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(54) Title: BALANCING OF ELECTROLYTES IN REDOX FLOW BATTERIES

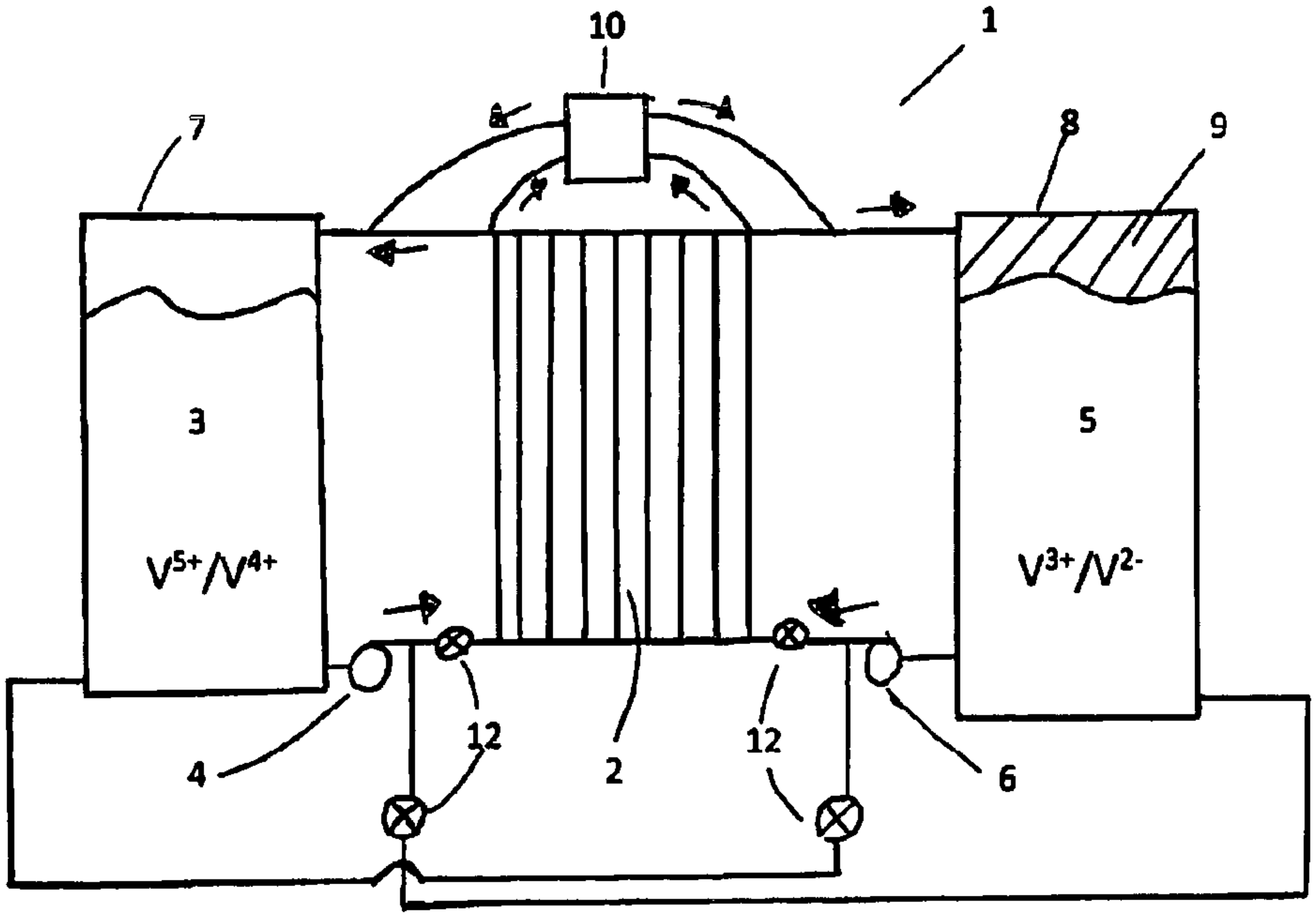

Figure 1

(57) Abrégé/Abstract:
According to the invention there is provided a method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte, including the steps of: measuring the extent of oxidation of the negative electrolyte, and; adding reducing agent to the positive electrolyte to reduce the V^{5+}/ $[VO_2]^+$ ions to $V^{4+}/[VO]^{2+}$ ions, the reducing agent combining carbon, oxygen and hydrogen in such ratios that the products of the reaction include $V^{5+}/[VO_2]^+$ ions reduced to V^{4+}/ $[VO]^{2+}$ ions, water and carbon dioxide. Wherein the reducing agent can be carboxylic acid or a precursor, or indeed an intermediate product, of a carboxylic acid.

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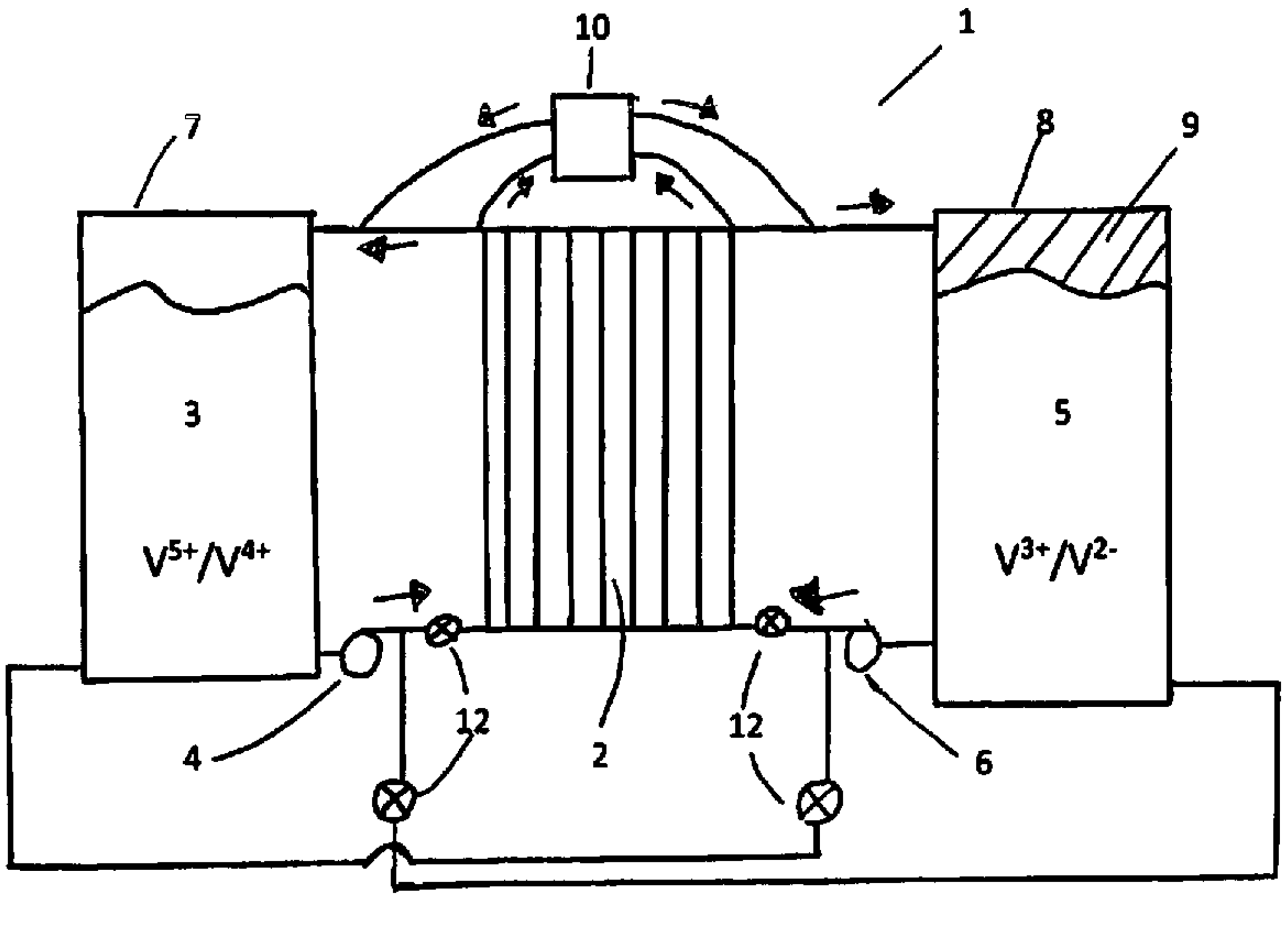

Figure 1

(57) Abstract: According to the invention there is provided a method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte, including the steps of: measuring the extent of oxidation of the negative electrolyte, and; adding reducing agent to the positive electrolyte to reduce the V^{5+}/ $[VO_2]^+$ ions to V^{4+}/$[VO]^{2+}$ ions, the reducing agent combining carbon, oxygen and hydrogen in such ratios that the products of the reaction include V^{5+}/$[VO_2]^+$ ions reduced to V^{4+}/ $[VO]^{2+}$ ions, water and carbon dioxide. Wherein the reducing agent can be carboxylic acid or a precursor, or indeed an intermediate product, of a carboxylic acid.

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BALANCING OF ELECTROLYTES IN REDOX FLOW BATTERIES

The present invention relates to a method of balancing the electrolytes of an unbalanced redox flow battery

In a redox flow battery, reagents are passed to opposite sides of an ionically selective and conductive membrane separator separating two reagent compartments, electrodes being provided in the respective compartments. The reagents are a complementary pair of electrolytes, i.e. an anolyte and a catholyte. Electricity flows between the reagents via the electrodes, as a result of ionic flow between the reagents through the separator. During discharge, these flows are in one direction and during charging they are reversed. Further, during discharge, the redox ions (not the ions passing through the separator) in the anolyte are oxidised and other redox ions in the catholyte are reduced. During conventional charging, the anolyte ions are reduced and the catholyte ions are oxidised. This is in accordance with the "anolyte" and "catholyte" meaning in accordance with US Patent 4,786,567 and European Patent No 0829104. The latter acknowledges that this is an unusual convention in that the anode is in catholyte and the cathode is in anolyte. For the purposes of the present invention, which concerns balancing the electrolytes per se, we use an alternative convention of the "negative electrolyte" being the one associated with the negative terminal or electrode in discharge of the battery, when this electrolyte gives up electrons, and the positive electrolyte being the one that absorbs electrons from the positive terminal or electrode during discharge.

In the preferred redox flow batteries the redox ions are of the same metal, vanadium, and as such their transfer between electrolytes causes no contamination. An understanding of the reactions in a vanadium redox flow battery can be found in US Patent 4,786,567.

Such a redox flow battery requires reservoirs of the electrolytes and means for supplying them to and from the reagent compartments, e.g. pipes and pumps.

As used in this specification, the term "redox flow battery" is used to mean at least one redox fuel cell per se, together with a pair of electrolyte reservoirs, i.e. one for anolyte and the other for catholyte, and electrolyte supply means, i.e. means for circulating anolyte from its reservoir, to its compartment in the cell and back to the reservoir and like circulating means for catholyte. Usually, the battery will have several cells each supplied with anolyte and catholyte from a single pair of reservoirs.

