Elastocaloric heat pump with specific cooling power of 20.9 Wg⁻¹, exploiting snap-through instability and strain-induced crystallization

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Abstract: Conventional refrigeration relies on hazardous agents, contributing to global warming. Soft, cheap, biodegradable solid-state elastocaloric cooling based on natural rubber offers an environmental friendly alternative. However, no such practical cooler has been developed, as conventional soft elastocaloric designs are not fast enough to ensure adiabaticity. In this work, we combine snap-through instability with strain-induced crystallization and achieve a sub-100 ms quasi-adiabatic cycling which is 30 times faster than previous design. Negligible heat exchange in expansion/contraction stages combined with the latent heat of phase transitions result in a giant elastocaloric crystallization effect. The rubber-based all-soft heat pump enables a specific cooling power of 20.9 W/g, a heat-flux of 256 mW/cm², a coefficient of performance of 4.7 and a single-stage temperature span between hot and cold reservoirs of 7.9 K (full adiabatic temperature change of rubber membrane exceeding 23 K). The pump permits a compact all-soft voltage-actuated setup, opening up the opportunity of a viable plug-in-ready cooling device.

Introduction

A substantial fraction of the world's cooling demand is provided by Vapor-compression refrigeration (VCR) systems. This outdated technology depends on hazardous gases and cooling fluids with high global warming potential and consumes large amounts of electricity often generated from fossil fuels^{1,2}. Even though more environment-friendly vapor-refrigerants are developed, such as hydrocarbons, hydrofluoric olefin and carbon dioxide, many restrictions still have to be balanced in applications, including long-term impact on the environment, cost,

efficiency, space, and safety²⁻⁵. This calls for the development of more efficient and greenhouse-gas-free systems, which are cheap enough to be employed on a global-scale.

Solid-state cooling based on different caloric effects (magneto-, electro-, baro- and elastocaloric) is a promising technology to fulfil these requirements and offer an environment friendly, efficient, and economic solution⁶⁻¹⁰. Mechanocaloric, in particular colossal barocaloric and elastocaloric materials, together with giant electrocaloric and magnetocaloric designs are expected to replace harmful fluids in refrigeration and heat pumping technologies¹⁰. The elastocaloric effect, in particular, has been identified as the most promising alternative by the US department of energy¹¹. However, the majority of devices developed so far raise a number of new environmental concerns. Magnetocaloric cooling is the most developed of all caloric solid-state technologies⁹. State of the art devices reach efficiencies competitive with VCR systems and are at the brink of market introduction^{6-8,10}. The materials used, especially the permanent magnets, contain large amounts of rare earth metals, which require high energy expenditure in production and leave behind considerable amounts of toxic waste⁶. Additionally, they are expensive and supply security is subject to considerable geopolitical risks⁶.

The electrocaloric (EC) effect is still in its infancy; furthermore, most EC materials contain lead, rendering them unsustainable. PVDF-based polymers and BaTiO₃ were identified as environmentally friendly alternatives, but only a few functioning devices have been reported to date⁶. Electrostatically actuated EC cooling devices based on PVDF¹² show high coefficient of performance (COP), the high cost of PVDF however hampers large scale market penetration. The colossal barocaloric effects in plastic crystals open up new possibilities with high entropy changes and an adiabatic temperature change ΔT of 50 K^{13,14}, but the required pressure

variations are hundreds of MPa, and a practical application is still far away. For elastocaloric devices, NiTi-based alloys are the most prominent active material. NiTi-based alloys exhibit a large elastocaloric effect with an isothermal entropy change ΔS of 35.1 J/(kg K), an largest ΔT of 40 K resulting from an austenite-martensite phase transformation^{15,16}. Several prototypes have been reported^{6,17}, including one using thin-walled Ni-Ti tubes under compression¹⁸ that reaches a maximum ΔT of 27 K at large strains, small-strain COP above 20 and a highest specific cooling power (SCP) of 18 W/g achieved by fast heat transfer and high operation frequency in a miniature-scale device¹⁹. However, the large forces required for operation pose a major engineering challenge; the stress required to drive NiTi SMAs is as high as 700 MPa²⁰ making scale-up difficult. Some of the NiTi SMAs demonstrate a maximum adiabatic temperature change as high as 31.5 K²¹, and COP in the range of 3.5-20, as well as practically unlimited lifetime in moderate-strain cycling compression¹⁸. The large-strain fatigue-life of such elastocaloric materials^{8,20,22}, typically a few thousand cycles⁷, may nonetheless be a limiting factor when large temperature spans and/or tensile cycling are required.

Current focus on SMAs overshadows a promising class of materials with exceptionally strong elastocaloric effect at room temperature: elastomers such as natural rubber (NR)^{6,12,23}. Contrary to most caloric materials, NR is soft, cheap and biodegradable, simultaneously solving some of the major engineering and sustainability issues of artificial cooling. The wide availability of NR, together with the low mechanical forces required for stretching, make it an ideal candidate for future large-scale, high-power cooling devices.

Constructing an elastomer heat pump that enables cooling is challenging, and attempts to build one are rare. The elastocaloric effect of NR was explored to build elastomer heat engines for classroom purposes early on²⁴⁻²⁶, with theoretical description following later^{27,28}. NASA patented a design for a manually operated device for use in space emergencies²⁹. A design based on uniaxial deformation of rubber stripes with a crankshaft was tested, but no cooling effect was achieved due to poor heat transfer and large frictional heating³⁰. More recently, a regenerative heat pump was developed³¹, which uses oscillatory stretching of a NR pipe with an oscillating fluid flow through it and an externally superimposed axial temperature gradient. The rubber is not adiabatic in this setup, as thermal contact with the fluid is permanent and the stretching rate is low.

