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(71) Applicant: **BATTELLE MEMORIAL INSTITUTE** [US/US]; P.O. Box 999, K1-53, Richland, Washington 99352 (US).

(72) Inventors: **RONNEBRO, Ewa Carin Ellinor**; 4208 Norma Loop, West Richland, Washington 99353 (US). **WHYATT, Greg A.**; 3401 Equestrian Drive, West Richland, Washington 99353 (US). **POWELL, Michael R.**; 2718 Kyle Road, Kennewick, Washington 99338 (US).

(74) Agent: **MATHESON, James D.**; P.O. Box 999, K1-53, Richland, Washington 99352 (US).

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(54) Title: REVERSIBLE METAL HYDRIDE THERMAL ENERGY STORAGE SYSTEMS, DEVICES, AND PROCESS FOR HIGH TEMPERATURE APPLICATIONS

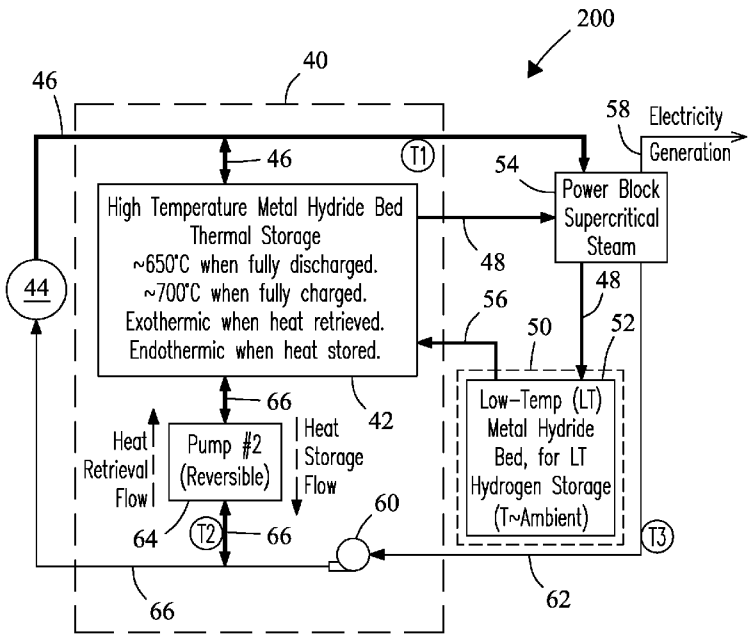


FIG. 3

(57) Abstract: High-temperature thermal energy storage and retrieval systems, devices, and processes are described that reversibly store high temperature heat in metal hydride beds composed of titanium containing metals or transition metal alloy that reversibly form metal hydrides at high temperatures above about 600°C and at low temperatures at or below 100°C. The present invention provides exergetic efficiency up to 96% or better.

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REVERSIBLE METAL HYDRIDE THERMAL ENERGY STORAGE SYSTEMS, DEVICES, AND PROCESS FOR HIGH TEMPERATURE APPLICATIONS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This is a Non-Provisional Application that claims priority from U.S. Provisional Application No.: 61/769,628 filed 26 February 2013 and U.S. Application No.: 14/189,942 filed 25 February 2014.

STATEMENT REGARDING RIGHTS TO INVENTION MADE UNDER FEDERALLY-SPONSORED RESEARCH AND DEVELOPMENT

[0002] This invention was made with Government support under Contract DE-AC05-76RLO1830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

BACKGROUND OF THE INVENTION

[0003] Currently, no commercial high-temperature thermal energy storage systems (TES) are available that operate above 600 °C for applications such as power generation. Some conventional thermal energy storage (TES) systems employ molten salts reported to operate at mid-level temperatures up to 500 °C. However, energy density for these systems is only about 153 kJ/kg. Thus, large

quantities of salts are required to operate. Medium temperature systems that employ magnesium hydride (MgH_2) are reported to operate at temperatures between 250 °C and 500 °C and hydrogen pressures between 20 bar (2.0 MPa) and 40 bar (4.0 MPa). However, at higher temperatures, magnesium hydride requires significantly increased pressures. For example, at a temperature of 520 °C, a pressure of 132 bar (13.2 MPa) is required. Elevated pressures significantly increase costs as containers must withstand the added pressures. Further, at a pressure of ~250 bar (25 MPa), storage as a hydride is not possible above a temperature of 566 °C due to a problematic phase transition from Mg + $\beta(MgH_2)$ to a mixture of Mg and H_2. Another system based on molten CaH_2 is reported that operates continuously at temperatures between 1000 °C and 1200 °C. However, to withstand these temperatures, reactor tanks must be constructed of costly nickel-based alloys. Accordingly, new systems, devices, and processes are needed that increase energy density, exergetics, and provide suitable commercial operation costs. The present invention addresses these needs.

SUMMARY OF THE INVENTION

[0004] The present invention includes a Reversible Metal Hydride (RMH) Thermochemical (RMHT) energy storage and retrieval system. The system may include at least one HT reservoir and at least one LT reservoir. The HT and LT reservoirs may each include a metal hydride bed. The HT metal hydride bed may include a titanium-containing metal in the presence of hydrogen gas that reversibly forms a metal hydride at a temperature at or above about 600 °C. The LT metal hydride bed may include a transition metal alloy that reversibly forms a metal hydride in the presence of hydrogen gas at a temperature at or below about 100 °C. The

system may include a hydrogen transfer device that is configured to transfer hydrogen gas between the metal hydride bed of the HT reservoir and the metal hydride bed of the LT reservoir or vice versa that maintains an ambient or near-ambient hydrogen pressure in the respective reservoirs during a thermal cycle operation.

[0005] The present invention may also include a reversible thermal energy storage and retrieval device. The device may a container constructed of a corrosion-resistant metal or metal alloy with an internal compartment that includes a selected density of adjacent conducting metal disks. The metal disks may be positioned a selected distance apart and span at least a portion of the length or internal volume of the internal compartment. The separation distance between the metal disks provides a gap or space that may receive a titanium-containing metal or a transition metal alloy. The metal or metal alloy with introduced into the container charges the metal hydride bed for operation and reversibly forms a metal hydride during operation at a temperature at or above 600 °C or at or below 100 °C. The metal disks enhance thermal conductivity through the metal hydride in the metal hydride bed in at least a radial direction during a thermal cycle. The separation distance between the conducting metal disks may be between about 0.25 inches (0.64 cm) and about 12 inches (30.5 cm).

[0006] The present invention may also include a process for performing reversible thermal energy storage and retrieval. The process may include delivering heat from a high-temperature heat source into a HT metal hydride bed of a HT reservoir at a temperature of at least about 600 °C to release hydrogen from the metal hydride in the metal hydride bed. Released hydrogen may be delivered into the metal hydride bed of the LT reservoir for absorption therein that stores the high-temperature heat. When heat is required, LT reservoir may release hydrogen

from the LT metal hydride bed within the LT reservoir, which may be delivered back to the HT metal hydride bed within the HT reservoir. When absorbed in the HT reservoir, hydrogen releases heat that can be sent to a power block to drive a Rankine stream cycle that produces electricity.

[0007] The process may include matching the hydrogen flow rate between the HT reservoir and the LT reservoir during operation.

[0008] The process may include recovering high-temperature heat from the hydrogen gas released from the HT metal hydride bed in a recuperation system to recuperate the heat that may be used to preheat feed water into a Rankine steam cycle.

[0009] The process may include maintaining a hydrogen gas pressure within the metal hydride beds of the HT reservoir and the LT reservoir between about 0.1 MPa and about 1 MPa during operation.

[0010] The process may include introducing the titanium-containing metal or the transition metal-containing metal alloy into the metal hydride beds of the HT and LT reservoirs between adjacent conducting metal disks within the storage containers.

[0011] The metal hydride beds of the respective HT and LT reservoirs may include one or more storage containers with an internal compartment comprising a selected density of adjacent conducting metal disks that are positioned a selected distance apart. The conducting metal disks may span at least a portion of the length or internal volume of the internal compartment. The separation distance between the conducting metal disks may be filled with a titanium-containing metal or a transition metal alloy that reversibly form metal hydrides during thermal cycle operation. The metal disks enhance thermal conductivity in at least a radial direction through the metal hydride beds of the HT and LT reservoirs during a thermal cycle operation.

The density of conducting metal disks is between 2% and 10% of the volume of the HT or LT reservoir, respectively.

[0012] The gas transfer device may be a sintered porous metal conduit with an inner bore of a selected dimension positioned within the metal hydride beds configured to deliver hydrogen into the metal hydride bed for formation of the metal hydride or to recover hydrogen released from the metal hydride bed during operation. The gas transfer device may include a selected metal or metal alloy such as stainless steel. The gas transfer device may couple to conducting metal disks positioned within the metal hydride beds of the HT and LT reservoirs. The sintered porous conduit maintains a hydrogen gas pressure in the metal hydride beds of the HT and LT reservoirs between about 0.1 MPa and about 1 MPa during a thermal cycle operation.

[0013] The HT and LT reservoirs may each include a fluid transfer device configured to deliver a heat transfer fluid that delivers heat into or retrieves heat from the HT metal hydride bed and the LT metal hydride bed within respective reservoirs.

[0014] Heat transfer fluids for the HT bed may include sodium metal, lead-bismuth, and tin-antimony. Heat transfer fluids for the LT bed may include water, propylene glycol, ethylene glycol, or mixtures of these fluids.

[0015] The metal positioned within the HT metal hydride bed may include titanium metal and the metal alloy within the LT metal hydride bed may include one or more metals selected from: Ti, Fe, Ni, Mn, or combinations. The titanium-containing metal reversibly forms a titanium metal hydride at a high temperature between about 600 °C and about 800 °C. The transition metal alloy may be a titanium-containing metal alloy that reversibly forms a metal hydride at a low temperature between about 20 °C and about 100 °C. The titanium-containing metal

and transition metal alloy may be in the form of compressed powder disks in the one or more HT and LT reservoirs, respectively.

[0016] The HT and LT metal hydride beds of the HT reservoir and the LT reservoirs may further include a conducting metal foam with a density of open pores of at least about 8% by weight or at least about 10 pores per inch (20.5 pores per cm) into which the metal or transition metal alloy powder may be dispersed. The metal foam may be a copper metal foam or an aluminum metal foam.

[0017] The system may provide an energy density of at least about 750 kJ/kg and a volumetric energy density of at least about 3,000 kWh/m^3. The system may provide a heat flux of at least about 3,000 W/m^2 during operation. The system may provide an exergetic efficiency of up to about 95% or better. The system may include a recuperation system that recuperates sensible heat for steam generation.

[0018] Various advantages and novel features of the present invention are described herein and will become further readily apparent to those of ordinary skill in the art from the following detailed description. Additional advantages and novel features of the present invention will be set forth as follows and will be readily apparent from the descriptions and demonstrations set forth herein. As will be realized, the invention is capable of modification in various respects without departing from the invention. Accordingly, the drawings and description of the preferred embodiment set forth hereafter are to be regarded as illustrative in nature, and not as restrictive.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] **FIG. 1** shows a thermal energy storage (TES) and retrieval system of a bench-scale design according to one embodiment of the present invention.

[0020] **FIG. 2** shows a single metal hydride storage reservoir for one embodiment of the present invention.

[0021] **FIG. 3** shows a thermal energy storage (TES) and retrieval system of an industrial-scale design according to another embodiment of the present invention.

[0022] **FIG. 4** shows an exemplary metal hydride storage tank of one embodiment that includes one or more metal hydride storage reservoirs for high-temperature or low-temperature operation.

[0023] **FIG. 5** shows a single metal hydride storage reservoir of the present invention used in HT and LT storage reservoirs.

[0024] **FIGs. 6A-6B** show exemplary system configurations for recuperation of heat used to desorb hydrogen from the low temperature hydride bed during thermal cycling.

