Adsorption-Enhanced Compressed Air Energy Storage

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ABSTRACT

Adsorption-Enhanced Compressed Air Energy Storage (AE-CAES) reduces the cost of surface (non-underground) CAES by adsorbing the air in nano-porous materials. This gives an air density equivalent to 100 bar at less than a fifth that pressure. It also changes the effective equation of state for air, which allows the air to be stored and released at constant pressure by cycling the temperature instead. A low and constant pressure greatly reduces the cost of the hardware needed for CAES. In addition, the desorption rate of air is intrinsically limited by diffusion, which together with the low pressure renders the system essentially explosion proof. Even though more heat must be moved around over the storage cycle than in conventional CAES, AE-CAES needs only low-grade heat at circa 100°C. This allows it to use cost- and carbon-free waste or solar heat, rather than heat from fossil fuels as in existing CAES systems. As a result, an AE-CAES system can be economically efficient even though it dissipates significant heat over each cycle.

Keywords: adsorption, compressed air, demand response, energy storage, zeolites

1 INTRODUCTION

Energy storage technologies for the electric power grid can be compared by mapping them onto a two-dimensional space. The first axis is the maximum discharge time at which they can be economically deployed, while the second is the minimum power (capacity) of an economically viable system. The approximate locations of most prominent energy storage technologies [1] in this coordinate system are shown in Fig. 1. Note the flexibility of a technology increases as one goes from the lower-left to the upper-right in such a plot.

This paper introduces a new kind of grid-scale energy storage which promises a degree of flexibility comparable to flow batteries, but provides additional value in many situations. It is a form of compressed air energy storage (CAES) which, like "surface" CAES in high-pressure tanks, does not have the site restrictions associated with storing the air in underground geological formations, but is better suited to long discharge durations. This is because it greatly reduces cost of the tanks needed to confine the compressed air, while at the same time making an explosive discharge almost impossible. Although it could mimic a battery by converting electrical energy to-and-from mechanical, its best applications probably will not require this.
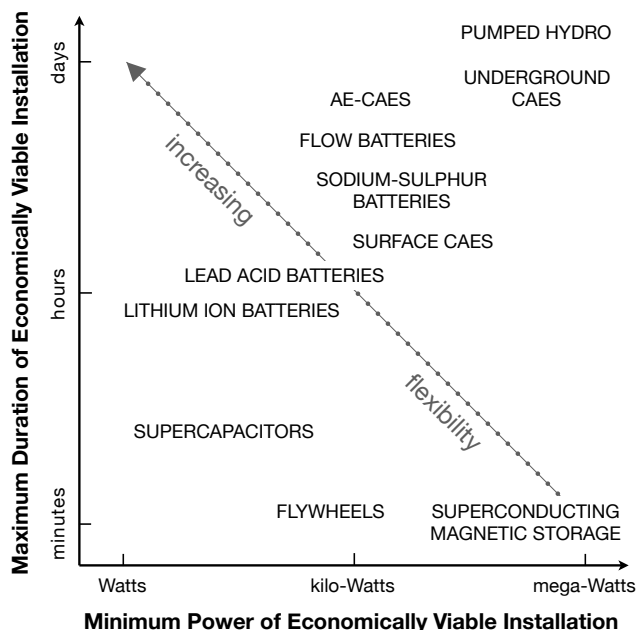

Figure 1. Two-dimensional coordinate system for grid-scale energy storage with the approximate locations of most prominent technologies plus AE-CAES mapped onto it. Flexibility increases as indicated (adapted from Ref. [1]).

This technology is known as *Adsorption-Enhanced Compressed Air Energy Storage* (AE-CAES). As its name implies, it achieves its advantages by adsorbing the compressed air in a nano-porous material. The best known class of materials that adsorb significant quantities of air are the zeolite minerals [2]. These are inexpensive, non-toxic, non-corrosive, non-flammable, environmentally benign, and contain only abundant elements. They also come in an astounding variety of chemical structures and compositions, some of which occur naturally but most of which are easily synthesized. The question of which zeolites are best suited to AE-CAES has received very little study, so the cost-benefit analysis given below is based on a standard zeolite variously known as sodium faujusite, NaX, or 13X. Significant improvements may be expected once the resources at our disposal permit this question to be properly addressed.

