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(54) Title: SIMPLIFIED PROCESS FOR PREPARING ELECTROLYTE FOR VANADIUM REDOX BATTERIES

(57) Abstract: This invention relates to an electrolyte preparation process that involves two stages, one is the thermal reduction of vanadium pentoxide (V_2O_5) to vanadium trioxide (V_2O_3) in a tubular reactor, and the other is the dissolution of the resulting V_2O_3 . It can be used in all types of vanadium redox batteries, also known as flow batteries. This process is simpler than the competing ones and requires, overall, less energy in the preparation of the electrolyte. The reduction step is thermal and uses reducing gases (hydrogen (H_2), carbon monoxide (CO), hydrogen sulphide (H_2S), methane (CH_4) and ammonia (NH_4^+)) or a combined mixture of these gases. It is followed by the dissolution stage. This invention can be used in the industrial manufacture of electric energy storage systems, particularly in vanadium redox batteries (similar to the lead battery sector).



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**Simplified process for preparing electrolyte for vanadium
redox batteries**

10 **Field of the invention**

Technical field to which the invention belongs

This invention belongs in the field of electric storage and consists of a simplified process for preparing electrolyte
15 for vanadium redox batteries.

State of the art

The preparation of electrolyte for vanadium batteries using conventional processes involves considerable technical
20 complexity. Hence the reason for the focus in the invention to be protected.

The most relevant documents in the state of the art are:

- US6143443 - This patent describes the process of preparing the electrolyte for vanadium redox batteries, in
25 which the reduction always takes place in an electrolytic medium, using a wide range of reducing agents along with stabilizing agents. The electrolyte preparation process in an electrolytic medium is lengthy, involves a complex electrolytic cell composed of many parts liable to
30 deteriorate during the course of the process, and requires monitoring the concentration of several chemical species throughout the process.

Compared with this patent, the process to be protected is not performed in an electrolytic medium but in a thermal
35 reduction reactor. The preparation time is shorter or equal to about half the time taken by the electrolytic process and requires, only at the end of the process, one weighing of the reactor after the set time has elapsed. Since the

5 cost of preparing the electrolyte can be between 10% and 70% of the cost of the final vanadium redox battery, the development of a simpler process that is less costly in terms of energy could be a considerable asset in the field of vanadium redox batteries.

10 * Zhang_2005_A-new-method-for-preparing-V₂O₃-nanopowder, Materials Letters 59 (2005) 2729 - 2731 - In this article, the authors describe the preparation of electrolytes as follows: Vanadium trioxide (V₂O₃) nanoparticles are prepared by dissolving vanadium pentoxide (V₂O₅) in aqueous
15 solution of sulfuric acid (H₂SO₄) with its subsequent reduction in aqueous medium using sulfur dioxide gas (SO₂). The V₂O₃ nanoparticles are then characterized through X-ray diffraction, showing that they had the desired crystal structure and there were no impurities. They further used
20 transmittance electron microscopy to determine the morphology and average particle size and concluded the structure was polycrystalline. The XPS spectrum was used to analyse the oxidation state of the oxide (X-ray photoelectron spectroscopy). The authors only mention the
25 preparation of the oxide by reduction in aqueous medium and perform its subsequent characterization. There is no reference to any application for the produced oxide.

In the invention to be protected, the electrolyte in which the V₂O₅ is reduced is prepared in hydrogen gas (H₂) medium,
30 the V₂O₃ is then dissolved in H₂SO₄ in order to prepare the final electrolyte, more specifically for a vanadium redox battery. The analytical techniques employed by the authors of the article could also be used at the end of the thermal reduction process of the invention to be protected, to
35 characterize the V₂O₃ crystals. In the present invention, the V₂O₅ used at the start of the process is already sufficiently pure and therefore only one weighing of the V₂O₃ is performed at the end of the process. It is possible

5 to know if all the V_2O_5 was reduced to V_2O_3 from the ratio of the masses of the reaction products.

• US2003143456 - In this patent, the electrolyte is prepared in solution by the reduction or oxidation of vanadium through an electrochemical route (electrolysis) in
10 liquid electrolyte; the SO_2 (in the form of gas bubbles) is mixed with the electrolyte to reduce the vanadium with the higher oxidation state (5+) to the lower state (3+). The need for stabilizing agents to ensure that the vanadium species in the various oxidation states remain stable
15 throughout the process of electrolyte preparation is also mentioned in this patent, reflecting all the additional complexity of this process.

In the invention to be protected, the V_2O_5 is converted by thermal reduction to V_2O_3 and it is subsequently dissolved
20 under well-controlled conditions in an acidic medium to yield the desired final electrolyte.

