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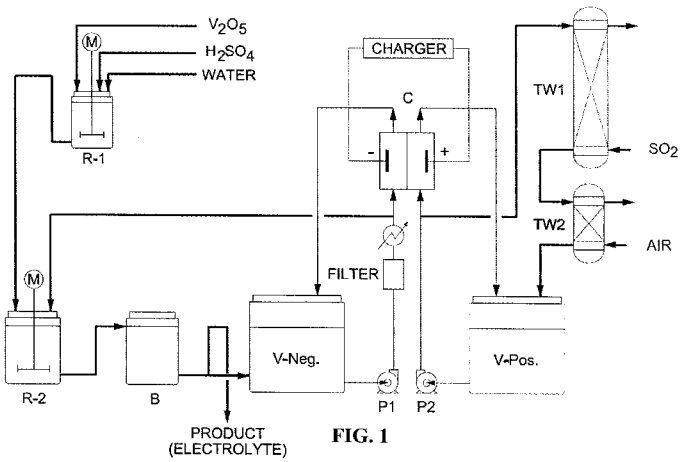

FIG. 1

(57) Abstract: An acid vanadium sulfate solution adapted to be used as electrolyte solution in separated positively and negatively charged electrolyte solution circulation circuits of a vanadium flow redox battery system is produced *in situ*, exploiting the working energy storing battery system by mixing vanadium pentoxide powder with sulfuric acid and water of dilution to form a suspension of vanadium pentoxide powder in sulfuric acid solution, and mixing it with negatively charged electrolyte solution, eventually diverted from the respective negative electrolyte circuit of the flow redox battery system, for dissolving and reducing the vanadium pentoxide, producing fresh acid vanadium sulfate solution there from. Simultaneously or whenever due, the state of charge of the two electrolyte solutions containing vanadium is rebalanced by absorbing sulfur dioxide in the positively charged electrolyte solution for reducing vanadium+5 contained therein. Exemplary embodiments and related examples of usable system schemes are described.

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"IN SITU" PRODUCTION OF ELECTROLYTE SOLUTION FROM VANADIUM PENTOXIDE FOR USE IN A FLOW REDOX BATTERY STORAGE SYSTEM

BACKGROUND

Technical Field

This disclosure relates to electrochemical energy storage based on the use of a flow redox battery system and in particular to a method of producing an acid solution of vanadium from vanadium pentoxide of mineral origin.

Introduction

With the demise of nuclear energy and the limited proven reserve of oil and gas the word is geared to produce more electricity from renewable sources, mainly solar and wind. Last year solar panels for more than 18 GW were produced and, with the advent of cheaper and more efficient solar panels, the amount of energy produced by renewable sources will be growing exponentially. However, renewable sources like solar and wind are hard to manage because of their inherent discontinuity and can hardly be fully exploited without associating to them efficient energy storage systems. Among the numerous energy storage options, the vanadium redox flow battery system is recognized as a particularly suitable solution.

In a flow redox battery system, energy is stored in the electrolyte solutions. The electrolyte solution consists of an aqueous solution of vanadium sulfate with vanadium ions (in concentration of 1 to 2 mole/liter) at different states of oxidation. At start, the two hydraulic circuits of the electrolyte solutions flowing into the negative and positive compartments of the electrochemical cells of a generally multi cell battery, may be filled with the same aqueous solution of vanadium sulfate as prepared or procured for the purpose. Generally, the loaded electrolyte solution consists of a mixture of about 50% trivalent vanadium [V^{+3}] sulfate vanadium and about 50% tetravalent [VO^{2+}]

vanadium sulfate. Basically, the two electrolyte solutions continuously circulate from a respective storage tank through the corresponding compartments of the cells and back to the tank.

A conditioning phase of the electrolyte solutions must be performed before energy may start to be reversibly stored consisting in passing an electric current across each cell's electrodes while the two electrolyte solutions are kept in circulation. The electric current forced through the cells reduces the tetravalent vanadium to trivalent vanadium in the negative electrolyte solution (that is to say the electrolyte solution flowing in the cell compartment containing the negatively biased electrode) until it contains only trivalent vanadium and, at the same time, the trivalent vanadium oxidizes to tetravalent vanadium in the positive electrolyte solution (that is to say the electrolyte solution flowing in the cell compartment containing the positively biased electrode) until it contains only tetravalent vanadium.

At the end of this conditioning period the negative electrolyte solution will contain only trivalent vanadium and the positive electrolyte solution will contain only tetravalent vanadium.

The battery charging process consists in further reducing (forcing a "charging" current) the trivalent vanadium to divalent vanadium in the negative electrolyte solution and further oxidizing the tetravalent vanadium to pentavalent vanadium in the positive electrolyte solution.

When most of the V^{+3} in the negative electrolyte has been reduced to V^{+2} and, at the same time, most of the tetravalent vanadium VO^{2+} has been oxidized to pentavalent vanadium [VO_2^{+}], the electrolyte solutions are considered completely charged and they can be discharged by a reverse current flowing across the battery cells through an electrical load connected to the battery, practically allowing the reverse electrode reactions of those of the charging process to occur.

The required fill amount of electrolyte solution (at a concentration of approximately 1.5 Mole of vanadium per liter) is between 50 and 60 liters per kWh. Normally, the solution is produced from commercially available vanadium pentoxide and the amount of vanadium pentoxide required for the storage of one kWh is approximately 16 lb.

The combined solar and wind renewable energy generation equipments that will be installed in the world in the next few years will be in the range of hundreds of GW and, considering an average requisite of about 10 hours night time or calm period storage, the average energy storage capacity may easily surge to the TWh order of magnitude. A vast amount of vanadium sulfate solution will be needed and it is indispensable to find a way of economically and quickly produce vanadium electrolyte solution from vanadium pentoxide.

PRIOR ART

Suitable vanadium sulfate electrolyte solution was originally produced by Mitsubishi (Japan) by reducing vanadium pentoxide using hydrogen at 700 °C.

Unisearch, Australia, proposed a rather complex method involving use of reducing chemicals like oxalic acid and eventual further reduction steps in an electrochemical cell. Oxalic acid reacts very slowly with vanadium pentoxide reducing it partially to tetravalent vanadium but the reaction may take several days and is never complete; a complete dissolution of V_2O_5 may be reached but yet only 70 to 90% of the pentoxide is reduced to tetravalent vanadium.

The document WO 2002/015317 discloses an entirely electrochemical way of reducing finely ground vanadium pentoxide in sulfuric acid solution in a diaphragm-less cell with asymmetric electrodes, where at the positive electrode (Ti coated with Ta-Ir oxides) nascent oxygen is produced. Efficiency could be enhanced by using a cationic membrane between the cell electrodes.

There is also a growing interest of vanadium pentoxide producers in supplying an acid sulfate solution of vanadium for use in redox flow battery systems. However, a price much higher than that of vanadium pentoxide and residues of reducing chemical compounds used for dissolving the vanadium pentoxide that impair electrode activity (cell electrodes poisoning) are problems yet to be solved.

Approximately up to 70% of the cost of an all-vanadium redox flow battery energy storage system is for the electrolyte solution, and this speaks for itself in stressing the importance of finding an easy and economical way of procuring it.

Last but not least, large shipments of a strong acid solution (from about 8% up to about 15 % of free sulfuric acid in the aqueous vanadium sulfate solution) pose safety problems and may be intolerably expensive. By contrast the solid vanadium pentoxide precursor is generally marketed in powder form and may be safely shipped without any problem. Considering that the volume of electrolyte capable of storing 1 kWh is about 40 to 50 liters (depending on the vanadium concentration, normally between 1.5 and 2 Mole/liter), and weighs approximately 70 kg, the corresponding powder of vanadium pentoxide would weigh just 7.00 kg/kWh (approximately one tenth of an electrolyte solution).

Preparation of electrolyte solution for filling a flow redox battery system up to full storage capability if carried out at the site could overcome the above recalled difficulties and associated costs. However, dissolving V_2O_5 in sulfuric acid solution, as discussed above, may be a costly, low yield and/or inefficient process or may require a specifically dedicated electrolyzer, according to prior art methods.

GENERAL DESCRIPTION OF THE INVENTION

Preparation of vanadium electrolyte solution consists in general terms in dissolving in sulfuric acid solution V_2O_5, reducing the vanadium ions from the state of charge +5 of V_2O_5 to the state of charge +3 [V^{+3}] and +4 [VO^{2+}].

The applicants have found a simple and outstandingly cost effective method that, in a highly preferred embodiment allowing a continuous mode of operation by maintaining a balanced state of charge between the two electrolyte solutions of a working all-vanadium flow redox battery system, may be defined as "hybrid" in the sense that it cunningly couples the action of chemical reducing vanadium +5 (reduction of vanadium +5, in its ionic form [VO_2^+], to vanadium +4 [VO^{2+}] using sulfur dioxide conducted in the positive electrolyte solution of an all-vanadium flow redox battery system, with the action of dissolving and reducing V_2O_5 in the negative electrolyte solution of the all-vanadium flow redox battery system containing V^{+2} that is electrochemically produced at the negative electrodes of a battery stack of cells used for energy storage. The surprising condition of fastness of both reduction reactions conducted in the two electrolyte solutions, allows yield rates of fresh vanadium sulfate solution from commercial powder of V_2O_5 outstandingly high and thus the equipments needed are relatively small.

