Energy Storage for Air-Conditioning Using CO$_2$ Gas Hydrates

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Abstract

The prevalence of air conditioning in buildings and its synchronicity within a geographic region causes peak load capacity problems for electricity transmission and distribution infrastructure. While solar photovoltaics can assist in mitigating midday and early afternoon peak loads, late afternoon and evening loads cannot be serviced in this way. Presently, battery storage is not as cost effective as thermal storage for air conditioning. However, thermal storage systems are not widely adopted in this field.

In this paper, we discuss a range of issues associated with the use of phase change energy storage at typical air conditioning evaporator temperatures. These issues include sub-cooling, melt-freeze hysteresis, thermal conductivity, energy density, cost and cyclic stability.

We present a phase change material tailored for storage of energy at a range of temperatures between 5°C and 12°C. The material is a type of gas hydrate formed from water, a salt and carbon dioxide gas. The energy store operates in a pressurized heat exchanger whereby the phase change temperature may be tuned by modifying the vessel pressure over a range of 4-8 bar. The gas hydrate has appearance and properties similar to ice.

Through systematic development, the material now exhibits an energy storage density of around 90 kWh/t, similar to conventional ice and superior properties to most other phase change materials. Additionally, the gas hydrate may be used with conventional chillers operating at conventional evaporating temperatures. The cost of the energy storage system, including material and heat exchanger is estimated to be around $250/kWh at lab scale.

The main field of application of the gas hydrate cold store material is to allow air conditioning chillers to run overnight, storing the cooling effect for deployment during the following day. Not only can the chiller operate on low cost off-peak electricity, but also the chiller runs more efficiently when heat is rejected to cooler overnight temperatures.

The next steps involve scale up to commercial air conditioning installations in the cooling capacity range 10-100 kW. The gas hydrate store would run in parallel with the chiller on a heat exchange loop, thereby providing fail-safe operation.

1.   Introduction

Conventional vapour compression chillers have undergone detailed development such that chiller efficiency is approaching its practical limits. For further improvements in energy efficiency for air conditioning of buildings, we must turn our attention to the whole air conditioning system. This system is comprised of the chiller, its energy supply infrastructure, the cooling distribution system, the building and the building occupants.

Cold thermal energy storage (CTES) provides a means to smooth supply of cooling service and demand of electricity for a building. CTES is also attractive for use in solar cooling applications where the supply of solar energy may be intermittent. CTES has other benefits: the chiller capacity can be reduced, thereby saving capital cost to offset the cost of CTES; off-peak electricity rates can be accessed; the chiller efficiency improves through operation overnight in cooler condensing conditions and a degree of resilience is provided to the air conditioning system.

Of the classes of CTES, phase change materials (PCMs) are ideal candidates for air conditioning applications due to their constant temperature freezing property (suits chiller evaporators that also operate a latent heat process), constant temperature melting property (suits air dehumidification) and high energy density.

Of the PCMs, the use of conventional ice is problematic because the chiller must operate its evaporator at much reduced temperature to freeze the water. This is detrimental to its efficiency. Many other PCMs are expensive (paraffins and hydrated salts) and some have cyclic stability problems due to phase segregation (hydrated salts) or have limited heat transfer capability.

In this work, we investigate gas hydrates as an option for CTES in air conditioning applications. Most small and non-polar gas molecules will form gas hydrates with water. We have selected CO_2 hydrate due to its high energy density, low cost, safety and low environmental impact. However not much is known about the suitability of CO_2 gas hydrates in CTES applied to air conditioning applications.

1.1.   Gas hydrates

Gas hydrates are non-stoichiometric, ice-like crystalline compounds formed through a combination of water molecules and small non-polar molecules (Sloan and Koh, 2008). Water molecules form closed cage-like structures and host the smaller "guest" molecules. Candidates for the guest molecules include low molecular weight hydrocarbon gases, small refrigerant gas molecules and natural gases such as CO_2.

Gas hydrate crystalline structures are classified as structure s-I, structure s-II, and structure s-H, where each structure is defined by the manner in which the host cages join together (Figure 1). The gas hydrate cages form through hydrogen bonding of the water molecules. Guest gas molecules can become trapped within the cages. The size of the cavity is the main determinant of the ability of a gas to be enclathrated.

