

A First and Second Law Analysis of a Thermoresponsive Polymer Desiccant Dehumidification and Cooling Cycle

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Abstract

We present a theoretical description for a new desiccant air conditioning cycle that uses thermoresponsive polymers instead of traditional desiccants. We use a combined first and second law analysis to demonstrate that this new cycle has three major advantages relative to the traditional case: (i) it can regenerate at lower temperatures, (ii) it can harvest liquid water and (iii) it has significantly higher coefficient of performances (COPs). For example, this new cycle can achieve a COP of 5.1 when regenerated at 95 °C, whereas the traditional desiccant cycle is limited to a COP of ~1. The fundamental origins of these advantages can be traced to the method of regeneration. The traditional desiccant cycle regenerates by flowing hot air over the desiccant, which provides a medium for gaseous water desorption. However, this also generates entropy and places a minimum temperature constraint on the hot air. In contrast, the thermoresponsive polymer cycle regenerates through a polymer phase transition. The polymer absorbs water vapor in humid air, and then it expels liquid water when raised above its transition temperature. This regeneration method generates liquid water that can be harvested and relaxes constraints on entropy generation and minimum temperature. The minimum regeneration temperature of the thermoresponsive cycle is only limited by the transition temperature of the polymer, which can be tuned through materials science. Due to its liquid water harvesting capability, the new cycle potentially eliminates water consumption when used with evaporative cooling, or it can be directly used for atmospheric water harvesting.

Keywords: Cooling, Air conditioning, Dehumidification, Desiccant, Thermoresponsive, LCST

1. Introduction

The adoption of efficient and environmentally sustainable space cooling technologies is a significant challenge facing society. Vapor compression systems remain the most widely adopted method of air conditioning, due to their scalability, reliability, and cost [1]. These systems, however, are not without their drawbacks. The refrigerants used in vapor compression systems have high global warming potentials, some being thousands of times greater than CO₂ [2], [3]. Vapor compression systems are also often inefficient at dehumidification. To remove moisture from humid air, vapor compression systems must cool the air below the dew point, forcing moisture to condense out of the air. To bring the air to a comfortable humidity, this often means the air must be cooled to a significantly lower temperature than is necessary [4]. This coupling of the sensible load (temperature) and latent load

(humidity) reduces the efficiency of vapor compression systems when they are used for dehumidification.

In order to circumvent this coupling of sensible and latent loads, many dehumidification cycles have been incorporated into air conditioning systems. Much like how heat pumps and refrigerators “pump” heat from a low temperature to a high temperature, these dehumidification cycles can be seen as “humidity pumps” that move moisture from a low humidity space to a high humidity space [5]. Just like heat pumps, these humidity pump cycles can be driven by work or heat. Of the work driven humidity pumps, one of the simplest is a compressor with water-selective membranes that actually pumps the water vapor from the low humidity building air to the high humidity outdoor ambient air [4], [6], [7]. Other work-driven dehumidification technologies include ultrasonic regeneration, electro dialysis regeneration, and reverse osmosis regeneration desiccant cycles [8]–[10]. These cycles use a solid desiccant, such as silica gel, or a liquid desiccant, such as LiCl, to dehumidify air, and then they regenerate the desiccant with mechanical or electrical work input.

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Nomenclature		Greek symbols	
C	Polymer water content (kg/kg)	ϵ	Heat exchanger effectiveness
COP	Coefficient of performance	<i>Subscripts</i>	
c_p	Specific heat (kJ/kg-K)	a	Dry air
g	Specific Gibbs free energy (kJ/kg)	amb	Ambient conditions
h	Specific enthalpy (kJ/kg)	$cool$	LCST cycle used for direct evaporative cooling
\dot{m}	Mass flow rate (kg/s)	$dehum$	LCST cycle used for dehumidification
\dot{Q}	Rate of heat transfer (kW)	des	Traditional desiccant
R	Specific gas constant (kJ/kg-K)	f	Saturated liquid
RH	Relative humidity	g	Saturated vapor
s	Specific entropy	H_2O	Water
\dot{S}_{gen}	Rate of entropy generation	$int, 1$	Cold side heat exchanger outlet
T	Temperature	$int, 2$	Hot side heat exchanger outlet
$T_{6,crit}$	Critical traditional desiccant regeneration temperature	p	Dry polymer
$T_{6,min}$	Minimum traditional desiccant regeneration temperature	rev	Reversible
T_C	Effective cooling temperature	$shrink$	Polymer shrinking
T_H	Effective heat rejection temperature	$swell$	Polymer swelling
T_S	Effective heat source temperature	t	Polymer phase transition
w	Humidity ratio (kg/kg)		

Heat-driven desiccant cycles [3], [11]–[16] have a key advantage over work-driven cycles in that they can be regenerated with low-grade, “free” heat sources, like solar-or waste-heat [17]. This significantly reduces the electricity consumption of the dehumidification cycle, which reduces the cost of operation for the user. This also reduces the strain on the electric grid, which can be especially impactful during peak hours. Unfortunately, traditional heat-driven desiccant cycles have been limited by low coefficients of performance (COPs) [1] and an inability to regenerate at temperatures near ambient [12].

A general drawback of desiccant cycles is that they must work in conjunction with additional technology to achieve complete air conditioning functionality (dehumidification and cooling). While desiccant cycles reduce the electricity consumption required to handle latent loads, they are incapable of handling sensible loads (*i.e.*, lowering the temperature of the building air). One option is to use vapor compression for the sensible load, but this again requires the use of refrigerants and their associated global warming potential.

Evaporative cooling is often paired with desiccants as an environmentally friendly method of lowering the air temperature without using refrigerants or consuming much electricity [1], [3], [17], [18]. However, evaporative cooling consumes large amounts of water, which is problematic given the increasing scarcity of this resource. In an ironic fashion, traditional heat-driven desiccant cycles absorb water vapor from the building air, but they then re-expel that water as vapor to the outdoor environment during regeneration due to the operational requirements of traditional desiccants. After discarding the water vapor from regeneration, these cycles then consume additional liquid water to operate the evaporative cooler.

If the desiccants could instead expel absorbed water as liquid during regeneration, this liquid water could then be used to offset or even eliminate the water consumed during evaporative cooling. This paper explores this concept of harvesting water from the desiccant regeneration process via novel thermoresponsive polymers. Thermoresponsive polymer gels have recently garnered attention for their ability to sorb water vapor from humid air and expel it as liquid [19], [20].

Thermoresponsive gels, like poly(N-isopropylacrylamide) (PNIPAm), have historically been used in biomedical applications [21]–[26], but concepts for using them in air conditioning applications have only just begun to emerge. Due to an enthalpy and entropy change during swelling, PNIPAm can absorb liquids at room temperature and then expel them when raised above a transition temperature of approximately 32 °C [19]–[26]. The gel swelling (liquid absorption) at room temperature and shrinking (liquid expulsion) at higher temperatures allow PNIPAm to be used in controlled drug delivery. This behavior arises from the phase separation of thermoresponsive polymer solutions at critical solution temperatures. Thermoresponsive polymers exhibit a lower critical solution temperature (LCST) [19]–[22], [27]–[32] or upper critical solution temperature (UCST) [21], [30]–[36]. In the case of polymers with an LCST, like PNIPAm, a single-phase polymer solution forms below the LCST, and a two-phase mixture forms above the LCST. UCST behavior is the reverse, where separation occurs below the UCST and mixing occurs above the UCST. Of these two behaviors, this paper focuses on LCST behavior. If an LCST polymer crosslinks, the resulting gel will have a transition temperature (T_t), below which swelling occurs and above which shrinking occurs [27], [37]. In general, the gel transition temperature is often near (or identical to) the polymer solution LCST. The phase behavior of LCST gels is explained in greater detail in Sec. I of the Supplementary Material. While PNIPAm is among the most well-known thermoresponsive polymers and has an LCST of approximately 32 °C, other LCST polymers have been demonstrated, some having LCSTs greater than 70 °C [30], [31], [38]–[41].

Materials research on thermoresponsive polymer gels has historically focused on swelling in liquid water; however, these gels should also swell upon exposure to water vapor as based on thermodynamic analysis [42]. This phenomenon was recently demonstrated by Matsumoto *et al.* [20] and Zhao *et al.* [19], where they created LCST polymer gels that absorbed water vapor from air below the gel transition temperature and expelled liquid water when raised above the transition temperature. Water vapor in humid air has an activity (and chemical potential) lower than liquid water. As such, when a

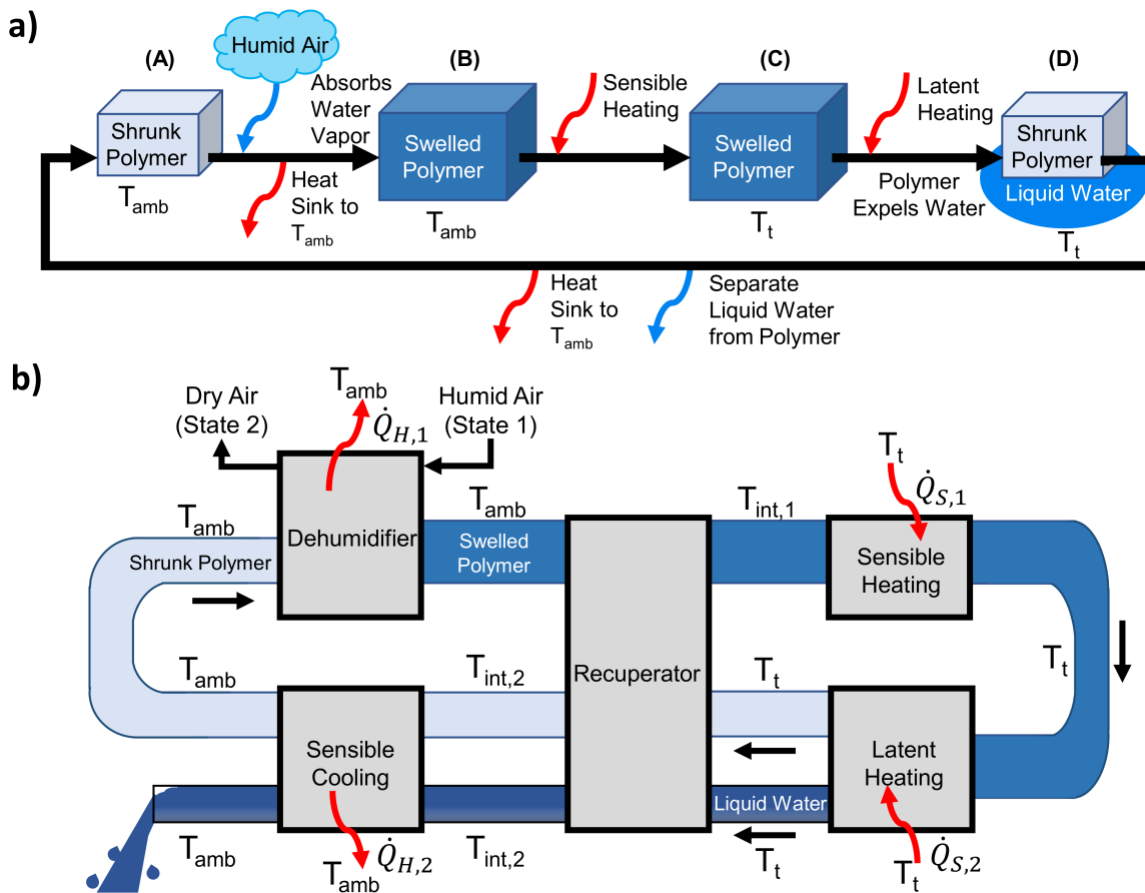


Fig. 1. Diagram of the LCST cycle for (a) sequential (cyclic) operation and (b) continuous operation.

