

A Functional Thermochemical Energy Storage System for Mobile Applications: Design and Performance Analysis

Jure Galović, Peter Hofmann

Abstract—Thermochemical energy storage (TCES), as a long-term and lossless energy storage principle, provides a contribution for the reduction of greenhouse emissions of mobile applications, such as passenger vehicles with an internal combustion engine. A prototype of a TCES system, based on reversible sorption reactions of LiBr composite and methanol has been designed at Vienna University of Technology. In this paper, the selection of reactive and inert carrier materials as well as the design of heat exchangers (reactor vessel and evapo-condenser) was reviewed and the cycle stability under real operating conditions was investigated. The performance of the developed system strongly depends on the environmental temperatures, to which the reactor vessel and evapo-condenser are exposed during the phases of thermal conversion. For an integration of the system into mobile applications, the functionality of the designed prototype was proved in numerous conducted cycles whereby no adverse reactions were observed.

Keywords—Mobile applications, LiBr composite, methanol, performance of TCES system, sorption process, thermochemical energy storage.

I. INTRODUCTION

THERMAL energy storage represents a possible approach to reduce the CO₂ emissions of mobile applications such as passenger vehicles with an internal combustion engine. It can enable the reuse of engine waste heat during operation for engine heating at the next cold start. As a result, the fuel consumption during the engine warm-up phase can be reduced [1].

For use in cars heat storage must meet high requirements in terms of specific storage capacity and long-term storage capability. Among the three heat storage principles, the highest energy densities can be achieved with TCES [2]. By way of reversible sorption reactions, long term storage without thermal insulation and with negligible heat losses can be possible. The attractive materials are salt hydrates which have a high theoretical energy density over 1 GJ/m³.

In the reversible reactions with salt hydrates, the thermal energy is stored by drying the salt hydrate and storing the dry salt and decomposed sorbate separately [3]. By connecting the

separated products during discharging, the heat is released in an exothermic reaction [4]. The heat for drying can be supplied from the internal combustion engine at operating temperature and the released heat during discharging can be used for engine heating at the cold start. For this purpose, a modular TCES prototype, based on reversible solid-gas sorption reactions with salt hydrate and sorbate alcohol, was developed [5].

This paper reviews the prototype design and selection of reactive materials as well as reports on achieved performance. The aims of the conducted investigations were to determine the performance of the module at different ambient temperatures as well as to prove its functionality and cyclic stability under real conditions, to which it can be exposed by integration in an internal combustion engine for passenger vehicles.

II. TCES PROTOTYPE

A. Reactive Materials

The materials working pair suitable for mobile applications such as heating of internal combustion engines of vehicles must meet several requirements which were highlighted in [6]. Crucial for reactive salts are high reaction enthalpies and reaction reversibility at operating temperatures of the coolant of internal combustion engines.

Although the salt hydrates offer high theoretical storage densities, several problems can occur. The induced stress within the heat exchanger and possible material pulverization due to volume variation as well as clogging of the salt grains due to deliquescence and a low melting point were reported in [7], [8]. To overcome those disadvantages, the impregnation of the salt hydrate into porous matrices was proposed in [2]. Through the impregnation of reactive salt into an inert carrier glass wool, an improved vapour transport along the reactive bed, material stability as well as fixation of salt in the structure were achieved in [1]. As a result, more than 50% of the theoretical energy density of the salt hydrate could be obtained.

Considering the sorbate material for a system which operates in a passenger vehicle, methanol (CH₄O) enables the heat storage system functionality at sub-zero temperatures due to a low melting point [7].

The composite materials with glass wool and salt hydrates which meet the listed requirements were in-situ investigated in the scope of prototype design [5]. Fig. 1 shows the obtained

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power release of composites (30 g of salts and 10 g of glass wool) with strontium bromide (SrBr_2), lithium chloride (LiCl), magnesium chloride (MgCl_2), lithium bromide (LiBr), and calcium chloride (CaCl_2). Thereby, methanol was used as sorbate material. The highest power release was reached with the salts LiBr and LiCl , while it was obviously lower with other reactive salts.