Here we propose a heat pump design to solve these issues and demonstrate a functioning elastomer-based cooling system. It combines strain-induced crystallization (SIC)^{32,33} of NR with snap-through instability^{34,35}, resulting in sub-100 ms quasi-adiabatic actuation 30 times faster than in conventional setups. This produces what we call a giant elastocaloric crystallization (geCC) effect, which includes entropy-elastic and SIC contributions^{6,23}. In brief, stretching rubber aligns its randomly coiled molecular chains, lowering the number of possible conformations. For adiabatic deformation, such a decrease in conformational entropy S_{config} increases the thermal entropy S_{thermal} , i.e., heats the material. This process is reversible, and the initial state is recovered upon relaxation. Strong stretching also leads to a partial transformation of the NR molecules into an ordered crystallized phase accompanied by the release of latent heat. This phase transition, too, is reversible to a high degree²³. Of these two effects (schematically illustrated in Fig. 1a), the SIC-related heating is dominant, which yields a high

SCP that exceeds other approaches^{4,12,19,36-42} (see Fig. 1e and Supplementary Table 1). Using voltage-controlled elastomer actuation³⁵, we also open up a path towards a plug-in-ready all-soft heat pump.

Operational principle and setup

We develop a setup, based on balloon inflation, with almost equal biaxial stretch, inherently efficient heat transfer, and no frictional losses, far superior to uniaxial stretch designs. IR-measurements (Fig. 1b-c & Supplementary Video V1) verify the temperature increase of the NR during the inflation (state 2), the temperature equilibration with the surroundings (states 1&3), as well as the temperature decrease upon deflation (state 4)^{34,43}. Fig. 1d shows the operating principle of our geCC device, further details on the experimental setup are given in the Methods section “Experimental realization of the geCC heat pump” and Supplementary Fig. 1. The active material is a thin latex membrane mounted onto a pressure vessel by a clamp with a central circular aperture. In the first step (1→2) the membrane is stretched during fast adiabatic inflation into a balloon, which leads to an increase in temperature. In the second step (2→3) the membrane exchanges heat with the high temperature reservoir (HTR). The HTR consists of an aluminium cylinder with a concave spheroidal cavity that precisely fits the shape of the inflated balloon. We varied the maximum stretch of the membrane using a small (HTR_S) and a large (HTR_L) version of this reservoir. In the third (3→4) and fourth (4→1) step the membrane contracts adiabatically and thus cools down, followed by heat absorption from the low temperature reservoir (LTR). The LTR is an aluminium spherical

cap with a mass of 1.9 g. This operational cycle possesses several major advantages. First, nearly spherical geometry of the pressurized balloon ensures efficient heat transfer, as the internal overpressure intrinsically applies a contact force perpendicular to the surface of the heat sink. Second, friction and associated dissipation and heating are reduced to a minimum, because the contact between the membrane and the heat reservoirs remains static during the heat exchange. This, in conjunction with the small thickness and weight of the NR membrane, results in a SCP of 20.9 W/g, outperforming other elastocaloric cooling device (Fig. 1e and Supplementary Table 1). Third, to minimize the impact of parasitic heat exchange with the surroundings (to ensure adiabaticity), strain rates need to be high. Pressure-driven actuation of a rubber membrane realizes quasi-instant stretching (within ~100 ms, area strain rates of 16000 %/s) by exploiting the snap-through instability³⁵.

This mechanical snap-through instability is observed for elastomer balloons with low viscoelasticity and can be theoretically described by constitutive models with stiffening, for example the hyperelastic Gent model for rubber⁴⁴. We discuss the pressure-volume ($p-V$) diagram of one inflation-deflation cycle with volume constraints (as imposed by the LTR and HTR) schematically (Fig. 2a) and compare it with the experimental data (Fig. 2b). At the onset (A), pressure rises steeply, while volume change remains minimal. When the pressure reaches the value p_B (B), the snap-through instability causes a rapid expansion of the balloon to the limiting volume determined by the HTR (C). Decrease in internal overpressure (D) leads to a similarly swift jump (E-F) towards the initial size (determined by the LTR). The hysteresis in the $p-V$ diagram is to a large extent caused by the SIC^{23,33,45} (see Supplementary Note 2 and Supplementary Fig. 2). Due to different dynamics of crystallization and melting, the crystalline

fraction for a given strain is higher during contraction (schematically shown in Fig. 2c)^{32,33,45-47}. The stress is lower there, because the extended crystallized parts of the chains allows the remaining amorphous fraction to relax (illustrated in Fig. 2c). The area enclosed by the $p - V$ diagram represents the mechanical input energy, used in COP and SCP calculation (eq. (22)-(24) in Supplementary Note 3). Measurements yielded 0.09 J (HTR_S) and 0.31 J (HTR_L) per cycle (see Supplementary Fig. 3). Due to high crack growth resistance of the crystalline phase, SIC also improves membrane fatigue properties. Though cyclic operation in the SIC regime (pre-stretch > 200 %) allows for lifetimes of $\sim 10^7$ cycles, which fulfils the requirement for commercial applications⁶, our demonstrative device operates partly in the fully amorphous range, resulting in shorter lifetime ($\sim 10^3$ cycles, Supplementary Video V2). However, since SIC provides the main contribution to the cooling power, there is a large potential for increasing lifetime and enhancing device performance⁶. The temperature-entropy ($T - S$) diagram in Fig. 2d represents a reversed Otto cycle for the membrane. It contains a SIC phase change and highlights the thermal aspects of the elastomeric heat pump. In contrast to a Rankine cycle⁴⁸ used in the majority of steam turbines and refrigerators, the heat exchange here happens at constant stretch, not pressure (stress).