This paper is structured as follows. First, we consider how the physics of CAES is altered by the use of an adsorbent, and some of its economic consequences. Next, we consider what an energy storage system based on AE-CAES might look like, and its performance characteristics. Finally, we discuss some of its possible applications.

2   OW AE-CAES WORKS

The physics of compressed air energy storage, in general, is very different from electrochemical forms of energy storage. Over the range of temperatures and pressures involved in CAES, the behavior of air is described quite well by the ideal gas law. The energy of an ideal gas, however, depends only on its temperature and not its pressure. Thus if one compresses a given mass of air and allows it to cool back to its original temperature, the amount of energy in the air is essentially the same as it was before it was compressed. No energy has been stored!

What has been stored is *free* energy, which for the compression of air is largely entropy, or more precisely, a lack thereof. The lower entropy of air after compression can be used to convert heat to work with an efficiency that is not limited by that of the Carnot cycle, for the simple reason that the expansion of air is not a cycle. Of course the compression of air followed by expansion is a cycle, but the "efficiency" of CAES is very different from the Carnot efficiency of a heat engine. The latter is the *net* work done over a cycle which transfers heat from a high- to a low-temperature reservoir, divided by the heat transferred. The former is generally the ratio of the work out to the work in. Hence if more heat is added to the air during expansion than was taken out during compression, the efficiency of CAES can actually exceed 100%! Moreover, any attempt to correct this by taking the heat added to the air into account would force us to conclude that even perfectly isothermal CAES must always be less than 100% "efficient".
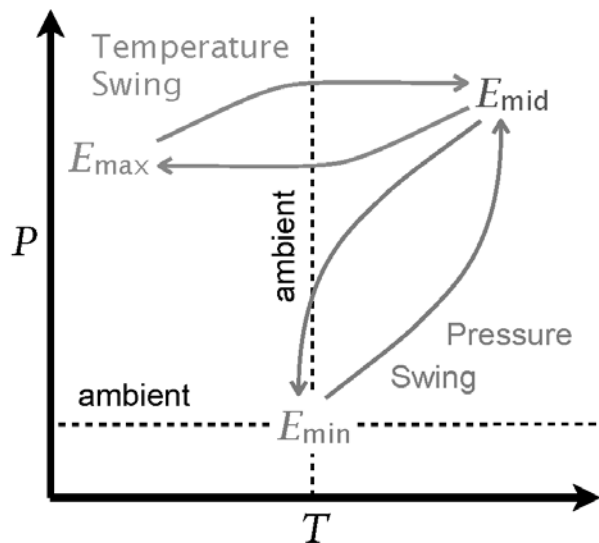
Figure 2. Illustration of the two-stage storage cycle utilized by AE-CAES. The first stage is quasi-isothermal compression / expansion, utilizing a conventional pressure swing, while the second stage is quasi-isobaric adsorption, i.e. a temperature swing at approximately constant pressure.

In short, the compression and expansion of air is essentially a transduction mechanism which converts work into heat and back, respectively. Various forms of CAES