Upon formation and dissociation of the gas hydrate, there is a substantial change in enthalpy between the reactant(s) and product(s). This large enthalpy change makes gas hydrates a potential candidate for cold thermal energy storage.
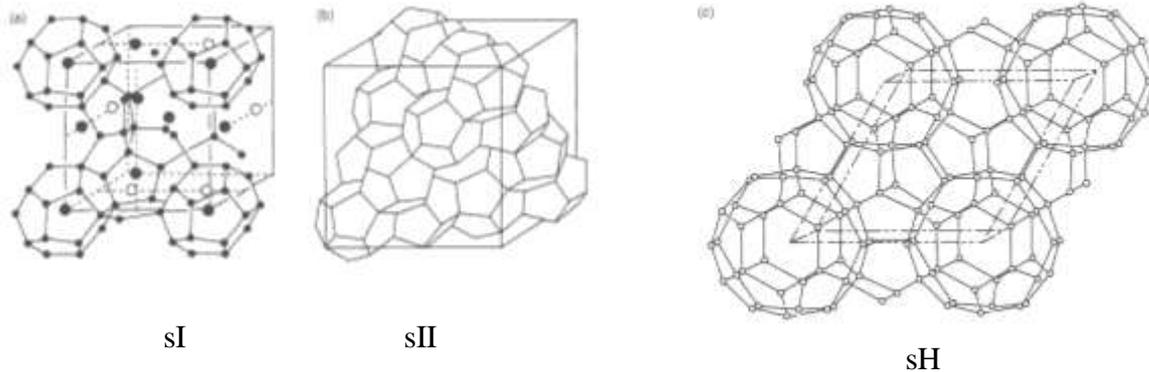
sI   sII   sH

Figure 1. Gas hydrate structures composed of hydrogen bonded water molecules (Sloan and Koh, 2008).

Although a large number of hydrate compounds can be formed, there are some practical restrictions on hydrates that are suitable for cold storage in air-conditioning applications. The main restrictions are that the hydrate should have a safe operating pressure, be non-flammable, be non-toxic, contain environmentally friendly constituents, have a phase transition temperatures in the range 5-10°C and exhibit high energy density.

Refrigerant hydrates are attractive because they can be directly coupled to a heat pump, thereby eliminating the additional cost and temperature loss associated with heat exchange with the hydrate. However, a large volume of refrigerant would be required because the resulting hydrate phase change enthalpy is not particularly high and this would expensive. There are also practical problems of water vapour carryover into the compressor and maintaining oil compatibility (Alshaibani, 2016).

After weighing up a number of considerations, we selected CO_2 as the guest molecule. Hydrates based on CO_2 are known to form sI hydrate structures and have high energy density (90 kWh/t) but form at rather high pressures, in the order of 40 bar corresponding to 8°C. However, we show that the use of hydrate formation promoters is able to reduce the formation pressure to a range of pressures below 10 bar.

2. Measured Behaviour of the CO_2 hydrate

We have measured the formation and dissociation properties of the CO_2 hydrate with sample volumes from 1 cm^3 to 8 L. We also report on experimental peculiarities we have observed and assess the material's suitability as a cold storage medium.

2.1. Hydrate formation

A gas hydrate spontaneously forms when the host water molecules and guest gas coexist at the formation pressure and below the formation equilibrium temperature.

Formation conditions are usually achieved by heat exchange into the constituents which are contained in a pressure vessel. In our work, we used a thermostatic bath to simulate the cooling action of a chiller on the cold store constituents. The thermostatic bath was operated at a temperature a few degrees lower than the expected hydrate formation temperature corresponding to the experimental pressure. This temperature difference is referred to as subcooling (Figure 2). Subcooling is undesirable since the air-conditioning chiller efficiency decreases as the subcooling increases.

