A Novel State of Charge Sensor Concept for Thermochemical Heat Storage

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Abstract

A functional prototype of a state of charge sensor for a solid sorption thermochemical heat storage was developed. The sensor concept is based on detecting the relative change of permittivity when water vapour adsorbs on the surface of the sorptive material. This is done by measuring the capacitance of a capacitor where the sorptive material is utilized as dielectric. We were considering Zeolite and Silica gel in the experimental validation of the sensor concept. The experiments showed a strong correlation between the measured capacity and the weight of the material which indicates the saturation with water, both in the adsorption and in the desorption stage. Several consecutive experiments proved the repeatability of the measurements which subsequently could be used to identify a sensor calibration function in order to relate the capacitance with the state of charge.

Keywords: Sorption thermal energy storage, solid adsorption

1. Introduction

Storage of heat is essential in industry as well as in domestic homes and can be realized through many different technological pathways. Sorption thermal storage methods and materials are a very active area of research (Aydin et al. 2015) and are often utilized in combination with solar energy production. The concept of storing surplus solar energy during summertime and using it in wintertime for e.g. space heating is referred to as seasonal storage (Scapino et al. 2017). Various different process types of thermochemical sorption energy storages for seasonal storage are compared against each other in (Fumey et al. 2019). The main process technologies can be subdivided into open and closed systems (Bott et al. 2019) depending on whether the thermochemical material is operating at atmospheric pressure or is contained inside of a vacuum chamber. Another distinction can be made whether the sorption material is continuously transported while reacting (Zettl et al. 2014, Zettl and Kirchsteiger 2018) or is stationary in a fixed bed reactor (Mette et al. 2014) without material movement. In this work, our prototype state of charge sensor is evaluated on an open process with a fixed bed.

There is a whole variety of material combinations where the thermochemical effect of storing and releasing energy through adsorption of a fluid (called *adsorbate*) on a solid material (called *adsorbent*) is utilized (Shmroukh et al. 2015). From a process handling point of view, the combinations of Zeolite or SilicaGel as adsorbent and water vapor as adsorbate are frequently used because the temperatures are in a reasonable range, there are no hazardous chemicals involved and the materials are relatively cheap. Those are the reasons why those combinations are considered in this study as well.

The basic and simplified working principle of an open solid sorption storage using the material combination zeolite and water vapor is shown in Fig. 1: When charging, a flow of hot and dry air dries the sorptive material, removing the adsorbed water atoms from the pores. This process is called *desorption*. The dried out material stores heat at low temperatures without losses as long as it does not get in contact with water vapor. For discharging, water vapor needs to be provided to the sorptive material where the water atoms adsorb in the pores thereby releasing large amounts of energy in the form of heat. This process is called *adsorption*. The whole process is repeatable without losses, although the hydrothermal stability of the zeolite powder or beads decreases with usage (Fischer et al. 2018). A more detailed process description can be found e.g. in (Do 1998).
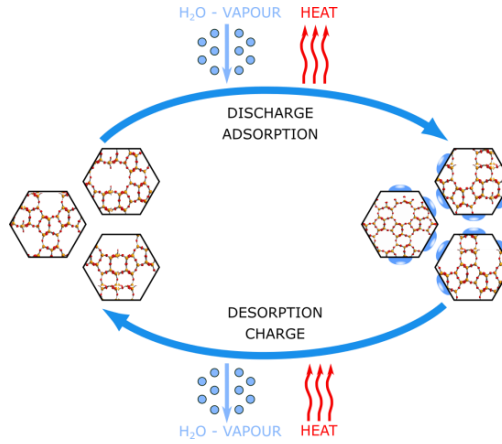
Fig. 1: Sorption working principle (the hexagons indicate Zeolite molecules)

Sorption thermal storage devices can play a significant role in future renewable energy system for domestic homes. Their efficient use requires advancements in materials science (development of adsorbents with high storage energy density), in process engineering (system layout, efficient material transportation, avoid mechanical stress to the adsorbents), and in overall process control (temperature regulation and humidity control). From the control point of view, sensors are required to measure the current state of charge of the system. The importance of sensing the state of charge has already been recognized in the battery storage community a long time ago (How et al. 2019). Recently, the phase change material (PCM) storage community focuses on state of charge sensors as well (Steinmaurer et al. 2014, Barz et al. 2018).

