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(54) Title: METHOD OF CONDUCTING AN ALL VANADIUM REDOX FLOW BATTERY AND IMPLEMENTING SYSTEM

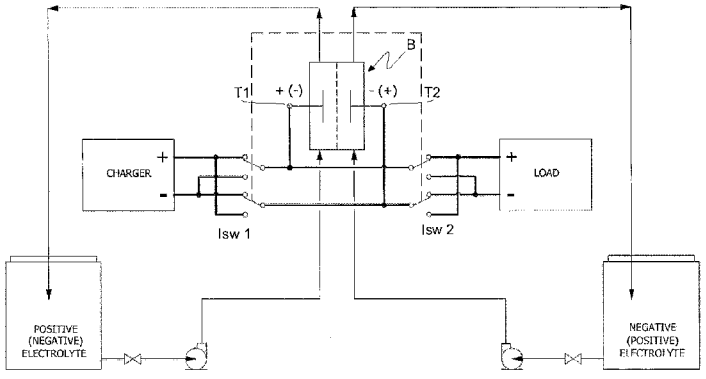

Fig.1

(57) Abstract: Accidental precipitation of vanadium pentoxide, progressive unbalancing of the vanadium content in the two electrolyte solutions, transfer of electrolyte solution through the permionic membrane when using a cationic membrane as cell separator are deleterious effects of different electro - chemical -physical mechanisms that are active when cycling an all vanadium redox flow battery as energy storage system. Any or all of them are effectively remedied with a method comprising a step of, inverting the connections of the electrical connection terminals of the battery to the recharging electrical source and to the electrical load at intervals of time. In practice, the electrode that is functioning as anode in a flow compartment of the cell during the current phase of operation, will be polarized as cathode, and vice versa for the other electrode of the cell or cells.

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"METHOD OF CONDUCTING AN ALL VANADIUM REDOX FLOW BATTERY AND IMPLEMENTING SYSTEM"

TECHNICAL FIELD

The present disclosure relates to an all-vanadium redox flow battery system and in particular to a method of conducting the system over prolonged periods of time countering a number of progressive alterations and unbalances in the electrolyte solutions.

BACKGROUND

Redox flow battery systems or briefly redox batteries, store energy in acid electrolyte solutions, namely a positive and a negative solution, that are flown through respective electrode compartments of the cells of a multi-cell electrochemical reactor during charge and discharge phases. Energy storage capacity is strictly tied to storage volumes of the two distinct positive and negative electrolyte solutions.

The unlimited possibility of storing large volumes of positively and negatively charged electrolyte solutions containing ions of the redox couple, make these systems exceptionally suitable for load-leveling (peak-shaving) in electric power generation and distribution industry, as storage battery in self standing wind farms or solar photovoltaic conversion plants as well as for powering vehicles. Most redox flow battery systems employ a multi-cell bipolar stack.

The redox couples used in a flow redox battery system are typically of multivalent metals dissolved in the two respective positive and negative electrolyte solutions, typically an acid electrolyte capable of dissolving the multivalent metal or metals in all states of oxidation. The above considerations are generally applicable to any multivalent metal providing a viable redox couple dissolved in an aqueous acid solution, wherein the redox couple metal ions sustain the anodic oxidation reaction and the cathodic reduction reaction, the product of which remains

dissolved in the acid electrolyte solution without undergoing any phase change, both during a charging phase as well as during a electrochemical discharge phase. Carbon electrodes are often used in redox flow cells because of the relative high hydrogen discharge over-voltage of carbon-base materials that helps preventing parasitic water electrolysis.

An "all vanadium" redox flow battery system offers a number of evident and undisputed advantages compared to redox flow systems using redox couples of distinct metals in the positively charged and in the negatively charged electrolyte solutions.