Hydrate formation is characterized by supercooling of the solution over a period known as the induction time. During this period, water molecules nucleate in a stochastic manner to form a critical nucleate size, after which the hydrate formation proceeds more rapidly. Hydrate formation is then exothermic at the formation temperature. Our experiments show that nucleation delay may be reduced by small additions of physical or chemical agents such as surfactants, nanoparticles, or by ultrasonic vibration.
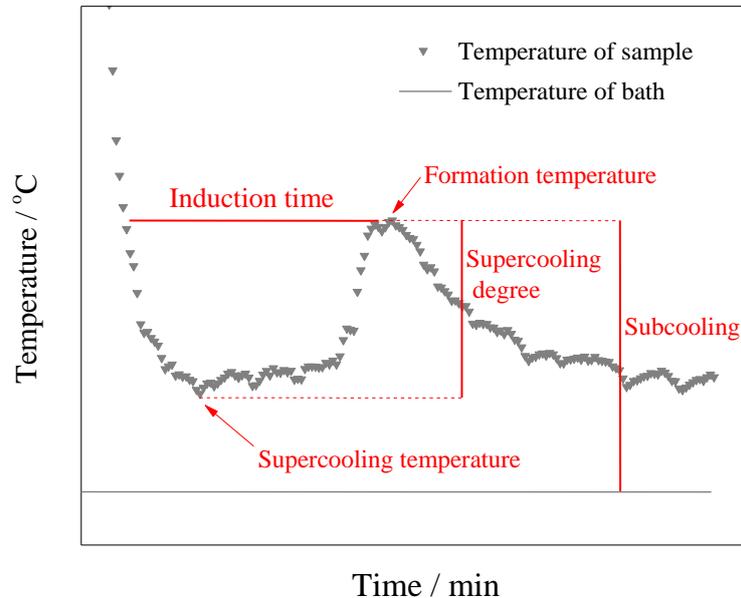

Figure 2. A typical hydrate formation process.

Hydrate formation is often represented in pressure-temperature coordinates (Figure 3). The red line indicates liquid-hydrate-vapour (L_w-H-V) phase equilibrium with liquid water and gas to the right of the red line and liquid water and solid hydrate to the left. Starting at ambient conditions (I), the water solution is pressurized (A) and then cooled (B). Some supercooling may be required and hydrate formation begins at point C. Between points C and D, gas is absorbed and the system pressure reduces if the system is closed. The location of point D depends on the formation conditions and subcooling conditions.
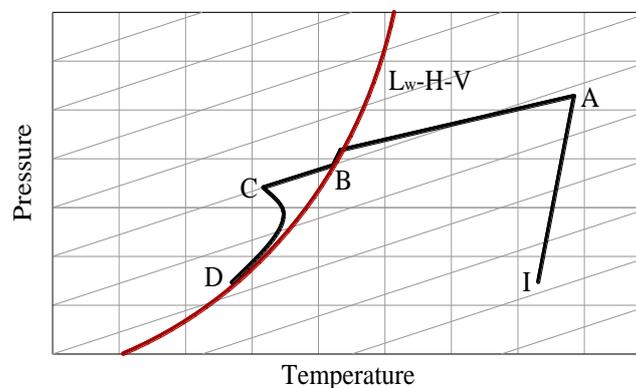

Figure 3. Hydrate formation shown in p-T coordinates. The solid red line is the L_w-H-V phase equilibrium curve.

When a gas hydrate is formed, there is a considerable reduction in entropy because the gas is, in effect, condensed into a small volume. This is offset by the availability of the kinetic

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energy of the gas molecules, and a contribution from the van der Waals attraction between host and guest, which can be turned into entropy in the surroundings (exothermic reaction). The net result is that the solid can be formed at temperatures above those of the formation of pure ice (Calvert, 2016).

CO_2 hydrate naturally forms at temperatures between 0^oC and 10^oC and at pressures of 15-40 bar (Eslamimanesh et al, 2011). Considerations of cost and safety led us to seek means to reduce the formation pressure. For use in air conditioning chilled water systems, we set a maximum operating pressures of 10 bar based primarily on cost considerations of storage tanks. Previous studies have established that the addition of quaternary alkyl halide salts as hydrate formation promoters and are able to reduce the formation pressure accordingly (Meysel et al, 2011). These promoters have similar morphology to the water cages and become part of the molecular cages in the hydrate.

