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(54) **THERMOCHEMICAL ENERGY STORAGE SYSTEM**

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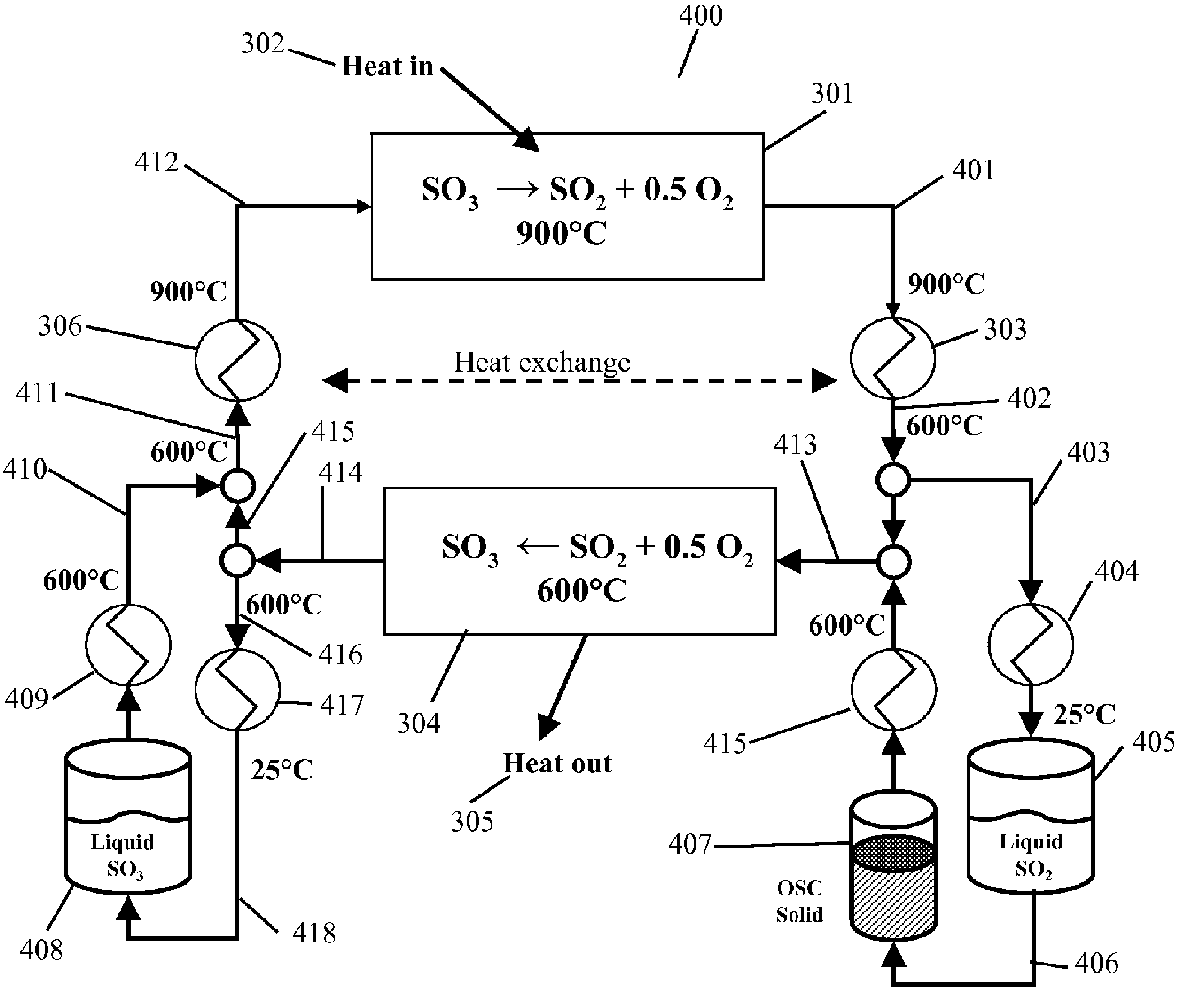
(57) **ABSTRACT**

A system is described for the thermochemical capture of heat energy and the transfer of this energy to a point of use using a cycle decomposing SO_3 to SO_2 and O_2 and the subsequent oxidation of SO_2 and O_2 to SO_3. This system can store this energy in the form of chemical energy by storing liquid SO_2. Embodiments are described wherein oxygen is stored by a solid oxygen storage material or removed and added to the process by selective membranes or by electrochemical pumping. In addition, an alternative embodiment uses an electrochemical generator for the direct conversion of SO_2 to electrical energy.



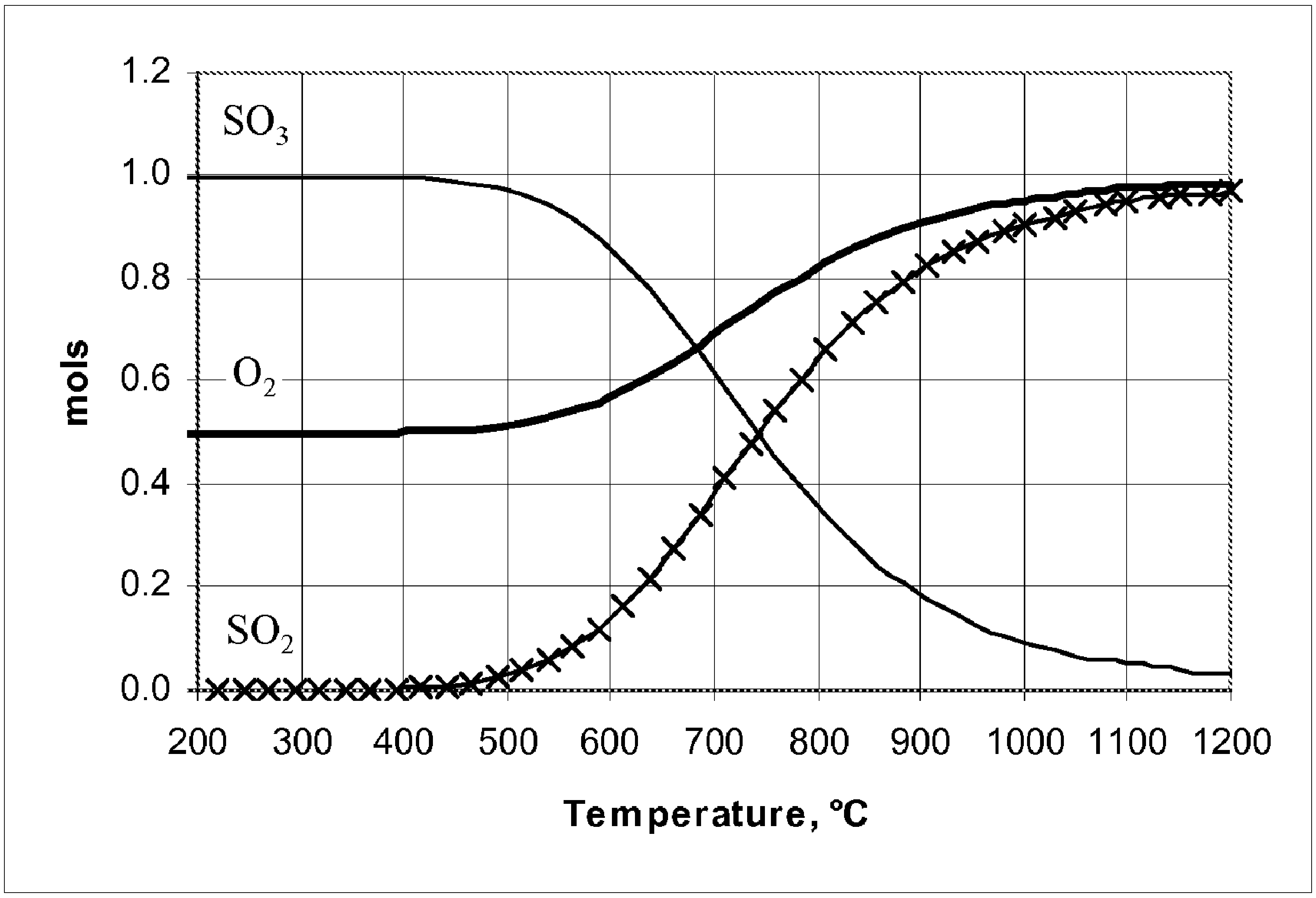

1.2
1.0
0.8
0.6
0.4
0.2
0.0
mols
SO_3
O_2
SO_2
200
300
400
500
600
700
800
900
1000
1100
1200
Temperature, °C

FIG. 1

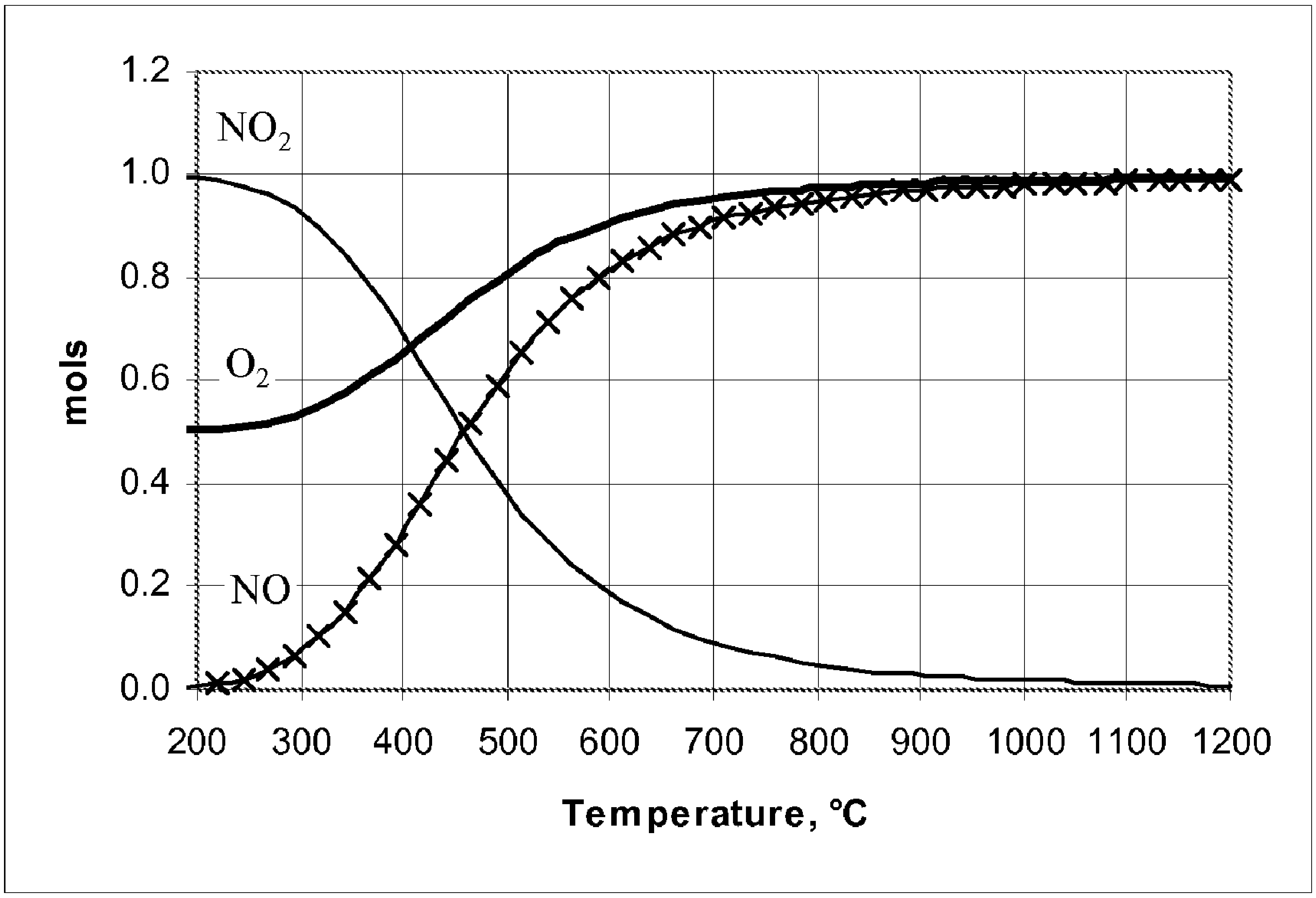

1.2
1.0
0.8
0.6
0.4
0.2
0.0
mols
NO_2
O_2
NO
200
300
400
500
600
700
800
900
1000
1100
1200
Temperature, °C