Thermodynamics of heat pump cycle with crystallization

In conventional elasticity of purely amorphous rubber, the entropy (density) of the elastomer additively separates into a purely configurational term S_{config} , which depends on stretch λ , and a purely temperature-dependent term S_{thermal} :

$$S = S_{\text{config}}(\lambda) + S_{\text{thermal}}(T) \quad (1)$$

In the presence of SIC the expression for the entropy is more complicated (see eq. (1) in the Supplementary Note 1)

$$S = -\chi \frac{U_{\text{ac}}}{T_{\text{c},0}} + S_{\text{ch}}[\lambda, \chi] + c \ln \frac{T}{T_s} \quad (2)$$

The first term reflects the decrease in configurational entropy due to crystallization of individual structural units, where χ is the crystalline fraction, U_{ac} is the latent heat of crystallization per unit volume and $T_{\text{c},0}$ is the unstretched crystallization temperature. The second term describes the configurational entropy of the partially crystallized chains (roughly equivalent to S_{config} in eq. (1) and the third term gives the thermal contribution, c being the volumetric heat capacity, and T_s some universal reference temperature. To obtain the adiabatic stretch-temperature relation, one has to compute the equilibrium entropy $S_{\text{eq}}(T, \lambda)$ and free energy $F_{\text{eq}}(T, \lambda)$ by substituting $\chi = \chi_{\text{eq}}(T, \lambda)$ from equilibrium condition (see eqs. (3)-(6) in Supplementary Note 1 for the detailed derivation).

$$cdT = U_{\text{ac}} d\chi + s[T, \lambda, \chi_{\text{eq}}(T, \lambda)] d\lambda \quad (3)$$

Here $s = \frac{\partial F_{\text{eq}}(T, \lambda)}{\partial \lambda}$ is the (equilibrium nominal, 1D) stress for a given temperature and stretch. Our thermodynamic cycle consists of two adiabats (expansion & contraction) and two iso-strain curves, where the heat exchange with LTR & HTR takes place.

In the adiabatic processes AC and DF ($dS = 0$, see Fig. 2d) the change in total configurational entropy (1st two terms on the r.h.s. in eq. (2)) is balanced by the opposite change in thermal entropy. Expansion reduces and contraction increases the configurational entropy of

the chains. Additionally, an entropy change of structural units upon SIC/amorphization is released/absorbed as latent heat, amplifying the change in membrane temperature (Fig. 3a-d & Supplementary Video V3). This is quantified by eq. (3), reflecting the adiabatic energy balance, because the internal energy is $U = cT - \chi U_{ac}$. The simplicity of the eq. (3) is misleading, as it implies the knowledge of the function $\chi = \chi_{eq}(T, \lambda)$, but both stretch and crystallization increase the temperature. The adiabatic temperature change depends on the maximum stretch defined by the HTR size (see end of the Supplementary Note 2, Methods section “Infrared temperature measurements of NR membranes”, Fig. 3e, and Supplementary Note 9); as expected, the cooling of the LTR is larger and faster for HTR_L with larger stretch (Fig. 2e).

During the heat exchanges CD and FA (Fig. 2d), the stretch λ remains constant ($d\lambda = 0$); therefore the stress s performs no work ($sd\lambda = 0$), and the energy balance similar to eq. (3) reads: $TdS = dU = cdT - U_{ac}d\chi$. As χ_{eq} decreases with T , the r.h.s. here increases with T . Thus, the total entropy also increases, and the slope of both iso-stretch legs in Fig. 2d is positive. The fully amorphous FA leg is steeper than segment CD (Fig. 2d) on the HTR (thin line with χ is shown for comparison), because changes in χ are opposite to changes in T and S there. During cooling χ increases, and latent heat diminishes the temperature drop. Highest crystallinity in a cycle is reached after cooling on the HTR, and the adiabatic temperature drop DF is larger than the AC increase. The thermal entropy always follows the temperature changes. The 1st entropy term in eq. (2) also increases with T , due to a decrease in $\chi_{eq}(T)$ for $\lambda = const$. The behaviour of the 2nd, chain term can be understood from the equilibrium condition (eq. 2 in Supplementary Note 1). It turns out, that S_{ch} increases with χ (for a fixed λ), while the total S_{config} (sum of the 1st and 2nd terms) decreases with it.

Figures of merit in a multi-cycle operation

In our setup, the HTR remains at room temperature, as its heat capacity is more than 100 times larger than that of the LTR and over 1000 times larger than that of elastomer membrane. We measure temperature curves of the LTR at different cycle frequencies, maximum stretches and membrane thicknesses. The heat pump characteristics COP and SCP are then determined from the time constants and the final temperatures of these curves in relation to the ideal, intrinsic membrane temperature changes (see Supplementary Note 3, particularly the final result in eqs. (22)-(24)). For quantification, we use the onset of the temperature curve, because later (for $\Delta T < 0$), parasitic heat exchange with the surroundings diminishes measured values. However, we can estimate the impact of parasitic heat, as shown in Fig. 2f (see also Supplementary Fig. 4). The results for different parameters are summarized in Table 1.

The highest COP of 4.7 is achieved for a 140 μm membrane with HTRs at 0.5 Hz. Larger frequency of 0.9 Hz moderately reduces COP, almost doubling the SCP to 10 W/g, while ΔT has its maximum HTRs value of 4.6 K. HTRs operation is highly efficient, because it limits the membrane expansion at the endpoint of the snap-through instability. Larger HTR_L increases the SCP and ΔT , at the cost of reducing COP, presumably because the crystallinity saturates at high stretches²³. Here, 0.9 Hz produces an SCP of 15.9 W/g and a ΔT of 6.8 K. Maximum SCP of 20.9 W/g is obtained at 1.1 Hz, for a slightly modified setup (with 0.3 s long pressure pulses of 6 bar).

