Electrocaloric Coolers: A Review

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Since the discovery of giant electrocaloric effects, researchers are intensively studying electrocaloric cooling as an alternative to vapor compression systems to develop more efficient heat pumps and mitigate climate change. Endorsed by its direct use of electricity, easy-handling, and compact design, recent advancements in the performance of electrocaloric coolers have finally displayed temperatures comparable to similar competing technologies, and the topic has regained attention and interest. In this work, the design, performance, and working principles of all electrocaloric prototypes before the year 2021 are reviewed, and hints and guidelines are given for future works to bring the development of these devices one step closer to real applications.

1. Introduction

The energy consumption of the humankind is increasing year after year and the world we live in cannot take it any longer. Most energy processes involve CO₂ emissions to the environment, causing global warming and its alarming consequences, as hot summers, floods, typhoons, or heavy snowstorms. Regardless of the kind of energy source, developing more efficient energy conversion technologies is essential for the planet’s future sustainability and viability. Out of the overall world’s electricity consumption, 10% of the share is destined only for cooling purposes. However, the refrigeration industry is still today governed by the vapor compression of gas refrigerants that, despite reaching remarkable efficiencies = 60%, tend to perform less efficiently (20–30%) when their size is reduced, and have little room for improvement after more than a century of advancements. In addition, they utilize powerful greenhouse gases (mostly hydrofluorocarbons) that greatly contribute to global warming when released to the environment, worsening the overall scene.

To fight this issue, some nations have agreed on gradually replacing these harmful refrigerants with natural ones that have a lower or zero global warming potential (Kigali amendment to the Montreal protocol). However, the use of some of these natural refrigerants (such as CO₂ or ammonia) still entails other side effects, such as flammability, the handling of high pressure, or toxicity. All in all, a highly efficient and eco-friendly new generation of coolers is thus in demand.

Caloric materials, which utilize entropy variations from solid-state phase transitions driven by the action of an external field, have emerged in the last decade as promising candidates to replace vapor compression coolers. Depending on the external field applied (magnetic, electric or mechanical stress), these materials are label correspondingly as magneto-calorics (MC), electrocalorics (EC), and mechanocalorics (mC), with the latter congregating elastocalorics (eC), if the stress is uniaxial, and barocalorics (bC), if hydrostatic pressure otherwise. Out of the three caloric families, EC are particularly interesting because of their direct utilization of electricity, high energy efficiency, and low cost. Moreover, with EC is easier to enhance the coefficient of performance (COP) of the resulting coolers (by recovering part of the work needed to drive the corresponding caloric effect) because of the handiness of dealing with electric charges with standard circuitry. At the same time, EC demonstrators are compact and suitable for miniaturization.

From a phenomenological point of view, the EC effect stands for the polar entropy variations ΔS_{EC} that the material experiences when an electric field is induced. If isothermal conditions are not respected, these entropy changes are manifested as a temperature difference ΔT_{EC}, which is highest if the field is fully adiabatically applied (ΔT_{ad}). The sweet spot for the EC effect is close to the Curie temperature, at the vicinity of the paraelectric (PE)–ferroelectric (FE) phase transition, where entropy is more eager to be changed and the pyroelectric coefficient diverges. The PE–FE is not unique to see EC effects, and other transitions are possible as well. An example is the antiferroelectric–FE phase transition, where recent works have shown inverse EC effects in the sense that the application of an electric field produces a negative temperature change instead of a positive one.

Differently from MC and eC prototypes though, EC demonstrators have struggled to maintain temperature spans (temperature difference between hot and cold side of the cooling device) larger than 10 K and have barely reported cooling power values. One of the reasons for these low and incipient performances is the relatively low EC effect of most common materials to date (<5 K). This is a similar situation to MC devices, which have
2. Electrocaloric Objects and Materials

To display EC effects, a voltage difference is needed to be applied between two adjacent electrode plates that contain the EC material. Generally, there are three different structures in which these electrode plates can be configured (Figure 1): bulk, thin films, and multilayer capacitors (MLCs). Hereunder, we provide more details on these structures, underlining their pros and cons, and debating their suitability for the development of EC coolers.