[0025] **FIG. 7** shows outer wall temperatures of the high-temperature and low-temperature metal hydride storage reservoirs obtained during thermal cycling.

[0026] **FIG. 8** shows model absorption and desorption curves obtained from an embodiment of the present invention.

[0027] **FIG. 9** shows experimental absorption and desorption curves obtained during thermal cycling of an embodiment of the present invention.

DETAILED DESCRIPTION

[0028] The present invention includes a new High Temperature Metal Hydride Thermochemical Storage system that stores high-temperature heat including, e.g., solar energy or waste heat for high-temperature energy production applications. The following description includes preferred embodiments of the invention that illustrate the best mode contemplated for carrying out the invention. It will be clear from this description of the invention that the invention is not limited to these illustrated embodiments but that the invention also includes a variety of modifications and embodiments thereto. Therefore the present description should be seen as illustrative and not limiting. Because the invention is susceptible of various modifications and alternative constructions, it should be understood that there is no intention to limit the invention to the specific form disclosed, but, on the contrary, the invention is to cover all modifications, alternative constructions, and equivalents falling within the spirit and scope of the invention as defined in the claims.

[0029] **FIG. 1** shows a cross-sectional view of a thermal energy storage (TES) and retrieval system **100** of a bench-scale design according to one embodiment of the present invention. System **100** may include a HT metal hydride storage tank (reservoir) **2** and a LT metal hydride storage tank (reservoir) **4**. HT storage reservoir **2** and LT storage reservoir **4** may be constructed of corrosion-resistant metals or metal alloys including, e.g., stainless steel alloys or Inconel alloys. In the instant embodiment, reservoirs **2** and **4** may be of a single-wall design with both an outer (exterior) surface and an inner surface. Dimensions of the HT reservoir and the LT reservoir are not limited. In the exemplary embodiment, HT reservoir **2** may include a diameter dimension of about 5 inches (12.7 cm) with an I.D. of 5.1 inches and O.D. of 5.6 inches, and a length of from 22.5 inches (57.9 cm) to 24 inches (60.9 cm). LT

reservoir **4** may include a diameter of 5 inches (12.7 cm) or less and a length of 22.5 inches (57.9 cm) to 24 inches (60.9 cm) or less. Dimensions are exemplary only, and other dimensions may be employed. No limitations are intended.

[0030] HT metal hydride storage reservoir **2** may include a HT metal hydride bed **6** composed of a metal foam **8** such as copper foam (e.g., DUOCEL® copper foam, ERG Materials and Aerospace Corp., Oakland, CA, USA) into which a selected titanium-containing metal **10** powder is introduced that reversibly absorbs hydrogen and forms a metal hydride at high temperatures. LT metal hydride storage reservoir **4** may include a LT metal hydride bed **12** composed of a metal foam **8** such as copper foam into which a selected transition metal or metal alloy **14** is introduced that reversibly absorbs hydrogen and forms a metal hydride at LT. In some embodiments, metal foam **8** may include a density of 8% with 10 pores per inch. Pores of foam **8** create interstitial spaces that may be filled with the metal hydride powder. Metal hydride powders loosely packed within the open cells (pores) of the copper foam enhances thermal conductivity or transfer of heat in both the radial and axial directions.

[0031] In some embodiments, titanium metal and transition metal alloy powders introduced into respective reservoirs may have a mesh size of about 60, but particle size is not intended to be limited.

[0032] Thermal energy is stored in the chemical bonds between the metal or metal alloy and hydrogen of the metal hydride in the selected reservoirs. Hydrogen acts as the energy carrier that may be released when needed. Thermal cycling between the HT metal hydride **10** formed in HT bed **6** of HT storage reservoir **2** and LT metal hydride **14** formed in LT bed **12** of LT storage reservoir **4** during operation are driven by gas-solid chemical reactions accompanied by heats of reaction that provide maximum exergetic efficiency.

[0033] Reservoirs may be operated at selected temperatures and ambient hydrogen pressures detailed herein. For example, the dual bed system of the present invention may employ selected metal hydrides that permit a wide range of temperatures and pressures to be used. In some embodiments, the high-temperature (HT) metal hydride may be a titanium-containing hydride. Titanium hydride is capable of forming hydrides over a range of [H : Ti] ratios from 0 to 2 or more. In the exemplary embodiment, heat storage may be accomplished with [H : Ti] ratios of from 1.0 to 1.5 where the phase diagram shows both β and δ phases present. Operation in this region allows a swing in hydrogen loading of about 1 wt% with only small changes in temperature at a constant pressure. In some embodiments, formation of the high-temperature (HT) metal hydride operates reversibly at temperatures exceeding 600 °C and pressures of at least about 1 bar (0.1 MPa). In some embodiments, formation of the HT metal hydride operates reversibly at a temperature of 640 °C and a hydrogen pressure of 1 bar (0.1 MPa). In some embodiments, HT metal hydride operates reversibly at a temperature from about 650 °C to about 700 °C. In some embodiments, formation of the HT metal hydride operates reversibly over temperatures in the range from about 450 °C to about 900 °C and is safe to handle at ambient temperature. Decomposition begins above 400 °C.

[0034] In some embodiments, the low-temperature metal hydride may be titanium iron hydride or another transition metal alloy. The LT metal hydride stores hydrogen until heat is needed. In some embodiments, formation of the LT metal hydride operates reversibly at a temperature between about 20 °C and about 100 °C.

[0035] HT reservoir **2** and LT storage reservoir **4** may each include a hydrogen gas transfer conduit **16** comprised of a sintered, porous metal positioned, e.g., at the centerline of HT metal hydride bed **6** of HT reservoir **2** and LT metal

hydride bed **12** of LT storage reservoir **4**. Transfer conduit **16** delivers and collects hydrogen gas to and from respective beds **6** and **12** during operation. In the exemplary embodiment, transfer conduit **16** includes a dimension (O.D.) of about ½ inch (1.3 cm), but dimensions are not intended to be limited. In the figure, transfer conduit **16** connects metal hydride bed **6** of HT storage reservoir **2** to metal hydride bed **12** of LT storage reservoir **4**. In some embodiments, HT reservoir **2** and LT storage reservoir **4** may be connected via interconnecting tubes with valves that connect the two metal hydride beds.

[0036] HT reservoir **2** and LT storage reservoir **4** may further include retention screens **18** or another retention device constructed of suitable materials including, e.g., metals or metal alloys with a mesh size sufficiently small to ensure retention of metal hydride particles. Retention screens **18** may be positioned at respective ends of HT reservoir **2** and LT storage reservoir **4** to retain metal hydride powders within the reservoirs. Screen mesh sizes are not limited. Screens **18** may be mounted to, e.g., metal support disks **20** that include a center perforation that permits mounting to hydrogen transfer conduit **16** at respective ends of metal hydride beds **6** and **12** within HT reservoir **2** and LT storage reservoir **4**.

[0037] HT reservoir **2** and LT storage reservoir **4** may include metal end caps **22** positioned at respective ends of the reservoirs that enclose the metal hydride beds **6** and **12** with their respective metal hydride powders **10** and **14** in the copper foam **8** within the respective reservoirs. During operation, metal end caps **12** may be filled with hydrogen gas at the reservoir operation pressure. Metal caps **22** may be secured to reservoirs **2** and **4** to form a leak tight seal. Hydrogen in end caps **22** is in communication with hydrogen in contact with or that otherwise surrounds metal hydride particles in hydride beds **6** and **12** of HT storage reservoir **2** and LT storage reservoir **4**, respectively.

[0038] HT reservoir **2** may be wrapped with a metal sheet **24** of a selected thickness composed of a conducting metal such as copper to increase thermal conductivity of the outside surface of HT reservoir **2** along the longitudinal direction.

[0039] An optional heater **26** may be employed to test performance of HT reservoir **2** for operation by coupling HT reservoir **2** to heater **26**. Heater **26** delivers heat into HT metal hydride bed **6** through the outer wall of HT reservoir **2** and tests release of hydrogen from the metal hydride bed. Heater **26** be constructed, e.g., of electrical heating wire [e.g., nickel-chrome (Ni-80/Cr-20), Pelican Wire Co., Naples, Fl, USA] that is insulated with, e.g., interlocking ceramic beads [e.g., salamander beads (0.2 in. x 0.094 in. x 0.21 in.), Mor Electric Heating Assoc., Inc., Comstock, MI, USA] that circumvolve the outer wall of HT reservoir **2** and form an insulation layer **28** around HT reservoir **2**. Insulation **30** composed of a selected high-quality material may also be positioned at respective ends of HT reservoir **2** around metal caps **22**. Need for insulation depends in part on the scale and components of the system. For industrial-scale systems and applications, for example, need for insulation decreases because heaters are not employed. In the instant embodiment, once testing is complete, heater **26** may be exchanged with an external heat source and heat transfer fluids described further herein. No limitations are intended.

[0040] For performance testing, LT reservoir **4** may also be introduced into an optional temperature-controlled water bath **32** or other temperature-controlled environment. Temperatures of reservoirs **2** and **4** in system **100** may be controlled with a thermal adjustment device **34** such as a temperature controller that maintains low temperatures in LT reservoir **4** and high temperatures in HT reservoir **2**. For industrial-scale operation, temperatures may be maintained with heat sources and recuperation systems described further herein. All system components as will be

selected by those of ordinary skill in the art in view of the disclosure are within the scope of the present invention. Thus, no limitations are intended.

[0041] In the instant embodiment, HT reservoir **2** and LT reservoir **4** each include a volumetric energy-storage density greater than 25 kWh/m^3. The present invention works at high exergetic efficiencies up to about 95% at operation temperatures between about 600 °C and about 800 °C.

[0042] **FIG. 2** shows a cut-away view of HT storage reservoir **2** of the system described previously in reference to **FIG. 1**. Reservoir **2** may include a metal hydride bed **6** filled with a metal foam (not shown). A metal hydride powder may be dispersed uniformly through the metal foam as described previously. Choice of metal powder configures the reservoir for either HT or LT operation. Reservoir **2** may include a hydrogen transfer conduit composed of a sintered metal positioned, e.g., at the center of the reservoir **2** to transfer and collect hydrogen gas released from or delivered to the HT metal hydride bed **6** of HT reservoir **2**. The LT reservoir (**FIG. 1**) may be constructed similarly with the introduction of a metal alloy into the metal hydride bed.

[0043] **FIG. 3** shows a reversible, high-temperature thermal energy storage (TES) system **200** of an industrial-scale thermochemical energy storage (TCES) design for high-temperature applications. System **200** may be integrated with, e.g., a solar-driven supercritical steam plant that provides electricity generation. System **200** may include one or more high-temperature (HT) storage reservoirs **40** and one or more low-temperature (LT) storage reservoirs **50**. Storage reservoirs and may each include metal hydride beds **42** and **52** constructed of one or more metal hydride storage containers detailed further in reference to **FIG. 5**. Metal hydride storage containers may be filled with selected metals or metal alloys during assembly that form metal hydrides during thermal cycling for storage and retrieval of energy.