In order to enhance performance of relatively poorly conductive and poorly catalytic carbon electrode surfaces, the electrodes or more particularly the active electrode surface thereof is generally in form of a porous felt of carbon fibers readily permeated by the flowing electrolyte solution and back-contacted by the generally planar surface of a carbon-base bipolar electrical interconnecting septum (briefly "interconnect") defining the respective flow compartment in cooperation with the opposing permionic membrane cell separator.

In the positive sulfuric acid electrolyte solution, normally contaiing the redox couple V[V]/V[IV], during a charging phase, the positive electrode of the battery behaves as anode extracting electrons from V[IV] in oxidizing vanadium to V[V] according to the reaction:

$$2VO^{2+} + H_2O = 2VO_2^{+} + 2H^{+} + e^{-} \qquad E^0_{Va} = 1.00 \text{ Volt} \qquad (1)$$

In the negative sulfuric acid electrolyte solution, normally containing the redox couple V[III]/V[II], during a charging phase, the negative electrode of the battery behaves as cathode giving out electrons to V[III] in reducing it to V[II] according to the reaction:

$$VO^{3+} + e^{-} = V^{2+} \qquad E^0_{Va} = -0.225 \text{ Volt} \qquad (2)$$

At the ultimate end of a charging process the negative electrolyte solution will

contain only divalent vanadium while the positive electrolyte solution will contains only pentavalent vanadium.

The permionic membrane cell separator may be either an anionic membrane or a cationic membrane.

In time, after numerous charge/discharge cycles of the battery, several problems of different nature have been found to arise.

Precipitation of vanadium pentoxide

This phenomenon occurs during a charging phase when the positive electrolyte approaches an almost completely charged state. At that point, small crystals of vanadium pentoxide begins to form, typically in the positive electrolyte flow compartment of the cells. The problem arise because during the successive discharging phase, V(IV) (i.e.VO^{+2}) does not reduce/dissolve the precipitated vanadium pentoxide. Precipitation often starts in cells where conditions may be more favorable (high concentration of VO_2^+ and high temperature).

This imposes careful control of operation conditions of the battery system to arrest the charging phases safely before approaching the theoretical full charge of the positive electrolyte solution and a consequent reduction of storage capacity. Large power systems employing a plurality of multi-cell stacks impose even more prudential limits, on account of possible hotter stacks than others.

Unbalancing of the electrolytes

While VO_2^+ / VO^{+2} in the positive are stable and not chemically reduced or oxidized by external elements, V+3/V+2 in the negative electrolyte storage tank are both readily oxidized by exposure to ambient air. As a matter of fact, if air is allowed in the tank, a relatively fast oxidation of V+2 to V+3 and a slow oxidation of V+3 to VO+2 are experienced. Therefore, it is necessary to "blanket" the liquid content in the negative electrolyte tank with nitrogen or float wax or oil on the surface of the liquid. This is bothersome.

Transfer of electrolyte through the permionic membrane

This phenomenon occurs only when using a cationic membrane. Indeed it does not occur or if it does with a negligible rate if anionic membrane is used in the cells. However, commercial anionic membranes, compared to commercial cationic membranes are more expensive, have higher electrical resistance, a shorter life and poorly withstand high temperature.

With cationic membrane separators, electrolyte transfers from the negative compartment to the positive compartment of the cells mainly during discharging phases. During discharge, not only the H^+ ions migrate from the negative to the positive compartment but also solvated V^{+2} and V^{+3} ions migrate at a non negligible rate from the negative to the positive compartment.

During charging phase the H^+ ions migrate in the opposite direction: from the positive to the negative compartment. However, the other positive ions in the positive electrolyte solution are VO_2^+ ions and VO^{+2} both relatively large solvated ions that substantially do not pass through the membrane because of a steric impediment. Therefore, at the end of each cycle not only the level of the positive electrolyte tank will be higher than that of the negative electrolyte tank but also the concentration of vanadium in the positive tank will slowly increase.

These phenomena inevitably lead, if not to laborious treatments for freeing the positive electrolyte circuit from precipitated vanadium pentoxide accumulated in the negative electrolyte flow compartments and in the relative storage tank, to the need of periodically re-equilibrating volumes and vanadium content in the two circuits.