“Bulk” structures consist of macroscopic flat samples with electrodes plates deposited at bottom and top surfaces (left object in Figure 1). The electrode deposition is usually done with techniques such as spin coating or sputtering, although simpler proceedings, such as handmade painting with conductive paste, epoxy, or similar conductive coatings, are possible as well. The main advantage of the bulk configuration is that the electrodes can easily cover almost the entire sample surface. Hence, the electric field is applied everywhere, and the sample is said to be nearly 100% electrocaloric active. The relatively large sample size generates a substantial amount of heat that can be directly measured either by differential scanning calorimetry, when the ECE is triggered isothermally, or by thermometry, when triggered adiabatically (thermocouples, thermistor, Infrared imaging...). Similarly, the object is handy and easy to be integrated into practical devices. The main disadvantage of EC bulk structures though is that the distance between the electrodes is large (>100 µm). This implies the appliance of high voltages (>1 kV), which challenges the experimental set-up and safety. Typical bulk materials reporting large EC effects are ferroelectric perovskite-like ceramics, such as PbSc0.5Ta0.5O3 (PST), (1-x)Pb(Mg1/3Nb2/3)O3–xPbTiO3 (PMN-100xPT), PbZr0.97Tio0.03O3 (PZT) or BaTiO3 (BTO). These kind of samples have been already implemented in a few EC coolers.

A solution to decrease the applied voltage is shortening the distance between electrode plates by growing thin films (right object in Figure 1). Thin films are layers of the EC material (<10 µm) grown on a substrate (red parts in Figure 1), which typically is a few orders of magnitudes thicker. While one of the electrodes (<100 nm) is deposited at the very top of the EC film, the other one can either be the substrate itself (if it is conductive) or a conductive thin layer that is placed between the substrate and the EC film. Because of the very low thickness of the films, much higher electric fields can be easily induced at relatively low applied voltages (<10 V) and larger EC effects are thus triggered. In fact, it was precisely works on thin films that lead to the discovery of giant EC effects (>10 K) in 2006 and 2008, which served to revive the topic. Since then, similar performances have been achieved in the aforementioned ferroelectric ceramics and the organic ferroelectric polymer polyvinylidene difluoride (PVDF). Because of the fast thermalization and low amount of heat produced, EC effects in thin films are normally characterized by indirect methods. A few direct measurements in thin films have been reported though, through high-resolution calorimetry or highly sensitive thin-film resistance thermometry with the so-called “3-omega” technique. On the other hand, direct characterization of ECE in thin films by thermometry is challenging because: a) film substrates impose nonadiabatic conditions and b) the temperature relaxation time is too short to be captured by the instrumentation currently available. To our knowledge, no works on the latter have been reported yet. In addition, the handling of thin films is challenging and farfetched, what makes them today unviable for realistic devices in which the continuously cooling of a macroscopic object is required (at least for the kind of devices that the EC community is envisioning now).

There is a third kind of object that lies in between bulk and thin films: the MLC configuration (centered object in Figure 1).
MLCs consist of an engineered-like structure constituted of EC thick films (between a few µm up to 50 µm) piled up with electrodes in between. The electrode sheets are connected in parallel through electric terminals, which are usually placed at the sides (Figure 1). Although the overall resulting object is macroscopic, with dimensions that fall typically in the millimeter or even centimeter range, reasonable voltages (<1 kV) are sufficient to trigger large ECEs, which is convenient and safer. While the resultant active volume is less than the overall sample volume (around 50–80% of the total volume, where negative and positive inner electrodes overlap), the quantity of heat generated is large enough to be directly measured and make use of it. Moreover, the metallic electrodes can conduct heat very efficiently thanks to thermal conductivity, roughly one hundred times larger than in EC ceramic layers, promoting heat exchange. The later drawback of this kind of structure though is that commercially available MLCs have not been developed for EC purposes yet and they exhibit rather poor EC effects (<1 KJ). To our knowledge, only the corporation Murata Electronics Ltd. has fabricated bespoke EC MLCs and only for scientific and collaborative purposes. All in all, MLCs mainly based on the common EC materials PST, PMN, BTO, and PVDF have proved to be the most convenient and practical objects for cooling applications, having been now exploited in several EC devices and achieving the best performances so far.