Currently, no specific sensors to measure or estimate the state of charge of sorption storages or sorptive material are available. Experimental prototype solutions were presented in (Luoma et al. 2017) where infrared spectroscopy was used to analyze the reflected light from specifically prepared zeolite tabs and conclude on the water content in the material. Besides physical measurement principles, there is the alternative option to employ software sensors which make use of mathematical models. In (Scapino et al. 2019) such a concept was introduced using neural networks, however, the method was only tested on datasets generated with another model (of higher complexity) but not on real data.

In this paper, an experimentally validated proof of concept sensor based on measuring the relative change in permittivity is described. We consider zeolite and silica gel in the form of small beads with a diameter between 2 and 5 mm and water vapor as adsorbate. A specific lab setup was designed to experimentally validate the sensor concept both in adsorption and in desorption mode.

2. Methods

The physical principle used to detect the water content of the sorption material is the difference in relative permittivity of water (Andryieuski et al. 2015) and the adsorbent. The relative permittivity of water up to 1 GHz is in the range of 50-90 (see Fig. 2) whereas the permittivity of sorption material is typically in the single digits. In (Zheng et al. 2013) it is stated that a direct correlation of adsorbed amount of water and the dielectric constant of the material is existent.

If sorption material is utilized as dielectric of a capacitor, the capacity is directly correlated to the relative permittivity of the material. The voltage V, i.e. the difference in the potential, is defined as the line integral across an electric field E. In a one-dimensional point of view (for plate-type capacitors) this is

$$V = \int E(z)dz = \int \frac{\sigma(z)}{\epsilon_0 \epsilon_r} dz \tag{2.1}$$

where ε_0 is the permittivity of vacuum, ε_r is the relative permittivity of the material used as dielectric of the capacitor and σ is the charge density. The capacity C is then given as:

$$C = \frac{Q}{V(Q)} \tag{2.2}$$

where Q denotes the electrical charge. Since most capacity measurement techniques work with transient input signals (rectangular or sine), the frequency range must be considered in order to get good sensitivity for the measurement i.e. higher values for the relative permittivity. As Fig. 2 shows, signals below approximately 1 GHz will be suitable in that regard.
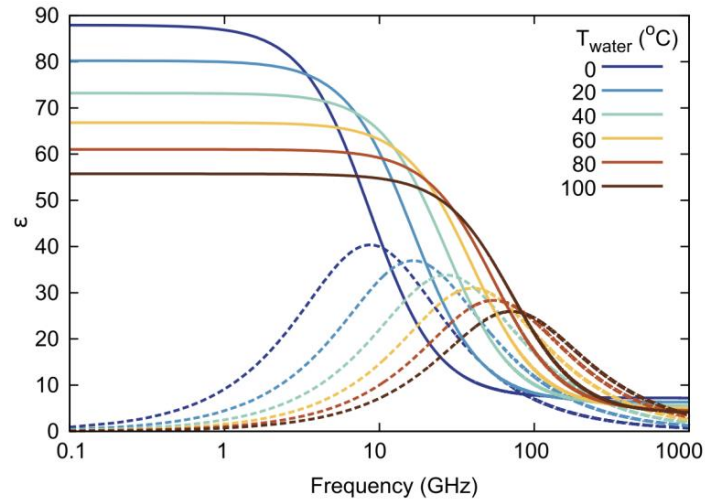

Fig. 2: relative permittivity of water (Andryieuski et al 2015)

3. Sensor prototype and lab setup

The conceptual lab setup to validate the experimental prototype is shown in Fig. 3. The main components are a radial fan, an electrical heater, the measurement capacitance filled with sorptive material, a scale and a flexible hose connection between the part resting on the scale and the rest of the setup.

