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(54) **THERMOELECTRIC ENERGY STORAGE SYSTEM**

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(57) **ABSTRACT**

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A thermoelectric energy storage system and method are provided for storing electrical energy by transferring thermal energy to a thermal storage in a charging cycle, and for generating electricity by retrieving the thermal energy from the thermal storage in a discharging cycle. The thermoelectric energy storage includes a working fluid circuit configured to circulate a working fluid through a heat exchanger, and a thermal storage conduit configured to transfer a thermal storage medium from a thermal storage tank through the heat exchanger. The working fluid includes a zeotropic mixture. The working fluid is in a mixed vapor and liquid phase and has continuously rising or continuously falling temperature during heat transfer due to the working fluid including the zeotropic mixture.

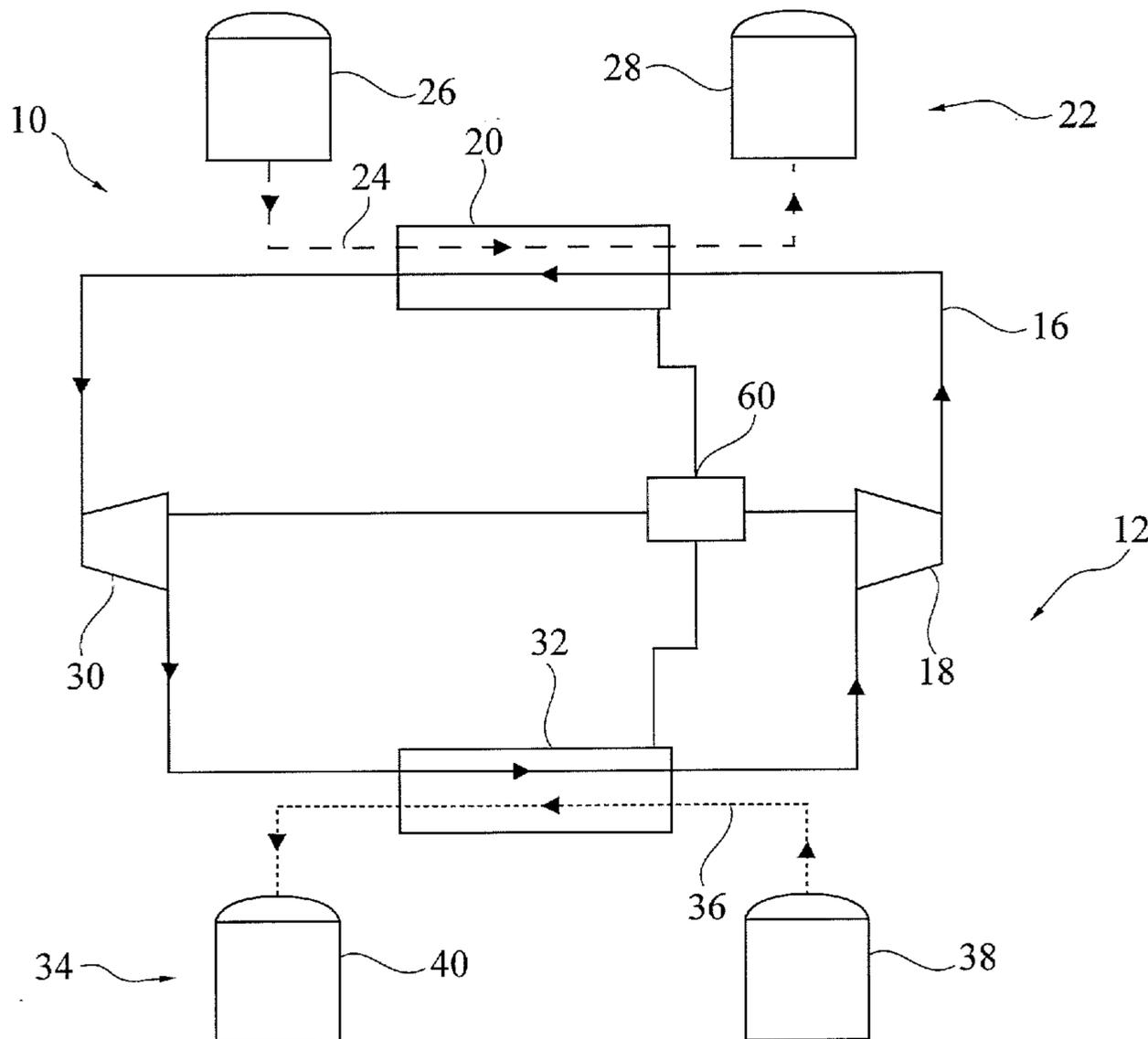
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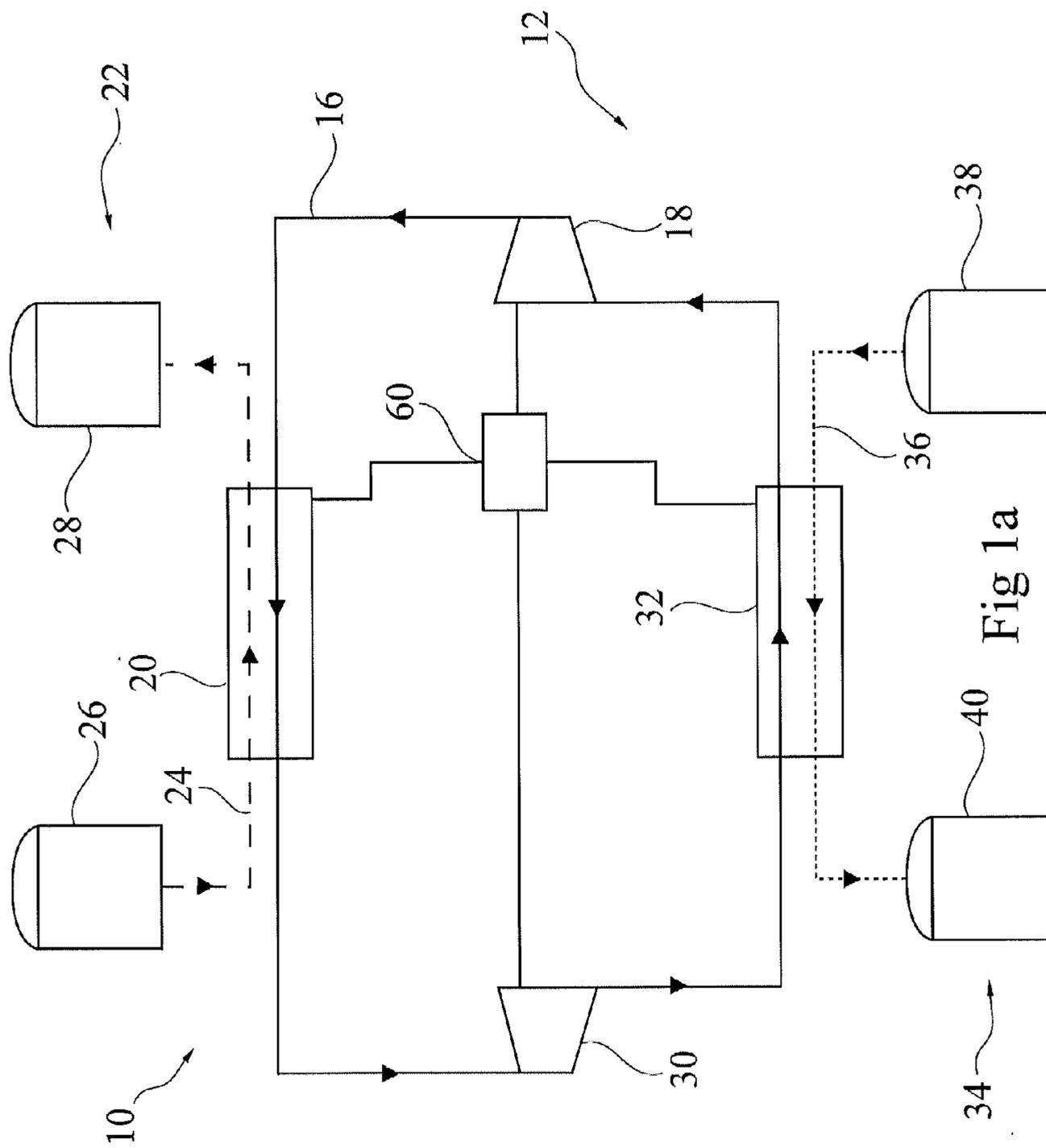