On top of that, MLCs are extremely reliable, as they have been initially developed to act as large values capacitors and are currently used in plenty of electronic devices. In addition, they are less fragile than bulk thanks to their inner electrodes. The main drawback of this kind of structure though is that commercially available MLCs have not been developed for EC purposes yet and they exhibit rather poor EC effects (<1 kV). To our knowledge, only the corporation Murata Electronics Ltd. has fabricated bespoke EC MLCs and only for scientific and collaborative purposes. All in all, MLCs mainly based on the common EC materials PST, PMN, BTO, and PVDF have proved to be the most convenient and practical objects for cooling applications, having been now exploited in several EC devices and achieving the best performances so far.

3. Thermodynamic Cycles and Working Principles

To make use of the EC effect, EC materials shall undergo thermodynamic cycles. The easiest one to implement is the Brayton cycle, which consists of 4 steps (2 adiabatic legs and 2 isofield legs), as depicted in Figure 2. In the first step (1-2) of the Brayton cycle, an electric field is applied adiabatically (which is feasible if the field is applied in a shorter time scale than the thermal relaxation time constant of the system). Consequently, the EC material experiences an increase of temperature ΔT_{ad}. In the second step (2-3), the field is maintained constant (isofield leg) and the material releases heat to the surroundings. Once the initial temperature is reached, the field is removed adiabatically (3-4), triggering the EC temperature decrease (−ΔT_{ad}). Finally, at E = 0 (4-1, isofield leg), the material absorbs heat from the surroundings and the material returns to its initial state. Devices following this strategy are the simplest kind of coolers, where heat can be continuously transferred from a heat source to a heat sink. Within such a design though, the temperature difference between source and sink cannot exceed the temperature change of the EC effect. Considering that practical EC materials display rather low EC effects (ΔT_{ad} < 5 K), the cycle described above is not sufficient for realistic cooling applications, where temperature spans larger than 20 K are required.

3.1. Passive and Active Regeneration

To reach such performances, regenerative cycles are typically implemented, allowing the temperature difference between sides to be several times larger than the temperature change of the EC effect. It is important to note that heat regeneration is not unique to EC devices. In fact, heat regeneration has been widely studied and exploited for more than decades in MC coolers, where maximum temperature spans (i.e., cooling power q_c = 0) as large as 40 K have been reached. Depending on its core nature, heat regeneration can be either passive or active (Figure 3). In passive regeneration (Figure 3a), the cooling material (EC material) is moved periodically throughout a regenerative fluid column, absorbing heat from the bottom of the column (cold end) and expelling it at the top (hot end). As a result, a temperature gradient along the fluid column is developed, and the temperature span can exceed the temperature change of the EC effect. In active regeneration (Figure 3b), hot and cold sides are instead separated by the cooling material embedded in a porous-like assembly, and heat is exchanged thanks to the oscillatory circulation of a heat transfer fluid in between. Similarly, a temperature gradient along the cooling material assembly is established, which can exceed the EC effect magnitude as well.

Active regeneration is implemented usually following a Brayton-like cycle, which provides the highest temperature span thanks to fast activation of the EC effect. More efficient cycles such as Ericsson or Ericsson–Brayton-like may be attempted as well, though they are difficult to realize because they require a precise control of the applied field distribution and time variation of the heat transfer fluid. Heat regeneration is mostly performed with the action of a heat transfer fluid because 1) the optimal thermal contact set between the active material and the pumping agent and 2) the apparent lower induced frictional heating (which becomes more stringent for high viscosity fluids or high-frequency operating devices). Utilizing a solid–solid regenerator is possible as well by the oscillatory movement of solid plates. The main interest of solid–solid regenerators lies on developing devices with an anisotropic thermal conductivity within the heat transfer media. The idea of such systems is to promote heat transfer in the material–regenerator interface (through-plane conduction) while diminishing it along the direction of the temperature gradient within the regenerator.

![Figure 2](image-url)  In red, the temperature of a PST-MLC sample, measured with an IR camera. In blue, the electric field applied to the sample by means of a sourcemeter.
(in-plane conduction), and larger regeneration factors (ratio between the temperature span and the EC effect) are expected. Although having an anisotropic-like heat transfer within the device is feasible only in solid–solid regenerators, it still requires a high degree of engineering and thus remain a rare type.