Considering the general availability of water and common chemicals like oleum (concentrated 98% sulfuric acid) and sulfur dioxide that is sold in bottles or is often made locally by burning sulfur or by reacting metabisulfite with sulfuric acid, the possibility of producing *in situ* the large volume of electrolyte needed to fill up the redox battery storage system to full rated capacity, after having started up the system with a limited amount of electrolyte solution, just enough to drive the recirculation pumps in the two electrolyte circuits, allows important savings.

Exploiting the working flow redox cell battery or batteries system for simultaneously produce the vanadium sulfate electrolyte solution up to completely fill the system or to add storage capacity of an existing system, simply coupling to the negative electrolyte solution circuit ancillary reactor means of vanadium pentoxide dissolution in aqueous sulfuric acid solution and to the positive electrolyte solution

circuit ancillary absorption-reaction means of sulfur dioxide in the circulating negative electrolyte solution for reducing pentavalent vanadium contained therein in ionic form (VO_2^+) to tetravalent vanadium, results in an outstandingly fast and effective method of *in situ* producing fresh vanadium sulfate electrolyte solution.

The novel method of this disclosure sparks from an intuition on a generally accepted explanation of puzzling experimental results relating to reaction between solid V_2O_5 and V^{+2}:

a) it has been reported that in the process of dissolution of V_2O_5 by V^{+3} it is important to avoid the presence of V^{+2} because V^{+2} would passivate the solid V_2O_5 preventing or at best negatively affect its dissolution rate and reduction process;

b) on the other hand, V^{+3} is under many aspects and behaviour a relatively modest reducing agent, it oxidizes slowly to VO^{2+} [V+4] at the same time reducing and causing solubilization of V_2O_5, according to the reaction: V_2O_5 (solid) + 2 V^{+3} + 2 $H^+ = 4\ VO^{2+} + H_2O$;

c) on the contrary V^{+2} is a very strong reducing agent as it reduces instantly atmospheric oxygen. Theoretically V^{+2} should instantly reduce solid V_2O_5;

d) however in a verification experiment conducted by the applicants, V_2O_5 (yellow powder) was suspended in a sulfuric acid solution containing V^{+2} (in practice the yellow powder was suspended in almost completely charged negative electrolyte solution of a working battery system, containing free sulfuric acid, approximately two mole of H^+ per mole of Vanadium ion). The reported behavior was found to be absolutely correct. The yellow V_2O_5 powder does not dissolve or dissolves very slowly and only partially in the V^{+2} containing acid solution, the color of the powder changes from orange to black. Even addition of sulfuric acid and/or heating of the suspension up to boiling point failed to produce any effect: the undissolved dark

powder appeared to be absolutely insoluble. Any such an occurrence in a circuit of a working all-vanadium flow redox battery is obviously recognized as a disastrous event. Closed case? No!

e) the dark powder solid residue could reasonably consist of V_2O_4 , V_2O_3 , both black solid, or a mixture of the two. Having worked on these two vanadium oxides and found that dissolution of V_2O_4 and V_2O_3 in concentrated or diluted sulfuric acid occurs only at temperatures above 115-120 C and that in any case remains very slow, it came to the mind of the applicants that in presence of very little free acid or in absence of it the following reactions would indeed be likely to occur:

$$V_2O_5 + 2\ V^{+2} + H_2O = 2\ V_2O_4 + 2\ H^+ \quad (1)$$

$$V_2O_5 + 4\ V^{+2} + 4\ H_2O = 3\ V_2O_3 + 8\ H^+ \quad (2)$$

justifying the observed generation of a dark solid residue in the suspension (probably a mixture of V_2O_4 and V_2O_3.

f) contrarily, the reactions one would like to have look like:

$$2V_2O_5 + 2V^{+2} + 8\ H^+ = 6\ VO^{2+} + 4\ H_2O \quad (3)$$

and

$$V_2O_5 + 4\ V^{+2} + 10\ H^+ = 6\ V^{+3} + 5\ H_2O \quad (4)$$

and these reactions would need the presence of at least 4 or 10 mole of H^+.

g) in the charged electrolyte solution used for checking the reported inadequacy of V^{+2} for reducing and dissolving V_2O_5 only 2.4 mole of H^+ (1.2 mole/liter of free sulfuric acid) were present and in these conditions of low acidity only reaction (1) and (2) may be expected to occur. The applicants found out that, by suspending the yellow powder of V_2O_5 in a commensurate amount of sulfuric acid and then adding it into the negatively charged electrolyte solution, the yellow powder V_2O_5 dissolves

immediately and a blue-green electrolyte solution is produced according to the reactions (3) and (4) or according to the sum reaction

$$3\ V_2O_5 + 6\ V^{+2} + 18\ H^{+} = 6\ VO^{2+} + 6\ V^{+3} + 9\ H_2O \qquad (5)$$

A second intuition of the applicants relates to the use of sulfur dioxide for the reduction of vanadium +5 contained in the positively charged electrolyte solution for electrically balancing the two electrolyte solutions during the phase of producing electrolyte solution to be eventually added into the two circuits to reach the rated energy storage capacity of the system.

According to the consequent highly preferred embodiment, periodic (batch) manoeuvres for rebalancing the state of charge of the two electrolyte solutions circulating in the battery cells become unnecessary.

i. The yellow powder of V_2O_5 reacts very slowly with SO_2. Even a solution of sodium metabisulfite that in presence of acid develops immediately sulfur dioxide according to the reaction: $Na_2S_2O_5 + H_2SO_4 = Na_2SO_4 + SO_2 + H_2O$, does not react or reacts very slowly with V_2O_5. However, if this sulfite solution is mixed with V^{+5}, in ionic form VO_2^{+}, the reaction with of pentavalent vanadium and sulfur dioxide becomes extremely rapid and substantially quantitative. Reduction of vanadium ions by sulfites is very well known because sulfites are used for reducing vanadium ions in the analytical procedure to evaluate the concentration and the state of charge of vanadium;

ii. sulfur dioxide that does not react or react extremely slowly with solid V_2O_5, reacts very rapidly with V^{+5} in solution, the reaction is fast and selective; the product is only VO^{2+}:

$$2\ VO_2^{+} + SO_2 + 2\ H{+} = 2\ VO^{2+} + SO_3 + H_2O = 2\ VO^{2+} + H_2SO_4 \qquad (6).$$

iii. An experiment was carried out by bubbling gaseous SO_2 in a tank containing the positive electrolyte solution completely charged (yellow color), the color of the electrolyte became immediately blue and the analysis revealed that all the V^{+5} [VO^{2+}] had been transformed into V^{+4} [2 VO^{2+}].

The method of this disclosure takes advantage of

1) fast reduction and dissolving of V_2O_5 in the negatively charged electrolyte solution of a flow redox battery system, according to the reactions (3) and (4) between V_2O_5 and V^{+2}, by pre-suspending the solid V_2O_5 in an amount of sulfuric acid sufficient to prevent the irreversible reactions (1) and (2) to occur when mixed with the negatively charged electrolyte solution;

2) fast reduction according to reaction (5) between sulfur dioxide and the V+5 ions in the positive electrolyte solution of the battery cells used for energy storage.

3) exploitation of the same multi cell battery stack designed for the charging and discharging of the electrolyte solutions normally used for the storage of energy.

In practice, the novel method of the applicants permits, after having introduced in an all-vanadium flow redox battery system to be brought to operate at full capacity, a limited amount of electrolyte solution in one or in both circuits, pre-conditioned and thence charged at least the negative electrolyte solution or both of them, to fill the two circuit completely with the contemplated amount of electrolyte solution that is quickly and economically produced, substantially by adding V_2O_5, sulfuric acid, water and SO_2 into the working all-vanadium flow redox battery system.

Process details and effective embodiments are given in the ensuing detailed description making reference to the attached drawings.

The invention is defined in the annexed claims, the content of which is intended to constitute part of this description and is herein incorporated by express reference.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a basic scheme of an all-vanadium energy storage flow redox battery system with the ancillary equipment adapted for producing *in situ* an acid vanadium sulfate solution from commercial vanadium pentoxide powder, according to an embodiment of the present invention.

FIG. 2 shows an alternative way of conducting the *in situ* production of fresh vanadium electrolyte solution, for filling up the circulation circuits of the two electrolyte solutions of a battery system to be brought to full storage capacity or for increasing its original storage capacity.

FIG. 3 is a possible alternative configuration employing a horizontal tubular absorber with ejector of SO_2 into streaming positive electrolyte solution and inner static mixing means instead of a packed column.

FIG. 4 is yet another alternative configuration employing a stirred mixer with liquid overflow outlet pipe with dynamic seal for adjusting its height to maintain a constant gaseous SO_2 residue at the top of the mixer, and an eventual stirred saturator in cascade of the mixer.

FIG. 5 is a further alternative configuration employing a turbulent flow tubular absorber.

