Electricity storage based on coupled thermochemical reactions: The Thermochemical Battery

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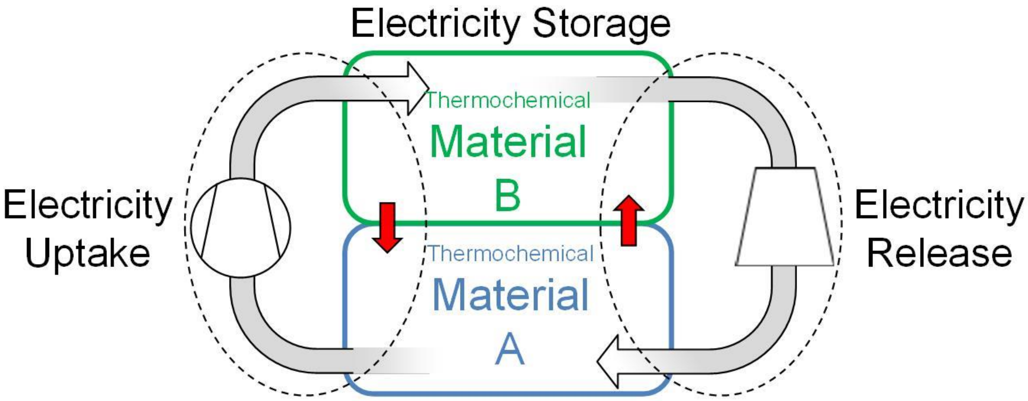

Abstract:

Thermochemical reactions are under investigation for a wide variety of applications. However, the system of two coupled gas-solid reactions exchanging both thermal energy and gas solely with each other has not been investigated yet. This approach allows realizing a compact thermochemical unit with two gas reservoirs at different pressure levels at approximately the same temperature. In this work, such a system is fundamentally analyzed and its technical potential as an energy storage component is investigated. While any two thermochemical gas-solid system can be used, this work exemplarily focusses on metal hydrides. Based on a thermodynamic analysis, it can be shown that the system is feasible, as the intrinsic difference in the reaction enthalpies of the metal hydrides can be compensated with heat integration of the compression unit. Following these findings, a thermochemical battery is investigated in more detail including an energetic analysis of efficiencies and potential storage densities. It is deduced that a higher pressure ratio between the hydrides yields in higher storage density but lower efficiency. Co-generation of cooling energy during discharging is feasible.

Keywords:

Hydrogen storage, thermochemical heat storage, thermochemical battery, metal hydride, Electricity storage

Highlights:

- Innovative principle for electricity storage is assessed
- A thermochemical battery is analyzed based on fundamental thermodynamics
- Two coupled thermochemical gas-solid reactions are used as gas pressure reservoirs
- Principle can be transferred to a variety of gas-solid reaction systems

Nomenclature

Symbol	Description	Unit
M	Molar mass	kg mol^{-1}
p	Pressure in reactor compartment 1	Pa
R	Universal gas constant	J mol^{-1} K^{-1}
T	Temperature	K
w	Work	J kg^{-1}
$\Delta_R H$	Reaction enthalpy	J mol^{-1}
$\Delta_R S$	Reaction entropy	J mol^{-1} K^{-1}
ΔT	Temperature difference for heat transfer between reactor compartments	K
η	Efficiency	-
κ	Specific heat ratio of the gas	-
Subscripts	**Description**	
Ref	Reference	
Isen	isentropic	
Comp	Compression	
Eq	Equilibrium	
Acronyms	**Description**	
CAS	Compressed air storage	
M	Metal	
MH	Metal hydride	

1 Introduction

With the change of the global energy system from fossil based to renewable, a need for energy conversion- and storage systems arises. Besides other technologies, thermochemical systems are under investigation for that purpose. In thermochemical systems, thermal energy drives the dissociation of a compound and combining the reactants again releases the thermal energy. The separation of the reactants should be easy, which is why gas-solid reactions are beneficial for that purpose.

Due to the nature of gas-solid reactions, during a cycle of absorption and desorption, the material can act as heat source and mass sink or heat sink and mass source, respectively. Subsequently, these system's thermal features can be used for heating or cooling. Especially hydrogen-metal systems are investigated to preheat fuel cell systems [1] or to utilize the potential energy of compressed hydrogen to drive an air conditioning unit in fuel cell vehicles [2]. Or, besides that, gas-solid reactions are also interesting for gas storage. Metal hydrides are in the discussion to serve as hydrogen storage compounds in a future hydrogen economy [3].

If the gaseous compound of a gas-solid reaction can be supplied to the material at varying pressures or temperatures, the range of applications extends even more. For this purpose, the system has to be coupled with a pressure dependent gas supply. For systems with a gaseous reactant easy to condense, such as water vapor, a temperature-dependent evaporator/condenser is beneficial. In case the gas is more difficult to condense, such as hydrogen, another thermochemical material can be used instead of an evaporator/condenser. In such a system, the gaseous side of two different thermochemical materials using the same gaseous reactant is coupled, while heat supply to the two beds is independent. In a setup like this, thermal energy can also be released at a higher temperature level than it has been stored before. This process is called heat transformation and has been investigated for both hydrogen- [4] and water vapor systems [5]. It is also possible to operate such a system as a heat pump [6].

Hence, single thermochemical systems can be used for thermal energy storage, gas storage, heating or cooling. Thermochemical systems coupled on the gaseous side while being independent on their thermal sides can additionally be applied for heat pumps and heat transformation. In this contribution we analytically investigate for the first time the potential applications and performance of a thermochemical system that is both coupled thermally and on the gaseous side. Hence, two different thermochemical materials working with the same gaseous reactant exchange both gas and thermal energy solely with each other. Such a setup offers two reservoirs for gas storage at different pressures that could be used e.g. for electricity storage. This paper outlines the newly developed storage concept. Taking basic systems properties into account, a first analysis on the concept´s general potential efficiency and storage densities has been carried out. By stepwise including more aspects of a real technical system, like inefficiencies of the compression and expansion and thermodynamic losses due to heat transfer, the impact of these factors on the energy efficiency and storage density has been identified.

2 Process analysis - Basic concept

In this section, the basic principles of the thermochemical battery are presented. The system consists of two thermochemical gas-solid reactions coupled both thermally and on the gaseous side. While any two reactions involving the same gaseous reactant, such as water vapor or ammonia, could be used, this work focuses on metal-hydrogen systems. Metal hydrides have been studied intensively for most of the applications mentioned in the previous paragraph. Therefore, a wide variety of different metals with different thermodynamic properties are available. This variety of materials is a sufficient data basis for analyzing the properties of the thermochemical battery.

Metal hydrides are able to reversibly store and release hydrogen via a thermochemical reaction. Generalized, they can be described with the following reaction equation, with M representing a metal [3]:

$$\mathrm{M} + \frac{\mathrm{x}}{2}\mathrm{H_2} \rightleftharpoons \mathrm{MH_x} \qquad (1)$$

Due to the nature of gas-solid reactions, the reaction temperature of a metal hydride can be adjusted with the gas pressure and vice versa. This characteristic is different for every metal hydride. The relationship between the pressure and so called equilibrium temperature of such a system is commonly visualized in a van't Hoff plot. Figure 1 qualitatively illustrates the distinct coherence between the pressure of the gas and the temperature of the reaction for two different metal hydrides.

The proposed thermochemical battery utilizes the pressure difference between two different metal hydrides at a given temperature $T_{\text{ini.}}$ The two hydrides are placed in separate compartments of the reactor operating as gas reservoir. They are in thermal contact to enable heat transfer between the materials. Additionally, they are coupled on the gaseous side.