Fig 1a

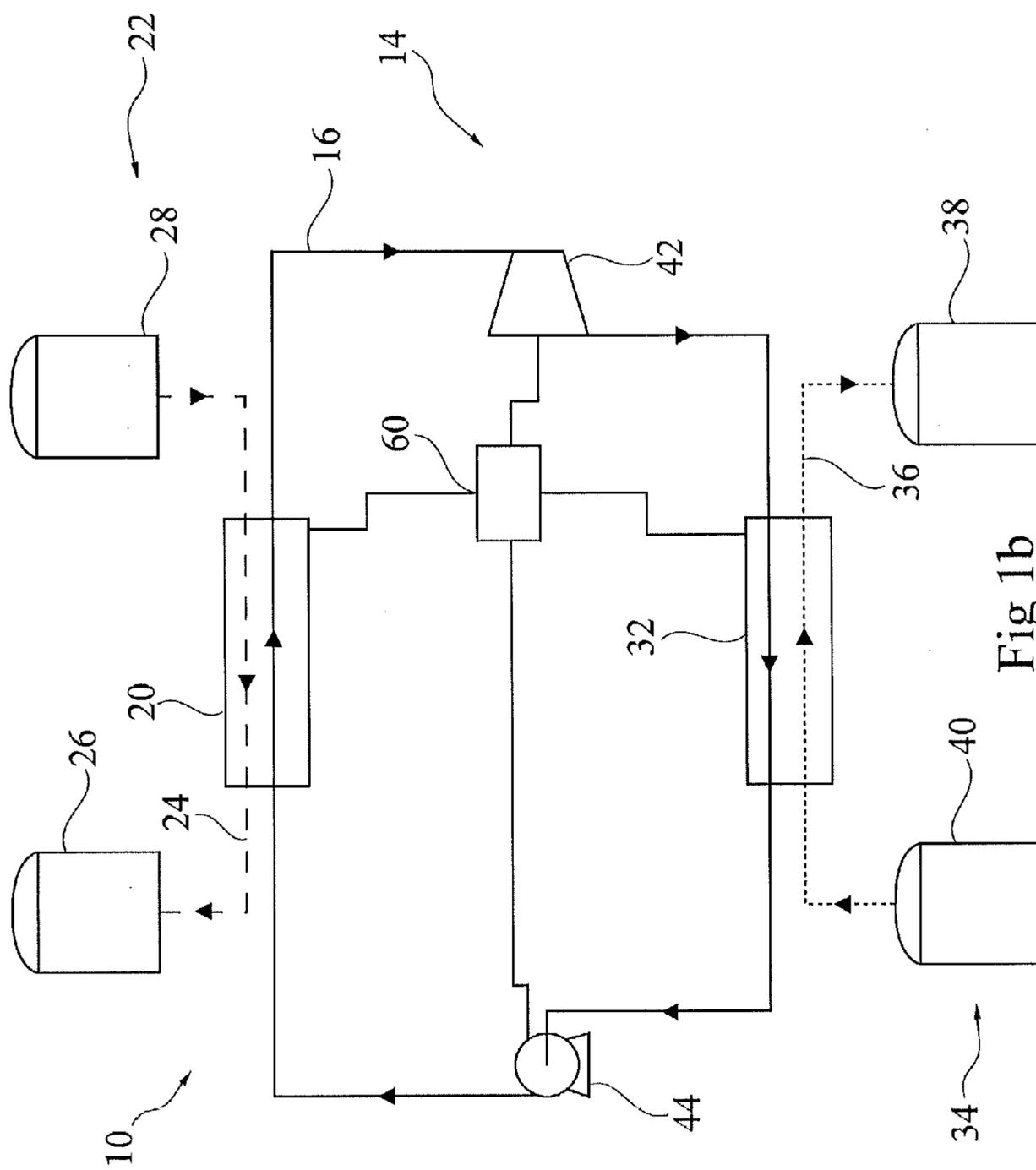


Fig 1b

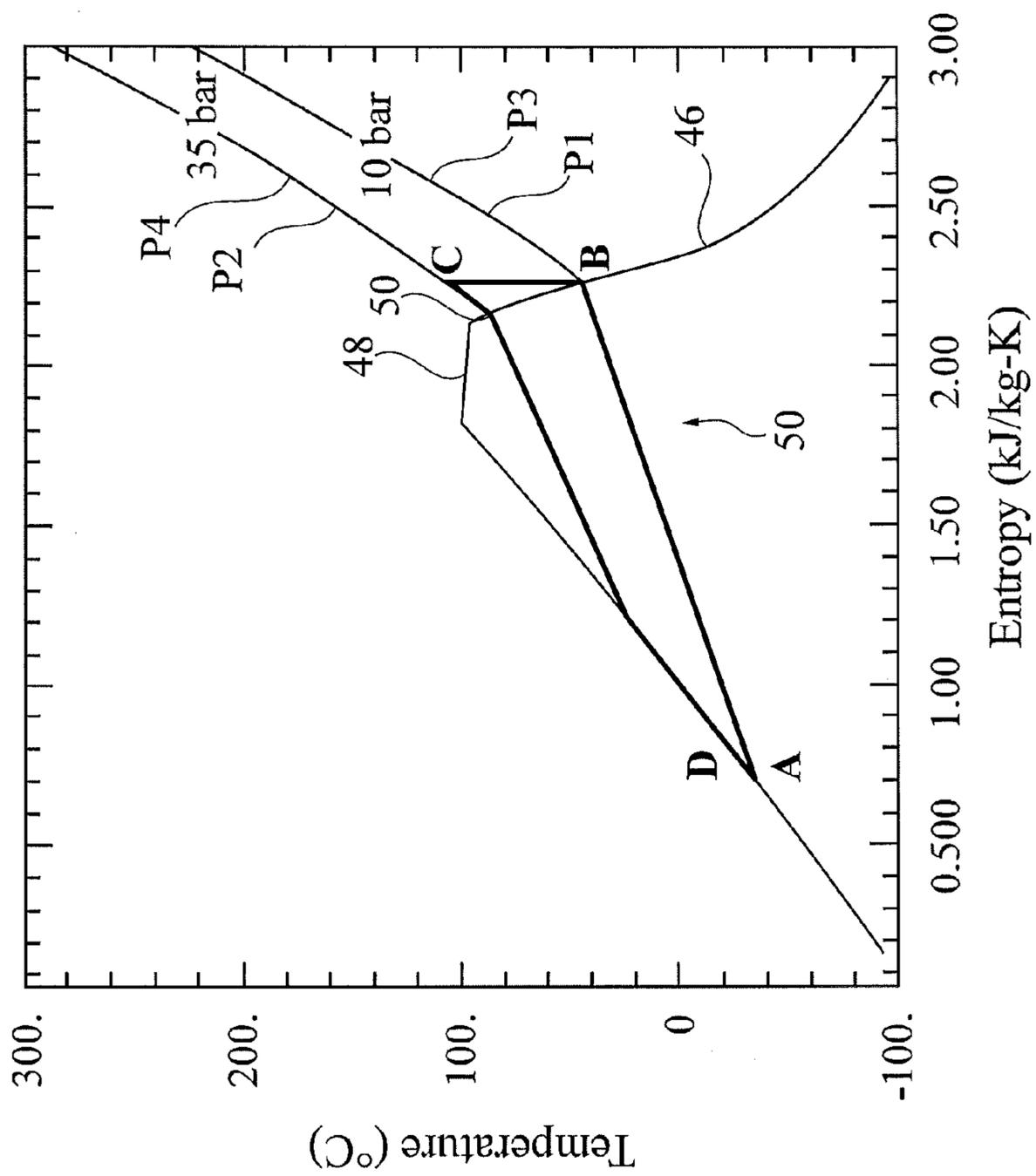


Fig. 2

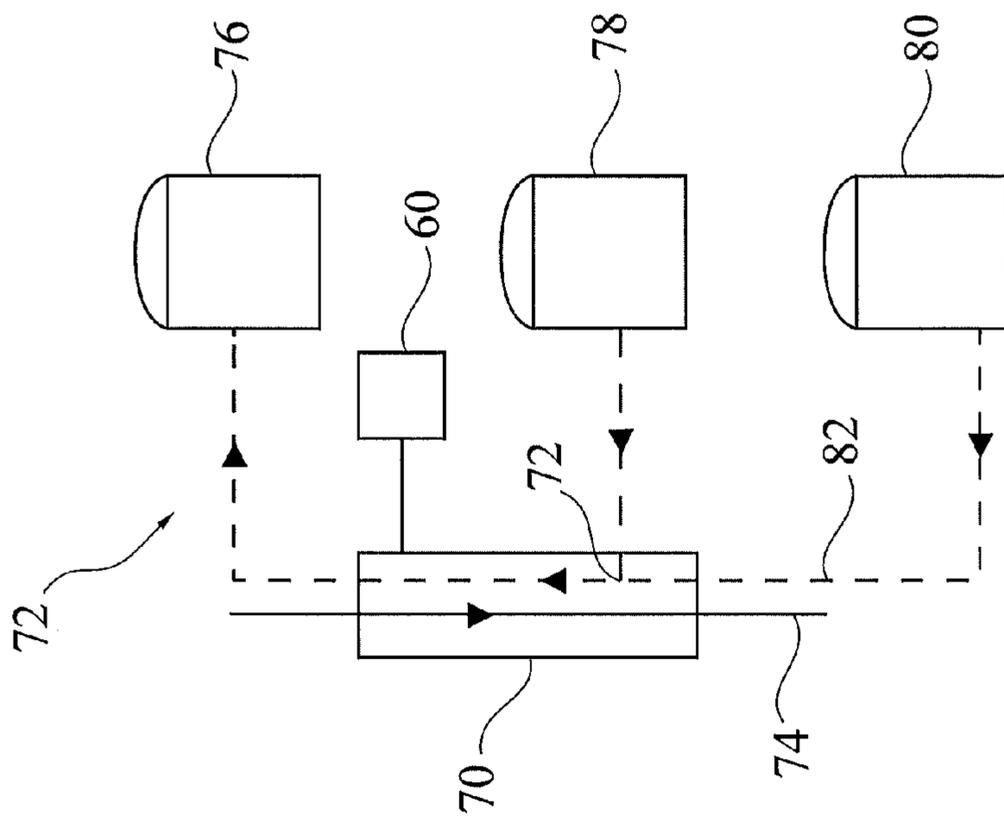


Fig. 3a

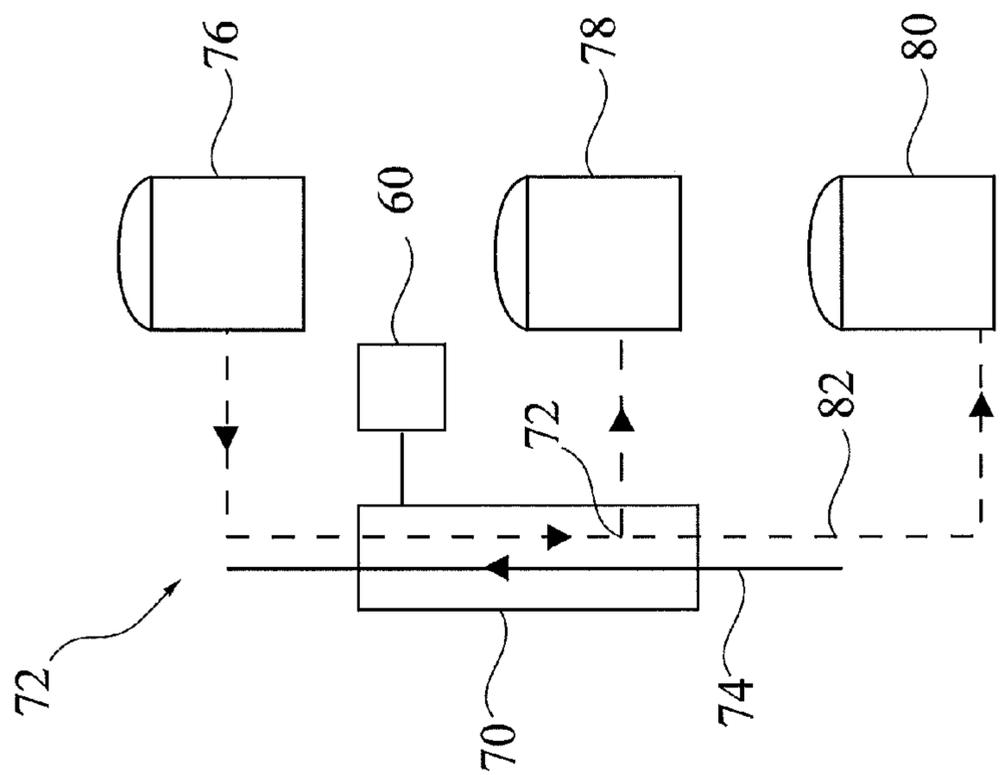


Fig.3b

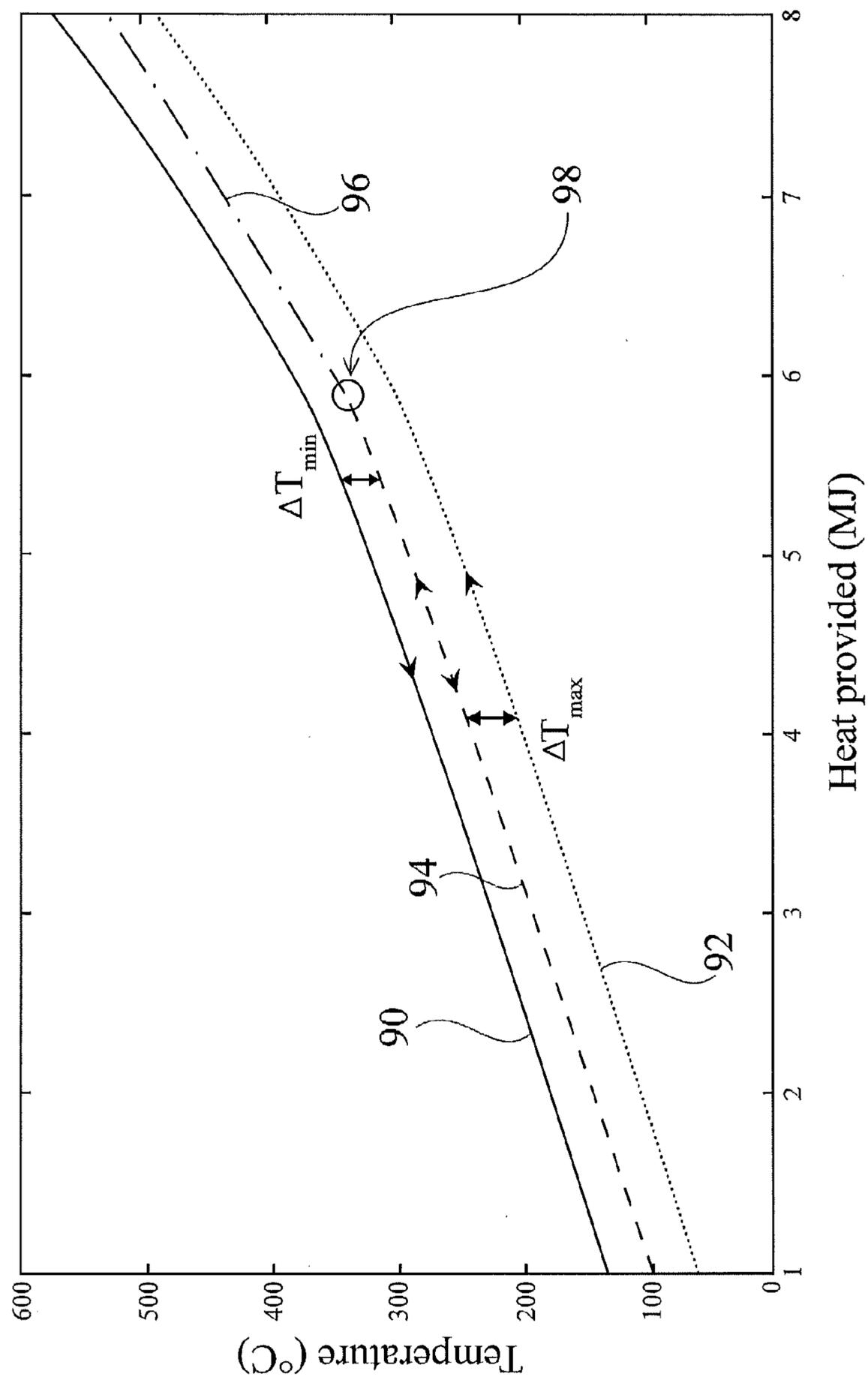


Fig. 4

THERMOELECTRIC ENERGY STORAGE SYSTEM

RELATED APPLICATIONS

[0001] This application claims priority as a continuation application under 35 U.S.C. §120 to PCT/EP2011/060323, which was filed as an International Application on Jun. 21, 2011 designating the U.S., and which claims priority to European Application 10167030.5 filed in Europe on Jun. 23, 2010. The entire contents of these applications are hereby incorporated by reference in their entireties.