Thicker 180 μm membrane produces the highest ΔT of 7.9 K and heat-flux of

256 mW/cm² (see Fig. 2f, Supplementary Fig. 4a,b and the discussion at the end of Supplementary Note 3); this flux value is much higher than reported for other solid-state cooling devices^{4,12}. The corresponding total flux, with the LTR area from the Supplementary Note 9 is 877 mW. In our setup, the LTR only covers ~45 % of the aperture area, leaving considerable potential for increasing heat transport without altering mechanical input energy. Simulations indicate a possible improvement of heat pump performance by up to a factor of 2 (see Supplementary Fig. 5 and Supplementary Note 4). The operational longevity should further increase using working membranes from high-quality rubbers, custom pre-cast into an almost spherical initial shape, operating in a narrower stretch range. This would reduce the harmful influences of stretch inhomogeneity, amorphous (non-SIC) stretch region, and defects, present in our commercial off-the-shelf samples (Supplementary Fig. 6). These factors decrease cycling lifetime, as discussed in the Supplementary Note 6 and Supplementary Fig. 7. Furthermore, the full inflation-deflation adiabatic temperature change of our membrane working body exceeds 23 K (see Fig. 3ac and Supplementary Video V3). Therefore, the LTR temperature difference of 7.9 K reached in our setup can potentially be more than doubled upon outlined improvements and optimization.

Our lab-scale demonstrator setup is designed to determine all relevant performance parameters. A feasible practical device remains conceptually similar: it requires an LTR, an HTR, a membrane, and a pressure vessel with a volume 5 to 10 times larger than the volume V_b of the inflated balloon on the HTR. For practical cooling applications the LTR can be connected with a regenerative fluidic heat exchanger. The pressure transducer can be a conventional linear or rotational piston transducer, a voltage-controlled elastomer actuator

(discussed in the next section), or any other transducer system capable of providing a volume change $\sim V_b$ and associated small pressure difference Δp between the snap-through and snap-back of a few kPa (only $\sim 20\%$ of the maximum pressure, see Fig. 2b). This is schematically shown in the Supplementary Fig. 8. Such a narrow pressure range opens up the possibility to operate a solid-state cooling system made from cheap, soft, biodegradable materials without the use of compressed air.

Voltage-controlled cycling

We demonstrate this approach by building a proof-of-concept all-soft electrical driving system using dielectric elastomer actuators (DEAs, schematic in Fig. 4a). Such a compact, cheap and all-soft plug-in-ready device directly converts electrical energy into a low-noise pneumatic actuation.

A DEA is a soft capacitor, made of a deformable dielectric material, sandwiched between two compliant electrodes⁴⁹. When a voltage is applied to the electrodes, the resulting Maxwell stress thins down the incompressible elastomer and consequently increases its area. We couple the DEA and the cooler membrane via a common sealed pressure vessel. Initial constant offset pressure inflates both the cooler membrane and the DEA at zero voltage. The overall amount of gas in the system remains constant. When voltage is applied to the DEA, its volume increases, reducing the volume of the elastomer balloon, until the snap-back is triggered. A decrease in voltage reverses this process (Fig. 4a). A high-voltage sine-wave signal allows for continuous device operation (Figs. 4b-c). The desired volume change can be adjusted by varying the

voltage amplitude and the number of DEAs. The voltage-induced pressure variations (Maxwell stress) should match the snap-through and snap-back pressure difference of the NR membrane. They can be modified changing the number of active layers in each individual (stacked) DEA (see Supplementary Fig. 9). We demonstrate actuation and successful cooling (Fig. 4d, Supplementary Fig. 10 & Supplementary Video V4) with a 140 μm and a 180 μm membrane for a slightly adapted setup geometry and frequencies of 1-3 Hz and 1-2 Hz respectively. Remarkably, a DEA achieves even higher actuating frequencies than the design using high-pressure pulses. The COP value in this proof-of-principle demonstration is about 0.1, due to low efficiency of electro-mechanical energy conversion. This performance metric can be further improved with more optimized transducer systems (see discussion at the end of the Supplementary Note 5).

Conclusion

We have demonstrated the capabilities of natural rubber in cooling applications by constructing a prototype with outstanding cooling power (20.9 W/g, and heat-flux of 256 mW/cm²), and good efficiency with a coefficient of performance of 4.7. Controlled use of SIC results in a geCC effect enabling devices that are stable over 10³ inflation-deflation cycles. Further performance and stability increase is feasible with design improvements and by employing low-hysteresis and low-fatigue rubbers. Optimization of elastomer materials (i.e. their SIC properties) promises to unlock the full potential of this technology. Due to the large stretches inherent to our elastomeric design, the necessary forces and pressures are small. This

allows compact and lightweight setups for mobile applications, robotics, aircraft- and even spacecraft-related tasks. The demonstrated performance numbers put mass-market applications such as room-temperature refrigeration and air conditioning within reach of the suggested framework.

Methods

Infrared temperature measurements of NR membranes

Infrared temperature measurements were performed using a FLIR A325sc thermal camera (FLIR Systems, Wilsonville, USA) for real-time analysis. The camera was enclosed with a sealed housing, which allowed cooling with cold nitrogen gas to slightly below room temperature. This prevents IR radiation from the warm camera and its reflection by the NR membrane back into the camera. The inflated membrane was shielded by Styrofoam walls, eliminating IR-reflections from various nearby thermal sources. In addition to the parasitic IR reflections, NR is semi-transparent in the IR⁵⁰. It is thus impossible to get consistent IR readings from the inflated balloon (where the membrane is thin) due to thermal contribution from the background (see Fig. 3a, and the initial inflation frames in Supplementary Video V3). For this reason, the temperature changes were monitored during deflation. Inflated balloons were thermalized with the surrounding (Fig. 3b) and adiabatically contracted within ~100 ms (Fig. 3c, see also Fig. 2b). For reliable measurements, thick enough membranes were used (420 μm), in an unstretched state it transmits below 7 % in the IR (thicker membranes yield similar temperatures). Membrane thickness does not affect the temperature changes for a given

balloon volume V_b , as both the membrane volume V and the balloon pressure p (see eq. 8 in Supplementary Note 1) are proportional to it. Temperature differences were referenced to the IR temperature of the unstretched patch of the same membrane. Supplementary Video V3 (3.75 frames/s, or 267 ms/frame) evidences the abrupt temperature change upon deflation (Figs. 3b-c). This change is larger in the central area, which comes in contact with the LTR (and HTR) and depends on the balloon volume (Fig. 3e). These contact thermal reservoirs are absent in this case; thus, the membrane thermalizes much slower than in the regular cyclic refrigerating experiments.