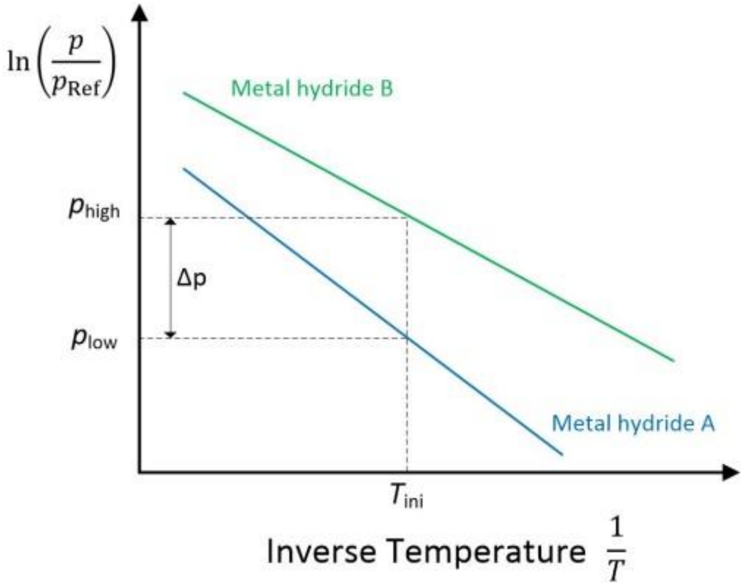

Figure 1 – Two metal hydrides – van't Hoff plots.

A similar system also operating with a setup that is coupled both thermally and on the gaseous side was proposed by Honigmann in 1883 [7]. He used a steam engine which was heated by the interaction of the exhaust water vapor with sodium hydroxide. The heat released thereby was used to generate steam in a boiler which was thermally connected to the sodium hydroxide. The setup was in practical operation to power fireless locomotives. During the process, the sodium hydroxide became more and more diluted. To regenerate the system, the diluted sodium hydroxide solution was drained, boiled down and refilled. In recent days that operation principle was picked up by Jahnke in 2019 [8] to investigate the process for thermochemical energy storage. In contrast to sodium hydroxide, she used LiBr and proposed several strategies to release energy from the system and to regenerate it. For example, discharging with the extraction of mechanical work or cold production is feasible. For regeneration, the utilization of thermal energy or mechanical work is proposed.

Differences to the process proposed in this manuscript can be identified. First, the setup in this paper utilizes two thermochemical reactions for the two compartments. In contrast, the Honigmann process utilized one chemical reaction and the evaporation of water on the other side. In addition, the chemical reaction in the Honigmann process is of gas/liquid nature, while here two gas-solid reactions are involved.

Second, the thermal characteristics of the water absorption in the Honigmann process and the present setup are different. As reported by Jahnke [8], the temperature level of the thermal energy release is not only dependent on the gas pressure, but also on the concentration of the solution. Therefore, the pressure has to rise during the water vapor absorption process, if the same temperature level shall be maintained. Subsequently, the pressure difference to extract work is reduced with the discharging time. That issue could be visualized with a distinct equilibrium line in Figure 1 for each concentration of the solution resulting in a series of curves. In the proposed setup in this work, it can be assumed that the temperature level of the exothermal reaction is independent of the loading of the metal hydride corresponding to a negligible plateau slope. Therefore, the same pressure difference can be maintained during the whole discharging process.

2.1 Reference Materials: Metal hydrides

For the thermochemical battery to be operable, two different metal hydrides have to be used. For these materials, the equilibrium pressure $P_{\mathrm{eq,H2}}$ at a given temperature T can be calculated using the standard enthalpy $\Delta_{\mathrm{R}}H$ – and entropy $\Delta_{\mathrm{R}}S$ of the hydride formation [9].

$$\frac{p_{\mathrm{Eq,H2}}}{p_{\mathrm{Ref}}} = \exp\left(\frac{-\Delta_{\mathrm{R}}H}{R \cdot T} - \frac{-\Delta_{\mathrm{R}}S}{R}\right) \tag{2}$$

with the reference pressure being $p_{\mathrm{Ref}} = 1\ \mathrm{atm}$.

The thermochemical battery couples two metal hydrides both thermally and on the gaseous side. That means that the two materials exchange heat and gas solely with each other. Therefore, for full conversion of both materials, their total hydrogen capacity and total thermal capacity have to be equal. This seems to be a contradiction since the metal hydrides have to differ in terms of enthalpy of reaction offering two pressure levels. In other words, if the reaction enthalpies are different, the overall amount of thermal energy cannot add up, and only viewing material properties, there is an intrinsic imbalance in thermal energy. This imbalance has to be accounted for in the process design and will be addressed in this manuscript.

2.2 Reactor

The reactor for the thermochemical battery has to exhibit two different compartments for the two materials. They have to be in thermal contact to enable rapid heat transfer. Additionally, they should be designed in a way that the reactive gas can be supplied to the solid bed without mass transfer limitations. For this study, an idealized reactor without heat- or mass transfer limitations is assumed. The temperature and pressure inside the reactor compartments is always at the equilibrium conditions of the respective material. Additionally it was assumed that the reaction kinetics are not limiting.

3. The Thermochemical Battery

The thermochemical battery consists of three major parts – the reactor, the compression- and expansion unit - as it is illustrated in Figure 2. For the storage of electrical energy, a compressor is powered to desorb hydrogen from metal hydride A (MH-A). The compressor increases the hydrogen's pressure and it is absorbed by metal hydride B (MH-B). The heat released during hydrogen absorption in MH-B is transferred to MH-A driving the desorption. For heat transfer, a temperature gradient between the materials is necessary. For the first part of this analysis, it is assumed that heat transfer can take place anyways without a temperature difference. This assumption will be dropped in the course of the paper.

For the release of the stored electrical energy, the process is reversed. Hydrogen desorbs from MH-B at the same pressure as it has been stored previously. Afterwards its pressure is reduced to the equilibrium pressure of MH-A in an expander. Thereby, the hydrogen performs work, which can be converted to electrical energy in a generator. The hydrogen is absorbed in metal hydride A, where the heat of absorption is released and being transferred to metal hydride B to drive the desorption. The system is completely closed and can flexibly switch between charging and discharging operation. With the selection of a metal hydride pair, and the temperature level, a wide variety of pressure ratios is feasible.

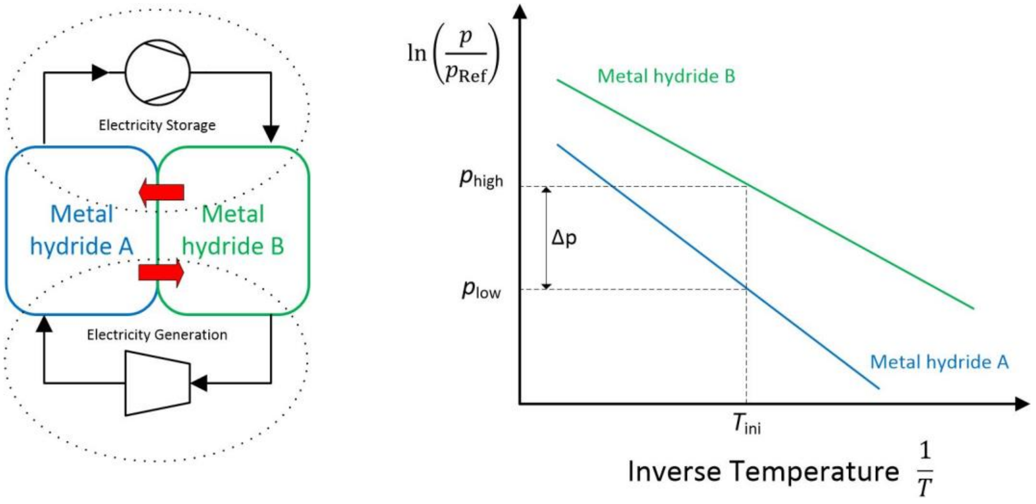

Figure 2 - Basic principle of the thermochemical battery.

