# SYSTEM AND METHOD FOR REINSTATING THE VALANCE OF ELECTROLYTE IN VANADIUM REDOX FLOW BATTERIES

## FIELD OF THE INVENTION

[0001] The present invention relates to electrolyte suitable for use in battery, to batteries comprising the electrolyte, deals with balancing the valance of electrolyte in vanadium redox flow batteries and to the use of batteries of the invention in energy storage.

## BACKGROUND OF THE INVENTION

[0002] Vanadium redox flow battery (VRFB / VFB) shows great potential as an energy storage solution because of its distinct ability to separate power and energy, its impressive efficiency and its exceptionally long lifespan for charge and discharge cycles. It utilizes the same element – vanadium – at different oxidation states in both the positive and negative side electrolyte solution, resolving the risk of irreversible contamination due to the mixing of electrolyte.

[0003] A VFB system generally has two components: an electrochemical cell and an electrolyte solution. The electrochemical cell consists of two half-cells (positive and negative half-cells) separated by an ion exchange membrane. A Vanadium salt solution dissolved in a sulfuric acid solution is used for energy storage. When the electrolyte solution goes through the cell, redox reactions occur in the positive and negative half cells. During long-term operation, an electrolyte imbalance of the VRB system is usually found, which subsequently causes an energy capacity loss.

[0004] This electrolyte imbalance is a result of the amount of oxidized species becoming unequal to that of the reduced species in the VRFB cell, leading to the incomplete utilization of the electro-active species. The inequality between the oxidized and reduced species is, in turn, a result of vanadium ions and water transfer across the ion exchange membrane and side reactions inside the electrochemical cell, resulting in decreases in the cell performance and energy capacity. Additionally, the cell may become damaged or destroyed with high levels of the electrolyte imbalance. While electrolyte rebalancing can normally restore the VRB system, its success largely depends on the level of the electrolyte imbalance.

[0005] Overtime, due to electrolyte transfer through the membrane or other forms of mixing, electrolyte imbalance may occur where the state of charge of the positive

and negative side electrolytes are not equal. This reduces the efficiency of the system by reducing the amount of energy it may store.

[0006] The other cause for the imbalance of the electrolyte might be due to the oxidation in the negative tank. The negative redox couple is very prone to oxidation when it is fully charged and decreases with the decreasing state of charge. The air entered during the repair or from deformities will also oxidize the negative redox couple.

[0007] The imbalance of the electrolyte state of charge reduces the efficiency and after heavy imbalance, the system does not deliver the power.

[0008] Precharge time difference here is defined as the time difference between the two points of inflections.

[0009] Precharge is defined as the time when the system is being charged when both the positive and negative side electrolyte are at an oxidation state between $V^{3+}$ and $VO^{2+}$ exclusive. This means that during precharge, the electrolyte in both positive and negative side is a mixture of $V^{3+}$ and $VO^{2+}$.

[0010] Open-Circuit Voltage (OCV) quantifies the potential difference between the positive and negative electrolyte sides. In the positive electrode during the charging process, $VO^{2+}$ undergoes conversion to $VO_2^+$, while in the negative electrode, $V^{3+}$ transforms into $V^{2+}$. This conversion process leads to a substantial increase in the potential difference, giving rise to distinctive inflection points.

[0011] For a perfectly balanced system, the precharge time difference between positive and negative tanks reaching zero percent state of charge is negligible as shown in **FIG. 1**.

[0012] In an imbalanced system, the time difference between the positive tank and negative tank reaching zero percentage state of charge results from the tank volume concentration and average valance. If the electrolyte is thoroughly mixed with OCV less than 10 mV with same amount in each tank and equal concentration and still the separation is observed than this is only arising from the SOC difference from each tank as shown in **FIG. 2**.

## SUMMARY OF THE INVENTION

[0013] To reinstate the valance of the vanadium electrolyte after severe System-of-Charge (SOC) imbalance, oxalic acid addition is performed in the positive half (positive redox couple). Addition of oxalic acid incurs lots of cost to the system.

[0014] Addition of fructose is the simplest technique to reduce the positive redox couple. This method can be easily implemented on/off site without any specific technical know-how. Simple food grade fructose can be used to achieve the required valance and it comes at the fraction of price while compared to oxalic acid addition.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0015] **FIG. 1** is an illustration of the imbalance system. Here, the imbalance system refers to the high difference of SOC in between the negative and positive electrolyte. The figure shows the time vs open circuit voltage plot.

[0016] **FIG. 2** shows the perfectly balanced valance of the electrolyte i.e. same SOC in negative and positive side. The Figure shows the time vs open circuit voltage plot.