• US5250158 - In this patent, the electrolyte is prepared from V_2O_5 reduction in acid electrolyte solution using inorganic acids with reducing agents, with a stated
25 preference for H_2SO_4 . An electrolytic reduction in an electrolytic cell is also part of this electrolyte preparation process. As in the patents mentioned earlier, this electrolyte preparation process is carried out in liquid medium, whereby V_2O_5 (5+) is reduced to V_2O_3 (3+)
30 through the use of a liquid reducing agent.

The invention to be protected is clearly different from the previous proposals in that it has a smaller number of process control parameters.

• US6362514 - This patent describes the preparation of
35 electrolytes for vanadium redox batteries stabilized with various additives that prevent the precipitation of vanadium salts. This patent also gives an extensive list of the reducing agents typically used in electrolytic

5 solutions to reduce vanadium to lower oxidation states. The reductions are always performed in electrolytic medium. In the invention to be protected, thermal reduction is carried out in gaseous medium.

10 **Summary of the invention**

The electrolyte in a vanadium redox battery is one of the basic constituents of this electric energy storage system. The various processes proposed to prepare the electrolyte are mostly in electrolytic medium and make use of
15 electrolysis processes to perform the reduction and oxidation of the reagents. These processes are usually complex in that they control and monitor all the concentrations of species to oxidize and reduce in solution. This invention relates to an electrolyte
20 preparation process that can be used in all vanadium redox batteries, as well as other redox batteries with other metals. The process described in the invention to be protected is a thermal reduction process in gaseous medium with subsequent dissolution in electrolytic medium under
25 well-controlled conditions. The well-controlled dissolution conditions may be achieved by mechanical agitation, or magnetic agitation, or ultrasonic agitation, in concentrated H_2SO_4 at a temperature between 30°C and 95°C for a period of more than 1 minute and less than 10 hours,
30 at a pressure between atmospheric and 50 bar. The dissolution process will be faster if the V_2O_5 is crushed in a mortar or ball mill.

Detailed description of the invention

35 The main advantage of this invention is that it is a much simpler process than the processes described in the state of the art since it enables the final electrolyte to be obtained through only two sequential stages, which are the

5 thermal reduction and dissolution in electrolytic medium. The sequential stages are straightforward to reproduce and repeat. It should be noted that the reactor used is not changed by oxidation during the preparation of the electrolyte, whereas in the other processes the
10 electrolyzers can suffer oxidation arising from the very process of preparing the electrolyte. The reduction reactor can be placed inside any furnace capable of imposing the above-mentioned temperature conditions. The reactor can be made of carbon steel with high chromium content or
15 stainless steel, 316 L or 304 L. It could also be a ceramic material such as zirconium or aluminium, or aluminium/glassy carbon, or zirconium/glassy carbon. The electrolyte obtained from this process may be marketed to various vanadium redox battery manufacturers.

20 The process begins by introducing V_2O_5 into a tubular reactor in the presence of an inert atmosphere consisting of an inert gas, helium (He), argon (Ar) or nitrogen (N_2) or of a combined mixture of these gases. The reactor should be heated from the ambient temperature to between 300°C and
25 1000°C. The temperature may increase at a rate between 1°C/minute and 20°C/minute until the desired temperature is reached, within the range mentioned above. After reaching the desired temperature the reducing atmosphere to replace the inert atmosphere should be introduced. The reducing
30 atmosphere should consist of a reducing gas, from among hydrogen (H_2), carbon monoxide (CO), hydrogen sulphide (H_2S), methane (CH_4) or ammonia (NH_4^+) or of a combined mixture of these gases diluted in N_2 or He or Ar. The mixture of reducing gas or gases diluted in the inert gas
35 or gases should have a volumetric percentage proportion of between 1% and 100%. The flow rate of the reducing gas mixture should be proportional to the amount of V_2O_5 within the tubular reactor. For example, for one gram V_2O_5 to be

5 completely reduced to V_2O_3 will require a flow of a 3% mixture of H_2 (V/V) diluted in 12 L N_2 over a reduction period between 1 minute and 10 hours.

The reducing gas should be chosen in accordance with these stoichiometric calculations: 1 mole of vanadium will need 2
10 moles of H_2 gas to yield 1 mole of V_2O_3 and 2 moles of water (36 g). If the vanadium is in the pure state of complete reduction, 1 mole of V_2O_3 should weigh 149.88 g ($M(V_2O_3)=149.88$ g/mol). The mass of 1 mole of V_2O_5 would initially be 181.88 g ($M(V_2O_5)=181.88$ g/mol). One can check whether
15 the reaction occurred completely or not by weighing the V_2O_5 at the start of the process and during the process so as to arrive at a mass ratio between the V_2O_5 at the start and the V_2O_3 at the end of 1.2135. When this mass ratio is reached it means that all the V_2O_5 has been converted to
20 V_2O_3 .