The actual realization of this concept in a lab-scale prototype is shown in Fig. 4 and was described in detail in (Bin Azman et al. 2020). The capacitance filled with sorptive material is made out of two concentric copper cylinders with diameters of 90mm and 60mm respectively. The air supply shown in the lower left part of Fig. 4 can be controlled with respect to temperature and air mass flow. The selectable temperature range is between ambient and a maximum of 300°C which enables to perform an efficient desorption while the material is inside of the storage. The air flow through the storage is continuously adjustable with a radial fan which sucks in ambient air. For process monitoring, temperature sensors and humidity sensors are installed at the outlet of the air stream after the storage.
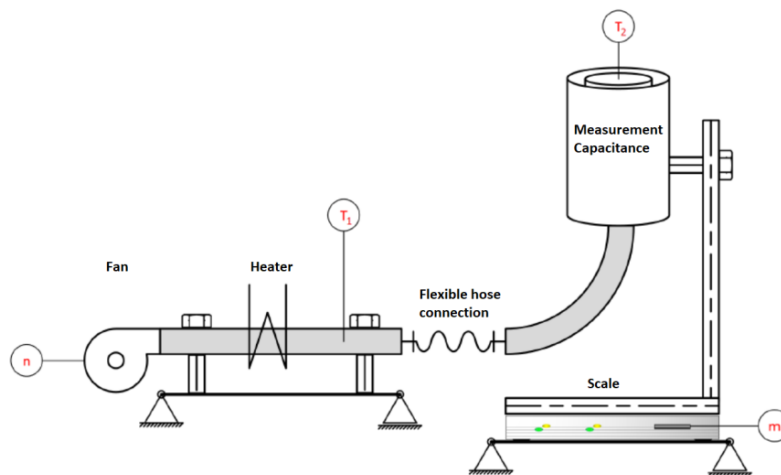

Fig. 3: Schematic of the entire experimental setup

The capacitance itself is evaluated with an oscillator circuit made out of a parallel connection of a known capacitance C and an inductance L that results in a resonance frequency

$$f_R = \frac{1}{2\pi\sqrt{LC}} \tag{3.1}$$

Connecting the unknown capacitance C_X of the storage in parallel to C results in a modified resonance frequency

$$f_R' = \frac{1}{2\pi\sqrt{L(C + C_X)}} \tag{3.2}$$

Based on those two frequencies and the known values of the components, the unknown capacity is evaluated:

$$C_X = \left(\frac{f_R}{f_R'} - 1\right) C \tag{3.3}$$

The whole setup is resting on a lab scale with a resolution of 0.05g, which continuously measures the weight. This weight measurement serves as a reference value for the unknown state of charge of the material since an adsorption or desorption of water vapor is directly reflected in the weight. The measurement capacitance cylinder is filled with approximately 500g material.

All measurements were cyclically recorded with an Almemo (Ahlborn Mess- und Regelungstechnik GmbH, Holzkirchen, Germany) data logging device connected to a standard desktop PC running MATLAB/Simulink (MathWorks, Natick, MA) which was used to implement the control loops for the temperature and fan speed.
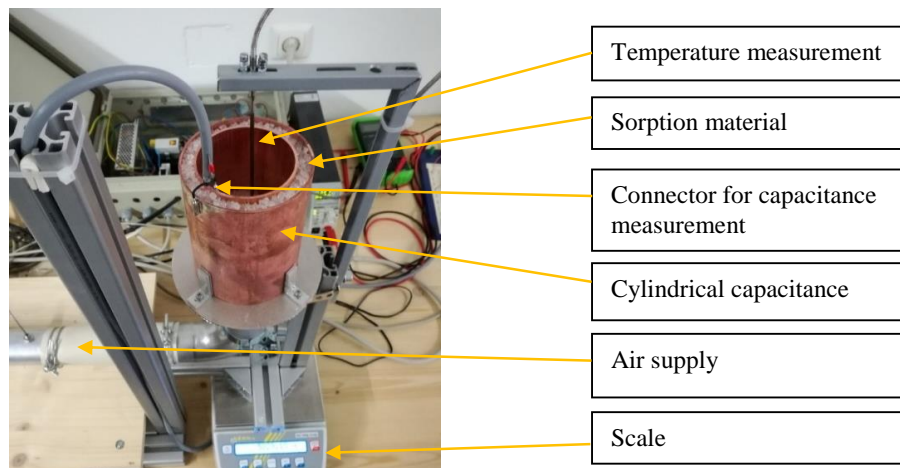

Fig. 4: Experimental setup used to validate the sensor concept

4. Evaluation Procedure and Results

In this section, we present the measurement results of the prototype capacitive sorption sensor evaluated on a fixed bed reactor using Zeolite and SilicaGel. The results are subdivided in adsorption and desorption results for both materials.

The measurement procedure started with filling the measurement cylinder (inside and annulus) with approximately 500g material with an initially unknown charge with water vapor. Then, the heater was set to a temperature of 300°C in the case of zeolite (180°C in the case of Silicagel) in order to achieve a desorption. The desorption stage was held until the weight did not change significantly anymore which was after around one hour. Subsequently, the temperature was set to 20°C (for both material types), effectively switching off the heater, and running into an adsorption stage. The switch from desorption to adsorption is not instantaneously, since the measurement cylinder and pipe connections initially need to cool down from the high desorption temperatures. The adsorption stage was again held until the weight did not increase significantly anymore which was after around two hours. This cycle of desorption and adsorption was repeated for five times in order to analyze the repeatability and reliability of the prototype sensor concept.