[0017] **FIG. 3** is an illustration of the system set up used in experimentations. Solid lines being electrolyte inlet while dashed being electrolyte outlet.

## DETAILED DESCRIPTION OF THE INVENTION

[0018] It has been shown that oxalic acid is suitable as a reducing agent to reduce $VO_2^+$ in the positive side to rebalance the system. However, oxalic acid may be costly and it being a corrosive substance poses storage concerns as well. As such, this disclosure uses fructose as a reducing agent in place of oxalic acid. Fructose addresses the issue of the corrosiveness of oxalic acid and the costliness as it is a readily available sugar in the food industry.

[0019] The oxidation state of vanadium in the solution used was between +3.5 to +4, the most common form of imbalance found to be in a vanadium redox flow battery system. The present disclosure can only be used when the valance of the electrolyte is more than 3.5.

[0020] The system is charged at constant current while logging the OCV values. Charging is stopped when the second point of inflection on the OCV-time curve is reached. **FIG. 3** illustrates the set up.

[0021] From the initial oxidation state of the electrolyte, there is a greater amount of $VO^{2+}$ as compared to $V^{3+}$. As such the first point of inflection signifies that all the $V^{3+}$ in the positive side has been oxidized to $VO^{2+}$ and the second point of inflection signifies that all $VO^{2+}$ has been reduced to $V^{3+}$ in the negative side.

[0022] Charging the electrolyte to this point will leave the negative side electrolyte as a solution with only $V^{-3}$ ions and the positive side as a mixture of both $VO^{2+}$ and $VO_2^{+}$ ions. Thus, to rebalance the system, the $VO_2^{+}$ ions will just have to be reduced back to $VO^{2+}$.

[0023] Before the addition of fructose, it is necessary to make sure that SOC of the positive side is more than 50% / half. Fructose reacts with $VO_2^{+}$ in a reversible reaction releasing only carbon dioxide and water with no other side products. The following equation describes the assumed (stoichiometric) reaction:

$$24VO_2^{+} + C_6H_{12}O_6 + 24H^{+} \rightarrow 24VO^{2+} + 6CO_2 + 18H_2O$$

[0024] The above reaction equation between fructose and $VO_2^{-}$ is used as a starting point to estimate the amount of fructose to add. The purity from the nutritional label and the stoichiometric ratio of the above reaction is a starting point to determine the amount of this concentrated fructose to add to the positive electrolyte.

[0025] After addition of fructose, the electrolyte should be allowed to circulate while logging OCV values. The reaction can be taken to have proceeded to completion if the OCV values remains constant with time. After the completion, both positive and negative electrolyte is mixed thoroughly, and this results in the electrolyte valance of $V^{+3.5}$.

[0026] It is important to ensure that the tanks containing the electrolyte are not sealed as a large volume of gas is evolved during the reaction.

[0027] The fructose of any grade can be used if it does not contain any foreign substance. Any purity of fructose from any supplier can be used according to the stoichiometric requirement.

**EMBODIMENTS**

[0028] Embodiment 1: A method for rebalancing an electrolyte in a vanadium redox flow battery system having a positive half-cell and a negative half-cell separated by an ion exchange membrane, the method comprising:

identifying an electrolyte imbalance in the vanadium redox flow battery system,

wherein the positive half-cell contains a positive electrolyte with vanadium ions in an average oxidation state greater than +3.5, and the negative half-cell contains a negative electrolyte;

adding fructose to the positive electrolyte as a reducing agent to reduce $VO_2^+$ ions to $VO^{2+}$ ions in the positive half-cell; and

circulating the positive electrolyte after the addition of fructose until an open-circuit voltage (OCV) between the positive half-cell and the negative half-cell stabilizes, indicating completion of a reduction reaction.

[0029] The embodiment 1, further comprising charging the vanadium redox flow battery system at a constant current until a second point of inflection is observed on an OCV-time curve prior to adding the fructose, wherein the second point of inflection indicating all $VO_2^+$ ions in the negative electrolyte have been reduced to $V^{+3}$ ions.

[0030] The embodiment 1, wherein the fructose is added in an amount determined based on a stoichiometric ratio of a reaction between fructose and $VO_2^+$ ions, represented by:

$$24VO_2^+ + C_6H_{12}O_6 + 24H^+ \rightarrow 24VO^{2+} + 6CO_2 + 18H_2O$$

[0031] The embodiment 1, further comprising ensuring that a state of charge (SOC) of the positive electrolyte is greater than 50% prior to adding the fructose.

[0032]The embodiment 1, further comprising mixing the positive electrolyte and the negative electrolyte after the OCV stabilizes to achieve an average vanadium oxidation state of approximately +3.5 across both electrolytes.

[0033] The embodiment 1, wherein the fructose is food-grade fructose having a purity level specified by a nutritional label.