Charging and discharging involves reduction and oxidation of the electrolytes. The negative electrolyte is oxidised also by exposure to air, and normally this is avoided by blanketing the electrolyte in its tank with inert gas. This can leak away (or the supply may become insufficient or non-existent, for a variety of reasons) enabling the negative electrolyte to be oxidised, with the result that the state of oxidation/reduction or charge/discharge of the two electrolytes becomes unbalanced and the useful capacity of the battery reduced.

The object of the present invention is to provide a method of balancing the electrolytes of an unbalanced vanadium redox flow battery.

According to the invention there is provided a method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte, including the steps of:

- measuring the extent of oxidation of the negative electrolyte and
- adding reducing agent to the positive electrolyte to reduce the V^{5+}/ $[VO_2]^+$ ions to V^{4+}/$[VO]^{2+}$ ions, the reducing agent combining carbon, oxygen and hydrogen in such ratios that the products of the reaction include V^{5+}/ $[VO_2]^+$ ions reduced to V^{4+}/ $[VO]^{2+}$ ions, water and carbon dioxide.

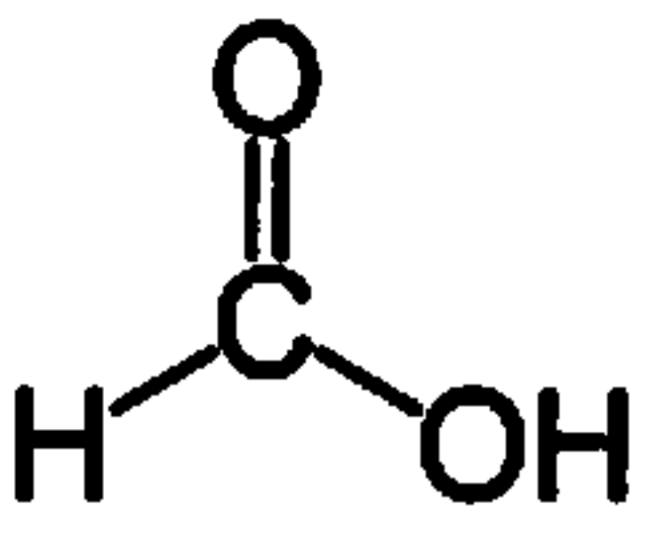
It should be noted that for the purposes of charging and discharging of the battery it is convenient to think in terms of the vanadium in the positive electrolyte passing between a V^{5+} charged state and V^{4+} discharged state and the vanadium in the negative electrolyte passing between a V^{2+} charged state and V^{3+} discharged state. Whilst V^{2+} ions and V^{3+} ions exist; V^{5+} and V^{4+} exist as $[VO_2]^+$ and $[VO]^{2+}$ ions in solution, although behaving for electrical charging and discharging purposes as V^{5+} and V^{4+} ions. For these reasons, the terms "V^{5+}/ $[VO_2]^+$ ions" and "V^{4+}/ $[VO]^{2+}$ ions" are used in the above statement of invention. However below they are mostly abbreviated to V^{5+} and V^{4+} ions.

It is not essential that there be no other reaction products. For instance gaseous products will provide no permanent contamination of the electrolytes once they have dissipated. However we prefer to use a reducing agent that produces no reaction products except V^{4+}/ $[VO]^{2+}$ ions, water and carbon dioxide.

Preferably, the reducing agent is a carboxylic acid or a precursor, or indeed an intermediate product, of a carboxylic acid.

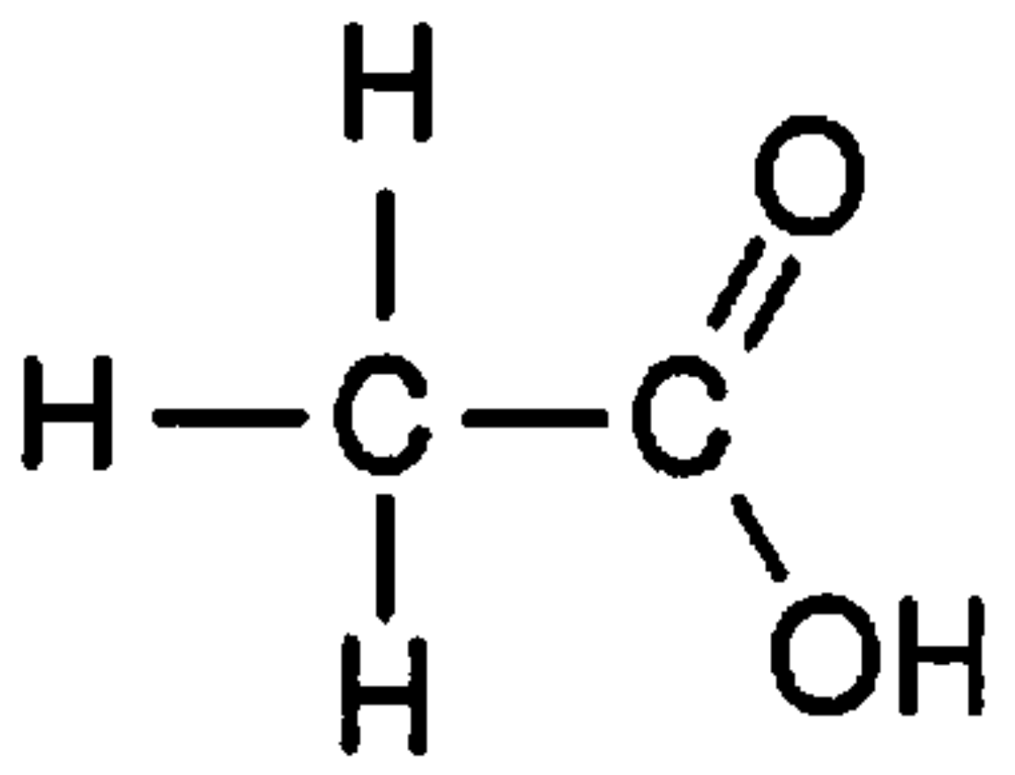
Whilst we can envisage using:

- methanoic acid (formic acid) – $C_2H_2O_4$ –



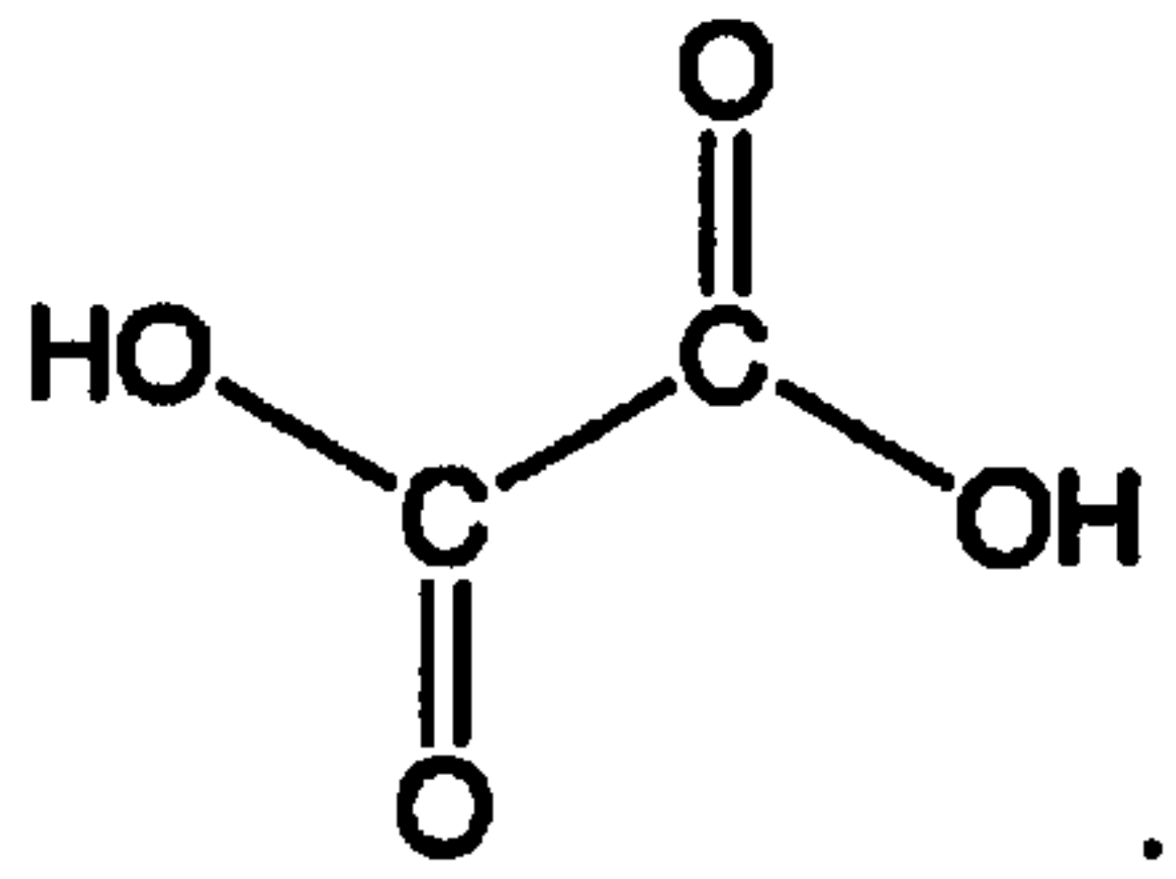
We should mention a concern that carbon monoxide may be released, or:

- ethanoic acid (acetic acid) – $C_3H_8O_3$ –



We have not tested this and have a concern that contaminants may be produced. We prefer to use as the carboxylic acid:

- oxalic acid –. $H_3CCOOH_3O_3$ –

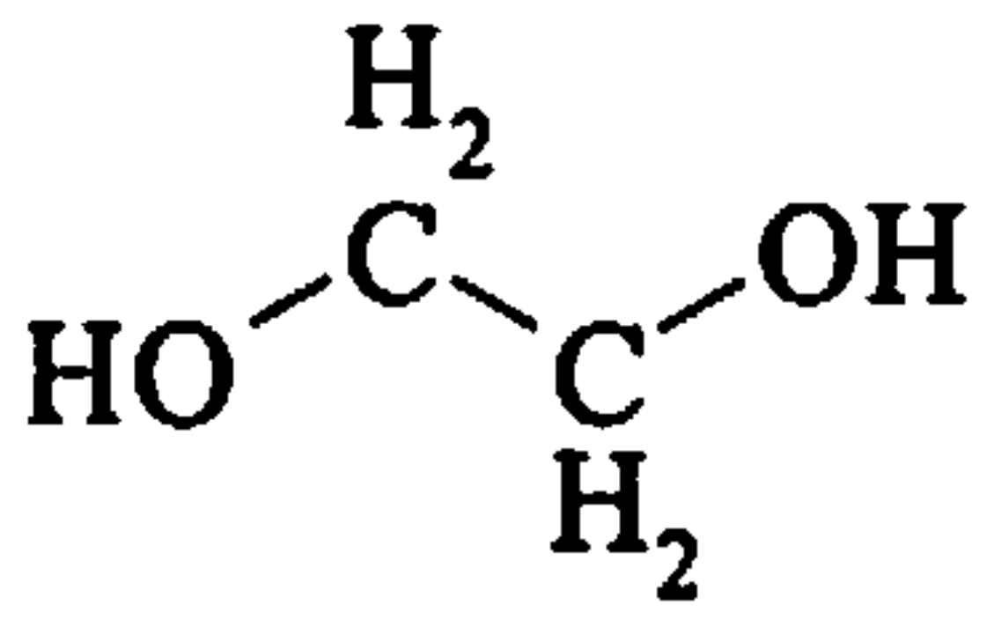


.