[0044] In the figure, a high-temperature heat source **44** or receiver including, e.g., solar collectors (e.g., 100 kW 16-facet solar dishes and 50 kW thermal dishes), advanced composite glass mirrors, heat generators, and other high-temperature thermal generators and heat sources may be used to heat a high-temperature heat transfer fluid **46**. Exemplary HT heat transfer fluids include, but are not limited to, e.g., sodium metal, lead-bismuth, and tin-antimony. Heat transfer fluid **46** delivers heat into the metal hydride bed **42** which releases high-temperature hydrogen **48** from HT metal hydride bed **42**. HT storage containers (**FIG. 5**) discharge and collect hydrogen efficiently and effectively at high temperatures selected between about 600 °C and about 900 °C. High-temperature hydrogen **48** released from HT storage reservoir **40** may be delivered to and passed through power block **54** (e.g., a Rankine cycle steam power) where sensible heat carried by hydrogen **48** may be used to raise temperature that preheats feed water delivered into a steam cycle in power block **54** before hydrogen **48** is stored in LT storage reservoir **50**. "Sensible heat" is heat that causes a direct increase in temperature of an object when introduced and a direct decrease in temperature of an object when heat is removed. Preheating feed water can reduce the quantity of high-temperature heat required generate steam needed to drive turbines that generate power in power block **54**. Sensible heat is a low duty heat (< 10% of exergy) compared to high quality heat delivered by hot HTF **46**, which allows sensible heat to be effectively used. As an example, feed water may be preheated to a temperature of, e.g., 291 °C before going to a boiler where steam is generated at a temperature of, e.g., 593 °C. In this scenario, about 30% (1/3) of the heat duty may be used to preheat feed water, mostly from steam taken from turbines. Sensible heat delivered from high-temperature hydrogen **48** may be about 8% of the total exergy delivered to steam block **54**.

[0045] Hydrogen **48** passing from power block **54** may then be introduced into LT metal hydride bed **52** of LT storage reservoir **50**. The transition metal in LT hydride bed **52** absorbs hydrogen **48** forming a transition metal hydride that stores heat during. LT metal hydride storage containers (**FIG. 5**) that make up LT hydride bed **52** discharge and collect hydrogen efficiently and effectively at low temperatures between about 20 °C and about 100 °C. LT heat transfer fluids (not shown) circulated through LT bed **52** maintain the temperatures. LT heat transfer fluids include, but are not limited to, e.g., water, propylene glycol, ethylene glycol, mixtures of these fluids, and like media.

[0046] When heat is needed, hydrogen **56** released from LT hydride bed **52** may be delivered from LT storage reservoir **50** back to HT storage reservoir **40** where it is adsorbed back into HT hydride bed **42** in an exothermic reaction that releases heat during thermal cycling. Hydrogen **56** returned to HT hydride bed **42** may flow directly from LT bed **52**. The hydrogen flow stream may be controlled by valves (not shown). Reversible chemical reactions in LT reservoir **50** are similar to those in HT reservoir **40**.

[0047] HTF **46** may transfer heat between HT storage bed **42** and power block **54**. For example, HTF **46** may deliver high temperature heat at a first (e.g., **T1**) high temperature of, e.g., ~650 °C from HT hydride bed **42** to power block **54** where water may be heated into supercritical steam to drive power turbines (not shown) that generate power **58**. A pump **60** (e.g., an electrodynamic pump) may set the circulation rate for HTF **46** to bring the high temperature of HTF **46** to the first temperature. In exemplary tests, a high-temperature heat transfer fluid may deliver 30 kW of heat with a flow of about 36.5 liters per minute (lpm) or about ~9.7 gallons per minute (gpm). Pump **60** may also be set at a flow rate that provides a predetermined temperature drop for the HTF **46** that generates steam within power

block **54** at a desired rate. For example, if flow of heat into steam block **54** is less than the flow of heat from solar collector **44** into HT reservoir **40**, inlet temperature (**T1**) at steam block **54** may increase above the temperature of HT bed **42**. Maximum temperature drop for HTF **46** through power block **54** may be also selected such that the HTF is returned at a lowest operation temperature (e.g., **T3**) as a low-temperature flow **62** to solar collector **44** for reheating. In various embodiments, maximum temperature drop may be up to about 50 °C. At the upper limit, the HTF may be returned to solar collector **44** at a temperature (**T3**) of about 600 °C. However, no limitations are intended.

[0048] Heat transfer fluids may be selected that have selected freezing points suitable for high temperature operation. For example, when power is not produced, pump **60** may maintain a sufficient flow of HTF **46** to prevent freezing of the HTF. For example, liquid sodium as an HTF becomes a solid metal (i.e., freezes) below 98 °C.

[0049] When heat is neither stored nor retrieved, HTF **46** does not flow through HT storage reservoir **40**. When heat is stored, a pump **64** may be positioned to produce a flow of HTF **46** through HT storage reservoir **40** and then back to heat source **44**. Here, as liquid sodium HTF **46** passes through HT bed **42**, HTF **46** heats the reservoir walls of the one or more HT metal hydride containers (**FIG. 5**) to a temperature (e.g., **T2**) that is at or near the temperature of the HTF. Heat from HTF **46** passes through the walls of the containers into the metal hydride bed **42**.

[0050] The HTF leaves HT bed **42**, e.g., at the bottom of HT storage reservoir **40** as a flow **66** that is at the temperature (**T2**) near the wall temperature of the storage containers back to heat source **44**. Over the heat loading cycle, wall temperature of metal hydride bed **42** may increase, e.g., from about 660 °C to about 703 °C.

[0051] HTF **46** delivered from HT-bed storage reservoir **40** at temperature (**T1**), e.g., at the top of HT bed **42**, closely matches the wall temperature of the storage reservoir. Temperature drop of HTF **46** from HT-bed **42** may be too fast or too large to maintain the HTF temperature entering steam block **54**. In the figure, pump **64** (e.g., an electrodynamic pump) may pump HTF **46** in an upward direction to restore temperature of HTF **46** entering steam block **54**. Flow to solar collector **44** may then be reduced to allow HTF **46** to maintain a desired temperature at a lower flow rate. Then, pump **60** may be set to deliver steam through power block **54** at a desired rate and a predetermined temperature.

[0052] When there is no solar input, pump **60** may be set to provide HTF **46** at a flow rate that is, e.g., ~10% higher than the flow through pump **64** so that some flow is provided through solar collector **44** to prevent freezing of HTF **46**. Pump **64** may also drive primary circulation of HTF **46** through HT bed **42** to power block **54**.

[0053] Pump **64** may also be operated to produce a flow rate for HTF **46** that maintains HTF **46** at a temperature ~10 °C above the temperature of HT storage bed **42**. For example, hot HTF **46** may flow down through HT storage reservoir **40** to allow HTF **46** to give up heat to HT bed **42** in storage reservoir **40**. Temperature differentials affect pumping costs. For example, if temperature of HTF **46** is too close to the temperature of HT bed **42**, more energy may be required to pump the fluid compared with the quantity of heat stored on a per unit basis. As will be appreciated by those of ordinary skill in the art, temperature differentials selected between HTF **46** and HT storage bed **42** are not limited. Temperature differentials are selected that optimize performance. Thus, no limitations are intended.

[0054] Modeled results indicate temperature of HT storage bed **42** may fall from about 691 °C to about 653 °C during retrieval of heat, but is not intended to be limiting.

[0055] When there is a shortage of heat delivered from solar collector **44**, a portion of HTF **46** returning to solar collector **44** may be withdrawn and pumped through HT bed **42** to provide sufficient heat to HTF **46** to permit it to be joined with the flow of HTF **46** sent to power block **54**. As heat is extracted from HT bed **42**, hydrogen from LT bed **52** may be delivered back to HT bed **42** to maintain hydrogen pressure in both HT bed **42** and in LT bed **52**. Hydrogen does not flow to power block **54** when heat is being retrieved. Hydrogen flows to power block **54** only when heat is introduced to HT bed **42**.

[0056] In the instant embodiment, H_2 gas may be stored in LT reservoir **50** which is advantageous. For example, practical storage volumes for the LT reservoir are lower than gas storage tanks by a factor of about 350 times compared with storage of H_2 at atmospheric pressure. LT bed **52** forms a metal hydride reversibly within a range of temperatures between about 20 °C and about 55 °C of the ambient temperature depending on selected operating conditions. Heat of reaction for formation of the metal hydride in LT bed **52** is in the range from about 25 KJ/mol to about 30 kJ/mol. Composition of the LT hydride bed may be tuned based on the choice of metal alloys so that hydrogen release rates and hydrogen diffusion rates match those of HT metal hydride bed **42**. As will be appreciated by those of ordinary skill in the art, temperatures and heats of reaction may vary depending on the choices of metal hydrides and selected conditions. Thus, no limitations are intended.

[0057] In some embodiments, LT metal hydride bed **52** may be filled with a Ti-Mn-Fe metal alloy configured to operate near ambient temperatures with hydrogen pressures that match the operating pressures of HT hydride bed **40**. During storage of hydrogen, low-grade (low-duty) heat may be rejected to atmosphere. The term "low grade heat" refers to heat with a sufficiently low temperature that is unusable to perform work. Heat at or below a temperature of

about 100 °C is considered low-grade heat. The term "high grade heat" refers to heat that is capable of doing work, e.g., to generate electrical power. Heat typically above a temperature above 100 °C can perform work.

[0058] During retrieval of hydrogen, cooling can occur in LT reservoir **50** as a side effect. Temperature in LT storage bed **52** may be maintained using heat (e.g., waste heat) dissipated, e.g., by a condenser (e.g., a Rankine cycle condenser) (not shown) in power block **54**.

[0059] In some embodiments, as an alternative to storing hydrogen in a LT hydride bed, H_2 gas released from the HT storage reservoir may be stored in a gas storage tank (not shown). In these embodiments, use of a gas storage tank for low-temperature storage presumes energy requirements for compression and storage of hydrogen are favorable.

[0060] The invention provides a thermal energy storage capacity defined by an energy density between about 700 kJ/kg and 800 kJ/kg or a volumetric energy density of between about 3000 kJ/m^3 and about 4000 kJ/m^3. Energy density values are a factor of ten times greater than those achieved with conventional molten salt systems known in the art. System **200** provides superior energy densities that provide operation costs below conventional systems. In various embodiments, operation costs may be below about $30/kWh. System **200** with its selection of titanium powders is also scalable. For example, titanium powders may be produced in scalable quantities up to ton quantities or greater at selected impurity levels. For example, at a higher impurity levels, if performance metrics can be maintained, operation costs may be reduced accordingly.

[0061] **FIG. 4** shows a HT storage reservoir **40** of an exemplary design used in the TES system described previously in reference to **FIG. 3**. Storage reservoir **40** may be of a cylindrical design constructed of a corrosion-resistant metal or metal

alloy such as stainless steel or another suitable structural material. However, shapes are not intended to be limited. HT storage reservoir **40** may include an internal metal hydride bed **42** that includes one or more metal hydride storage containers **72** of a selected design each filled with one or more selected metal hydrides, described further in reference to **FIG. 5**. In one exemplary configuration, metal hydride bed **42** may include 31 metal hydride containers **72**, but number is not intended to be limited. Each metal hydride container **72** may be mounted into a top support plate **74** and a bottom support plate **76**. Plates **74** and **76** are preferably in a horizontal position within storage reservoir **40**, but orientation is not intended to be limited. Top plate **74** and bottom plate **76** may each include fluid flow channels or holes **78** positioned around each metal hydride reservoir **72** that allow a heat transfer fluid (not shown) when introduced into reservoir **40** to fill and surround hydride storage containers **72** of metal hydride bed **42**. Fluid flow channels or holes **78** further allow heat transfer fluid to drain from HT reservoir **40** when reservoir **40** is emptied.

[0062] Storage reservoir **40** may include an HTF inlet **80** for introduction of heat transfer fluid and a second HTF outlet **82** for release of heat transfer fluid from storage reservoir **40** during operation. Inlet **80** (or outlet) and outlet **82** (or inlet) are reversible depending on the direction of flow of HTF into reservoir **40**. Thus, no limitations are intended. In the figure, baffles **84** may be placed at selected locations along the inside wall of storage reservoir **40** to prevent pooling of HTF introduced into storage reservoir **40**. As HTF enters HTF inlet **80**, a corresponding quantity of HTF may exit from HTF outlet **82** or vice versa. Flow of HTF through reservoir **40** may be controlled to maintain temperature differences within storage reservoir **40**. For example, during heat storage, HTF may be flowed in a downward direction through storage reservoir **40** and in an upward direction during heat retrieval. However, flows of HTF are not intended to be limited.