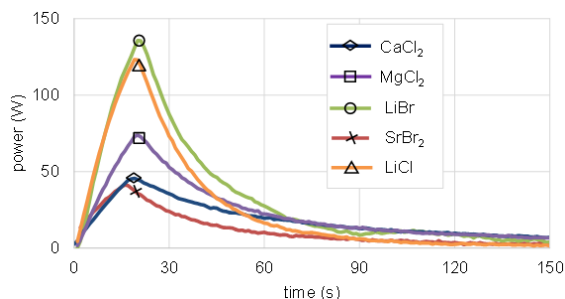


Fig. 1 Achieved power release with different reactive salts [9]

Although LiBr and LiCl were tagged as inappropriate for a system based on solid-gas hydration reactions due to their low deliquescence relative humidity in [10], a high potential of these materials was demonstrated in this research work. Therefore, LiBr was chosen for this application.

A theoretical energy density of a closed system based on the hydration reaction of LiBr and water of 1.37 GJ/m^3 was calculated in [8]. A hydration temperature of 103°C (at 12 mbar water pressure) and a dehydration temperature of 110°C (at 20 mbar water pressure) were determined. It was reported that with an increase of the evaporator temperature, the maximum hydration temperature increases as well. Generally, lower dehydration temperatures are needed at lower sorbate vapour pressures. However, in a system with methanol as sorbate, the lower dipole moment of methanol might sink the dehydration temperature [7].

B. Prototype Design

The TCES modular prototype developed in [5] was investigated to determine the performance and its suitability for mobile applications. The assembled module consists of a reactor vessel, a sorbate pipe, and a sorbate reservoir (see Fig. 2 (a)).

The reactor vessel was designed as a cylinder (cartridge) and was 3D printed of AlSi-Alloy. The sorbent composite of LiBr (80 g - anhydrous) and glass wool (40 g) formed the porous reactive bed which was placed into the 3D printed reactor on the thin ribs for better heat exchange (see Fig. 2 (b)).

The sorbate (30 g of methanol) was placed in a reservoir (constructed of Al) which acts as evapo-condenser. It ensures the supply of vaporization heat and removal of condensation heat through the cooling ribs during the operation. With a limited amount of methanol (30 g) in the sorbate reservoir, an over-hydration and material clogging were avoided. The module from [5] was adapted with a sorbate pipe. It aims as thermal insulation between the reactor and the sorbate

reservoir. In that way, lower sorbate temperatures were ensured during charging. An electrically actuated magnet valve system was situated within the sorbate reservoir. It consists of a magnetic steel core (armature) with a valve disc on top and a coil which pulls the steel core and the valve opens [5].

The reactor, sorbate pipe, and sorbate reservoir were sealed and evacuated. The module must be vacuum-tight since the inert gases strongly reduce the performance [8], [11]. An advantage of a closed system is an extremely fast vapour transport which results in high power density [8]. The module has a total mass of 1.25 kg and a volume of 0.9 liters. There is still room for improvement here in order to reduce the high passive mass of metal components (1140 g) compared to the mass of reactive materials (110 g).

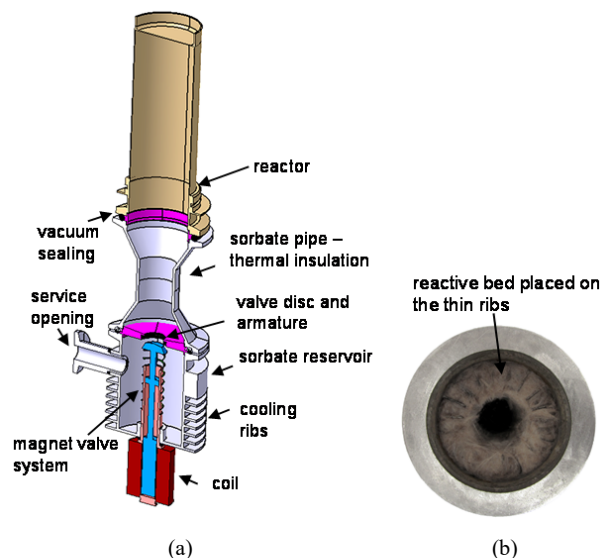


Fig. 2 (a) TCES modular prototype and (b) reactor with the reactive bed – adopted from [5]

The module operates in two phases – discharging and charging with a heat storage phase in between. During the discharging, the liquid methanol evaporates in the sorbate reservoir by consuming heat from the environment and flows to the reactor due to a pressure difference. The vapour gets absorbed by the reactive salt into the crystal lattice and the sorption heat is released in an exothermic reaction. During charging, the heat is supplied to the reactive bed, whereby a decomposition reaction occurs. The separated sorbate vapour flows to the sorbate reservoir where it condenses by releasing the heat into the environment.