The hydrates formed with promoters are not pure water based hydrates and are thus known as semi-clathrate hydrate compounds. The cages are formed when the halide ions form hydrogen bonds with water molecules. The alkyl cation is encaged at the centre of four water-framed cages, leaving the remaining cages to be occupied by the guest gas molecules. Like gas hydrates, semi-clathrate hydrates are capable of selectively trapping large volumes of gases within a molecular framework of water molecules. However, semi-clathrate can be formed at a substantially lower pressure than pure water based gas hydrates.

2.2. *Hydrate formation reactors*

Most hydrate researchers use a differential scanning calorimeter (DSC) to analyse properties of phase change materials such as gas hydrates (Delahaye et al (2006), Zhang and Lee (2009), Deschamps and Dalmazzone (2009), Klancnik et al (2010)). Since hydrates form at elevated pressure, a high pressure DSC is required. The main problem with this equipment is the small sample size. Hydrate nucleation is a stochastic process and we have noticed inconsistent results in the sample volumes below a few cm^3. Our initial studies were conducted with pressurised test tubes with a volume of 0.07 L. The results reported in this paper relate to a larger pressure vessel that produced hydrate volumes of around 8 L.

The pressure vessel pressure vessel was constructed to facilitate study of hydrate formation and dissociation (Figure 4 and Figure 5). The vessel was equipped with a viewing window so the crystal morphology could be studied during freezing and melting. A heat exchange coil within the vessel was supplied alternately with chilled water or heated water from a thermostatic bath to facilitate hydrate formation and dissociation respectively.

Gas pressure in the vessel could be regulated to maintain constant gas pressure as the gas became enclathrated in the hydrate (constant pressure reaction), or isolated from the vessel to conduct a constant mass reaction.

An external pumped liquid loop was connected to the reactor. Within this loop, there was a crystallizer. The crystallizer was equipped with an ultrasonic vibrator to assist with formation of hydrate nuclei. The liquid was returned to the vessel through a spray nozzle to further increase the interaction between the gas and hydrate nuclei.

A typical hydrate formation characteristic is shown in time coordinates (Figure 6) and pressure-temperature coordinates (Figure 7).

Firstly, the contents of the vessel are pressurised with the guest gas and cooled to just above the hydrate formation temperature, usually in a step-wise manner. Hydrate nucleation is then

initiated by subcooling the water solution. Hydrate formation is indicated by a sudden rise in temperature and decreasing gas pressure (for constant mass reactions).
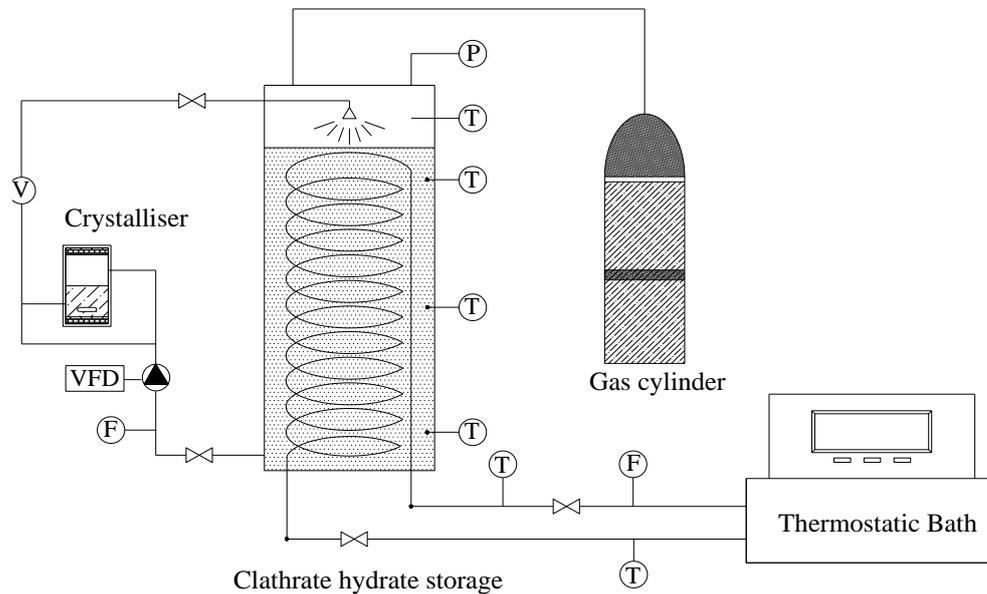

Figure 4. Schematic of the hydrate pressure vessel.