FIG. 6 is another alternative configuration employing a gas bubbler absorber

DESCRIPTION OF EMBODIMENTS

Process details like chemical reactions, parameters affecting their selectivity and/or rates, and alike conditions have obviously a general character and apply also to other embodiments of the method of this disclosure, using dedicated equipments, possibly designed for the sole purpose of producing vanadium sulfate solution from

commercial powder of V_2O_5 to be eventually used for filling up the circuits of an all-vanadium flow redox battery system. However, also to stress the exceptional adaptability of the method of this disclosure to best meet the quest of energy storage plant operators of abating the cost of the vanadium electrolyte inventory, the new method of preparation of the electrolyte will be exemplarily described for the case of exploiting the energy storage hardware itself for self-producing on site the needed volume of acid vanadium sulfate solution to fill up the two circuits of the all-vanadium flow redox battery system, to bring the system to the rated energy storage capacity.

With reference to **FIG. 1**, the additional equipments and related piping that are required for making the all-vanadium flow redox battery system adapted to produce the needed volume of acid vanadium sulfate solution to fill up the two circuits of the all-vanadium flow redox battery system, that is to say to fill the two tanks **V-Neg.** and **V-Pos.**, were the negatively charged and the positively charged electrolyte solutions are respectively stored, in order to bring the system to the rated energy storage capacity, are made more immediately recognizable by being drafted with thicker lines.

These added equipments comprise:

- a stirred vessel **R-1** for mixing the feed powder of V_2O_5 with the required amount of sulfuric acid and dilution water;
- a stirred reactor **R-2** where a portion of the negatively charged electrolyte solution, spilled from the delivery side pipeline of the circulation pump **P1**, is made to react with the V_2O_5 suspended in sulfuric acid solution, spilled from the vessel **R-1**;
- a first absorption tower **TW1** of SO_2 in a portion of the positively charged electrolyte solution, diverted from the delivery side pipeline of the circulation pump **P2** of the respective battery circuit;

- a second absorption tower **TW2** for stripping with air any unreacted residue of SO_2 from the electrolyte solution before returning to the respective battery circuit e.g. into the **V-Pos**. tank;
- a maturation vessel B into which collecting the freshly produced acid vanadium sulfate electrolyte solution providing for a residence time adapted to ensure a complete reduction and dissolution of V2O5 and means for returning the diverted volume of negatively charged electrolyte solution to the respective circuit, e.g. into the V-Neg. tank, and for conveying the freshly generated volume of solution to a reservoir (not shown in the scheme);
- a filter in the delivery pipeline of the circulation pump P1 to prevent any undissolved particle to circulate in the negative electrode compartments of the cells of the battery.

According to an alternative embodiment depicted in **FIG. 2**, the freshly produced volume of acid vanadium sulfate electrolyte solution is distributed to the **V-Neg** and to the **V-Pos**. tanks of the respective circulation circuits of the flow redox battery, taking into account the diverted volume to be returned to the negative electrolyte circuit together with the fleshly generated vanadium solution.

Of course, the means used for absorbing gaseous sulfur dioxide in the positively charged vanadium sulfate electrolyte solution may be chosen among many alternative apparatuses known to the expert technician.

FIG. 3 is a possible alternative configuration employing a horizontal tubular absorber with ejector of SO_2 into streaming positively charged electrolyte solution and inner static mixing means instead of a packed column.

FIG. 4 is yet another alternative configuration employing a stirred mixer **R-3** provided with a liquid overflow outlet pipe with dynamic seal for adjusting its height as far as to maintain a constant volume sac of gaseous SO_2 residue at the top of the mixer,

and an eventual stirred saturator **R-4**, in cascade of the mixer.

FIG. 5 is a further alternative configuration employing a turbulent flow tubular absorber of easy scalability. Flow rate of the liquid in the conduit that may even be conveniently coiled, is maintained well above Reynolds 5000 to ensure a turbulent regime that favors gas absorption-reaction.

FIG. 6 is another alternative configuration employing a gas bubbler absorber with overflow discharge.

In order to start the on site production of fresh vanadium electrolyte solution from commercial powder of V_2O_5, according to the method of this disclosure, a minimum amount of electrolyte solution sufficient to safely operate the pumps **P1** and **P2** and the battery cells **C**, the flow compartments of which are hydraulically separated by a membrane permeable to anions, must be introduced in the two circuits of the flow redox battery system. Of course this amount of electrolyte solution must be procured or taken from a reserve stock.

The priming positive and the negative electrolyte solutions are then conditioned and charged to a state of charge of at least 40 to 60% and preferably at least 50%.

Meanwhile, the feed powder of V_2O_5 that may be of quantity equivalent to the amount of vanadium to be loaded in the energy storage system for providing the rated energy storage capacity (less the amount already loaded with the priming volumes of electrolyte solutions introduced for making operable the battery), is suspended in a first purposely added stirred vessel **R-1** in sulfuric acid in a molar ratio that may preferably be of 4 to 5 mole of sulfuric acid per mole of vanadium pentoxide, though a slightly lower or a higher ratios may be practiced.

When, preferably, at least the 50% state of charge is reached, a small amount of the negative electrolyte is diverted from the delivery line of the pump **P1** and sent into a stirred reactor **R-2** together with a commensurate amount of V_2O_5 suspended in sulfuric

acid spilled from the vessel **R-1**. Of course appropriate valve means (not shown in the basic diagram of the figure) may be deployed for controlling the process of production of the vanadium electrolyte solution.

The following fast reactions will occur (already discussed as equation (5) and equation (6) in the chapter General Description):

$V_2O_5 + 4\ VSO_4 + 5\ H_2SO_4 = 3\ V_2(SO_4)_3 + 5\ H_2O$ (i.e.: eq. 5)

$V_2O_5 + VSO_4 + 2\ H_2SO_4 = 3\ VOSO_4 + 2\ H_2O$ (i.e.: eq. 6)

However, assuming to be using a negatively charged electrolyte solution at 50% state of charge, there will be an equal percentage of V^{+2} and of V^{+3} in the spilled negatively charged electrolyte solution; therefore the condition of 50% V^{+3} and 50% VO^{2+} is achieved with reaction (5) multiplied by two and reaction (6) multiplied by 10.

Therefore the wanted reactions are:

$2V_2O_5 + 8\ VSO_4 + 10\ H_2SO_4 = 6\ V_2(SO_4)_3 + 10\ H_2O$ (7)

$10\ V_2O_5 + 10\ VSO_4 + 20\ H_2SO_4 = 30\ VOSO_4 + 20\ H_2O$ (8)

Summing to

$12\ V_2O_5 + 18\ VSO_4 + 30\ H_2SO_4 = 30\ VOSO_4 + 6\ V_2(SO_4)_3 + 30\ H_2O$ (9)

A typical vanadium electrolyte solution is prepared with about 2 mole of sulfuric acid per mole of vanadium, therefore 4 mole of sulfuric acid are needed for each mole of vanadium pentoxide. The amount of sulfuric acid to be added to 1 mole of vanadium pentoxide is, in generally between 4 to 5 mole (of sulfuric acid per mole of V_2O_5).

What follows is the balance of the system for the preparation of electrolyte corresponding to 1 mole (182 g) of vanadium pentoxide powder per hour.

The amount of sulfuric acid that we need to add to the vanadium pentoxide powder in the mixer vessel R-1(on the left side of the diagram) is 4 to 5 mole of sulfuric acid per mole of vanadium minus the mole of sulfuric acid that are produced in the positively charged electrolyte solution circuit of the battery cells when reducing V^{+5} to

V^{+4} using sulfur dioxide, and that are transferred with the ionic current through the permionic membrane separator of the cells. This means that 400 to 500 g of sulfuric acid at 98% concentration must be added for every 182 g of V_2O_5, minus the mole of sulfuric acid produced on the anodic side and that will migrate through the anionic membrane used in the battery cells.

Since it is necessary to reduce the vanadium ion of the V_2O_5 from an oxidation state of +5 to an oxidation state of +3.5, the total amount (in mole) of vanadium to be reduced is 2 x (5-3.5) = 2 x1.5 = 3 mole/h. The electric current required for this reduction is exactly 3 mole/h x 96450 Coulombs = 3 mole/h x 96500/3600 (sec/h) = 80.4 Ah.

Forcing this current through the cells, 3 mole (per hour) of vanadium ions will be oxidized from V^{+4} to V^{+5} according to the reaction: $VO_2^+ + H_2O = VO^{2+} + 2\ H^+ + e^-$ that therefore becomes $3VO_2^+ + 3H_2O = 3VO^{2+} + 6\ H^+ + 3e^-$.

At the same time it is necessary to reduce 3 mole of V^{+5} [i.e. $3VO_2^+$] to V^{+4} [i.e. $3VO^{2+}$] and this reduction is carried out using sulfur dioxide according the reaction:

$2VO_2^+ + SO_2 + 2\ H+ = 2\ VO^{2+} + H_2SO_4$ that becomes

$3VO_2^+ + 3/2\ SO_2 + 3\ H+ = 3\ VO^{2+} + 3/2\ H_2SO_4$

The amount of SO_2 required to reduce al the V^{+5} to V^{+4} is: 3/2 mole or 3/2 x 64 = 96 g and the sulfuric acid produced will be 150 g.