FIG. 2

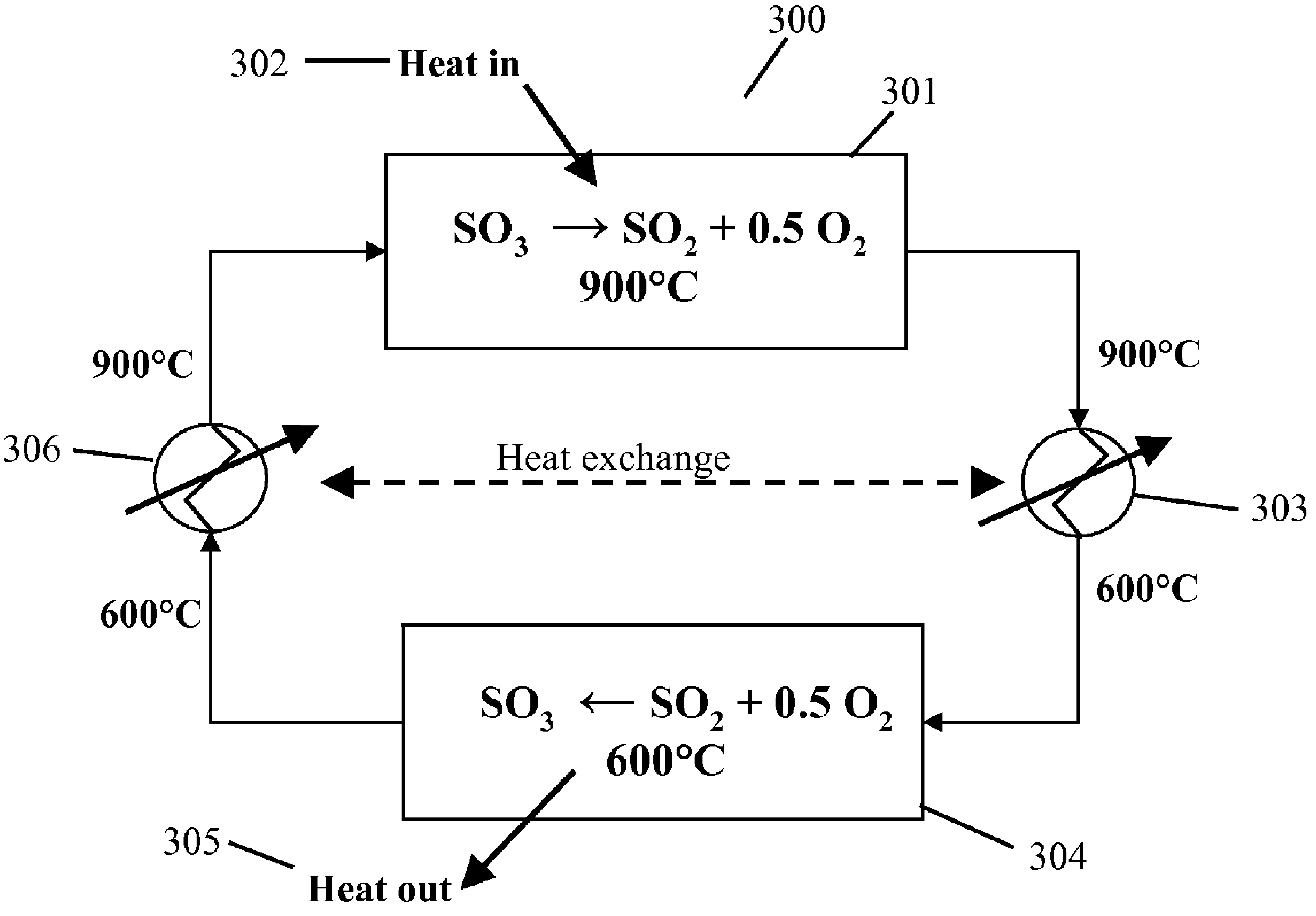

300
302
Heat in
301
$SO_3 \rightarrow SO_2 + 0.5\ O_2$
900°C
900°C
900°C
306
Heat exchange
303
600°C
600°C
$SO_3 \leftarrow SO_2 + 0.5\ O_2$
600°C
305
Heat out
304

FIG. 3

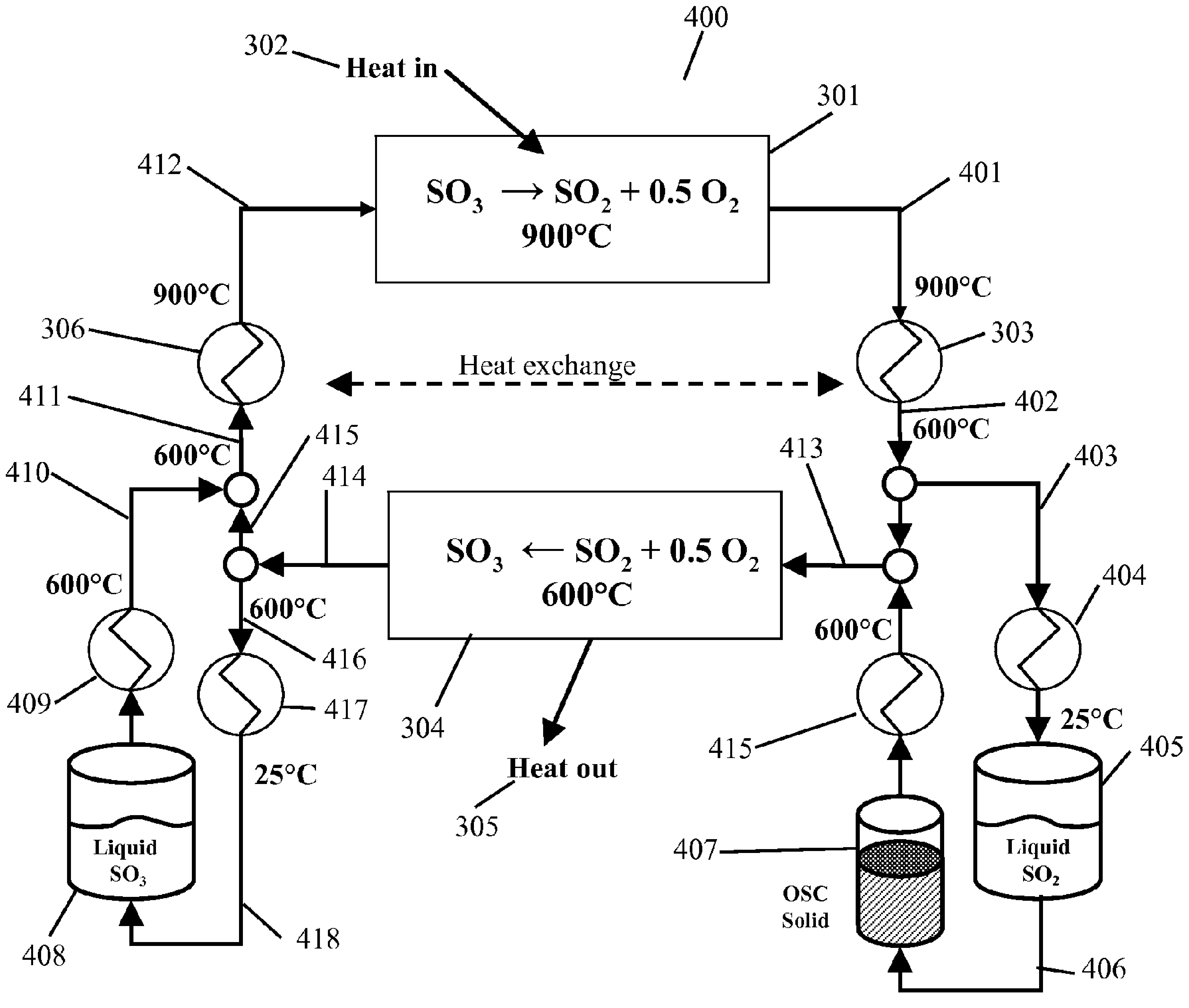

400
302
Heat in
301
412
$SO_3 \rightarrow SO_2 + 0.5\ O_2$
900°C
401
900°C
900°C
306
303
Heat exchange
411
402
600°C
415
600°C
413
403
410
414
$SO_3 \leftarrow SO_2 + 0.5\ O_2$
600°C
404
600°C
600°C
600°C
416
417
409
304
415
25°C
405
25°C
Heat out
305
407
Liquid SO_3
OSC Solid
Liquid SO_2
408
418
406

FIG. 4

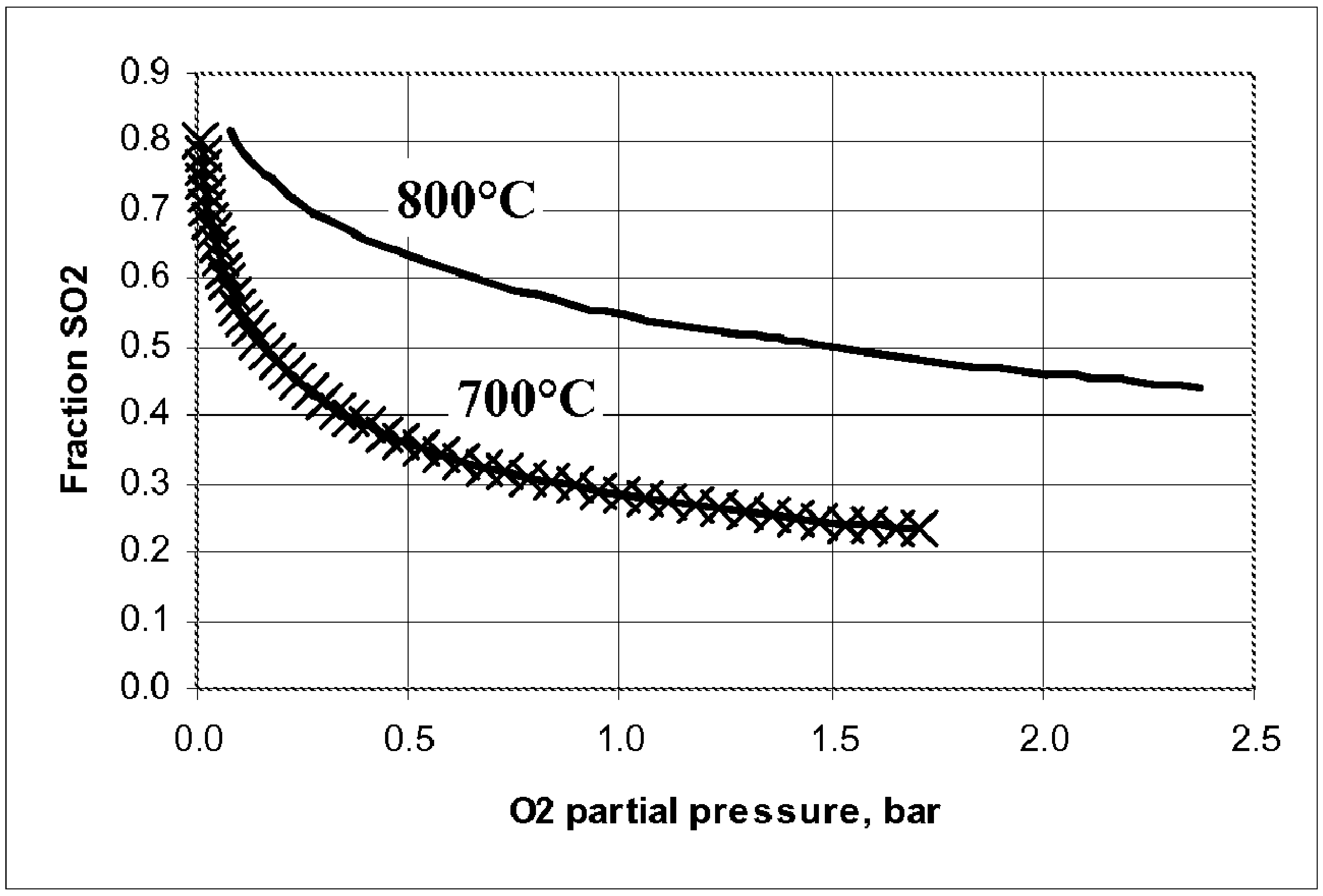

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Fraction SO2
0.0
0.5
1.0
1.5
2.0
2.5
O2 partial pressure, bar
800°C
700°C