3.1 Isothermal compression/expansion

An idealized description for compression of a gas is isothermal compression. For isothermal compression of an ideal gas, the work required to compress one kilogram of gas from pressure p_1 to a pressure p_2 at temperature T is calculated with R being the universal gas constant and M the molar mass of the gas:

$$w_{\mathrm{isothermal}} = \frac{R \cdot T}{M} * \ln\left(\frac{p_2}{p_1}\right) \tag{3}$$

Isothermal compression is the minimum work that is required to compress an ideal gas [10]. Since it is an idealized process requiring that the thermal energy is dissipated to the environment instantly, technical realization is challenging. The equilibrium pressure of a thermochemical material at a certain temperature

T can be calculated with equation (2). Therefore, using the thermodynamic properties $\Delta_{\mathrm{R}}H$ and $\Delta_{\mathrm{R}}S$, the pressure ratio between the materials $\frac{p_2}{p_1}$ can be calculated with

$$\frac{p_2}{p_1} = \frac{\exp\left(\frac{-\Delta_{\mathrm{R}}H_2}{R \cdot T} - \frac{-\Delta_{\mathrm{R}}S_2}{R}\right)}{\exp\left(\frac{-\Delta_{\mathrm{R}}H_1}{R \cdot T} - \frac{-\Delta_{\mathrm{R}}S_1}{R}\right)} \tag{4}$$

The indices 1 and 2 refer to the compartments of the two metal hydrides. Assuming that the change of entropy ΔS_{R} is the same for every metal hydride [11], resulting in $\Delta_{\mathrm{R}}S_2 = \Delta_{\mathrm{R}}S_1$, equation (4) simplifies to:

$$\frac{p_2}{p_1} = \exp\left[\frac{1}{R \cdot T}\left(\Delta_{\mathrm{R}}H_1 - \Delta_{\mathrm{R}}H_2\right)\right] \tag{5}$$

Combining equations (3) and (5) gives:

$$w_{\mathrm{isothermal}} \cdot M = \Delta_{\mathrm{R}}H_1 - \Delta_{\mathrm{R}}H_2 \tag{6}$$

Therefore, it can be concluded that the work required compressing one mol hydrogen isothermally from p_1 to p_2 is equal to the difference in the reaction enthalpies of the two materials. It can be seen that the amount of energy required for that increases with the difference of the materials' reaction enthalpies. Therefore, more energy can be stored compressing the same amount of gas.

The temperature does not change during isothermal compression/expansion. Additionally, the pressure ratio is the same for compression and expansion. Therefore, in this idealized case, the efficiency η is calculated using equation (3):

$$\eta_{\mathrm{el,isothermal}} = \frac{\left|w_{\mathrm{Expander,isothermal}}\right|}{\left|w_{\mathrm{Compressor,isothermal}}\right|} = 100\% \tag{7}$$

It can be seen that for every pressure ratio and temperature, the efficiency of the thermochemical battery is 100% assuming isothermal compression.

3.2 Adiabatic compression/expansion

Temperature difference for heat transfer ΔT = 0 °C

Another idealized process is the adiabatic compression, at which no heat is dissipated into the environment. In case the entropy of the gas does not change, it can be referred to as isentropic compression. The work to compress one kilogram of an ideal gas from pressure p_1 and temperature T_1 to a pressure p_2 is calculated with R being the universal gas constant and M the molar mass of the gas using the specific heat ratio $\kappa = \frac{c_\mathrm{p}}{c_\mathrm{v}}$ and assuming that κ is independent of the temperature [12]:

$$w_{\text{adiabatic,isentropic}} = \frac{R \cdot T_1}{M} \cdot \frac{\kappa}{\kappa - 1} \left[\left(\frac{p_2}{p_1} \right)^{\frac{\kappa-1}{k}} - 1 \right] \tag{8}$$

The work for adiabatic compression is higher than for isothermal compression [10]. Both isothermal and adiabatic compressions are idealized processes. The real energy demand for gas compression is in between of those [10]. For the present analysis, the focus is on these idealized ways of compression since they serve as starting points to judge the potential of the thermochemical battery.

For the calculation of the efficiency in the adiabatic case, it was assumed that no temperature gradient is required for heat transfer between the two materials and the following roundtrip process takes place:

- Isentropic compression from T_1 and p_1 to $p_{2,\Delta T=0}$.
- Isobaric cool-down to the initial temperature T_1.
- Thermochemical hydrogen storage in metal hydride B at temperature T_1 and pressure $p_{2,\Delta T=0}$.
- Release of the hydrogen from metal hydride B at temperature T_1 and pressure $p_{2,\Delta T=0}$.
- Isentropic expansion from $p_{2,\Delta T=0}$ to p_1.
- Isobaric heat-up to the initial temperature T_1.

The electric efficiency of the process can be calculated using equation (8).

$$\eta_{el,\text{isentropic},\Delta \text{T}=0°\text{C}} = \frac{\left| w_{\text{Expander,isentropic}} \right|}{\left| w_{\text{Compressor,isentropic}} \right|} = \frac{\left| \left(\frac{p_1}{p_{2,\Delta T=0}} \right)^{\frac{\kappa-1}{k}} - 1 \right|}{\left| \left(\frac{p_{2,\Delta T=0}}{p_1} \right)^{\frac{\kappa-1}{k}} - 1 \right|} \tag{9}$$

The indices 1 and 2 refer to the compartments of metal hydrides A and B in Figure 2, respectively. It can be seen that the efficiency is independent of the temperature since the temperature before the compressor and expander as well as the reactor is assumed to be identical.

Temperature difference for heat transfer ΔT ≠ 0 °C

If the assumption of no temperature difference being necessary is dropped, the equations have to be adapted. Hydrogen is now being stored at a temperature T_3 which is ΔT higher than the initial temperature T_1.

$$T_3 = T_1 + \Delta T \tag{10}$$

Subsequently, the compartment B of the thermochemical battery now operates at T_3 with the corresponding equilibrium pressure $p_{2,\Delta T \neq 0} = p_3$, which is higher than in the case without a temperature gradient. Again it is assumed that the conditions at which hydrogen is stored and released are identical. The qualitative *T-S* diagram and the pressure/temperature levels are visualized in Figure 3.

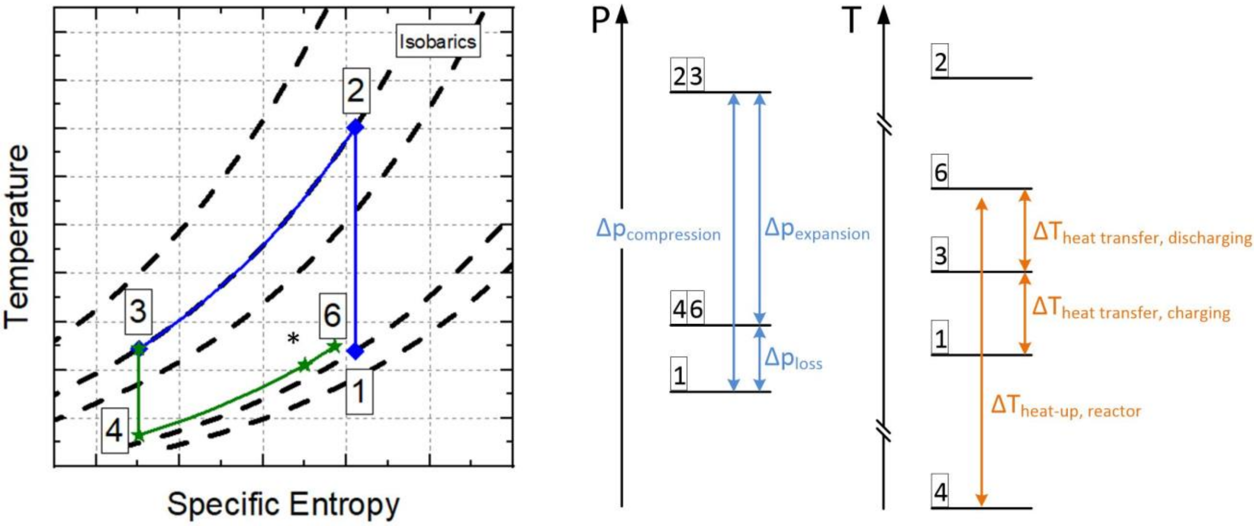

Figure 3 - Temperature and pressure levels during adiabatic compression/expansion; * Point 5 will be introduced later.