Figure 5. The hydrate vessel and hydrate seen through the top view port.

The hydrate formation rate is limited by the ability of the system to transfer heat and mass (Yang et al, 2011). The gas hydrate is a poorer thermal conductor compared to ice and so a large heat transfer surface area needs to be available. Further, mass transfer of gas into the hydrate structure is limited by the extent of the mixing interface. In principle, the mixing interface can be enhanced by the use of solution recirculation and nozzles that spray the water mixture into cooled gas.

The hydrate formation rate must match the rate of cooling produced by the air conditioning chiller. Our experiments show that hydrate formation is naturally too slow for air conditioning CTES. However, the formation rate may be enhanced by increasing the gas pressure above the equilibrium formation pressure and by decreasing the temperature of the heat transfer medium. Sustained increases in gas pressure during formation are helpful to increase both the extent of formation (and hence the energy stored) and the rate of formation.
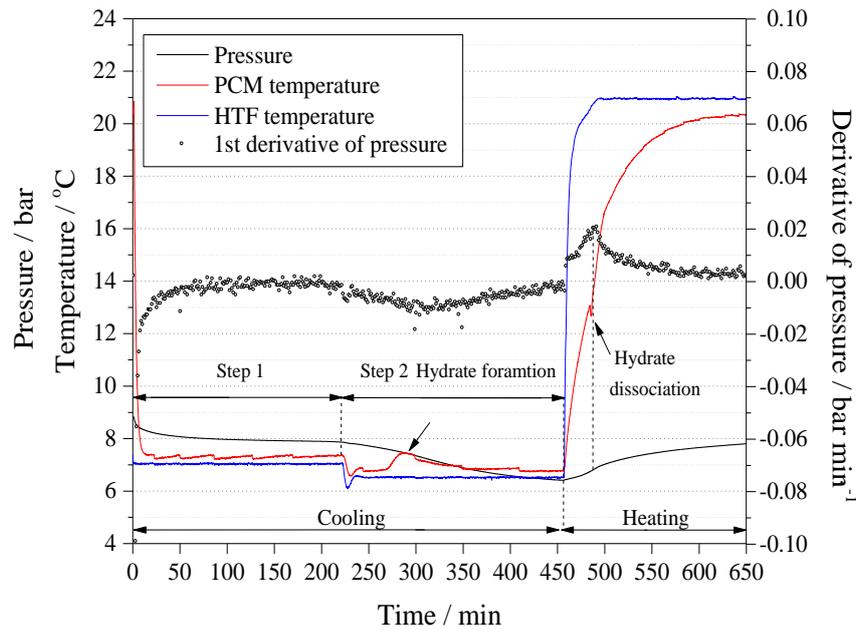
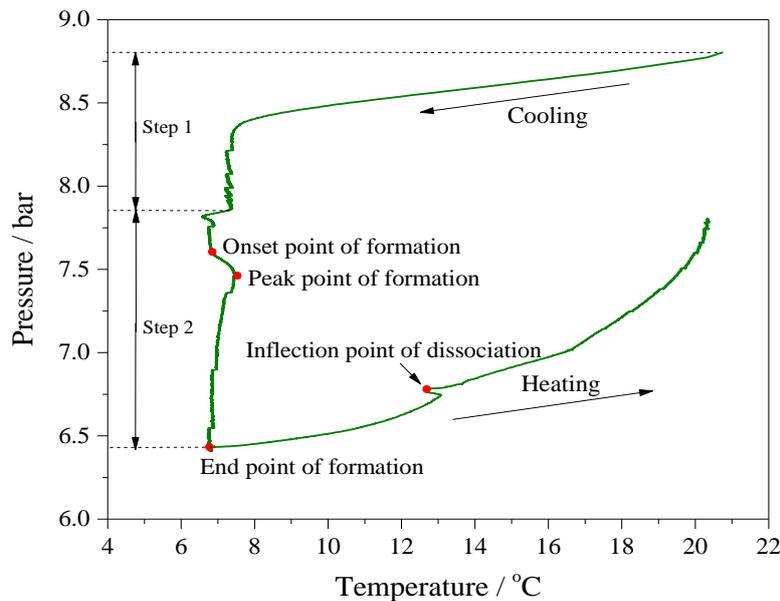**Figure 6. Hydrate formation and dissociation in time coordinate.**

Figure 7. Hydrate formation and dissociation in p-T coordinates.