FIG. 5

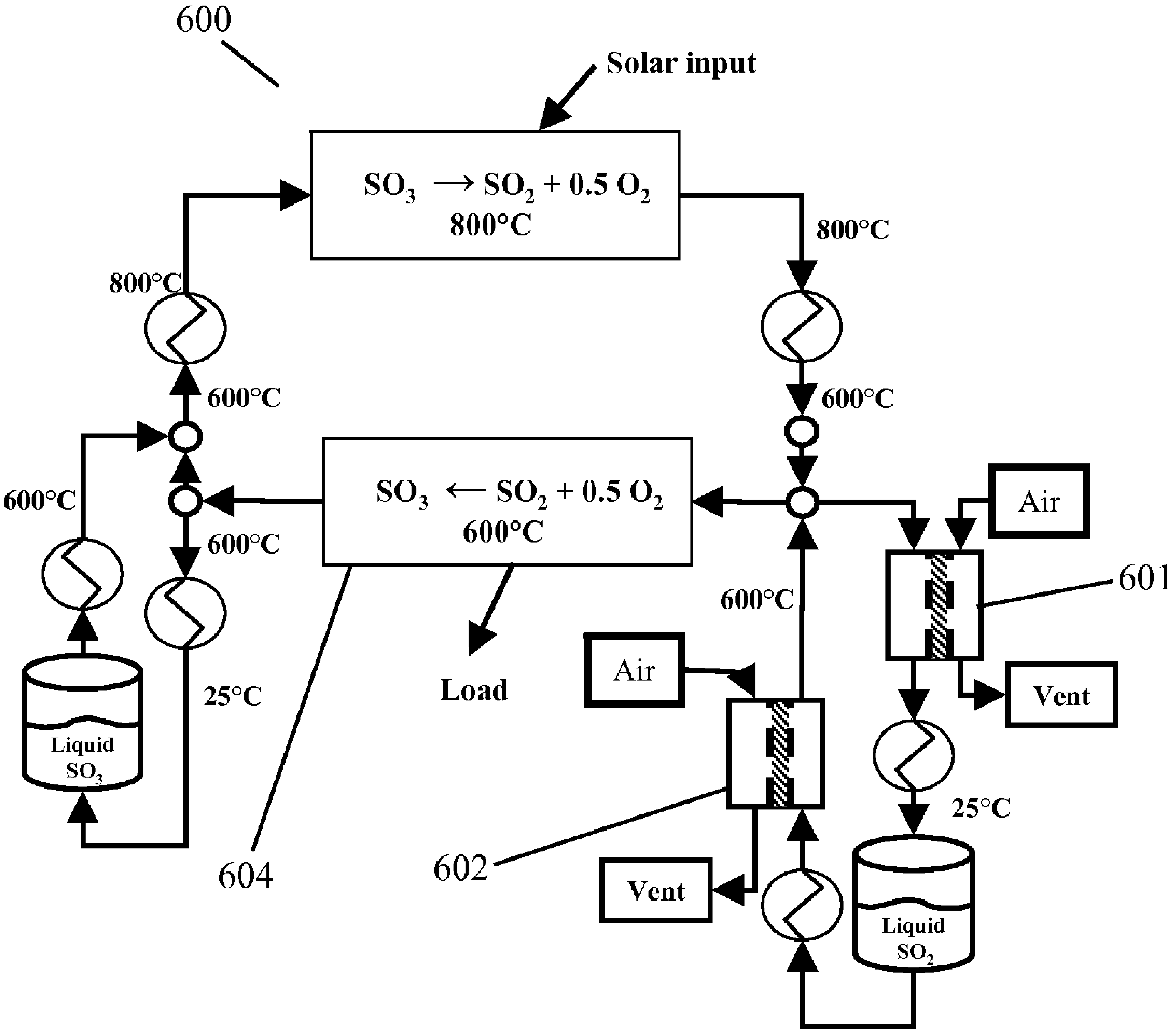

600
Solar input
SO3 → SO2 + 0.5 O2
800°C
800°C
800°C
600°C
600°C
600°C
600°C
SO3 ← SO2 + 0.5 O2
600°C
600°C
Air
601
600°C
Air
Load
Vent
25°C
Liquid SO3
25°C
604
602
Vent
Liquid SO2

FIG. 6

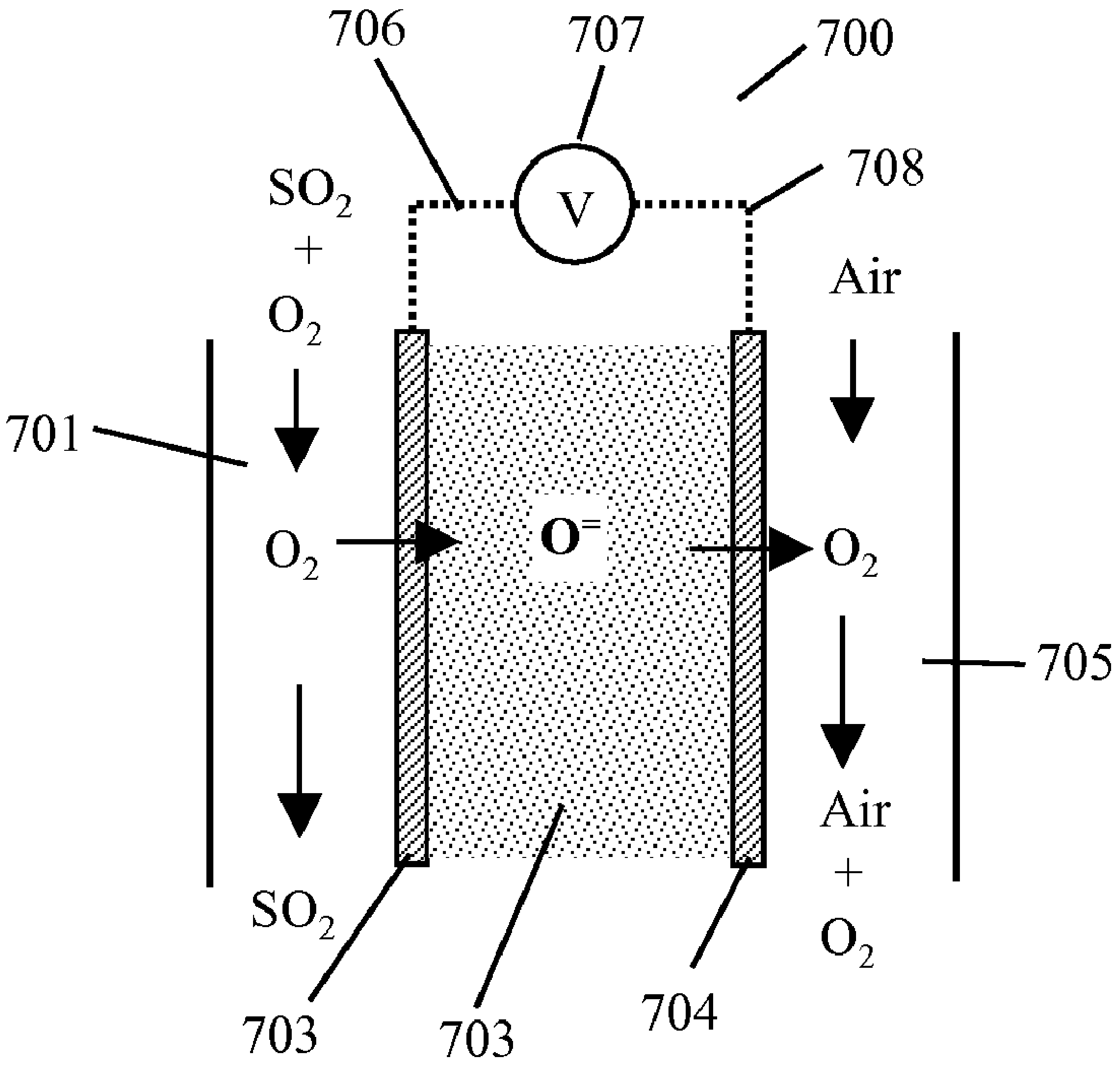

706
707
700
708
V
SO_2
+
O_2
Air
701
O_2
$O^=$
O_2
705
Air
+
O_2
SO_2
703
703
704