[0063] Hydride storage containers **72** may each include a porous hydrogen gas transfer conduit **16** that is constructed of a sintered metal or metal alloy that introduces and collects hydrogen gas from the metal hydride contained with the storage containers. Gas transfer conduits **16** couple to manifold (header) **86** positioned, e.g., at the top of storage reservoir **40** to distribute or collect hydrogen gas uniformly into or from transfer conduits **16** during operation. Hydrogen gas may enter or return through a hydrogen inlet/outlet **88** through manifold (header) **86** into and from each metal hydride container **72** within storage reservoir **40** at selected temperatures during operation.

[0064] HT metal hydride storage containers **72** that configure reservoir **40** for operation may each be filled with a metal hydride that operates reversibly at high temperatures. In some embodiments, the metal selected for HT operation may be titanium metal that forms TiH at temperatures greater than 600 °C. In various embodiments, metal hydride storage containers **72** of the HT bed may operate at temperatures selected above 600 °C and at hydrogen gas pressures at or above 1 bar (0.1 MPa). In some embodiments, the HT bed may operate at a temperature between about 600 °C and about 750 °C. In some embodiments, the HT bed may operate at 640 °C. In some embodiments, the HT bed may operate at temperatures between about 600 °C and about 800 °C.

[0065] LT reservoir (**FIG. 3**) may include a configuration similar to that described here for the HT reservoir. Differences between the respective reservoirs may include the number of metal hydride containers, different metal hydride(s), and different heat transfer fluids described herein. All other components may be identical. No limitations are intended. For example, LT reservoir may include one or more metal hydride storage containers that configure the LT bed for operation. Each LT

storage container may be filled with a selected metal alloy containing a transition metal configured to form a metal hydride at a low temperature.

[0066] In some embodiments, the metal alloy may be a titanium-containing alloy. In some embodiments, the metal alloy may be a metal TiFeNi alloy. In some embodiments, the LT metal alloy may be a TiFeMn alloy.

[0067] In some embodiments, the LT metal hydride bed may operate at a temperature near ambient temperature to store H_2 desorbed from the HT bed. In some embodiments, the low temperature containers of the LT metal hydride bed may be configured to operate at temperatures above about 20 °C. In some embodiments, the low temperature containers of the LT metal hydride bed may be configured to operate at temperatures between about 20 °C and about 100 °C. In various embodiments, the LT bed may operate at a temperature selected above 20 °C and at hydrogen pressures at or above 1 bar (0.1 MPa). In some embodiments, the LT bed may operate at a temperature between about 20 °C and about 100 °C at hydrogen pressures at or above 1 bar (0.1 MPa).

[0068] HT reservoirs and LT reservoirs when coupled may store thermal energy for a time greater than about 8 hours on average. HT reservoirs can be charged for operation in a time of less than about 6 hours on average.

[0069] In operation, HT reservoirs and LT reservoirs provide an energy density of between about 700 kJ/kg and 800 kJ/kg, or a volumetric energy density between about 3000 kJ/m^3 and about 4000 kJ/m^3.

[0070] **FIG. 5** shows a HT metal hydride container **72** of an exemplary design that configures the HT metal hydride bed of the HT storage reservoir (**FIG. 4**) for operation. Differences between the components of the HT metal hydride container and the LT metal hydride container may include the metal hydride selected for use in the container and selected operation temperatures.

[0071] In the figure, metal hydride container **72** may be constructed of a corrosion-resistant metal or metal alloy such as stainless steel. In the figure, container **72** may include a cylindrical design. Container **72** may include an internal compartment **90** and a container lid **92** that seals container **72**. Inner compartment **90** may include a selected quantity or density of adjacent conducting metal disks **94** that span at least a portion of the length within the container. Conducting metal disks **94** may be constructed of copper or aluminum or another conducting metal to increase thermal conductivity within the container and enhance transfer of heat from the inside of the container wall to the metal hydride within the container. Metal disks **94** may be positioned a selected distance apart within the container. Separation distances between adjacent metal disks may be selected that allow a metal or metal alloy powder to be inserted between the metal disks in the container.

[0072] In some embodiments, metal or metal alloys may be in the form of a powder introduced or inserted between adjacent conducting metal disks in the HT container **72** that charge the container for operation. In some embodiments, the powder may be in the form of a compressed powder disk or disks (not shown) that allow for convenient and rapid exchange. Metal or metal alloy powders may be compacted, e.g., with a press. In some embodiments, powder disks may each include a diameter selected to maximize the packing density in the HT container. Compressed powder disks and metal disks **94** may be stacked in the thickness dimension to fill the container.

[0073] In various embodiments, spacing between adjacent conducting metal disks **94** may be selected between about 0.25 inches (0.64 cm) and about 5 inches (12.7 cm). Spacing depends in part on the distribution of heat into the metal or metal alloys positioned within the container and ease of exchange for compressed metal or metal alloy powders.

[0074] Conducting metal disks **94** enhance thermal heat conductivity in both radial direction and the axial direction through the metal hydride powder in the container. Conducting metal disks may displace a within inner compartment at or below about 10% on average. However, densities are not intended to be limited. For example, higher densities may be employed when increased thermal cycling is desired. No limitations are intended.

[0075] Diameter of conducting metal disks **94** and powder disks may each match or be below the inside diameter of storage container **72**. In some embodiments, diameter of conducting metal disks and powder disks may be selected between about 3 inches (7.6 cm) and about 12 inches (30.5 cm). In some embodiments, diameter of conducting metal disks and powder disks may be about 5 inches (12.7 cm) or greater. Diameter of conducting metal disks and powder disks may also be selected to maximize contact between the metal disks and the powder disks to maximize thermal conductivity in the container.

[0076] HT container **72** may further include indexing slits **96** introduced at selected locations along the length of the inner wall of container **72** and/or container lid **92**. Indexing slits **96** serve to secure conducting metal disks **94** when the container lid is closed and secured for operation at selected temperatures and pressures. In some embodiments, metal disks and compressed powder disks may be alternatively stacked within the container without a need of indexing slots within the container. In other embodiments, metal or metal alloys may be in a compressed form in the form of a single disk that may be introduced as a single unit into the container.

[0077] Metals and metal alloys may include a particle size selected to provide optimum cycle life, capacity, and flat plateau pressures during operation. In some embodiments, metal or metal alloy powder may include a particle size of about 60

mesh, but mesh size is not intended to be limited. Particle size can be expected to change during thermal cycling due to the change in volume during formation of the metal hydride during operation.

[0078] Systems of the present invention achieve a (net) exergetic efficiency (e.g., in a round trip thermal cycle) of up to about 96% in operation based on an enthalpy for the HT metal hydride (operating at temperatures in the HT reservoir between about 600 °C to about 800 °C) of about 150 kJ/mol and an enthalpy for the LT metal hydride (operating at temperatures in the LT reservoir of about room temperature or above) of about 25 kJ/mol. Such efficiencies lower costs of operation. For example, as heat is withdrawn from storage, high exergetic efficiency is achieved because the temperature at which heat is removed from the reservoir is maintained at a high temperature by the hydride reaction and does not fall as would the temperature of a sensible heat storage medium. Heat withdrawn from the HT storage reservoir thus allows each Watt of extracted heat to do a sustained level of work in contrast with sensible heat in which a falling temperature reduces the work that can be done. The present invention also extracts sensible heat from high-temperature hydrogen leaving the HT storage reservoir during heat storage may be delivered to the steam power block to assist in the production of electricity. An exemplary system for recovery of sensible heat from hydrogen released from the HT metal hydride bed will now be described.

[0079] **FIG. 6A** shows an exemplary system **300** for recovery of sensible heat during heat storage mode. At the start of the heat storage cycle, working hydrogen capacity resides in HT bed **42**. Recovery system **300** may employ three different heat transfer fluids or media, including, but not limited to, e.g., carbonate salts **114**, nitrate salts **122**, and mineral oil **130**. At the start of the storage cycle, heat transfer fluids **114**, **122**, and **130** reside in their respective low temperature (cool)

temperature reservoirs **116**, **124**, and **132**. In the figure, high-temperature heat **110** may be added to HT hydride bed **42** at ~700°C. Heat absorbed by the HT hydride bed results in endothermic decomposition of some fraction of the metal hydride in the bed, which results in release of hydrogen **48**. Released hydrogen **48** may be delivered through a recuperator **112** (e.g., a counter-current recuperator) where sensible heat may be transferred from the hydrogen to a heat transfer medium composed of or including, e.g., a carbonate salt **114**. The carbonate salt may be drawn from a cool reservoir **116** and passed through recuperator **112** where heat from the hydrogen is transferred. Carbonate salt released from recuperator **112** may be stored in a hot (e.g., carbonate salt) reservoir **118** at a temperature, e.g., of about ~700 °C. Flow of carbonate salt **114** may be adjusted to match the flow rate of the hydrogen gas in order to minimize temperature differences (so-called temperature approaches) between the various flows delivered to and from recuperator **112**, to and from cool fluid reservoir **116**, and to and from hot fluid reservoir **118**. For example, matching the flows of fluids permits a close approach at either end of recuperator **112** such that carbonate salt **114** may leave recuperator **112** at a temperature near (e.g. within ~20 °C) the hydrogen inlet temperature. Hydrogen may further leave recuperator **112** at a temperature near (i.e. within ~20°C) the inlet temperature of cool carbonate salt reservoir **116**.

[0080] Hydrogen leaving recuperator **112** may then enter recuperator **120** at a lower temperature. Transfer of heat from the hydrogen may be repeated with, e.g., a molten nitrate salt **122** collected from a cool nitrate salt reservoir **124**. Cool nitrate salt **122** may be heated by flowing through recuperator **120** and be subsequently stored in hot nitrate salt reservoir **126**. Transfer of heat from hydrogen to the nitrate salt cools the hydrogen to a temperature near (e.g. within ~20 °C) the storage temperature of the cool nitrate salt **122**. Hydrogen may then be released from

recuperator **120** and enter recuperator **128** where mineral oil **132** from cool reservoir **134** may be heated by exchanging heat with the flowing hydrogen. Heated mineral oil **130** may be stored in a hot (mineral oil) reservoir **134**. Hydrogen may be released from recuperator **128** at a temperature near (i.e. within ~20°C) of the ambient temperature, which may then be received into low temperature metal hydride bed **52**. Absorption of hydrogen into LT hydride bed **52** generates heat **136**, which may be rejected to the ambient environment due to its low exergetic value. For example, at an ambient temperature of 25 °C, each Watt of heat rejected at 50 °C may have an exergetic value of about 0.08 Watts). A typical heat loss target may be about 1% of the total heat input to the system during any 24 hour thermal cycle. At the end of the storage cycle, the working capacity of hydrogen resides in LT bed **52** and heat transfer fluids **114**, **122**, and **130** reside in their respective high temperature reservoirs **118**, **126**, and **134**.