The hydrate phase change enthalpy is measured using the T-History method developed by Yinping for PCM enthalpy testing (Yinping, 1999) and developed by the authors for hydrate testing at elevated pressure. Essentially, the thermal history of the gas hydrate sample undergoing phase transition is compared to the simultaneous temperature change of pure water in a shared environment. Knowledge of the thermal properties of pure water allows the phase change enthalpy of the hydrate to be determined. Phase change enthalpy of the CO_2 gas hydrate was found to be 318 kJ/kg (~90 kWh/t). This enthalpy is close to that of pure water ice (330 kJ/kg) and double that of common PCM materials. Moreover, it is a factor of 15-20 greater than the energy density of chilled water.

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From the result of a trial operation in the hydrate vessel, the energy storage capacity during hydrate formation can be enhanced using a constant pressure mode instead of constant mass mode, as shown in Figure 8.
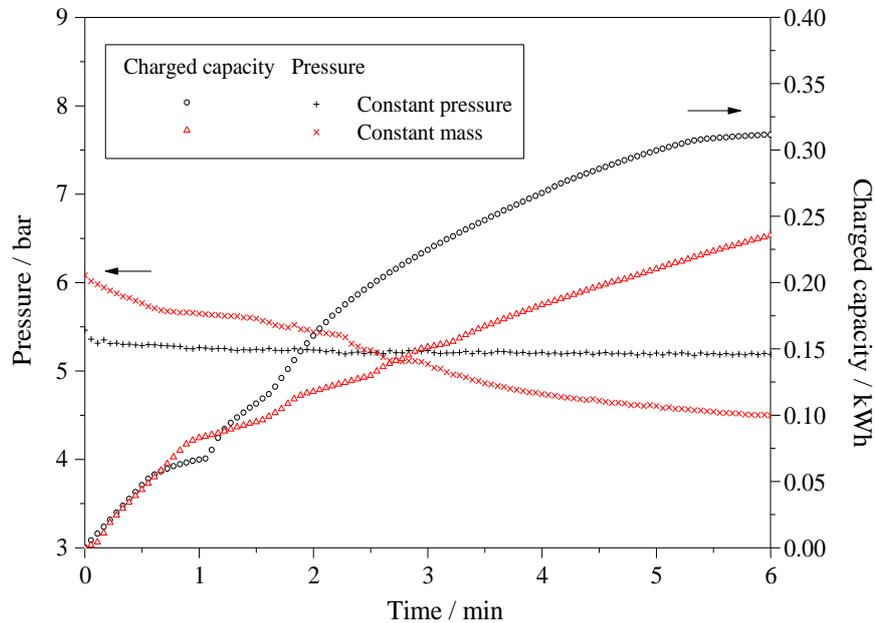

Figure 8. Energy storage capacity depends on the mode of charge.

2.3. *Hydrate Dissociation*

The CTES may be discharged by thermally dissociating the hydrate. Heat transfer fluid is supplied to the CTES at a temperature that exceeds the formation equilibrium temperature.

Upon dissociation, the cage structures unwrap and release the gas molecules. However, fragments of the cages remain. Through repeated thermal cycling of the CTES, these fragments assist re-formation of the hydrate and so repeated cycling of the CTES largely eliminates the nucleation delay. This is known as the memory effect of a hydrate (Buchmann et al (2005), Duchateau et al (2010)).

Some of our experiments showed hysteresis in the formation and dissociation temperatures that could not be dismissed as non-equilibrium behaviour. For example, a hydrate that froze at 7°C was found to thaw at 9°C. This is an undesirable feature in a CTES application. Fortunately, we noticed this effect to be less pronounced as the sample size increased.