dry polymer gel is placed in humid air, it will absorb moisture from the air, but it will absorb less than if it were in contact with liquid water. When an LCST gel absorbs water vapor below the transition temperature, it incorporates the water as liquid into the bulk of the gel. Then, when the gel is raised above the transition temperature, it expels the water as liquid.

This paper presents the description and theoretical analysis of a new thermodynamic cycle that uses LCST materials to dehumidify air and then regenerates the LCST materials through phase separation. While the swelling of LCST gels in humid air has been previously demonstrated [19], [20], we present the governing thermodynamics of this behavior and explain how it can be leveraged in a thermodynamic cycle. We note that Zeng *et al.* very recently performed a computational analysis on the use of LCST gels in rotary desiccant wheels [12]. However, in their work, the gels would be regenerated with hot air (just like traditional desiccants), while the cycle in this paper regenerates using the thermoresponsive phase transition and separation of liquid water. Some work has been done to measure [27] or model [42] the thermophysical properties of a few thermoresponsive gels, but this paper describes the thermodynamic limits that govern the swelling of all LCST materials in humid air. Matsumoto *et al.* [20] and Zhao *et al.* [19] combined thermoresponsive polymer networks with highly hygroscopic polymer networks to increase the polymer's water uptake in lower humidities. However, the authors did not measure important thermophysical properties such as the enthalpy of polymer swelling. In this paper, we

show that water vapor sorption of thermoresponsive polymers in lower humidities must be accompanied by a change in certain properties, such as the enthalpy of swelling, entropy of swelling, or transition temperature.

To analyze this new cycle, we describe the processes that the polymer undergoes and apply mass, energy, and entropy balance to each process. In our cycle, the gels absorb water vapor, after which they are heated, which causes a phase transition in which the gels expel liquid water. The gel volume phase transition serves to dry the gel out for reuse and to harvest liquid water, which can be used for evaporative cooling. We apply mass balances to the air, polymer, and water, along with the first and second laws of thermodynamics to relate the heat flow and entropy generation in each component of the cycle. We also set the entropy generation to zero to find the minimum enthalpy and entropy of polymer swelling that are required to produce the desired dehumidification for a given polymer transition temperature. Though very little data exists on the swelling of existing thermoresponsive polymers in humid air, our results explain the sub-optimal behaviors that have been previously reported. We hope our analysis of the required polymer properties can also serve as a roadmap for the development of future thermoresponsive polymers that can more fully realize the potential of this new cycle. We also use the theoretical minimum enthalpy of swelling to identify the limits of the cycle efficiency.

Lastly, we utilize the first and second laws to analyze a traditional desiccant cycle and compare it to the new

thermoresponsive polymer cycle. We show that the traditional desiccant cycle is subject to a lower limit to the regeneration temperature, whereas the thermoresponsive polymer desiccant cycle circumvents this limit. In addition, the traditional desiccant cycle must be regenerated with temperatures higher than this lower limit in practice. We show that higher regeneration temperatures necessarily introduce entropy generation in the traditional desiccant cycle and limit the COP of these cycles to approximately 1. Conversely, the thermoresponsive polymer cycle can (theoretically) be regenerated without entropy generation at higher temperatures. This means that the COP of this new cycle is not limited to a value of 1 and can be significantly higher than the traditional desiccant COP. For example, this new cycle can theoretically achieve a COP of 5.1 when regenerated at 95 °C.

2. The LCST Cycle

Herein, we detail a heat-driven thermoresponsive polymer desiccant cooling and dehumidification cycle that utilizes an LCST polymer gel as the desiccant. For brevity, we refer to this cycle as “the LCST cycle”, as this cycle requires a desiccant material that exhibits LCST behavior.

In general, the LCST cycle receives humid air at ambient temperature and separates it into dry air and liquid water (also at ambient temperature). As with any heat-driven cooling or dehumidification cycle, some heat is rejected to the ambient (\dot{Q}_H), and some heat must be delivered to the cycle (\dot{Q}_S) from a heat source with a temperature greater than ambient. To achieve this overall cycle, the gel must undergo four main processes, illustrated in Fig. 1(a): (A – B) swelling of the gel in humid air, (B – C) sensible heating of the gel, (C – D) shrinking of the gel to expel liquid water, and (D – A) sensible cooling back to the original temperature. The swelling process serves to dehumidify the air, while the other three processes (sensible heating, shrinking, and cooling) serve to regenerate the gel by removing the water.

In many cases it is desirable to both dehumidify and cool the air inside a building. The ability to do both of these tasks separately is one of the main benefits of the LCST cycle. The polymer first dehumidifies the air by absorbing water vapor. Then, the polymer goes through a phase transition that expels water during regeneration. The liquid water harvested during regeneration could then be used with an *indirect* evaporator that lowers the building air temperature without affecting building air humidity. This is one of the major benefits of the LCST cycle that traditional desiccant cycles cannot accomplish. Traditional desiccant cycles remove water vapor from a conditioned space and exhaust it as vapor to outside air. When these cycles are coupled with evaporative cooling, they need an external water source. The LCST cycle conveniently condenses the water vapor to liquid, which can be used in the evaporative cooler, eliminating the need for an external water source.

Occasionally, either dehumidification or sensible cooling is not needed. If it is desirable to use the cycle only for dehumidification (*i.e.*, the ambient temperature is comfortable, but the ambient humidity is too high for comfort), then the liquid water expelled by the gel during regeneration can be discarded. If it is desirable to use the cycle only for cooling (*i.e.*, the ambient humidity is comfortable, but the ambient temperature is too high for comfort), then the water harvested

during regeneration can be evaporated directly back into the building air. This will rehumidify the air but lower its temperature. For simplicity, we limit our analyses to these two cases: solely dehumidification and solely direct evaporative cooling.

While Fig. 1(a) represents the cyclic or sequential operation of the LCST cycle, Fig. 1(b) illustrates the continuous mode of operation. During continuous operation, the gel physically moves through different control volumes. Here, a recuperator can be added to decrease the required sensible heat input, which allows the thermodynamic limits of the cycle to be analyzed. While this recuperation process may be difficult to implement in practice, the cycle can be analyzed without recuperation by setting the recuperator effectiveness, ϵ , to zero.

At the materials-level, this cycle uses the LCST polymer’s free energy of swelling to condense water out of humid air, thereby dehumidifying the air. The free energy change during isothermal swelling is $\Delta g_{swell} = \Delta h_{swell} - T\Delta s_{swell}$. The opposite process of swelling is deswelling, or shrinking, in which the gel expels liquid water. The free energy of shrinking is equal in magnitude and opposite in sign of the free energy of swelling: $\Delta g_{shrink} = \Delta h_{shrink} - T\Delta s_{shrink} = -\Delta g_{swell}$. Below the transition temperature of an LCST gel, Δg_{swell} is negative and the gel swells. Above the transition temperature, Δg_{shrink} is negative (meaning Δg_{swell} is positive), which causes the polymer to shrink, thereby expelling the water. The enthalpies and entropies of swelling and shrinking are what allow the LCST cycle to exist, and they serve as variables in our first and second law analysis of this cycle.

Generally, the enthalpy and entropy of swelling can vary with temperature. Grinberg *et al.* observed a roughly 20% decrease in specific heat (Δc_p) across the shrinking phase transition of PNIPAm. This caused the enthalpy and entropy of swelling and shrinking to vary with temperature [27]. Other works, however did not report any change in specific heat across volume phase transitions [28], [43], and some authors assume the swelling enthalpy and entropy to be invariant with temperature [42]. For completeness, we include the term Δc_p in our derivations to allow for this potential temperature dependence of the enthalpy and entropy of swelling and shrinking. As such, we use the subscript “amb” to denote the swelling and shrinking enthalpy and entropy at ambient temperature and “t” to denote the enthalpy and entropy at the transition temperature. For simplicity, all of the results in the main text of our paper correspond to $\Delta c_p = 0$, thereby assuming that the enthalpy and entropy of swelling are invariant with temperature. We additionally provide results in Sec. III of the Supplementary Material for $\Delta c_p \neq 0$.