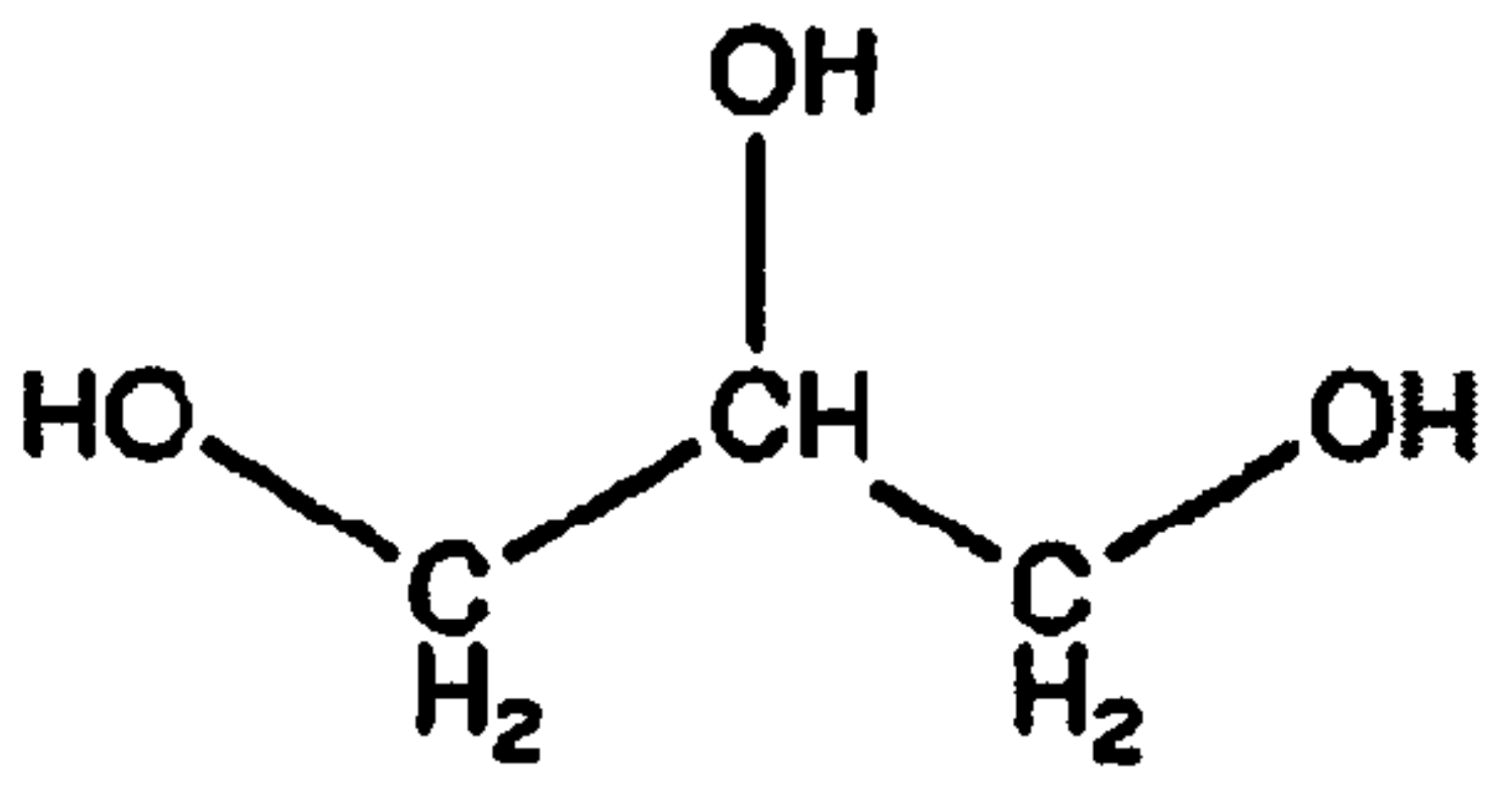
It has the advantage of producing no reaction products except V^{4+}/ $[VO]^{2+}$ ions, water and carbon dioxide.

The precursors of oxalic acid that we can envisage being useful in our method are:

- ethylene glycol – $(CH_2OH)_2$ – and

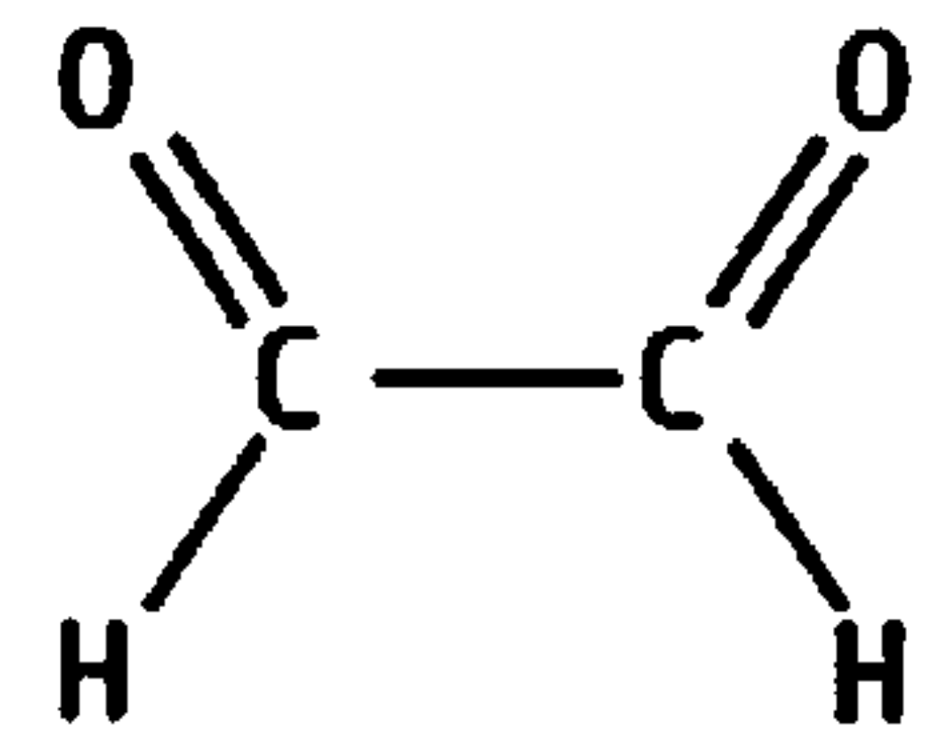


- glycerine – $C_3H_8O_3$ –

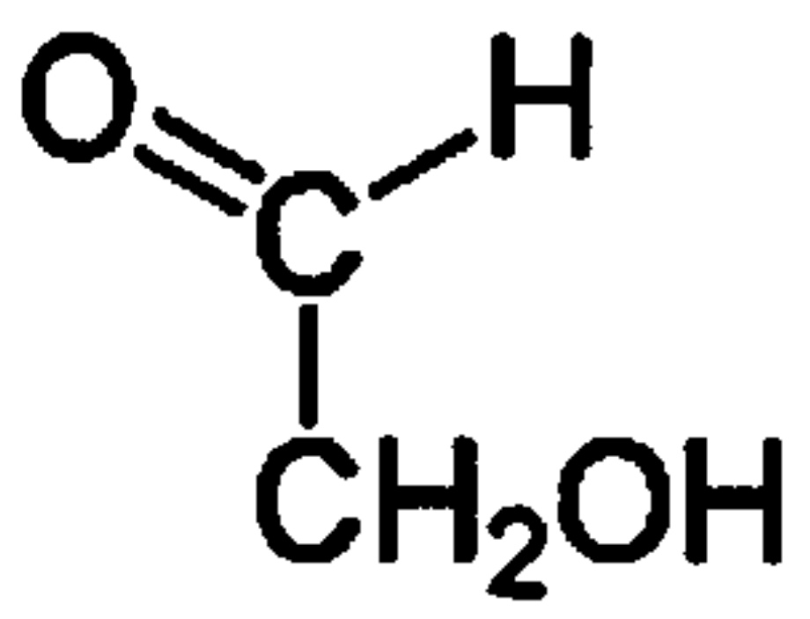


Similarly the intermediate products that we can envisage for our method are:

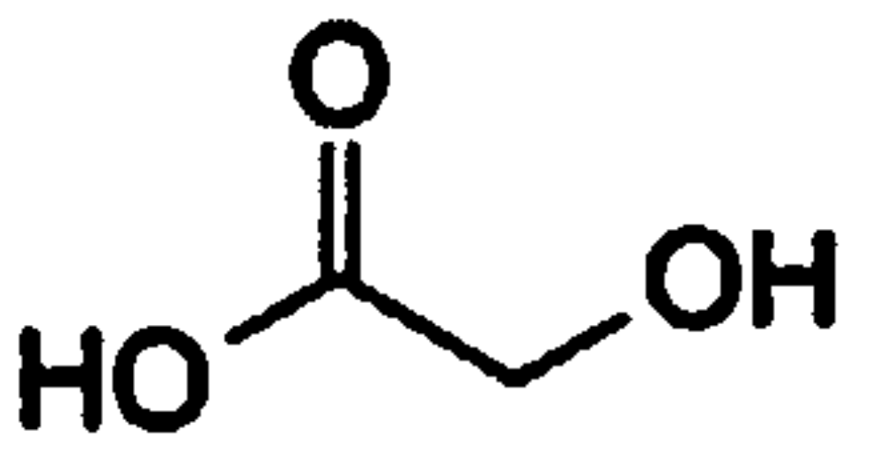
- glyoxal – OCHCHO –



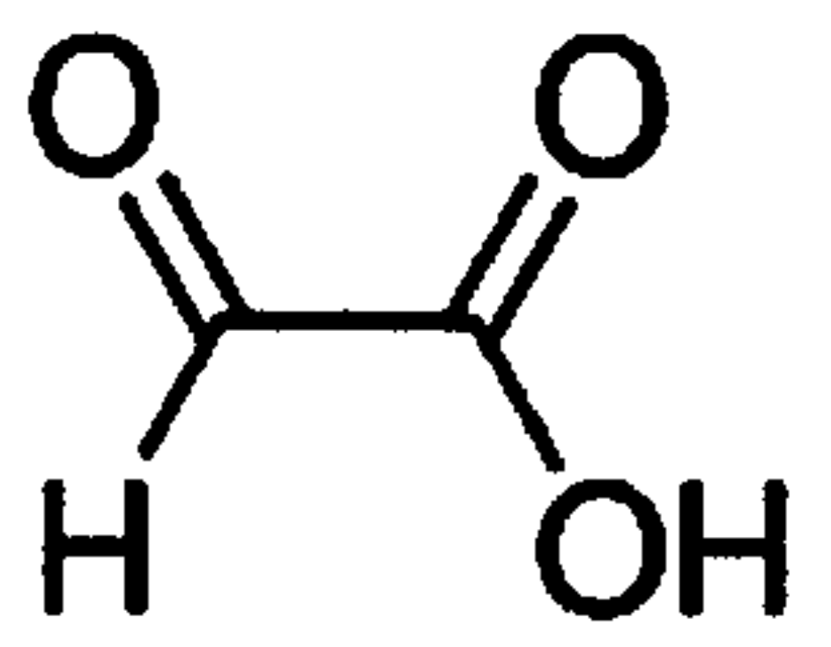
- glycoaldehyde – $C_2H_4O_2$ –



- glycolic acid – $C_2H_4O_3$



- glyoxylic acid – $C_2H_2O_3$



Our preferred method of measuring the extent of oxidation of the negative electrolyte is to