GENERAL DESCRIPTION OF THE INVENTION

The applicants have found an outstandingly simple and effective manner of correcting the deleterious effects of the above discussed phenomena that manifest themselves during the protracted cycling of an all vanadium redox flow battery

system, and that in time lead to out-of- service conditions for restoring correct working conditions of the two electrolyte solutions.

A surprising aspect of the solution found by the applicants is that the restoring action of such a simple implementation demonstrates that all the three different mechanisms that may be acting during normal cycling of the battery appear to be substantially reversible, which renders the solution found exceptionally effective.

Basically the novel method of this disclosure consists in inverting the connections of the electrical connection terminals of the battery to the recharging electrical source and to the electrical load at intervals of time. In practice, the electrode that is functioning as anode in a flow compartment of the cell (all similarly polarized electrodes in case of a multi-cell stack) during the current phase of operation, for example during a charging phase, will be polarized as cathode, and vice versa for the other electrode of the cell or cells. The interval between successive inversions of the battery polarity may correspond to the total duration of a number of charge/discharge cycles that may be set in consideration of the prevailing working conditions of the energy storage system.

Of course the inversion implies that V^{+3}/V^{+2} in what had been the negative electrolyte circuit, including the storage tank, will progressively transform into VO_2^{+}/VO^{+2}, becoming the positive electrolyte solution. Vice versa, in what had been the positive electrolyte circuit, including the storage tank, the VO_2^{+}/VO^{+2} will progressively transform into V^{+3}/V^{+2}, becoming the negative electrolyte solution. This process of inversion of the state of charge of the two electrolyte solutions requires time and has a cost. In terms of waste of residual exploitable charge the cost is practically null, given that, in the normal practice, a discharge phase necessarily ends when the battery output voltage drops below a pre-established lowest acceptable value, though the battery system is still in a state of charge. A relatively small amount of electrical energy may be deliberately spent for accelerating the complete discharge that if left to occur by short circuiting the battery would take a relatively long time (in the order of hours or tens of hours). A

re-conditioning, in an inverted polarity the two electrolyte solutions, making them ready for undergoing a new ordinary charge phase of the battery system (as would have happened without effecting the inversion) represents a necessary remake of the normal "initial investment" charge of the redox flow battery system at a fresh start-up, and its cost in terms of electrical energy consumption may be in the order of about 35-65% of the total charge/discharge energy storage capacity of the system.

Of course, the above cost evaluation applies for the case in which the polarity inversion is performed when the energy storage system is approaching the customary end of a discharge phase of its normal cycling. For this reason, the periodic inversion of polarity according to the novel method of the applicants once, it has become due, will be advantageously carried out upon approaching the customary end of a discharge phase that is generally dictated by a tolerable limit of decline of the output DC voltage of the battery.

Considering that the inversions would be scheduled or automatically programmed every 50, 100, 1000 or more charge/discharge cycles, or whenever regularly monitored parameters of operation of the energy storage system detect a no longer tolerable unbalance or an excessive accumulation of precipitated vanadium pentoxide in the positive electrolyte circuit, the cost of restoring optimal working conditions and energy conversion performance according to this disclosure can be considered negligible or in any case insignificant compared to cost of maintenance work for clearing the positive electrolyte flow compartments of the cells and felt electrodes from likely cloggings and/or periodically rebalancing volumes and vanadium content in the two distinct electrolyte solutions.

According to a preferred embodiment requiring a limited and inexpensive modification of the two distinct hydraulic circuits, cost in terms of electrical energy and duration of re-charging phase that would need to be carried out at every changeover of polarity of the battery according to the novel method of the applicants, can be reduced down to a residual proportion of the above-discussed

amounts. Moreover, the energy storage system will be back to a condition of ability to deliver electrical energy to a load in a similarly shortened time after the switch over of polarity of the battery.