are defined by how any heat dissipated during compression is made up for during expansion. This issue is even more complicated for AE-CAES, however, since of necessity it uses a thermodynamic cycle that is quite different from all other forms of CAES. If the usual pressure swing were used, most of the air would come off the adsorbent at low pressures and thus do very little work in the process. So, instead of using the pressure to control how much air is adsorbed, AE-CAES uses a cycle in which the temperature is varied while the pressure remains largely constant. This works because, according to the van't Hoff relation, the amount of air in a volume filled with an adsorbent depends exponentially on the inverse absolute temperature, rather than linearly as with an empty volume according to the ideal gas law. Of course the air must subsequently be expanded to obtain useful work, as indicated in Figs. 2 & 3.
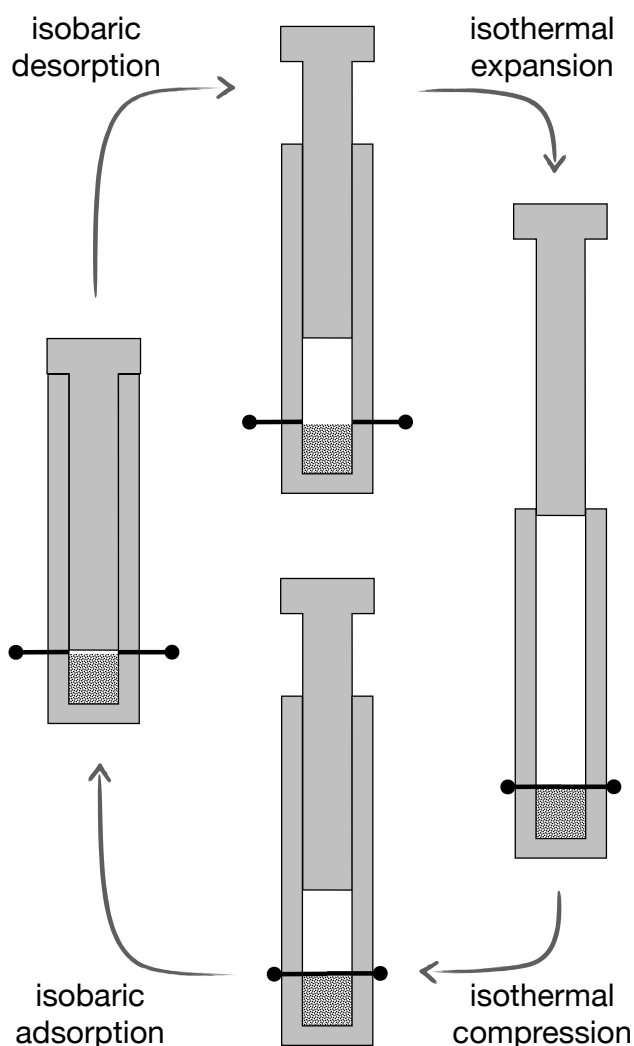
Figure 3. Idealized implementation of the two-stage storage cycle utilized by AE-CAES, using a piston with a movable barrier at the bottom to isolate the zeolite during compression and expansion. Note work is done on the system during adsorption and by it during desorption.

Besides the energy "stored" on compressing the air, AE-CAES stores energy in a form not found in conventional CAES. This comes from the change in volume which accompanies the exothermic process of adsorption, and may most easily be grasped by examining the idealized implementation shown in Fig. 3. Whereas the isothermal expansion of air converts virtually all the heat taken from its surroundings into work, only part of the heat consumed during desorption is converted into work. This is just the PV contribution to the enthalpy of adsorption. Additional sensible heat must be added to the adsorbent to drive the temperature swing, but this heat produces no work. It is however expected that the temperature swing's minimum will be well below ambient, so that a portion of this heat will flow spontaneously from the surroundings. This means the cold adsorbent can be used to provide valuable cooling as a portion of the air desorbs from it and expands.

We conclude that AE-CAES is actually a combined thermal and mechanical energy storage system. The same could perhaps be said for any form of CAES, but if the expanding air is used for cooling one will per force get less work out of it. In AE-CAES however, both the sensible cold in the adsorbent and part of the heat of desorption can provide cooling with no reduction in the work performed.

3 AE-CAES IMPLEMENTATION ESTIMATES AND OPTIONS

All of the science behind AE-CAES is well established, and no basic research is needed to implement it. In particular, several kinds of zeolites are known to adsorb substantial quantities of air, and are widely used to separate oxygen and nitrogen from air since they adsorb the latter gas preferentially. The most significant engineering challenge involved in developing a commercially viable system is to find a cost-effective means of cooling and heating a large quantity of zeolite in a pre-programmed fashion. This issue is intimately tied to the available sources of cold and heat, and hence to the built environment of the commercial application targeted, as well as to the climate where it is located, the season of the year, etc.
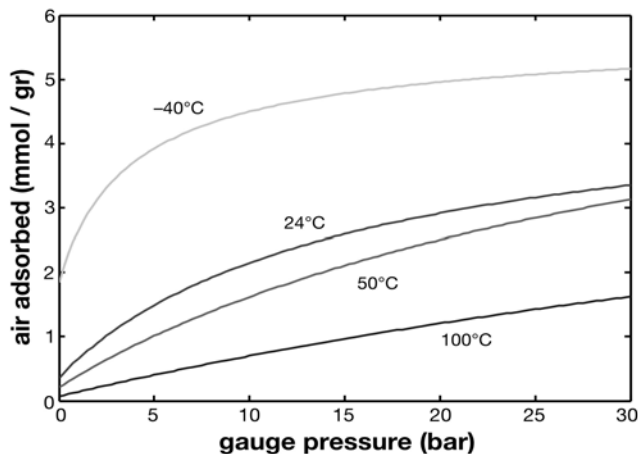
Figure 4. Isotherms for air on NaX zeolite (see text).