Therefore, instead of adding 400 g of sulfuric acid into the mixer vessel R-1, only 250 g are needed.

Every mole of vanadium pentoxide requires 3 mole of sulfur dioxide for electrically rebalancing the two electrolyte solutions.

In practice the preparation of electrolyte corresponding to 1 mole of V_2O_5, (approximately 1 liter (1.34 kg) of electrolyte having concentration of vanadium of 2 mole/liter) will require:

V_2O_5: 182 g (2 mole of vanadium every 1 mole of V_2O_5)

H_2SO_4 98%: 400 – 150 = 250 g per mole of V_2O_5 : 2.5 mole

SO_2 (gas): 96 g per mole of V_2O_5: 1.5 mole

Water: 700 – 800 g per mole of V_2O_5 (depending on evaporation, etc.).

The ratio between vanadium and sulfuric acid will remain equal to 1 mole of vanadium per 2 mole of sulfuric acid.

The amount of sulfuric acid that will pass through the membrane as SO_4^{-2} will be (80.4 Ah) / (26.8 Mole/Ah) = 3 mole that divided by 2 (charges carried by SO_4^{-2}: $2e^-$), becomes 1.5 mole.

Therefore 2.5 mole will be added as sulfuric acid and 1.5 mole are the mole of sulfuric acid that will be produced using sulfur dioxide and that will transfer through the anionic membrane.

Sulfuric acid has a variable price ranging from about 100 to 350 US$/Metric ton, the price is very variable because in general sulfuric acid is not transported over long distances and it is locally produced all over the world. The production is exclusively from sulfur (or pyrite) via oxidation to sulfur dioxide and then oxidation to sulfuric acid with vanadium pentoxide catalysts. By contrast, sulfur dioxide is the precursor of sulfuric acid and is readily available everywhere (usually in pressure cylinders).

In the process of this disclosure, instead of purchasing 400 g of sulfuric acid (per mole of V_2O_5 or per liter of electrolyte with vanadium 2 molar), 250 g of sulfuric acid and 96 g of sulfur dioxide need to be purchased, with an evident saving.

A different analysis could be as follows.

The global reaction being used is:

$$2\ V_2O_5 + 3\ SO_2 + 2\ H_2SO_4 = 2VOSO_4 + V_2(SO_4)_3 + 2\ H_2O \qquad (10)$$

that written in ionic form becomes:

$$2\ V_2O_5 + 3\ SO_2 + 2\ H_2SO_4 = 2VO^{2+} + 2V^{+3} + 5\ SO_4^{-2} + 2\ H_2O \qquad (11)$$

This reaction as such is very slow because sulfur dioxide does not react easily with vanadium pentoxide or the reaction is so slow that it is unusable.

By contrast, alike the reactions (3) and (4) between V_2O_5 and V^{+2}, also the reaction between SO_2 and VO^{2+} is also very rapid

$$2\ VO^{2+} + SO_2 + 2\ H+ = 2\ VO^{2+} + H_2SO_4 \qquad (12)$$

According to this invention, the flow redox battery cells are exploited for providing V^{+2} generated at the negative electrode that is thence exploited for dissolving and reducing vanadium pentoxide according to the reactions (3) (4) and simultaneously, at the positive electrode VO^{2+} is generated that is thence exploited for reacting with SO_2 injected into the positive electrolyte solution, according to the fast reaction (12).

EXAMPLE 1

The task was to produce on site the electrolyte solution required to store 60 kWh of energy at a rated power of 5 kW with a charge time of 12 hours.

For a normal vanadium concentration of 1.6 mole/liter, the quantity of electrolyte solution required is 25 liter/kWh for each of the two battery circuits of the negatively charged and of the positively charged electrolyte solutions, thus a total of 50 liter/kWh.

Theoretically, storing of 1 kWh requires 55.28 mole of vanadium (1,000 kVAh divided by 1.35 Volt (average cell voltage), divided by 26.8 Ah/mole and multiplied by 2). However, by considering the efficiency of the cells and the reduced range of utilization for energy storage of the state of charge, in practice 80 mole (instead of 55.28 mole) of vanadium are required and this correspond to a real world volume requisite of 50 liters (containing 1.6 mole of vanadium/liter) of electrolyte solution per kWh.

The total amount of electrolyte solution to be prepared is therefore 3,000 liters.

The 5 kW battery system consisted of 42 cells operated, in charge mode, at 100 Ampere (50 Volt); the total current is 4,200 Ampere.

Reduction of a vanadium ion from a degree of oxidation +5 to +3.5 requires 1.5

Faraday (1.5 x 26.8 Ah [26.8 = 96459 Coulomb/3600 sec/h]), therefore the reduction of 1 mole of V_2O_5 requires 3 x 26.8 Ah = 80.4 Ah. Therefore, 4200 A reduce 4200/80.4 = 52.24 moles/h or 47 mole/h of V_2O_5, at 90% efficiency.

47 moles of V_2O_5 are equivalent to 94 mole of vanadium and produce 94/1.6 = 58.75 l/h of electrolyte containing 1.6 moles of vanadium.

47 moles of V_2O_5 require a minimum of 70.5 (= 47 x 3 / 2) moles of V^{+2} [or VSO_4] according to the reaction: $2\ V_2O_5 + 3\ VSO_4 + 5\ H_2SO_4 = 5\ VOSO_4 + V_2(SO_4)_3 + 5\ H_2O$.

Since the concentration of V^{+2} in the 50% charged electrolyte is (by definition of the 50% state of charge) 0.8 mole/l, only 70.5 mole will require (70.5/0.8=) 88.15 liters/hour of negatively charged electrolyte solution to be diverted from the recirculation circuit of the working battery into the reduction reactor into which the suspension of V_2O_5 in sulfuric acid solution is fed and admixed to the negatively charged electrolyte solution.

The two electrolyte circuits of the 5 kW energy storage system were filled with 40 liters of standard electrolyte solution per tank sufficient to fill the battery circuit, namely: cell compartments, pumps and piping (approximately 12 liters) and to have sufficient liquid (28 liters) in the tank for safely operating the recirculation pumps. (Standard electrolyte solution contains 1.6 mole/liter of vanadium of which 0.8 mole/liter of V^{+3} [0.4 mole of $V_2(SO_4)_3$] and 0.8 mole/liter of V^{+4} or VO^{+2} [0.8 mole/liter of $VOSO_4$]).

Keeping the two electrolyte pumps **P1** and **P2** in continuous operation (each pump operated with a flow of approximately 3,000 liter/h) the two electrolyte solutions (40 liter per circuit) were charged up to a state of charge of 50% (open circuit battery voltage of 1.35 Volt).

Once the 50% state of charge was reached, 88 liters/h of negatively charged

electrolyte solution (out of a total of 3,000 liter/hour being pumped in the circuit) were diverted from the delivery pipe of the negative electrolyte pump to flow through a cylindrical 30 liter stirred plastic reactor, into which 8.55 kg/h (equivalent to 47 mole) of V_2O_5 were added after premixing it with sulfuric acid 6.26 liter/h (11.5 kg/h) and water 51.6 liter/h inside a smaller 10 liter plastic vessel also provided with a stirrer. Both the 30 liter reaction vessel and the 10 liter mixing vessel were provided with a stainless steel cooling pipe coil.

The overflow stream of solution (88.15 liter/h) from the reactor was partially returned to the negative electrolyte tank in order to keep a constant level of electrolyte therein and a balance stream of about 58.75 l/h, collected and stored in a separate tank represented the fresh vanadium electrolyte solution produced.

The analysis of the electrolyte solution produced showed a vanadium concentration of 1.61 mole/liter, and a state of oxidation of + 3.48.

At the same time, while part of the negative electrolyte solution was being diverted from the delivery side of the negative electrolyte recirculation pump through the stirred reactor, 530 liters per hours of the positively charged electrolyte solution were diverted from the delivery pipe of the positive electrolyte pump and conveyed to the top of a 6" PVC tower **TW1** packed with 15 mm Rashig rings. The height of the packing was 700 mm. At the bottom of the tower sulfur dioxide from a pressurized cylinder was introduced at a rate of 30 liter/minute (corresponding to approximately 70 mole/h of sulfur dioxide). The SO_2flow was regulated in order to keep the state of charge of the positive electrolyte solution equal or higher than 50%. The state of charge of the positive electrolyte was also measured using an ORP probe. The value of the oxidation-reduction potential was kept between 650 and 800 mV. An excessive flow rate of SO_2 would bring the ORP below 650 mV, which would indicate a lower than 50% state of charge of the electrolyte and a too low flow rate would bring the ORP to

exceed the set value, which would indicate a higher than 50% state of charge.

A state of charge below 20% would drastically reduce the rate of absorption of sulfur dioxide and a very high state of charge could deteriorate the positive electrode of the cell as oxygen may be evolved if the electrolyte solution is overcharged.

The liquid leaving the bottom of the tower was conveyed to the top of a similar tower **TW2**, packed with Rashig rings (height of the packing 500 mm) and air was blown at the bottom of the second tower at the same rate of 30 liter/minute. The liquid outlet at the bottom of the second tower was conveyed to the positive electrolyte solution tank **V-Pos**.