Experimental realization of the geCC heat pump

For a comprehensive description and a detailed schematic of the experimental setup see Supplementary Fig. 1. Our geCC heat pump consists of a pressure vessel connected to two pressure reservoirs p_{high} and p_{low} via externally triggered valves (Supplementary Fig. 1a). The pressure vessel has an opening where the elastomer membrane is fixed with a clamp, so that the pressure p inside the pressure vessel is equal to the balloon pressure. The LTR was inserted from beneath (Supplementary Fig. 1b). We measured the temperature with a type-K thermocouple fixed at the bottom of the LTR (Supplementary Fig. 1c). In order to expand the membrane, the inlet valve was opened ($p = p_{\text{high}}$) while the outlet valve stayed closed. When the membrane reached its maximum volume, the inlet valve was closed and, after a specified equilibration time, the outlet valve was opened ($p = p_{\text{low}}$) to initiate contraction. The experiment was controlled by a custom LabVIEW program.

p-V measurements

We measured the common pressure p inside the pressure vessel and the balloon using a Jumo dTrans p30 pressure sensor (JUMO, Fulda, Germany). High-speed determination of the volume required an indirect approach. The pressure vessel was connected to an external volume of 300 l in an airtight fashion with the NR membrane facing inside (Supplementary Fig. 1a). The expansion and contraction of the membrane causes a pressure change Δp_{ext} within the external volume V_0 , which we measured and converted to the change in the balloon volume ΔV_b applying the ideal gas equation. The large size of the volume reservoir (300 L) in Supplementary Fig. 1 was chosen to keep the pressure increase at the low end of the sensor range. In this way, the change in the external pressure can be neglected in the key elastic eq. 8 in Supplementary Note 1 and the associated equations. The sensor was connected to the reservoir via a 1100 mm long tube with 3 mm diameter, in order to damp resonant oscillations of the reservoir body.

We assumed an adiabatic change of state and used the adiabatic index (heat capacity ratio) of an ideal diatomic gas $\kappa = 1.4$.

$$\Delta V_b = V_0 \left[1 - \left(\frac{p_0}{p_0 + \Delta p_{\text{ext}}(t)} \right)^{1/\kappa} \right] \quad (4)$$

Here, p_0 is the atmosphere pressure and t is time. The mechanical input energy per cycle W_{in} follows from the integral work of the varying pressure during the inflation (p_{infl}) and deflation (p_{defl}) (listed in the Supplementary Note 9):

$$W_{\text{in}} = \int_0^{V_{\text{max}}} p_{\text{infl}} dV_b - \int_0^{V_{\text{max}}} p_{\text{defl}} dV_b \quad (5)$$

The maximum volume V_{max} of the inflated membrane used as upper integration limit in eq. (5)

was determined separately by the displacement of a water column, which yields more accurate results. The result yielded 115 cm³ (HTR_S) and 200 cm³ (HTR_L). The maximum volumes, measured with the indirect pressure conversion method using eq. (4), were 5-10 % lower than with the water column method. Therefore, all measured values were multiplied by a linear correction factor in order to normalize them to the accurate maximum volume.

DEA setup and assembly

The actuator setup is schematically illustrated in Supplementary Fig. 9a. Up to five DEAs were supported by a cuboid acrylic mount. The DEAs were fixed on the mount with clamps, as shown in Supplementary Figs. 9b-c.

Each of the DEAs driving the heat pump consisted of a layered stack of VHB 4905-F (3M, Saint Paul, USA) and carbon grease, shown in Supplementary Fig. 9d. One actuator layer consists of two sandwiched VHB tapes (each with thickness 0.5 mm, this improves dielectric breakdown strength and reliability as the defect overlap probability is low). Prior to DEA assembly, each VHB double-layer was biaxially pre-stretched by a factor of 1.8 (areal stretch 1.8×1.8). Next, the adhesive pre-stretched tape was firmly pressed against the rear side of the actuator clamp. A 2 mm wide copper tape (100 μm thick) was attached onto the membrane at the rear side of the clamp. The membrane was coated on both sides with a thin layer of carbon grease (also contacting the copper strip) (Supplementary Fig. 9e right). The copper strips were attached alternately on opposing sides (Supplementary Fig. 9d). All conductors of one side were connected to the same pole of the voltage source in order to subject every VHB-layer to an electric field. In this work, three- and four-layer actuators were used.

For the carbon grease, Black Pearls 2000 Carbon Black (CABOT, Boston, USA) was mixed with Elbesil 50 silicon oil (Quax GmbH, Oetzberg, Germany) in a weight ratio of 1:15 using a planetary mixer for 10 min at 2000 rpm with 5 steel balls (~5 mm diameter) added and another 20 min at 2000 rpm without steel balls. Blending was interrupted in ten-minute intervals to allow cooling of the mixture for 10 min.

DEA operation

To reach a comparable degree of inflation for both the actuator and the NR membrane, the elastic response of both elements at a given common pressure p has to be similar. For comparable sizes and geometries used, the stiffness of a newly assembled DEA was found to be slightly higher than that of the NR balloon. We used two methods to adjust the DEA elasticity to better match the membrane response: One is to let the DEA rest for several hours, allowing the silicon oil of the carbon grease electrodes to diffuse into the VHB layers acting as a softener. The other is to initially inflate the DEA to volumes larger than the typical operating volumes for a few times, causing softening of the membranes due to Mullins effect. We applied an offset pressure of 5500-7500 Pa for operation and electrically actuated the DEA system with a high-voltage sine-wave signal (TREK 610D HV AMPLIFIER) at an amplitude of up to 3700 V and frequencies between 1-3 Hz (see Supplementary Video V4).