- mix the two electrolytes, preferably having fully discharged the battery first and then
- pre-charge it noting the time taken to the pre-charge voltage step of the negative tank electrolyte and then the pre-charge voltage step of the positive tank electrolyte.

Provided that the rate of charge remains constant – and it if not adjustments can be made accordingly – the percentage state of oxidation of the negative electrolyte is given by the ratio of the difference in the times divided by their sums.

For the avoidance of doubt, construction of the cell stacks forms no part of this invention, and will not be described here. Details can be found at our WO 2006/111704 patent application.

To help understanding of the invention, a specific embodiment thereof will now be described by way of example and with reference to the accompanying drawings, in which:

Figure 1 is a diagrammatic view of a Vanadium Redox Flow Battery (VRFB);

Figure 2 is a graph showing a reference cell voltage during the pre-charging of the VRFB when balanced;

Figure 3 is a similar graph showing the reference cell voltages for the individual positive and negative electrolytes and their combined reference cell voltages during the pre-charging of the VRFB when un-balanced;

Figure 4 is a diagrammatic view of the electrolyte states of the VRFB when fully discharged;

Figure 5 is a diagrammatic view of the electrolyte states after mixing of the electrolytes;

Figure 6 is a diagrammatic view of the electrolyte states at an intermediate stage in pre-charging, when the positive electrolyte is pre-charged and the negative electrolyte is not yet fully pre-charged;

Figure 7 is a diagrammatic view at the end of pre-charging, with the positive electrolyte partially charged (after pre-charging) and the negative electrolyte fully pre-charged; and

Figure 8 is a diagrammatic view of the state of the electrolyte after reduction of the partly charged V^{5+} ions to V^{4+} ions, by addition of reducing agent to the positive electrolyte.

Referring to the drawings, a Vanadium Redox Flow Battery (VRFB) 1 has a cell stack 2 into which positive electrolyte 3 having a useful concentration of V^{5+} ions is pumped by a positive pump 4 to positive sides of diaphragms in individual cells (not separately shown) and negative electrolyte 5 having a useful concentration of V^{2+} ions is pumped by a negative pump 6 to negative sides of the diaphragms in the cells. The electrolytes are pumped from and return to respective positive and negative electrolyte reservoirs 7,8. These are closed, but not be completely hermetically sealed to avoid build-up of pressure for instance due to temperature change in use. In practice there is no disadvantage in the positive electrolyte being exposed to the ambient atmosphere, but access of oxygen to the negative electrolyte can result in oxidation. Normally this is avoided by providing a blanket 9 of inert gas, typically nitrogen, over the negative electrolyte. The physical arrangements for this form no part of the invention. However they can fail.

If for instance 60% of the V^{2+} ions of the VRFB when fully charged have been oxidised to V^{3+} ions, during discharge the limit of useful concentration of V^{2+} ions will be reached substantially before that of V^{5+} ions and the capacity of the battery will be adversely affected, in practice reduced by more than 60%. Before the remedy for this situation in accordance with the invention is described, the steps of "pre-charging" and normal charging of a VRFB should be noted.

When the VRFB is prepared for use, both the positive and negative electrolyte reservoirs are filled with identical electrolyte, that is to say one having a balanced, equal concentration of V^{4+} ions and V^{3+} ions. If these electrolytes are pumped through the cell stack, the voltage across the stack will be zero. In a pre-charging step, the electrolytes are pumped, charging voltage is applied and electrical charge is absorbed by the VRFB. The result is that the V^{3+} ions on the positive side are converted to become V^{4+} ions and vice versa. During pre-charging, the voltage across a reference cell 10 to which a sample of the electrolytes is pumped remains close to zero as shown in Figure 2, until close to the end of the pre-charging. Then there is a step change 11 in the reference cell voltage as shown in the figure. It should be noted that the reference cell voltage has a direct correlation to the open circuit voltage of the VRFB, which is much higher due to the number of individual cells in the stack, but slight reduced from the reference cell voltage times the number of cells due to internal shunt current losses.

It is possible to measure the effect on the reference cell voltage of the individual electrolyte and their state of charge. For this single individual electrolyte reference cells which use a reference electrode, known in themselves to the skilled reader but for the avoidance of doubt available from BASi, www.basinc.com, can measure the positive and negative electrolyte voltages individually. The difference of these voltages is the normal reference cell voltage. The step change in reference cell voltage occurs when all of the ions are changed to their normal discharge state, i.e. V^{4+} in the positive electrolyte and V^{3+} in the negative electrolyte, as described above. In a balanced battery, the positive and negative electrolytes reach this state together and the step changes in their individual changes occur together.

Once the pre-charging has finished, with all V^{4+} ions in the positive electrolyte and all V^{3+} ions in the negative electrolyte, the former are progressively charged to V^{5+} ions and the latter to V^{2+} ions without further step change in reference cell voltage or open circuit voltage across the stack (until full charge is reached, when a further step change in reference cell voltage occurs).

In an imbalanced battery, the positive electrolyte reaches pre-charged state before the negative electrolyte, as explained in more detail below. This is shown in Figure 3.

To remedy the imbalance in the VRFB having oxidised negative electrolyte, the following steps are performed:

1. From the state of full charge – or a partially discharged state – the VRFB is fully discharged to the ions in the electrolytes being in the state as shown in Figure 4. The shown result is that whilst all of the vanadium ions in the negative reservoir are V^{3+} ions, 40% of the positive reservoirs ions will be V^{4+} ions, with 60% V^{5+} ions remaining in their undischarged state. These are the ions that could not be discharged due to the lack of corresponding negative electrolyte V^{2+} ions, i.e. the 60% of the V^{2+} ions having been oxidised in the charged state;
2. The discharged positive and negative electrolytes are now mixed, by opening the normally closed crossover valves 12 and using the positive pump to pump electrolyte from the positive reservoir to the negative reservoir and vice versa.

Whilst V^{4+} ions remain in equilibrium in the same solution with both V^{3+} ions and V^{5+} ions, the latter two ions react with each other on mixing to produce more V^{4+} ions. In the case of 60% of the V^{2+} ions oxidised to V^{3+} ions, the remaining 60% V^{5+} ions from the positive electrolyte react with 60% of the V^{3+} ions from the negative electrolyte; all of these ions become V^{4+} ions. The percentages quoted above are percentages per individual electrolyte. On mixing, the V^{4+} ions come from both electrolytes with half the concentration of the reagents per electrolyte. The result is that each electrolyte has 60% V^{4+} ions from the reaction. Also the positive electrolyte had 40% before mixing. This is distributed as 20% to each electrolyte, with the result that each mixed electrolyte has 80% V^{4+} ions and 20% V^{3+} ions, as shown in Figure 5;

3. The unbalanced electrolytes are then pre-charged. This can be thought of as involving three sets of ions:
    a. The first set are 20% which undergo no change in pre charging, namely the 20% V^{3+} ions in the negative electrolyte which are in the state which they should be at the end of the pre-charge, together with a corresponding 20% of V^{4+} ions in the positive reservoir. The latter represent only a quarter of the total of 80% of V^{4+} ions in the positive reservoir after mixing. Since these ions undergo no change in valency state, no pre-charging charge or energy is imparted to them;
    b. Provision of a first amount of charge, in equal and opposite measure to the two electrolytes in the two reservoirs, addition of electrons to ions in the negative electrolyte and removal of electrons from ions in the positive reservoir. This amount of charge converts the 20% V^{3+} ions in the positive reservoir to V^{4+} ions and 20% of V^{4+} ions in the negative electrolyte to V^{3+} ions. At this stage, all the ions in the positive electrolyte are V^{4+} ions. This is the pre-charge state of the positive electrolyte and it results in a step in the reference cell voltage, corresponding to the positive voltage electrolyte stepping up if measured in an individual electrolyte cell. This is the step 14 in Figure 3. However, the latter measurement does not have to be made, because the effect can be seen in the reference cell voltage, as its first step 15. The actual pre-charge occurs at a steady current and therefore a time plot of voltage against time is an indication of a certain quantum of

charge having been transferred to the electrolytes during the time to the step from the start of charging. This time is also proportional to the quantum of ions pre-charged to the step, namely 20% of the ions in the electrolytes.

The imbalance at the end of this stage is shown in Figure 6 by the 60% of V^{4+} ions in the negative electrolyte. Pre-charge these to V^{3+} ions. requires provision of a second amount of charge and indeed partial normal charging of the positive electrolyte;

c. Provision of this second amount of charge converts all the negative electrolyte ions to V^{3+} ions. It also converts 60% of the already all V^{4+} ions in the positive electrolyte to V^{5+} ions, as shown in Figure 7. At the end of this charge, the voltage at the reference cell steps up again 16, corresponding to the negative electrolyte reaching its pre-charge state, as shown in Figure 3, with the negative electrolyte stepping down 17, corresponding with the voltage difference stepping up.

Analysis of when the steps 15,16 occur as shown in Figure 3 enables the state of imbalance to be identified. In a normal pre-charge of balanced electrolytes, the starting ratio of V^{3+} ions to V^{4+} ions is 50%/50% and 50% of the ions change state of valency by one unit of charge. In the example above the pre-charge is from 20% V^{3+} ions and 80% V^{4+} ions. During the first amount of pre charge 20% of the ions change valency by one step; and during the second step 60% of the ions also change valency by one step. The total is 80% compared to 50%.

By observation we know that as the amount of imbalance increases, the two pre-charge voltage steps move away from the balanced electrolytes voltage step. Intuitively the extent of the movement is proportional to be extent of imbalance.