The T-s diagram of a polymer undergoing the LCST cycle (Fig. 2) is analogous to the Ericsson cycle. The entropy of the polymer first decreases with a magnitude of $\Delta s_{swell,amb}$ as it absorbs water vapor at T_{amb} (A – B). Then, when the polymer is sensibly heated, the entropy and temperature both increase (B – C). Next, as the polymer undergoes latent heating at T_t , the entropy increases by $\Delta s_{shrink,t}$ as liquid water is expelled (C – D). Finally, the polymer is sensibly cooled, and entropy and temperature decrease (D – A). The shape of the LCST cycle T-s diagram in Fig. 2 is the same as the Ericsson cycle, and similarities between the two cycles exist. Just as the Ericsson cycle approaches the Carnot efficiency when recuperation is

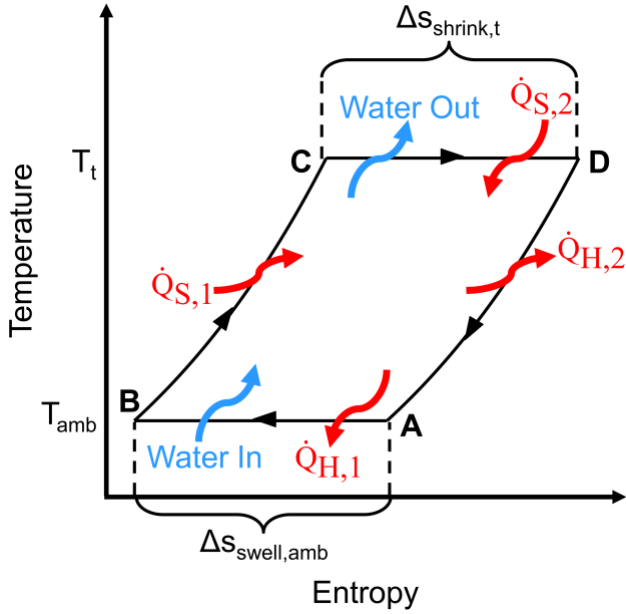


Fig. 2. T-s diagram of the LCST polymer gel in the LCST cycle. The lettered states in this figure match the lettered states in Fig. 1(a). The T-s diagram of the LCST cycle has the same shape as the Ericsson cycle. Much like the Ericsson cycle, the LCST cycle approaches the Carnot limit when a recuperator is used to transfer heat from the polymer being sensibly cooled (D - A) to the polymer being sensibly heated (B - C).

used, the LCST cycle approaches the COP of a heat-driven Carnot humidity pump when recuperation is used, as we show in our results. To evaluate the upper limits of the LCST cycle, we analyze a continuous configuration of the cycle that contains a recuperator.

The work by Matsumoto *et al.* [20] and Zhao *et al.* [19] can be seen as early, small-scale demonstrations of the LCST cycle: the experiments consisted of isothermal polymer swelling in humid air, followed by regeneration heating to expel the sorbed water. Both Matsumoto *et al.* and Zhao *et al.* found that PNIPAm by itself (*i.e.*, PNIPAm homopolymer) did not swell significantly in humid air. As such, Matsumoto *et al.* created an interpenetrating polymer network with PNIPAm and hygroscopic sodium alginate to improve the sorption capacity. They found that the gels absorbed water from the atmosphere when below the transition temperature and expelled liquid water when the temperature was raised [20]. Similarly, Zhao *et al.* created a gel with a PNIPAm network and a polypyrrole chloride network. In their experiments, they placed the gels outside to absorb water vapor in the shade, and then they moved them to a sunny area to heat and expel the water. They found that their gels swelled with a significant amount of water per unit mass of dry polymer [19].

While the work in this paper focuses on the usefulness of the LCST cycle for air conditioning, Zhao *et al.* explored its use for atmospheric water harvesting [19]. In this paper, we show that the LCST cycle requires polymers with higher enthalpies of shrinking, and thus more heat input, when the polymer sorbs water from low humidity air. Consequently, the LCST cycle will be less efficient when used in dry areas, like those where water is scarce and atmospheric water harvesting might be attractive. Conversely, the LCST cycle will be more efficient in

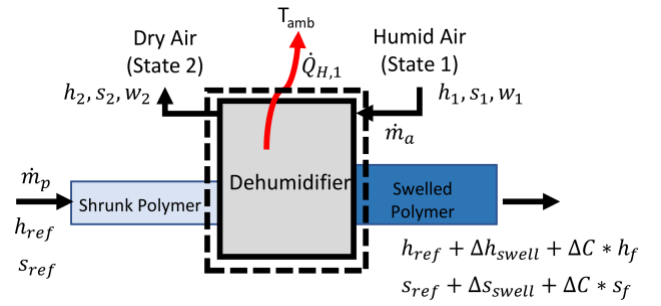


Fig. 3. Dehumidifier control volume. Humid air enters with a humidity ratio of w_1 and leaves as dry air with a humidity ratio of w_2 . The enthalpies and entropies h_1 , h_2 , s_1 , and s_2 are evaluated for moist air (*i.e.*: air/water vapor mixture). Shrunk gel enters the dehumidifier and leaves with an enthalpy and entropy change of Δh_{swell} and Δs_{swell} , respectively. The swelled gel also carries liquid water with an enthalpy and entropy of h_f and s_f , respectively. The dehumidifier is isothermal, so at all points the temperature is T_{amb} .

highly humid regions, where air conditioning use is highly desirable.

3. Methods

3.1. Mass balance of the LCST cycle

We start with a mass balance on this new cycle in Fig. 1(b). The LCST cycle's mass balance is achieved by relating the air mass flow rate (\dot{m}_a), liquid water mass flow rate (\dot{m}_{H_2O}), polymer mass flow rate (\dot{m}_p), inlet and outlet humidity ratios (w_1 and w_2 , respectively), and the polymer water uptake (ΔC , the ratio of increase in water content to dry polymer mass). The resulting mass balance equation is $\dot{m}_p = \frac{\dot{m}_{H_2O}}{\Delta C} = \frac{\dot{m}_a(w_1 - w_2)}{\Delta C}$.

3.2. First and second law analysis of the LCST cycle

Applying the first and second laws of thermodynamics to various control volumes in Fig. 1(b) allows the LCST cycle performance to be analyzed. This can be used to predict the performance of existing thermoresponsive polymers when used in the LCST cycle. Our analysis can also be used to find the enthalpies and entropies of swelling of a theoretical thermoresponsive polymer that would dehumidify air from a specified inlet humidity to a specified outlet humidity. While little literature data exists on these properties for thermoresponsive polymers other than PNIPAm homopolymers, this analysis allows us to make statements about the thermophysical properties that future LCST gels must possess to dehumidify air to desired humidities.

The LCST cycle begins with the dehumidification process, in which the LCST gel swells while absorbing water from humid air. The dehumidifier control volume is depicted in Fig. 3. The dry gel enters with some enthalpy and entropy per unit dry polymer mass (h_{ref} and s_{ref} , respectively). Upon swelling, the gel enthalpy and entropy change by values of Δh_{swell} and Δs_{swell} , respectively. Additionally, the gel incorporates liquid water upon swelling, which has an enthalpy of h_f and an entropy of s_f . Then, at the outlet, the gel has an enthalpy per unit dry polymer mass of $h_{ref} + \Delta h_{swell} + \Delta C * h_f$ and an entropy per unit dry polymer mass of $s_{ref} + \Delta s_{swell} + \Delta C * s_f$.

Meanwhile, the air enters with an enthalpy of h_1 and leaves with an enthalpy of h_2 . These are moist air enthalpies, which are given per unit mass of dry air but contain the enthalpy of both the dry air and water vapor and are functions of temperature and humidity. Similarly, the air enters with an entropy of s_1 and leaves with an entropy of s_2 . The dehumidification process is isothermal, so the entire dehumidifier control volume is at T_{amb} .

Since no shaft work is done in this control volume, application of the first law yields an equation for the heat released during dehumidification: $\dot{Q}_{H,1} = -\dot{m}_p \Delta h_{swell} + \dot{m}_a (h_1 - h_2 - (w_1 - w_2) h_f)$. Assuming the ideal gas model can be applied to the moist air, the inlet air enthalpy is $h_1 = h_a + w_1 h_g$ and the outlet air enthalpy is $h_2 = h_a + w_2 h_g$, where h_a is the dry air enthalpy at T_{amb} and h_g is the enthalpy of saturated water vapor at T_{amb} . Once the ideal gas model is applied, the heat released becomes $\dot{Q}_{H,1} = -\dot{m}_p \Delta h_{swell} + \dot{m}_a (w_1 - w_2) h_{fg}$. Because Δh_{swell} is negative, the swelling of the gel in humid air is more exothermic than condensation.

Applying the second law to the dehumidifier control volume yields Eq. (1) for the entropy generation during dehumidification.

$$\frac{\dot{S}_{gen,dehum}}{\dot{m}_a} = \frac{w_1 - w_2}{\Delta C} \left(\Delta s_{swell,amb} - \frac{\Delta h_{swell,amb}}{T_{amb}} \right) + \left(\frac{h_1 - h_2}{T_{amb}} - (s_1 - s_2) - (w_1 - w_2) \left(\frac{h_f}{T_{amb}} - s_f \right) \right) \quad (1)$$

Certain thermoresponsive polymer gels undergo first-order shrinking upon a single transition temperature T_t (explained by [42], demonstrated by [27], and described in greater detail in Sec. I of the Supplementary Material). When swelling and shrinking are limited to this first-order behavior, the entropy of swelling can be written as $\Delta s_{swell,t} = \Delta h_{swell,t} / T_t$. This behavior is ideal for the LCST cycle, as explained in Sec. I of the Supplementary Material. As such, we limit our analysis to this behavior and assume the gel in the cycle is regenerated with a first-order phase transition at a temperature T_t . This allows the entropy generation equation to be rewritten in terms of $\Delta h_{swell,t}$ and T_t , as shown in Eq. (2).

$$\frac{\dot{S}_{gen,dehum}}{\dot{m}_a} = \frac{h_1 - h_2}{T_{amb}} - (s_1 - s_2) - (w_1 - w_2) \left(\frac{h_f}{T_{amb}} - s_f \right) + \frac{w_1 - w_2}{\Delta C} \Delta h_{swell,t} \left(\frac{1}{T_t} - \frac{1}{T_{amb}} \right) + \frac{w_1 - w_2}{\Delta C} \Delta c_p \left(\frac{T_{amb} - T_t}{T_{amb}} - \ln \left(\frac{T_{amb}}{T_t} \right) \right) \quad (2)$$

Eq. (2) corresponds to a drop in relative humidity between the inlet and outlet of the dehumidifier control volume. However, if the amount of water removed from the air is small relative to the air mass flow rate, then the relative humidity can be treated as approximately constant across the dehumidifier. The entropy generation given for the constant relative humidity case is given in Eq. (3), found using the ideal gas law (detailed in Sec. IV of the Supplementary Material).

$$\frac{\dot{S}_{gen,dehum}}{\Delta \dot{m}_{H_2O}} = R_{H_2O} \ln(RH) + \frac{\Delta h_{swell,t}}{\Delta C} \left(\frac{1}{T_t} - \frac{1}{T_{amb}} \right) + \frac{\Delta c_p}{\Delta C} \left(\frac{T_{amb} - T_t}{T_{amb}} - \ln \left(\frac{T_{amb}}{T_t} \right) \right) \quad (3)$$

If the value of $\Delta h_{swell,t}$ is known for a particular LCST gel, it can be plugged into Eq. (2) or (3) to evaluate the performance of said gel. Intuitively, however, there should be some limit to $\Delta h_{swell,t}$ that any LCST gel must obey. The enthalpy of swelling is the impetus that causes the gel to absorb water from humid air. It also ends up being the amount of latent heat that must be supplied to the cycle during regeneration. Since the LCST cycle must obey the Carnot limit of a heat-driven cooling cycle, there is a minimum amount of heat that must be supplied to drive the cycle. We use our first and second law analysis to find this limit. Not only does this allow us to find the maximum COP of the LCST cycle, it also allows us to find the enthalpy of swelling that any gel must possess to absorb moisture from air of a given humidity.