FIG. 7

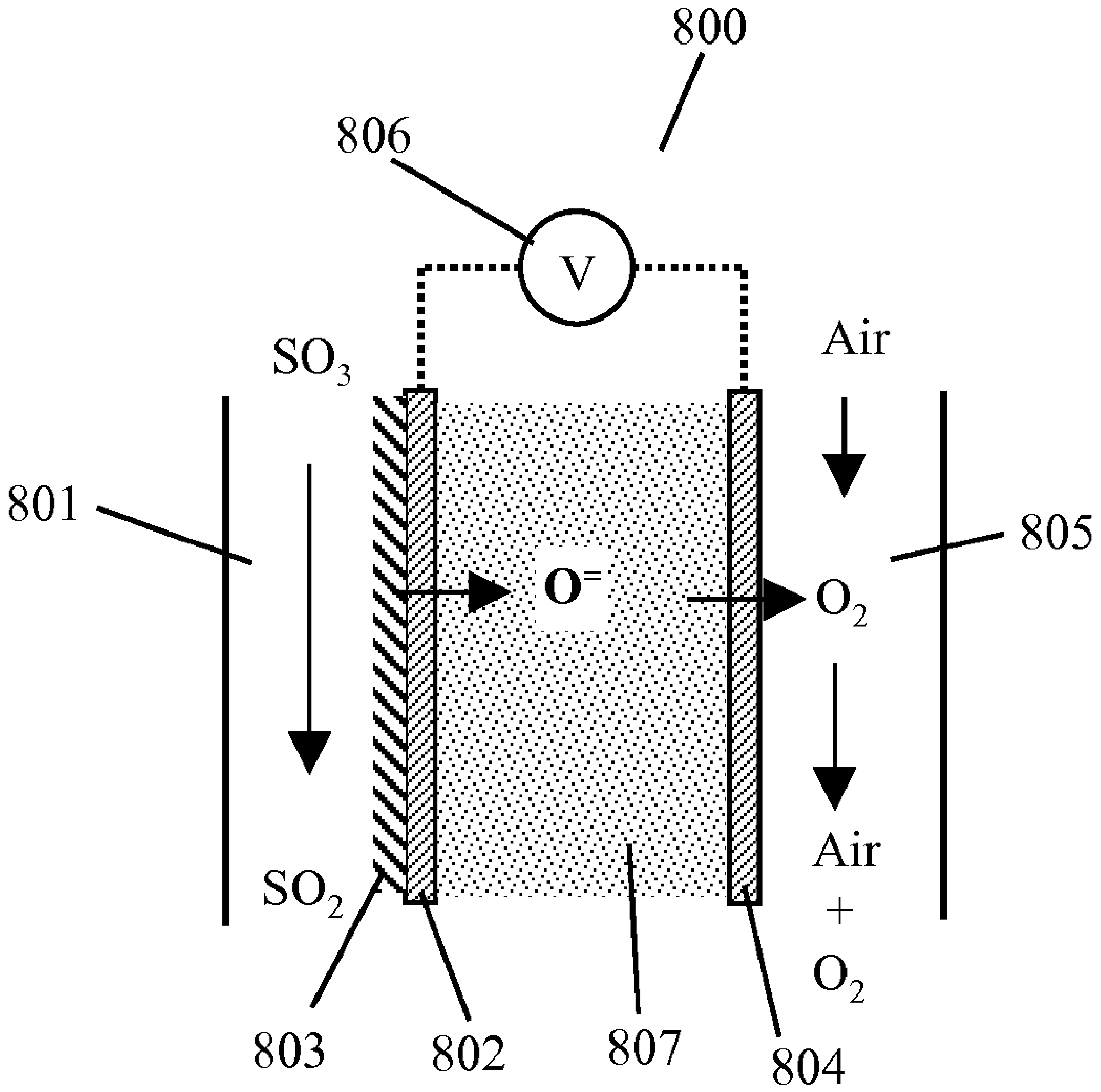

800
806
V
SO_3
Air
801
$O^=$
O_2
805
Air
+
O_2
SO_2
803
802
807
804

FIG. 8

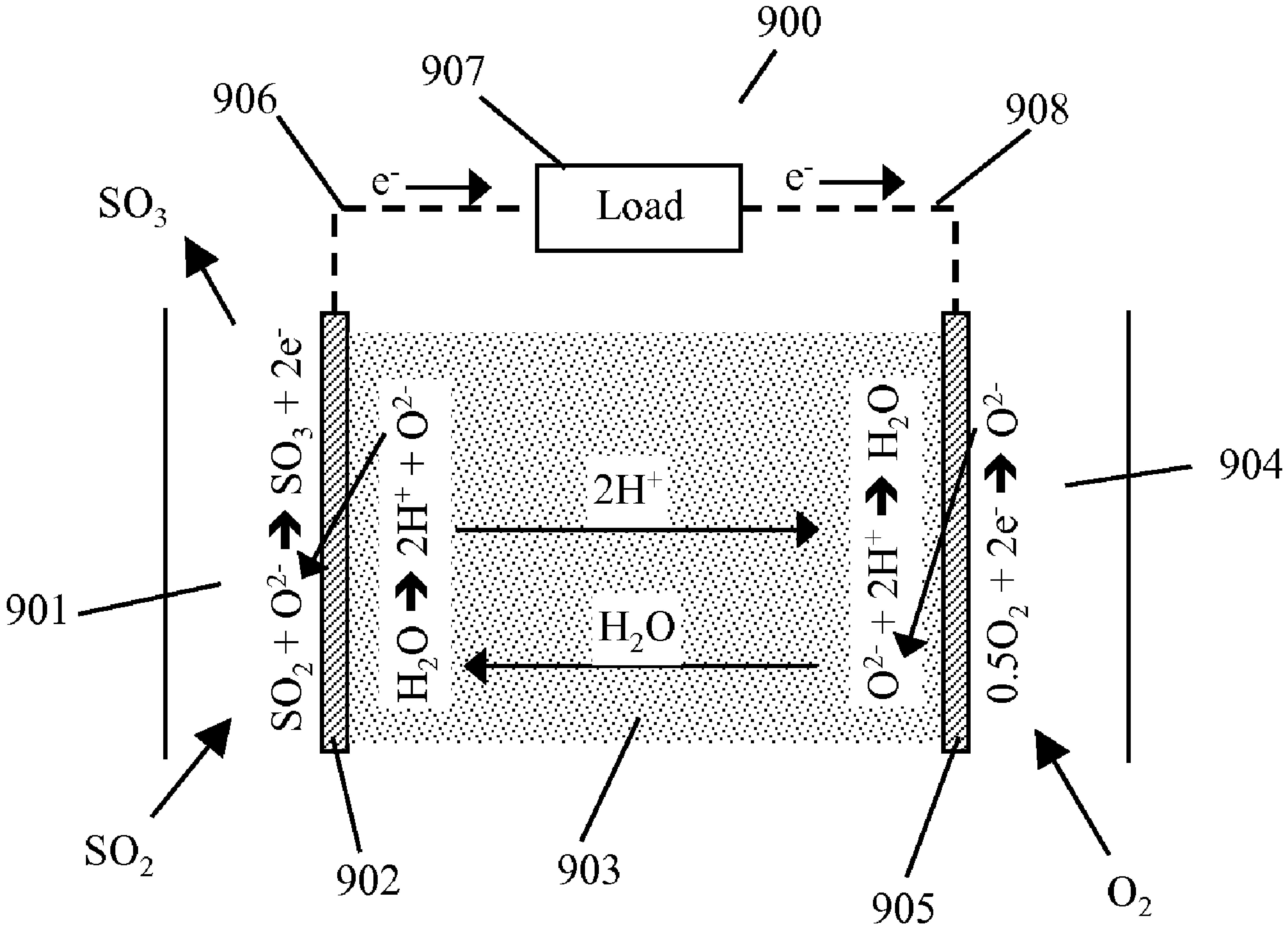

900
907
906
908
e-
Load
e-
SO3
2H+
H2O
SO2 + O2- → SO3 + 2e-
H2O → 2H+ + O2-
O2- + 2H+ → H2O
0.5O2 + 2e- → O2-
901
904
SO2
902
903
905
O2

FIG. 9

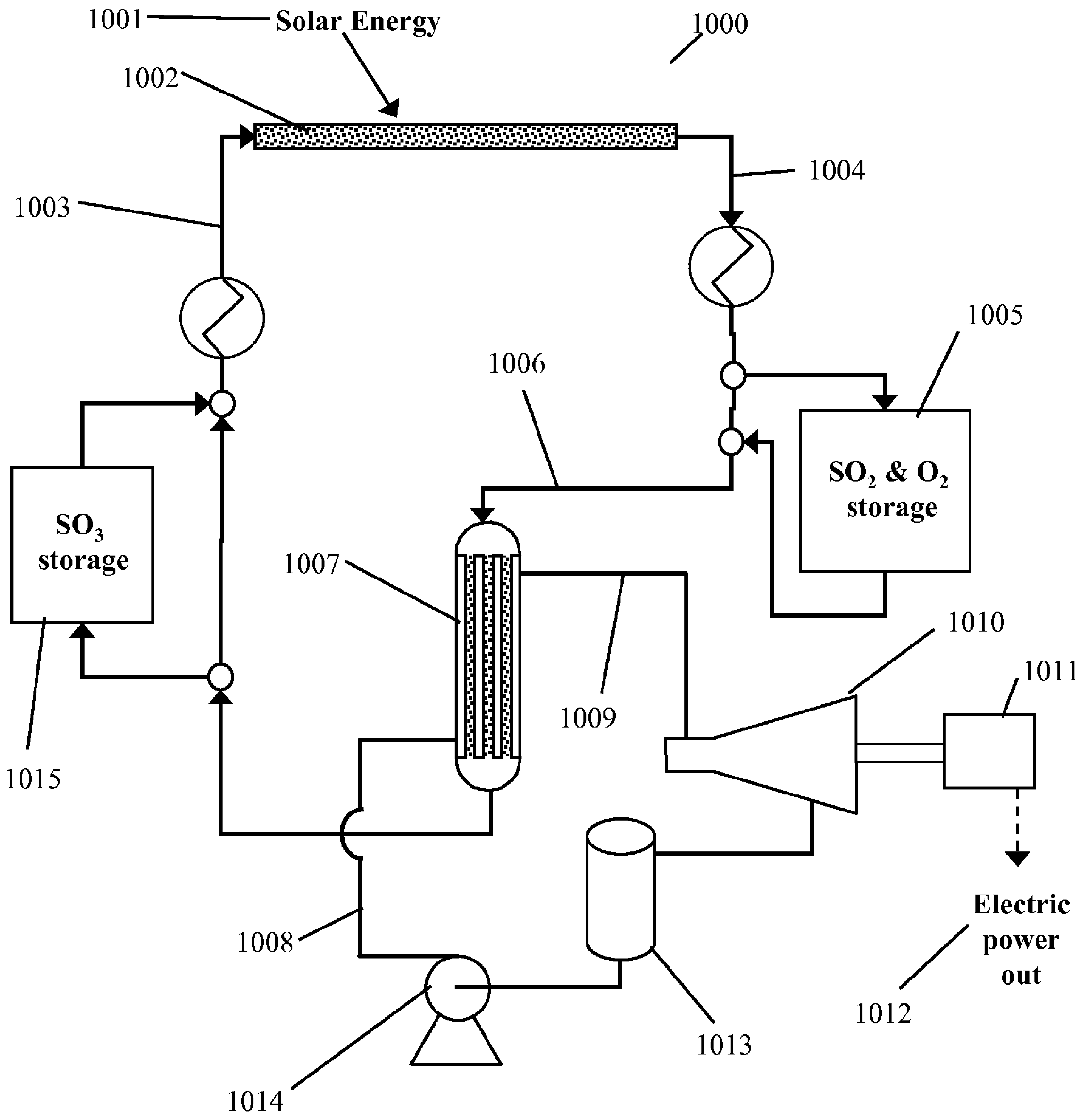

1001
Solar Energy
1000
1002
1003
1004
1005
1006
SO_2 & O_2 storage
SO_3 storage
1007
1009
1010
1011
1015
1008
1013
1014
Electric power out
1012

FIG. 10

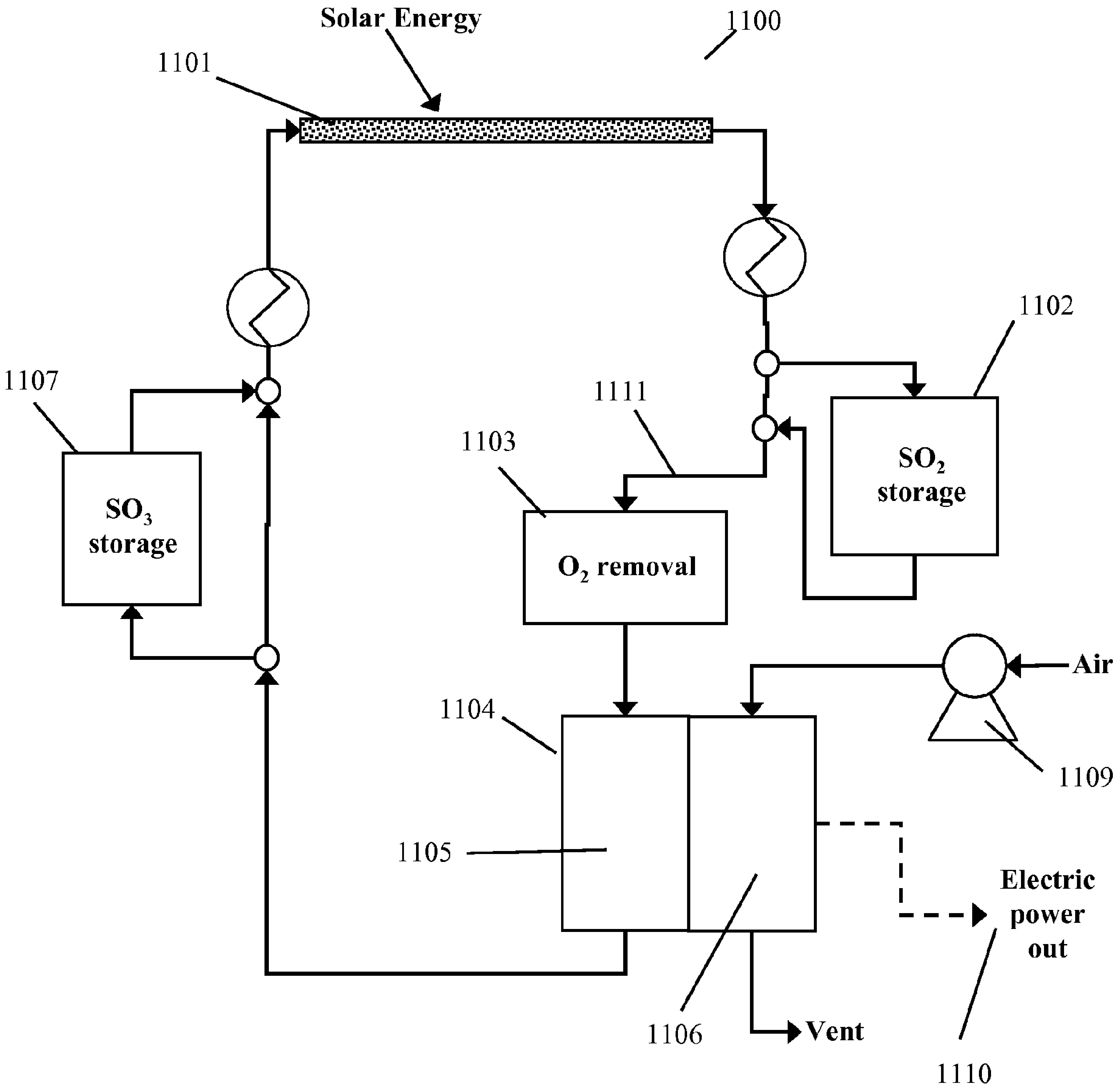

Solar Energy
1100
1101
1102
1107
1111
1103
SO$_2$ storage
SO$_3$ storage
O$_2$ removal
Air
1104
1109
1105
Electric power out
1106
Vent
1110