For the sake of discussion we will take a common zeolite known as NaX or 13X, and consider some published air adsorption data on it [3]. These data imply the isotherms plotted in Fig. 4, which specify the amount of air adsorbed per gram of NaX versus pressure at a fixed temperature. As previously noted, most of the air comes off at low pressures, but the amount of air adsorbed at any given pressure depends strongly on temperature. These adsorption estimates lead to the energy storage density estimates plotted in Fig. 5 [4], assuming a fairly extreme temperature swing going all the way from –40°C to +100°.

Unfortunately these data do not cover many of the intermediate temperatures, and so do not permit precise energy density estimates for less extreme swings. More recent data indicates that the estimates are probably on the low side [5], but the new data were aimed at pressure-swing separation of O_2 and N_2 from air and cover an even smaller temperature range. What we can say with confidence at this point in time is that the mechanical energy storage density of a packed zeolite bed will be roughly 10% the electrical energy density of a lead acid battery.
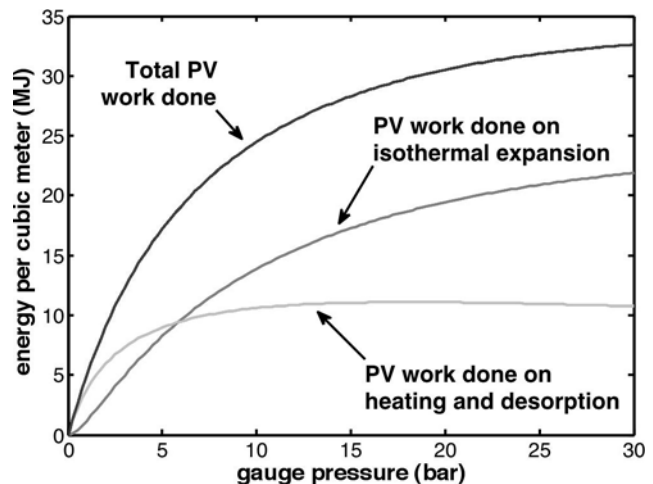
Figure 5. Estimates of the mechanical energy storage density in a packed bed of zeolite vs. pressure, given a temperature swing of –40-to-100°C (see text).

Assuming again a –40-to-100°C temperature swing, the amount of heat that must be moved around while charging or discharging the system with air is approximately 5 times the stored mechanical energy. Fortunately, in many possible applications (see below) much of the heat needed could be obtained at near-zero variable cost. Specifically, temperatures approaching 100°C may be reached using low-grade waste or solar thermal heat. In other cases they could be attained with a conventional hot water heater, and much of the heat recovered while charging by using the heat in the zeolite bed to pre-heat the water going into the heater.

Reaching temperatures well below ambient without using additional (unrecoverable) mechanical energy is less straightforward. At sites where refrigerators capable of similar temperatures are in regular use, however, the cold they produce will be simply stored in the zeolite bed while