[0081] **FIG. 6B** shows operation of heat recovery system **300** during heat retrieval. Heat released during heat retrieval mode may be used to drive a Rankine steam cycle **54** that generates electricity. At the start of the heat retrieval cycle, heat transfer fluids **114**, **122**, and **130** reside in their respective high temperature (hot) reservoirs **118**, **126**, and **134**. In the figure, high-temperature heat **110** may be withdrawn from HT bed **42** and used for generation of steam **140**. Steam **140** drives turbines **142** that produce electricity **58** as an output. Steam **140** may then be condensed **144** using, e.g., a steam condenser **146** (e.g., ~40 °C Rankine cycle condenser). Condenser **146** may be used since it operates at a temperature slightly above ambient (e.g. <100°C, and preferably < 50 °C). A fraction of heat **148** obtained from condensation may be delivered to LT hydride bed **52** which releases LT hydrogen **56** from LT bed **52**. Hydrogen

[0082] Hydrogen **56** from LT bed **52** may be heated in recuperator **128** by flowing mineral oil **130** from hot (mineral oil) reservoir **134** through recuperator **128** back to cool reservoir **132**. Hydrogen released from recuperator **128** may be introduced to recuperator **120** where the hydrogen may be heated to a higher temperature by flowing molten nitrate salt **122** from hot reservoir **126** to cool reservoir **124**. Hydrogen released from recuperator **120** may be introduced to recuperator **112** to heat the hydrogen further. The hydrogen may be heated by flowing molten carbonate salt **114** from hot reservoir **118** through recuperator **112** to cool reservoir **116**. Hydrogen released from recuperator **112** may then be absorbed into HT hydride bed **42** where the heat of reaction maintains the temperature of the bed as heat is withdrawn for production of electricity. While three transfer fluids have been shown, the present invention is not intended to be limited thereto. For example, use of multiple heat transfer fluids overcomes the difficulty of identifying a single heat transfer fluid that can be used over a temperature range from ambient to 700 °C. Nitrate salts cannot be used at ambient temperature because they solidify and cannot be used above about 500 °C because they thermally decompose. In some embodiments, two heat transfer fluids may be employed including, e.g., liquid sodium metal as the HT transfer fluid and mineral oil as the LT transfer fluid to span the entire temperature range.

[0083] Rate at which heat is transferred into or out of the metal hydride beds of the respective storage reservoirs determines at least in part the rate at which a hydride can absorb or release hydrogen, and thus absorb or release thermal energy. Thermal conductivity dictates the design of the respective storage reservoirs. An optimized heat transfer structure optimizes the thermal conductivity and determines the efficiencies attained.

[0084] **FIG. 7** shows outer wall temperatures of the HT metal hydride reservoir and the LT metal hydride reservoir described previously in reference to **FIG. 1**. Temperatures of both the outer wall and inner wall and inner core are important. For example, if thermal conductivity is low, metal hydride beds within the HT and LT storage reservoirs can have a decreased capacity; cycle lifetimes can also decrease. Exergetic efficiency of the metal hydride beds within the HT and LT storage containers depend on efficient thermal conductivity through the metal hydride beds and exterior and interior walls of respective HT and LT containers. As such, a low temperature gradient is preferred that achieves heat transfer within the metal hydride beds. Temperature of the metal hydride beds and reservoirs may be controlled by balancing heat loss with heat input. For example, heating of the HT metal hydride bed may be accomplished by increasing input heat to a level above the steady-state heat loss. Cooling may be accomplished by reducing input heat to a level immediately below the steady state heat loss. Modeling results predict the outer wall temperature of the LT bed ($TiFe_{0.925}Ni_{0.075}$) can vary from about ~20 °C to ~55 °C during the thermal cycle. Heating to 55 °C can occur via the bottom of the steam cycle (i.e. heating with steam exiting the low pressure turbine or using steam condensate). Simulation results show that the system can be charged or discharged over a period of 8 hours with the hydrogen pressure remaining constant and the HT hydride bed varying from ~660 °C to 700 °C while the LT bed varies from 55 °C to 20 °C. The small overshoot in the transition to idle state indicates a small thermal gradient is required to achieve the thermal flux. Isotherms and cycling behavior are described further in reference to **FIG. 8** and **FIG. 9**.

[0085] **FIG. 8** plots adsorption isotherms and desorption isotherms predicted based on a model using a measured adsorption isotherm as a basis. The model uses data on the reaction enthalpy for titanium hydride as a function of hydride

loading determined by Danzter, [*J. Phys. Chem. Solids*. Vol. 44, No. 9, pp. 913-923, 1983] to extrapolate conditions where actual data are not available. The model was incorporated in a multi-physics model (e.g., COMSOL Multiphysics® Software, COMSOL Inc., Burlington, MA, USA) that simulated formation/decomposition of the hydride in response to changes in temperature with simultaneous heat and mass transport within storage reservoirs. In the figure, hydrogen pressure (psia) is plotted against moles of H_2 absorbed/desorbed in the metal hydride bed. Operation pressures were selected at 2.4 bar (0.24 MPa). Isotherm data were then fitted for titanium hydride (Ti-H). Model isotherms show that equilibrium loading may be optimized in the Ti-H bed at pressures of about 2.4 bar (0.24 MPa) and temperatures between about 650 °C and about 700 °C. Swings in equilibrium hydrogen loading (dashed lines) can occur at temperatures between 650 °C and 700 °C. Plateau pressures are observed at an average hydrogen pressure of about 2.4 bar (0.24 MPa) over the selected temperature range. Model isotherms also show average atomic ratios between [H: Ti] at the plateau pressures between about 0.88 and about 1.55. For example, equilibrium loading is predicted to swing from 0.88 mol H : mol Ti at 700°C to 1.55 mol H: mol Ti at 650°C for a swing of 0.67 mol H/mol Ti. The swing corresponds to a hydrogen loading swing of about 1.4 wt% with respect to titanium mass. Actual loading swings achieved in the model depend on local temperatures reached during the loading/unloading cycle.

[0086] **FIG. 9** shows adsorption/desorption isotherms (hydrogen loading curves) from tests conducted of the thermal energy storage and retrieval system of **FIG. 1** during thermal cycling over the temperature range from about 650 °C to about 700 °C. In the figure, pressure (psia) is plotted against moles of H_2 in the metal hydride bed. Performance tests were conducted using an automated hydrogenation system controlled with a programming environment (e.g., LabVIEW, National

Instruments Corp., Austin, TX, USA). Optimum temperature for the HT reactor tank was selected between about 650 °C and about 700 °C. A pressure of 2.4 bar (0.24 MPa) is typical. Experimental data agree with model data (**FIG. 8**). In particular, plateau temperatures are reached in the temperature range from about 630 °C to about 670 °C and selected hydrogen pressures between about 5 psia (0.03 MPa) and about 40 psia (0.28 MPa) over the selected temperature range. Results show a cycle lifetime of over 100 thermal cycles with no loss adsorption/desorption capacity.

[0087] The dual bed TES system of the present invention finds applications: in conversion of renewable energies (e.g., concentrated solar power), in nuclear power plants, in the electrical power grid, in buildings, and in the transportation sector including the automotive sector.

EXAMPLES

[0088] The following Examples provide a further understanding of various aspects of the present invention.

EXAMPLE 1

[Bench-scale thermal energy storage system]

[0089] A 2.5 gram sample of titanium hydride (TiH) was loaded into a temperature controlled sample container with the ability to add or remove hydrogen to maintain pressure over the sample. Operating temperature was between about 640 °C and about 650 °C. Hydrogen pressure was 1 bar (0.1 MPa). Results showed a minimum of 100 thermal cycles without a loss in capacity.

EXAMPLE 2

[Lab-scale thermal energy storage system]

[10 kg test bed, 3kWh prototype]

[0090] The TES system of **FIG. 1** was used for performance testing. Prior to operation, the TES system was positioned vertically with a protective Plexiglas® cover positioned at one end of the TES system in a fume hood. The high-temperature (HT) reservoir and the low-temperature (LT) reservoir were each filled with a dense (8% nominal density) copper metal foam containing 10 pores per inch (ppi) (e.g., DUOCEL® copper foam, ERG Materials and Aerospace Corp., Oakland, CA, USA). Titanium powder was introduced into the HT reservoir by vibrating the reservoir which facilitated uniform distribution and loose compaction of the powder into the open cells of the copper metal foam. Argon gas was flowed through the test beds during filling. A total of 9.4 kilogram of metal foam was loaded with titanium powder.

EXAMPLE 3

[Full-scale system (~1,000 kg)]

[0091] A full-scale system conceptual of a 240 kWh prototype design is envisioned illustrated in **FIG. 3**. A HT metal hydride storage tank and a LT metal hydride storage tank described herein will be constructed. Each tank will comprise a metal hydride bed containing up to 1,000 kg of a selected metal powders in compressed form. The storage tanks will be connected to a solar collector/solar collector that will collect heat from solar collection (i.e., an On-Sun Test) and provide energy to the selected MH tanks.

[0092] While various preferred embodiments of the invention have been shown and described, it is to be distinctly understood that this invention is not limited thereto but may be variously embodied to practice within the scope of the following claims. From the foregoing description, it will be apparent that various changes may be made without departing from the spirit and scope of the present invention as defined by the following claims.

CLAIMS

What is claimed is:

1. A reversible thermal energy storage and retrieval system, comprising:

at least one HT reservoir and at least one LT reservoir, each reservoir including a metal hydride bed, the metal hydride bed of the HT reservoir comprises a titanium-containing metal in the presence of hydrogen gas that reversibly forms a metal hydride at a temperature at or above about 600 °C, the metal hydride bed of the LT reservoir comprises a transition metal alloy that reversibly forms a metal hydride in a hydrogen gas environment at a temperature at or below about 100 °C; and

a hydrogen transfer device configured to transfer hydrogen gas between the metal hydride bed of the HT reservoir and the metal hydride bed of the LT reservoir or vice versa that maintains an ambient or near-ambient hydrogen pressure in the respective reservoirs during a thermal cycle operation.

2. The system of Claim 1, wherein the metal hydride bed of the respective HT and LT reservoirs include one or more storage containers with an internal compartment comprising a selected density of adjacent conducting metal disks disposed a selected distance apart therein that span at least a portion of the length or internal volume of the internal compartment, the separation distance between the metal disks defines a space configured to receive a titanium-containing metal or a transition metal alloy therein configured to reversibly form a metal hydride during operation, the metal disks enhance thermal conductivity

through the metal hydride in the metal hydride bed in at least a radial direction during a thermal cycle.

3. The system of Claim 2, wherein the titanium-containing metal and transition metal alloy are in the form of compressed powder disks disposed between the conducting metal disks in the one or more storage containers within the HT or LT reservoirs, respectively.

4. The system of Claim 1, wherein the gas transfer device is a sintered porous conduit with an inner bore of a selected dimension disposed within the metal hydride bed configured to deliver hydrogen into the metal hydride bed for formation of the metal hydride and to recover hydrogen released from the metal hydride bed during a thermal cycle.

5. The system of Claim 1, wherein the metal disposed within the HT metal hydride bed comprises titanium metal and the metal alloy within the LT metal hydride bed comprises one or more metals selected from: Ti, Fe, Ni, Mn, or combinations thereof.

6. The system of Claim 1, wherein the HT reservoir includes a heat transfer fluid configured for transfer of heat within the HT metal hydride bed selected from sodium metal, lead-bismuth, tin-antimony, and the LT reservoir includes a heat transfer fluid configured for transfer of heat within the LT metal hydride bed selected from water, propylene glycol, ethylene glycol, or mixtures thereof.

7. The system of Claim 1, wherein the energy density is at least about 750 kJ/kg and the volumetric energy density is at least about 3,000 kWh/m^3.

8. The system of Claim 1, wherein the exergetic efficiency is up to about 95% or better.

9. A reversible thermal energy storage and retrieval device, comprising:

a container constructed of a corrosion-resistant metal or metal alloy with an internal compartment comprising a selected density of adjacent conducting metal disks disposed a selected distance apart therein that span at least a portion of the length or internal volume of the internal compartment, the separation distance between the metal disks defines a space configured to receive a titanium-containing metal or a transition metal alloy that when introduced defines a metal hydride bed configured to reversibly form a metal hydride during operation at a temperature at or above 600 °C or at or below 100 °C, the metal disks enhance thermal conductivity through the metal hydride in the metal hydride bed in at least a radial direction during a thermal cycle.

10. The device of Claim 9, wherein the metal or metal alloy is in the form of compressed powder disks that are insertable in the space disposed between the conducting metal disks.