[0034] The embodiment 1, wherein the positive half-cell and the negative half-cell are configured with unsealed tanks to allow the release of carbon dioxide gas produced during the reduction reaction.

[0035] The embodiment 1, wherein identifying the electrolyte imbalance includes measuring a precharge time difference between the positive half-cell and the negative half-cell reaching a zero percent state of charge, wherein the precharge time difference exceeds a predetermined threshold.

[0036] Embodiment 1: A method for correcting a state of charge (SOC) imbalance in a vanadium redox flow battery system, the method comprising:

determining an SOC imbalance between a positive electrolyte and a negative electrolyte in the vanadium redox flow battery system, wherein the positive electrolyte contains a mixture of $VO_2^+$ and $VO^{2+}$ ions with an average oxidation state greater than +3.5;

introducing fructose into the positive electrolyte to reduce a portion of the $VO_2^+$ ions to $VO^{2+}$ ions, thereby adjusting the average oxidation state of the positive electrolyte;

circulating the positive electrolyte while monitoring an open-circuit voltage (OCV) until the OCV remains constant; and

combining the positive electrolyte and the negative electrolyte to achieve a balanced SOC across the vanadium redox flow battery system.

[0037] The embodiment 2, wherein the fructose is added in an amount proportional to an excess of $VO_2^+$ ions in the positive electrolyte, calculated based on a molar ratio derived from a reaction of fructose with $VO_2^+$ ions.

[0038] The embodiment 2, wherein the SOC imbalance is detected by observing a separation in inflection points on an OCV-time curve during a charging process of the vanadium redox flow battery system.

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# CLAIMS

**We Claim:**

1. A method for rebalancing the electrolyte in a vanadium redox flow battery system comprising:

identifying an electrolyte imbalance where the oxidation state of vanadium in the electrolyte in the vanadium redox flow battery is greater than at least a value of +3 and / or preferably +3.5;

determining that a state of charge (SOC) of a positive half-cell of the battery is more than 50%;

on the determination of the SOC being more than 50%,

adding fructose to the positive half-cell of the battery;

allowing the fructose to react with $VO_2^+$ ions in the positive half-cell to reduce to $VO^{2+}$;

circulating the electrolyte while monitoring Open-Circuit Voltage (OCV) values; and

mixing the electrolyte from the positive and negative half-cells to achieve a balanced electrolyte valance of approximately $V^{+3.5}$.

2. The method of claim 1, wherein when the OCV values are constant, the reaction is complete and the positive and negative electrolytes are mixed after the OCV stabilizes is nearly constant.

3. The method of claim 1, wherein the fructose is food-grade fructose.

4. The method of Claim 1, wherein the amount of fructose added is determined based on a stoichiometric ratio of the reaction between fructose and $VO_2^+$.

5. The method of claim 1, wherein the electrolyte imbalance is determined by either by measuring a pre-charge time difference between the positive and negative tanks reaching 0% of SoC or by observing a difference in the SOC between the positive and negative electrolytes.

6. The method of Claim 1, wherein the reaction between fructose and $VO_2^+$ produces $CO_2$ and water as byproducts.

7. The method of claim 1, wherein the fructose is added in an amount determined based on the stoichiometric reaction:

$$24VO_2^+ + C_6H_{12}O_6 + 24H^+ \rightarrow 24VO^{2+} + 6CO_2 + 18H_2O$$

8. The method of claim 1, wherein the electrolyte imbalance is determined by: charging the battery at a constant current;
monitoring the OCV of the VRFB system; and
identifying a pre-charge time difference between the positive and negative electrolytes reaching a predetermined SOC, wherein the predetermined SOC is between $V^{3+}$ and $VO_2^+$.

9. The method of claim 9, wherein the pre-charge time difference is determined by identifying inflection points in the OCV versus time curve during charging.

10. A vanadium redox flow battery (VRFB) system rebalanced by the method of any of claims 1–9.

11. A system for rebalancing the electrolyte in a vanadium redox flow battery, comprising:
a vanadium redox flow battery with positive and negative half-cells;
means for detecting an electrolyte imbalance where the oxidation state

of vanadium in the electrolyte is greater than at least a value of +3 and / or preferably +3.5;

a source of fructose for addition to the positive half-cell;

means for circulating the electrolyte; and

means for monitoring Open-Circuit Voltage (OCV) values to determine completion of the rebalancing process.

12. The system of Claim 11, wherein the means for detecting electrolyte imbalance includes measuring a pre-charge time difference between positive and negative tanks of the battery reaching 0% of state of charge (SoC).

13.The system of Claim 11, wherein the means for monitoring OCV values includes a sensor and a data logging system.

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