Setting the entropy generation in the dehumidifier to zero ($\dot{S}_{gen,dehum} = 0$) yields the reversible limit for the enthalpy of swelling. Recognizing that the enthalpy of swelling and enthalpy of shrinking are equal in magnitude and opposite in sign, we derive the reversible enthalpy of shrinking, $\Delta h_{shrink,t,rev}$, shown in Eq. (4). This is the minimum enthalpy of shrinking that an LCST gel would need to bring air from the inlet humidity of w_1 to the outlet humidity of w_2 , when sorption occurs at T_{amb} and the polymer has a transition temperature of T_t . This reversible enthalpy of shrinking is a function of the inlet air (state 1) and outlet air (state 2) humidity ratios, enthalpies, and entropies, the enthalpy and entropy of liquid water (h_f and s_f , respectively), the ambient temperature, the polymer transition temperature, the change in polymer specific heat that accompanies the shrinking transition (Δc_p), and the polymer water uptake. The enthalpies h_1 and h_2 and entropies s_1 and s_2 are evaluated for humid air (*i.e.*, a mixture of dry air and water vapor) and are fixed by the temperature and humidities at states 1 and 2.

$$\Delta h_{shrink,t,rev} = \frac{\Delta C}{\frac{1}{T_{amb}} - \frac{1}{T_t}} \left(\frac{s_1 - s_2 - \frac{h_1 - h_2}{T_{amb}}}{w_1 - w_2} - \left(s_f - \frac{h_f}{T_{amb}} \right) \right) + \frac{\Delta c_p}{\frac{1}{T_{amb}} - \frac{1}{T_t}} \left(\frac{T_t - T_{amb}}{T_{amb}} - \ln \left(\frac{T_t}{T_{amb}} \right) \right) \quad (4)$$

The enthalpy of shrinking is expressed in Eq. (4) in units of energy per unit mass of dry polymer. Alternatively, the enthalpy of shrinking can be expressed per unit mass of water absorbed by the polymer, given in Eq. (5). When expressed in this way, we refer to the enthalpy of shrinking as $\Delta h_{shrink,t,rev,H_2O}$.

$$\Delta h_{shrink,t,rev,H_2O} = \frac{s_1 - s_2 - \frac{h_1 - h_2}{T_{amb}} - \left(s_f - \frac{h_f}{T_{amb}} \right) + \frac{\Delta c_p}{\Delta C} \left(\frac{T_t - T_{amb}}{T_{amb}} - \ln \left(\frac{T_t}{T_{amb}} \right) \right)}{\frac{1}{T_{amb}} - \frac{1}{T_t}} \quad (5)$$

$$\Delta h_{shrink,t,rev,H2O} = -\frac{R_{H2O} \ln(RH)}{\left(\frac{1}{T_{amb}} - \frac{1}{T_t}\right)} + \frac{\Delta c_p}{\Delta C \left(\frac{1}{T_{amb}} - \frac{1}{T_t}\right)} \left(\frac{T_t - T_{amb}}{T_{amb}} - \ln\left(\frac{T_t}{T_{amb}}\right)\right) \quad (9)$$

The expressions for the reversible enthalpy of shrinking in Eq. (4) and (5) are given in terms of the moist air enthalpy and entropy at states 1 and 2. Since the moist air properties are functions of relative humidity, Eq. (4) and (5) are implicitly functions of relative humidity. However, if the ideal gas law is employed, these equations can be rewritten explicitly in terms of relative humidity. This simplification is detailed in Sec. IV of the Supplementary Material, and Eq. (6) results for the reversible enthalpy of shrinking (per unit mass of dry polymer) as an explicit function of relative humidity.

$$\begin{aligned} \Delta h_{shrink,t,rev} &= \frac{\Delta C}{(w_1 - w_2) \left(\frac{1}{T_{amb}} - \frac{1}{T_t}\right)} \left(R_a \ln \left(\frac{P_{tot} - RH_2 P_{sat}}{P_{tot} - RH_1 P_{sat}} \right) \right. \\ &+ R_{H2O} (w_2 \ln(RH_2) - w_1 \ln(RH_1)) \left. \right) \\ &+ \frac{\Delta c_p}{\left(\frac{1}{T_{amb}} - \frac{1}{T_t}\right)} \left(\frac{T_t - T_{amb}}{T_{amb}} - \ln\left(\frac{T_t}{T_{amb}}\right) \right) \end{aligned} \quad (6)$$

The enthalpy of shrinking in Eq. (6) is expressed per unit mass of dry polymer. It is instead expressed per unit mass of water absorbed during swelling in Eq. (7).

$$\begin{aligned} \Delta h_{shrink,t,rev,H2O} &= \frac{1}{(w_1 - w_2) \left(\frac{1}{T_{amb}} - \frac{1}{T_t}\right)} \left(R_a \ln \left(\frac{P_{tot} - RH_2 P_{sat}}{P_{tot} - RH_1 P_{sat}} \right) \right. \\ &+ R_{H2O} (w_2 \ln(RH_2) - w_1 \ln(RH_1)) \left. \right) \\ &+ \frac{\Delta c_p}{\Delta C \left(\frac{1}{T_{amb}} - \frac{1}{T_t}\right)} \left(\frac{T_t - T_{amb}}{T_{amb}} - \ln\left(\frac{T_t}{T_{amb}}\right) \right) \end{aligned} \quad (7)$$

Eq. (6) and (7) were derived for a drop in relative humidity between the inlet and outlet. Eq. (8) and (9) give the reversible enthalpy of shrinking for no drop in relative humidity (the gel swells in constant humidity air). Eq. (8) is given per unit mass dry polymer, and Eq. (9) is given per unit mass water absorbed during swelling.

$$\begin{aligned} \Delta h_{shrink,t,rev} &= -\Delta C \frac{R_{H2O} \ln(RH)}{\left(\frac{1}{T_{amb}} - \frac{1}{T_t}\right)} \\ &+ \frac{\Delta c_p}{\left(\frac{1}{T_{amb}} - \frac{1}{T_t}\right)} \left(\frac{T_t - T_{amb}}{T_{amb}} - \ln\left(\frac{T_t}{T_{amb}}\right) \right) \end{aligned} \quad (8)$$

The cooling power of the cycle, \dot{Q}_C , depends on its intended use. When used as a dehumidifier, the LCST cycle's useful effect is the removal of water vapor from the air: $\dot{Q}_{C,dehum} = \dot{m}_{H2O} h_g = \dot{m}_a (w_1 - w_2) h_g$, where h_g is the enthalpy of water vapor (the reference point for h_g is discussed in Sec. II of the Supplementary Material). In this use case, the outlet liquid water stream is discarded. When the system is used for cooling, the liquid water is adiabatically recombined with the air to lower its temperature (through evaporative cooling). In this case, the useful cooling effect is $\dot{Q}_{C,dehum} = \dot{m}_{H2O} h_{fg} = \dot{m}_a (w_1 - w_2) h_{fg}$, since the liquid water enthalpy is being added back to the air.

Following the analysis of the dehumidifier control volume, the first and second laws of thermodynamics are used to find the heat inputs required to drive the regeneration of the LCST cycle. From Fig. 1(b), there are sensible and latent heat inputs. The sensible heat is required to bring the swelled polymer and absorbed liquid water from the temperature they possess as they leave the recuperator, $T_{int,1}$, to the transition temperature, T_t . For all the cases analyzed in the main text of this paper, the specific heat increment of polymer swelling is assumed to be zero ($\Delta c_p = 0$), but we provide some results for a gel with a non-zero Δc_p in Sec. III of the Supplementary Material. When $\Delta c_p = 0$, $T_{int,1}$ is related to the recuperator effectiveness through the expression given in Eq. (10). When the recuperator effectiveness is unity, no sensible heating is required.

$$T_{int,1} = T_{amb} + \epsilon (T_t - T_{amb}) \quad (10)$$

The second heat input to the LCST cycle is the latent heat, or the enthalpy of shrinking of the thermoresponsive polymer, $\Delta h_{shrink,t}$. The reversible limit to this value is given per unit mass polymer in Eq. (4) as a function of ambient temperature, gel transition temperature, and inlet and outlet humidities. Sec. I of the Supplementary Material gives literature values for the enthalpies, entropies, and transition temperatures of existing LCST polymer gels, as well as thermal conductivity and permeability data.

The heat supplied to the system is the sum of the sensible heat to raise the swelled polymer temperature and the latent heat (enthalpy of shrinking): $\dot{Q}_S = \dot{m}_p \left((c_{p,swell} + \Delta C * c_{p,H2O}) (T_t - T_{int,1}) + \Delta h_{shrink,t} \right)$.