11. The device of Claim 9, wherein the metal alloy comprises one or more metals selected from the group consisting of: Ti, Fe, Ni, Mn, and combinations thereof.

12. The device of Claim 9, wherein the titanium-containing metal reversibly forms titanium metal hydride at a high temperature between about 600 °C and about 800 °C.

13. The device of Claim 9, wherein the transition metal alloy is a titanium-containing metal alloy that reversibly forms a metal hydride at a low temperature between about 20 °C and about 100 °C.

14. The device of Claim 9, further includes a sintered porous metal conduit that couples to the conducting metal disks disposed therein constructed of a selected metal or metal alloy with an inner bore of a selected dimension configured to deliver hydrogen into the metal hydride bed for formation of the metal hydride and to recover hydrogen released from the metal hydride bed during a thermal cycle operation.

15. The device of Claim 9, wherein the density of conducting metal disks comprises between 2% and 10% of the volume of the internal compartment of the container.

16. A process for operating the system of Claim 1, comprising the steps of:

contacting the titanium-containing metal hydride in the HT reservoir with heat introduced from a high-temperature heat source to release hydrogen from the metal hydride therein;

absorbing hydrogen released from the HT reservoir in the transition metal hydride bed of the LT reservoir to store same therein; and

releasing high-temperature heat at a temperature above 600 °C from the titanium-containing metal hydride bed of the HT reservoir to generate power.

17. The process of Claim 16, wherein providing the HT reservoir and the LT reservoir includes inserting the titanium-containing metal or the transition metal-containing metal alloy between adjacent conducting metal disks disposed within one or more storage containers within the metal hydride beds of the HT and LT reservoirs, respectively.

18. The process of Claim 16, wherein releasing heat from the HT metal hydride bed includes delivering the heat to a Rankine steam cycle to generate power.

19. The process of Claim 18, further including recovering high-temperature heat from the hydrogen gas released from the HT metal hydride bed in a recuperation system to recuperate heat used to preheat feed water in the Rankine steam cycle.

20. The process of Claim 16, wherein the hydrogen gas pressure in the metal hydride beds of the HT and LT reservoirs is between 0.1 MPa and 1 MPa.

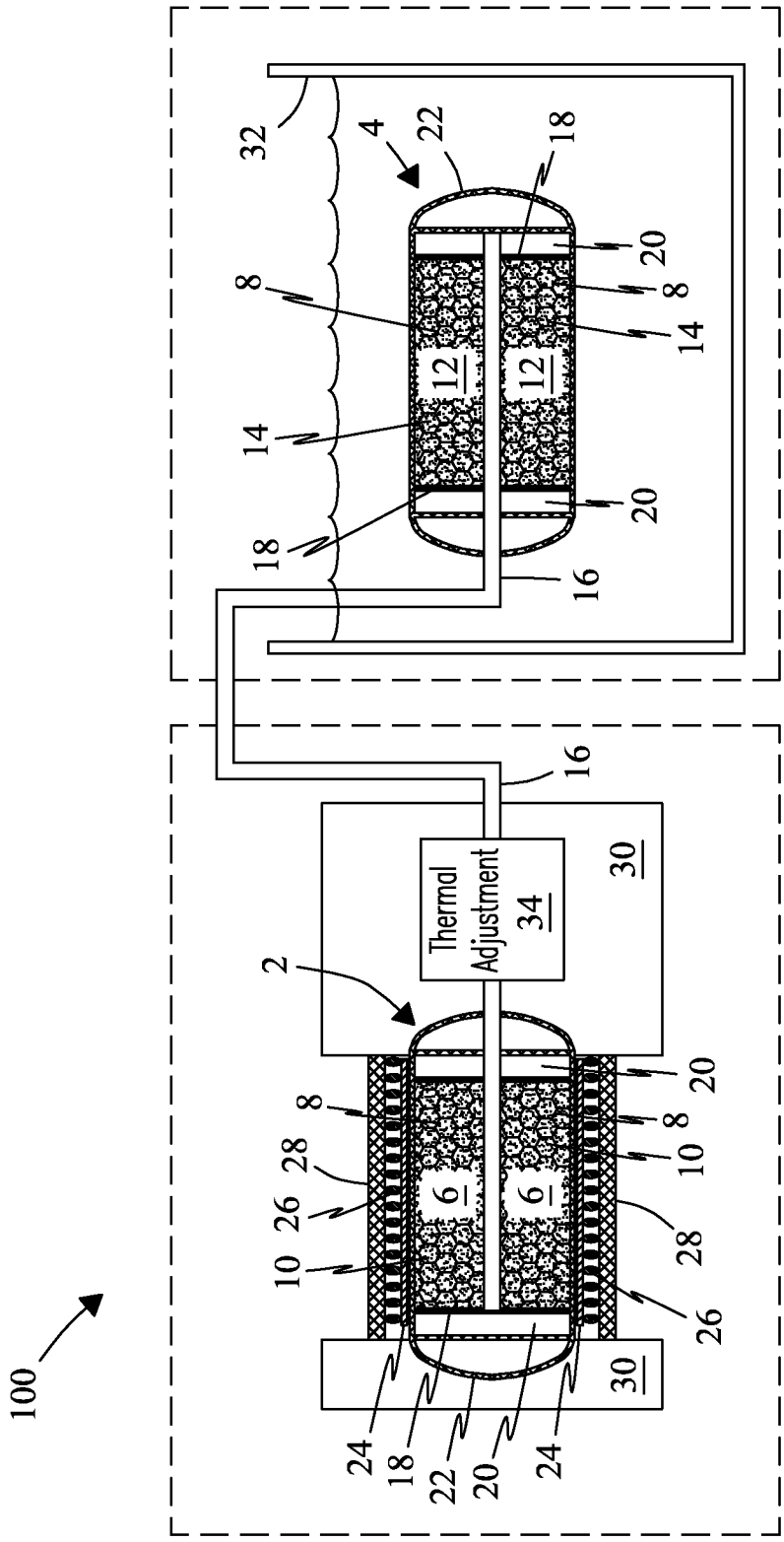

100
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
Thermal Adjustment

FIG. 1

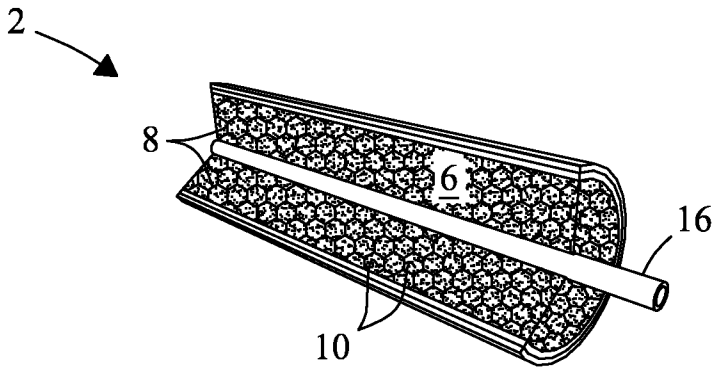

2
8
6
16
10

FIG. 2

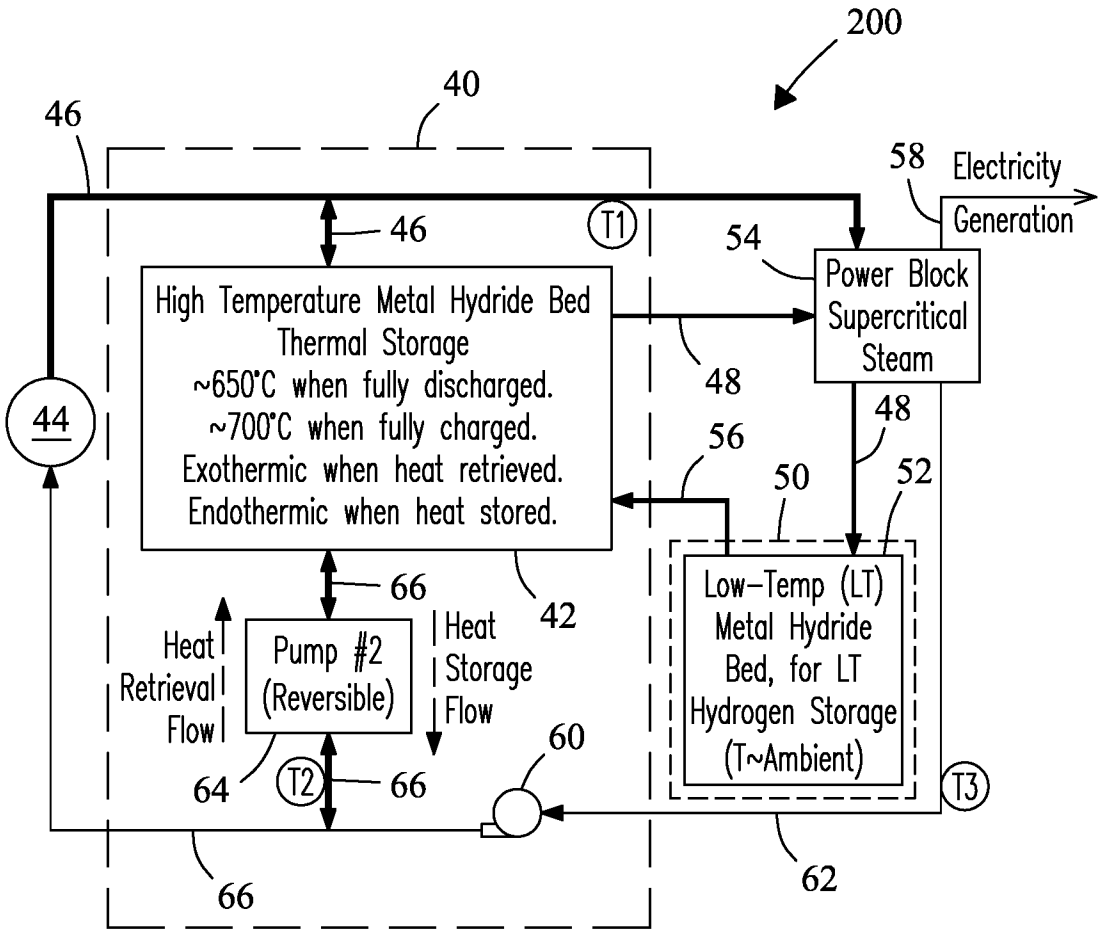

200
40
46
58
Electricity
Generation
46
T1
54
Power Block
Supercritical
Steam
High Temperature Metal Hydride Bed
Thermal Storage
~650°C when fully discharged.
~700°C when fully charged.
Exothermic when heat retrieved.
Endothermic when heat stored.
48
48
44
56
50
52
66
42
Heat
Retrieval
Flow
Pump #2
(Reversible)
Heat
Storage
Flow
Low-Temp (LT)
Metal Hydride
Bed, for LT
Hydrogen Storage
(T~Ambient)
60
64
T2
66
T3
66
62