FIG. 11

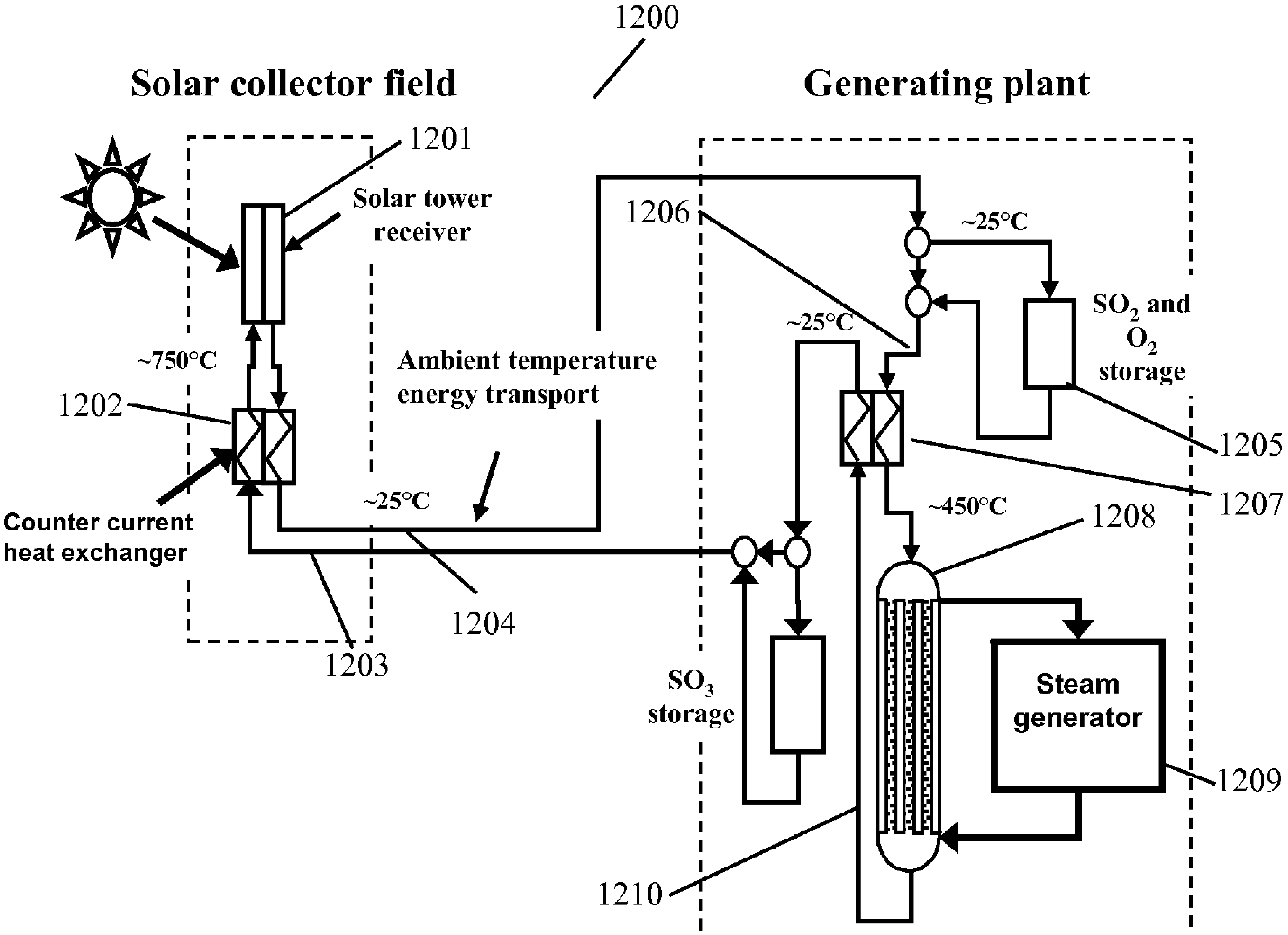

1200
Solar collector field
Generating plant
1201
Solar tower receiver
~750°C
1202
Counter current heat exchanger
~25°C
1203
1204
Ambient temperature energy transport
1206
~25°C
~25°C
SO_2 and O_2 storage
1205
1207
~450°C
1208
SO_3 storage
Steam generator
1209
1210

FIG. 12

THERMOCHEMICAL ENERGY STORAGE SYSTEM

FIELD OF THE INVENTION

[0001] The present invention relates to a concept and system design for thermochemical energy storage.

BACKGROUND

[0002] The headings used herein are for illustrative purposes and do not limit the interpretation of the following specification.

[0003] Thermal solar systems generate thermal energy when the sun is shinning but when the sun sets, solar thermal energy is not available and such system must either rely on conventional stored carbon based fuels or stored energy generated during the period when solar energy is available. Energy can be stored in a variety of ways such as electrical energy stored in batteries or capacitors, pumped storage where water is pumped to an elevated storage area for later use to generate electrical energy through a water powered turbine generator, pressurized storage of compressed gas etc. Another such energy storage technique is to use the solar energy to convert a chemical substance from a low energy state to a high energy state, storing this chemical compound and later use this chemical compound to generate energy through a chemical reaction that returns the chemical to it initial state and release energy, typically heat. One such process is the ammonia synthesis reaction and ammonia decomposition reaction shown in equations 1 and 2 as described in published articles by Luzzi, Lovegrove and coauthors (Solar Energy 66(2) pp. 91-101 (1999)).

$$H_2+3N_2 \rightarrow 2\ NH_{3l\ +heat} \tag{1}$$

$$3\ NH_3+\text{heat} \rightarrow 3\ H_2+N_2 \tag{2}$$

Both of these reactions are carried out over a catalyst. This reaction can transport energy from the solar collector where energy input dissociates HN_3 to H_2 and N_2, The H_2 an N_2 are then transported to the location where the heat is needed where the ammonia synthesis reaction releases heat. To store energy for use during periods when solar energy is not available, for example at night or during cloudy periods, this system has to produce and store excess H_2 and N_2. This is not an ideal situation since at ambient temperatures, H_2 and N_2 can only be stored as compressed gases since ambient temperature is above the critical temperature of these species. Storage as liquids would require additional energy input to liquefy these gases and storage at very low temperatures would have additional energy costs or require additional process equipment to deal with continual liquid evaporation. Also, storage of gas at high pressure results in high capital costs for the storage facilities and expenditure of considerable energy for compression as the gas is stored.

[0004] An alternative type of energy storage is described by Azpiazu and coauthors (Applied Thermal Engineering 23 (2003) p. 733-741) which uses the hydration of calcium oxide as the energy cycle. CaO is hydrated by reaction with water to release heat and then dehydrated using solar energy to regenerate the CaO and release the water.

$$Ca(OH)_2+\text{heat} \rightarrow CaO+H_2O \qquad (^{3})$$

$$CaO+H_2O \rightarrow Ca(OH)_2+\text{heat} \tag{4}$$

In operation as a solar thermochemical storage system, the calcuim hydroxide is contained in a reactor as a packed bed or similar solid mass. Heat from solar energy collector is used to heat a gas or liquid heat transfer medium that transfers the heat energy to a heat exchange system installed in the calcium hydroxide bed to dehydrate the calcium hydroxide to calcium oxide and free water vapor at approximately 500° C. When heat energy is required from the stored chemical energy, the calcium oxide bed temperature is lowered to 25° C. and water added back to form calcium hydroxide and release the sorted energy. The energy is extracted by gas or fluid flow through a heat exchange system installed in the storage bed. A wide range of such adsorption-desorption reactions can be envisioned. U.S. Pat. No. 4,365,475 describes a number of such reaction couples for NH_3 adsorption-desorption. The reaction couple can be selected to collect energy and release energy over a variety of temperature ranges. The CaO—$Ca(OH)_2$ couple described above releases heat near ambient temperature so it would be a good cycle for space heating and adsorption chillers. Cycles described in U.S. Pat. No. 4,65,475 involving the formation of NH_3 complexes, could release energy at higher temperatures, for example 200 to 250° C., allowing the released heat to be used to generate steam for electrical power generation using a steam turbine. One major disadvantage of these adsorption-desorption systems is that the energy storage and release requires that a massive solid bed be heated and cooled to the required cycle temperatures thus wasting significant energy. Also, the large change in volume of the solid upon hydration-dehydration or ammonia complexation-decomposition make it difficult to prepare durable solid materials that can go through many cycles. Azpiazu and coauthors describe the calcium oxide-hydroxide couple as limited to 20 cycles before performance degradation was excessive.

[0005] Another system that has been described in U.S. Pat. Nos. 3,972,183 and 3,997,001 is the conversion of SO_3 into SO_2 and O_2 and the subsequent oxidation of SO_2 with O_2 to SO_3. The process described uses a catalyst in the solar energy collector to decompose SO_3 to SO_2 and O_2 at about high temperature with the adsorption of heat, transport of the SO_2 and O_2 gas to the process or an energy storage unit where the SO_2 and O_2 is coverted to SO_3 and heat and the heat stored. These references describe the storage of energy as sensible heat in a thermal mass such as a bed of hot rocks or heat of phase change in a molten salt. Storage of energy as a hot thermal mass or as a hot molten salt requires insulation to retain the heat and also results in a slow loss of the stored energy through loss of heat.

SUMMARY

[0006] In embodiments of the invention, thermochemical energy storage cycles are provided that use the a reaction couple of a gaseous species that is catalytically decomposed to a less oxidized species and free oxygen with the adsorption of heat to store thermochemical energy followed by the catalytic oxidation of this less oxidized species to release energy. One embodiment of such the cycle is shown in equations 5 and 6.

$$SO_3+\text{heat} \rightarrow SO_2+0.5\ O_2 \tag{5}$$

$$SO_2+0.5\ O_2 \rightarrow SO_3+\text{heat} \tag{6}$$

Another embodiment of the cycle employs NO and NO_2 as shown in equation 7 and 8.

$$NO_2+heat \rightarrow NO+0.5\ O_2 \quad (7)$$

$$NO+0.5\ O_2 \rightarrow NO_2+heat \quad (8)$$

[0007] For the SOx couple of equations 5-6, SO_2 is the stable species above 700 to 800° C. and SO_3 is the stable species below about 600° C. Thus, reaction 5 would be operated at 700 to 1000° C. with energy input from a solar or other energy source supplying heat and reaction 6 at 600° C. or lower with energy output to the target process. This would allow the production of high quality steam for power generation or process heat. The NOx cycle is similar with the NO_2 the preferred chemical species above 600° C. and NO the preferred chemical form below 300 to 400° C. SO_2 and NO plus O_2 provide thermochemical energy transport methods. The inventive cycles use the SO_2 to SO_3 interconversion combined with liquid storage of the SO_2 and SO_3 to provide a thermochemical energy storage system with a high energy density and low capital cost. Since the SO_2 and SO_3 can be stored at ambient temperature as a liquid, this eliminates the need for thermal energy storage at high temperature, eliminates the need for insulation to retain this high temperature stored heat and eliminates any loss of energy through slow loss of heat with time. In addition, inventive methods for the storage of the O_2 or removal and supply of the O_2 are described. In addition, an inventive electrochemical generator for the electrochemical oxidation of SO_2 into SO_3 and electricity is described.

[0008] A number of other aspects of these cycles will be described and systems described for energy transfer from the energy source (solar) to the process and for high density energy storage and release.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIG. **1** shows the equilibrium distribution of SO_3, SO_2 and O_2 over a range of temperatures for 1 bar pressure starting with 1 mole SO_3 and 0.5 mole O_2.