In practice, the circulation pipelines of the two electrolyte solutions from the respective storage tanks to the respective flow compartments of the cells of a multi-cell battery stack and similarly the return pipeline to the storage tanks are functionally duplicated and path selecting electro valves allows to exchange the source and destination tank, simultaneously to the inversion of polarity of the battery.

In this way, the full discharging and re-conditioning of the two electrolyte solutions in a reversed state of charge after switching over the polarity of the battery no longer needs to be done for the large amount of electrolyte solution contained in the two respective storage tanks that will continue to store one, the positive charge electrolyte and the other, the negative charge electrolyte, irrespectively of the periodic inversion of the battery.

According to this preferred embodiment, the amount of electrolyte solutions that will undergo full discharge, re-conditioning in an inverted state of charge will be the total volumes of solutions contained in the flow compartments of the multi-cell stack and in the circulation pipelines upstream and downstream of the set of path-selecting electro-valves in the return lines and in the feed lines of the two solutions.

The outstanding simplicity of the implementing devices for running an all-vanadium redox flow battery system according to the novel method of the applicants will emerge even clearer in the ensuing description of different embodiments.

The invention claimed is defined in the annexed claims, the recitation of which is considered to be part of this description and herein incorporated by express reference.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a scheme of a flow redox battery system according to a first embodiment the method of this disclosure.

Figure 2 is a scheme of a flow redox battery system according to an alternative embodiment.

DESCRIPTION OF EXEMPLARY EMBODIMENTS

A classic functional scheme of an all vanadium redox flow battery system normally employing a multi-cell battery stack B, symbolically illustrated, having electrical connection terminals T1 and T2 at extreme end electrodes of a bipolar arrangement of cells in series, is shown in **Fig. 1**.

Of course, the energy storage system may include several multi-cell battery stacks B, interconnected according to a series-parallel arrangement best suited for the intended use of the energy storage system, in order to increase peak power and voltage ratings.

The scheme clearly illustrates the two distinct hydraulic circuits each including a storage tank of the respective positive and negative electrolyte solution and the circulating pumps that force the solutions to flow in parallel or in series through the respective flow compartments of the individual cells composing the multi-cell stack B.

For sake of simplicity of illustration and clarity of the concepts, a single cell is symbolically depicted in the figures, making more clearly observable the cell electrodes in the respective flow compartments of each cell of a typically multi-cell battery stack, the polarization of which in the streaming electrolyte solution is periodically inverted in sign according to this disclosure.

The above described method of conducting the energy storage system found by the present applicants is implemented by introducing in the electrical connection

of the two terminals T1an T2 of the battery B to a DC source POWER CHARGER, for charging the redox flow battery system, and for connecting the same terminals T1 and T2 to an electrical circuit LOAD, supplied by the battery, inverting switches Isw1 and Isw2, respectively.

The polarity notation +(-) and -(+) at the terminal ends of the battery B signify the periodically effected polarity inversion of the battery according to the method of conduction of this disclosure.

Similarly, the alternated notation POSITIVE (NEGATIVE) and NEGATIVE (POSITIVE) of the two storage tanks, referred to the distinct electrolyte solutions flown through the respective cell compartments of the multicell battery stack B, signify the accompanying inversion of the state of charge of the electrolyte solutions in the two distinct hydraulic circuits that takes place upon switching the polarity of the battery cells.

Fig. 2 depicts the basic functional scheme of the all vanadium redox flow battery system of Fig. 1. according to an alternative and in many respect preferred embodiment that avoids a complete reconditioning and recharging of the entire volume of each of the two distinct electrolyte solutions circulating in the respective hydraulic circuits and cell compartments.

As may be easily observed, readily implemented duplication of flow paths in the return lines and in the feed lines of the two distinct electrolyte solutions to the respective flow compartments of the cells composing the multi-cell battery stack B, and deployment of two pairs of electro-valves in the return lines to the storage tanks and in the feed lines of the two distinct electrolyte solutions to the respective cell compartments, allows changing the flow paths of the two solutions such to maintain the volume of electrolytes stored in the two tanks with unchanged state of charge upon inverting polarity of the battery cells. As already discussed above, this minimizes the cost of the energy needed for restoring the state of charge of the two distinct electrolyte solutions they had before inverting the battery polarity.