The pressure after the expander is now denoted with p_4. Due to the temperature gradient, metal hydride A in Figure 2 has to operate at $2 * \Delta T$ higher during its absorption than during desorption. Since temperature and pressure of a metal hydride correlate via the van't Hoff relation, the pressure p_4 can be calculated based on the reaction enthalpy and the desorbing temperature T_1. Pressure p_4 is the pressure in the metal hydride if the temperature is raised by $2 * \Delta T$ from p_1 and T_1.

$$p_4 = p_1 * e^{\frac{\Delta_R H_1}{R} * \left(\frac{1}{T_1} - \frac{1}{T_1 + 2 * \Delta T}\right)} = p_6 \tag{11}$$

Therefore, the roundtrip for the case with a temperature difference can be described as follows:

- Isentropic compression from T_1 and p_1 to $p_{2,\Delta T \neq 0}$.
- Isobaric cool-down to the temperature T_3.
- Thermochemical hydrogen storage in metal hydride B at temperature T_3 and pressure $p_{2,\Delta T \neq 0}$.
- Release of the hydrogen from metal hydride B at temperature T_3 and pressure $p_{2,\Delta T \neq 0}$.
- Isentropic expansion from temperature T_3 and $p_{2,\Delta T \neq 0}$ to p_4.
- Isobaric heat-up to the temperature T_6.

The efficiency regarding a temperature difference for heat transfer calculates with:

$$\eta_{el,\mathrm{isentropic},\Delta\mathrm{T}\neq 0°\mathrm{C}} = \frac{\left| T_3 \left[\left(\frac{p_4}{p_{2,\Delta T\neq 0}} \right)^{\frac{\kappa-1}{k}} - 1 \right] \right|}{\left| T_1 \left[\left(\frac{p_{2,\Delta T\neq 0}}{p_1} \right)^{\frac{\kappa-1}{k}} - 1 \right] \right|} \qquad (12)$$

The dependencies of the roundtrip efficiency on the pressure ratio for all three previously discussed cases are shown in Figure 4. The roundtrip efficiency for the isothermal process is 100% for every pressure ratio. For single stage adiabatic, isentropic compression/expansion the threshold value for the efficiency at a given pressure ratio is determined by setting the temperature gradient for heat transfer to zero which is independent of the material pair. It can be seen that the electric efficiency drops with increasing pressure ratio (black curve, square markers). This is due to the temperature increase of the hydrogen during isentropic compression. That heat-up is more pronounced at high pressure ratios. Therefore, at high pressure ratios, more thermal energy has to be dissipated to the environment since it cannot be utilized otherwise, which reduces the electric efficiency. The calculations for cases with ΔT ≠ 0 °C are dependent on material A in Figure 2 as equation (**11**) reveals. The sharp initial rise in these cases is attributed to the fact that a certain pressure ratio is necessary to establish the desired temperature gradient. Below that pressure ratio, the process is impossible. That rise increases to a maximum after which it starts to decline again. Therefore, in terms of efficiency, an optimal system design can be identified. Note that the lines for isothermal the isothermal case (grey, equation (7)) and the isentropic case without temperature difference (black, equation (9)) are valid for every material pair, while the other curves were calculated for $LaNi_{4.8}Sn_{0.2}$ with the properties listed in Table 1.

If a temperature gradient is introduced, the efficiency decreases with larger temperature difference. This is due to the temperature difference that translates into a reduced pressure difference for expansion. The difference between pressures p_1 and p_4 increases which is not available for expansion which is visualized with Δp_{loss} in Figure 3.

With an increased temperature difference in the same reactor design, the power increases, as heat transfer proceeds faster. Therefore, increasing the power of the thermochemical battery coincides with a reduced efficiency and vice versa. The pressure ratio translates directly in the amount of energy that can be stored with one unit of hydrogen. A high pressure ratio requires a high amount of energy for compression and results in a high amount of energy withdrawal during expansion. Hence, increasing the pressure difference results in higher storage densities, but reduced efficiency. Therefore, a correlation between efficiency, storage density and pressure ratio can be observed.

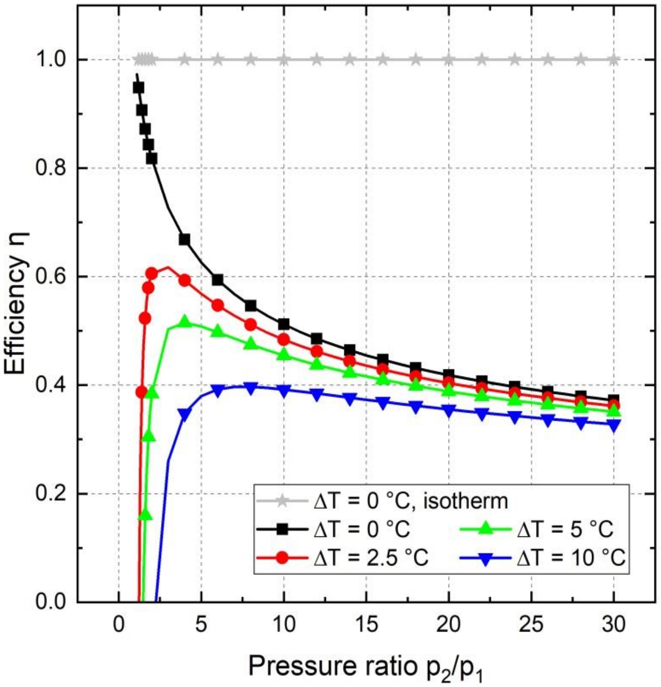

Figure 4 - Pressure ratio and efficiencies at different temperature differences for heat transfer; grey line: Isothermal compression/expansion; other lines: adiabatic, isentropic, single stage compression/expansion; Cases with ΔT: $LaNi_{4.8}Sn_{0.2}$ as Material A with appropriate partner.

3.3 Thermal integration of the compression unit

So far, it was assumed that the charging and discharging processes are feasible even though the demand and supply of thermal energy for the involved thermochemical reactions are different. During charging, more thermal energy is required to desorb hydrogen from metal hydride A than released by the absorption in metal hydride B. This imbalance has to be accounted for.

There is a surplus of thermal energy in the hydrogen after the compressor, since the hydrogen is heated up during non-isothermal compression. It would be beneficial for the process efficiency to store the thermal energy of this compressed hydrogen. The stored thermal energy could then be used to heat the hydrogen before the expander during discharge. The proposed system is able to partially store this thermal energy in the reactor itself without requiring an additional device. Storing thermal energy is even a necessity to drive the process. As introduced before, the reaction enthalpy per mole of hydrogen in MH-A (desorbing) in Figure 2 has to be higher than the one of MH-B (absorbing). Thermal energy of the compressed hydrogen can now be used to compensate for that difference. For the reverse reaction, MH-A releases more thermal energy than required by MH-B. This excess thermal energy can be used for intermediate heating of the hydrogen between several stages of expansion and to heat up hydrogen after the final stage to the reactor temperature of MH-A, which will be analyzed later. The amount of stored thermal energy is only dependent on the selected materials. It is independent of the compression ratio or the temperature level the process occurs.

Isothermal compression is the minimum of work required for compression. It was found that the energy required to compress hydrogen isothermally from the lower to the higher pressure reservoir is exactly the same as the difference in the reaction enthalpies regarding the mentioned assumptions. Adiabatic compression requires more energy than isothermal compression. That energy remains in the gas increasing its temperature. Therefore, it can be concluded that there is enough thermal energy in the hot gas after the compression to compensate for the difference in the reaction enthalpies. Even after compensating that, there is still a surplus of thermal energy in the hot gas. If that thermal energy cannot be utilized, it has to be dissipated to the environment, which lowers the electrical storage efficiency.

3.4 Optimization and operational strategies

So far, mostly qualitative data was presented. In this section selected cases for a material pairing are evaluated quantitatively, involving temperatures, pressures, storage densities and efficiencies. First, a case is shown with single stage adiabatic compression. Thereby, the influence of the isentropic and mechanical efficiencies of the machineries on the thermochemical battery will be evaluated. Afterwards, a case with three-stage compression and expansion will be presented, to reduce the fraction of unused thermal energy. Thereby, the compression work and the electricity output can be reduced and increased, respectively.