3.2. Cascading or Multistage

Another possibility for cooling devices to display large temperature spans, though less common in EC prototypes,\cite{12,13,63} is cascading (or multistage) systems. Cascading systems consist of several stages of active cooling material connected in such a way that each stage undergoes the same unique thermodynamic cycle. To pump heat through the stages, two requirements need to be fulfilled. First, the electric field is applied to consecutive stages with a phase shift of 180°. That means that if the field is applied to stage \( s_n \), none is at the neighboring stages \( s_{n-1} \) and \( s_{n+1} \). The second requirement is that consecutive stages \( s_n \) and \( s_{n+1} \) are thermally contacted when the field is applied at the lower-indexed stage \( s_n \) (within these notation, \( s_1 \) is next to the source and \( s_0 \) to the sink). The thermal contact between stages can be done either with the circulation of a fluid, as has been shown recently in an EC prototype (with a record temperature span of 28 K)\cite{77} or just by direct physical contact of every adjacent stage. The latter is depicted by Figure 4, which consists of a solid-state cascading system made of four stages (labeled A,B,C,D instead of 1,2,3,4 to avoid confusion with cycle steps)\cite{65}. Recently, very innovative highly efficient cascading EC coolers have been presented, with very promising perspectives\cite{12,13} as explained later on. Moreover, cascading systems can be operated with heat switches as well placed in between the stages as inner layers\cite{61,78}. Heat switches are interesting because they have the capability to swap between good thermal conductors and good thermal insulators, and hence create or annihilate thermal routes as appropriate.

4. Fluid-Based Electrocaloric Coolers

Prototypes utilizing a heat transfer fluid to pump heat are the most common kind of caloric coolers (including MC, EC, and eC), and their vast majority are based on the active heat regeneration principle.\cite{7,11,27} Five different laboratories have attempted EC prototypes based on the circulation of a heat transfer fluid. The performances of all of them are summarized in Table 1 and described hereunder.

4.1. Moskov Power Engineering Institute Prototypes

The first EC prototype dates from 1989.\cite{40} It was developed by Sinyavsky’s team in Moskov Power Engineering Institute (MPEI) in collaboration with Shebanov, from Latvian State University. The EC material was \( 20 \times 10 \times 0.5 \) mm\(^3 \) bulk plates of \( \text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3 \) (PST) with an ordering degree of scandium and tantalum anions \( \Omega = 0.8–0.9 \). The material displayed a \( \Delta T_{\text{ad}} \) of 1.3–1.5 K under the application of \( E = 25 \) kV cm\(^{-1} \) at its optimal temperature \( T_{\text{op}} = 274 \) K. The EC prototype itself consisted of two main blocks, each made of 10 PST plates, structured in a parallel plate matrix of two rows and five columns, with each block having a total PST mass of 7 g. A gap of 0.5 mm was set in between the PST plates to let a heat transfer fluid flow through. The two blocks operated with a 180° out of phase electric field and were connected in series in a closed fluid tubing with heat exchangers in between the blocks, as depicted in Figure 5a. The heat transfer fluid was helium, which pressure was set at 0.8 MPa. The direction of the fluid circulation was alternated simultaneously with the applied field cycle, as required by the regenerative principles. The authors called their method quasi-regeneration. This device was able to build a temperature difference between the heat exchangers (temperature span) of 2 K and a cooling power of 10 mW for an electric field strength \( E = 15 \) kV cm\(^{-1} \) and a cycle frequency of 3–5 Hz.

An upgraded version following the same design and principle was presented a few years later.\cite{61,83} The PST plates where thinner (0.3 mm), and the total PST ceramic mass was increased (35 g). The fluid slits were thinner as well (0.05 mm) by using copper wires as spacers in between the plates. The heat transfer fluid was replaced by Hexane, permitting higher electric fields to be applied. The resulting device produced a maximum temperature span of 5 K for an electric field of 60 kV cm\(^{-1} \), which is about twice as large as the EC effect displayed by the EC material (considering that \( \Delta T_{\text{ad}} = 1.5 \) K at \( E = 25 \) kV cm\(^{-1} \)).