[0010] FIG. **2** shows the equilibrium distribution of NO_2, NO and O_2 over a range of temperatures for 1 bar pressure starting with 1 mole NO_2 and 0.5 mole O_2.

[0011] FIG. **3** is a schematic diagram of thermochemical energy cycle using SO_2 and SO_3 where the decomposition of SO_3 to SO_2 and O_2 adsorbs thermal energy and the oxidation of SO_2 to SO_3 releases the thermal energy at the point of use.

[0012] FIG. **4** is a schematic diagram of a thermochemical energy cycle including energy storage using liquid SO_2 and SO_3 in one embodiment of the invention.

[0013] FIG. **5** is a graph showing the effect of oxygen partial pressure on the equilibrium fraction of SO_2 at **10** bar pressure for temperatures of 700 and 800° C. in one embodiment of the invention.

[0014] FIG. **6** is a schematic diagram of a thermochemical energy cycle including energy storage using an oxygen pump to remove and add O_2 to the process stream in one embodiment of the invention.

[0015] FIG. **7** is a schematic diagram of an electrochemical O_2 pump in one embodiment of the invention.

[0016] FIG. **8** is a schematic diagram of an electrochemical O_2 pump combined with a catalytic process to decompose SO_3 into SO_2 and O_2 in one embodiment of the invention.

[0017] FIG. **9** is a schematic diagram of an electrochemical process for converting SO_2 and O_2 into SO_3 and electric power in one embodiment of the invention.

[0018] FIG. **10** is a schematic diagram of a thermochemical energy cycle including energy storage and electrical power generation using thermal energy to generate steam and the steam to drive a turbine generator in one embodiment of the invention.

[0019] FIG. **11** is a schematic diagram of a thermochemical energy cycle including energy storage and an electrochemical generator that directly converts SO_2 and O_2 into electricity in one embodiment of the invention.

[0020] Use of the same reference numbers in different figures indicates similar or identical elements.

DETAILED DESCRIPTION

Basic System Design

[0021] FIG. **1** illustrates the thermodynamic species balance for the oxidation of SO_2 to SO_3 and FIG. **2** illustrates the thermodynamic balance for the NO to NO_2 couple, both at 1 bar pressure and with a starting composition of 1 mole of NO and SO_2 and 1 mole of O_2. FIG. **1** shows that for the oxidation of SO_2 to SO_3, equation 10, the equilibrium lies far to the left with SO_2 the preferred species at temperatures below about 750° C. and SO_3 the preferred species above 750° C. The oxidation of SO_2 to SO_3 is highly exothermic and the decomposition of SO_3 into SO_2 and O_2 is highly endothermic. By employing a catalyst that can facilitate the oxidation of SO_2 to SO_3 (equation 10) or the decomposition of SO_3 into O_2 and SO_2 (equation 9), this interconversion can form a thermochemical cycle.

$$SO_3 \rightarrow SO_2+0.5\ O_2 \quad (9)$$

$$SO_2+0.5\ O_2 \rightarrow SO_3 \quad (10)$$

[0022] FIG. **3** shows a system **300** using thermochemical energy cycle of SO_2 and SO_3. SO_3 is decomposed in a reactor **301** to SO_2 and O_2 at a temperature of about 900° C. with heat input **302** since the process is endothermic. The SO_2 can then be circulated through a heat exchanger **303** to reduce the stream temperature to about 600° C. and then to a second reactor **304** which operates at a lower temperature where SO_3 is thermodynamically preferred species and where the SO_2 is oxidized to SO_3 with the release of heat **305**. To complete the cycle, the process stream from reactor **304** is circulated through heat exchanger **306** to raise the stream temperature to 900° C. and back to the SO_3 decomposition reactor **301**. This thermochemical cycle moves energy from one site where heat is adsorbed to a second site where energy is released.

[0023] This energy transfer cycle can also be an energy storage cycle by storing the high energy species, SO_2. FIG. **4** shows a system **400** similar to system **300** of FIG. **3** but offers energy storage in one embodiment of the invention. System **400** similarly uses reactor **301** to decompose SO_3 to SO_2 and O_2 to produce process stream **401** which passes through heat exchanger **303** to reduce the stream temperature to 600° C. at point **402** prior to entering reactor **304**. However, a portion of stream **402** can be split off to process stream **403** which then passes through heat exchanger **404** to drop the stream temperature to about 25° C. where a substantial portion of the SO_2 will change phase to a liquid and be collected in tank **405**. The actual temperature of this stream and the temperature of the liquid SO_3 will depend on the system pressure and the overall process design. The temperature could range from

−50 to 250° C. In addition, the O_2 in process stream **403** will pass through tank **405**, through line or process passage **406** to a vessel **407** containing an oxygen storage material which will adsorb or otherwise trap a substantial portion of the O_2. Such an oxygen storage material is sometimes referred to as an oxygen storage compound (OSC). In addition, **407** can refer interchangeable to the oxygen storage material and the vessel containing the oxygen storage material. It should be noted that line and process passage are used interchangeably. In this manner, energy input **302** can be stored by producing a large amount of SO_2 and O_2 that is stored in vessels **405** and **407**. Such an energy storage system must also have a source of SO_3 to convert to SO_2. This is also shown in FIG. **4** where liquid SO_3 is stored in vessel **408**. During this energy storage operation, the liquid SO_3 in vessel **408** is vaporized and heated to 600° C. in heat exchanger **409** and then passes through line **410** and line **411** to heat exchanger **306** to be heated to 800° C. and then through line **412** to decomposition reactor **301** to complete the cycle. The overall process for energy storage then consists of vaporizing liquid SO_3 from vessel **408**, heating this stream to 800° C., passing this process stream through reactor **301** to decompose the SO_3 to SO_2 and O_2 using a heat input source, then cooling this SO_2+O_2 stream to 25° C. where the SO_2 is condensed to be stored as a liquid and the O_2 is stored in an oxygen storage material. This energy storage process can have a high energy density since the high energy phase, SO_2 is stored as a liquid and the O_2 can be stored as an absorbed phase in an oxygen storage material at reasonable pressures without the need for high pressure gas storage.

[0024] This stored energy can then be utilized by vaporizing SO_2 in vessel **405**, desorbing O_2 from the oxygen storage material in vessel **407**, passing this stream through heat exchanger **415** and on to reactor **304** where heat is generated. The SO_3 is then passes through line **416** to heat exchanger **417** where it condenses to a liquid, then through line **418** to vessel **408** where the SO_3 is stored as a liquid.

[0025] It should be noted that in operation, this process can operate in a variety of modes. All of the heat input from solar or other heat sources can be converted to heat output by directing all of the SO_2 and O_2 to process stream **413**, through reactor **304** and then on through process stream **414** and **415** back to the decomposition reactor **301** where the cycle is completed. Another alternative is to split a portion of the SO_2 and O_2 to each of the process streams **403** and **413** so that some of the heat input is used to provide heat output and some of the energy input is stored as liquid SO_2. Of course the third operating mode is to have no heat input **302** and just produce heat output by using the stored SO_2 in vessel **405** flowing through reactor **304** to produce heat output.

[0026] System **400** in FIG. **4** would be useful as a solar energy storage system where solar energy can be collected and supplied to reactor **301**, this energy can be stored as liquid SO_2 in vessel **405** or used in reactor **304** to produce heat for any needed purpose. It can provide heat output when there is limited or no solar energy or other energy input by consuming stored SO_2 from vessel **405** to produce heat and then store the product SO_3 in vessel **408** for later use. Thus, this system can be used as a means to transfer energy from a solar collector to the point of use, store solar energy during periods when solar radiation exceeds current thermal needs, and produce thermal energy at the point of use from stored chemical energy when the solar radiation does not meet the thermal requirements.

[0027] To store energy using the process design shown in FIG. **4**, the operating pressure has to be sufficiently high to allow SO_2 and SO_3 to liquefy at reasonable temperatures. It is desirable to store the energy at ambient temperatures, for example below about 50° C. so that it can be stored for long periods without needing energy to maintain a low temperature or to thermally insulate or heat the storage vessels to maintain a higher temperature. If the process in FIG. **4** is operated at about 10 bar total pressure, then both SO_2 and SO_3 will condense to form a liquid if cooled below about 50° C. Pressures from 1 bar to above 100 bar could be used. In one embodiment, the operating pressure is in the range of 3 to 20 bar. In another embodiment, the operating pressure is in the range of 5 to 15 bar.

[0028] Reactors **301** and **304** may be thermal reactors or catalytic reactors. To obtain a fast rate of conversion from the input species to the output species, a catalyst may be used. Catalyst for the decomposition of SO_3 to SO_2 and O_2 and for the oxidation of SO_2 and O_2 to SO_3 are well known in the art and are discussed elsewhere in this specification. The temperature of operation of reactor **301** will depend on the level of conversion desired and on other process variables such as total pressure, partial pressure of O_2 and the temperature of the storage vessels **405** and **408**. At 10 bar pressure, approximately 80% conversion of SO_3 to SO_2 can be obtained at about 1000° C. If the oxygen partial pressure is reduced, then the temperature for 80% conversion will decrease. The operating temperature of reactor **301** is in the range of 600 to 1200° C. In one embodiment, the operating temperature is in the range of 700 to 1000° C. In another embodiment, the operating temperature is in the range of 800 to 1000° C. Similarly, the operating temperature of reactor **304** is in the range of 300 to 800° C. In one embodiment, the operating temperature is in the range of 500 to 700° C. In another embodiment, the operating temperature is in the range of 500 to 600° C.

Operation at Reduced Oxygen Partial Pressures

[0029] At 10 bar pressure with excess O_2 in the circulating streams, reactor **301** must operate at quite high temperatures to obtain a high level of conversion from SO_3 to SO_2. A high operating temperature may not be desirable for thermal solar systems since this would reduce efficiency and increase cost. One strategy to reduce the temperature of reactor **301** is to decrease the oxygen concentration. FIG. **5** shows the equilibrium fraction of sulfur species versus O_2 partial pressure at several temperatures and at 10 bar total pressure in one embodiment of the invention. At 800° C., if the O_2 partial pressure is below 0.25 bar, then the SO_2 fraction will be >70%. If the O_2 partial pressure can be reduced below 0.1 bar, then the SO_2 fraction could be greater than 80%. Similarly, at 700° C., the SO_2 fraction can be increased substantially if the O_2 partial pressure is reduced. By operating the process at lower O_2 partial pressure, the equilibrium conversion of SO_3 to SO_2 would be much higher. This could be achieved by operating the process with lower average O_2 pressure. A lower O_2 partial pressure could be accomplished by the choice of the oxygen storage material in vessel **407** or the operating temperature of this oxygen storage material. The actual magnitude of the O_2 partial pressure would be given by a tradeoff between the optimal pressure for the decomposition reaction, equation 10, in reactor **301** and the oxidation of SO_2, equation 9, in reactor **304**. A lower O_2 partial pressure will drive equation 10 and allow reactor **301** to operate at a reasonable temperature, say 700 to 800° C. A higher O_2 partial pressure will drive equation 10 to the right producing more SO_3 so the actual choice of O_2 partial pressure is a trade off between the needs of the two processes shown in equation 9 and 10. The main driver for the selection of the O_2 partial pressure will probably be equation 9, the decomposition of SO_3 to SO_2. The partial pressure of O_2 for system **300** or **400** would be in the range of 0.01 to 3 bar. In one embodiment, the partial pressure of O_2 for system **300** or **400** is in the range of 0.01 to 1.5 bar. In another embodiment, the partial pressure of O_2 is in the range of 0.01 to 0.75 bar.

[0030] The O_2 partial pressure could be controlled by controlling the temperature of the oxygen storage material **407**. This vessel containing oxygen storage material could be placed upstream of heat exchanger **404** to operate at 600° C. or heat exchanger **404** could be divided into several sections, the first section reducing the temperature of stream **403** to some intermediate temperature for oxygen storage material **407** placed in this location downstream of this first heat exchanger section. A second heat exchanger section would then reduce the temperature of this process stream to the temperature required to liquefy SO_2 for storage in vessel **405**. Oxygen storage material containing vessel **407** could also be placed in other locations in the process loop. For example it could be placed just downstream of reactor **301** in line **401** for operation at very high temperature. Alternatively, the oxygen storage material **407** could be divided into several vessels and placed in different locations to control the O_2 partial pressure to different levels in different parts of the process stream.