FIG. 3

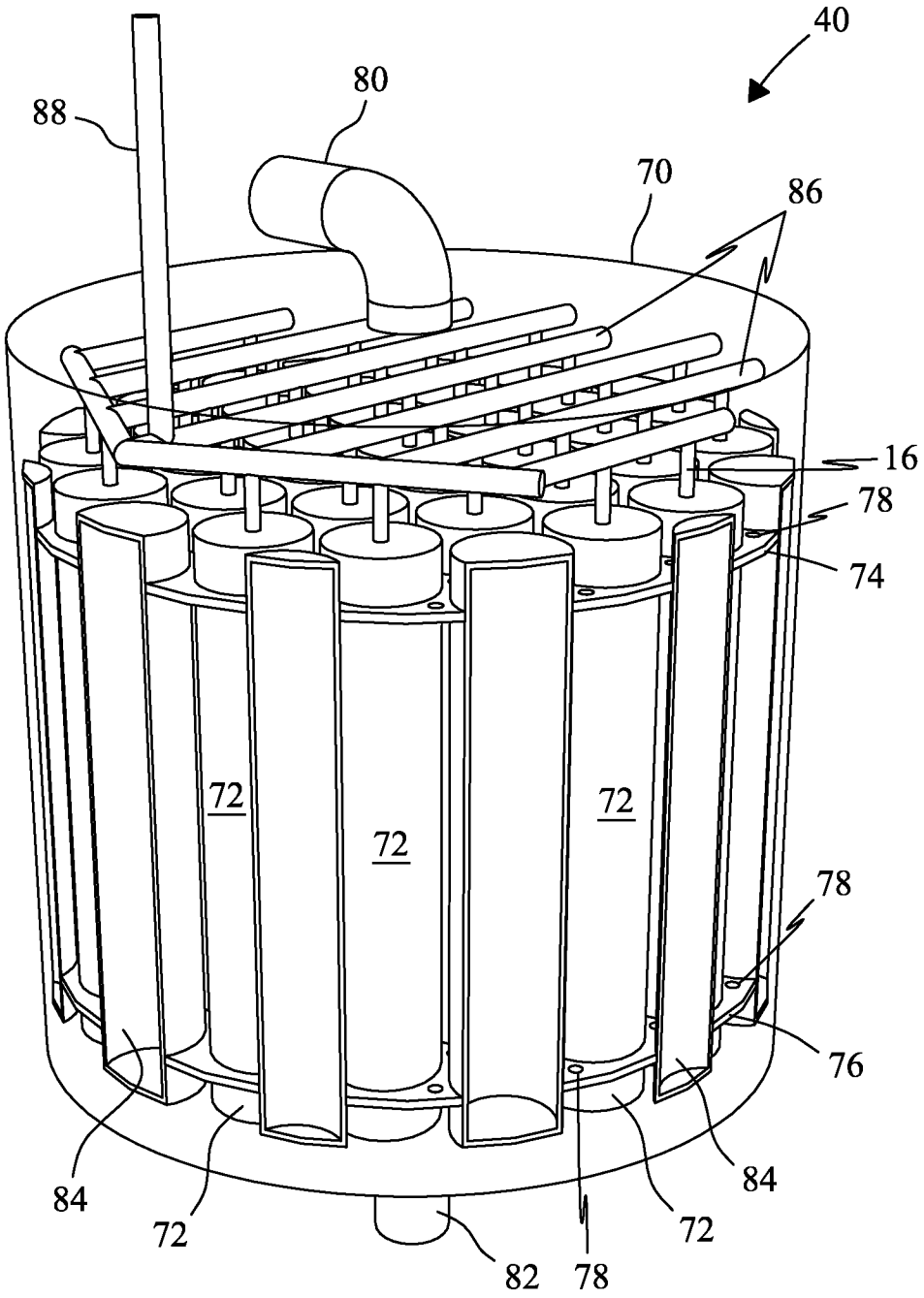


FIG. 4

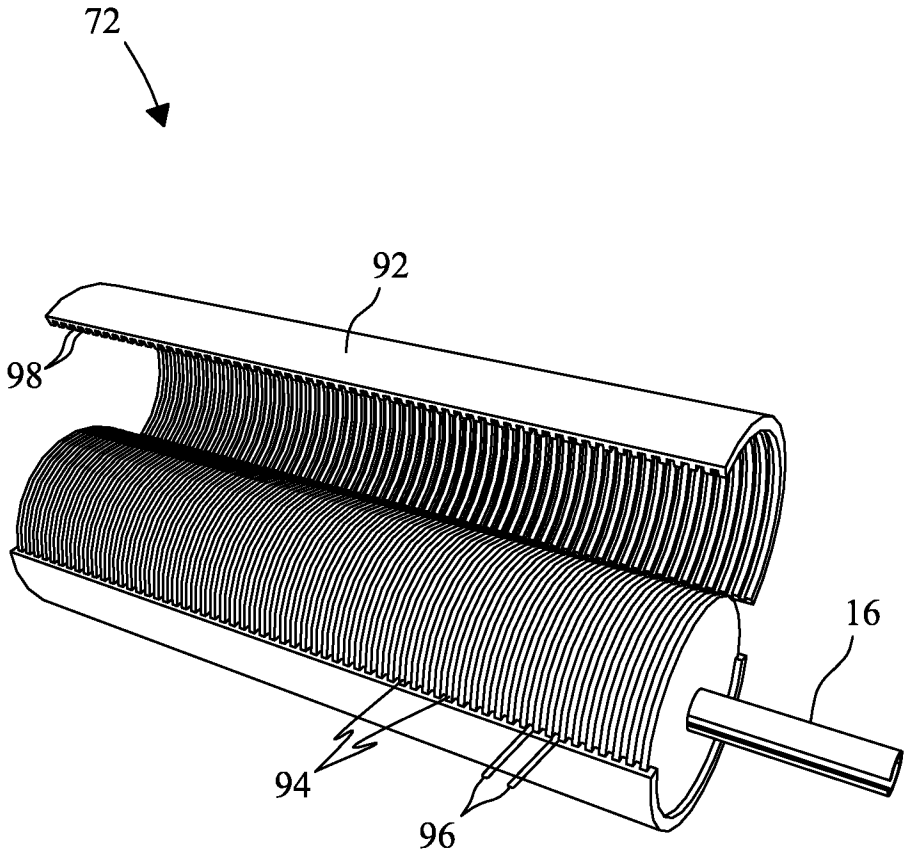


FIG. 5

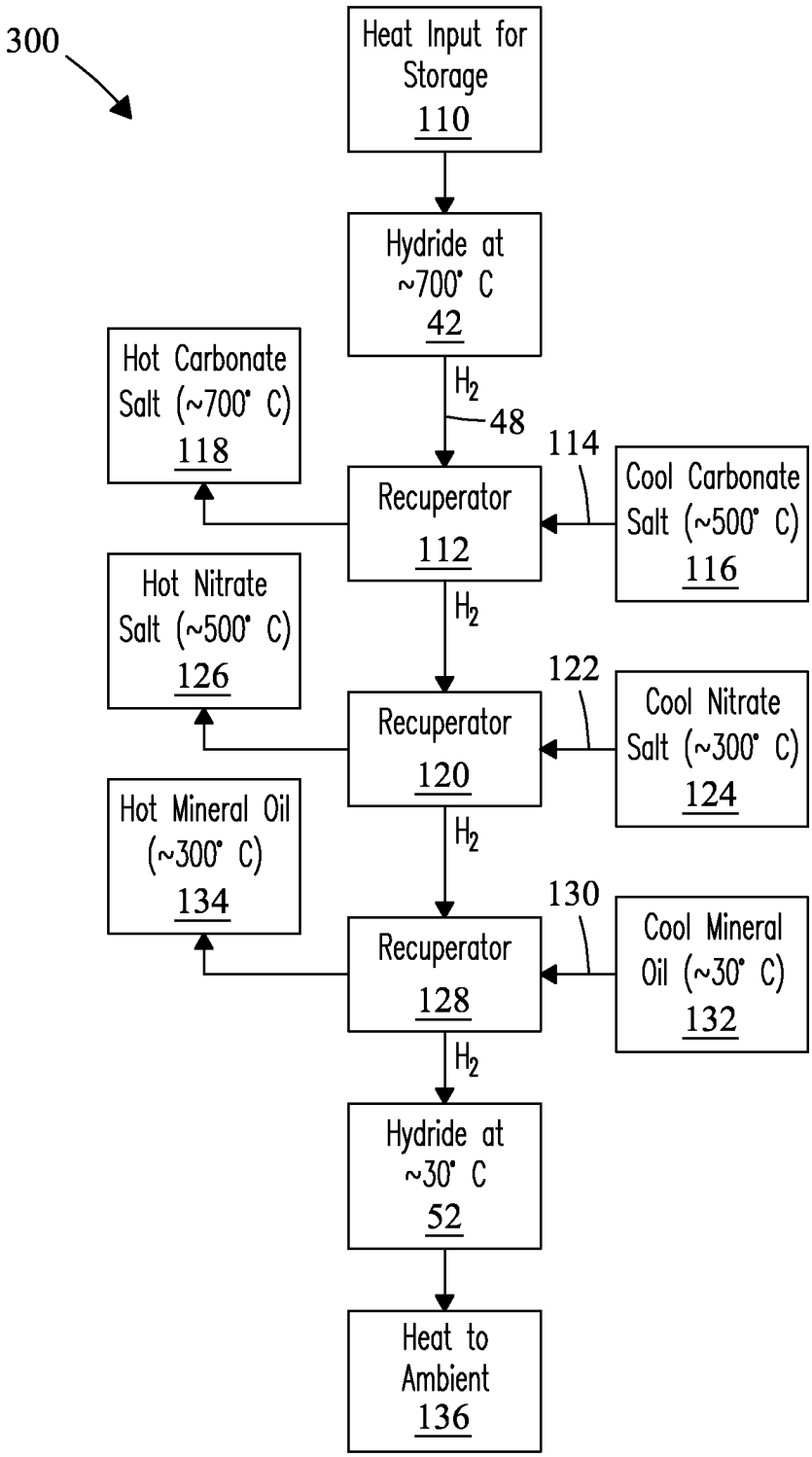

300
Heat Input for Storage 110
Hydride at ~700° C 42
H2
48
Hot Carbonate Salt (~700° C) 118
114
Cool Carbonate Salt (~500° C) 116
Recuperator 112
Hot Nitrate Salt (~500° C) 126
H2
122
Cool Nitrate Salt (~300° C) 124
Recuperator 120
Hot Mineral Oil (~300° C) 134
H2
130
Cool Mineral Oil (~30° C) 132
Recuperator 128
H2
Hydride at ~30° C 52
Heat to Ambient 136