The concentration of vanadium+5 at the top of the first tower **TW1** was measured and found to be 0,81 mole/liter (this was consistent with the 50% state of charge of the electrolyte) while at the bottom of the second tower **TW2** the concentration of vanadium+5 in the liquid was only 0.54 mole/liter. The difference (0.27 mole/liter) had reacted with the sulfur dioxide according to the reaction: $(VO_2)_2SO_4 + SO_2 = 2\ VOSO_4$, thus and transformed into vanadium+4. This was confirmed by analysis proving that the concentration of V^{+4} in the electrolyte that was 0.79 mole/liter, at the top of the absorbing tower, and 1.06 mole/liter, at the outlet of the second tower **TW2** (residual SO_2 stripper).

EXAMPLE 2

The same preparation was carried out in a semi-batch mode consisting of two phases.

At the beginning the preparation is the same as in Example 1; the two electrolyte recirculating tanks are each filled with 50 liters of available standard electrolyte.

The electrolyte has the following composition: vanadium: 1.6 mole/l, total sulfuric acid: 3.2 mole/liter (2 mole per mole of vanadium) and water 52 mole/liter (specific weight about 1.34 kg/l).

Therefore, 3000 liters (4,020 kg) of standard electrolyte contain: vanadium: 4800 mole, equivalent to 438 kg of V_2O_5, sulfuric acid: 9,600 mole, equivalent to 960 kg and water 2800 liters.

Therefore, the used feed materials are:

Vanadium pentoxide: 438 kg;

Sulfuric acid: 600 kg as liquid concentrated sulfuric acid corresponding to 326 liters and 360 kg generated by the oxidation of 230 kg of sulfur dioxide.

Water: 2800 liters

The preparation of the electrolyte is carried out in the following way:

First Phase (using only half of the water, half of the V_2O_5 and all the sulfuric acid)

200 liter of water are added in the positive electrolyte tank **V-Pos**. and mixed with the 50 liters of standard electrolyte solution.

1,200 liters of water are added in the negative electrolyte tank **V-Neg**. to the 50 liters of electrolyte and mixed slowly with 326 liter (600 kg) of sulfuric acid and the tank is allowed to cool down to room temperature.

Keeping the two electrolyte solution pumps **P1** and **P2** in continuous operation (each pump operated with a flow rate of approximately 3,000 liter/h) the two electrolytes are then charged up to a state of charge of at least 50% (open circuit voltage 1.35 Volt).

When the 50% or higher state of charge is reached, 88 liters/hour of negatively charged electrolyte (out of a total of 3,000 liter/hour) are diverted from the delivery pipe of the negative electrolyte pump **P1** to a 30 liter plastic cylindrical stirred reactor where 5.7 kg/h (equivalent to 30 mole) of V_2O_5 are slowly added. The overflow stream of solution from the reactor vessel is returned entirely to the negative electrolyte tank. Normally, it should take approximately 38 to 40 hours to dose the 218.4 kg of V_2O_5 at a

rate of 5.7 kg/hour into the stirred reactor.

The 5 kW battery storage system provides 4,200 Ah (100 Ampere x 42 cells). The vanadium of V2O5 is reduced from the oxidation state +5 to the oxidation state +2 and +3 (average +2.5). Therefore, the reduction from +5 to +2.5 is a reduction of -2.5. The reduction of 1 mole requires 26.8 Ah for each unit variation of state of oxidation, therefore every ion of vanadium requires 26.8 Ah x 2.5 = 67 Ah/mole. Therefore, 4200 Ah reduce 4200 Ah / 67 Ah/mole = 62.69 mole of vanadium. Since V_2O_5 has two atoms of vanadium only 31.34 mole per hour of V_2O_5 are reduced or 31.34 x 182 = 5.7 kg.

At the same time, while part of the negative electrolyte is diverted from the delivery side of the negative electrolyte recirculation pump **P1** to the stirred reactor, 530 liter/hours out of a total of 3,000 liter/hour of the positive electrolyte solution are diverted from the delivery side of the positive electrolyte pump **P2** and conveyed to the top of the 6" PVC tower packed with 15 mm Rashig rings for a height of the packing of 700 mm. At the bottom of the tower sulfur dioxide, from a pressurized cylinder, is introduced at a rate of 79 mole/h = 5 kg/h = 32 liter of SO_2 gas/min. This uses 190 kg of SO_2 out of the 230 kg required.

At the end of the first phase, the negative electrolyte tank **V-Neg.** will contain approximately 1,600 liters of electrolyte while the positive electrolyte tank **V-Pos.** will contain approximately 150 liters.

Second Phase:

1,500 liters of electrolyte solution are transferred from the negative electrolyte tank **V-Neg.** to the positive electrolyte tank **V-Pos.**. Therefore at the beginning of the second batch phase, the negative electrolyte tank contains approximately 100 liters of electrolyte solution while the positive tank contains approximately 1,650 liters.

The remaining 1400 liters of water are thence added to the negative electrolyte

tank **V-Neg.** , which thus now contain 1,500 liter of solution.

The pumps **P1** and **P2** of the system are restarted and charging of the battery system is resumed at 100 Ampere. At start, the negative electrolyte solution will have a state of charge of approximately 50% while the state of charge of the positive electrolyte solution will be below zero.

Only a by-pass stream of 88 liters/hour of the positive electrolyte (out of a total of 3,000 liter/hour) are diverted from the delivery pipe of the positive electrolyte pump to the stirred reactor and again 5.7 kg/h (equivalent to 30 mole) of V_2O_5 are slowly added. The overflow stream from the reactor is wholly returned to the negative electrolyte tank **V-Neg.**.

Contrarily, the positive electrolyte is normally circulated through the battery cells **C** and the respective tank until it state of charge will raise from below zero to + 50%.

The time required for the state of charge of the positive electrolyte solution to reach 50% during this second phase, is approximately 30 hours. As soon as the state of charge of the positive electrolyte exceeds 50%, the diverting of a stream of 530 liter/hours is resumed and SO_2 is dosed at the bottom of the packed tower at the same rate of 79 mole/h = 5 kg/h = 32 liter of SO_2 gas/min. The whole duration of the second batch phase is of about 38 hours.

At the end of the two batch phases each tank will contain approximately 1,550 to 1,600 liters of electrolyte solution at approximately 50% state of charge.

In both the examples, the battery system was then discharged by connecting an electrical load to the battery and the electrolytes solution of the two circuits were mixed together.

The analysis of the mixed electrolyte solution revealed that the concentration of vanadium was 1.6 mole/liter and the state of oxidation +3.51.

The concentration of vanadium in the two solutions even of an energy storage

flow redox battery system working at full volumetric capacity can be increased and the state of charge can be modified by recharging the system at 50% state of charge and by diverting streams of the two electrolyte solutions to carry out the same reactions as during the preparation of fresh electrolyte solution.

In practice, the existing concentration of vanadium can be increased by adding V_2O_5 to the 50% charged negatively charged electrolyte solution and absorbing SO_2 in the positively charged electrolyte solution. To maintain a balance between the solutions, it must be considered that for every 2 mole of vanadium pentoxide, 5 moles of sulfur dioxide need to react in the positively charged solution, according to the reaction

$2V_2O_5 + 5\ SO_2 = V2(SO_4)_3 + 2VOSO_4$

The presence of the ancillary sub-system of treatment of the positively charged electrolyte solution with SO_2 may even have a general utility for re-balancing the electrical state of charge of the two electrolyte solutions of an all-vanadium energy storage battery system, whichever the cause.

When the two electrolyte solutions (negative and positive electrolytes) are mixed, the state of oxidation of vanadium in the mixture should always be +3.5 (50% V+3 and 50% V+4 or VO+2). Often though, the state of oxidation of vanadium in the mixed electrolyte is higher than +3.5 because during operation of the battery system V+2 in the negative electrolyte tends to be oxidized to V+3 if exposed to atmospheric air. This cause of unbalancing of charges between the two electrolyte solutions reduces the energy storage capacity of the battery system. The state of oxidation of the electrolyte may be lowered back to +3.5 by charging the system up to 50% and then treating the 50% positively charged electrolyte solution with gaseous SO .

CLAIMS

1. A method of producing *in situ*, from vanadium pentoxide, an acid vanadium sulfate solution adapted to be used as electrolyte solution in separated positively and negatively charged electrolyte solution circulation circuits of an all-vanadium flow redox battery system, comprising the separate or unified actions of:

mixing vanadium pentoxide powder with sulfuric acid and water of dilution to form a suspension of vanadium pentoxide powder in sulfuric acid solution; and

mixing the vanadium pentoxide suspension in sulfuric acid with negatively charged electrolyte solution, having a non null state of charge, of the all-vanadium flow redox battery system, for dissolving and reducing the vanadium pentoxide, producing fresh acid vanadium sulfate solution there from.

2. The method of claim 1, wherein the actions are performed in two separate steps and the mixing of the vanadium pentoxide powder sulfuric acid suspension with the negatively charged electrolyte solution is carried out with part of the negatively charged electrolyte solution purposely diverted from the negatively charged electrolyte circuit of the flow redox battery system and thence returned to it.