Oxygen Storage Materials

[0031] The oxygen storage materials used in system **400** will depend on the specific system design and operating conditions. Metal oxides and peroxides offer one type of oxygen storage material. BaO and BaO_2 is one example. At about 825° C., BaO_2 would have an O_2 partial pressure of about 1 bar. Lower temperatures would provide lower equilibrium O_2 partial pressures. Cerium oxides, manganese oxides, cerium and palladium oxides and mixed oxides can also provide embodiments of oxygen storage materials. One embodiment of a mixed oxide O_2 storage material is the mixed oxide $REBaCo_4O_{7+}$ as described by Motohashi et. al. (Materials Science and Engineering B 148 (2008) 196-198) where this material can store up to 3% of the oxygen storage material's weight as oxygen in the temperature range of 200 to 400° C. RE is one of the rare earth elements, in particular Y, Dy, Yb, and Lu (elements of the periodic table).

Electrochemical Control of O_2 Partial Pressure

[0032] The storage of oxygen is a critical aspect of the inventive process since storage as a gas would not be cost effective since it would require very large vessels or compression to high pressures which would consume energy and reduce efficiency. A significant observation is that the O_2 does not have to be stored within the process but can be removed from the process as excess SO_2 is generated and stored in vessel **405** and then added back to the process when the SO_2 is oxidized. FIG. **6** shows a system **600** similar to system **400** of FIG. **4** but replaces the oxygen storage material **407** with single or multiple electrochemical cells or electrochemical oxygen pumps in one embodiment of the invention. Electrochemical oxygen pump and electrochemical oxygen cell are used interchangeably in this disclosure. In system **600**, electrochemical pumps **601** and **602** replace the oxygen storage material vessel **407**. These electrochemical pumps function as O_2 pumps. Cell **601** pumps O_2 out of the process when excess SO_3 is decomposed to SO_2 and O_2 moving the O_2 to an air purge stream and into the atmosphere. Cell **602** pumps O_2 into the process when the SO_2 is vaporized and is to be oxidized to SO_3 to generate heat. In this case, the electrochemical cell **602** pumps O_2 from the air purge stream into the process. FIG. **7** is a schematic diagram of such an electrochemical cell **700** in one embodiment of the invention. In FIG. **7**, electrochemical pump **700** operates in the mode required for oxygen removal pump **601** of FIG. **6**. SO_2 and O_2 pass through channel **701**. Electrode **702** dissociates the O_2 into oxygen ions, O^{2-} and electrons, the oxygen ions are then transported through electrolyte **703** to the opposite electrode **704**. At electrode **704** the oxygen ions are recombined with electrons to produce O_2 which is then extruded into the gas phase, a flowing purge stream of air in channel **705**. The electrons travel from electrode **702** through conductors **706** and **708** to electrode **704**. The pumping of O_2 from channel **701** to channel **705** is driven by the applied voltage, V, **707**. The applied voltage controls the O_2 pumping rate and the oxygen partial pressure that can be achieved in channel **701**. By increasing the voltage, the O_2 partial pressure can be driven to a very low value if desired and the pumping rate can be very high. For a given voltage, the pumping rate and the ultimate O_2 partial pressure can be also be influenced by the O_2 partial pressure in the air purge channel **705**. If the purge air is at 1 bar pressure, then the O_2 partial pressure would be approximately 0.21 bar. If a vacuum is applied to channel **705**, then the O_2 partial pressure can be reduced to any desired value. For example, by operating the air purge channel **705** at 0.25 bar, the effective O_2 partial pressure would be 0.05 bar in the process flow stream.

[0033] The electrochemical pump **602** in FIG. **6** is essentially similar to pump **700** shown in FIG. **7** except that the O_2 flow is in the direction to move O_2 from the air purge stream to the process flow stream, pumping O_2 into the process flow stream. The current flow would be in the opposite direction and the effect of the O_2 partial pressure on the air purge side would be opposite. A higher air pressure in the air purge channel **705** would help drive the O_2 into the process flow stream and require a lower pumping voltage.

[0034] The use of an electrochemical pump to move O_2 from air into the process and from the process out to air would eliminate the need to store O_2 in the process equipment and reduce the overall equipment size for energy storage. The only stored chemical is the liquid SO_2. Ambient air becomes the source and sink for the required O_2 reactant. The design of the electrochemical oxygen pump can take many forms. A possible form is a zirconium oxide solid electrolyte cell such as that described in U.S. Pat. No. 5,378,345 and U.S. Pat. No. 4,877,506 which are incorporated into this application in their entirety. These cells use a stabilized zirconium oxide electrolyte that can transport oxygen ions and porous electrodes that act to dissociate O_2 into oxygen ions and recombine the oxygen ions to form O_2 and also act as the electron conductor. A typical electrode material is a porous platinum layer. Other platinum group metals or mixtures of platinum group metals could be used.

[0035] An alternative embodiment using an electrochemical oxygen pump to remove oxygen from and add oxygen to the process stream would replace the ambient air purge at **601** and **602** of FIG. **6** with two vessels containing an oxygen storage material that would absorb and release the oxygen as the electrochemical pump removes it from or adds it to the process stream. This could provide an advantage if any SO_3 or SO_2 were to leak across the electrochemical cell or pump since it would be trapped within the vessels holding the oxygen storage material and would not be released to the ambient air. The oxygen storage material could be contained in two vessels, one for each electrochemical pump **601** and **602** or it could be a single vessel connected to both electrochemical pump **601** and **602**.

[0036] It should also be noted that while an electrochemical oxygen pump or cell is described herein, an alternative embodiment is to use an oxygen permeable membrane to selectively remove O_2 from the process stream to an external purge stream. Oxygen could also be added back using a similar oxygen permeable membrane. The driving force for movement of O_2 into the process stream or out of the process stream would be the O_2 partial pressure on the opposite side of the membrane. A high O_2 pressure or high air pressure would drive O_2 into the process and a low O_2 partial pressure or air pressure would drive O_2 out of the process.

Electrochemical SO_3 Decomposition Reactor

[0037] The decomposition of SO_3, equation 9, is limited by thermodynamics at the selected operating temperature. This is shown in FIG. **1** for a pressure of 1 bar as one embodiment of the invention. At the operating pressure of 5 to 15 bar, these curves would be shifted to the right and the equilibrium limited conversion to SO_2 can be low as shown in FIG. **5**. Reducing O_2 partial pressure allows a higher equilibrium conversion. One approach to reducing the O_2 partial pressure is to make the reactor **301** in FIG. **4** a combined O_2 cell to pump oxygen and SO_3 decomposition reactor. FIG. **8** shows such a reactor **800** that can be placed in the location occupied by reactor **301** in FIG. **4** in one embodiment of the invention. The SO_3 enters reactor through channel **801**. One wall of the reactor is formed by the electrode **802** that is coated with a catalyst layer **803**. The SO_3 reacts on the catalyst **803** to decompose into SO_2 and O_2. The O_2 diffuses to electrode **802**, is dissociated into oxygen ions at electrode **802**, is pumped through electrolyte **807** to the opposite electrode **804** where it is recombined to form O_2 and passes into channel **805** where it is swept away in the flowing air purge stream. By controlling voltage **806**, the O_2 partial pressure at the interface between the catalyst layer **803** and electrode **802** can be controlled to the desired value. The O_2 partial pressure in the catalyst layer could be lowered to a very low value and as shown in FIG. **5**, the equilibrium SO_2 conversion can be very high. This could also allow the reactor **800** to operate at a lower temperature ranging from 650 to 800° C.

Direct Electrochemical Conversion of SO_2 to Electrical Power

[0038] The process shown in FIG. **6** produces energy by oxidation of the stored SO_2 oxidation with O_2 to produce heat in reactor **604**. This heat can then be used to produce steam which would power a steam turbine to produce electricity. Direct conversion of the SO_2 into electrical energy would be more desirable and could be substantially more efficient. FIG. **9** shows a system **900** with direction conversion of SO_2 into electrical energy in one embodiment of the invention. This device can be referred to as an SO_2 fuel cell or an SO_2 electrochemical generator. For the anode of the SO_2 fuel cell, SO_2 enters channel **901** and reacts on electrode **902** with oxygen ion, O^{2-}, to form SO_3 and 2 electrons, $2e^-$. The O^{2-} is supplied through the electrode **902** from electrolyte **903**. For the cathode of this fuel cell, O_2 enters channel **904** and reacts at electrode **905** to receive 2 electrons per O atom and form O^{-2} at the electrode. The electrons flow from the anode **902** through electric line **906** to the load **907** and electric line **908** to the cathode **905**. The electrolyte **903** must transport O^{2-} from the cathode **905** to the anode **902**. In one embodiment of the invention, this is done by the reactions shown in FIG. **9**. At the cathode, O^{2-} reacts with $2H^+$ in the electrolyte to form H_2O. The H^+ is transported from the anode and H_2O is transported to the anode through the electrolyte **903**. At the anode, H_2O dissociates to $2H^+$ and O^{2-} thus supplying the H^+ for transport to the cathode and oxygen ion, O^{2-}, for the anode reaction to oxidize SO_2 to SO_3. An appropriate electrolyte for the SO_2 fuel cell of FIG. **9** would be sulfuric acid, H_2SO_4 or any electrolyte that transports H^+ and H_2O. The sulfuric acid could range from a dilute sulfuric acid to a nearly 100% concentrated sulfuric acid. The electrolyte could also be formed of a membrane or other porous material that is impregnated or filled with sulfuric acid. Alternatively the electrolyte could be a membrane or porous medium with the ability to transport H_2O and H^+. One such embodiment would be Nafion, a sulfonated tetrafluoroethylene copolymer. The transport of H^+ is equivalent to the transport of hydronium ion, H_3O^+. The overall electrochemical process shown in FIG. **9**, identical to reaction equation 10, has a standard Gibbs free energy of reaction of −70.9 kJ/mol at 25° C. Using the Nernst equation, this equates to a standard cell potential of +0.37 volts. The operating temperature of this cell in one embodiment of the invention can vary over a wide range from 0° C. to 300° C. A lower temperature will provide a higher driving force and a larger cell voltage. In one embodiment, the operating temperature is in the range of 25° C. to 200° C.

[0039] An alternative embodiment of the invention to the process shown in FIG. **9** where the electrolyte transports protons, H^+, and water, H_2O, the electrolyte could transport only protons and use water supplied with the SO_2 flow in channel **901**. In this case the reaction of water to form H^+ and O^{2-}, $H_2O \rightarrow 2H^+ + O^{2-}$, would occur on the electrode in channel **901** using water supplied in the stream flowing through channel **901**.

Thermal Solar Energy Storage System

[0040] The process and system design described above can be used as system for the capture and storage of solar energy. FIG. **10** illustrates one such of a system **1000** in one embodiment of the invention. In system **1000**, solar energy **1001** is captured in the collector **1002** as high temperature heat. SO_3 flows into collector **1002** through stream **1003**. Collector **1002** is filled with a catalyst for the conversion of SO_3 to SO_2 and O_2 and captures the thermal energy from solar radiation. The SO_2 and O_2 flow through process stream **1004** and then is split into section **1005** or to process stream **1006**. In section **1005**, the SO_2 and O_2 are stored for use during low solar energy periods. The SO_2 and O_2 that flow through process stream **1006** flow into reactor **1007** where the SO_2 and O_2 react to produce SO_3 and release thermal energy, heat. Reactor **1007** could be a heat exchange reactor such as a tube and shell reactor containing a catalyst for the conversion of SO_2 and O_2 into SO_3 and heat. Water or low temperature steam could flow into reactor through line **1008** to produce high temperature steam that exits reactor **1007** through line **1009** to steam turbine **1010** where the energy is extracted to drive electric generator **1011** to produce electric power output

1012. The steam or condensed water flows out of the steam turbine **1010** to storage vessel **1013** and to circulation pump **1014** and back to reactor **1007**. The SO_2 and O_2 storage section **1005** and the SO_3 storage section **1015** are not shown in detail as they can take any of the forms described in other parts of this specification and other forms that can be implemented by those familiar with the art.