Arithmetically, the distance of the steps from the balanced step 18, shown dashed and notionally between them, as a percentage of the distance to the balanced step is:

$$30 / (20 + 30) = 0.6, \text{ i.e. } 60\%.$$

This is the oxidised proportion of V^{2+} ions and indeed the proportion of V^{5+} ions in the positive electrolyte after pre-charge.

It is convenient to state here therefore that the percentage imbalance can be measured with reference to Figure 3,

1. measuring the time t_1 to the first step;
2. measuring the time t_2 to the second step;
3. calculating the time T to the mid-point between the steps;
4. calculating the time t from the first step to the mid-point;
5. calculating the percentage imbalance as the percentage t is of T.

The following equations can be written:

(1) $t = (t_2 - t_1) / 2$

(2) $T = t_1 + (t_2 - t_1) / 2$

(3) $t / T = ((t_2 - t_1) / 2) / (t_1 + (t_2 - t_1) / 2) = t_2 - t_1 / t_2 + t_1$

In other words, ratio of t/T is the difference in the times to the steps divided by their sum, and the % imbalance is the ratio times 100.

Given the total volume of the positive electrolyte and the concentration of ions in it, and using the imbalance percentage, the quantity of oxalic acid, or equivalent chemical, to reduce the V^{5+} ions to V^{4+} ions can be calculated. For this is should be noted that:

- The electrolytes are in the form of solution of a vanadium sulphate and sulphuric acid. Thus vanadium and hydrogen ions are available for oxidation and reduction reactions;
- Whilst V^{2+} and V^{3+} ions exist in solution as free ions, V^{4+} and V^{5+} exist as $[VO]^{2+}$ and $[VO_2]^+$ ions respectively, that is with one or two oxygen atoms covalently attached;
- The equation for reduction of V^{5+} / $[VO_2]^+$ ions to V^{4+} / $[VO]^{2+}$ ions is as follows:

  $C_2O_4H_2 + 2[VO_2]^+ + 2H^+ \rightarrow 2[VO]^{2+} + 2H_2O + 2CO_2$
- The reaction involves absorption of H^+ ions from solution and release of carbon dioxide gas;

- Further each oxalic acid molecule reduces two V^{5+} / $[VO_2]^+$ ions to V^{4+} / $[VO]^{2+}$ ions.

Accordingly, for each mole of oxalic acid 2 moles of V^{5+} can be reduced. Conversely, if the positive electrolyte contains 1 mole of vanadium ions and is 60% imbalanced, then ½ x 0.6 = 0.3 moles of oxalic acid are required to reduce the V^{5+} ions to V^{4+} ions. The relative molecular mass of oxalic acid is 126.08 g mol^{-1}. The mass of oxalic acid for this reduction is then 0.3 x 126.08 = 37.82 g.

The final step of remedying the imbalance is then:

4. Addition of the calculated quantity of oxalic acid to the positive electrolyte, slowly in four equal portions, to return it to its normal, balanced pre-charge state. The addition is in small portions, to avoid excessive effervescence and spillage of the electrolyte, which is both expensive and corrosive. The state of the electrolytes after addition of the oxalic acid is shown in Figure 8.

For the avoidance of doubt, the oxalic acid is not a strong enough reducing agent to reduce V^{4+} ions to V^{3+} ions nor V^{3+} ions to V^{2+} ions if added to the negative electrolyte at the imbalance stage of Figure 4, quite apart from the extent of the imbalance and the quantity of oxalic acid required being unknown prior to measurement.

In this document, reference to VRFBs is not intended to exclude other redox flow batteries for which the balancing method may be applicable, such as, but not limited to iron-chromium systems.

CLAIMS:

1. A method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte, including the steps of:
    - measuring the extent of oxidation of the negative electrolyte and
    - adding reducing agent to the positive electrolyte to reduce the V^{5+}/ $[VO_2]^+$ ions to V^{4+}/$[VO]^{2+}$ ions, the reducing agent combining carbon, oxygen and hydrogen in such ratios that the products of the reaction include V^{5+}/ $[VO_2]^+$ ions reduced to V^{4+}/ $[VO]^{2+}$ ions, water and carbon dioxide.
2. A method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte, as claimed in claim 1, wherein reaction products in addition to water and carbon dioxide are produced.
3. A method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte, as claimed in claim 1 or claim 2, wherein the reducing agent is any one of:
    - a carboxylic acid,
    - a precursor of carboxylic acid, or
    - an intermediate product of a carboxylic acid.
4. A method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte, as claimed in claim 3, wherein the reducing agent is a carboxylic acid and any one of:
    - oxalic acid,
    - ethanoic acid, or
    - methanoic acid.
5. A method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte, as claimed in claim 3, wherein the reducing agent is a precursor of a carboxylic acid, and any one of:
    - Ethylene glycol, or
    - Glycerine.
6. A method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte, as claimed in claim 3, wherein the reducing agent is an intermediate product of a carboxylic acid, and any one of:
    - glyoxal,

- glycoaldehyde,
- glycolic acid, or
- glyoxylic acid.

7. A method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte, as claimed in any preceding claim, wherein the method of measuring the extent of oxidation of the negative electrolyte comprises the following steps:

- mixing the two electrolytes, preferably having fully discharged the battery first, and then
- pre-chargeing it noting the time taken to the pre-charge voltage step of the negative tank electrolyte and then the pre-charge voltage step of the positive tank electrolyte.

8. A method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte as claimed in claim 7, wherein the rate of charge is held constant, and is adjusted to remain constant if it is not, and the percentage state of oxidation of the negative electrolyte is given by the ratio of the difference in the times divided by their sums.

9. A method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte, as claimed in claim 7, wherein during the pre-charging step, the electrolytes are pumped, charging voltage is applied and electrical charge is absorbed by the redox flow battery.

10. A method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte as claimed in claim 7, wherein during pre-charging the voltage across a reference cell, to which a sample of the electrolytes is pumped, remains close to zero until close to the end of charging.

11. A method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte, as claimed in claim 7, wherein once the pre-charging has finished, with all V^{4+} ions in the positive electrolyte and all V^{3+} ions in the negative electrolyte, the V^{4+} ions are progressively charged to V^{5+} ions and the V^{3+} ions to V^{2+} ions without further step change in reference cell voltage or open circuit voltage across the stack, until full charge is reached, a further step change in reference cell voltage occurs.

12. A method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte, as claimed in any preceding claim wherein to remedy the imbalance in the redox flow battery having oxidised negative electrolyte, the following steps are performed:

- fully discharging the redox flow battery from a state of full charge, or a partially discharged state, to the ions in the electrolytes as follows:
  - in the negative reservoir are V^{3+} ions, and
  - in the positive reservoir, 40% of the ions will be V^{4+} ions, with 60% being V^{5+} ions,
- mixing of the discharged positive and negative electrolytes by opening the normally closed crossover valves and using a positive pump to pump electrolyte from the positive reservoir to the negative reservoir and vice versa.
- pre-charging of the unbalanced electrolytes, which can be any one of the following sets of ions:
  - the first set are 20% which undergo no change in pre charging, the 20% V^{3+} ions in the negative electrolyte are in the state which they should be at the end of the pre-charge, together with a corresponding 20% of V^{4+} ions in the positive reservoir, the latter represent only a quarter of the total of 80% of V^{4+} ions in the positive reservoir after mixing;
  - provision of a first amount of charge, in equal and opposite measure to the two electrolytes in the two reservoirs, addition of electrons to ions in the negative electrolyte and removal of electrons from ions in the positive reservoir, this converts the 20% V^{3+} ions in the positive reservoir to V^{4+} ions and 20% of V^{4+} ions in the negative electrolyte to V^{3+} ions, and the actual pre-charge occurs at a steady current, the imbalance is the 60% of V^{4+} ions in the negative electrolyte, these re pre-charged to V^{3+} ions by provision of a second amount of charge and indeed partial normal charging of the positive electrolyte;
  - provision of this second amount of charge converting all the negative electrolyte ions to V^{3+} ions, the second charge also converts 60% of the V^{4+} ions in the positive electrolyte to V^{5+} ions, at the end of this charge, the voltage at the reference cell steps up again, corresponding

to the negative electrolyte reaching its pre-charge state, with the negative electrolyte stepping down, corresponding with the voltage difference stepping up.

13. A method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte, as claimed in claim 12 wherein, as the amount of imbalance increases, the two pre-charge voltage steps, a first step and a second step, move away from the balanced electrolytes voltage step, and the extent of the movement is proportional to be extent of imbalance.

14. A method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte, as claimed in claim 12 wherein, a final step for remedying an imbalance is achieved by the addition of a calculated quantity of oxalic acid to the positive electrolyte, slowly in four equal portions, to return it to its normal, balanced pre-charge state.

15. A method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte, as claimed in claim 14 wherein, the addition of oxalic acid or an equivalent is in small portions, to avoid excessive effervescence and spillage of the electrolyte.

16. A method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte, as claimed in claim 12 wherein, the percentage imbalance can be measured with the following steps:

1. measuring the time t_1 to the first step;
2. measuring the time t_2 to the second step;
3. calculating the time T to the mid-point between the steps;
4. calculating the time t from the first step to the mid-point;
5. calculating the percentage imbalance as the percentage t is of T.

17. A method of balancing an imbalanced redox flow battery having partially oxidised negative electrolyte, as claimed in claim 14, wherein, the following equations can be written:

- $t = (t_2 - t_1) / 2$
- $T = t_1 + (t_2 - t_1) / 2$
- $t / T = ((t_2 - t_1) / 2) / (t_1 + (t_2 - t_1) / 2) = t_2 - t_1 / t_2 + t_1$

such that the ratio of t/T is the difference in the times to the steps divided by their sum, and the % imbalance is the ratio times 100.