3. The method of claim 2, wherein the steps are conducted in continuous mode using a stream of negatively charged electrolyte solution diverted from the respective circuit of the flow redox battery system, for passing through at least a stirred reactor, into which said vanadium pentoxide suspension is continuously dosed, before returning a volume of the negative electrolyte solution and fresh acid vanadium sulfate solution produced equivalent to the diverted volume to the negative electrolyte circuit of the working battery and collecting the freshly produced volume of acid vanadium sulfate solution, and further including the steps of

diverting a stream of positively charged electrolyte solution from the respective circulation circuit of the battery for passing it in an absorber fed with gaseous sulfur

dioxide for reducing vanadium+5 (VO^{2+}) contained in the positively charged electrolyte solution at a rate adapted to maintain a balanced state of charge of the two electrolyte solutions of the battery system during the process of producing fresh electrolyte solution from vanadium pentoxide.

percolating the positively charged electrolyte solution leaving the absorber through an air fed packed column stripper of any residue of un-reacted sulfur dioxide before returning the diverted stream of positively charged electrolyte solution to the respective circulation circuit.

4. The method of claim 1, wherein the collected volume of freshly produced acid vanadium sulfate solution is distributed to the two separated electrolyte solution circuits of the flow redox battery system.

5. The method of claim 1, wherein the collected freshly produced volume of acid vanadium sulfate solution is accumulated and successively distributed into the two separated vanadium electrolyte solution circuits of the flow redox battery system.

6. A modified all-vanadium flow redox battery system for *in situ* production of fresh acid vanadium sulfate solution adapted to be used as electrolyte solution in separated positively and negatively charged vanadium electrolyte solution circulation circuits of the flow redox battery system for increasing storage capacity, comprising.

a) a flow redox battery system composed of at least a plurality of flow redox cells (C) having a positive electrode flow compartment (+) and a negative electrode flow compartment (-), separated by an anionic membrane, separate circulation circuits, including at least a storage tank (V-Neg., V-Pos.) and a pump (P1, P2), of an acid vanadium sulfate electrolyte solution in the two electrode compartments of the cells for positively charging the electrolyte solution of one circuit and negatively charging the electrolyte solution of the other circuit;

b) a stirred vessel (R-1) for blending together sulfuric acid, water of dilution and vanadium pentoxide powder forming an acid suspension thereof;

c) a stirred reactor (R-2) having an inlet and an outlet coupled to the circulation circuit of the negatively charged electrolyte solution of the battery system;

d) a sulfur dioxide fed absorber (TW1) coupled to the circulation circuit of positively charged electrolyte solution, through which part of the circulating electrolyte is diverted for absorbing sulfur dioxide and chemically reducing vanadium+5 (VO^{2+}) contained in the positively charged electrolyte solution to vanadium+4 ($VOSO_4$);

e) an air fed packed column stripper (TW2) of un-reacted residue of sulfur dioxide, connected in cascade of a liquid outlet of said absorber (TW1) and having a liquid outlet connected to the respective circulation circuit for returning therein the diverted stream of positively charged electrolyte solution;

f) means adapted to dose said vanadium pentoxide suspended in sulfuric acid solution into said negatively charged electrolyte solution flowing through said stirred reactor (R-2) for dissolving and reducing the suspended vanadium pentoxide (V_2O_5) to soluble compounds of vanadium+3 (V^{+3}) and vanadium+4 (VO^{2+}), at a rate adapted to maintain a balanced state of charge between the two electrolyte solutions circulating in the respective circuits of the flow redox battery system.

7. The system of claim 6, wherein said absorber is chosen among the group composed of gravity operated packed columns, tubular absorber with gas ejector and inner static mixing means, stirred mixer with adjustable overflow liquid outlet, turbulent flow tubular absorber and gas bubbler absorber.

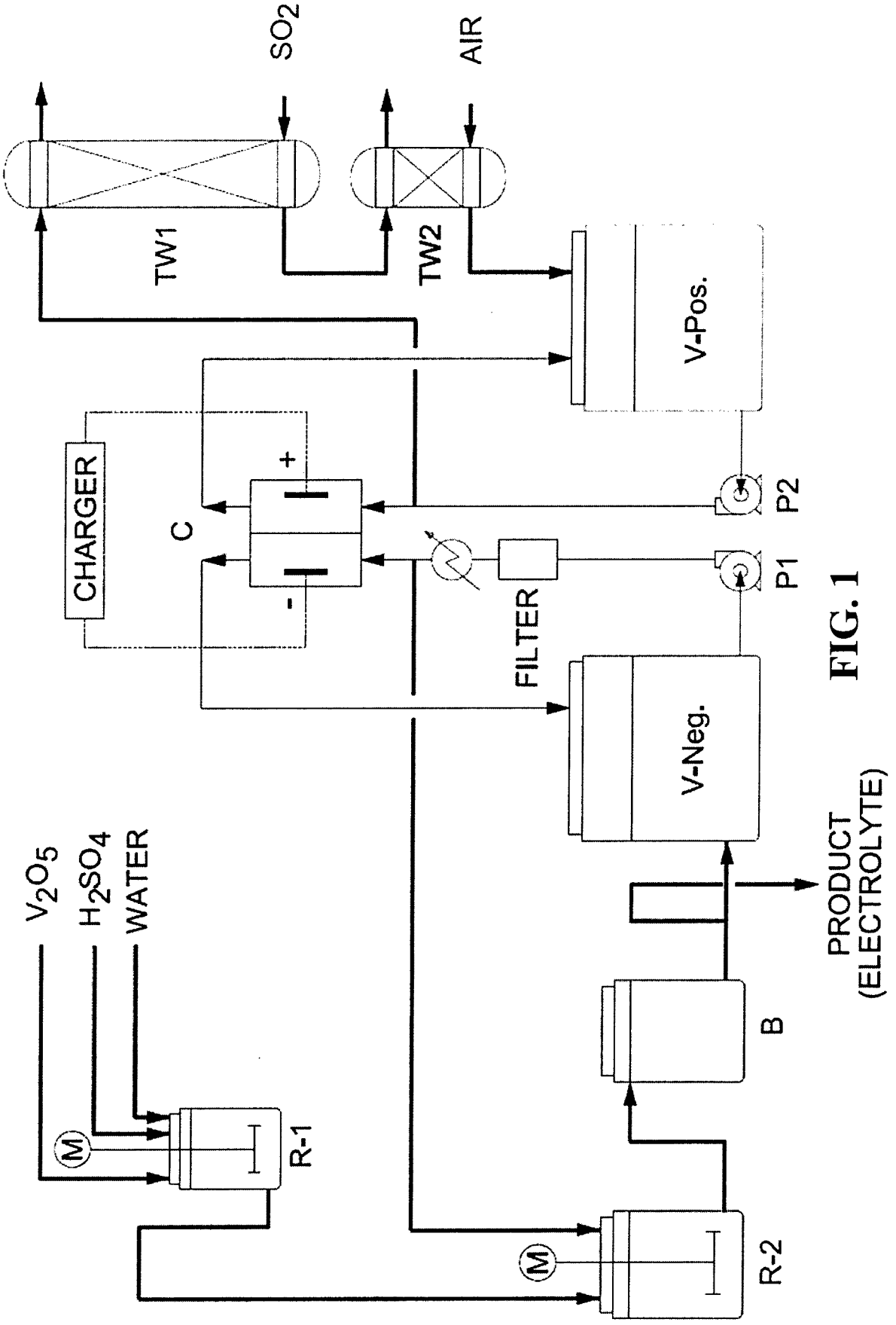
SO2
AIR
TW1
TW2
V-Pos.
CHARGER
C
+
-
P2
P1
FILTER
V-Neg.
V2O5
H2SO4
WATER
M
R-1
B
PRODUCT
(ELECTROLYTE)
M
R-2