III. EXPERIMENTAL METHODS

To investigate the performance at different ambient temperatures and the cycle stability under real operating conditions, the module was installed into an experimental test bench as presented in Fig. 3. The reactor was immersed into a coolant bath and the sorbate reservoir into a tap-water bath for sorbate cooling. The data acquisition occurred with

temperature elements and pressure gauge.

During discharging (300 s), the absorption heat was released to coolant bath and the average bath temperature was measured. Thereby, the sorbate cooling was inactive and the heat for the vaporization was consumed from the ambient air.

During charging (1800 s), the coolant bath was heated with an electric heater up to a dehydration temperature of 95°C which meets an operating temperature of the coolant of an internal combustion engine. Beside, the sorbate was cooled to a sorbate temperature of 12 °C. The sorbate vapour pressure in the system equivalent to the sorbate temperature, i.e. 83 mbar was measured.

Before the first use (initial test), the reactor was charged (heated) in a convection oven at a temperature of 190 °C in presence of ambient. In that way, the reactor was completely dehydrated.

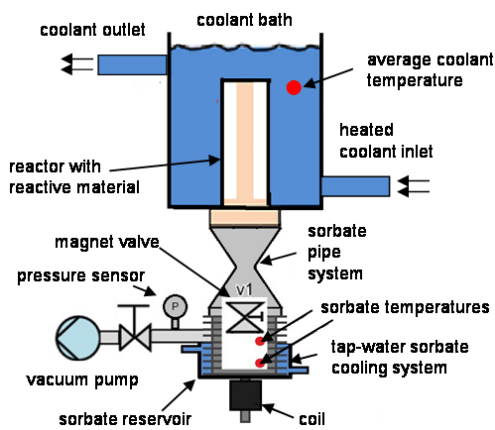


Fig. 3 TCES modular prototype on experimental test bench

The heat output (P), which was released during the discharge of the module in the coolant bath was used for the evaluation. It was calculated using (m_c) mass of the coolant, (c_p) heat capacity of the coolant and (θ_i) average temperature rise in (dt) time step measured in the coolant bath as shown in (1). The (Q) heat represents the released heat during discharging.

$$P = \frac{dQ}{dt} = \frac{m_c \cdot c_p \cdot (\theta_{t+1} - \theta_t)}{dt} \quad (1)$$

Characteristic power and heat release curves were reported in [5]. Since the prototype is designed to enable e.g. fast heating of an internal combustion engine which would occur approximately over 90 s, the average achieved powers over 30 s, 60 s, and 90 s were compared.

IV. RESULTS AND DISCUSSION

A. Performance at Different Ambient Temperatures

For mobile applications, the TCES module needs to release high discharging powers under different conditions. To investigate prototype performance at different ambient temperatures, the discharging was carried out at ambient

temperatures of -10 °C, 0 °C, 10 °C, 20 °C and 30 °C, maintained in a climate chamber. For the purpose of this investigation, the reactor was completely charged in the convection oven.

The achieved average powers over 60 s and released heat during discharging (300 s) are presented in Fig. 4. The average power increased linearly as the module discharging occurred at higher ambient temperature. Higher ambient temperatures during discharge lead to a higher sorbate temperature and thus also to a higher sorbate vapour pressure (see Table I). This improves the reaction kinetics as well as the sorbate vapour flow through the porous reactive bed. This is apparent from the fact that the sorbate flow along the reactive bed is mainly driven by the pressure gradient [12].

Since the reactor was completely charged in the conducted tests, the achieved average power represents the maximum prototype performance at each ambient temperature. Comparison of the achieved power at ambient temperatures of -10 °C and 30 °C shows a reduction of 60%.

The released heat in 300 s raised as the ambient temperature increased as well. Although the average power (60 s) obviously increased, the released heat (300 s) was in the same range at ambient temperatures of 20 °C and 30 °C, (see Fig. 4). That indicates that although the absorption occurred “faster” at an ambient temperature of 30 °C, the reactor was capable to deliver only a certain amount of heat which was limited with the amount of reactive materials and the duration of the discharging. Therefore, the maximum released heat (23.6 kJ) represents the maximum heat capacity of the module.

