Energy saving thermal adaptive liquid gating system

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GRAPHICAL ABSTRACT

PUBLIC SUMMARY
- An energy saving thermal adaptive liquid gating system is constructed
- The system uses functional liquid to exhibit high metastability, providing durability
- The system is used as an energy saving patch to greenhouse by sandwich configuration
- The system shows energy consumption reduction of ~11.6% than traditional greenhouse
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Thermal transfer systems involving temperature control through heating, ventilation, and air conditioning applications have emerged as one of the largest energy issues in buildings. Traditional approaches mainly comprise closed and open systems, both of which have certain advantages and disadvantages in a single heating or cooling process. Here we report a thermal adaptive system with beneficial energy-saving properties, which uses functional liquid to exhibit high metastability, providing durability in a temperature-responsive liquid gating system. With an efficient use of energy, this system achieves smart "breathing" during both heating and cooling processes to dynamically tune the indoor temperature. Theoretical modeling and experiments demonstrate that the adaptive, sandwich-structured, membrane-based system can achieve temperature control, producing obvious advantages of energy saving compared with both closed and open systems through the bistable interfacial design of the liquid gating membrane. Further energy saving evaluation of the system on the basis of simulation with current global greenhouse plantation data shows a reduction of energy consumption of 7.9 \times 10^{11} \text{kJ/year, a percentage change of} \approx -11.6\%.

Because the adaptive system can be applied to a variety of thermal transfer processes, we expect it to prove useful in a wide range of real-world applications.

RESULTS AND DISCUSSION

Temperature control involves processes to detect changes in the temperature of a space and regulate the passage of energy into and out of this space to achieve a desirable temperature. Although temperature controls using HVAC (heating, ventilation, and air conditioning) facilities have been commonly applied to actively increase or decrease the temperature in order to meet a user-defined setpoint, the use of façade materials to envelop constructions that react by blocking or accelerating energy exchange in response to temperature or environmental variations is becoming more attractive given increasing energy concerns.2–8

Thermal exchange between an enclosed space and its ambient environment can take place in the forms of conduction, convection, and radiation.9,10 Although conduction and radiation prevail, convection usually plays a dominant role in the heat transfer of air in space through the movement of fluids to spread heat.10–12

As a result, a closed space can be effectively heated by blocking the fluid motions in a closed space, whereas air can freely flow continually in an open system. By contrast, with adaptive opening produced by a liquid form-gate, when the internal temperature is above the desired temperature as a user-defined setpoint, the porous matrix stabilizing the liquid through wetting is in a flaccid state, rendering a moderate affinity with the liquid filler. A mild pressure gradient led by the temperature difference between the internal and the external space is provided adequately to force the air to open the liquid-sealed pores. In contrast, when the internal temperature is lower than the desired temperature, the matrix becomes turgid, with stronger affinity to the liquid filler, and the openings are immediately sealed and require comparatively strong pressure to open in the lower range below the setpoint temperature. In this way, a single system capable of switching the passage of thermal transfer in response to temperature variation to a desired temperature can be achieved (Figures S1 and S2).