The hydrate dissociation rate (CTES discharge) may be increased to match the cooling rate required by the application. Primarily, the dissociation rate may be enhanced by lowering the CTES vessel pressure below formation pressure and maintaining this lowered pressure during dissociation by pumping gas from the CTES vessel to an external store, as shown in Figure 9. The gas re-compression work consumes electrical energy. Over the course of a discharge cycle, the electrical energy consumption is equivalent to less than 0.5% of the thermal energy stored.

Another method to enhance hydrate dissociation is to increase the temperature of the heat exchange water being cooled by the CTES. In this way, very high discharge rates can be realised provided that the heat transfer rate and gas re-compression rate can keep up.
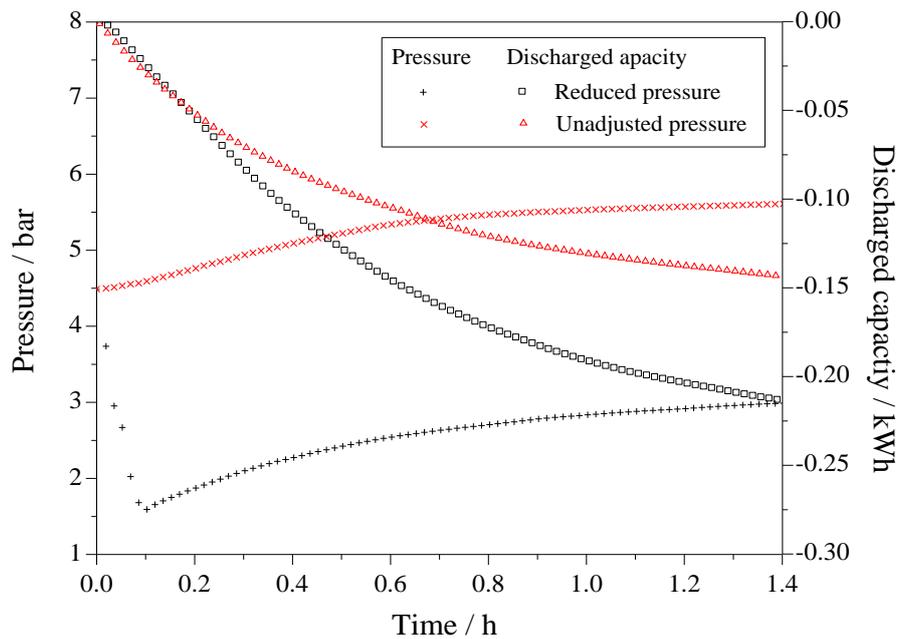
Figure 9. Energy storage capacity depends on the mode of discharge.

3.   Discussion and practical considerations

The hydrate energy storage is achieved by a gas/liquid to solid phase transition. This implies that a volume of gas will need to be accommodated while the system is in the dissociated state. The required volume can be large, in the order of 700 L/kWh at ambient pressure. This volume may be reduced by raising the pressure of the gas store to at least the hydrate formation pressure. However, a costly pressure vessel will be required to store the gas. A gas compressor may also be required if there is a difference in gas pressure between storage conditions and hydrate formation conditions. This gas storage requirement is the main impediment to the practical application of hydrate CTES.

For practical application, it is also important for a system controller to understand the state of charge of the CTES and control the rates of charge and discharge to integrate with the operating conditions of the system. The gas hydrate CTES offers a great deal of operational flexibility not available in chilled water or conventional ice CTES arrangements. In a constant volume hydrate CTES, state of charge is measured by the gas pressure. However, in a constant pressure configuration, the pressure in the separate gas store is used as an indication of the gas transferred to the hydrate and hence the amount of hydrate ice in the CTES.

After a limited period of operation (20 thermal cycles), no deterioration in store capacity, formation or dissociation has been observed.

4.   Conclusions

We have conducted some fundamental experiments with CO_2 gas hydrates to determine their suitability for cold thermal energy storage in air-conditioning applications. With hydrate samples over 0.1 L, we have been able to overcome most practical issues facing the use of CO_2 hydrate as a CTES solution. These issues included supercooling, melt-thaw hysteresis, nucleation delay, formation rate, discharge rate and state of charge estimation. However, challenges remain in realising a reasonable system volume. This volume relates to storage of CO_2 gas that is cyclically absorbed and evolved from the hydrate.

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