FIG. 6A

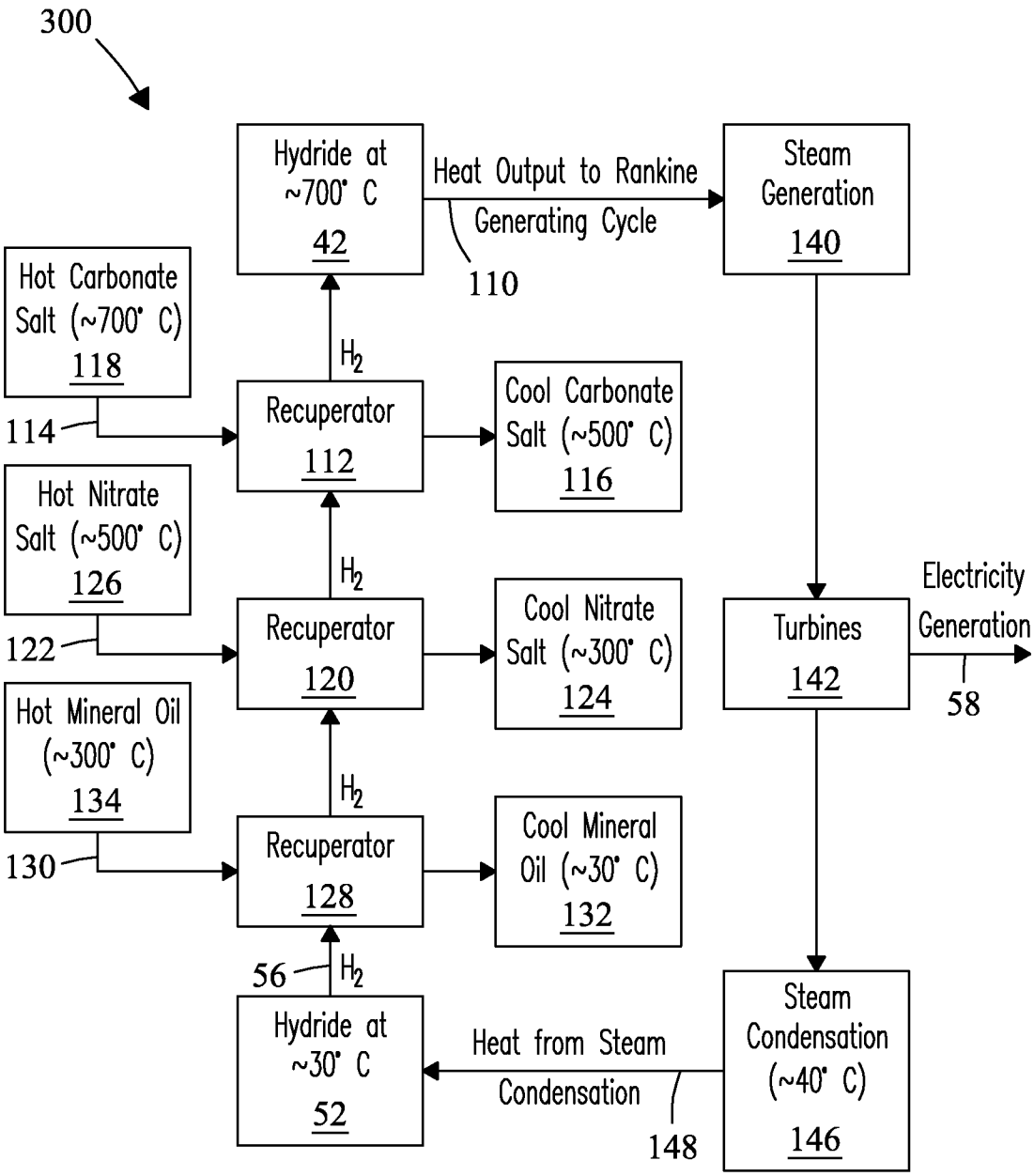

300
Hydride at ~700° C
42
Heat Output to Rankine Generating Cycle
110
Steam Generation
140
Hot Carbonate Salt (~700° C)
118
114
H2
Recuperator
112
Cool Carbonate Salt (~500° C)
116
Hot Nitrate Salt (~500° C)
126
122
H2
Recuperator
120
Cool Nitrate Salt (~300° C)
124
Turbines
142
Electricity Generation
58
Hot Mineral Oil (~300° C)
134
130
H2
Recuperator
128
Cool Mineral Oil (~30° C)
132
56
H2
Hydride at ~30° C
52
Heat from Steam Condensation
148
Steam Condensation (~40° C)
146

FIG. 6B

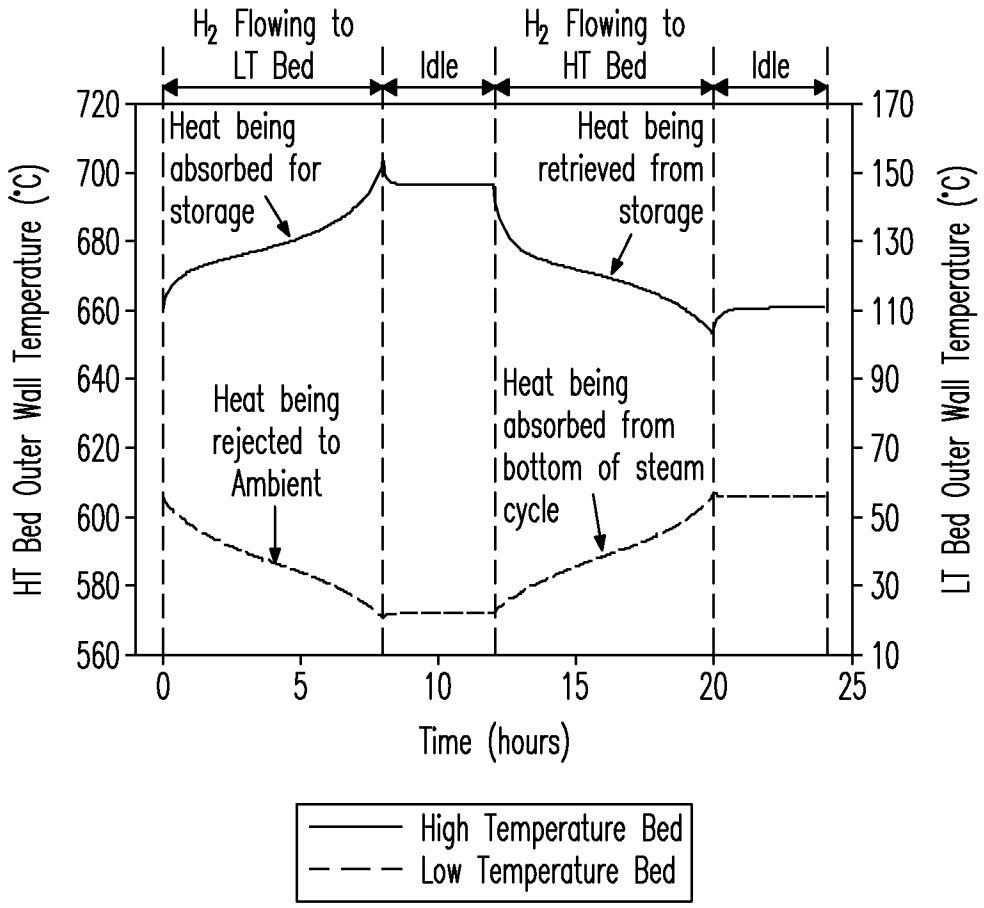

H_2 Flowing to LT Bed
Idle
H_2 Flowing to HT Bed
Idle
Heat being absorbed for storage
Heat being retrieved from storage
Heat being rejected to Ambient
Heat being absorbed from bottom of steam cycle
HT Bed Outer Wall Temperature (°C)
LT Bed Outer Wall Temperature (°C)
720
700
680
660
640
620
600
580
560
170
150
130
110
90
70
50
30
10
0
5
10
15
20
25
Time (hours)
High Temperature Bed
Low Temperature Bed

FIG. 7

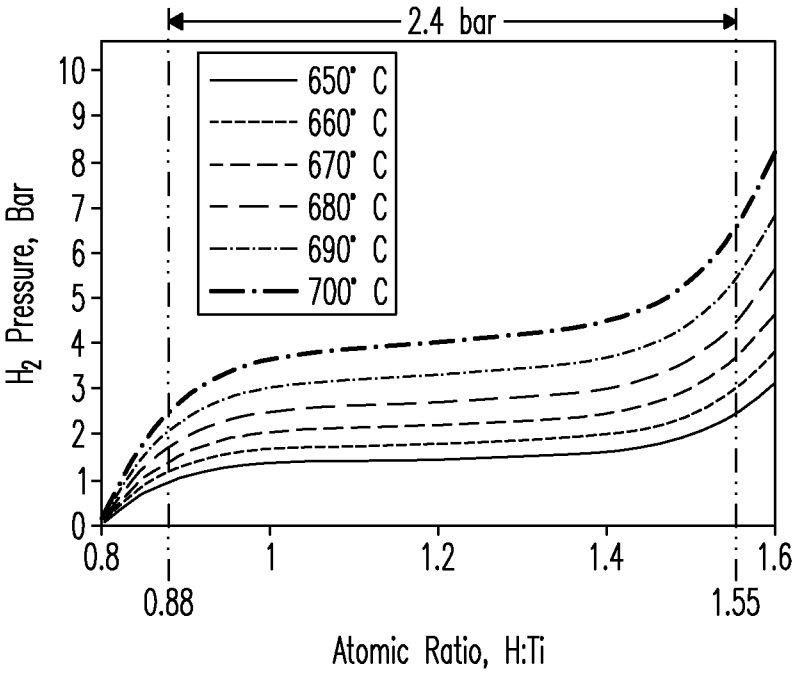

2.4 bar
650° C
660° C
670° C
680° C
690° C
700° C
H2 Pressure, Bar
0
1
2
3
4
5
6
7
8
9
10
0.8
1
1.2
1.4
1.6
0.88
1.55
Atomic Ratio, H:Ti

FIG. 8

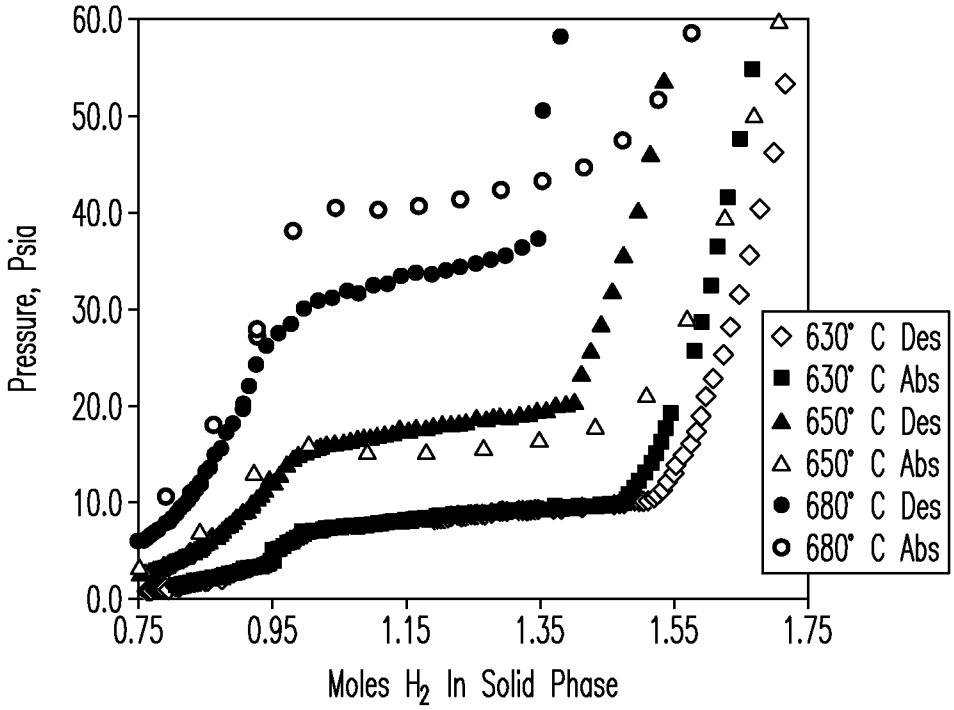

Pressure, Psia
0.0
10.0
20.0
30.0
40.0
50.0
60.0
0.75
0.95
1.15
1.35
1.55
1.75
Moles H2 In Solid Phase
630° C Des
630° C Abs
650° C Des
650° C Abs
680° C Des
680° C Abs

FIG. 9

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/018723

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B3/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 220 678 A1 (ENERGY CONVERSION DEVICES INC [US]) 6 May 1987 (1987-05-06)	1,5-8,16
Y	page 3, lines 14-20 page 14, lines 11-18 claim 1; figure 1	2-4, 17-20

X	US 5 797 269 A (NISHIMURA KOUICHI [JP] ET AL) 25 August 1998 (1998-08-25)	9-15
Y	column 5, lines 41-44 column 6, line 49 - column 7, line 6	2-4, 17-20
A	column 2, lines 37-45 figures 2,3	5-8

X	EP 1 286 406 A2 (ASIA PACIFIC FUEL CELL TECH [TW]) 26 February 2003 (2003-02-26)	9-15
Y	paragraphs [0009], [0017], [0019], [0021], [0023], [0028]	2-4, 17-20
A		5-8,16

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

[X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 June 2014	02/07/2014

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

1

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/018723

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 122 338 A (WALLACE W EDWARD [US] ET AL) 16 June 1992 (1992-06-16) column 2, lines 39-52; figures 1,2 column 3, lines 1-11 -----	1-20
A	US 4 995 235 A (HALENE CLEMENS [DE]) 26 February 1991 (1991-02-26) column 4, lines 7-51; figure 1 -----	1-20

1

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