3.4.1 Stages of compression and expansion

For the calculation of the hydrogen's properties and the machinery, the EBSILON®Professional software was used. The following assumptions and considerations have been taken into account:

- Hydrogen is assumed to behave as an ideal gas.
- Pressure- and heat losses in the heat exchangers and piping are disregarded.
- The reactors are not limited by heat or mass transport. They are always operating at their respective equilibrium conditions.
- Efficiencies of the compression and expansion units are regarded as listed in Table 1.
- Material properties are listed in Table 1.
- The temperature difference for heat transfer between the metal hydrides was set to 5 K.
- The temperature difference for inter-stage cooling/heating between the hot/cold hydrogen and the reactor was set to 10 K.
- Steady state and energetic analysis only.
- Ambient temperature is 20 °C.

Table 1 - Parameters for the machinery and materials. Material data from [9].

Parameters	Value
Motor electrical efficiency	0.95
Motor mechanical efficiency	0.998
Pump isentropic efficiency	0.85
Pump mechanical efficiency	0.99
Turbine isentropic efficiency	0.9
Turbine mechanical efficiency	0.99
Generator efficiency	0.9857
$LaNi_{4.8}Sn_{0.2}$ $-\Delta_R H$	$32.80\ \mathrm{kJ\ mol_{H2}^{-1}}$
$LaNi_{4.8}Sn_{0.2}$ $-\Delta_R S$	$105.0\ \mathrm{J\ mol_{H2}^{-1} K^{-1}}$
$MmNi_{4.15}Fe_{0.85}$ $-\Delta_R H$	$25.00\ \mathrm{kJ\ mol_{H2}^{-1}}$
$MmNi_{4.15}Fe_{0.85}$ $-\Delta_R S$	$105.4\ \mathrm{J\ mol_{H2}^{-1} K^{-1}}$

Single stage process

In this subsection, the performance of the thermochemical battery is analyzed for a specific case. The previously taken assumption that the efficiency of the machinery is 100% is eliminated now. Hence, the efficiency losses is the machinery are also accounted for. In that specific case, the metal hydride pairing $LaNi_{4.8}Sn_{0.2}$ and $MmNi_{4.15}Fe_{0.85}$ are used. They were chosen, since they are both operable around ambient temperature and their reported specific changes of entropy are almost identical. It can be seen that their reaction enthalpies differ for $7.8\ \mathrm{kJ\ mol_{H2}^{-1}}$ or $3900\ \mathrm{kJ\ kg_{H2}^{-1}}$. Hence, for full conversion during the charging process of the thermochemical battery, $3900\ \mathrm{kJ\ kg_{H2}^{-1}}$ additional thermal energy is required which is approximately 24% of the thermal energy required for desorption. Subsequently, a surplus of, $3900\ \mathrm{kJ\ kg_{H2}^{-1}}$ thermal energy is available during discharge.

The roundtrip process for charging and discharging can be described as follows. The corresponding *T-S*-Diagram is shown in Figure 5.

Charging

1: Hydrogen desorption from $LaNi_{4.8}Sn_{0.2}$ at 39 °C. The majority of the thermal energy required for that process is provided by the hydrogen absorption in $MmNi_{4.15}Fe_{0.85}$.

1 -> 2: Adiabatic hydrogen compression to the absorption pressure of $MmNi_{4.15}Fe_{0.85}$ of 24.6 bar. This is the equilibrium pressure of the $MmNi_{4.15}Fe_{0.85}$ at a temperature of 44 °C. The gas temperature increases.

2 -> 3: Isobaric hydrogen cool-down to the hydrogen absorption temperature of $MmNi_{4.15}Fe_{0.85}$ of 44 °C. The thermal energy can partially be used to account for the difference in reactions enthalpies between the two materials ($3900\ \mathrm{kJ\ kg_{H2}^{-1}}$). Additional surplus thermal energy is dissipated into the environment.

3: Hydrogen absorption in $MmNi_{4.15}Fe_{0.85}$ at 44 °C. For heat transfer between the materials, the temperature level of hydrogen absorption in $MmNi_{4.15}Fe_{0.85}$ has to be ΔT = 5 K higher than the temperature level of hydrogen desorption in $LaNi_{4.8}Sn_{0.2}$.

Discharging

3: Hydrogen desorption from $MmNi_{4.15}Fe_{0.85}$ at 44 °C and 24.6 bar. The thermal energy for that process is fully provided by the hydrogen absorption in $LaNi_{4.8}Sn_{0.}2$. Excess thermal energy is available.

3 -> 4: Adiabatic hydrogen expansion to the absorption pressure of $LaNi_{4.8}Sn_{0.2}$ of 1.5 bar. The gas temperature drops subzero to -117 °C. Hydrogen remains gaseous at these conditions and does not liquefy or freeze which might damage the machinery

4 -> 5: Isobaric hydrogen heat-up close to the ambient temperature. Thermal energy of 1770 $\mathrm{kJ\ kg_{H2}^{-1}}$ is withdrawn from the environment.

5 -> 6: Further isobaric hydrogen heat-up to the reactor temperature of $LaNi_{4.8}Sn_{0.2}$ of 49 °C partially using the previously stored thermal energy. The temperature level of the ambient is not high enough. Therefore, the reactor itself has to heat up the hydrogen. This is possible, since the absorption of the hydrogen releases more thermal energy than is required for full desorption. For that purpose, $3900\ \mathrm{kJ\ kg_{H2}^{-1}}$ are available, but due to preheating via the environment only 561 $\mathrm{kJ\ kg_{H2}^{-1}}$ are required.

Alternatively: 4 -> 6: Instead of using energy from the ambient, the hydrogen can also be heated up directly with the excess thermal energy that is available during hydrogen absorption. This is illustrated with the numbers in brackets in Figure 5.

6: Hydrogen absorption in $LaNi_{4.8}Sn_{0.2}$ at 49 °C. For heat transfer between the materials, the temperature level of hydrogen absorption in $LaNi_{4.8}Sn_{0.2}$ has to be ΔT = 5 K higher than the temperature level of hydrogen desorption in $MmNi_{4.15}Fe_{0.85}$ at 44 °C. Compared to the electricity charging, the temperature gradient between the beds is reversed.

Table 2 - Efficiencies and energy densities of the thermochemical battery for single stage adiabatic compression/expansion.

Roundtrip efficiency electric electric	26%
Additional cooling power	1770 kJ kg_{H2}^{-1}
Storage Density w.r.t. hydrogen	2205 kJ kg_{H2}^{-1}
Storage Density w.r.t. material volumes	22.2 Wh L_{Mat}^{-1}

It can be seen that in this single stage process, the thermal energy in the hydrogen after the compressor is being stored thermochemically in the $LaNi_{4.8}Sn_{0.2}$ to about 50%. The other half has to be dissipated to the environment, which negatively affects the efficiency. Additionally, the stored thermal energy cannot be converted into electricity, since the temperature level is not high enough to preheat the hydrogen before the expander. A fraction of it can be used for reheating after the expander. The other fraction cannot be used which is detrimental with respect to efficiency. Additionally, it has to be noted that a hot gas temperature of 583 °C after the compressor poses significant engineering effort. The efficiencies and storage densities are reported in Table 2. The values for the energies in Figure 5 are shown with respect to the working fluid hydrogen. The actual storage density of the thermochemical battery is dependent on the weight and volume of the two materials storing that hydrogen. With the material properties of the $LaNi_{4.8}Sn_{0.2}$ (ρ_{solid} = 8400 kg m^{-3} [13], 1.4 wt% [13]) and $MmNi_{4.15}Fe_{0.85}$ (ρ_{solid} = 8100 kg m^{-3} [13], 1.14 wt% [13]), and assuming 30% porosity, the storage density with respect to the materials can be calculated as it is listed in Table 2.