We quantitatively investigate temperature changes in the three systems under heating and cooling processes by controlling variables of energy input and start temperature (Figure 1B, Table S1). It is shown that during the heating process, with the same amount of thermal energy input, the temperature increase in the adaptive system is significantly lower than that in a closed system and approximate to that in an open system. During the cooling process, starting from the same temperature, the temperature in the adaptive system diminishes more slowly than that in an open system and tends to parallel that in a closed system. As the liquid openings in the adaptive system display different opening behaviors, when the temperature increases above the set temperature, the system autonomously operates the openings to allow convective fluid movement,
The feasibility of temperature control with a thermal adaptive system relies on the temperature responsiveness of the porous membrane and the stability and thermal adaptive gating performance of the gating liquid. We illustrate temperature-responsive controllability by using the wettability change of the thermo-responsive polymer (poly[N-isopropylacrylamide], or PNIPAAm), because its lower critical solution temperature (LCST), the response temperature of the polymer, also functions as the set temperature of the thermal adaptive system and is approximate to the optimal greenhouse temperature (~30°C), which is a practical example of a desired temperature. Hydrophobic or hydrophilic monomers (HBM or HLMs) are copolymerized with the PNIPAAm monomer to adjust LCST (Figure 2A, left). LCST of the copolymer linearly increases with increasing HLM molar ratio and linearly decreases with increasing HBM molar ratio because of the changes of the hydrogen bond donor content in copolymer (Figures 2A, right; Figure S4). However, the change in temperature will lead to a change in the wettability of the membrane, and the change in wettability will inevitably affect the stability of the gating liquid to the membrane, which presented a special design challenge to the system, as the stability of liquid gate cannot be sustained with single structure-based membrane materials. As shown in Figure 2B (left), the gating liquid has good adhesive properties (being close to the optimal straight line) and spreading behavior (being in 65° wetting envelope) on PNIPAAm when the temperature is below its LCST, because of the strong interaction between the aqueous functional liquid and the hydrophilic polymer molecules. But when above the LCST, the gating liquid shows poor wetting performance and a high contact angle, because the molecular polarity of PNIPAAm decreases, and the polar interaction between the liquid and solid phases weakens, which leads to the loss of gating liquid and diminished performance of the liquid gating system. Therefore, we propose dual-complex structure-based materials with a permanent hydrophilic part and a responsive wettability conversion part that can be prepared to achieve stable interfaces regardless of temperature changes (Figures 2B, right; Figure S5; Note S3). This dual-complex structure possesses both temperature- and wettability-responsive properties and low interfacial tension to the gating liquid; the temperature- and wettability-responsive properties cause variation of the adhesion force between the solid substrate and gating liquid below and above the LCST, which produces the change in air transmembrane pressures; the permanent hydrophilic part provides bistability of wettability and adhesion between the membranes.
porous membrane and gating liquid regardless of the variation of temperature, which ensures the working stability of the liquid gating system. This design allows a unique strategy to solve problems concerning wetting and adhesion of liquids on solids in a quick and cost-effective way.

It is worth mentioning that with the dynamic nature of liquid, thermal adaptive gating performance is variably affected by porous geometries, surface chemistries, pore sizes, and gating liquids. In order to optimize gating performance, we use a sandwich configuration design (Figure S6). Compared with the original dual-complex structure, which achieved both stable interfacial adhesion and thermal adaptive wettability to the gating liquid, the sandwich configuration with specific geometries and surface chemistries (Figure S7) further improves the functionality and stability of the TA system through continuous Au sputtering on the dual-complex structure. That is, the sandwich configuration with specific geometries and surface chemistries increases the active modification sites of thermo-responsive PNIPAAm, thus producing more sensitive responses while ensuring the stability of the gating liquid inside the porous membrane, thereby enlarging the threshold difference of the liquid gating substantial air transmembrane critical pressures ($P_{\text{Critical \ [air]}}$), the forces required to overcome the capillary pressure at the liquid-air interface under different temperatures (Figure 2C, left). As shown in Figure 2C (right), the air must deform the pore-filling gating liquid

Figure 2. Design, evaluation, and working principles of the TA system (A) Design and conformation transition of the thermo-responsive polymer responding to the temperature change (left). Controllable LCST of the thermo-responsive copolymer with different molar ratio of HLM and HBM incorporation (right). (B) Interfacial design of the TA system with bistability. Adhesion work analysis with the wetting envelope and the corridor for optimal adhesion, as well as the value for gating liquid on single (left) and dual-complex (right) structures. Inset diagrams depict the wetting behavior of the gating liquid on single and dual-complex structures. (C) Transmembrane critical pressures required for the air to force through TA systems with original dual-complex structure and sandwich configuration, below and above the LCST, respectively (left); insets show the geometry and chemical modification hypothesis of porous membrane cross-section. Schematic illustration of gating liquid reconfiguration for realizing intelligent control of air movement below and above the LCST (right). (D) Transmembrane critical pressures for air through TA systems with different pore sizes. Inset shows the ratio of pressure difference versus different membrane sizes. All error bars indicate SD. LCST, lower critical solution temperature of thermo-responsive polymer; HLM, hydrophilic monomer; HBM, hydrophobic monomer.
interface to enter the pores. Because of the stronger affinity for gating liquid to the thermo-responsive membrane below the LCST, a mild pressure difference ($\Delta P$) between internal and external spaces is higher than the air transmembrane critical pressure ($P_{AS}$), the TA system opens, cool air from outside enters the greenhouse, and ventilation starts. When the temperature is below the setpoint, and $\Delta P$ is lower than the air transmembrane critical pressure ($P_{BS}$), the TA system is sealed by gating liquid and thermally insulated. Conceptual simulations using COMSOL Multiphysics also show the air velocity and temperature change at open and closed states. (B) Transmembrane critical pressure required for air movement through the TA system at different temperatures. Error bars indicate SD (top). Cyclability of the TA system for air through temperatures alternating below and above the setpoint (bottom). (C) Optical image of a self-designed experimental greenhouse prototype for internal temperature monitoring. Scale bar: 1 cm. Energy saving of the TA system in a greenhouse application. 