The measurement results of one such cycle for zeolite are shown in Fig. 5. On the left side is the desorption stage and on the right side the adsorption. Those two stages follow each other immediately, however, there is a small time

gap in the measurements due to saving the data and restarting the measurement hardware. The desorption figure to the left shows that the 300°C air temperature after the heater leads to a temperature of approximately 200°C at the outlet of the storage which is high enough to enable a significant desorption. The activity of the sorptive material can be monitored by the relative humidity of the outlet air stream: initially (between 0 and 5 minutes) large absolute quantities of water vapour are released (note that in this period the temperature is already increasing up to almost 100°C). Later on, the released water vapour diminishes and eventually reaches a steady state which depends on the desorption temperature and the partial pressure of H_2O of the surrounding air. From the bottom graphs in Fig. 5 it already becomes evident that the weight measurement and the proposed capacity measurement are highly correlated. From the top graph on the right side of Fig. 5 the cool down phase of the equipment can be observed between 0 and approximately 5 minutes. Additionally, heat is actively produced by the zeolite because of the supply with humid air at ambient temperature. All measurements were done in January 2018, during Wintertime in Austria where there is a typical relative humidity of ambient air of approximately 30% and an ambient temperature of approximately 22° indoors. This low humidity is the reason why the desorption part of the experiment takes relatively long and would be much faster if larger amounts of water vapour would be provided. This does, however, not affect the validation of the sensor principle in any way.
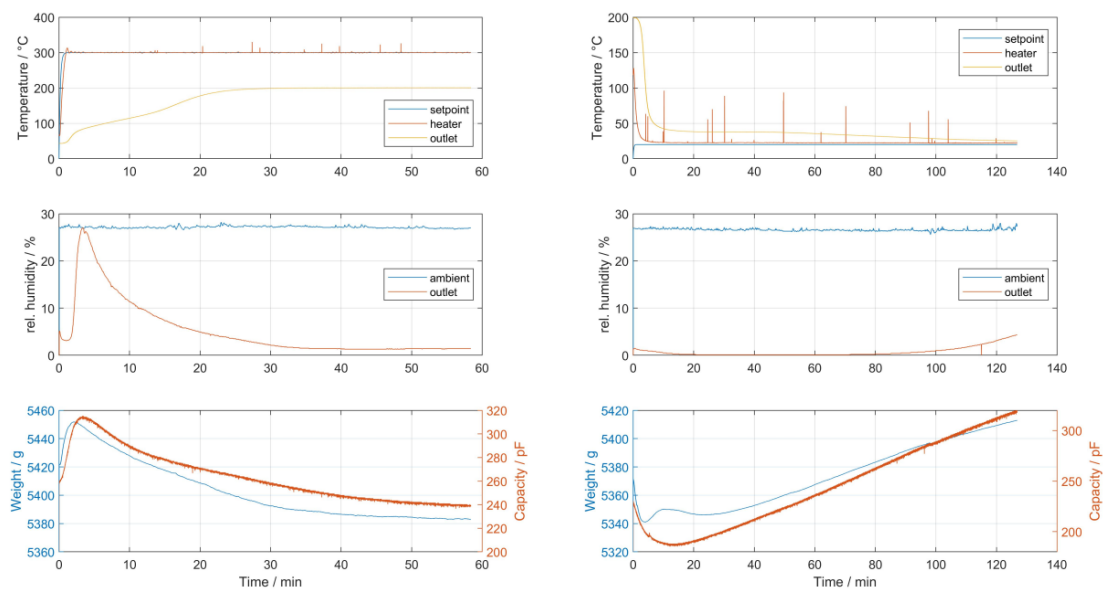

Fig. 5: One cycle of zeolite desorption (left) followed by adsorption (right)

To better evaluate the connection between the measured capacitance and the weight, they were plotted against each other as shown in Fig. 6 for Zeolite and Fig. 7 for Silica gel. Under the assumption that the weight is an indicator for the state of charge of the material, an ideal sensor would result in a straight line in those graphs providing a linear relationship between the sensed quantity and the reference value. In the case of zeolite adsorption such a linear relationship indeed occurs, however, in the case of zeolite desorption the resulting graph is only piecewise linear consisting roughly of a combination of two linear functions. For silica gel the relationship is following a polynomial shape for adsorption (see Fig. 7) and is linear in a large range for desorption followed by a slightly steeper increase for higher masses, i.e. higher state of charge.