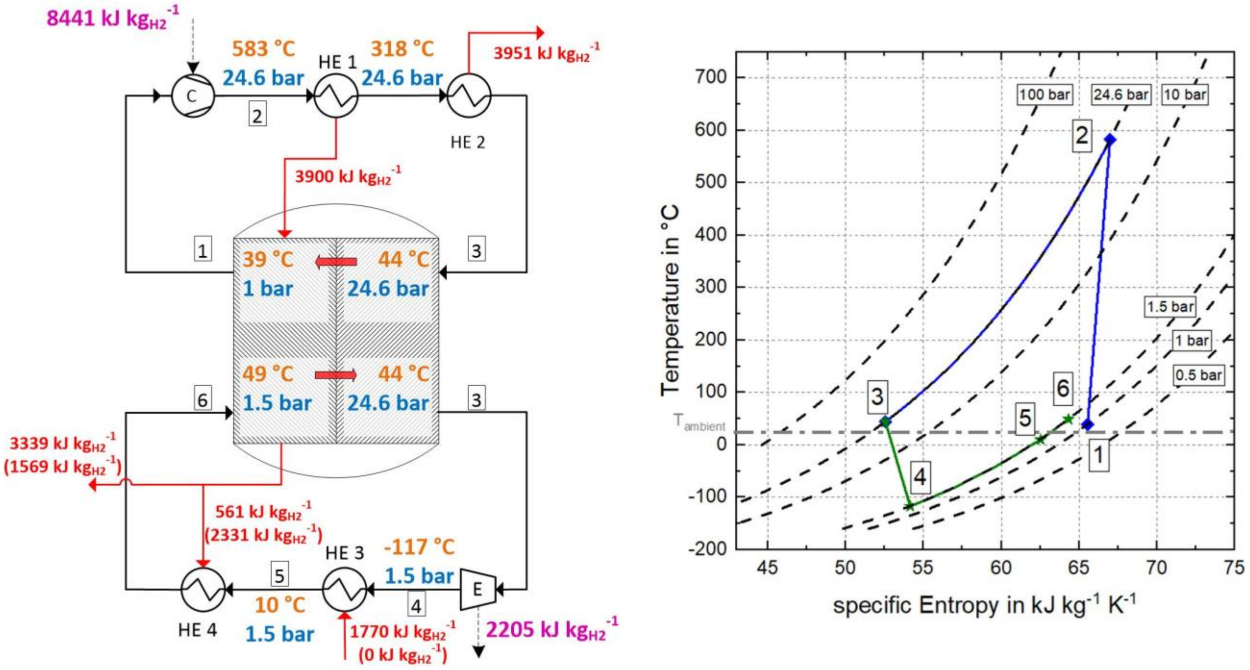

Figure 5 - Case 1, singe stage adiabatic compression/expansion, $LaNi_{4.8}Sn_{0.2}$ and $MmNi_{4.15}Fe_{0.85}$.

Three stage process

Due to the high temperature increase in the single stage compressor, and subsequent loss of thermal energy, a three stage compression/expansion with intermediate cooling/heating is analyzed. Apart from that, the system's parameters and materials are identical. The pressure ratio for each stage is approximately the same for all compressors (2.9) and expanders (2.5). The expander's pressure ratio is lower since the overall pressure drop is lower due to the temperature gradient as it has been discussed before. The flow chart and *T-S* diagram for that case are shown in Figure 6. In contrast to the single stage case, the compression ratio for each compressor is lower. Therefore, the outlet temperature of the compressor is lower (approximately 170 °C). The hot gas after each compression stage is cooled down to 49 °C, and the thermal energy is transferred to the reactor. Since the desorbing metal hydride operates at 39 °C, 10 K are available for heat transfer. Once the difference in reaction enthalpies has been balanced, the additional thermal energy has to be dissipated to the environment. After the last compression stage, the gas is still too hot to enter the reactor. Therefore, this surplus energy of $1825\ \mathrm{kJ\ kg_{H2}^{-1}}$ has to be dissipated to the environment. Note that this value is lower than the dissipation of $3951\ \mathrm{kJ\ kg_{H2}^{-1}}$ in the single stage case. Due to the multiple stages with intermediate cooling, the overall energy to compress the hydrogen from 1 bar to 24.6 bar is lower than in the single stage process. However, the amount of stored thermal energy to account for the difference in the reaction enthalpies of $3900\ \mathrm{kJ\ kg_{H2}^{-1}}$ is the same.

Table 3 - Efficiencies and energy densities of the thermochemical battery for three stage and one stage adiabatic compression/expansion.

	Three stage process	**One stage process**
Efficiency electricity to electricity	45%	26%
Storage Density w.r.t. hydrogen	2803 kJ $\mathrm{kg_{H2}}^{-1}$	2205 kJ $\mathrm{kg_{H2}}^{-1}$
Storage Density w.r.t. material volumes	28.2 Wh $\mathrm{L_{Mat}}^{-1}$	22.2 Wh $\mathrm{L_{Mat}}^{-1}$

For the discharging of the battery, the previously stored thermal energy is available again. Its temperature level is too low to preheat the hydrogen before the first expander. However, it can be used to reheat the hydrogen between the stages up to 39 °C, assuming 10 K for heat transfer. Therefore, the previously stored thermal energy can be partially converted to electricity. Again, after the last stage, the environment can be cooled via heating the hydrogen to 10 °C. Since the temperature drop in the expander stages is much lower compared to the single stage process, the cooling power is reduced. An overview of the results of the three-stage process can be found in Table 3. It is evident that for the efficiency of electricity to electricity, the three stage process is beneficial, since less energy is needed for compression and the thermochemically stored thermal energy can partially be converted to electricity. This is an intrinsic feature of the thermochemical battery, and since the thermal energy is stored thermochemically, long-term loss free storage is possible.

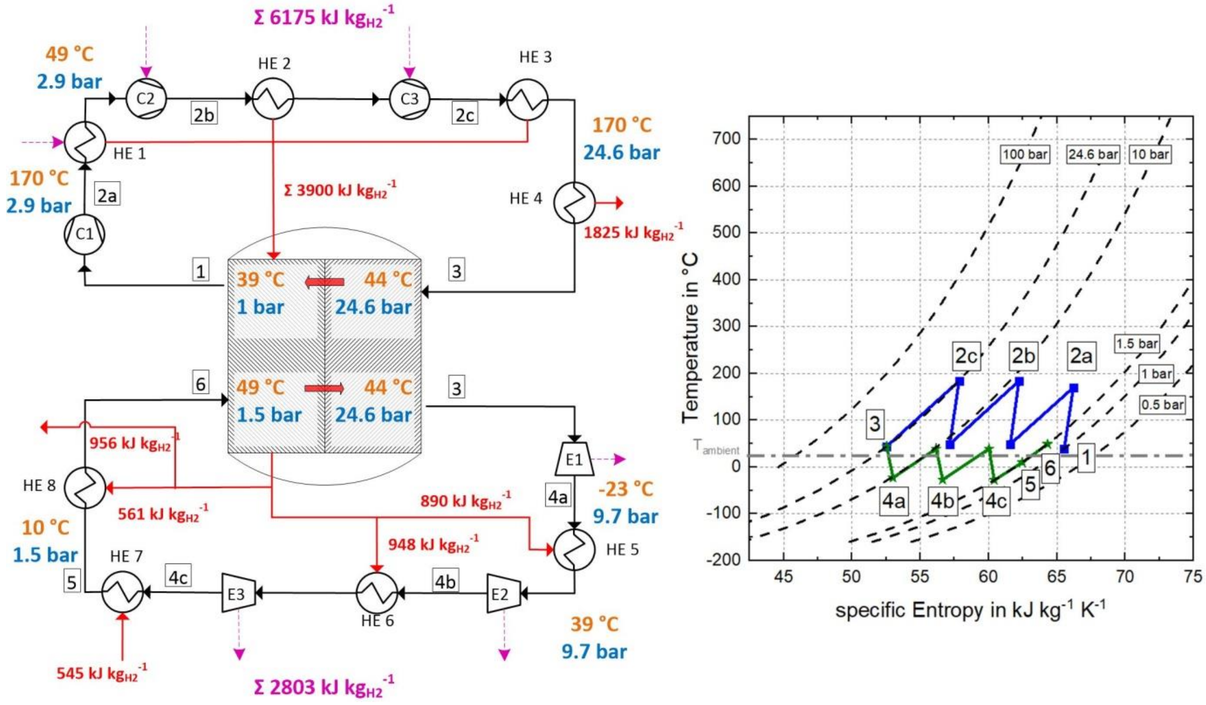

Figure 6 - Case 2, three stage adiabatic compression/expansion with intermediate cooling/heating, $LaNi_{4.8}Sn_{0.2}$ and $MmNi_{4.15}Fe_{0.85}$.