Due to more inconvenient reaction kinetics and vapour transport during discharging at lower ambient temperature, the power release occurred slowly. As a result, heat released over 300 s was lower. From the maximum heat capacity and mass of the module, a gravimetric energy density of 19 kJ/kg was determined.

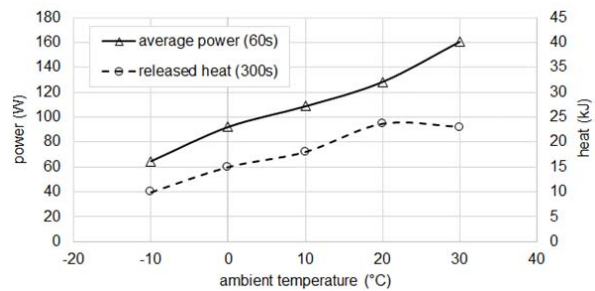


Fig. 4 Average power release and released heat at different ambient temperatures

B. Cycle Stability

In addition to high power release at different ambient temperatures, the reaction reversibility and discharging/charging cycle stability are important criteria for integration of the developed TCES prototype into a mobile application. To investigate the prototype functionality and cycle stability, a cycle consisted of an initial test and the following test 1 – 10 was carried out at an ambient temperature of 20 °C. Thereby,

the reactor charging was conducted in a convection oven at a temperature of 190 °C, in the initial test. In each following test 1 – 10, the charging was conducted on the test bench for 1800 s. The sorbate temperature was set at 12 °C and the reactor was exposed to a dehydration temperature of 95 °C. Equivalent to sorbate temperature, the sorbate vapour pressure in the system was 83 mbar. The obtained average powers over 30 s, 60 s, and 90 s in the cycle test are represented in Fig. 5.

TABLE I METHANOL VAPOUR PRESSURE	
ambient temperature	methanol vapour pressure determined according to [13]
10°C	21 mbar
0°C	40 mbar
10°C	74 mbar
20°C	130 mbar
30°C	219 mbar

The highest average power release of 130 W over 60 s was achieved in the initial test due to the completely charged reactor in the convection oven. In further tests 1-10, the achieved average discharging powers were below the power in the initial test and ranged between 75 W and 95 W (60 s). Therefore, it is apparent that the dehydration temperature of 95 °C was insufficient high for a complete reactor dehydration under sorbate pressure of 83 mbar. However, a comparison of

tests 1-10 shows satisfying cycle stability and reaction reversibility. The light fluctuations in achieved powers between tests occurred due to slightly different dehydration temperatures (95-100 °C) and sorbate temperatures (11-15 °C) during charging.

Compared to the maximum heat capacity of the module, the released heat in 300 s decreased to 15 kJ in tests 1–10. Thus, the achieved powers represent the prototype performance under real conditions possible in the internal combustion engine. For all eleven tests conducted in a row, no adverse effects on performance and reaction reversibility were observed. The tests were carried out over 72 hours, thereby no pressure rise in terms of air leakage into the system was observed. This result proves the functionality of the developed module and indicates the suitability of the TCES for mobile applications.

V. CONCLUSION

The performance of a developed modular TCES prototype based on reversible sorption reactions of LiBr and methanol was investigated. The prototype aims to be integrated into a mobile application such as heating of an internal combustion engine of a vehicle and therefore, the highest possible performance under different conditions is crucial.

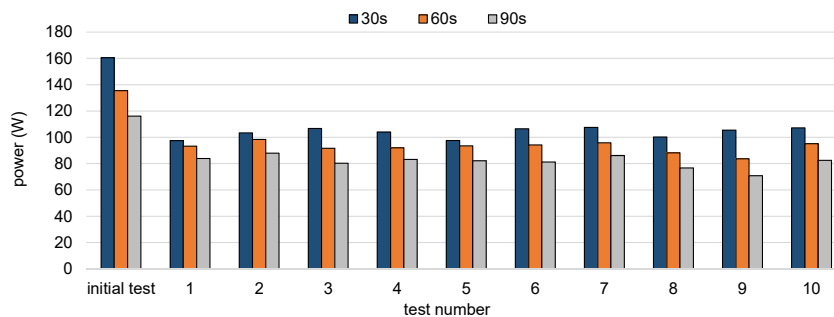


Fig. 5 Average powers in eleven discharging/charging tests in a row under real operating conditions