![Figure 3](image-url)

**Figure 3.** a) Passive regeneration. The EC material is moved through a fluid column back and forth. The movement of the EC material is synchronized with the EC cycle, so that a temperature gradient is established along the fluid column. b) Active regeneration. A heat transfer fluid is moved back and forth through a porous-like structured EC material. The movement of the fluid is synchronized with the EC cycle, so that a temperature gradient is established along the EC structure. Adapted with permission.\cite{72} Copyright 2020, University of Cambridge.
In the same publication, the authors disclosed: “at their present time, a new model of a large scale electrocaloric cooler had been assembled”. This new device consisted of a single unit of 400 g, made of 0.3 mm thick PST plates “modified by different elements” to achieve different optimum temperatures, similar fluid slit size (0.06 mm) and the same heat transfer fluid (hexane), but with a larger cross-section (11 × 11 mm) and a longer total length (300 mm). Preliminary results reported a temperature span of almost 8 K for an applied electric field of 15 kV cm\(^{-1}\) and a fluid flow rate of 2.5 cm\(^3\) per cycle. The authors claimed that when increasing the field from 15 to 18.5 kV cm\(^{-1}\) (and we understand that keeping constant the other parameters as well, but this is not explicitly mentioned), they measured a temperature span of 12.7 K. Cooling power values were not reported for any of the two last versions. Regarding the electric consumption, 750 W was required to induce an electric field of 25 kV cm\(^{-1}\) in the material (unfortunately, the power for the electric fields of 15 and 18.5 kV cm\(^{-1}\) in the experiment was not disclosed). According to their calculations, the authors explained that such an electric field of 25 kV cm\(^{-1}\) (which was too high to be applied experimentally) should produce a temperature span in the device larger than 15 K. Up to now, this is the last communication that Sinyavsky’s team disclosed on electrocaloric cooling and further works confirming these preliminary results have not been reported yet.

Figure 4. Cascading (multistep) system. In step 1, field is applied to EC stages A/C, and removed from B/D, whereas thermal contact is established between stages B/C, so that heat flows from C to D (black arrow). In step 2, thermalization occurs in stages B and C, stage D absorbs heat from a heat source and stage A repels it to a heat sink. In step 3, the field is removed from stages A/C and applied to stages C/D, and thermal contact is established between stages A/B and C/D (black arrows). In step 4, stages A/B and C/D are thermalized, and the cycle finished. Adapted with permission. Copyright 2021, Elsevier.

Table 1. Summary of the performance of all experimental EC fluid-based coolers proposed to date.

| Institution     | Reference | EC material | \(m_{EC}\) [g] | \(E\) [kV cm\(^{-1}\)] | \(\Delta T_{ad}\) [K] | Fluid | \(\Delta T_{span}\) [K] | \(q_{c}\) [W kg\(^{-1}\)] | \(q_{c}\) [W L\(^{-1}\)] |
|----------------|-----------|-------------|--------------|----------------|----------------|-------|----------------|----------------|----------------|
| MPEI           | [40]      | PST bulk   | 14           | 15             | 1.5\(^{a}\)   | Helium | 2               | 0.7            | 6              |
| MPEI           | [79]      | PST bulk   | 35           | 60             | –              | Hexane | 5               | –              | –              |
| MPEI           | [41]      | PST bulk   | 400          | 18.5           | 1.5            | Hexane | 12.7            | –              | –              |
| U. of Ljubljana| [42]      | PMN bulk   | 10           | 50             | 0.9            | Silicone oil | 3.3           | –              | –              |
| U. of Ljubljana| [43]      | PMN bulk   | 14.6         | 57             | 1              | Silicone oil | 3.3           | 15\(^{b}\)     | 122\(^{b},c\) |
| LIST           | [62]      | BTO MLCs   | 13           | 200          | 0.5            | Silicone oil | 0.16          | –              | –              |
| LIST           | Unpublished results | PMN MLCs | 35           | 175          | 1.7            | Silicone oil | 1.4           | –              | –              |
| LIST           | [11]      | PST MLCs   | 42           | 160          | 2.2            | Silicone oil | 13            | 12\(^{d}\)     | 105\(^{d}\)    |
| U. of Hannover | [80]      | PMN MLCs   | 4.5          | 32           | 0.39           | Silicone oil | 1.12          | –              | –              |
| UTRC           | [82]\(^e\) | PVDF MLCs  | –            | 1500         | 8.9            | Air      | 8.4            | –              | –              |