[0041] The system shown in FIG. **10** is one example of a solar energy generation system using the aspects described in this specification. This system uses the solar energy to generate high temperature steam that is used to drive a steam turbine to produce electrical power. This system is only described for illustration purposes and the system can take many forms. In other embodiments of the invention, the solar energy collection components can be a central tower structure with surrounding solar reflectors that concentrate the solar energy on the central energy collector. An alternative embodiment is a parabolic trough collector that concentrates the solar energy on a linear tube reactor. A third embodiment would be a circular parabolic mirror that concentrates the solar energy on a central thermal collector. The SO_2 and O_2 storage system could be a system that liquefies the SO_2 and stores the SO_2 as a liquid at temperatures near ambient. The O_2 can be stored by absorption on an oxygen storage material or by adsorption on the surface of an adsorbent. The gaseous O_2 can be compressed at high pressure to store the O_2 in a pressure vessel. An alternative embodiment is to use an oxygen transfer membrane to extract O_2 from the process stream and move it into the surrounding air. Such a membrane could take the form of an electrochemical cell or pump that transfers the O_2 as oxide ions such as stabilized ZrO_2 membranes operating at high temperatures. The electrical power generation process can also take many forms. It can take the form of a thermal process wherein the oxidation of SO_2 to SO_3 produces heat that is used to produce steam that then drives a turbine and electric generator as shown in FIG. **10**. Alternatively the heat from the decomposition reactor can be used to heat a heat transfer fluid which is then used to generate steam in a boiler or to heat other fluid to drive a turbine or other engine to produce electrical power. The engine can take the form of a turbine, reciprocating engine, sterling engine etc.

Direct Electrochemical Solar Energy System

[0042] FIG. **11** illustrates an alternative solar energy system in one embodiment of the invention. System **1100** is similar to system **1000** in FIG. **10** but with a modification in the method of electric power generation from the oxidation of SO_2 to SO_3. The SO_2 generated in solar energy collection reactor **1101** will flow to SO_2 storage system **1102** or to the O_2 removal section **1103** and electrochemical generator **1104** which produces an electrical power output **1110**. Electrochemical generator **1104** could be similar to that described in FIG. **9**. The SO_2 stream flows to the anode side **1105** of the cell and an oxygen containing stream such as air flows to the cathode side of the cell **1106**. The SO_3 oxidation product from the electrochemical generator **1104** is either recycled to the solar energy collector **1101** or stored in SO_3 storage section **1107** where the SO_3 is stored for use during low solar energy periods. The cathode side **1106** of the electrochemical generator **1104** can be supplied with oxygen by a purge air stream using blower **1109**. Other oxidants could be used. The O_2 removal section **1103** could be similar to the oxygen storage material or the electrochemical pump described elsewhere in the specification and shown in FIG. **7**. Alternatively, it could be a membrane based system that uses oxygen partial pressure difference to extract O_2 from stream **1111**. The level of oxygen removal required will depend on the sensitivity of the anode **1105** to O_2. In general, the O_2 level does not have to be extremely low since any oxygen present at the anode will probably just react directly with the SO_2 to form SO_3 thus bypassing the electrochemical conversion and lead to a lower electrical generation efficiency. It is not expected that low levels of O_2 at the anode will inhibit the anode electrochemical reaction.

[0043] In one embodiment of this invention, catalysts for the oxidation of SO_2 to SO_3 would be platinum, palladium or other platinum group metals supported on a oxide or other high surface area support such as aluminum oxide, silicon oxide, titanium oxide, zirconium oxide or mixtures of these oxides with or without additional additives. Vanadium is also a preferred catalyst, again supported on oxides such as described for the platinum group metal catalysts. An optimal catalyst used commercially for this reaction is vanadium oxide supported on silica support containing potassium, sodium and aluminum oxide additives.

[0044] The decomposition of SO_3 to SO_2 and O_2 would be done on similar catalysts as for the oxidation as described above.

[0045] Anode materials for the electrochemical generator described in FIG. **9** would be similar to the catalysts used for the catalytic oxidation of SO_2 and described above. A preferred catalyst would be a porous platinum layer since this would act as an electron conducting layer as well as a catalyst for the oxidation of SO_2 using oxide ions transported by the electrolyte.

[0046] Cathode catalysts for the electrochemical generator of FIG. **9** would be similar to those described for the hydrogen oxygen fuel cell and are well described in the literature and well known.

Alternative System Design

[0047] One alternative embodiment is shown in FIG. **12**. In this embodiment, system **1200** shows a solar tower or parabolic trough solar collector **1201** located proximate to a counter current heat exchanger **1202** that reduces the process flow streams **1203** and **1204** to a temperature near ambient temperature so that the process streams connecting the solar collectors to the generating plant will be near ambient temperature. This provides the advantage of reducing cost and complexity of the piping system by eliminating the need for high temperature insulation and high temperature materials. The counter current heat exchanger **1202** can be located at each solar collector unit or at groups of closely spaced solar collectors depending on collection system design and cost requirements. Heat exchanger **1202** could be combined with solar collector **1201** as a single unit or an integrated unit.

[0048] Stream **1204** from the solar collector field will then either split a portion of the flow to the SO_2 and O_2 storage section **1205** or to process stream **1206** and then to heat exchanger **1207**. Heat exchanger **1207** could also be a counter current heat exchanger which would increase the temperature of the process stream **1206** to the required temperature for the SO_2 oxidation reactor **1208** where the chemical energy is converted to heat. This temperature of reactor **1208** would be in the range of 350 to 600° C. The SO_3 leaving the SO_2 oxidation reactor **1208** flows through process stream **1210** back to heat exchanger **1207** where the temperature is adjusted to near ambient temperature for SO_3 storage or return to the solar collector field through process stream **1203**.

[0049] In one embodiment steam generator section **1209** could consist of a steam turbine and an electric power generator. In another embodiment the heat release and electric power generating section shown as reactor **1208** and steam generator **1209** could be replaced with the direct electrochemical generator **1104** shown in FIG. **11**.

[0050] In other embodiments, the heat exchangers shown in FIG. **12** could be co-current heat exchangers or combinations of heat exchangers. Also, the heat exchangers could be separated into several heat exchangers to provide an intermediate temperature for SO_2, O_2 and SO_3 storage or for other purposes.

[0051] Various other adaptations and combinations of features of the embodiments disclosed are within the scope of the invention. Numerous embodiments are encompassed by the following claims.

1. A thermochemical system that transports energy from a first location to a second location where the energy is used to generate steam for a steam turbine, comprising:

a thermal source providing a first thermal energy;

a first reactor at the first location converting the first thermal energy to chemical energy by decomposing SO_3 into SO_2 and O_2;

a second reactor at the second location converting the chemical energy to a second thermal energy by oxidizing SO_2 with O_2 to produce SO_3, the second reactor evaporating water into the steam for the steam turbine;

liquid SO_2 storage of; and

liquid SO_3 storage of;

wherein an output of the first reactor is coupled to both an input of the second reactor and the liquid SO_2 storage, and an output of the sec reactor is coupled to both an input of the first reactor and the liquid SO_3 storage;

wherein a flow split of SO_2 and O_2 from the first reactor to the second reactor and the liquid SO_2 storage is variable, and a flow split of SO_3 from the second reactor to the first reactor and the liquid SO_3 storage is variable.

2. The system of claim **1** wherein the thermal source is a solar concentrator that focuses sunlight on a receiver to produce a temperature high enough to decompose SO_3 into SO_2.

3. The system of claim **1** wherein at least one of the first reactor and the second reactor comprises a catalyst for converting SO_3 into SO_2 and O_2 or SO_2 and O_2 to produce SO_3.

4. The system of claim **1** wherein the first reactor converts SO_3 into SO_2 and O_2 at a temperature in the range of 600 to 1200° C.

5. The system of claim **1** wherein the second reactor converts SO_2 and O_2 to produce SO_3 at a temperature below about 800° C.

6. The system of claim **1** further comprising an oxygen storage material that chemically binds and stores a substantial portion of O_2 produced by the first reactor converting SO_3 into SO_2 and O_2.

7. The system of claim **1** wherein pressures in the first reactor and the second reactor are maintained in the range of 1 bar to 100 bar.

8. The system of claim **7** wherein the pressures are maintained in the range of 5 to 15 bar.

9. The system of claim **6** wherein at least one of the oxygen storage material and a temperature of the oxygen storage material is chosen to adsorb and release O_2 at an O_2 partial pressure in the range of 0.01 to 3 bar.

10. The system of claim **1**, further comprising:

a first electrochemical cell being located downstream of the first reactor, the first electrochemical cell being exposed on one side to a process stream and on the other side to the ambient air, the first electrochemical cell removing O_2 formed by the first reactor from the process stream and pumps it into the ambient air; and

a second electrochemical cell being located upstream of the second reactor, the second electrochemical cell begin exposed on one side to the process stream and on the other side to the ambient air, the second electrochemical cell pumping O_2 from the ambient air into the process stream to be used by the second reactor.

11. The system of claim **1**, further comprising:

a first electrochemical cell being located downstream of the first reactor, the first electrochemical cell being exposed on one side to a process stream and on the other side to a vessel containing an oxygen storage material; and

a second electrochemical cell being located upstream of the second reactor, the second electrochemical cell being exposed on one side to the process stream and on the other side to an other vessel containing an other oxygen storage material wherein:

the first electrochemical cell removes O_2 formed decomposing SO_3 into SO_2 and O_2 from the process stream and pumps it into the vessel containing the oxygen storage material;

the second electrochemical cell pumps O_2 from the other vessel containing the other oxygen storage material into the process stream to be used in oxidizing SO_2 and O_2 to produce SO_3.

12. The system of claim **1** wherein the first reactor includes an electrochemical cell that removes oxygen from the first reactor to allow a higher conversion of SO_3 to SO_2.

13. The system of claim **1**, wherein the second reactor includes an electrochemical cell that produces electrical power from the conversion of SO_2 and O_2 to produce SO_3.

14. A method of transporting energy from a first location to a second location where the energy is used to generate steam for a steam turbine, the method comprising:

converting the thermal energy at the first location to chemical energy in a first reactor by decomposing SO_3 into SO_2 and O_2;

converting the chemical energy to one of thermal energy or electrical energy in a second reactor at the second location by oxidizing SO_2 with O_2 to produce SO_3;

using stored SO_3 liquid for the first reactor and storing a portion of SO_2 from the first reactor as a liquid when more energy is available at the first location then is required at the second location; and

using stored SO_2 liquid for the second reactor and storing SO_3 liquid from the second reactor when more energy is needed at the second location then is available at the first location;

wherein using stored SO_3, storing a portion of the SO_2, using stored SO_2 liquid, and sorting SO_3 liquid comprise:

controlling a flow split of SO_2 and O_2 from the first reactor to the second reactor and a liquid SO_2 storage; and

controlling a flow split of SO_3 from the second reactor to the first reactor and a liquid SO_3 storage.

15. The method of claim **14**, further comprising using a solar concentrator to focus sunlight on a receiver to produce a temperature high enough to decompose SO_3 into SO_2.

16. The method of claim **14** wherein at least one of the first reactor and the second reactor comprise a catalyst for converting SO_3 into SO_2 and O_2 or SO_2 and O_2 to produce SO_3.

17. The method of claim **14**, further comprising operating first reactor at a temperature in the range of 600 to 1200° C.

18. The method of claim **14**, further comprising operating second reactor at a temperature below about 800° C.

19. The method of claim **14**, further comprising chemically binding at least a portion of O_2 produced in the first reactor by the decomposition of SO_3 into SO_2 and O_2 in an oxygen storage material.

20. The method of claim **14**, further comprising maintaining pressures in the first reactor and the second rector are in the range of 1 to 100 bar.

21. The method of claim **20** wherein the pressures are maintained in the range of 5 to 15 bar.

22. The method of claim **14**, further comprising:

pumping, with a first electrochemical cell, O_2 produced in the first reactor by the decomposition of SO_3 into SO_2 and O_2 to one of ambient air and a vessel containing an oxygen storage material;

pumping, with a second electrochemical cell, O_2 from one of the ambient air and another vessel containing another oxygen storage material to react with SO_2 in the second reactor to produce SO_3.

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