Reference

- 1 The Future of Cooling. (OECD/IEA, 2018).
- 2 Goetzler, W., Zogg, R., Young, J. & Johnson, C. Alternatives to vapor-compression HVAC technology. *ASHRAE Journal* **56**, 12 (2014).
- 3 Wang, R. *et al.* Torsional refrigeration by twisted, coiled, and supercoiled fibers. *Science* **366**, 216-221, doi:10.1126/science.aax6182 (2019).
- 4 Wang, Y. *et al.* A high-performance solid-state electrocaloric cooling system. *Science* **370**, 129-133, doi:10.1126/science.aba2648 (2020).
- 5 Kasaeian, A. *et al.* Applications of eco-friendly refrigerants and nanorefrigerants: A review. *Renewable and Sustainable Energy Reviews* **96**, 91-99, doi:<https://doi.org/10.1016/j.rser.2018.07.033> (2018).
- 6 Xie, Z. J., Sebal, G. & Guyomar, D. Comparison of elastocaloric effect of natural rubber with other caloric effects on different-scale cooling application cases. *Appl. Therm. Eng.* **111**, 914-926, doi:10.1016/j.applthermaleng.2016.09.164 (2017).
- 7 Imran, M. & Zhang, X. Recent developments on the cyclic stability in elastocaloric materials. *Materials & Design* **195**, 109030, doi:<https://doi.org/10.1016/j.matdes.2020.109030> (2020).
- 8 Greco, A., Aprea, C., Maiorino, A. & Masselli, C. A review of the state of the art of solid-state caloric cooling processes at room-temperature before 2019. *International Journal of Refrigeration* **106**, 66-88, doi:<https://doi.org/10.1016/j.ijrefrig.2019.06.034> (2019).
- 9 Kitanovski, A., Plaznik, U., Tomc, U. & Poredoš, A. Present and future caloric refrigeration and heat-pump technologies. *International Journal of Refrigeration* **57**, 288-298, doi:<https://doi.org/10.1016/j.ijrefrig.2015.06.008> (2015).
- 10 Mañosa, L. & Planes, A. Solid-state cooling by stress: A perspective. *Applied Physics Letters* **116**, 050501, doi:10.1063/1.5140555 (2020).
- 11 Goetzler, W., Zogg, R., Young, J. & Johnson, C. Energy savings potential and RD&D opportunities for non-vapor-compression HVAC technologies. *Navigant Consulting Inc., prepared for US Department of Energy*, 199 (2014).
- 12 Ma, R. *et al.* Highly efficient electrocaloric cooling with electrostatic actuation. *Science* **357**, 1130-1134 (2017).
- 13 Li, B. *et al.* Colossal barocaloric effects in plastic crystals. *Nature* **567**, 506-510, doi:10.1038/s41586-019-1042-5 (2019).
- 14 Carvalho, A. M. G., Imamura, W., Usuda, E. O. & Bom, N. M. Giant room-temperature barocaloric effects in PDMS rubber at low pressures. *Eur. Polym. J.* **99**, 212-221, doi:10.1016/j.eurpolymj.2017.12.007 (2018).
- 15 Tušek, J., Engelbrecht, K., Mikkelsen, L. P. & Pryds, N. Elastocaloric effect of Ni-Ti wire for application in a cooling device. *J. Appl. Phys.* **117**, 124901 (2015).
- 16 Pieczyska, E., Gadaj, S., Nowacki, W. & Tobushi, H. Phase-transformation fronts evolution for stress- and strain-controlled tension tests in TiNi shape memory alloy. *Experimental Mechanics* **46**, 531-542 (2006).
- 17 Frenzel, J., Eggeler, G., Quandt, E., Seelecke, S. & Kohl, M. High-performance elastocaloric materials for the engineering of bulk-and micro-cooling devices. *MRS Bull.* **43**, 280-284 (2018).

