increase of the chloride ion concentration, but at the same time, it has a significant protective effect on the electrode. Referring further to FIGs. 2-3, the electrode corrosion conditions of Comparative Example 1 and Example 1 are shown, respectively. It can be seen from the FIGs. that when no chloride ions are added to the electrolyte, the electrode corrosion is serious, and

when the concentration of chloride ions is 3.9~5.3mol and the range of $[c(\text{Cl}^-)+c(\text{SO}_4^{2-})]/c(\text{V}^{n+})$ is 2.9~3.6, the electrode can be protected by a small amount of chlorine gas generated. However, when the concentration of chloride ions in the electrolyte solution is too high and the range of $[c(\text{Cl}^-)+c(\text{SO}_4^{2-})]/c(\text{V}^{n+})$ is out of 2.9~3.6, as in Comparative Example 4, the rate of chlorine gas production is too high, gas binding will occur, making it difficult to control the chlorine gas in the battery system, which will affect the performance of the battery.

[0167] Regarding Examples 9-12, when the concentrations of vanadium ions and chloride ions remain unchanged, the energy density of the battery gradually increases with the increase of the concentration of sulfate ions, and the energy efficiency increases. When the concentration of sulfate ions increases to 2.1 mol/L, the energy density no longer increases significantly, and the change in energy efficiency is also close to stable.

[0168] Regarding Examples 13-17, when the concentrations of sulfate ions and chloride ions remain unchanged, the energy density of the battery gradually increases with the increase of the concentration of vanadium ions, but when the concentration of vanadium ions increases to 2.2 mol/L, the upward trend becomes flat. It can be seen that the increase in viscosity caused by the concentration of vanadium ions increases the concentration polarization of the solution, making it difficult to further increase the energy density. At the same time, it can be seen from the energy efficiency that after the concentration of vanadium ions reaches 2.1 mol/L, the efficiency appears an inflection point and begins to decrease.

[0169] Referring to Table 3, for Example 30 and Comparative Example 4, it can be seen that: when the V^{n+} concentration in the mixed acid solution is too

high, that is, when it cannot meet the range of $2.9 \leq [c(\text{Cl}^-) + c(\text{SO}_4^{2-})] / c(\text{V}^{n+}) \leq 3.6$, the mass transfer resistance caused by the increase in viscosity of the solution cannot continue to increase the energy density of the solution. At the same time, the further increase of Cl^- results in the evolution of a large amount of Cl_2 , which
5 makes the system circulation pump severely gas bound and difficult to operate stably.

[0170] The electrolyte solution and all-vanadium redox flow battery provided by the embodiments of this disclosure have been introduced in detail above. Specific examples are used in this disclosure to illustrate the principles and
10 implementation of this disclosure. The description of the above embodiments is only to help understand the technical solution and its core ideas of this disclosure. Those skilled in the art should understand that they can still modify the technical solutions recorded in the foregoing embodiments, or make equivalent substitutions for some of the technical features. However, these modifications or
15 substitutions do not cause the essence of the corresponding technical solutions to depart from the scope of the technical solutions of the embodiments of the present disclosure.

WHAT IS CLAIMED IS:

1. An electrolyte solution, characterized in that the electrolyte solution comprises: a positive electrolyte solution and a negative electrolyte solution, the positive electrolyte solution and the negative electrolyte solution comprise
5 chloride ions, sulfate ions and vanadium ions; both the positive electrolyte solution and the negative electrolyte solution satisfy:

$$2.9 \leq [c(\text{Cl}^-) + c(\text{SO}_4^{2-})] / c(\text{V}^{n+}) \leq 3.6;$$

- wherein the $c(\text{Cl}^-)$ represents a concentration of the chloride ions, the $c(\text{SO}_4^{2-})$ represents a concentration of the sulfate ions, and the $c(\text{V}^{n+})$ represents a
10 concentration of the vanadium ions.

2. The electrolyte solution according to claim 1, characterized in that the $c(\text{Cl}^-)$ satisfies: $1.5 \text{ mol/L} \leq c(\text{Cl}^-) \leq 6.5 \text{ mol/L}$.

3. The electrolyte solution according to claim 1, characterized in that the $c(\text{Cl}^-)$ satisfies: $2.5 \text{ mol/L} \leq c(\text{Cl}^-) \leq 5.5 \text{ mol/L}$.

- 15 4. The electrolyte solution according to claim 1, characterized in that the $c(\text{Cl}^-)$ satisfies: $3.0 \text{ mol/L} \leq c(\text{Cl}^-) \leq 5.0 \text{ mol/L}$.

5. The electrolyte solution according to claim 1, characterized in that the $c(\text{Cl}^-)$ satisfies: $3.5 \text{ mol/L} \leq c(\text{Cl}^-) \leq 4.5 \text{ mol/L}$.