\(^{a}\)For an \(E = 25\) kV cm\(^{-1}\); \(^{b}\)For a \(T_{span} = 1\) K; \(^{c}\)We used PMN bulk density of 8.13 g cm\(^{-3}\); \(^{d}\)For a \(T_{span} = 0\) K, obtained with a different prototype of \(m = 19\) g and \(E = 37.5\) kV cm\(^{-1}\); \(^{e}\)Not peer-reviewed.
Figure 5. Fluid-based EC prototypes. a) Sketch of Sinyavsky’s second prototype, based on modified-PST plates with hexane as a heat transfer fluid. The two blocks worked in an antiphase fashion (called quasi-regeneration by the authors). Such a device achieved a temperature span of 5 K.[41,82] Reproduced with permission.[82] Copyright 1992, Elsevier. b) Zenithal image of Slovenia’s prototype, with 5 EC stacks, each formed by 10 PMN-PT plates, and the hot side heat exchanger (HHX) and the electric heater in the cold side.[43] c) LIST first device based on passive regeneration with commercial BTO MLCs and silicone oil.[62] d) LIST first active regenerator based on PMN MLCs from Murata. The figure on the left shows the PMN MLC matrix, whereas the image on the right shows the EC capsule that sealed and thermally insulated the system. e) LIST’s second active regenerator, with 1280.5 mm thick PST MLCs from Murata and silicone oil. The simplification of the structure and reduction of the inactive mass allowed the device to reach 13 K of temperature span. Adapted with permission.[11] Copyright 2020, AAAS. f) Blumenthal’s prototype based on customized PMN MLCs and silicone oil. Reproduced with permission.[79] Copyright 2018, John Wiley and Sons. More details about these prototypes can be consulted in Table 1.
4.2. University of Ljubljana Prototypes

After the discovery of giant ECE in ceramic and polymers thin films in 2006 and 2008,[44,45] the electrocaloric community underwent a renaissance that triggered the development of more EC devices.[13–15,42,43,60,62,76,80] Kitanovski’s group attempted in 2015 the first Slovenian EC prototype, which followed the principle of active regeneration (active electrocaloric regenerator (AER)).[42] The device was based on bulk 0.9Pb(Mg1/3Nb2/3)O3–0.1PbTiO3 (PMN-10PT) rectangular plates (each was 20 × 10 × 0.2 mm²) that were stacked in a parallel plate matrix of ten rows and three columns of these plates. The space between the rows for the fluid to flow through was set to 0.1 mm and the heat transfer fluid was dielectric silicone oil. For an applied electric field $E = 50 \text{ kV cm}^{-1}$ and a cycle frequency of 0.75 Hz, the device showed a maximum temperature span of 3.3 K, which is more than 3 times the ECE magnitude (around 1 K at room temperature). The authors showed as well the results of a 2D-based dynamic numerical model which simulated the performance of other heat transfer fluids. Their model showed that, by using deionized water, enlarging the AER length to 0.2 m and increasing both cycle frequency to 1.25 Hz and applied electric field to 118 kV cm⁻¹, the device should reach a temperature span of 14 K, entailing a regeneration factor of almost 10.

In 2018, a very similar device was presented accompanied with a more detailed numerical modeling.[43] The experimental device consisted of 45 identical bulk PMN plates, distributed in a parallel plate matrix of 9 rows and 5 columns, with a total length of 110 mm (Figure 5b). In between the plates, 0.125 mm fluid slits were set. Contrary to the previous design, a heat exchanger was placed at the hot end of the AER (by means of a copper tube) and a thin-film heater in the cold end of the AER as a heat load to report on cooling power. This device achieved a maximum temperature span of 3.3 K for an applied electric field of 57 kV cm⁻¹ (very similar to their design from 2015) for a cycle frequency of 0.65 Hz and a ratio of the fluid displaced over the total regenerator fluid volume, $v^\text{R}$, of 0.2. When turning the heat load on, with the same frequency but a $v^\text{R} = 0.4$, a maximum cooling power of 16 W kg⁻¹ (of electrocaloric material) was measured at the same applied field, reducing thus the temperature span down to 1 K. The numerical modeling consisted of a 2D transient simulation of the AERs performance and included the effect of electric-polarization hysteresis and the effect of the irreversibility of the system for electric-energy recovery. Their model showed that, whereas the cooling power remained unchanged, the COP decreased between 10% and 15% when electric hysteresis was included in the model. This result was unexpected by the authors because of the slim hysteresis loop of PMN in comparison to other EC materials, such as BaTiO₃ or PVDF,[38,81] highlighting the need to include these irreversibilities to properly predict the efficiency of EC cooling devices. The model showed as well that by assuming 100% electric charge recovery, the COP could be enhanced by a factor of 10. The study ended with an experimental verification of the numerical modeling, for which heat losses to the surrounding where considered. Even though the model overpredicted the experimental data, it properly describes the trends of the temperature span versus $v^\text{R}$ parameter and cooling power versus temperature span graphs. Overprediction of data in 2D models is common because heat losses in the in-plane direction cannot be contemplated in any case. In addition, experimental inhomogeneities, such as irregular fluid channels, uneven plate surface or fluid dead volume, tend to diminish experimental performances, so that some parameters in the model need to be adjusted if one looks for an experimental data match.