FIG. 1

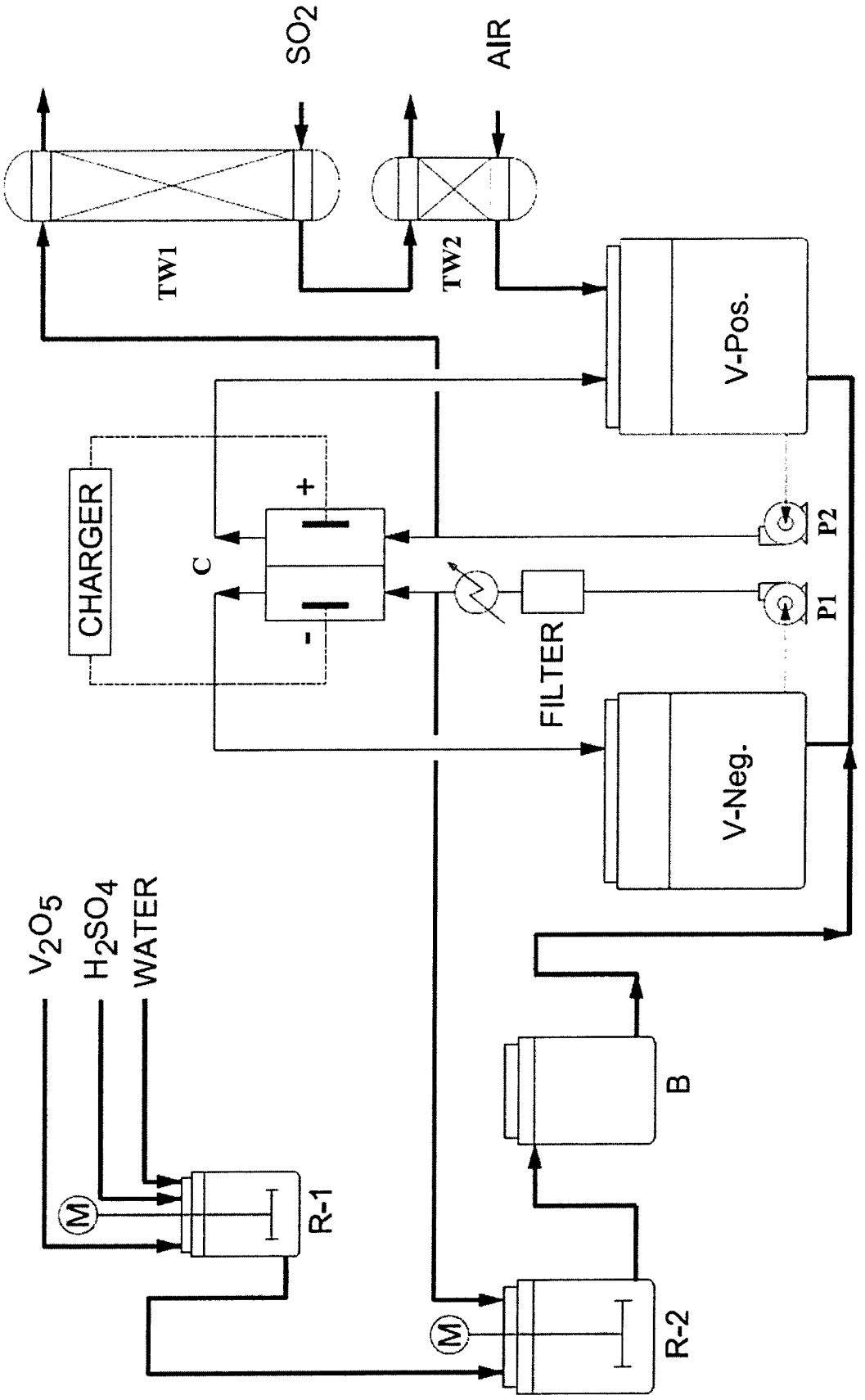
SO_2
AIR
TW1
TW2
V-Pos.
CHARGER
+
-
C
P2
P1
FILTER
V-Neg.
V_2O_5
H_2SO_4
WATER
M
R-1
B
R-2
PRODUCT
(ELECTROLYTE)