FIELD

[0002] The present disclosure relates to the storage of electric energy. More particularly, the present disclosure relates to a thermoelectric energy storage system, a method for storing and retrieving electrical energy with a thermoelectric energy storage system, and usage of a zeotropic mixture as a working fluid.

BACKGROUND INFORMATION

[0003] With thermoelectric storage systems, the useful concept of storing electrical energy is implemented by converting electric energy into thermal energy that may be stored for a required time (charging of the storage). The electric energy may be restored by reversed conversion from thermal energy into mechanical work and subsequently into electricity (discharging of the storage).

[0004] The storage of electrical energy may become more and more important in the future. Base load generators such as nuclear power plants and generators with stochastic, intermittent energy sources, such as wind turbines and solar panels, may generate excess electrical power during times of low power demand. Large-scale electrical energy storage systems may be a means of diverting this excess energy to times of peak demand and balance the overall electricity generation and consumption.

[0005] There may be several possibilities of storing heat. Thermal energy may be stored in the form of sensible heat via a change in temperature or in the form of latent heat via a change of phase or a combination of both. The storage medium for the sensible heat may be a solid, liquid or a gas. The storage medium for the latent heat occurs via a change of phase and may involve any of these phases or a combination of them in series or in parallel.

[0006] One of the most important characteristics of a thermoelectric storage system may be the round-trip efficiency. The round-trip efficiency of a thermoelectric storage system may be defined as the percentage of electrical energy that can be discharged from the storage in comparison to the electrical energy used to charge the storage, provided that the state of the energy storage system after discharging returns to its initial condition before charging of the storage. The round-trip efficiency may be increased when thermodynamic reversibility factors are maximized. However, it may be important that all electric energy storage technologies inherently have a limited round-trip efficiency due to thermodynamic limitations. Thus, for every unit of electrical energy used to charge the storage, only a certain percentage may be recovered as electrical energy upon discharge. The rest of the electrical energy is lost. If, for example, the heat being stored in a thermoelectric storage system is provided through resistor heaters, it has approximately 40% round-trip efficiency.

[0007] The charging cycle of a thermoelectric storage system may be referred to as a heat pump cycle, and the discharging cycle of a thermoelectric storage system may be referred to as a heat engine cycle. In a thermoelectric storage system, heat may have be transferred from a hot working fluid to a thermal storage medium during the heat pump cycle and back from the thermal storage medium to the working fluid during the heat engine cycle. A heat pump may require work to move thermal energy from a cold source to a warmer heat sink. Since the amount of energy deposited at the hot side may be greater than the work required by an amount equal to the energy taken from the cold side, a heat pump may multiply the heat as compared to resistive heat generation. The ratio of heat output to work input may be called a coefficient of performance (COP) with a value larger than one. In this way, the use of a heat pump will increase the round-trip efficiency of a thermoelectric storage system.

[0008] The efficiency of a thermoelectric storage system is limited for various reasons rooted in the second law of thermodynamics. Firstly, the conversion of heat to mechanical work in a heat engine is limited due to the Carnot efficiency. Secondly, the coefficient of performance of any heat pump declines with increased difference between input and output temperature levels. Thirdly, any heat flow from a working fluid to a thermal storage and vice versa requires a temperature difference in order to happen. This fact inevitably degrades the temperature level and thus the capability of the heat to do work.

[0009] Usually, a thermoelectric storage system has a working fluid circuit with which heat is transferred with a working fluid to a thermal storage medium (or vice versa) via one or more heat exchangers. The transfer of heat over large temperature differences is a thermodynamic irreversibility factor. This means that the larger the temperature differences between the working fluid and the thermal storage medium in the heat exchangers are, the lower the round-trip efficiency will be. In order to minimize the maximal temperature difference, relatively large heat exchangers may be constructed or phase change materials can be used for thermal storage. However, these solutions may result in high costs and may generally not be practical.

[0010] A reduction of heat transfer losses may be of particular importance in the considered application of thermal energy storage with charging based on a heat pump cycle. In such an application, any increase of heat exchange temperature losses during charging and discharging may directly translate into a loss of useful work and reduction of the round trip efficiency of the system.

[0011] For example, one solution to overcome at least some of the above mentioned problems may be the transcritical thermoelectric storage system introduced by the applicant. When a heat pump system runs transcritical, the working fluid on the high pressure side of the system does not change its phase from vapor to liquid while passing through the heat rejecting heat exchanger. Therefore, in a transcritical cycle, the heat rejecting heat exchanger may operate like a gas cooler, rather than as an isothermal condenser. This may enable the storage of the rejected heat by means of sensible heat storage (heat storage based on a temperature change rather than on a phase change) through a known fluid-to-fluid heat exchanger. This may be advantageous since the technology for fluid-to-fluid heat exchangers is advanced and enables very small approach temperatures in compact volumes resulting in high efficiencies at reduced costs.

[0012] However, if the cooling effect of the heat pump operation on the low pressure side is also desired to be utilized in parallel to create a cool thermal storage, the transcritical cycle usually has a known isothermal evaporator and therefore may have to be used to charge a PCM (phase change material) thermal storage such as ice at constant temperature. Ice is an excellent thermal storage medium but ice storage systems have to use heat exchangers which have to grow ice on the heat transfer surfaces (low heat transfer efficiency) or have to limit ice formation per heat exchanger pass (large flow rates) to prevent clogging.

[0013] Another disadvantage of known ice storage systems may be that these systems usually cannot exceed an ice content of 50%, which means that half of the thermal storage is unused, increasing both the capital cost of the system and also its footprint.

[0014] Another solution to thermoelectric storage system design without isothermal evaporation or condensation is to use the reverse Brayton cycle for charging and the known Brayton cycle for discharging of the thermal storage. The working fluid of the Brayton cycle is always in the gas phase and therefore all heat transfer steps of a “Brayton cycle thermoelectric storage system” can be matched with heat transfer to a sensible heat thermal storage. The downside is that due to its high back-work ratio, a Brayton cycle thermoelectric storage system may suffer from increased losses in the heat pump expansion and heat engine compression steps compared to other thermoelectric storage system designs. These losses can be counteracted by pushing the operating temperatures of the cold side and hot side of the cycles respectively to very low and very high values, which in turn may make it necessary to store the sensible heat to solid materials such as rocks or sand via special purpose contraptions eventually losing the potential benefit of sensible heat storage through a known fluid-to-fluid heat exchanger.

[0015] It is known that zeotropic refrigerant mixtures may increase the energy efficiency of certain refrigeration and heat pump equipment under optimized conditions.

[0016] For heat engine operation, the Kalina cycle was proposed to be used in power stations. Because temperature differences across a heat exchanger may be more uniform with the Kalina cycle compared to classical pure working fluid Rankine cycle, the system efficiency increases around 10% for a normal power station, but for special low-temperature applications by more than 30%.

[0017] However, in thermoelectric energy storage systems, the heat pump cycle and the heat engine cycle have to be optimized with respect to each other. Thus, it may be problematic to apply the optimization principles of a refrigerator system or a heat engine system to a thermoelectric storage system, because the optimization of the one cycle may degrade the efficiency of the other cycle.

[0018] A major hurdle in achieving high efficiencies in thermoelectric storage system operation may be large temperature differences between the hot side and cold side in heat exchangers.

[0019] Minimizing temperature differences in heat exchangers may become especially challenging when latent heat storage systems are used and the heat transfer involves conduction through the solid phase of the storage material which might be the case with the above mentioned transcritical thermoelectric storage system. However, such phase change material based thermal storage systems are an optimal

way to match temperature profiles of thermoelectric storage system thermodynamic cycles involving isothermal evaporation or condensation steps.

[0020] In view of the above, exemplary embodiments of the present disclosure provide a thermoelectric storage system which does not have to rely on isothermal evaporation or isothermal condensation of the working fluid.