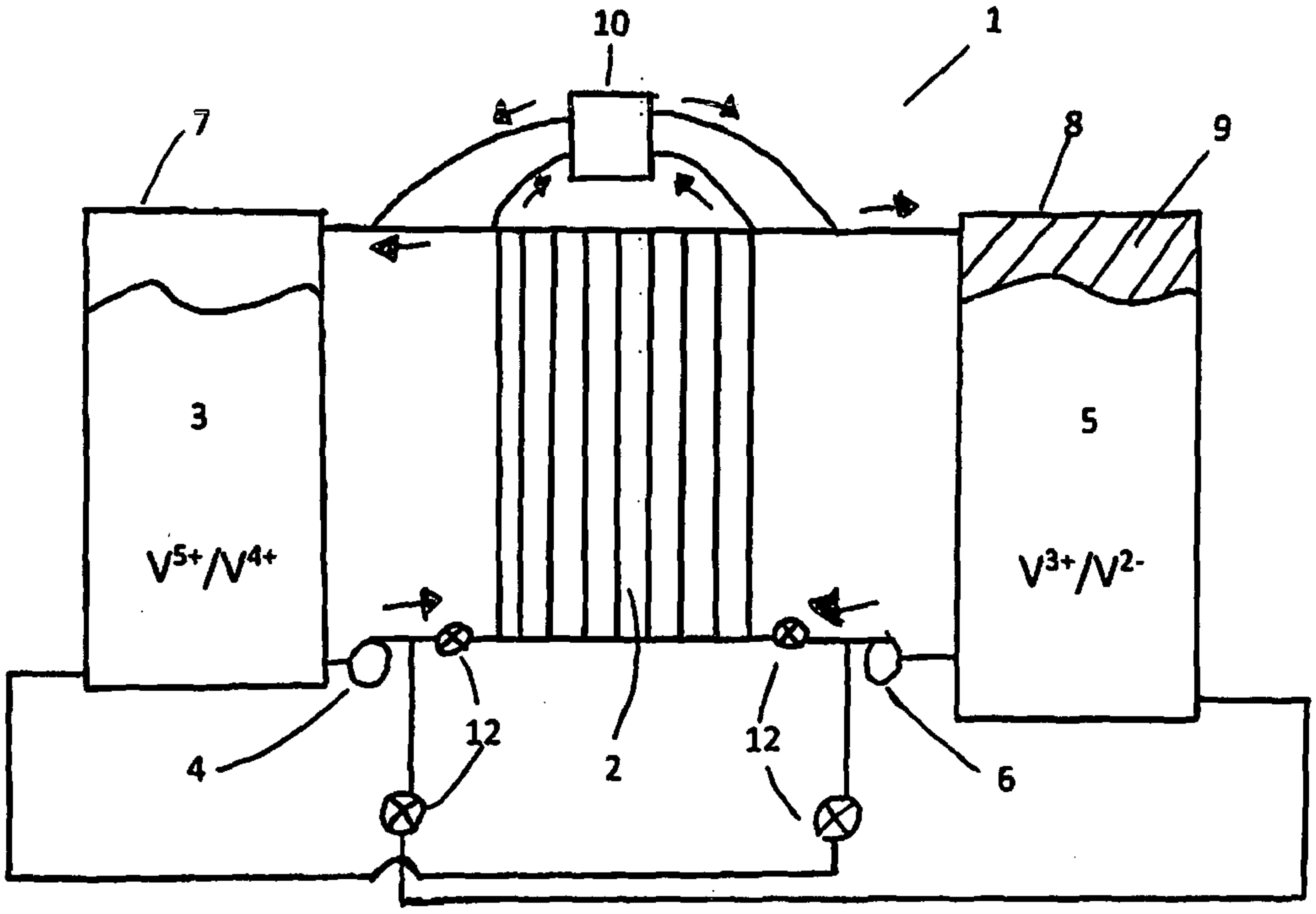


Figure 1

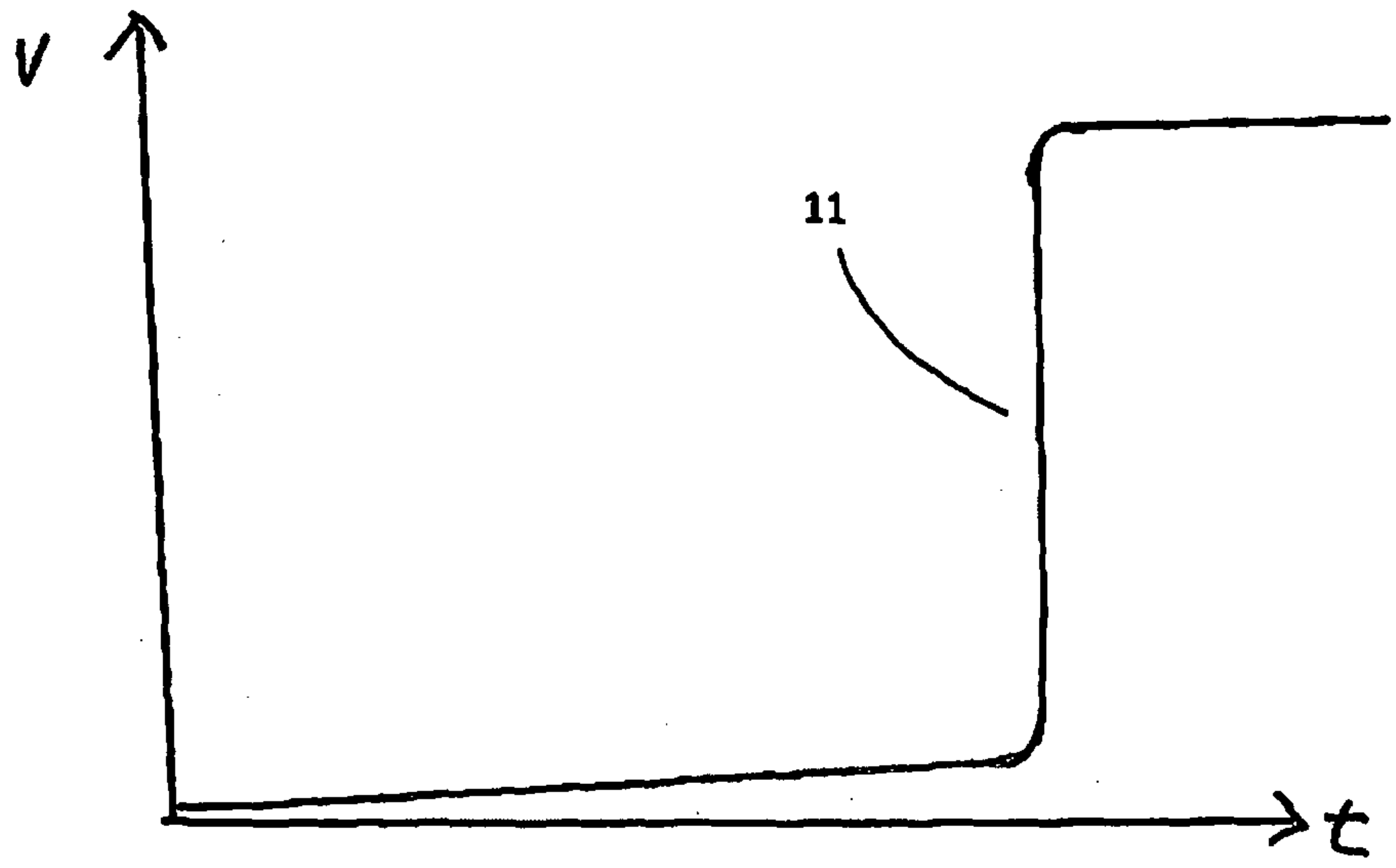


Figure 2

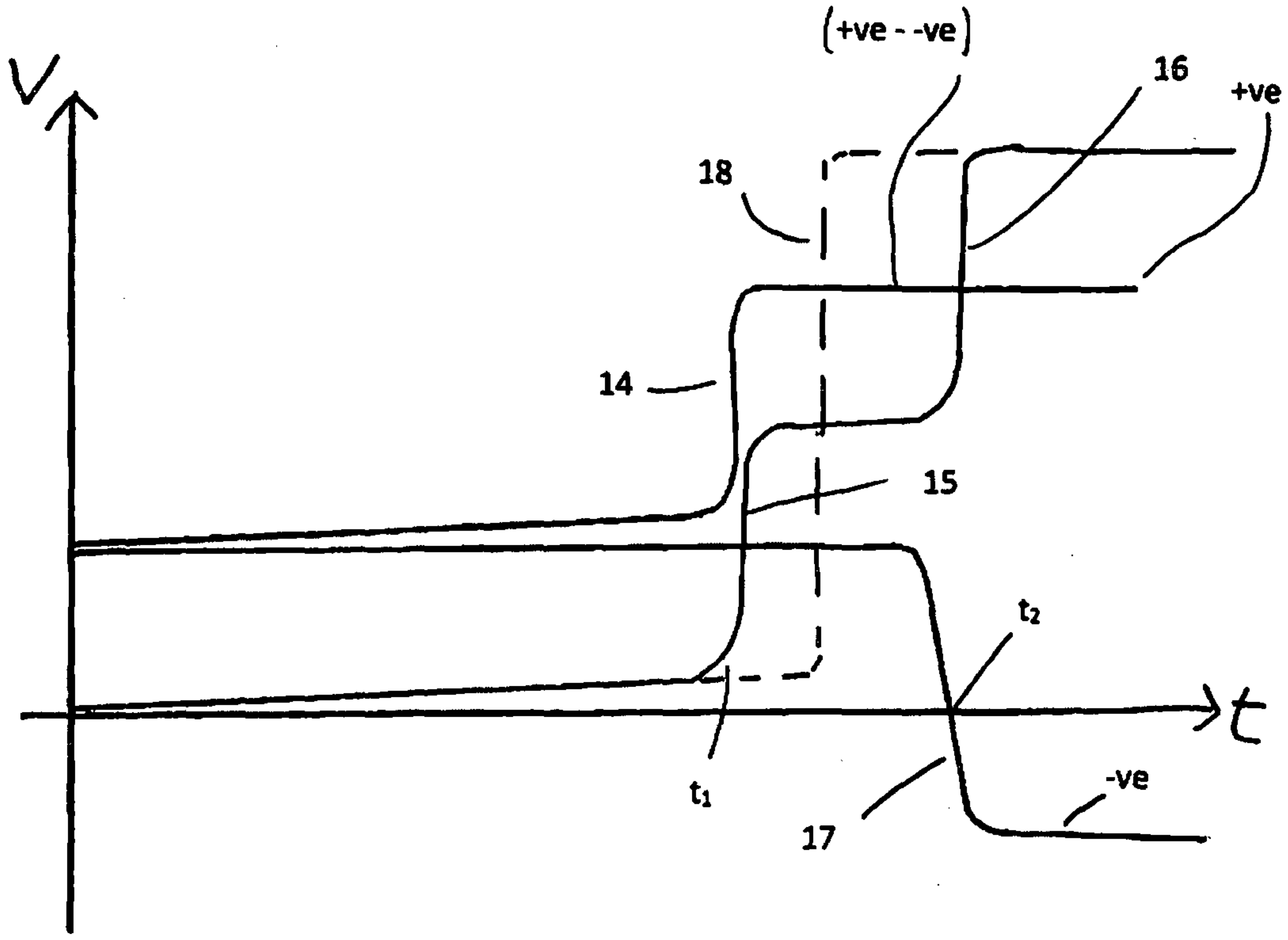


Figure 3