**Figure 3**. Schematic of a TA system with temperature control used in a greenhouse application (A) Adaptive ventilation of a TA system-patched greenhouse. If the internal temperature is above the setpoint and the pressure difference ($\Delta P$) between internal and external space is higher than the air transmembrane critical pressure ($P_{AS}$), the TA system opens, cool air from outside enters the greenhouse, and ventilation starts. When the temperature is below the setpoint, and $\Delta P$ is lower than the air transmembrane critical pressure ($P_{BS}$), the TA system is sealed by gating liquid and thermally insulated. Conceptual simulations using COMSOL Multiphysics also show the air velocity and temperature change at open and closed states. (B) Transmembrane critical pressure required for air movement through the TA system at different temperatures. Error bars indicate SD (top). Cyclability of the TA system for air through temperatures alternating below and above the setpoint (bottom). (C) Optical image of a self-designed experimental greenhouse prototype for internal temperature monitoring. Scale bar: 1 cm. Energy saving of the TA system in a greenhouse application.

**Fluid temperature control in greenhouse application**

Because greenhouse structures are not open to the atmospheric environment, the temperature inside can be easily built up and maintained. However, ventilation that ensures the movement of air to regulate temperature and CO$_2$ concentration can be the key to a successful greenhouse, and proper ventilation techniques can save considerable energy by reducing heating and cooling expenses. Thus, a TA system that responds to temperature stimuli to open and close a liquid gate can be provided as an adaptive ventilation system for greenhouse applications, with energy-saving features (Figure 3A). When using a TA system patched on a greenhouse, a constant pressure difference ($\Delta P$) is applied between the internal and external spaces, which is higher than the air transmembrane critical pressure ($P_{AS}$) above the set temperature and lower than that ($P_{BS}$) below the set temperature. The cool air from outside would open the TA system patch and penetrate into the greenhouse, providing ventilation when the internal temperature is higher than the setpoint and creating a thermally insulated space by liquid-sealing the TA system patch when the temperature falls. Additionally, the motion of air can be quantitatively predicted by the change of $\Delta P$ instantaneously, and the maximum velocity of convective flow can reach a higher rate when the TA system opened (1.64 times than that of closed state), even with a small temperature difference. The modified greenhouse model displays thermal adaptive pressure control and stable performance (Figures 3B and 3C, Figures S9–S11). Thus, the TA system patch with adaptive
opening produced by a liquid filler can be obtained for the potential application of a smart greenhouse.

Additionally, in our systems, thermal energy relates to temperature $T$ only when the temperature gradient $\Delta T$ is small, so we can directly use the microcosmic internal energy equation to quantitatively compare the energy consumption of the three systems to maintain a set temperature (Figures 4A and 4B):

$$U(T, V) = nC_{V,m} T = C_{V,m} TV/V_m$$  (Equation 1)

Here, we assume air as a typical diatomic gas, and $C_{V,m}$ can be set at $5/2n$. $n$ denotes the amount of substance of the air. $V_m$ is the molar volume of air, which depends on its temperature and pressure. $R$ is the gas constant. The internal temperature detections of the three systems in real time reveal that the TA system with self-regulated open and closed thermal transfer passages consumes less energy to maintain the set temperature under a heating-cooling cycle than the other two systems (Figure S12).