SUMMARY

[0021] An exemplary embodiment of the present disclosure provides a thermoelectric energy storage system for storing electrical energy by transferring thermal energy to a thermal storage in a charging cycle, and for generating electricity by retrieving the thermal energy from the thermal storage in a discharging cycle. The thermoelectric energy storage includes a working fluid circuit configured to circulate a working fluid through a heat exchanger, and a thermal storage conduit configured to transfer a thermal storage medium from a thermal storage tank through the heat exchanger. The working fluid includes a zeotropic mixture.

[0022] An exemplary embodiment of the present disclosure provides a method for storing and retrieving electrical energy. The exemplary method includes storing electrical energy by transferring thermal energy to a thermal storage in a charging cycle, and retrieving electrical energy by changing the thermal energy from the thermal storage into mechanical energy in a discharging cycle. The charging cycle and the discharging cycle include transferring heat between a working fluid and a thermal storage medium. The working fluid is in a mixed vapor and liquid phase and has continuously rising or continuously falling temperature during heat transfer due to the working fluid including a zeotropic mixture.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] Additional refinements, advantages and features of the present disclosure are described in more detail below with reference to exemplary embodiments illustrated in the drawings, in which:

[0024] FIG. 1a shows a simplified schematic diagram of a charging cycle of a thermoelectric storage system according to an exemplary embodiment of the present disclosure;

[0025] FIG. 1b shows a simplified schematic diagram of a discharging cycle of a thermoelectric storage system according to an exemplary embodiment of the present disclosure;

[0026] FIG. 2 shows a T-S-diagram of a thermoelectric storage system according to an exemplary embodiment of the present disclosure;

[0027] FIG. 3a shows a simplified diagram of a heat storage for a thermoelectric storage system according to an exemplary embodiment of the present disclosure during charging;

[0028] FIG. 3b shows a simplified diagram of the heat storage of FIG. 3a during discharging, according to an exemplary embodiment of the present disclosure; and

[0029] FIG. 4 shows a heat flow-temperature diagram of the heat transfer in a heat exchange according to FIG. 3a or FIG. 4a in accordance with an exemplary embodiment of the present disclosure.

DETAILED DESCRIPTION

[0030] Exemplary embodiments of the present disclosure provide an efficient thermoelectric energy storage having a high round-trip efficiency and a minimal approach tempera-

ture, while minimizing the amount of required thermal storage medium, and also minimizing the cost.

[0031] An exemplary embodiment of the present disclosure provides a thermoelectric energy storage system for storing electrical energy by transferring thermal energy to a thermal storage in a charging cycle, and for generating electricity by retrieving the thermal energy from the thermal storage in a discharging cycle.

[0032] According to an exemplary embodiment of the present disclosure, the thermoelectric energy storage system includes a working fluid circuit configured to circulate a working fluid through a heat exchanger, and a thermal storage conduit configured to transfer a thermal storage medium from a thermal storage tank through the heat exchanger. The working fluid includes a zeotropic mixture.

[0033] In other words, a zeotropic mixture is used as a working fluid for the thermoelectric energy storage system. The zeotropic mixture may be selected such that the temperature of the working fluid in the heat exchanger is continuously changing (e.g., rising or falling) from a first temperature to a second temperature.

[0034] For a zeotropic mixture the concentrations of the liquid phase and the vapour phase are never equal at different temperatures. This creates a temperature glide during phase change (at which point the concentrations of the vapour and the liquid are continually changing). Thus in a T-S-diagram equal pressure lines are increasing and thus, the temperature difference between the working fluid and the storage fluid in a heat exchanger can be made very small. For example, the system may be controlled such that the temperature of the working fluid in the heat exchanger is rising like the temperature of the storage fluid in the heat exchanger.

[0035] The advantage of increasing constant pressure lines in the T-S-diagram may be better understood with respect to the Lorenz cycle that also has two such processes with increasing slope. Similar to the Carnot cycle that optimizes heat engines operating between two constant-temperature sources, the Lorenz cycle optimizes heat engines operating between two gliding-temperature sources by adjusting the thermal capacity of the working fluid to that of the finite-capacity sources. That is, the Lorenz cycle has four processes like the Carnot cycle that for a heat engine are: isentropic compression, heating at constant thermal capacity matching that of the heat source (and its temperature variation), isentropic expansion, and cooling at constant thermal capacity matching that of the heat sink (and its temperature variation). Similar inverse cycles apply for refrigeration and heat pumping. However, for thermodynamic cycles operating at two constant pressure levels with a change of phase, realization of a Lorenz cycle with a pure working fluid is not possible.

[0036] From another perspective, an exemplary embodiment of the present disclosure combines the sensible heat storage possibility of a Brayton cycle thermoelectric storage system with the low back-work ratio of a Rankine cycle thermoelectric storage system in one thermodynamic machine.

[0037] If the working fluid is a zeotropic mixture, a constant pressure phase change takes place with a variation of temperature, with the temperature variation between the saturated vapor and the saturated liquid conditions being a function of the composition of the mixture and the components of the mixture.

[0038] In other words, the zeotropic mixture may have the advantage that the temperature differences between the work-

ing fluid and the thermal storage medium may be made very small. For example, the flow of the working fluid through the heat exchanger may be controlled (for examples through a valve before or after the heat exchanger) such that the temperature difference at any point of contact between the thermal storage medium and the working fluid in the heat exchanger, and during both charging and discharging cycles, is less than 50° C. For example, this temperature difference is below 10° C., or even below 3° C.

[0039] According to an exemplary embodiment of the present disclosure, a reversible thermodynamic machine is used to store electrical energy by utilizing an electrically driven vapor compression heat pump cycle with a zeotropic mixture as the working fluid to provide heat into a hot thermal storage while removing heat from a cold thermal storage, where the heat provided to the hot thermal storage is used to increase the temperature of the hot thermal storage and the heat removed from the cold thermal storage is used to reduce the temperature of the cold thermal storage.

[0040] According to an exemplary embodiment of the present disclosure, the hot and cold thermal storage materials are fluids such as liquids, which are pumped from their initial temperature states into heat exchangers, for example for counter current heat exchange, with the zeotropic working fluid mixture undergoing condensation during heat provision to the hot storage fluid and evaporation during heat removal from the cold storage fluid. For retrieval of the electrical energy back from the hot and cold thermal storage the thermodynamic machine may be operated in reverse and heat is removed from the hot thermal storage and added to the cold thermal storage.

[0041] According to an exemplary embodiment of the present disclosure, the temperature profiles of both the hot and cold thermal storage fluids are matched with the zeotropic working fluid mixture. The matching may be done very closely by utilizing very efficient counter flow heat exchangers hence reducing the irreversibility and increasing the roundtrip efficiency of electrical energy storage.

[0042] Carbon dioxide is by far the most benign working fluid available today. Other candidates to add to carbon dioxide to achieve the desired behavior described in this disclosure disclosure are hydrocarbons. According to an exemplary embodiment of the present disclosure, a zeotropic mixture may include carbon dioxide and hydrocarbons, for example, 50% carbon dioxide and 50% butane.

[0043] The constituent components of the working fluid mixture may be chosen to realize different operating conditions but in general the thermodynamic behavior of the two or more components may have to be close enough to ensure proper solubility and to avoid unwanted separation into multiple liquid phases while being different enough to ensure a significant glide during the evaporation and condensation phases. The higher the temperature difference between the bubble and dew points of the mixture the more significant the temperature glide and therefore the lower the required flow of the thermal storage fluids. The composition of the working fluid mixture may also impact on the thermodynamic behavior. When two components are used together as a working fluid mixture the glide is largest when equal mass fractions are used. As the fraction of one of the components is increased the behavior of the mixture will start approaching the behavior of the component with the larger mass fraction eventually becoming a single component working fluid when the fraction is increased to 1. These guidelines are useful when the

components of the working fluid mixture are forming a near ideal mixture. The behavior of mixtures may be unpredictable when they show non-ideal behavior but it may be possible to realize a very efficient thermoelectric storage system also with non-ideal mixtures.

[0044] According to an exemplary embodiment of the present disclosure, the charging cycle and/or the discharging cycle may be executed transcritically. This may mean that the heat exchanging step at the hot storage side in the T-S-diagram may be above the critical point dome of the phase envelope leading to a transcritical cycle. This possibility may be used if higher temperatures are desired at the hot side or if the glide on the hot side is desired to be increased further to minimize the mass of required storage fluid.