The method found by the applicants, besides offering a simple way of preventing accumulation of precipitated vanadium pentoxide, and periodically correcting unbalances of the state of charge of the two electrolyte solutions, makes the use of less expensive, durable and less resistive cationic membranes unplagued by the phenomenon of progressive volumetric and mass disproportionation, being the phenomenon reversible and correctable with the method of conduction of this disclosure, whenever it surpasses a tolerable measure.

CLAIMS

1. Method of conducting an all-vanadium redox flow battery having first and second electrical terminals adapted to connect the battery to positive and negative poles of an electrical source charging it and/or to electrical supply positive and negative poles of an electrical load discharging it, and distinct hydraulic circuits adapted to circulate a positive electrolyte acid solution containing the redox coupleVO_2^+/VO^{+2} and a negative electrolyte solution containing the redox coupleVO^{+3}/VO^{+2}, each including at least a respective tank adapted to store a volume of the respective chargeable and dischargeable electrolyte solution, the battery undergoing repeated cycles of charge and discharge phases, the method comprising the step of inverting the connections to said electrical terminals of the battery at intervals of time.

2. The method of claim 1, wherein said interval of time corresponds to the completion of a given number of charge/discharge cycles of the battery.

3. The method of claim 1, wherein upon switching the electrical polarity of the battery by inverting said electrical connections, the sign of charge of the electrolyte solutions contained in the respective storage tanks is maintained unchanged by simultaneously exchanging the flows paths of circulation of the distinct electrolyte solutions through the flow compartments of each cell of the battery upon changing the sign of the respective cell electrodes.

4. An all vanadium redox flow battery system comprising at least a multi-cell stack having first and second electrical terminals adapted to connect the battery cells to an electrical source charging the system and to an electrical load discharging it, and distinct hydraulic circuits adapted to circulate a positive electrolyte acid solution containing the redox coupleVO_2^+/VO^{+2} and a negative electrolyte solution containing the redox coupleVO^{+3}/VO^{+2}, each including at least a respective tank adapted to contain a volume of the electrolyte solution in respective electrode compartments of all the cells of the stack, characterized in

that the system comprises polarity inverting electrical switches of said terminals to said electrical source and/or electrical load adapted to change polarity of the multi-cell stack at intervals of time.

5. The all vanadium redox flow battery system of claim 4, further comprising hydraulic flow path selecting electrically controlled valves adapted to switch the flows paths of the distinct electrolyte solutions to and from the two storage tanks of the positively charged electrolyte solution and of the negatively charged electrolyte solution through the cell flow compartment containing the electrode of functionally correct sign, simultaneously with said change of polarity of the multi-cell stack.