6. The electrolyte solution according to any one of claims 1 to 5,
20 characterized in that the $c(\text{Cl}^-)$ and the $c(\text{V}^{n+})$ further satisfy: $0.5 \leq c(\text{Cl}^-) / c(\text{V}^{n+}) \leq 3.0$.

7. The electrolyte solution according to any one of claims 1 to 6, characterized in that the $c(\text{SO}_4^{2-})$ satisfies: $0.5 \text{ mol/L} \leq c(\text{SO}_4^{2-}) \leq 5.5 \text{ mol/L}$.

8. The electrolyte solution according to any one of claims 1 to 7,
25 characterized in that the $c(\text{V}^{n+})$ satisfies: $1.6 \text{ mol/L} \leq c(\text{V}^{n+}) \leq 2.65 \text{ mol/L}$.

9. The electrolyte solution according to any one of claims 1 to 8, characterized in that the $c(\text{Cl}^-)$ and the $c(\text{SO}_4^{2-})$ further satisfy: $0.4 \leq c(\text{Cl}^-)/c(\text{SO}_4^{2-}) \leq 3.1$.

10. The electrolyte solution according to any one of claims 1 to 9, characterized in that the positive electrolyte solution further comprises phosphate ions, and the positive electrolyte solution further satisfies: $2.9 \leq [c(\text{Cl}^-) + c(\text{SO}_4^{2-}) + c(\text{PO}_4^{3-})]/c(\text{V}^{n+}) \leq 3.7$; wherein the $c(\text{PO}_4^{3-})$ represents a concentration of the phosphate ions.

11. The electrolyte solution according to claim 10, characterized in that the $c(\text{PO}_4^{3-})$ further satisfies at least one of the following features:

- a) $0.01 \text{ mol/L} \leq c(\text{PO}_4^{3-}) \leq 0.15 \text{ mol/L}$;
- b) $0.02 \leq c(\text{PO}_4^{3-})/c(\text{V}^{n+}) \leq 0.06$;
- c) $[c(\text{Cl}^-) + c(\text{SO}_4^{2-}) + c(\text{PO}_4^{3-}) - 0.8 \times c(\text{V}^{n+})] \geq 4.2 \text{ mol/L}$;

wherein $0.8 \times c(\text{V}^{n+})$ represents an average molar concentration of acid group ions bound by the vanadium ions in the positive electrolyte solution.

12. The electrolyte solution according to any one of claims 1 to 11, characterized in that the negative electrolyte solution further comprises phosphite ions, and the negative electrolyte solution further satisfies: $2.9 \leq [c(\text{Cl}^-) + c(\text{SO}_4^{2-}) + c(\text{PO}_3^{3-})]/c(\text{V}^{n+}) \leq 3.7$; wherein the $c(\text{PO}_3^{3-})$ represents a concentration of the phosphite ions.

13. The electrolyte solution according to claim 12, characterized in that the $c(\text{PO}_3^{3-})$ further satisfies at least one of the following features:

- d) $0.01 \text{ mol/L} \leq c(\text{PO}_3^{3-}) \leq 0.15 \text{ mol/L}$;
- e) $0.03 \leq c(\text{PO}_3^{3-})/c(\text{V}^{n+}) \leq 0.1$;
- f) $[c(\text{Cl}^-) + c(\text{SO}_4^{2-}) + c(\text{PO}_3^{3-}) - 1.5 \times c(\text{V}^{n+})] \leq 4.5 \text{ mol/L}$;

wherein $1.5 \times c(V^{n+})$ represents an average molar concentration of acid group ions bound by the vanadium ions in the negative electrolyte solution.

14. The electrolyte solution according to any one of claims 1 to 13, characterized in that the positive electrolyte solution and the negative electrolyte solution further comprise an additive, and the positive electrolyte solution and the negative electrolyte solution further satisfy: $2.9 \leq [c(Cl^-) + c(SO_4^{2-}) + c(A)] / c(V^{n+}) \leq 3.7$; wherein the $c(A)$ represents a concentration of the additive.

15. The electrolyte solution according to claim 14, characterized in that the additive satisfies at least one of the following features:

g) the concentration of the additive $c(A)$ satisfies: $0.02 \text{ mol/L} \leq c(A) \leq 0.2 \text{ mol/L}$;

h) the additive is one or more of additives containing $-OH$, $-COOH$, or $-NH_2$ functional group.

16. The electrolyte solution according to any one of claims 1 to 15, characterized in that a temperature stability range of the electrolyte solution is $-30 \sim 60^\circ\text{C}$.

17. The electrolyte solution according to any one of claims 1 to 16, characterized in that the chloride ions are provided by an acid or salt containing the chloride ions; the sulfate ions are provided by an acid or salt containing the sulfate; the vanadium ions are provided by a vanadate.

18. An all-vanadium redox flow battery, characterized in that the all-vanadium redox flow battery comprises the electrolyte solution according to any one of claims 1-17.