[0045] A large temperature range may be covered by thermal storage materials in liquid phase. According to an exemplary embodiment of the present disclosure, ammonia and water mixtures may be used as the cool side thermal storage fluids, which, for example, may go from as low as -100°C . and can go as high as $+50^{\circ}\text{C}$. Other possibilities for hot and cold storage media are water at atmospheric pressure without additives, which can cover from 0 to 100°C ., thermal oils (e.g. Dowtherm J), which can cover a very wide range -80 to 315°C ., and molten salt mixtures, which can go as high as 566°C .

[0046] According to an exemplary embodiment of the present disclosure, the storage tank includes an intermediate storage tank, wherein the heat exchanger has a stream splitter configured to divide (or join) the flow of the thermal storage medium from a first (or second) storage tank into a flow to the intermediate storage tank and to a second (or first) storage tank. In this way, even in the case when the temperature of the working fluid is not continuously rising or falling in the heat exchanger, the temperature difference, at any point of contact between the thermal storage medium and the working fluid in the heat exchanger, and during both charging and discharging cycles, may be adjusted to be very small, for example below 3°C .

[0047] An exemplary embodiment of the present disclosure provides a method for storing and retrieving electrical energy.

[0048] According to an exemplary embodiment of the present disclosure, the method includes the steps of storing electrical energy by transferring thermal energy to a thermal storage in a charging cycle, and retrieving electrical energy by changing the thermal energy from the thermal storage into mechanical energy in a discharging cycle.

[0049] According to an exemplary embodiment of the present disclosure, the charging cycle and the discharging cycle include the steps of transferring heat between a working fluid and a thermal storage medium, wherein the working fluid is in a mixed vapor and liquid phase and has continuously rising or continuously falling temperature during heat transfer, because the working fluid includes a zeotropic mixture.

[0050] It is to be understood that features of the method as described in the above and in the following may be features of the system as described in the above and in the following.

[0051] If technically possible but not explicitly mentioned, combinations of exemplary embodiments of the present disclosure described above and in the following may be embodiments of the method and the system.

[0052] These and other aspects of the present disclosure will be apparent from and elucidated with reference to the exemplary embodiments described hereinafter.

[0053] In principle, identical parts are provided with the same reference symbols in the drawings.

[0054] FIGS. 1a and 2a show exemplary embodiments of a thermoelectric storage system 10. FIG. 1a shows the charging cycle system or heat pump cycle system 12, and FIG. 1b the discharging cycle system or heat engine cycle system 14.

[0055] The thermoelectric storage system 10 is adapted for performing a charging cycle with the system 12, during which electrical energy to be stored is converted into heat, and for performing a discharging cycle with the system 14, during which the thermal energy is retrieved from the storage and converted back into electricity. Furthermore the charging cycle can be followed by a storage period during which neither the charging nor the discharging cycle has to take place.

[0056] With respect to FIG. 1a, the thermoelectric charging cycle system 10 includes a working fluid circuit 16, which includes a zeotropic mixture as working fluid. The working fluid is compressed to a higher pressure by a compressor 18 and injected into a heat exchanger 20 for exchanging heat with a hot storage 22. The heat exchanger 20 is a counter flow heat exchanger in which a hot storage medium (e.g., a liquid) is transferred in a thermal storage conduit 24 from a first hot storage tank 26 to a second hot storage tank 28. After leaving the heat exchanger 20, the working fluid is expanded to lower pressure with expansion device 30 and enters a heat exchanger 32 for heat exchange with a cold storage 32. The heat exchanger 32 may be a counter flow heat exchanger in which a cold storage medium (for example a liquid) is transferred in cold storage conduit 36 from a first cold storage tank 38 to a second cold storage tank 40.

[0057] With respect to FIG. 1a, except the storage tanks 22, 26, 38, 40 all other components of the discharging cycle system 14 may be different from the components of the charging cycle system 12. However, it may be a cost advantage to use as many of them as possible in both systems 12 and 14. For example, the compressor 18 may be used as turbine 42.

[0058] The turbine 20 is used for generating electrical energy out of the heated working fluid by expanding the working fluid to a lower pressure. After leaving turbine 20, the working fluid is condensed in heat exchanger 32 by discharging heat to the cold storage system 34 and pumped to higher pressure by pump 44. After that the working fluid is heated with heat exchanger 20 to be injected into turbine 42.

[0059] During discharging, the working fluid, the hot storage medium and the cold storage medium are circulating in the reverse direction with respect to charging of the system 10.

[0060] The operation of the thermoelectric storage system 10 will be explained more detailed with reference to the T-S-diagram of FIG. 3. FIG. 3 shows a state change diagram of the thermoelectric storage system 10 with a working fluid composition of 50% carbon dioxide and 50% butane as zeotropic mixture.

[0061] In the diagram of FIG. 2, the vapor dome of the working fluid is indicated by line 46. Left of the vapor dome 46 the working fluid is in its liquid phase, right of the vapor dome 46 the working fluid is in its gas phase. Below curve 46, the working fluid is in a mixed gas/liquid state. On top of the vapor dome, the critical point 48 of the working fluid is indicated.

[0062] During the charging cycle, the charging cycle system 12 of FIG. 1a follows the thermodynamic cycle 50 counter-clockwise.

[0063] For charging of the storages **22**, **34** the zeotropic mixture at its bubble point is first evaporated at constant pressure **P1** (for example 10 bar) in the counter current heat exchanger **32**. This corresponds to going from point A to point B in the T-S-diagram. As may be derived from the diagram, the temperature of the working fluid is continuously rising during phase change from about -20°C . to about 40°C .

[0064] The zeotropic mixture vapor is then compressed with the compressor **18** to a higher pressure level **P2** (for example 35 bar). The compression corresponds to going from point B to point C in the T-S-diagram and it is the main point where electrical energy to drive the compressor **18** is injected into the thermoelectric energy storage system **10**.

[0065] According to an exemplary embodiment, the thermoelectric energy storage system **10** may include a compressor **18** for compressing the working fluid (e.g., the zeotropic mixture) in vapor phase from a lower pressure to a higher pressure during the charging cycle, such that electrical energy for driving the compressor is injected into the thermal energy storage system.

[0066] Following the compression, the zeotropic mixture is cooled at constant pressure **P2** in the counter current heat exchanger **20** corresponding to going from point C to point D in the T-S-diagram. During this cooling process, the superheated zeotropic mixture from the compressor **18** is first cooled to its dew point **50**, followed by condensation and subcooling of the liquid phase. At the pressure **P2** the temperature of the working fluid is continuously decreasing during phase change from about 90°C . to about 10°C . Point D is to the left of the boiling curve **46**. The subcooled zeotropic mixture in liquid phase is then expanded back to the pressure level **P1** via an expansion device **30**, which can be a work recovering expander or a thermostatic expansion valve. The expansion process corresponds to going from point D back to point A in the TS diagram. Point D and point A are very close to each other because the liquid phase of the working fluid is nearly incompressible.

[0067] According to an exemplary embodiment, the thermoelectric energy storage system **10** may include an expansion device (e.g., an expansion valve) **30** for expanding the working fluid (e.g., the zeotropic mixture) in liquid phase from a higher pressure to a lower pressure during the charging cycle.

[0068] It is important to note that the extent of subcooling has to be controlled to prevent vapor formation or flashing at the end of the expansion process to ensure reversible operation during the discharging cycle. This controlling may be performed by a control device **60** connected to a sensor for measuring the temperature of the working fluid at the end of the heat rejection process after heat exchanger **20** and adjusting the thermal storage flow rate. This may be done by changing the pump speed if a variable speed pump **30** is used or a valve located on the thermal storage fluid flow line.

[0069] During the operation of the charging cycle system **12**, external heat is provided to carry out the evaporation in the heat exchanger **32**, and heat is removed to carry out the cooling in the heat exchanger **20**. Since both the evaporation in the heat exchanger **32** and cooling (e.g., desuperheating-condensation-subcooling) in the heat exchanger **20** are constant pressure but variable temperature processes they can be closely matched with thermal storage fluids undergoing cooling in the heat exchanger **32** and heating in the heat exchanger **20**. This may also be controlled by the control device **60**.