recharging it with air. It may be recovered and utilized upon discharge by transferring it, for example, to a stream of water (plus antifreeze) while at the same time warming the zeolite and so desorbing air from it. The resulting chilled water could be used directly or as a low-temperature heat sink to make the external refrigeration more efficient. An implementation using this strategy is illustrated in Fig. 6.
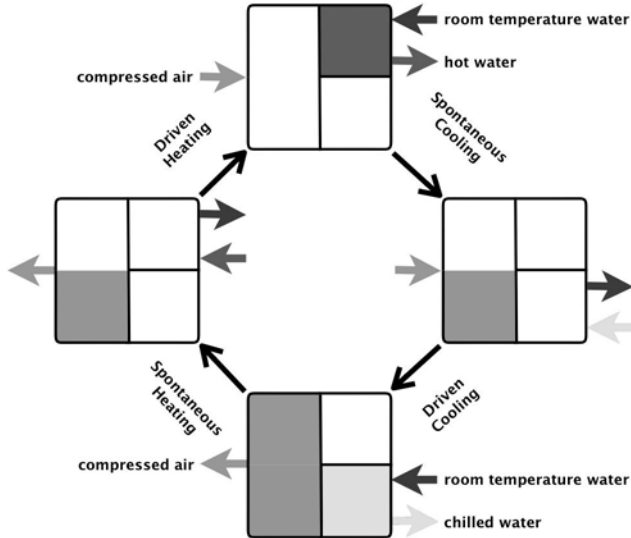

Figure 6. Black-box implementation with 3 compartments, 5 ports and a 4-step cycle, that could easily be adapted to a variety of applications (see text). The discharged state is at the top of the diagram, the charged state at the bottom, and states with the zeolite at near-ambient temperature between.

Another interesting option is to implement at least one stage of the cooling process by a well-known technology called *adsorption refrigeration* [6]. This is likewise driven directly by low-grade heat, so no extra mechanical energy is needed. Like energy storage itself, adsorption refrigeration is a batch process with temporally distinct recharging and discharging phases. In the latter, the vapor pressure of the refrigerant in a evaporator is kept low by allowing the vapor to be adsorbed in a suitable porous material (possibly a zeolite). To recharge, the adsorbent is heated to drive off the refrigerant and condense it back into a liquid for use in the next cycle. This is depicted schematically in Fig. 7.

4 SOME POSSIBLE APPLICATIONS

We close by describing three possible commercial applications for AE-CAES, albeit very briefly.

4.1 Wind Po er Capacity Firming

The wind often blows more at night when electricity is least needed, while in many locations non-concentrating solar thermal panels can provide the heat needed to drive the AE-CAES storage cycle most of the time. Under these circumstances one could use excess power from the wind to compress air which is stored in an AE-CAES system, while an adsorption refrigerator is used to cool the zeolite and so

promote adsorption. During the day, solar hot water could then be used to heat the zeolite and so desorb the air, while at the same time recharging the refrigerator's adsorbent.

4.2 Demand Response via Industrial Pneumatics

Between 5 & 10% of industrial electricity is used to compress air to the same modest pressures (6-10 bar) at which zeolites typically yield the greatest benefit. Another 10-to-15% is used to run compressors in refrigerators, most often to chill water. Low-grade waste heat, which can make AE-CAES economical, is also widely available in factories and other industrial facilities. Last but not least, a growing number of such facilities are able to monetize the value of energy storage by participating in a *demand response* program. These pay them to cut their power usage when the load on the grid spikes, a major generator goes down, etc. Industrial pneumatics has the further advantages of leveraging the factory's existing compressor investment, and being able to use the compressed air directly without the losses and costs of converting it back to electricity.

4.3 Energy Management for Buildings

As the "smart grid" comes into being, many homes and offices will acquire the ability to buy their electricity when it is least expensive, to participate in demand response programs, or benefit from other incentives to coordinate their energy use with the grid's needs. As was seen in the Wind Power Capacity Firming example, the storage cycle of AE-CAES synchronizes nicely with the diurnal cycle. In buildings, this would enable owners to recharge their system at night when electricity was least expensive and cooling most efficient, while using the stored energy and cooling power during the day. In effect, the zeolite would be the heat sink for a ground-source heat pump that could also store compressed air and, by conversion, electricity.
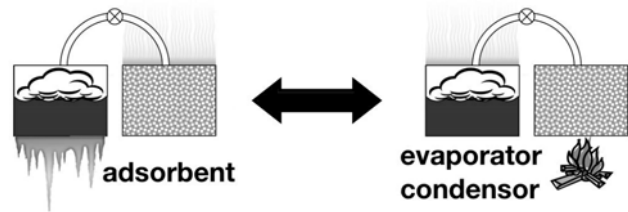

Figure 7. Schematic showing how adsorption refrigerators work (see text). Discharging left, recharging right.

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