FIG. 2

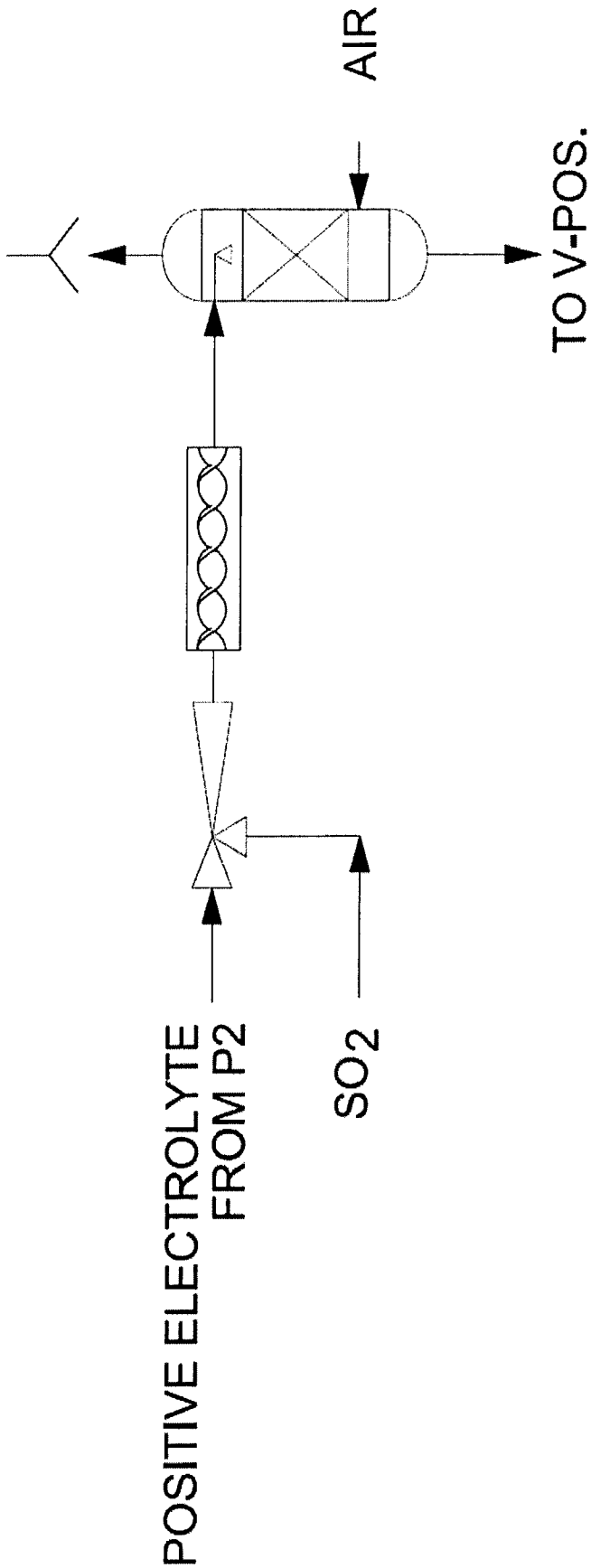

FIG. 3

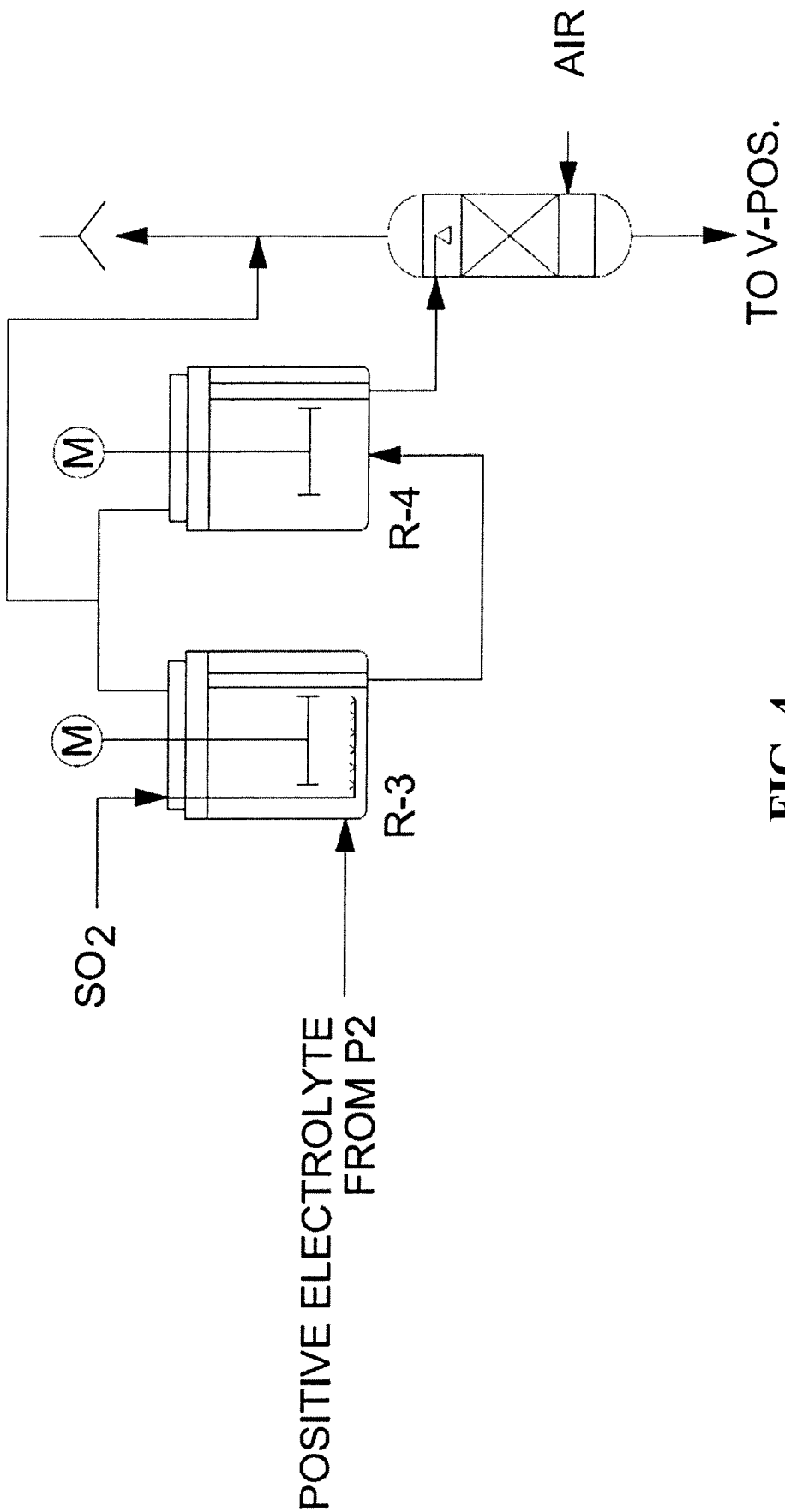

FIG. 4

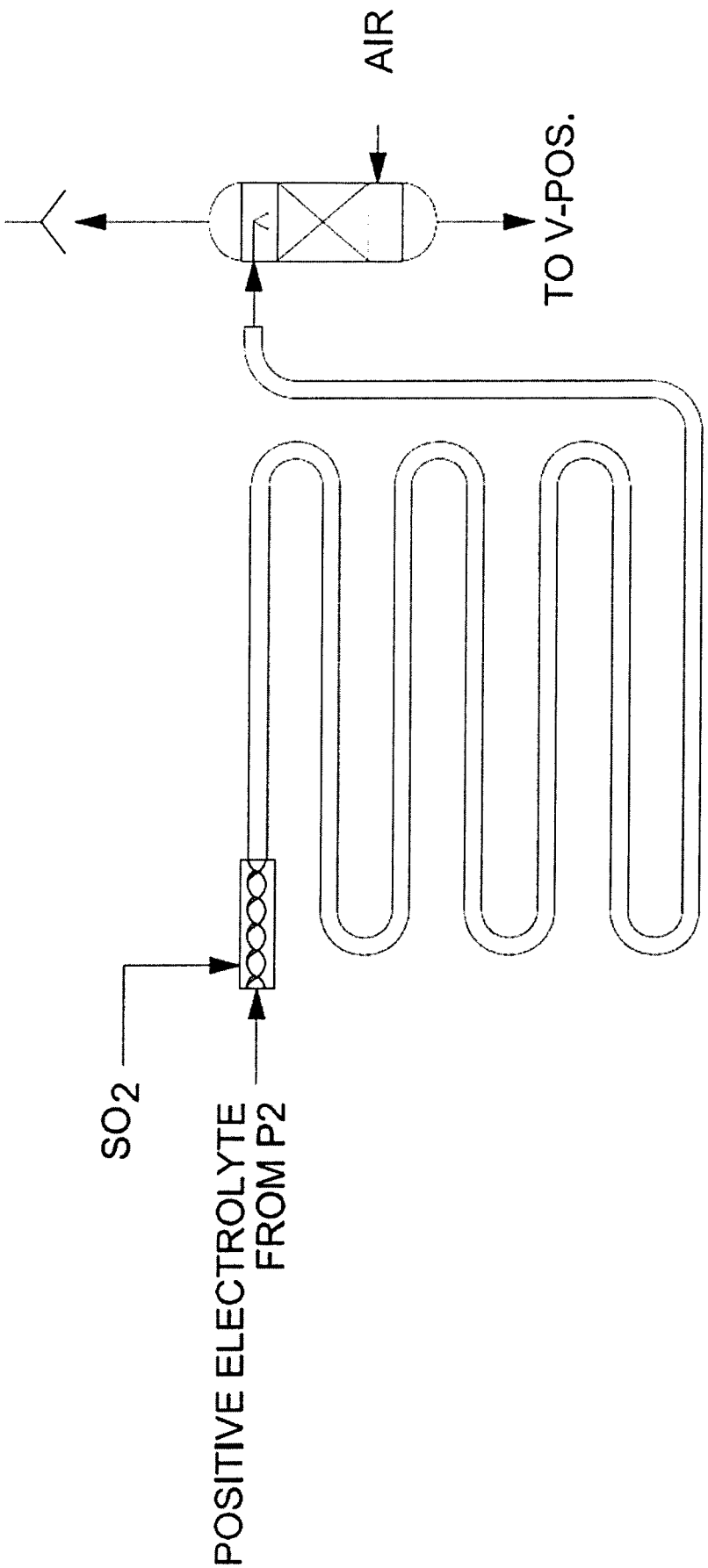

FIG. 5

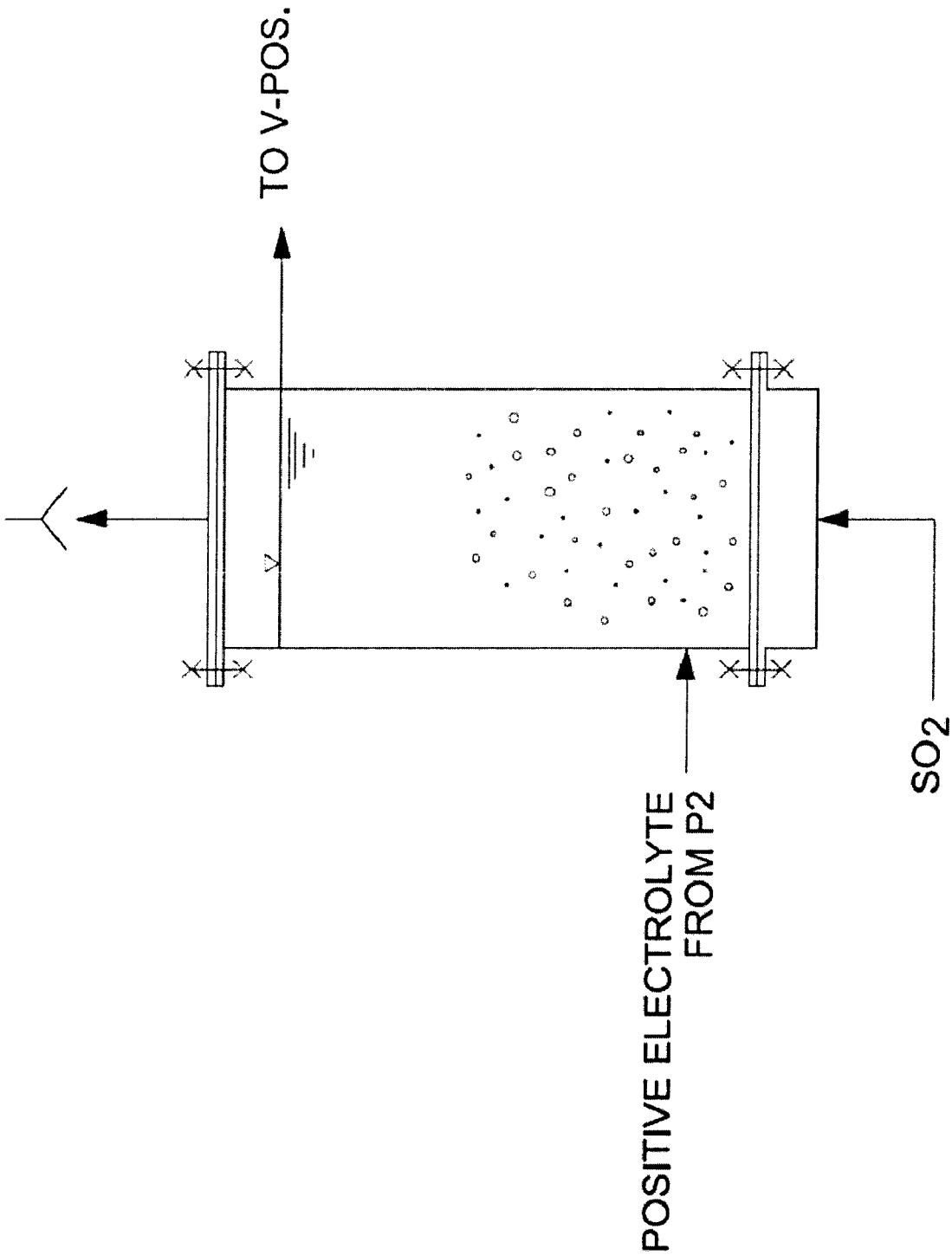

FIG. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2011/001928

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M8/18 C01G31/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01M C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 89/05363 A1 (UNISEARCH LTD [AU]) 15 June 1989 (1989-06-15)	1
Y	page 13, line 1 - page 17, line 14; claims 1-19; examples 1-8	2
Y	US 5 250 158 A (KANEKO HIROKO [JP] ET AL) 5 October 1993 (1993-10-05) claims 1-10; examples 1-7	2
A	WO 02/15317 A1 (SQUIRREL HOLDINGS LTD [GB]; PELLEGRI ALBERTO [IT]; BROMAN BARRY MICHAE) 21 February 2002 (2002-02-21) claims 1-7; figure 1	1-7
A	US 2002/048546 A1 (TANAKA YASUYUKI [JP] ET AL) 25 April 2002 (2002-04-25) the whole document	1-7

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 January 2012	24/01/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Wiedemann, Eric

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2011/001928

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 10 2007 011311 A1 (MTU CFC SOLUTIONS GMBH [DE]) 26 June 2008 (2008-06-26) claims 1-17	1-7
A	EP 0 713 257 A1 (KASHIMA KITA ELECTRIC POWER CO [JP]) 22 May 1996 (1996-05-22) claims 1-9	1-7

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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