The COP of the cycle (COP) is defined as $COP = \dot{Q}_C / \dot{Q}_S$, where \dot{Q}_C is different for the dehumidification and cooling use cases as described earlier. The COP takes the form of Eq. (11) and Eq. (12) when the cycle is being used as a dehumidifier and direct evaporative cooler, respectively.

$$COP_{dehum} = \frac{\Delta C * h_g}{(c_{p,swell} + \Delta C * c_{p,H2O})(T_t - T_{int,1}) + \Delta h_{shrink}} \quad (11)$$

$$COP_{cool} = \frac{\Delta C * h_{fg}}{(c_{p,swell} + \Delta C * c_{p,H2O})(T_t - T_{int,1}) + \Delta h_{shrink}} \quad (12)$$

The COP can also be calculated using effective temperatures of heat transfer and the “second law” COP in Eq. (13), which is derived from an energy and entropy balance on a general, heat-driven cooling cycle in Sec. II of the Supplementary Material. The first term on the right-hand side of Eq. (13) is the Carnot COP of a heat-driven cooling cycle, while the second term accounts for internal irreversibility. The temperatures in Eq. (13) are effective temperatures, derived from a second law analysis of the cycle, and must be expressed in absolute units of temperature. T_S is the effective temperature of heat addition, T_C is the effective temperature of dehumidification/cooling, and T_H is the effective temperature of heat and mass rejection to the ambient. These effective temperatures can be used to identify entropy generation external to the cycle, while \dot{S}_{gen} is the internal entropy generation. Eq. (13) can be used to find either COP_{dehum} or COP_{cool} , where the equations for T_H and T_C are different depending on whether dehumidification or cooling is being considered.

$$COP = \left(1 - \frac{T_H}{T_S}\right) \frac{T_C}{T_H - T_C} - \frac{\dot{S}_{gen}}{\dot{Q}_S} \frac{T_H T_C}{T_H - T_C} \quad (13)$$

The effective temperatures are derived by applying the first and second laws to the cycle (detailed further in Sec. II of the Supplementary Material). The expression for the effective temperature of heat addition, T_S , is given in Eq. (14).

$$T_S = \frac{(c_{p,swell} + \Delta C * c_{p,H2O})(T_t - T_{int,1}) + \Delta h_{shrink}}{(c_{p,swell} + \Delta C * c_{p,H2O}) \ln\left(\frac{T_t}{T_{int,1}}\right) + \Delta s_{shrink}} \quad (14)$$

The effective temperature of dehumidification/cooling, T_C , and the effective temperature of heat and mass rejection to the ambient, T_H , depend slightly on the intended use of the cycle. When the cycle is used for dehumidification, the expression for T_C takes the form in Eq. (15). When the cycle is used for cooling, T_C is described by Eq. (16).

$$T_{C,dehum} = \frac{h_1 - h_2}{s_1 - s_2} \quad (15)$$

$$T_{C,cool} = \frac{h_1 - h_2 - (w_1 - w_2)h_f}{s_1 - s_2 - (w_1 - w_2)s_f} \quad (16)$$

Eq. (17) gives the expression for T_H when the cycle is used for dehumidification, and Eq. (18) describes T_H when the cycle is used for cooling.

$$T_{H,dehum} = \left(h_2 - h_1 + \frac{w_1 - w_2}{\Delta C} (\Delta h_{swell,amb} + (c_{p,shrunk} + \Delta C * c_{p,H2O})(T_{amb} - T_{int,2})) \right) * \left(s_2 - s_1 + \frac{w_1 - w_2}{\Delta C} (\Delta s_{swell,amb} + (c_{p,shrunk} + \Delta C * c_{p,H2O}) \ln\left(\frac{T_{amb}}{T_{int,2}}\right)) \right)^{-1} \quad (17)$$

$$T_{H,cool} = \left(h_2 + (w_1 - w_2)h_f - h_1 + \frac{w_1 - w_2}{\Delta C} (\Delta h_{swell,amb} + (c_{p,shrunk} + \Delta C * c_{p,H2O})(T_{amb} - T_{int,2})) \right) * \left(s_2 + (w_1 - w_2)s_f - s_1 + \frac{w_1 - w_2}{\Delta C} (\Delta s_{swell,amb} + (c_{p,shrunk} + \Delta C * c_{p,H2O}) \ln\left(\frac{T_{amb}}{T_{int,2}}\right)) \right)^{-1} \quad (18)$$

When the system is internally reversible, Eq. (13) reduces to the Carnot COP of a heat-driven cycle: $COP = \left(1 - \frac{T_H}{T_S}\right) \frac{T_C}{T_H - T_C}$. If the recuperator has an effectiveness less than unity, the need to sensibly heat the gel makes the cycle both externally and internally irreversible. External irreversibility increases the value of T_H and reduces the value of T_S . When the system is externally reversible, T_H and T_S reach their ideal values. For example, when the LCST cycle is externally reversible and used for cooling, $T_H = T_{amb}$ and $T_S = T_t$. Even though Eq. (13) yields the same value as Eq. (11) or (12) (depending on the equations used for T_C and T_H), it provides important insight. Specifically, the rate of entropy generation and the effective temperatures are useful for identifying points of internal and external irreversibility and their effect on the cycle COP.

3.3. Mass balance, first law, and second law analysis of the traditional desiccant cycle

A simple configuration of the traditional desiccant cycle is given in Fig. 4(a). Humid, ambient air enters a rotating wheel filled with solid desiccant. The air enters with ambient conditions at state 1 and leaves hot and dry at state 1a. The hot and dry air at state 1a is sent through a heat exchanger, which has humid regeneration air at state 3 entering on the other side. The hot and dry supply air is cooled to the ambient temperature by the heat exchanger, which results in dry air at ambient temperature leaving the system (just as in the LCST cycle) at state 2. On the other side of the heat exchanger, the humid regeneration air is preheated to state 4. We note that our choice of state numbers is deliberately chosen such that states 1 and 2 in the traditional desiccant cycle are equivalent to states 1 and

The effective temperatures of heat transfer can be derived for the traditional desiccant cycle in the standard approach. Heat addition occurs from states 5 to 6, where the effective temperature $T_{S,des}$ is given in Eq. (21). The useful effect of the cycle, dehumidification, occurs between states 1 and 2, resulting in Eq. (22) for $T_{C,des}$. Regeneration air enters the cycle at state 3 and is exhausted to ambient at state 8; Eq. (23) gives the expression for $T_{H,des}$. These effective temperatures are for dehumidification, not cooling, as the traditional desiccant cycle does not harvest liquid water for evaporative cooling.

$$T_{S,des} = \frac{h_6 - h_5}{s_6 - s_5} \quad (21)$$

$$T_{C,des} = \frac{h_2 - h_1}{s_2 - s_1} \quad (22)$$

$$T_{H,des} = \frac{h_8 - h_3}{s_8 - s_3} \quad (23)$$

We take care to delineate the difference between our use of the phrases “regeneration temperature”, “transition temperature”, and “heat source temperature”. The regeneration temperature of both the LCST and traditional desiccant cycles is the highest temperature that is achieved within the cycle. This is the highest temperature that the LCST gel is brought to during regeneration of the LCST cycle, and it is the highest temperature that the regeneration air is brought to in the traditional desiccant cycle. For the traditional desiccant cycle, we label this as state 6, and the traditional desiccant regeneration temperature is T_6 . The transition temperature pertains only to the LCST cycle, as this is a material property of the LCST gel. The transition temperature, T_t , is the temperature at which the gel goes through a first order volume phase transition, expelling its water content upon isothermal heat addition. Because we assume that all of the water is expelled from the gel at the transition temperature, this ends up being the highest temperature within the LCST cycle. As such, the transition temperature is equal to the regeneration temperature for the LCST cycle. The effective heat source temperature, T_S , is a fictitious temperature derived from a second law analysis of the heat-driven cycles in this paper. This can be seen as the “thermodynamic average” (though not a true arithmetical average) temperature at which heat is supplied to the cycle. For the traditional desiccant cycle, the regeneration air increases in temperature as it is heated, so the effective heat source temperature is lower than the regeneration temperature. When the LCST cycle has a perfect recuperator, only latent heat is supplied at a temperature of T_t . In this case, the effective heat source temperature is equal to the transition temperature, which is equal to the regeneration temperature. This is the ideal (reversible) scenario.

4. Results and Discussion

The equations derived from the first and second law analysis of the LCST cycle are used in several ways. First, we use Eq. (4) to find the minimum enthalpy of swelling/shrinking that an LCST polymer gel must possess to dehumidify air. We

find this value for various inlet and outlet humidities, as well as various gel transition temperatures. Next, we use that minimum enthalpy of shrinking to find the maximum COP that the LCST cycle could possess for the humidities that would likely be seen in building applications. Then we compare the LCST cycle to a traditional desiccant cycle on a second law basis. We show that these two cycles would achieve different COPs under the same external conditions, due to differences in entropy generation and effective temperatures. Finally, we analyze the LCST cycle with the known enthalpy of swelling/shrinking of PNIPAm homopolymer, a common LCST polymer.

4.1 Reversible enthalpy of shrinking

Fig. 5 shows that absorbing water vapor requires higher enthalpies of shrinking in dry air than in humid air. This figure was made using Eq. (4) and all curves correspond to the same decrease in relative humidity (2% between the inlet and outlet), but the relative humidity at the inlet is different for each curve. As the inlet relative humidity decreases for a given transition temperature, higher enthalpies of shrinking are required to achieve the same decrease in relative humidity from inlet to outlet.

Fig. 5 also shows that the minimum possible enthalpy of shrinking increases rapidly as the transition temperature (T_t) approaches the temperature at which swelling occurs (T_{amb}); as the difference between T_t and T_{amb} decreases, so does the polymer’s affinity for swelling. Thus, Δh_{swell} must be very large in magnitude to compensate and drive the swelling process when T_t is near T_{amb} .

Fig. 5 highlights how the thermodynamic analysis in this paper can guide the materials science needed to allow the LCST cycle to perform desirably. For the LCST cycle to dehumidify to low humidities, it must have a gel with a high transition temperature and/or a high enthalpy of shrinking. Condensation of water out of unsaturated humid air is non-spontaneous and can only occur when accompanied by a thermodynamically favorable (negative free energy) process. The enthalpy of swelling/shrinking can be seen as the driver of the process that

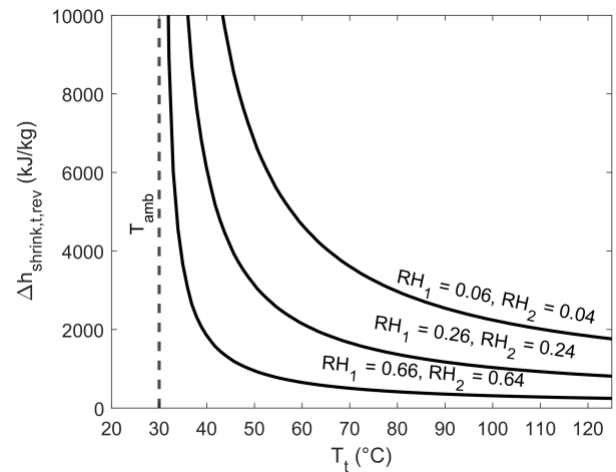


Fig. 5. Reversible (or minimum possible) enthalpy of shrinking for varying relative humidities (RH) at an ambient temperature of 30 °C and a polymer water uptake of 1 kg/kg. To give a sense of scale, we note that the enthalpy of vaporization of water is roughly 2340 kJ/kg at 30 °C.

allows the water vapor to condense and swell the polymer. The enthalpy of shrinking is also the penalty that must be paid during regeneration (in the form of heat input). The drier the air, the more difficult it is to condense water from the air; as such, the enthalpy of shrinking (or gel transition temperature) must increase to compensate. In other words, “there is no free lunch.”