[0070] In FIG. **1a**, the cold side thermal storage fluid is taken from tank **38** at a temperature **T1**, passed through the heat exchanger **32** providing the heat of evaporation for the zeotropic working fluid mixture, and placed at tank **40** at a temperature **T2**, where **T1** is greater than **T2**. Similarly the hot side thermal storage fluid is taken from tank **26** at a temperature **T3**, passed through the heat exchanger **20** absorbing the heat released by the zeotropic working fluid mixture, and placed at tank **28** at a temperature **T4**, where **T4** is greater than **T3**. For heat exchange, the temperature difference of the working fluid is a bit lower (for heating the working fluid) or a bit higher (for cooling the working fluid) as the temperature of the storage medium.

[0071] The temperature difference may be between 1°C . to 3°C ., between 3°C . and 10°C . or much larger. The temperature difference may be chosen by a cost-benefit analysis. I.e. Small temperature differences such as 1°C . to 3°C . may result in high efficiency (for example around 75%) but maybe also high costs due to large heat exchangers, a larger temperature difference such as 3°C . to 10°C . may result in low efficiency (for example around 40%) but maybe also low costs due to small heat exchangers.

[0072] The discharging is the reversed operation of the charging process. The discharging cycle system **14** of FIG. **1b** follows the cycle **50** in FIG. **3** clockwise.

[0073] The zeotropic working fluid mixture at its bubble point is first pumped via a pump **44** from a pressure **P3** (for example 10 bar) to a higher pressure **P4** (for example 35 bar), corresponding to going from point A to point D in the T-S-diagram. Due to the pumping there may be a minimal temperature rise. The zeotropic mixture then enters the heat exchanger **20**. Here the zeotropic mixture is heated to its new bubble point at the elevated pressure level **P4**, subsequently evaporated and superheated at constant pressure **P4**. These processes correspond to going from point D to point C in the T-S-diagram.

[0074] According to an exemplary embodiment, the thermoelectric energy storage system **10** may include a pump **44** for pumping the working fluid from a lower pressure to a higher pressure during the discharging cycle.

[0075] Next, the superheated zeotropic vapor mixture is expanded in the turbine **42** from the higher pressure level **P4** to the initial pressure level **P3**. This step corresponds to going from point C to point B in the T-S-diagram and it is the main point where electrical energy generated at the turbine **42** is retrieved from the thermal energy storage **10**. Finally, the expanded zeotropic vapor mixture is condensed at constant pressure **P3** in the heat exchanger **32** back to a liquid in its bubble point to be pumped again to complete the heat engine cycle. This final step corresponds to going from point B to point A in the T-S-diagram.

[0076] According to an exemplary embodiment, the thermoelectric energy storage system **10** may include a turbine **42** for expanding the working fluid from a higher pressure to a lower pressure level for generating electrical energy during the discharging cycle.

[0077] During the operation of the discharging cycle system **14**, external heat is provided to carry out the heating, evaporation, and superheating in the heat exchanger **20**, and heat is removed to carry out the condensation in the heat exchanger **32**. Since the heating, evaporation, and superheating in the heat exchanger **20** and condensation in the heat exchanger **32** are constant pressure but variable temperature

processes, they can be closely matched with thermal storage fluids undergoing cooling in the heat exchanger 20 and heating in the heat exchanger 32.

[0078] In FIG. 1*b*, the cold side thermal storage fluid is taken from tank 40 at the temperature T2, passed through the heat exchanger 32 absorbing the heat of condensation for the zeotropic working fluid mixture, and placed at tank 38 at the temperature T1, where T1 is greater than T2. Similarly the hot side thermal storage fluid is taken from tank 28 at the temperature T4, passed through the heat exchanger 20 providing the energy to heat, evaporate, and superheat the zeotropic working fluid mixture, and placed at tank 26 at the temperature T3, where T4 is greater than T3.

[0079] Although depicted in FIG. 1 and FIG. 1*b*, a thermal storage system without one of the storages 22 and 34 may also be an exemplary embodiment of the present disclosure, for example the thermal storage system with the hot storage 22 or the thermal storage system with the cold storage 34. According to an exemplary embodiment, the cold storage 34 can be replaced by a large thermal reservoir such as a river or a lake, and according to another exemplary embodiment, the hot storage can be replaced by a waste heat source greater than the ambient.

[0080] To summarize, the system 10 may include a hot storage tank 22 and the thermal storage conduit includes a hot storage conduit 24 for transferring a hot storage medium between a first hot storage tank 26 and a second hot storage tank 28 through the heat exchanger 20. Further, the thermal storage tank of the system 10 may include a cold storage tank 34, and the thermal storage conduit includes a cold storage conduit 36 for transferring a cold storage medium between a first cold storage tank 38 and a second cold storage tank 40 through the heat exchanger 32.

[0081] FIGS. 1*a* and 1*b* are simple versions of practical implementations. For example, instead of the heat exchangers 20, a split stream heat exchanger 70 as shown in FIGS. 3*a* and 3*b* may be used. With such a heat exchanger 70, the varying heat capacity and hence the slope of temperature variation of the zeotropic working fluid mixture in the heat exchanger 70 may be compensated by varying the flow rate of the thermal storage fluid via an intermediate storage tank in addition to tanks 26 and 28. Additionally or alternatively, also the heat exchanger 32 may be replaced by heat exchanger 70.

[0082] The heat storage system 72 system includes a heat exchanger 70 having an internal stream splitter 72. For example, the heat exchanger 70 may include two basic heat exchangers interconnected by a stream splitter 72. The zeotropic mixture 74 as working fluid circulates through these components as indicated by the solid line with arrows in FIGS. 3*a* and 3*b*. Further, a cold-fluid storage tank 76, an intermediate storage tank 78 and a hot-fluid storage tank 80 containing a fluid thermal storage medium 82 are connected together via the heat exchanger 70.

[0083] During heat transfer from the working fluid 74 to the thermal storage medium 82, the thermal storage medium, represented by the dashed line in FIG. 3*a*, is flowing from the cold-fluid storage tank 76 through the heat exchanger 72 into the hot-fluid storage tank 80 and partially into the intermediate storage tank 78. The temperature of the thermal storage medium is detected on either side of the stream splitter 72 by temperature sensors such as thermocouples or resistive sensors coupled to the control device 60. The heat discarded from the working fluid 74 into the thermal storage medium 82 is stored in the form of sensible heat.

[0084] Following detection of the temperature of the thermal storage medium 82 on either side of the stream splitter 72, the flow rate of the thermal storage medium 82 into the intermediate storage tank 78 and the hot-fluid storage tank 80 is adjusted. This is achieved by means of appropriate piping and valve arrangements controlled by control device 60. The initial valve openings are determined according to the desired temperature profile and the valve openings are fine-tuned during operation according to the temperature measurements.

[0085] The heat exchanger system 72 is designed such that the position of the stream splitter 72 within the heat exchanger 70 coincides with the point of the heat exchanger 70 at which the storage medium 82 is at the temperature level of the intermediate storage tank 78. The diverted stream is stored in the intermediate tank 78. The second stream continues through the rest of the heat exchanger 70 into the hot storage tank 80.

[0086] As shown in FIG. 3*b*, during heat transfer from the thermal storage medium 82 to the working fluid 74, the thermal storage medium 82 is pumped from the hot-fluid storage tank 80 and from the intermediate storage tank 78 into the cold-fluid storage tank 76. The temperature of the thermal storage medium 82 is detected and monitored on either side of the internal stream splitter 18 by the control device 60. The flow rate of the streams of the thermal storage medium 82 within the heat exchanger 70 can be controlled and modified to optimize round-trip efficiency of the thermoelectric storage system 10 with the control device 60. This will be explained more detailed with respect to FIG. 4.

[0087] Summarized, the thermoelectric energy storage system 10 may include an intermediate storage tank 78, wherein the heat exchanger 70 has a stream splitter 72 adapted to divide or join the flow of the thermal storage medium from a first or second storage tank 76, 80 into a flow to the intermediate storage tank 78 and to the second or first storage tank 76, 80.

[0088] FIG. 4 shows a heat flow-temperature diagram of the heat transfer in the heat exchanger 70 during heating and cooling of the working fluid. The solid line 90 indicates the temperature profile of the working fluid 74 during cooling. The dotted line 92 indicates the temperature profile of the working fluid 74 during heating. The lines 90 and 92 are not straight lines, since in general there is no linear interrelationship between the inner heat and the temperature of the zeotropic mixture 74.