- 18 Porenta, L. *et al.* Thin-walled Ni-Ti tubes under compression: ideal candidates for efficient and fatigue-resistant elastocaloric cooling. *Applied Materials Today* **20**, 100712, doi:<https://doi.org/10.1016/j.apmt.2020.100712> (2020).
- 19 Bruederlin, F. *et al.* Elastocaloric Cooling on the Miniature Scale: A Review on Materials and Device Engineering. *Energy Technology* **6**, 1588-1604, doi:10.1002/ente.201800137 (2018).
- 20 Engelbrecht, K. Future prospects for elastocaloric devices. *Journal of Physics: Energy* **1**, 021001, doi:10.1088/2515-7655/ab1573 (2019).
- 21 Cong, D. *et al.* Colossal Elastocaloric Effect in Ferroelastic Ni-Mn-Ti Alloys. *Physical Review Letters* **122**, 255703, doi:10.1103/PhysRevLett.122.255703 (2019).
- 22 Kirsch, S.-M. *et al.* NiTi-Based Elastocaloric Cooling on the Macroscale: From Basic Concepts to Realization. *Energy Technology* **6**, 1567-1587, doi:10.1002/ente.201800152 (2018).
- 23 Le Cam, J. B. Energy storage due to strain-induced crystallization in natural rubber: The physical origin of the mechanical hysteresis. *Polymer* **127**, 166-173, doi:10.1016/j.polymer.2017.08.059 (2017).
- 24 Wiegand, W. & Snyder, J. The rubber pendulum, the Joule effect, and the dynamic stress-strain curve. *Rubber Chem. Technol.* **8**, 151-173 (1935).
- 25 Archibald, P. B. quoted in Stong, CL “The Amateur Scientist: Some Delightful Engines Driven by the Heating of Rubber Bands.”. *Sci. Am.* **224**, 118-122 (1971).
- 26 Lyon, R. E., Wang, D., Farris, R. & MacKnight, W. Polyurethane-urea elastomers as working substances in rubber heat engines. *J. Appl. Polym. Sci.* **29**, 2857-2872 (1984).
- 27 Mullen, J., Look, G. W. & Konkell, J. Thermodynamics of a simple rubber-band heat engine. *Am. J. Phys.* **43**, 349-353 (1975).
- 28 Farris, R. J. Rubber heat engines, analyses and theory. *Polymer Engineering & Science* **17**, 737-744 (1977).
- 29 Hutchinson, W. D. Manually operated elastomer heat pump. Report No. NPO-10677, 2 (NASA, USA, 1970).
- 30 Gerlach, D. W. in *ASME 2009 International Mechanical Engineering Congress and Exposition*. 289-293 (American Society of Mechanical Engineers).
- 31 Sebal, G., Komiya, A., Jay, J., Coativy, G. & Lebrun, L. Regenerative cooling using elastocaloric rubber: Analytical model and experiments. *J. Appl. Phys.* **127**, doi:10.1063/1.5132361 (2020).
- 32 Huneau, B. Strain-Induced Crystallization of Natural Rubber: A Review of X-Ray Diffraction Investigations. *Rubber Chem. Technol.* **84**, 425-452, doi:10.5254/1.3601131 (2011).
- 33 Le Cam, J. B. Strain-induced crystallization in rubber: A new measurement technique. *Strain* **54**, e12256, doi:ARTN e12256, 10.1111/str.12256 (2018).
- 34 Keplinger, C., Li, T. F., Baumgartner, R., Suo, Z. G. & Bauer, S. Harnessing snap-through instability in soft dielectrics to achieve giant voltage-triggered deformation. *Soft Matter* **8**, 285-288, doi:10.1039/c1sm06736b (2012).
- 35 Baumgartner, R. *et al.* A Lesson from Plants: High-Speed Soft Robotic Actuators. *Adv. Sci.* **7**, 1903391, doi:ARTN 1903391, 10.1002/advs.201903391 (2020).
- 36 Jacobs, S. *et al.* The performance of a large-scale rotary magnetic refrigerator. *International journal of refrigeration* **37**, 84-91 (2014).
- 37 Clot, P. *et al.* A magnet-based device for active magnetic regenerative refrigeration. *IEEE Trans. Magn.* **39**, 3349-3351 (2003).
- 38 Tura, A. & Rowe, A. Permanent magnet magnetic refrigerator design and experimental characterization. *International Journal of Refrigeration* **34**, 628-639 (2011).

- 39 Defay, E. *et al.* Enhanced electrocaloric efficiency via energy recovery. *Nature communications* **9**, 1827 (2018).
- 40 Bruederlin, F., Ossmer, H., Wendler, F., Miyazaki, S. & Kohl, M. SMA foil-based elastocaloric cooling: from material behavior to device engineering. *J. Phys. D: Appl. Phys.* **50**, 424003 (2017).
- 41 Tušek, J. *et al.* A regenerative elastocaloric heat pump. *Nature Energy* **1**, 16134 (2016).
- 42 Ossmer, H. *et al.* Energy-efficient miniature-scale heat pumping based on shape memory alloys. *Smart Materials and Structures* **25**, 085037, doi:10.1088/0964-1726/25/8/085037 (2016).
- 43 Merritt, D. R. & Weinhaus, F. The Pressure Curve for a Rubber Balloon. *Am. J. Phys.* **46**, 976-977, doi:10.1119/1.11486 (1978).
- 44 Gent, A. N. A new constitutive relation for rubber. *Rubber Chem. Technol.* **69**, 59-61, doi:10.5254/1.3538357 (1996).
- 45 Khiêm, V. N. & Itskov, M. Analytical network-averaging of the tube model: Strain-induced crystallization in natural rubber. *J. Mech. Phys. Solids* **116**, 350-369, doi:10.1016/j.jmps.2018.04.003 (2018).
- 46 Gros, A., Verron, E. & Huneau, B. A physically-based model for strain-induced crystallization in natural rubber. Part II: Derivation of the mechanical model. *J. Mech. Phys. Solids* **125**, 255-275, doi:10.1016/j.jmps.2018.12.014 (2019).
- 47 Plagge, J. & Kluppel, M. A Theory Relating Crystal Size, Mechanical Response, and Degree of Crystallization in Strained Natural Rubber. *Macromolecules* **51**, 3711-3721, doi:10.1021/acs.macromol.8b00177 (2018).
- 48 Moran, M. J., Shapiro, H. N., Boettner, D. D. & Bailey, M. B. *Fundamentals of engineering thermodynamics*. 9th edn, (Wiley, 2018).
- 49 Suo, Z. G. Theory of Dielectric Elastomers. *Acta Mechanica Solida Sinica* **23**, 549-578 (2010).
- 50 Williams, D. & Dale, B. Further Studies of the Infrared Absorption of Rubber. *Rubber Chem. Technol.* **18**, 10-19, doi:10.5254/1.3543183 (1945).

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Figure and legends

Figure 1. Illustration of the geCC effect in elastomers, heat pump design principle and performance comparison. (a) Ordering of coil-like molecular chains and strain induced crystallization (black rectangles) in an adiabatic stretching (1-2) and contraction (3-4) leads to release/absorption of heat and reversible heating (red) and cooling (blue). The direction of changes in entropy S and temperature T is indicated by arrows behind the corresponding symbols. States of the system are the same in a-d, and the change in size is indicated by black arrows in a and d. (b-c) IR-measurements of rapid membrane inflation and deflation show the deformation induced temperature changes. After both deformation steps, the membrane temperature is allowed to equilibrate with the surroundings, and is poorly visible. It is indicated by the dashed lines in sub-panels 1 and 3. Scale bar is 1 cm. (d) To utilize geCC effect in a heat pump, a cooling target (LTR) is placed beneath the membrane. The HTR further accelerates

heat exchange with the surroundings. **(e)** The SCP of our device surpasses that of other solid-state cooling systems^{4,12,19,36-42}. Individual dots refer to different setups, grouped into bars for various classes (See also Supplementary Table 1).