Examples

The preparation of 1 litre of solution with 1 mole of V_2O_5 involves weighing 181.88 g of V_2O_5 . 2 moles of H_2 represent
25 44.8 L of H_2 considering the molar volume of an ideal gas at standard temperature and pressure (STP). It will, however, be necessary to supply excess H_2 . Therefore, 1.5 times more H_2 than needed will be supplied, which is around 67.2 L throughout the whole reduction process.

30 Around 6 hours (360 minutes) at a temperature of 500°C are estimated to be needed to reduce the whole amount of V_2O_5 to V_2O_3 . For this, pure H_2 will have to be supplied to the V_2O_5 powder at a flow rate of 0.19 L/min. If it is decided to use a mixture of reducing gases such as 5% of H_2 in N_2 ,
35 flow rates of 0.19 L/min for H_2 and 3.8 L/min for N_2 will be needed.

Once 100% of V_2O_5 has been converted into V_2O_3 , the latter is dissolved in a solution of H_2SO_4 with a concentration of

5 between 0.1 molar and 10 molar, previously degassed with N₂
or Ar or He. Dissolution is achieved by heating to a
temperature between 30°C and 95°C and using a magnetic
stirring bar and plate or ultrasonic bath or preferably a
combination of the two previous pieces of mixing apparatus,
10 with the preferred temperature being 90°C.

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1. Simplified process for preparing electrolyte for vanadium redox batteries characterised in that it comprises two stages: a first thermal reduction of vanadium pentoxide (V_2O_5) to vanadium trioxide (V_2O_3) with a mixture of reducing gases in a tubular reactor, in which the inert atmosphere is replaced by the reducing atmosphere during heating, and a second one of dissolution of the resulting V_2O_3 into sulfuric acid (H_2SO_4).
10
2. Process according to claim 1 characterised in that the inert atmosphere inside the reactor consists of an inert gas, from among helium (He), argon (Ar) or nitrogen (N_2), or of a combined mixture of these gases.
15
3. Process according to claim 1 characterised in that the reducing atmosphere consists of a reducing gas, from among hydrogen (H_2), carbon monoxide (CO), hydrogen sulphide (H_2S), methane (CH_4) or ammonia (NH_4^+), or of a combined mixture of these gases diluted in He or Ar or N_2 .
20
4. Process according to the previous claims characterised in that the mixture of reducing gas or gases is diluted in the mixture of inert gas or gases with a volumetric percentage proportion of between 1% and 100%.
25
5. Process according to claim 1 characterized in that the reactor temperature is between 300°C and 1000°C.
30
6. Process according to the previous claims, characterised in that the rate of increase of the reactor temperature is between 1°C/minute and 20°C/minute until the desired temperature, within the range mentioned in claim 5, is achieved.
35

- 5 7. Process according to the previous claims
characterised in that the flow rate of the reducing
gas mixture is proportional to the amount of V_2O_5
within the tubular reactor.
- 10 8. Process according to the previous claims
characterised in that the end of the reaction is
verified by weighing the V_2O_5 at the start of the
process and the resulting V_2O_3 at the end of the
process, until a mass ratio of 1.2135 is obtained.
- 15 9. Process according to claim 1 characterised by the
dissolution of the resulting V_2O_3 in a solution of
 H_2SO_4 with concentration between 0.1 molar and 10
molar, previously degassed with N_2 or Ar or He.
- 20 10. Process according to claims 1 and 9, characterised in
that the dissolution of the resulting V_2O_3 is effected
through heating at a temperature between $30^\circ C$ and
 $95^\circ C$ for a period greater than 1 minute and less than
10 hours at a pressure between atmospheric and 50
bar, with the help of mechanical agitation, or
magnetic agitation or ultrasonic agitation or a
25 combination thereof.

INTERNATIONAL SEARCH REPORT

International application No

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A. CLASSIFICATION OF SUBJECT MATTER

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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 practicable, search terms used)

EPO-Internal, WPI Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2004 168560 A (SUMITOMO ELECTRIC INDUSTRIES) 17 June 2004 (2004-06-17)	1,3,5
Y	paragraph [0023] - paragraph [0036]; claims 1-5	1-10
Y	----- CN 102 092 786 A (INST PROCESS ENG CAS) 15 June 2011 (2011-06-15) page 3, line 8 - page 6, line 25	1-10
X	----- EP 0 713 257 A1 (KASHIMA KITA ELECTRIC POWER CO [JP]) 22 May 1996 (1996-05-22) page 6, line 10 - page 8, line 40	1-5,7,9, 10
Y	----- CN 102 092 787 A (SHENYANG INST OF CHEMICAL TECH) 15 June 2011 (2011-06-15) page 7, line 1 - page 8, line 22	1-10



Further documents are listed in the continuation of Box C.



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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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CN 102092786	A	15-06-2011	NONE

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