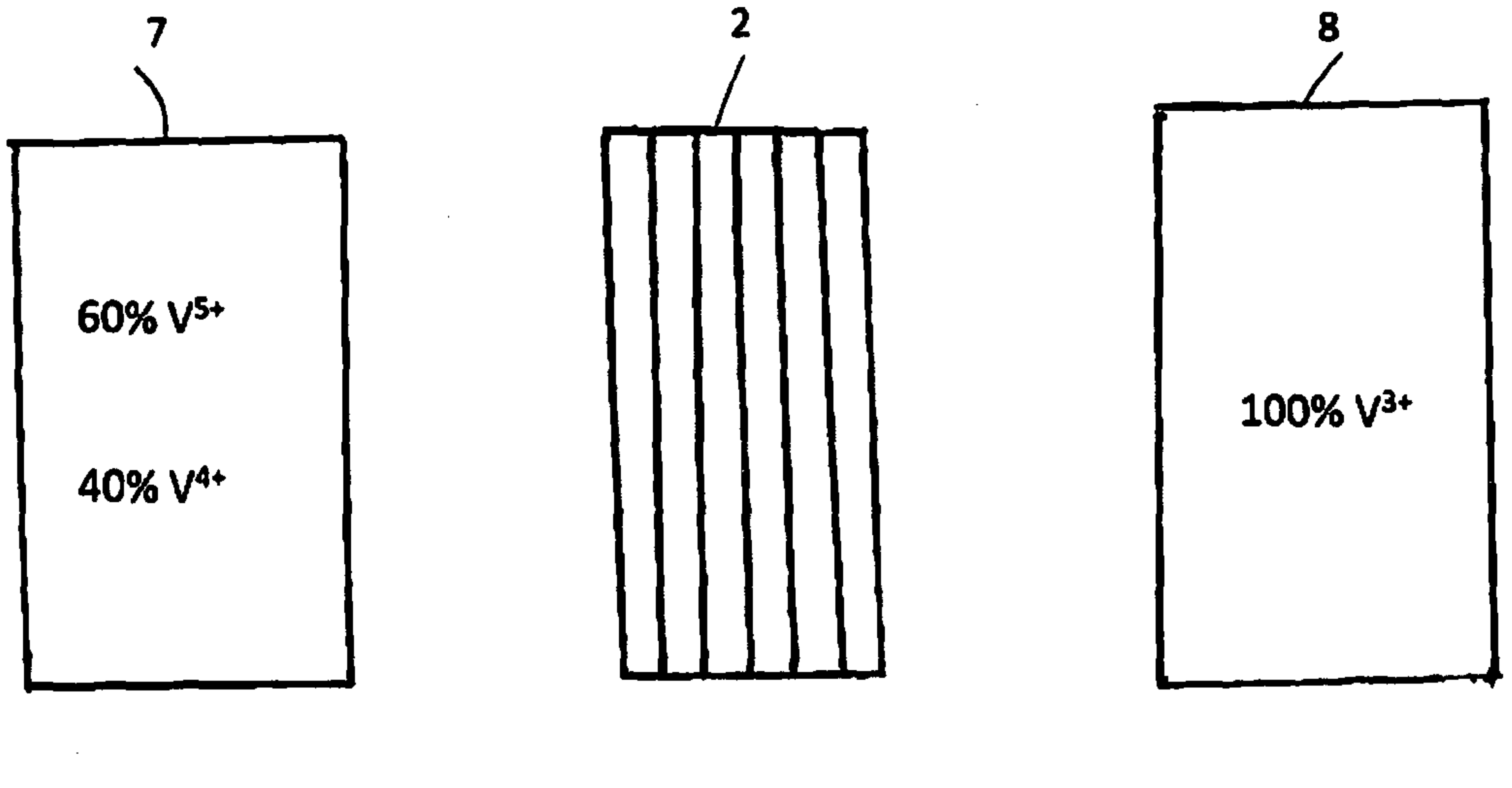


Figure 4

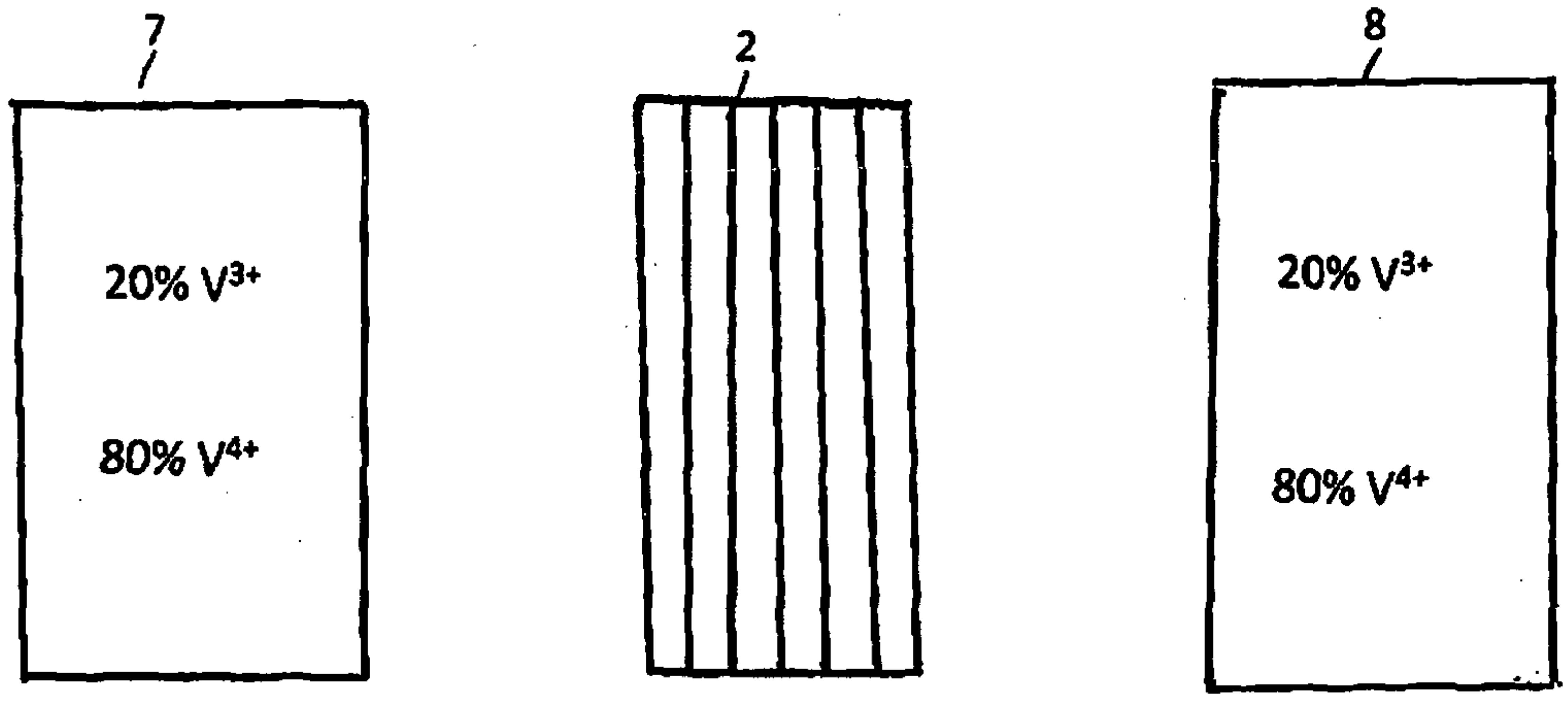


Figure 5

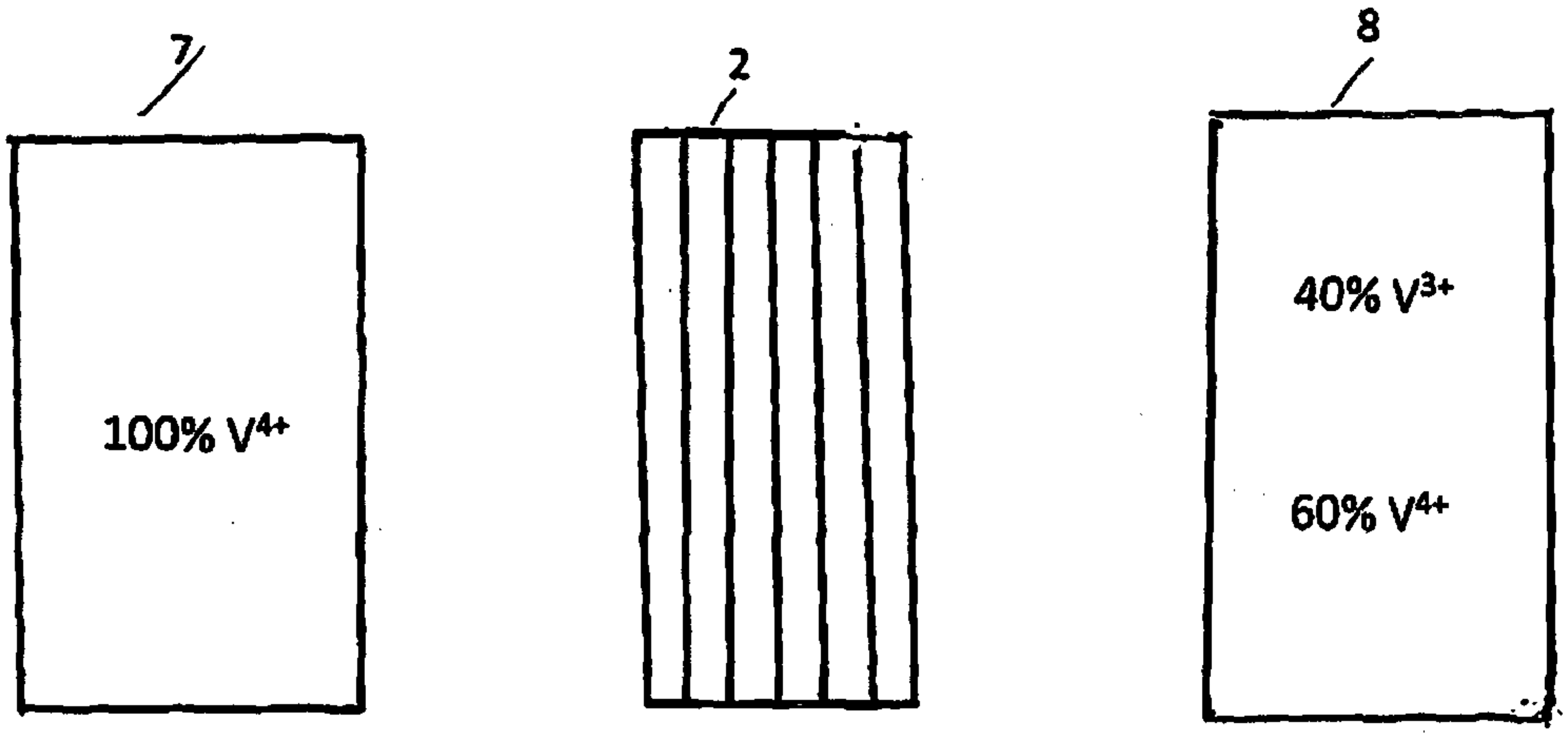


Figure 6