Figure 2. Elastic and thermal properties of a NR membrane and resulting cooling

performance of the heat pump. (a-b) Theoretical and measured p - V diagram of one actuation

cycle with 140 μm membrane and HTR_s. BC and EF indicate the adiabatic snap-through and

snap-back (initiated at the corresponding pressures p_B and p_E) with the measured snapping

times (the whole deflation leg DEF lasts 80 ms), while CD and FA represent the heat exchange

with the HTR and LTR (inset). The letters correspond to those used in the T - S diagram of the

cycle in d, and the hatched area in a and d corresponds to the work performed in a cycle. **(c)**

Schematic illustration of crystallization and hysteresis in the stress-stretch relation for NR. The

sample starts from the unstretched state (i) with fully amorphous coiled chain conformations towards a state of maximum crystallinity (around 25 %) (iii), where an appreciable fraction of chains is aligned along the stretch direction (in 1D case), as schematically indicated. For a given stretch, the crystallinity during expansion (ii) is always lower than for relaxation (iv), where it vanishes at lower stretch (v), resulting in a different elastic response for both stages.

(d) T - S diagram of the refrigerating Otto-cycle with phase change. The idealized cycle (blue tetragon) is constrained by the iso-strain $T(S)$ curves of the membrane (green), and adiabats. Thicker lines between the points ii and v (see panel c) indicate parts of the cycle where crystallinity is present. T_H and T_L indicate the temperature of the HTR and LTR, respectively. S_{defl} and S_{infl} denote the constant entropies during the adiabatic deflation and inflation of the membrane. **(e)** Measured multi-cycle cooling curves of the LTR (purple and blue lines) with corresponding fits by the exponential eq. (12) in the Supplementary Note 3 (black lines) for the small (S) as well as large (L) HTR with 140 μm membrane at 1.1 Hz. The inset shows individual cycles at the initial stage of cooling for the small and large HTR. The shape of the used HTR is indicated next to the cooling curve. **(f)** Estimation of the parasitic heat flow for the LTR (green line), which leads to a deviation of the measured ideal, intrinsic heat flow (averaged over cycles, blue line) from the effective heat flow (purple line). Here we used a 180 μm membrane on HTR_L at 1.1 Hz.

Figure 3. Adiabatic snap-back cooling. (a) The balloon immediately after the fast inflation to about 200 cm³. IR readings underestimate the quasi-adiabatic temperature increase, because the membrane is thin and semi-transparent. The dashed oval indicates the background and dashed circles, the initial relaxed membrane and the part of it which comes in contact with the LTR (see panel c). The bottom part of the balloon with the clamp setup can be seen in this region. (b) Inflated membrane, thermalized with the surrounding, right before the fast deflation. (c) Fully relaxed membrane immediately after the fast, adiabatic snap-back contraction. The time difference between the adjacent frames b, and c, is 267 ms. The membrane is colder in the area, which lies on the LTR in cycling experiments, and even colder in the very centre (see panel e). (d) Contracted membrane after the thermal equilibration with the surrounding, which proceeds much slower in these IR measurements, as there is no LTR or HTR present. All frames are from Supplementary Video V3, temperature colour coding and scale is common for a-d. Scale bar: 1 cm. (e) Intrinsic temperature changes of the membrane upon deflation, measured with the IR camera, as described in the text. The measurements were performed for the expansion volumes close to the balloons on HTR_S and HTR_L. Magenta diamonds - the *average* temperature change ΔT_{av} for the *whole* membrane, used for crystallinity estimations in eq. (10) in Supplementary Note 1. Green circles - the changes for the part of membrane in contact with

the LTR (see panel c), ΔT_{mem} , used for the heat transfer calculations in eq. (11)-(26) in Supplementary Note 3. The ΔT_{av} and ΔT_{mem} values used in calculations were obtained by extrapolation for the volumes 115 and 200 cm³ in both cases. Blue triangles – the maximum observed temperature change in the very centre of the membrane. The full inflation-deflation adiabatic temperature change exceeds 23 K.

Figure 4. Actuator-cooler design, characteristics and thermal properties. (a) Schematic illustration of the DEA-actuated cooler design and functional principle. The magenta arrows indicate the exchange of gas between both balloons and the pressure vessel. The upper panel corresponds to a snap-through at low DEA voltage, and the lower panel to snap-back near the maximum applied DEA voltage, as indicated in b. (b-c) Applied sinusoidal voltage U , measured current I , and the pressure, common for both balloons, measured within the pressure vessel. Vertical coloured bars indicate the fast snap-through expansion and snap-back stages. Segments with increasing voltage (low pressure segments) correspond to a relaxed membrane on the HTR, and with large pressure to a stretched membrane on the LTR. (d) Multi-cycle temperature evolution measured for the DEA-driven system. Temperature variations are lower than for direct pneumatic actuation due to larger LTR with a different holder layout.

Table 1 | Summary of the experimental results for different parameters.

Thickness H (μm)	Frequency f (Hz)	Final LTR ΔT_{meas} (K)	COP	SCP (W/g)	Heat flux q (mW/cm^2)
140	0.9	4.6	4.5	10	104
140	0.5	4.3	4.7	5.4	63
140	1.1	7	1.0 ⁱ	20.9	205
140	0.9	6.8	1.9	15.9	156
180	1.1	7.9	0.9 ⁱ	19.2	256
180	0.9	7.9	0.7 ⁱ	15.6	222

ⁱThese values are smaller due to larger outlet diameter, as explained in the Supplementary Note 8.

Supplementary Materials:

Supplementary Notes 1-9

Supplementary Figures 1-10

Supplementary Table 1

Supplementary Video V1-V4