Fig. 5 also gives a sense of the energy scales needed to drive the shrinking (regeneration) process of the LCST polymer gel. We note that water’s enthalpy of vaporization is ~ 2340 kJ/kg at 30°C and this serves as a relevant value for context. Fig. 5 shows that the enthalpy of shrinking can be less than water’s enthalpy of vaporization for high transition temperatures and/or high relative humidities. However, this enthalpy of shrinking can also exceed water’s enthalpy of vaporization at polymer transition temperatures near ambient and/or if low relative humidities are needed.

The enthalpy requirements shown in Fig. 5 apply to any thermoresponsive polymer (regardless if it is a homopolymer, copolymer, or interpenetrating polymer network), as our analysis makes no assumptions regarding the polymer material, other than that it is thermoresponsive. We treat the polymer as a black box that exhibits three traits: (i) a negative enthalpy of swelling, (ii) a negative entropy of swelling, and (iii) a first order swelling/shrinking phase transition at a temperature T_t . These traits are common to LCST behavior and are what drive the vapor absorption/liquid expulsion of any LCST polymer (homopolymer or otherwise). As such, any LCST polymer that converts humidity to liquid water via heat input must obey Eq. (4) and the corresponding results in Fig. 5. Moreover, we note that the enthalpy values in Fig. 5 were derived for reversible operation. As such, these values are not unique to the LCST cycle. This is the same heat input that would be required for *any* reversible heat-driven dehumidification cycle with the same boundary conditions.

4.2 LCST cycle COP

Fig. 6 was calculated using Eq. (4), (10), and (12), and it shows that in the reversible limit, the LCST cycle COP increases monotonically as a function of transition temperature.

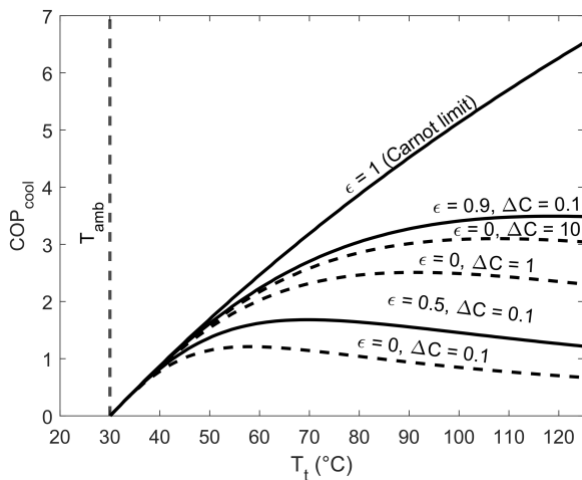


Fig. 7. LCST cycle COP_{cool} as a function of transition temperature, with different curves for various recuperator effectiveness values and water uptakes. For all curves, ambient temperature is 30°C , inlet relative humidity is 66%, and outlet relative humidity is 40%.

To calculate the COP, we used the reversible enthalpy of shrinking from Eq. (4) and set $\Delta c_p = 0$. When $\Delta c_p = 0$ and $\epsilon = 1$, the recuperator is reversible, and no entropy is generated; thus, the $\epsilon = 1$ curve in Fig. 6 represents the Carnot COP. At low transition temperatures, the COP is low, because the enthalpy of shrinking must be large in magnitude to drive dehumidification.

The COP peaks at a finite transition temperature for recuperator effectiveness values less than unity (Fig. 6). Below the peak temperature, the COP is limited by a large $\Delta h_{shrink,t}$ value, while above the peak temperature the COP is limited by sensible heating.

The COP increases with increasing water uptake when the recuperator effectiveness is less than unity (dotted lines in Fig. 6). A polymer with a higher water uptake would require less polymer mass to remove the same amount of water from the air. Less polymer mass reduces the sensible heating, which increases the system COP. The solid lines in Fig. 6 illustrate that an increased recuperator effectiveness leads to an increased COP. Fig. 6 also shows that a polymer with a water uptake of 10 kg/kg and no recuperator would have a COP nearly equal to the COP of a polymer with a water uptake of 0.1 kg/kg and a recuperator effectiveness of 0.9. When the water uptake is high, the recuperator can be eliminated without significantly affecting the COP.

4.3 Comparing the LCST and traditional desiccant cycles

The COPs of the LCST cycle (calculated using Eq. (11)) and traditional desiccant cycle (calculated using Eq. (19)) are plotted as functions of regeneration temperature in Fig. 7. The COPs of the two cycles are close when both cycles have a regeneration temperature equal to $T_{6,min}$ (the minimum possible regeneration temperature for the traditional desiccant cycle).

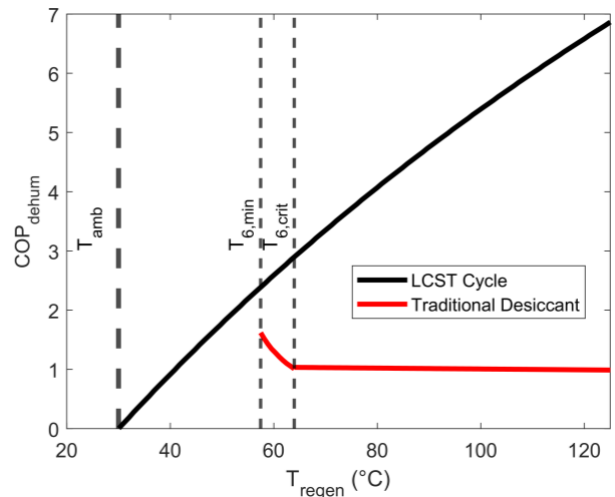


Fig. 6. LCST cycle (black) and traditional desiccant (red) COP_{dehum} as a function of regeneration temperature. For all curves, ambient temperature is 30°C , inlet relative humidity is 66%, and outlet relative humidity is 40%. For both cycles, the recuperator effectiveness values are 1. The regeneration temperature on the x-axis is T_t for the LCST cycle and T_6 for the traditional desiccant cycle.

Table 1. Effective temperatures of heat transfer, rate of entropy generation, and COP_{dehum} of two traditional desiccant cycle scenarios and two LCST cycle scenarios. For all four cases, the ambient temperature is 30 °C, the inlet relative humidity is 66%, the outlet relative humidity is 40%, the mass flow rate of air is 1 kg/s, and $\epsilon = 1$. Effective temperatures are kept in Kelvin, as they do not represent measurable temperatures; rather, they are equivalent temperatures derived from the second law that must be in absolute units when used to find the COP in Eq. (13). The minimum regeneration temperature for the traditional desiccant, $T_{6,min}$, is 56.8 °C, so the $T_{regen} = 32$ °C is blank for the traditional desiccant, as it is thermodynamically impossible. The critical regeneration temperature for the traditional desiccant ($T_{6,crit}$), which is the temperature above which the recuperator becomes useful, is 63.6 °C.

	T_C (K)	T_H (K)	T_S (K)	\dot{S}_{gen} (W/K)	COP_{dehum}
LCST Cycle ($T_t = 32.0$ °C)	292.2	303.0	305.2	0	0.19
LCST Cycle ($T_t = 56.8$ °C)	292.2	302.6	330.0	0	2.34
LCST Cycle ($T_t = 63.6$ °C)	292.2	302.6	336.8	0	2.87
LCST Cycle ($T_t = 95.0$ °C)	292.2	302.5	368.2	0	5.08
Traditional Desiccant ($T_{regen} = 32.0$ °C)	-	-	-	-	-
Traditional Desiccant ($T_{regen} = 56.8$ °C)	292.2	301.9	324.4	0.5	1.67
Traditional Desiccant ($T_{regen} = 63.6$ °C)	292.2	304.5	327.9	4.2	1.03
Traditional Desiccant ($T_{regen} = 95.0$ °C)	292.2	304.7	364.9	7.2	1.01

Fig. 7 highlights two advantages of the LCST cycle. Firstly, the LCST cycle can operate with lower regeneration temperatures than the traditional desiccant cycle. The LCST of PNIPAm, a common thermoresponsive polymer, is 32 °C [19]–[26], and Fig. 7 shows that the LCST cycle could operate with such a polymer. The COP would be low for such a polymer, but the regeneration temperature is low enough that almost any common heat source could be used to regenerate the polymer, including "free" heat sources like solar- and waste-heat. On the other hand, the traditional desiccant cycle could not operate with a regeneration temperature of 32 °C, as the minimum regeneration temperature ($T_{6,min}$) is greater than 32 °C. In other words, if the traditional desiccant were regenerated with a 32 °C heat source, it would not be able to dehumidify the air at state 2 to 40% relative humidity, but the LCST cycle could.

The second major advantage of the LCST cycle is that the LCST cycle COP increases with regeneration temperature, while the traditional desiccant cycle COP decreases. To improve the cycle COP, an LCST gel with a higher transition temperature could be synthesized and utilized in the LCST cycle. At these higher regeneration temperatures, it is clear that the LCST cycle could achieve COPs several times higher than traditional desiccant cycles. For example, the LCST cycle has a maximum COP of 5.1 when the polymer transition temperature is 95 °C, compared to the traditional desiccant cycle maximum COP of 1 at the same regeneration temperature. When the recuperator effectiveness is unity, the LCST cycle COP monotonically increases with the regeneration temperature (T_t), approaching an COP-asymptote far greater than 1. The existence of this asymptote can be seen in the functional form of Eq. (13), and it occurs at temperatures far greater than what would be used in the LCST cycle. As such, we limit the Fig. 5, Fig. 6, and Fig. 7 results to typical desiccant regeneration temperatures (<125 °C) [15]. Though PNIPAm, the most common thermoresponsive polymer, has an LCST of 32 °C, other polymers have been demonstrated with LCSTs as high as 73 °C [31]. We believe that LCST polymer gels with higher transition temperatures than historically well-researched gels (like PNIPAm) can be created. We note that in practice it would not make sense to use gels with transition temperatures greater than 100 °C in the LCST cycle, as the water would boil during

regeneration and could not be recollected as liquid. Still, we provide results for T_t up to 125 °C to show the behavior of Δh_{shrink} and COP at these higher temperatures.