[0089] The dashed line 94 and dot-dashed line 96 indicate the temperature profile of the thermal storage medium 82 during both processes. The arrows indicate the flow directions in the heat exchanger 70. Heat can only flow from a higher to a lower temperature. Consequently, the characteristic profile 90 for the working fluid 74 during cooling is above the characteristic profile 94 for the thermal storage medium 82, which in turn has to be above the characteristic profile 92 for the working fluid 74 during heating.

[0090] The stream splitting/joining point 98 (due to the stream splitter 72) is indicated at a thermal storage medium temperature of approximately 340° C. On the right hand side of this point on the graph, the gradient of the temperature profile 94, 96 increases. This relatively increased gradient is a consequence of a different flow rate of the thermal storage medium 82 after the stream splitting/joining point 98.

[0091] In this particular embodiment, the temperature of the cold-fluid storage tank 76 is approximately 100° C., the temperature of the intermediate storage tank 78 is approxi-

mately 340° C., and the temperature of the hot-fluid storage tank **80** is approximately 520° C. A minimum approach temperature of around 25° C. is assumed (e.g., the minimum temperature difference between the two fluids exchanging heat is 25° C.). In such an embodiment, the flow rates of the thermal storage medium between the cold-fluid storage tank and the stream splitter, and between the stream splitter and hot storage tank, are controlled such that they have a ratio approximately 2:1.

[0092] It can be seen from FIG. 4 that the isobars **90**, **92** representing the working fluid closely follow the form of the isobar **94** representing the thermal storage liquid **82**. Thus, the temperature differences at any point of contact between the thermal storage medium and the working fluid in the heat exchanger, and during both charging and discharging cycles (denoted ΔT_{min} and ΔT_{max}), are minimized. Advantageously, a minimization of the temperature differences is thereby facilitated with the heat storage system **72**, maximizing the roundtrip efficiency of the thermoelectric storage system **10**, regardless of the size of the heat exchanger.

[0093] The skilled person will be aware that, a heat flow-temperature diagram of the heat transfer in the heat exchanger may have a different form in an alternative embodiment of the present disclosure. For example, it is possible the gradient of the working fluid isobar on the left of the stream splitting point is greater than the gradient of the working fluid isobar to the right of the splitting point. This would indicate that the streams output from the cold storage tank and the intermediate tank are joined at the stream splitter during heating, and divided at the stream splitter during cooling.

[0094] It will be appreciated by those skilled in the art that the present invention can be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The presently disclosed embodiments are therefore considered in all respects to be illustrative and not restricted. The scope of the invention is indicated by the appended claims rather than the foregoing description and all changes that come within the meaning and range and equivalence thereof are intended to be embraced therein.

What is claimed is:

1. A thermoelectric energy storage system for storing electrical energy by transferring thermal energy to a thermal storage in a charging cycle, and for generating electricity by retrieving the thermal energy from the thermal storage in a discharging cycle, the thermoelectric energy storage system comprising:

a working fluid circuit configured to circulate a working fluid through a heat exchanger; and

a thermal storage conduit configured to transfer a thermal storage medium from a thermal storage tank through the heat exchanger,

wherein the working fluid includes a zeotropic mixture.

2. The thermoelectric energy storage system of claim **1**, wherein the zeotropic mixture is selected such that the temperature of the working fluid in the heat exchanger changes from a first temperature to a second temperature.

3. The thermoelectric energy storage system of claim **1**, wherein the heat exchanger includes a counter flow heat exchanger.

4. The thermoelectric energy storage system of claim **1**, wherein the flow of the working fluid through the heat exchanger is controlled such that a temperature difference between the working fluid and the thermal storage medium is less than 50° C.

5. The thermoelectric energy storage system of claim **1**, comprising:

a valve configured to control the flow in the working fluid circuit.

6. The thermoelectric energy storage system of claim **1**, wherein the thermal storage tank includes a hot storage tank, and the thermal storage conduit includes a hot storage conduit configured to transfer a hot storage medium between a first hot storage tank and a second hot storage tank through the heat exchanger.

7. The thermoelectric energy storage system of claim **1**, wherein:

the storage tank includes an intermediate storage tank; and the heat exchanger includes a stream splitter configured to divide the flow of the thermal storage medium from a first storage tank into a flow to the intermediate storage tank and to a second storage tank.

8. The thermoelectric energy storage system of claim **1**, comprising:

a compressor configured to compress the working fluid in vapor phase from a lower pressure to a higher pressure during the charging cycle, such that electrical energy for driving the compressor is injected into the thermal energy storage system.

9. The thermoelectric energy storage system of claim **1**, comprising:

an expansion device configured to expand the working fluid in liquid phase from a higher pressure to a lower pressure during the charging cycle.

10. The thermoelectric energy storage system of claim **1**, comprising:

a pump configured to pump the working fluid from a lower pressure to a higher pressure during the discharging cycle.

11. The thermoelectric energy storage system of claim **1**, comprising:

a turbine configured to expand the working fluid from a higher pressure to a lower pressure level for generating electrical energy during the discharging cycle.

12. A method for storing and retrieving electrical energy, the method comprising:

storing electrical energy by transferring thermal energy to a thermal storage in a charging cycle; and

retrieving electrical energy by changing the thermal energy from the thermal storage into mechanical energy in a discharging cycle,

wherein the charging cycle and the discharging cycle comprise transferring heat between a working fluid and a thermal storage medium, and

wherein the working fluid is in a mixed vapor and liquid phase and has continuously rising or continuously falling temperature during heat transfer due to the working fluid including a zeotropic mixture.

13. The method of claim **12**, comprising:

controlling the flow through the heat exchanger such that a temperature difference between the working fluid and the thermal storage medium is less than at least one of 50° C., 10° C. and 3° C.

14. The method of claim **12**, comprising:

dividing the flow of the thermal storage medium in the heat exchanger such that heat transfer in the heat exchanger has two different rates.

15. The thermoelectric energy storage system of claim **2**, wherein the zeotropic mixture is selected such that a tempera-

ture of the working fluid in the heat exchanger continuously changes from a first temperature to a second temperature.

16. The thermoelectric energy storage system of claim **4**, wherein the flow of the working fluid through the heat exchanger is controlled such that the temperature difference between the working fluid and the thermal storage medium is less than 10° C.

17. The thermoelectric energy storage system of claim **4**, wherein the flow of the working fluid through the heat exchanger is controlled such that the temperature difference between the working fluid and the thermal storage medium is less than 3° C.

18. The thermoelectric energy storage system of claim **4**, comprising:

a valve configured to control the flow in the working fluid circuit.

19. The thermoelectric energy storage system of claim **1**, wherein the thermal storage tank includes a cold storage tank, and the thermal storage conduit includes a cold storage conduit configured to transfer a cold storage medium between a first cold storage tank and a second cold storage tank through the heat exchanger.

20. The thermoelectric energy storage system of claim **6**, wherein the thermal storage tank includes a cold storage tank, and the thermal storage conduit includes a cold storage conduit configured to transfer a cold storage medium between a first cold storage tank and a second cold storage tank through the heat exchanger.

21. The thermoelectric energy storage system of claim **20**, wherein:

the storage tank includes an intermediate storage tank; and the heat exchanger includes a stream splitter configured to divide the flow of the thermal storage medium from a first storage tank into a flow to the intermediate storage tank and to a second storage tank.

22. The thermoelectric energy storage system of claim **20**, comprising:

a compressor configured to compress the working fluid in vapor phase from a lower pressure to a higher pressure during the charging cycle, such that electrical energy for driving the compressor is injected into the thermal energy storage system.

23. The thermoelectric energy storage system of claim **20**, comprising:

an expansion device configured to expand the working fluid in liquid phase from a higher pressure to a lower pressure during the charging cycle.

24. The thermoelectric energy storage system of claim **20**, comprising:

a pump configured to pump the working fluid from a lower pressure to a higher pressure during the discharging cycle.

25. The thermoelectric energy storage system of claim **20**, comprising:

a turbine configured to expand the working fluid from a higher pressure to a lower pressure level for generating electrical energy during the discharging cycle.

26. The method of claim **12**, comprising:

joining the flow of the thermal storage medium in the heat exchanger such that heat transfer in the heat exchanger has two different rates.

27. The method of claim **13**, comprising:

dividing the flow of the thermal storage medium in the heat exchanger such that heat transfer in the heat exchanger has two different rates.

28. The method of claim **13**, comprising:

joining the flow of the thermal storage medium in the heat exchanger such that heat transfer in the heat exchanger has two different rates.

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