The maximum discharging powers were determined under different ambient temperatures in the climate chamber. It has been shown that the performance increased as the ambient temperature, i.e. the equivalent sorbate vapour pressure before discharging, increased. The maximum power achieved at an ambient temperature of 30 °C decreased for 60% at -10°C. Thus, a strong decrease in performance at low ambient temperature might shrink the attractiveness of the system. The maximum heat capacity of 23.6 kJ was determined. The heat capacity was limited with the amount of reactive materials and the duration of the discharging phase. However, the released heat decreased during discharging at lower ambient temperature due to the limited ambient heat for evaporation of the sorbate. An enhanced heat exchange could diminish this problem.

To evaluate the prototype performance and reaction reversibility on repeated discharging/charging phases, cycles

were performed under real operating conditions, which are probable in an internal combustion engine. Although complete dehydration of the reactor was not possible at dehydration temperature of 95 °C and under the sorbate vapour pressure of 83 mbar, a stable and reversible reaction resulted in constant power release over eleven discharging/charging tests. Therefore, the functionality of the developed system was proved and suitability for the integration into a mobile application was indicated.

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REFERENCES

- [1] M. Jakobi and P. Hofmann, "Residual Heat Utilisation in Vehicles by Thermochemical Energy Storage," *Motortechnische Zeitschrift (MTZ)*, no. 77, 2016, pp. 44–49.
- [2] M.-M. Druske et al., "Developed Materials for Thermal Energy Storage: Synthesis and Characterization," *Energy Procedia*, vol. 61, Jan. 2014, pp. 96–99.
- [3] F. Trausel, A.-J. de Jong, and R. Cuypers, "A Review on the Properties of Salt Hydrates for Thermochemical Storage," *Energy Procedia*, vol. 48, 2014, pp. 447–452.
- [4] K. E. N'Tsoukpoe, T. Schmidt, H. U. Rammelberg, B. A. Watts, and W. K. L. Ruck, "A systematic multi-step screening of numerous salt hydrates for low temperature thermochemical energy storage," *Applied Energy*, vol. 124, Jul. 2014, pp. 1–16.
- [5] J. Galovic, F. Havlik, and P. Hofmann, "Modular Thermochemical Heat Storage for Engine Preheating," *ATZ*, Nov. 2018 pp. 96–101.
- [6] M. Jakobi and P. Hofmann, "Restwärmenutzung im Fahrzeug durch thermochemische Energiespeicher," in *Proc. FVV Spring Conference*, Germany, 2015.
- [7] M. Jakobi, "Entwicklung eines thermochemischen Wärmespeichers auf Basis von Salzhydraten zur Verwendung in Kraftfahrzeugen" Dissertation, Institut für Fahrzeugantriebe und Automobiltechnik der TU Wien, Wien, 2015.
- [8] P. A. J. Donkers, L. C. Söğütoglu, H. P. Huinink, H. R. Fischer, and O. C. G. Adan, "A review of salt hydrates for seasonal heat storage in domestic applications," *Applied Energy*, vol. 199, Aug. 2017 pp. 45–68.
- [9] P. Hofmann and F. Havlik, "Heat Recovery in Passenger Cars by Thermochemical Heat Storage Materials," in *Proc. FVV Spring Conference*, Germany Project no. 1155, 2018.
- [10] N. Yu, R. Z. Wang, and L. W. Wang, "Sorption thermal storage for solar energy," *Progress in Energy and Combustion Science*, vol. 39, no. 5, Oct. 2013, pp. 489–514.
- [11] K. E. N'Tsoukpoe, H. Liu, N. Le Pierrès, and L. Luo, "A review on long-term sorption solar energy storage," *Renewable and Sustainable Energy Reviews*, vol. 13, no. 9, Dec. 2009, pp. 2385–2396.
- [12] A. Fopah Lele, "A Thermochemical Heat Storage System for Households: Thermal Transfers Coupled to Chemical Reaction Investigations," Dissertation, Leuphana University of Lüneburg, Germany, 2015.
- [13] International Union of Pure and Applied Chemistry, Ed., *International thermodynamic tables of the fluid state. 12: Methanol*. Oxford: Pergamon Press, 1993.