In contrast to the LCST cycle COP, the traditional desiccant cycle COP monotonically decreases with regeneration temperature (T_6), approaching an asymptote of 1. While Fig. 7 shows that the traditional desiccant cycle would be fairly efficient if regenerated at $T_{6,min}$, this is unrealistic, as most traditional desiccants must be regenerated at temperatures closer to 100 °C, depending on the operating conditions [15]. When the regeneration temperature is above $T_{6,crit}$, the traditional desiccant cycle COP approximately reaches the limit of 1. This limitation is illustrated in Fig. 4(d); the cooling effect (represented by the length between points 1a and 2) is equal to the heat supplied (represented by the length between points 5 and 6). Thus, traditional desiccants have been historically limited to COPs near 1 [1].

It is worth noting that a third major advantage of the LCST cycle, not highlighted in Fig. 7, is that the LCST cycle harvests liquid water, which can be used to create an evaporative cooler with net-zero water consumption. This is an important advantage that sets the LCST cycle apart from traditional desiccant cycles, even in situations where the first two advantages of the LCST cycle do not prove to be important. For example, the DEVap system created at the National Renewable Energy Laboratory (NREL) is a liquid desiccant system that can achieve a COP of 1.2 - 1.4 and can be regenerated with solar- or waste-heat [3]. While the LCST cycle could reach a COP higher than the DEVap system, that becomes less important when considering solar- and waste-heat are "free". In that case, a higher COP (and thus a lower rate of heat input) becomes less impactful. However, even if the possibility of lower regeneration temperatures and higher COPs is not important, the liquid water harvesting of the LCST cycle is important. For example, the DEVap system uses evaporative cooling and thus consumes water. Regeneration of traditional desiccants involves the exhausting of water as vapor to outside air. The LCST cycle expels liquid water during regeneration which can be harvested and reused with evaporative cooling. This presents the potential for a dehumidification and cooling cycle with net-zero water consumption (in sufficiently humid environments),

which is something that traditional desiccant cycles cannot achieve.

In addition to evaporative cooling, the liquid water given off during regeneration of the LCST cycle can be used for atmospheric water harvesting. Researchers are already investigating LCST polymer gels for their ability to harvest potable water from humid air [19]. When the LCST cycle is used for atmospheric water harvesting, $\Delta h_{shrink,t,rev,H_2O}$ (given in Eq. (5)) becomes an important quantity, since this is the enthalpy needed to harvest a unit mass of water from an LCST polymer that absorbed water from humid air at state 1, bringing the air to state 2. We anticipate this equation will be useful to researchers who are using LCST gels for water harvesting.

From a second law perspective, it is not immediately evident why the LCST cycle COP deviates from the traditional desiccant cycle COP in Fig. 7. Both cycles dehumidify air to the same outlet conditions, reject heat to the same ambient temperature, and can be regenerated with the same heat source. To explain the difference between the two cycles, we present Table 1, where we show the effective temperatures, entropy generation, and COP of four LCST cycle scenarios and four traditional desiccant cycle scenarios. To make the cycles comparable, all were given recuperator effectiveness values of unity, and the inlet air (state 1) and outlet air (state 2) conditions were the same. All cycles in Table 1 have the same value for T_C , as they provide the same amount of dehumidification. The difference arises in the effective temperatures of the heat source and heat rejection, as well as the entropy generation.

The LCST cycle results in Table 1 were calculated using the reversible enthalpy of shrinking from Eq. (4), which corresponds to zero entropy generation in the dehumidifier. Since the results were calculated for a recuperator effectiveness of unity, no entropy is generated in the recuperator. This means $\dot{S}_{gen} = 0$ for the LCST cycle, regardless of the regeneration temperature.

Initially, it may seem unfair to compare the LCST cycle with zero entropy generation to the traditional desiccant cycle with nonzero entropy generation. However, this is a consequence of the undesirable behavior of traditional desiccants. Entropy will be generated in the traditional desiccant cycle when the desiccant is regenerated with a temperature greater than $T_{6,min}$. Because traditional desiccants have adsorption isotherms that are nearly independent of temperature [12], $T_{6,min}$ is determined by the relative humidity of the conditioned air. As such, $T_{6,min}$ is fixed by the desired humidity and cannot be increased to fit the desired regeneration temperature. Similar to the traditional desiccant cycle, the LCST cycle would generate entropy if the regeneration temperature were higher than the gel transition temperature, T_t . However, unlike $T_{6,min}$ for the traditional desiccants, T_t can be selected to fit the regeneration temperature by choosing an LCST gel with the right T_t . In fact, the LCSTs of certain thermoresponsive polymers have been shown to be tunable through various synthesis methods and LCSTs ranging from 18 to 73 °C have been demonstrated in the materials literature [30], [31], [38], [40]. As such, the polymer gel in the LCST cycle can be engineered to have properties that approach reversibility in ways that traditional desiccants cannot.

The highest temperature in the cycle is T_t , so the actual temperature of the heat source must be at least T_t . When $T_S <$

T_t , not all of the exergy from the heat source is being utilized, and exergy is being destroyed (*i.e.*, entropy is being produced) external to the cycle. When the recuperator in the LCST cycle has an effectiveness less than unity, the heat source (at a temperature of T_t) is used to increase the temperature of the swelled polymer to T_t . This means heat is being transferred between two bodies at different temperatures, and entropy is being externally generated, which reduces the value of T_S . The results in Table 1 were calculated for a recuperator effectiveness of 1, meaning no sensible heating is required. The lack of sensible heating maximizes T_S ; in fact, $T_S = T_t$ for all of the LCST cycle results in Table 1. This means that the effective and actual heat source temperatures are equal, and all of the exergy from the heat source is being used.

The ambient temperature for the results presented in Table 1 is 30 °C, or 303.15 K; however, the effective temperature T_H is lower than 303.15 K for all of the LCST cycle results. This may seem impossible at first: heat cannot be rejected to ambient at a temperature lower than the ambient temperature. However, it is important to note that the effective temperature T_H also includes mass (namely, liquid water) that is exhausted to ambient, and that reduces the value below the actual ambient temperature. If Table 1 were recreated for COP_{cool} , all of the T_H values would be equal to 303.15 K for the LCST cycle. This is because the cooling configuration of the cycle considers the liquid water as part of the useful cooling effect and not as being rejected to ambient.

It should be noted that the liquid water exhausted to ambient actually has some exergy (as it does not have the same chemical potential as the 66% relative humidity ambient air). Thus, when used for dehumidification, the LCST cycle described in Fig. 1(b) is externally irreversible and is not 100% exergy efficient. A 100% efficient version of the dehumidification configuration of the LCST cycle would have some way of scavenging the exergy from the exhausted liquid water, but that is beyond the scope of this paper. If the exergy of the liquid water were used instead of lost to ambient, the T_H values would be lower than those in Table 1.

While there is some small difference in T_H when comparing the LCST and traditional desiccant cycles, T_S and \dot{S}_{gen} are the major factors that explain the deviation in performance between the LCST and traditional desiccant cycles. For the same regeneration temperature, the T_S value is lower for the traditional desiccant than for the LCST cycle. Thus, the traditional desiccant cycle is not able to use all of the exergy from the heat source that the LCST cycle is able to use.

While the traditional desiccant T_S values are lower than those of the LCST cycle, they still increase with increasing regeneration temperature. Despite the increasing T_S values, it is clear from Table 1 that the COP decreases as regeneration temperature increases. This might seem counterintuitive; a higher temperature heat source tends to increase the COP of a heat-driven cooling cycle, as seen in Eq. (13). However, it is also clear from Eq. (13) that internal entropy generation decreases the COP, and Table 1 shows that entropy generation in the traditional desiccant cycle increases with increasing regeneration temperature. This entropy generation is why the

Table 2. The thermophysical properties of the shrinking volume phase transition of PNIPAm gel and several theoretical gels that would reversibly swell in constant RH air at an ambient temperature of 20 °C. The PNIPAm enthalpy and transition temperature were measured by Schild and Tirrell [28], the entropy was calculated from $\Delta s = \Delta h/T_t$, and the water uptake was estimated from Moerkerke et al. [42]. The properties of the ideal gels were calculated from Eq. (8) for $\Delta C = 8.64 \text{ kg}_{\text{H}_2\text{O}}/\text{kg}_p$ (the water uptake of PNIPAm). The gel that would reversibly swell in 99.8% RH has an enthalpy of swelling very near PNIPAm; as such, we label it as “PNIPAm-like”.

	Δh_{shrink} (kJ/kg _p)	Δs_{shrink} (kJ/kg _p -K)	T_t (K)	ΔC (kg _{H2O} /kg _p)
PNIPAm Homopolymer Gel	41.84	0.1356	308.65	8.64
Ideal 99.8% RH Gel (PNIPAm-like)	46.59	0.1509	308.65	8.64
Ideal 99% RH Gel ($T_t = 35.5 \text{ }^\circ\text{C}$)	233.9	0.7577	308.65	8.64
Ideal 90% RH Gel ($T_t = 35.5 \text{ }^\circ\text{C}$)	2452	7.943	308.65	8.64
Ideal 70% RH Gel ($T_t = 35.5 \text{ }^\circ\text{C}$)	8300	26.89	308.65	8.64
Ideal 50% RH Gel ($T_t = 35.5 \text{ }^\circ\text{C}$)	16129	52.26	308.65	8.64
Ideal 50% RH Gel ($T_t = 51.7 \text{ }^\circ\text{C}$)	8300	25.55	324.85	8.64
Ideal 50% RH Gel ($T_t = 70.0 \text{ }^\circ\text{C}$)	5559	16.20	343.15	8.64

traditional desiccant cycle COP decreases as T_{regen} increases, while the lack of entropy generation in the LCST cycle is why its COP increases with T_{regen} . The reason why entropy generation increases with regeneration temperature in the traditional desiccant cycle is due to the method of regeneration.

The conditions of the regeneration air, namely the relative humidity or chemical potential, determine the amount of entropy generation in the traditional desiccant cycle. The ideal case is when the desiccant dehumidifies the process air to the same relative humidity (RH) as the regeneration air entering the desiccant (*i.e.*, $RH_{1a} = RH_6$). This condition is described by $T_6 = T_{6,\text{min}}$. Because the relative humidities are the same, the entropy generation is approximately zero (a small amount of entropy is generated in the cycle’s heat exchanger). Hence the traditional desiccant cycle COP is approximately the Carnot COP at this minimum possible regeneration temperature. For the inlet and outlet conditions in Table 1, the minimum regeneration temperature was found to be 56.8 °C. At this minimum, the effective source temperature of the cycle (T_S) is low, which is undesirable, but the entropy generation is nearly zero, which is desirable.