The energy losses directly affecting the efficiency of the three setups are shown in Figure 7. It is evident that the majority of the losses occur in terms of thermal losses after the compressor and non-utilization of the excess heat of absorption during the discharging process. In comparison, losses in the machinery contribute only a fraction. The overall energy demand for compression decreases and the recoverable electric energy increases with increasing stages with isothermal compression as threshold. Since there is a lot of thermal energy that has to be dissipated to the environment in the presented cases, it would be beneficial to use it in another process.

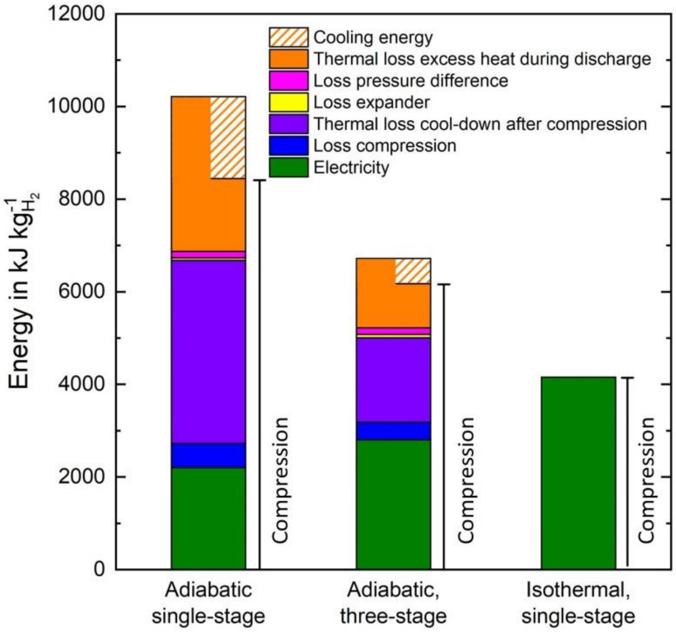

Figure 7 – Losses during a cycle of charging and discharging.

3.4.2 Utilization of heating- & cooling energy

As it has been derived before, adiabatic compression/expansion coincides with a temperature increase/drop of the hydrogen, respectively. Therefore, thermal energy at a high temperature level is available during the charging process while thermal energy can be withdrawn from the ambient during discharge. Viewing Figure 5 and Figure 6, the cool-down of the hydrogen after the compressor takes place between points 2 und 3. That thermal energy has to be used to make up the difference in the reaction enthalpies. The additional surplus can be used for additional heating purposes. The amount- and temperature level of that surplus thermal energy is strongly dependent on the specific case. Obviously, more thermal energy is available for heating if fewer stages for compression are used.

After the expander the hydrogen temperature is below the temperature level of the reactor. In contrast to other energy storage systems working with the expansion of a gas, even subzero temperatures are possible and feasible with the thermochemical battery, since hydrogen´s critical temperature is 33.2 K [14]. Therefore, the cold hydrogen can be used to withdraw thermal energy from the ambient. Heating the hydrogen with thermal energy from the ambient is shown in Figure 5 and Figure 6 between points 4 and 5. It is 1770 kJ kg_{H2}^{-1} and 545 kJ kg_{H2}^{-1} for the single stage and three stage expansion, respectively. Referring these values to the electric energy for compression, an additional cooling efficiency of 21% and 9% can be calculated which is a benefit on top of the electric efficiency. For the three stage expansion, the values are lower since the temperature drop of the hydrogen is less pronounced. The temperature until which the hydrogen can be heated up depends on the ambient temperature. In addition, the temperature of the hydrogen after the expander is strongly dependent on the specific process design, especially on the number of expansion stages. It can be concluded here, that the thermochemical battery can be designed in a way to co-generate high temperature heat during charging and cooling energy during discharge.

3.4.3 Thermal energy storage

As it has been demonstrated in the previous sections, a characteristic of the thermochemical battery is its ability to partially store the thermal energy of the hot gas after the non-isothermal compressor. This feature is based on the differences in the reaction enthalpies of the two materials. With a larger difference in enthalpy, more thermal energy has to be stored during the charging process of the thermochemical battery. It would be beneficial for the efficiency if that thermal energy can be converted to electricity during the discharging process. For the reference material combination that fraction is shown in Figure 8. For that analysis it was assumed that all expansion stages are operating at the same pressure ratio. Furthermore, it was assumed that the hydrogen is reheated to the reactor temperature after each compressor using the thermochemically stored thermal energy from the reactor. The thermochemically stored thermal energy is $3900\ \mathrm{kJ\ kg_{H2}^{-1}}$ which corresponds to 100%.

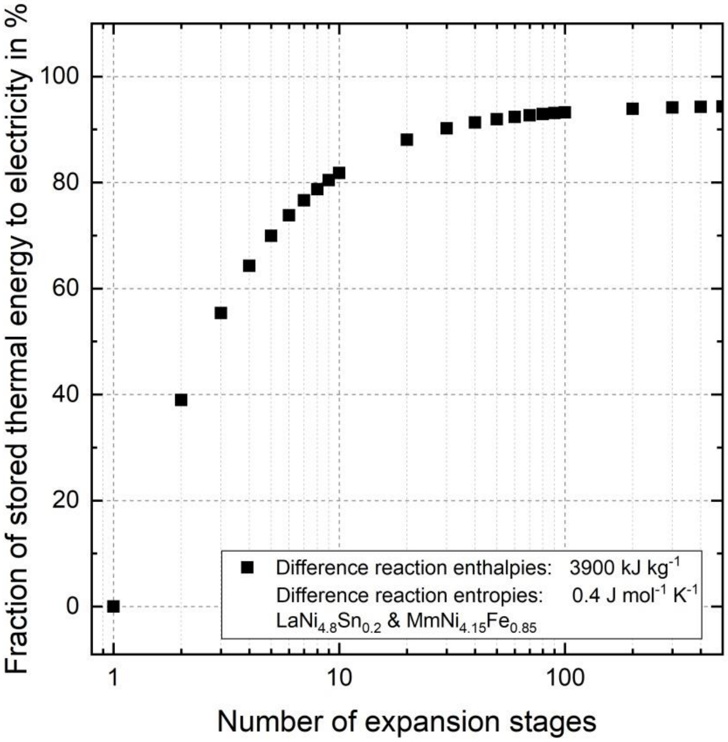

Figure 8 - Fraction of thermochemically stored thermal energy converted to electric energy depending on the number of expansion stages for the reference material pair – Without regarding machinery losses.

It can be seen that with only one expansion stage, utilization of the stored thermal energy is not possible because it can only be used to reheat the gas after the expander. Increasing the theoretical number of expansion stages reveals that there is a threshold value for the fraction of the stored thermal energy that can be converted to electricity that way. Without regarding the efficiencies of the machinery, the threshold value is 94% for the selected case. The missing fraction to 100% is attributed to the temperature difference which is required for heat transfer and subsequent reduction of the available pressure difference during expansion which is denoted with Δp_{loss} in Figure 3.

4 Discussion and technological classification

After the presented thermochemical battery has been discussed, the technology will be classified in comparison with existing technologies for energy storage.

The proposed thermochemical battery exhibits several features making it a technology worthy of investigation. The three main components of the system, which are the compression unit, the reactor and the expansion unit, can be dimensioned independently. A separation of power and capacity is possible. For example, the capacity of the reactors can be increased without affecting the machinery. Subsequently, the energy storage capacity can be increased while keeping the power constant. Additionally, the power uptake and release are independent since the compression unit can be dimensioned independently of the expansion unit. Therefore, it is possible to consume energy from the grid with high power and supplying it at a lower power to a consumer when there is demand. Since the storage is based on thermochemical reactions, loss-free long time storage is possible. Hence, the thermochemical battery is suited for both short term and seasonal energy storage.