5. Discussion and Conclusion

From the results presented in the previous section, the general conclusion is that the measured capacitance is a good indicator of the material weight, which in turn is directly connected with the state of charge. Therefore, the hypothesis of using a capacitance measurement as substitute for the state of charge of the material proves to be true. For the piecewise linear and polynomial relationship, a simple sensor calibration function needs to be developed and implemented in the sensor hardware. Such a sensor calibration function seems to be a possible approach since the non-linear behavior could be reproduced within small margins in five independent experiments.
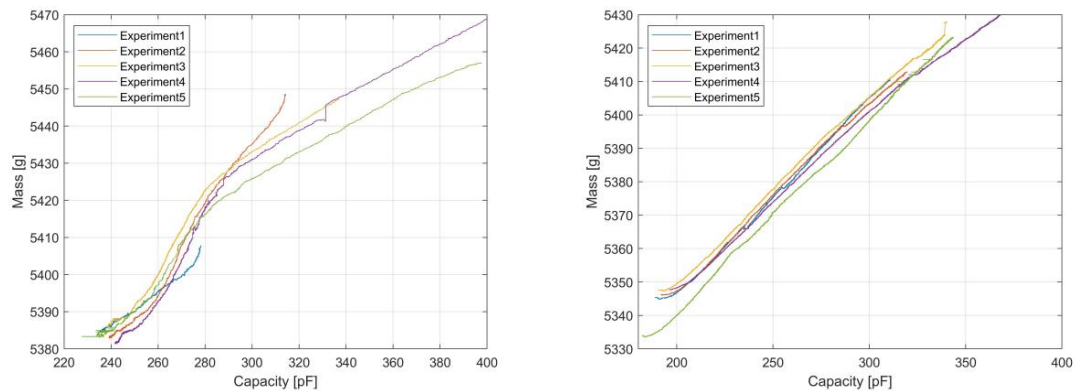
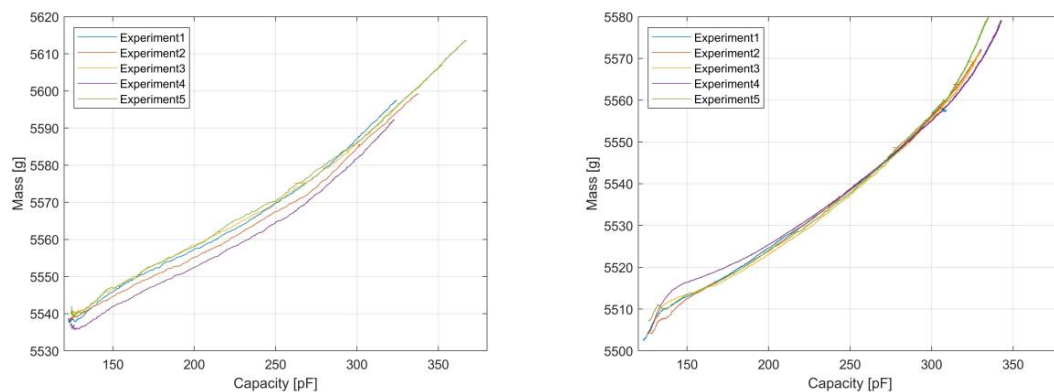**Fig. 6: Zeolite desorption (left) and adsorption (right)**

Fig. 7: Silica gel desorption (left) and adsorption (right)

The results presented prove the general validity of a concept of a state of charge sensor based on a capacitance measurement, however, several issues need further investigation:

- In the current prototype, the sensor itself is the storage. In future applications, especially for large scale storages, it should be aimed for to miniaturize the sensor.

- Miniaturized sensors based on the proposed concept could be placed at several locations inside a large scale storage providing a distributed information of the state of charge, similar to Li-ion batteries where the state of charge of individual cells is monitored and an overall state of charge is calculated.

- The sensor reading is by construction an average of the state of charge of the whole material inside the active area of the capacitance. Making the capacitance smaller could lead to a higher variance.

- A miniaturized sensor leads to smaller values of the capacity, which makes the evaluation more difficult.

- The sensor prototype was already tested on a moving bed reactor where material is continuously passing through the capacitance; however, this also needs further investigation.

None of those issues seems to be jeopardizing the general concept, thus we are working to expand the possibilities and accuracy of the current prototype.

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