In practical operation, traditional desiccants must be regenerated with temperatures greater than the theoretical minimum. As the regeneration temperature increases, the relative humidity of the regeneration air decreases. A regeneration temperature greater than the minimum creates a mismatch in relative humidity (and, correspondingly, a mismatch in chemical potential) between the process outlet air and regeneration inlet air. This increases the rate of desorption required to operate a practical, finite-sized system. It also results in mass transfer of water vapor across a non-zero chemical potential difference, which results in entropy generation. Thus, for high temperature regeneration sources, the traditional desiccant cycle COP becomes limited by entropy generation and cannot reach the Carnot COP for that source

temperature. Because the LCST cycle is regenerated with a phase transition, as opposed to dry air, it does not suffer from the entropy generation that hinders the traditional desiccant cycle at higher regeneration temperatures.

To this point, we have presented results pertaining to ideal polymer gels that would reversibly swell in humid air. However, we believe it is also useful to analyze the theoretical performance of real polymer gels. Specifically, we analyze the performance of PNIPAm homopolymer, based on measurements made by other researchers on the enthalpy of shrinking [28], transition temperature [28], and water uptake [42]. The measured properties of PNIPAm homopolymer are presented in Table 2, along with the values of ideal gels that would reversibly swell in 99.8% RH, 99% RH, 90% RH, 70% RH, and 50% RH air, as determined by Eq. (8). The enthalpy of PNIPAm homopolymer in Table 2 comes from measurements made by Schild and Tirrell [28], and they did not report a change in specific heat across the shrinking transition, so we used $\Delta c_p = 0$ for the calculation of our ideal gel properties. The 99.8% RH gel has properties very near PNIPAm. As such, we call this gel “PNIPAm-like”. We also use this to deduce that PNIPAm would not swell in humidities lower than 99.8% RH. This can also be seen through an entropy generation analysis.

We analyzed the entropy generation of the PNIPAm gel for swelling at 20 °C and varying humidity using Eq. (3). First, when swelling in a constant humidity of 99.9% RH, analysis reveals that the PNIPAm gel generates 3.7×10^{-4} kJ/K of entropy per kg of water removed from the air. This reveals that PNIPAm can indeed swell in 99.9% RH air. However, when analyzed for swelling in 99.8% RH air, the PNIPAm gel generates -9.4×10^{-5} kJ/K of entropy per kg of water removed from the air. The entropy generation is negative, revealing that this process is not possible. The entropy generation becomes more negative at lower humidities, as the PNIPAm cannot swell at those humidities either. As such, we deduce that PNIPAm

can only swell in very high humidities (>99.8% RH) if the gel is regenerated with the shrinking phase transition. This is qualitatively consistent with experimental data from other researchers, showing very little water uptake when PNIPAm is exposed to humid air [19], [20]. For a thermoresponsive gel to swell in low humidities after being regenerated by the shrinking phase transition, it would need a far higher enthalpy of shrinking than PNIPAm, as seen in Table 2. To absorb moisture in 50% RH, a gel with the same transition temperature as PNIPAm would need an enthalpy of shrinking several orders of magnitude greater than PNIPAm.

Alternatively, the gel will also swell in lower humidities if the transition temperature is increased instead of the enthalpy. From Table 2, a gel with an enthalpy of shrinking of 8300 kJ/kg could absorb moisture in 70% RH if the transition temperature were 35.5 °C. However, if the transition temperature were increased to 51.7 °C without changing the enthalpy of shrinking, it could absorb moisture in 50% RH. Both gels would require the same latent heat input, but the gel with the higher transition temperature can dehumidify to lower humidities. Another comparison can be made between the three “Ideal 50% RH” gels in Table 2. All of them can absorb moisture from 50% RH air, but the gel with the highest transition temperature would require the lowest enthalpy (and the least amount of heat input). If a higher temperature heat source is available, a gel with a higher transition temperature is desirable, since it would require less heat to absorb the same humidity or would dehumidify to lower humidities than gels with the same enthalpy.

While the analysis of the swelling of PNIPAm homopolymer in humid air may seem discouraging, it is important to keep in mind that existing thermoresponsive polymers have not been optimized for this application. PNIPAm has seen widespread use for controlled drug delivery due to its ability to absorb liquids, not vapors. Additionally, the transition temperature of PNIPAm is very useful in biomedical applications, since it is near the body temperature of humans. However, our analysis shows that the transition temperature of PNIPAm is likely too near ambient temperature to perform well in the LCST cycle. A thermoresponsive gel with the transition temperature of PNIPAm would need a very high enthalpy of shrinking to absorb water vapor at the humidities seen in building applications. Unless materials can be made with incredibly high enthalpies of shrinking, higher transition temperatures will be desirable for the LCST cycle. As such, the current state of thermoresponsive gels does not reflect the potential of the LCST cycle, as these gels have not been optimized for this new application.

Our previous discussion regarding PNIPAm refers to a PNIPAm homopolymer, but other PNIPAm polymers have been documented. We analyze the performance of a PNIPAm homopolymer gel since there is robust literature data on this thermoresponsive material. Other PNIPAm based polymers, such as interpenetrating polymer networks [19], [20] and copolymers [38], exist, as do thermoresponsive polymers that do not contain PNIPAm [40]. However, there is little information on the thermophysical properties relevant to our analyses, such as the enthalpy of swelling/shrinking, for these other polymers.

Other researchers have recently created interpenetrating polymer networks with a PNIPAm network and a hygroscopic

network [19], [20]. This has been done with the hope that the hygroscopic network increases moisture absorption, while the PNIPAm maintains the thermoresponsive behavior. It may be tempting to assume that the interpenetrating network will be able to absorb water at lower humidities while expelling liquid water upon heating and possessing the same enthalpy of shrinking as PNIPAm homopolymer. However, our thermodynamic analysis shows this to be impossible. An enthalpy increase is the penalty that must be paid for operating this cycle (water vapor absorption and liquid water expulsion) at lower humidities. The interpenetrating network will either initially absorb more water vapor than PNIPAm homopolymer but be unable to give it off as liquid, or it will give the water off as liquid, but will have a greater enthalpy of shrinking than PNIPAm homopolymer.

It should be noted that Zhao *et al.* [19] and Matsumoto *et al.* [20] both reported that the sorption isotherms of their interpenetrating polymer networks showed greater water uptake than PNIPAm homopolymer. However, the enthalpy of the volume phase transition was not reported. Based on the analyses in this paper, an increased enthalpy of shrinking and/or increased transition temperature must accompany the changes that cause an LCST material to absorb and harvest moisture from lower humidities. We anticipate that a measurement of the heat required to expel a unit mass of water from the Matsumoto [20] and Zhao [19] interpenetrating polymer networks would be greater than that of PNIPAm homopolymer.

For the LCST cycle, the basic design parameters are the regeneration heat input and regeneration temperature, which are implicitly related to the LCST polymer properties (enthalpy of shrinking and transition temperature, respectively). The regeneration heat and temperature determine the outlet humidity for a given inlet humidity and ambient temperature. As such, a polymer with the necessary transition temperature and enthalpy must be selected for the cycle to provide the desired performance.

It is important to note that the COP values we present in Fig. 7 and Table 1 are the maximum possible COPs that both the LCST and traditional desiccant cycles could achieve for the given operating conditions. Thus, our results should not be used to predict the COPs that these cycles could reach if practically implemented (as practical operation will introduce irreversibilities that we do not consider). Rather, our results should be used to draw general conclusions about the cycles. Namely, the LCST cycle has a far greater ceiling for the COP at higher regeneration temperatures, owing to the favorable method of regeneration. Another important result from our analysis is that the synthesis of LCST polymers with transition temperatures greater than PNIPAm would result in better performance when attempting to implement the LCST cycle. This result is important to researchers attempting to use LCST polymer gels for atmospheric water harvesting, as gels with low transition temperatures will require a significant amount of heat to harvest a unit mass of liquid water, or they will be unable to absorb moisture unless the air humidity is very high. Finally, we point out that researchers should attempt to make LCST polymers with higher enthalpies of swelling. This will enable the LCST cycle to dehumidify air to lower humidities than could be achieved with existing LCST gels like PNIPAm.

5. Conclusion

In summary, a thermoresponsive polymer desiccant dehumidification and cooling cycle that utilizes LCST polymer gels is presented, and we refer to this as “the LCST cycle”. This cycle uses a thermoresponsive gel to absorb moisture out of humid air. The gel is then heated to a transition temperature, at which point it expels and harvests the absorbed moisture as liquid water. This liquid water harvesting is an efficient method of regeneration, and it can be used for evaporative cooling without the need for an external water source.

We provide the thermodynamic equations necessary to analyze the performance of this cycle. Generally, the cycle COP improves as the gel transition temperature increases, until sensible heating begins to dominate. The sensible heating can be mitigated by using a highly effective recuperator or a gel with a high water uptake. When the gel transition temperature is high, the gel can absorb water vapor from humid air with little heat input required. This means the LCST cycle could achieve high COPs (a value of 3 or above) when the gel transition temperature is above 70 °C, which is something traditional desiccant cycles cannot achieve.

On the other hand, the LCST cycle can also be used with regeneration temperatures only slightly above ambient. These low transition temperature gels would need high heat inputs to dehumidify the air to comfortable humidities, but the low regeneration temperature would allow for the use of “free” heat sources like solar- or waste-heat. This is a benefit over traditional desiccant cycles, since they cannot operate below some minimum regeneration temperature (often near 60 °C for building applications [12], [15]).

While the majority of our analysis dealt with the reversible limit of swelling, we also presented an analysis of a common existing LCST polymer gel, PNIPAm homopolymer. Our analysis shows that the combination of a low transition temperature and a low enthalpy of shrinking cause PNIPAm to be unable to absorb moisture from anything other than very high humidities (> 99% RH). However, it is important to keep in mind that the pervasiveness of PNIPAm is predominately due to its biomedical applications, and hence it was never designed for swelling in humid air. We believe that LCST polymer gels can and eventually will be created with higher enthalpies and/or higher transition temperatures. These gels would then be able to swell in much lower humidities than PNIPAm homopolymer, which would then enable the LCST cycle to dehumidify air to a comfortable humidity for air conditioning applications.

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Appendix A. Supplementary material

Supplementary data to this article can be found online version at [url will be inserted by publisher]

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