An intrinsic feature of the thermochemical battery is the co-generation of high-temperature heat during charging and the co-supply of cooling energy during discharging. Depending on the desired application and surrounding, it is possible to adapt the thermochemical battery to specific requirements. With the proper selection of materials, pressure ratio and operating temperature, it can be dimensioned with focus on efficiency, storage density or cooling/heating power. An overview of potential focusses is shown in Table 4 where two additional scenarios for three-stage adiabatic compression are presented. The presented values can be understood as the threshold values that can be achieved at most. For example, a comparatively high storage density but lower efficiency can be achieved if a metal hydride pair with a high pressure ratio is chosen. The higher pressure ratio yields in more thermal energy that has to be dissipated to the environment after the compression unit. Another option is to increase the overall working temperature of the thermochemical battery. Table 4 shows another material pair with the same pressure difference as in the reference case, but operating at a higher temperature. Even though the densities of the materials are similar, higher storage densities can be achieved, because the temperature before the expansion stage is higher. In comparison with the previously analyzed reference case, no cooling power is provided with respect to 20 °C ambient temperature, but the storage density increases with approximately the same electric efficiency.

As it has been mentioned before, probable limitations of the overall process like heat- or mass transfer or kinetic limitations have not been addressed in this manuscript. Considering any of the mentioned limitations would affect the speed of the overall process, which translates into the power density. The scope of this work is an energetic analysis only, without drawing conclusion on the power of the energy storage or release process. For an evaluation of the power density, the limiting process has to be known. Using a reactor which does not exhibit heat- or mass transfer limitations, the reaction kinetics of the metal hydrides are the limiting factor. Therefore, the kinetics of the metal hydrides should be considered for the material selection [3]. The reaction kinetics are sensitive on the operating conditions as it was exemplarily shown by Perejón *et al.* [15] for magnesium hydride.

As it has been demonstrated previously, the storage density of the thermochemical battery is in the range of 22-62 Wh L_{mat}^{-1} and 5-11 Wh kg_{mat}^{-1} with respect to electrical output. These values involve the materials only. For a final value, the data of the compression- and expansion units have to be taken into account as well. Since their dimensioning is strongly dependent on the overall storage capacity and desired power, reliable values for those are not educible. The volumetric storage density of the thermochemical battery is in the rage of NiCd batteries [16]. The advantage of metal hydrides in general is their large volumetric hydrogen storage density while their gravimetric hydrogen storage density is a few percent at most. Therefore, the gravimetric storage density of the thermochemical battery cannot compete with other energy storage systems and is at the lower end of flywheel energy storage range [16]. Another aspect that has to be considered judging energy storage system is the cycling stability. Depending on the metal hydride cycling stability can vary a lot [3] and should be considered during material selection.

When it comes to energy storage via compression and expansion of a gas in the thermochemical battery, compressed air storage (CAS) has a similar working principle. For energy storage, air is compressed to a higher pressure, cooled down and stored in a cavity. The thermal energy of the hot air is either dissipated to the environment or it is stored in a thermal energy storage device [17]. To avoid liquefaction or freezing, the air has to be preheated before the expander either with additional combustion of a fuel or using the previously stored thermal energy. The similarities to the working principle of the thermochemical battery are evident. Both technologies work with the compression and expansion of a gas. While the volumetric storage density of the thermochemical battery potentially exceeds the CAS's one, the volume has to be filled with metal hydride increasing the cost and weight. In contrast, an empty cavern can be utilized for gas storage in CAS systems. Hence, the gravimetric energy density of CAS systems is higher than in the thermochemical battery. Since water-free hydrogen is the working fluid in the thermochemical battery, subzero temperatures are feasible. Unlike in CAS, an additional characteristic of the thermochemical battery is the incorporated thermochemical heat storage feature due to the difference in the reaction enthalpies of the materials. During multi-stage expansion the thermal energy can be used to reheat the fluid after the expansion stages. Therefore, the stored thermal energy can be partially converted into electricity without the necessity of an additional thermal energy storage device as in CAS. On the one hand, in comparison to CAS, the combustion of fuel or an additional thermal energy storage device can be avoided. On the other hand, CAS systems are able to reach higher temperatures of the air before the expansion unit. Therefore, higher efficiencies can be archived. Additionally, the feasibility of CAS systems has already been demonstrated in large scale [17].

The thermochemical battery was analyzed with respect to metal hydrides and hydrogen as working fluid. However, the system can also be designed utilizing other gas-solid reactions. It is important that two different materials reacting with the same gas are used. Therefore, material pairs using other gases such as ammonia, carbon dioxide or water vapor are theoretically feasible as well.

Table 4 – Selection of several scenarios of the thermochemical battery; Values calculated only regarding materials; Three stage, adiabatic compression/expansion, each with approx. identical pressure ratio for each stage; Efficiencies reported in Table 1. Material properties used (TD: Thermodynamic properties, 30% porosity assumed): * TD [9], ρ_{solid} = 8400 kg m^{-3} [13], 1.4 wt% [13]; $^{+}$ TD [9], ρ_{solid} = 8100 kg m^{-3} [13], 1.14 wt% [13]; $^{\#}$ TD [9], ρ_{solid} = 8000 kg m^{-3} [Assumption], 1.33 wt% [18]; $^{\sim}$ TD [9], ρ_{solid} = 8000 kg m^{-3} [Assumption], 1.7 wt% [19].

Metal hydride A	**Metal hydride B**	**MH-A (des) Pressure Temp.**	**MH-B Pressure Temp.**	**Pressure Ratio Compression**	**Efficiency electricity to electricity**	**Storage density w.r.t. energy output**
*LaNi$_{4.8}$Sn$_{0.2}$ *Reference*	$^{+}$MmNi$_{4.15}$Fe$_{0.85}$	1.0 bar 39 °C	24.6 bar 44 °C	24.6	45%	28.2 Wh L_{mat}^{-1} 4.9 Wh kg_{mat}^{-1}
$^{\#}$MmNi$_{4.8}$Al$_{0.2}$ *High pressure ratio*	~ZrFe$_{1.8}$Ni$_{0.2}$	0.1 bar 12 °C	241 bar 17 °C	2410	31%	62.6 Wh L_{mat}^{-1} 11.2 Wh kg_{mat}^{-1}
$^{\#}$MmNi$_{4.8}$Al$_{0.2}$ *High operating temperature*	$^{+}$MmNi$_{4.15}$Fe$_{0.85}$	5.8 bar 112 °C	143 bar 117 °C	24.6	47%	34.2 Wh L_{mat}^{-1} 6.1 Wh kg_{mat}^{-1}

5 Conclusions

In this work, a system based on two thermochemical reactions coupled both thermally and on the gaseous side has been presented. The two reactions exchange heat and gas solely with each other. Due to the different characteristic pressure at a certain temperature, a pressure difference between the materials arises. Compression of gas from the lower pressure to the upper one consumes electrical energy while its expansion recovers it. Therefore, such a system can act as a thermochemical battery when it is combined with a compression and expansion device. It was analyzed in general and an energetic potential analysis with respect to two metal hydrides as thermochemical materials was carried out. Configurations with comparatively high storage densities yield in competitively low electrical efficiencies and vice versa. With a three-stage compression/expansion unit and two metal hydrides as thermochemical materials, electric efficiencies of up to 47% can be reached. The maximum storage density of the investigated cases was 62.6 Wh L_{mat}^{-1} based on the two reactive materials only, without the compression/expansion unit. Additionally, the thermochemical battery acts as a thermochemical energy storage device. The stored thermal energy can be utilized during multistage expansion for intermediate reheating of the gas. During electricity charging and discharging, high-temperature heat and cold is co-generated, respectively. The amount of heat and cold generated is strongly dependent on the material chosen, the design of the compression and expansion unit as well as the temperature level of the process. Depending on one's preferences, the system can be designed with focus on electrical efficiency, storage density or cold/heat production. The qualitative behavior of the thermochemical battery is transferable to material combinations reaction with different gasses than hydrogen.

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