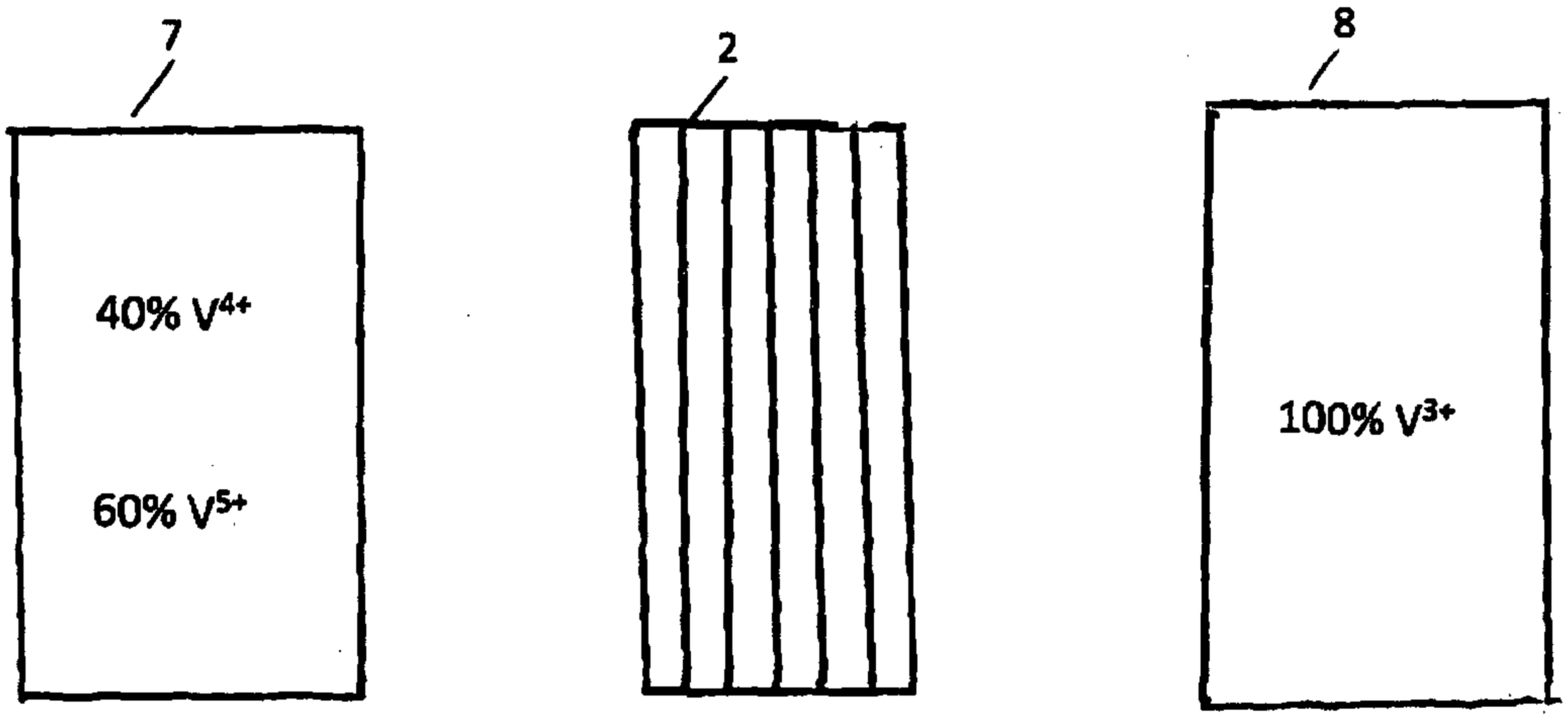


Figure 7

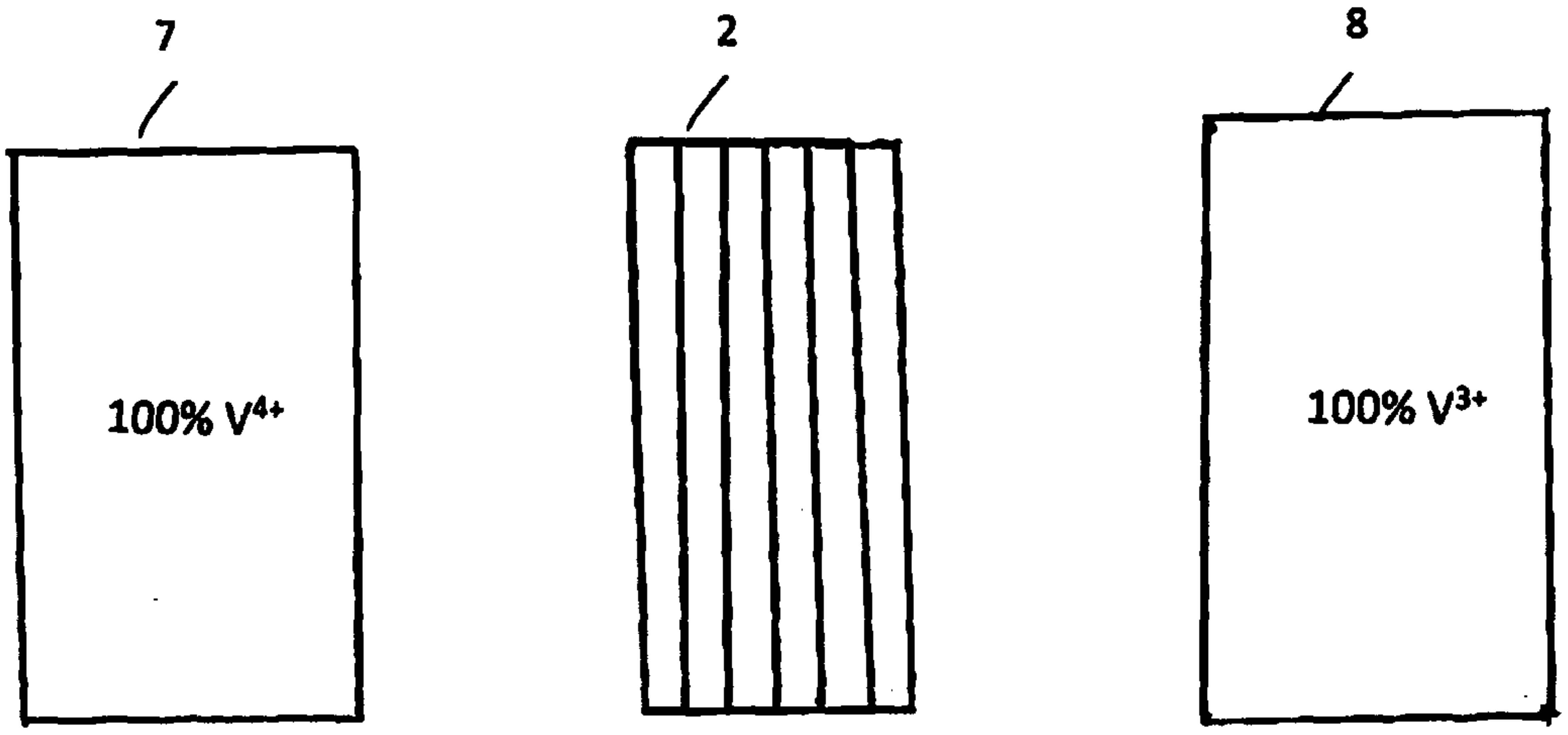


Figure 8

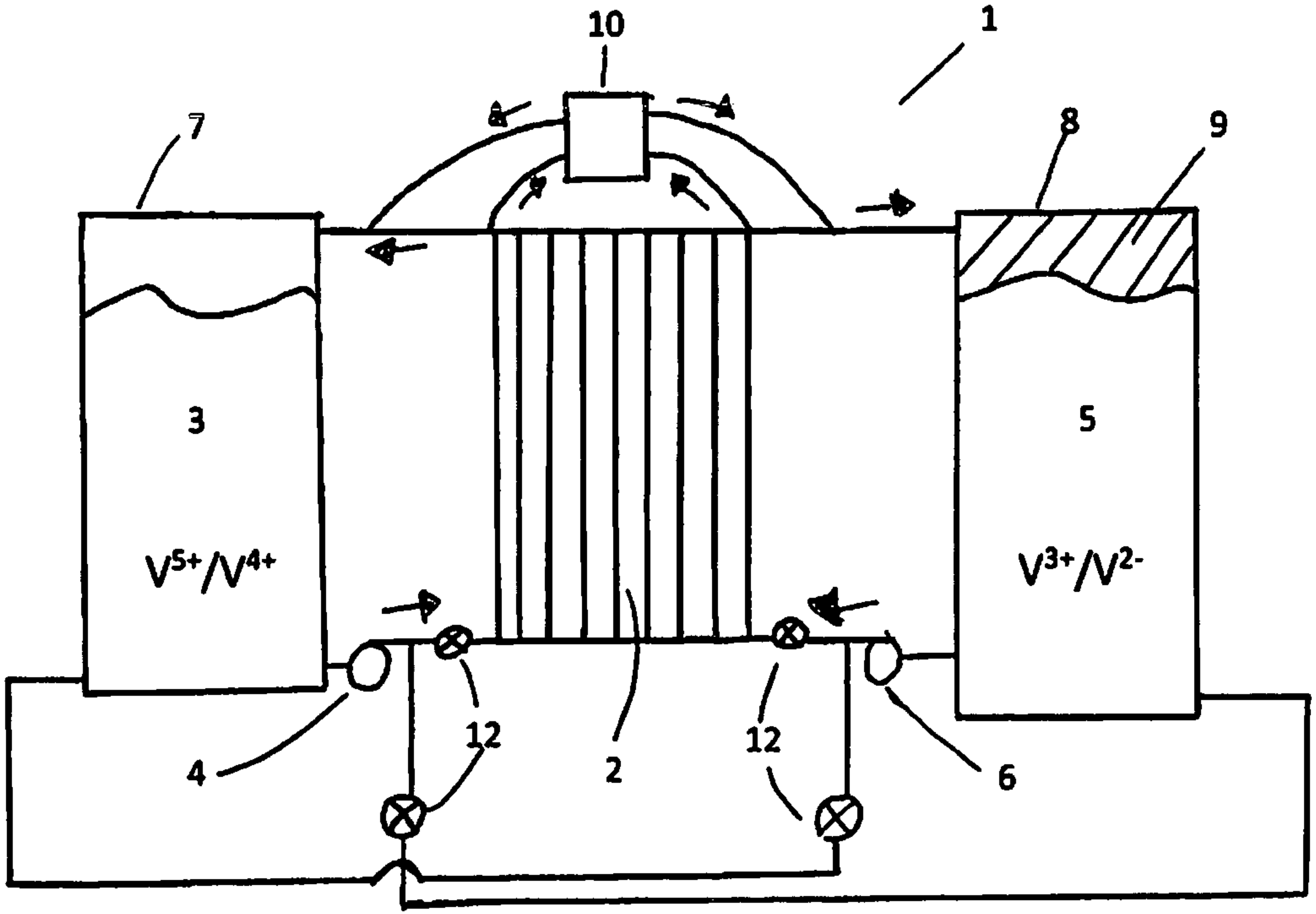


Figure 1