Considering the compromises between the cost and time duration in maintaining optimal energy performance, we conduct a model from our experimental device to demonstrate that the optimal use-area ratio of the TA membrane to the area of the whole greenhouse membrane is 22.7% (Figure S13; Note S4). According to the theory of heat transfer, heat transfer efficiency relates to the effective contact area only when the total heat energy is constant, which indicates that the optimal use-area ratio can be generally suitable for any structural greenhouse. Therefore, to take a commercial dome-structured greenhouse as an example, analysis and simulations, including thermal, laminar fluid, and solar radiation of this greenhouse with the TA system patch or traditional insulation materials for 24 h, are conducted using COMSOL Multiphysics, as shown in Figure 4C (left) (Note S5). Convective mass transfer, heat transfer of conduction, and radiation occur in all three systems. The energy balance leads to

$$q_{\text{input}}S + Q_{\text{initial}} = q_{\text{conv}}TS\phi + q_{\text{cond}}th + q_{\text{rad}}S(1 - \phi),$$  (Equation 2)

where $q_{\text{input}}$, $q_{\text{conv}} = h_{\text{conv}}(T-T_a)$, $q_{\text{cond}} = \lambda(T-T_a)$, and $q_{\text{rad}} = \epsilon(G-\epsilon_b[T])$ are the heat flux of input, convection, conduction, and radiation, respectively, $h_{\text{conv}}$ and $\lambda$ are the convective and conductive heat transfer coefficients, which are different among the three systems. $T$ is transient temperature, and $T_a$ is ambient temperature. $S$ is the area of the membrane, $\phi$ is porosity, $t$ is time, $\epsilon$ is surface emissivity, $G$ is irradiation, and $\epsilon_b(T)$ is the blackbody hemispherical total emissive.

**Figure 4.** Energy consumption for the closed, open, and TA systems to maintain a set temperature in a greenhouse application and simulation of energy-saving mechanism (A and B) Internal temperature monitoring in real time and comparison of energy consumption for maintaining a set temperature of the closed, open, and TA systems during heating and cooling processes. (C) Thermal transfer simulations of typical dome structural greenhouse for 24 h. The left panel shows the temperature changes in traditional and TA system-patched greenhouses, the dome structure is exhibited as an inset. The right panel shows temperature distributions of the two greenhouses at 4:00, 12:00, and 20:00.
The amount of energy saved in the greenhouse with the TA patch for maintaining the set temperature is about 2.6 x 10^3 J per day (Note S3). The temperature distribution comparison at 4:00, 12:00, and 20:00 (Figure 4C, right) for the two greenhouses shows the energy-saving mechanism of the TA system-patched greenhouse (Table S1). At 12:00, when solar radiation is intense, the average temperature of the greenhouse with the TA patch is lower compared with the other model, and the temperature difference is especially obvious at the TA membrane, which is caused by its adaptive ventilation and indicates better performance in thermostat applications. The total energy saving could be evaluated by transient heat transfer simulation. As the 2020 estimate statistics show that the global greenhouse plantation area accounts for 6,550 km² (1,618,400 acres), and by adopting these data in our simulation, the result shows that the use of the thermal adaptive system could lead to an energy saving of 7.9 x 10^3 kJ/year (a percentage change of -11.6%).

CONCLUSIONS
To sum up, we have established an energy-saving thermal adaptive system with a bistable, interfacial, sandwich-structured design, which displays adjustable openings for thermal convection passages, allowing a shift between closed and open systems. Enabled by the sandwich configuration of thermo-responsive porous membranes with affinitive gating liquids, the proposed thermal adaptive system produces different opening behaviors for different temperature ranges around the setpoint and exhibits temperature control by minimizing the variations between the actual and desired temperatures. Additionally, by using the sandwich configuration of porous membranes with affinitive gating liquids, the TA system is demonstrated to be an energy-efficient greenhouse patch, achieving smart "breathing" to provide proper ventilation. We believe that this prototype of an energy-saving thermal adaptive mechanism can open new avenues for further extending the scope of using liquid-based adaptive systems in practice to achieve the goal of carbon neutrality.

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