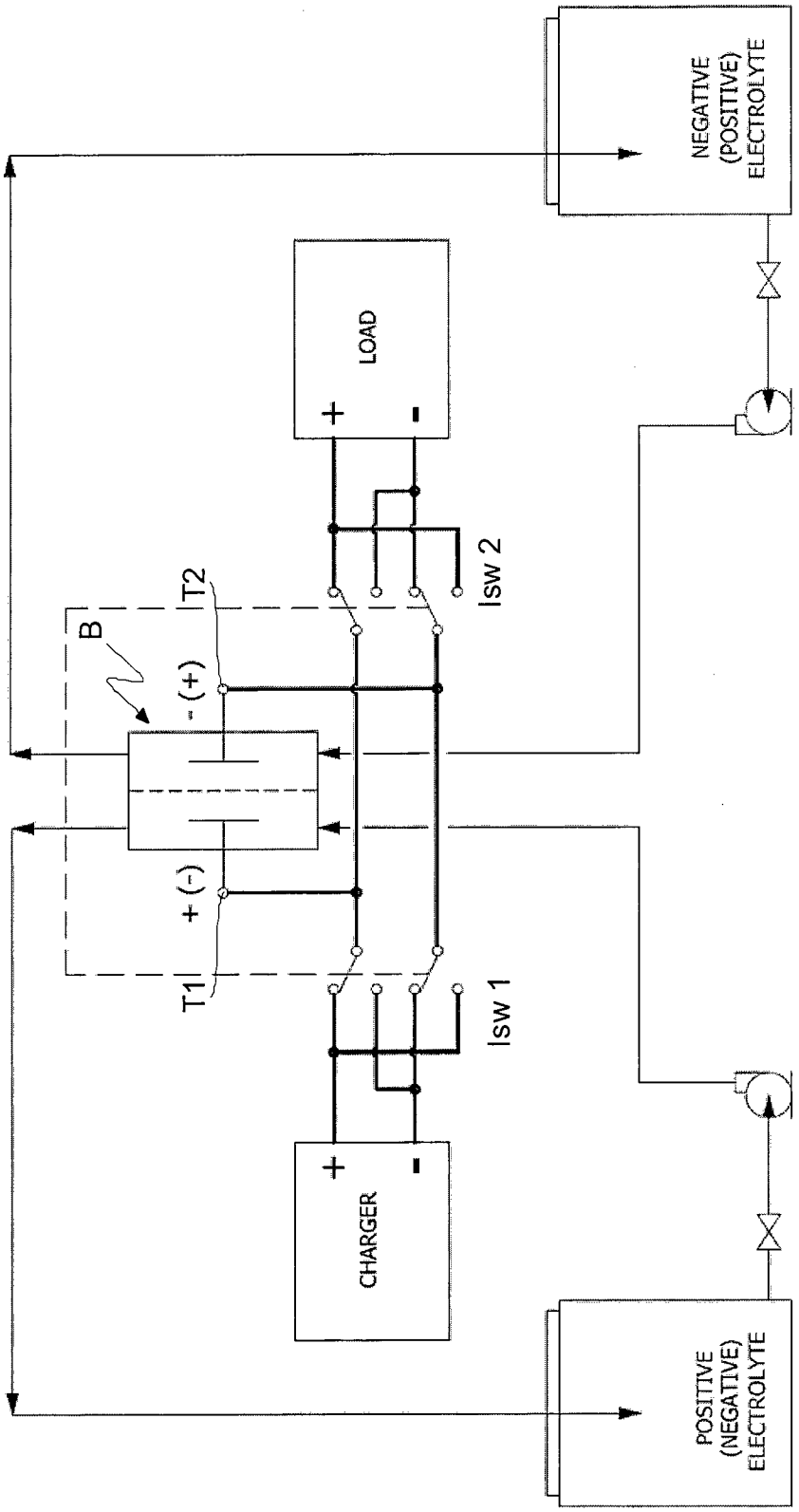
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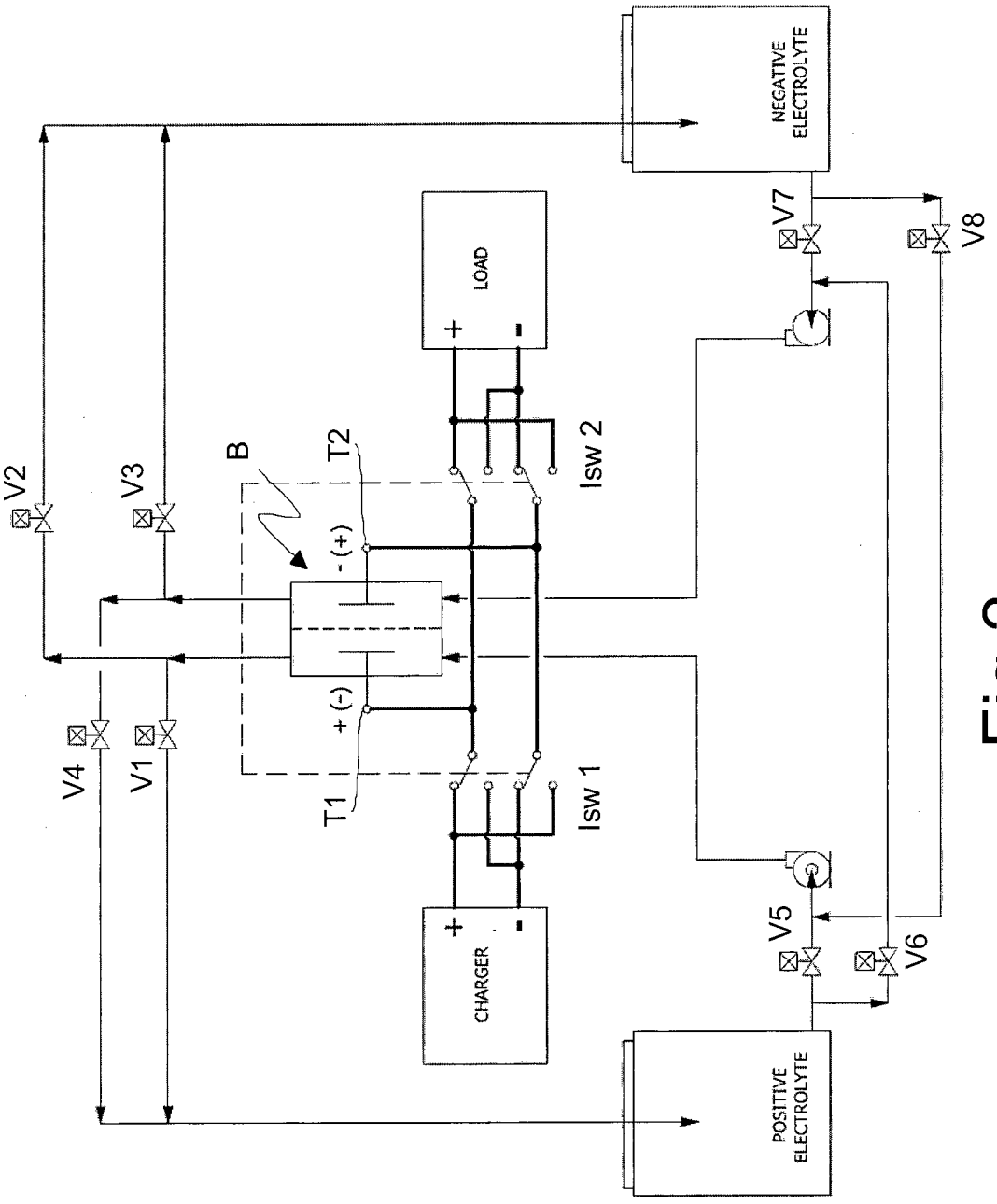
Fig.1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V8
V2
V3
B
T2
- (+)
Isw 2
+ (-)
T1
Isw 1
V4
V1
V5
V6
CHARGER
+
-
POSITIVE ELECTROLYTE

Fig.2

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2011/001141

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M8/04 H01M8/18
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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 2003/143456 A1 (KAZACOS MICHAEL [AU] ET AL) 31 July 2003 (2003-07-31) paragraphs [0001], [0003], [0200], [0270], [0372], [0373], [0394]; figure 13	1,2,4 3,5
X Y	JP 62 163270 A (SUMITOMO ELECTRIC INDUSTRIES) 20 July 1987 (1987-07-20) abstract; figure 1	1,2,4 3,5
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Y	JP 61 173468 A (MITSUI SHIPBUILDING ENG) 5 August 1986 (1986-08-05) abstract; figure 1	3,5

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

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2011/001141

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2002 216833 A (KANSAI ELECTRIC POWER CO) 2 August 2002 (2002-08-02) the whole document -----	1-5

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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