4.3. Luxembourg Institute of Science and Technology Prototypes

The first cooler from Luxembourg Institute of Science and Technology (LIST) was presented in 2016.[62] It was conceived to validate the basic principle of passive regeneration, i.e., to create a thermal gradient in a fluid column. The prototype was based on commercially available Zr-doped BaTiO₃ (Zr-BTO) MLCs, each being 3.2 × 2.5 × 2 mm³ and 0.087 g, which exhibited an ECE of 0.54 K at 200 V. Three plates of 5 × 10 BTO MLCs (making a total of 150 MLCs) were attached to copper foils and displaced throughout a fluid column containing dielectric fluid silicone oil (Figure 5e). The movement of the plates was carried out with a pneumatic piston. Thermocouples placed at the top and bottom of the fluid column measured a maximum temperature span of 0.13 K when 200 V were applied to the 150 EC samples, which is an electric field $E = 200 \text{ kV cm}^{-1}$. As described by the authors, the thermodynamic cycle the device underwent consisted of a modified Brayton cycle, constituted of 2 adiabatic legs, two isofield legs in stationary position and two isofield legs during the plate’s movement. According to the authors, the optimal experimental frequency of 25 mHz was a clear indicator of the poor heat exchange of the overall system, which forced the duration of the isofield legs to be excessively long (37 s) in comparison to the adiabatic legs (1.3 s), and justified the low regeneration factor (<1), even though their hypothesis of creating a thermal gradient in a fluid column was successfully proved.

An AER (inspired by previous works)[41,42] was attempted in 2017 with a parallel plate matrix of ten columns and six rows of PMN MLCs fabricated by Murata Electronics Ltd. (Figure 5d).[55,56] Each MLC was 10.4 × 72 × 0.9 mm³. This parallel plate matrix was assembled within a rectangular casing formed by 4 polyether ether ketone (PEEK) plates, with grooves symmetrically spaced to support the MLCs in two of these plates. Bespoke shaped brass plates were placed at the edges of the grooves to ensure mechanical locking of the MLCs and provide electrical connection at the same time. The resulting cell was fitted into an outer PEEK housing that provided sealing and thermal insulation. A maximum temperature span of 1.4 K was measured in the AER at 700 V ($E = 180 \text{ kV cm}^{-1}$), which triggered Δ$T_{\text{ad}} = 1.6 \text{ K}$ in the material. Despite the improvements with respect to the first design, such as utilizing a larger EC material mass with higher EC effects, heat exchange was still compromised because of MLCs’ large thickness and fluid slits irregularities (Figure 5d).

Recently, an evolution of this AER has been carried out with thinner PST-MLCs (0.5 mm).[31] The final parallel plate matrix consisted of 128 samples, distributed in 8 rows and 16 columns (Figure 5e). The fluid slits between the PST MLCs rows were set to 0.25 mm. Fluid slits irregularities were still present because of the uneven and curved shape of the EC samples at such low
thickness, but improved respect to the previous device. The design was based on a 2D finite element model, which provided important insights on the role of thermal insulation and inactive mass. As a result, none of the structural pieces and EC housings parts from the previous prototype were utilized. Instead, double-sided tape stripes were used to assemble the parallel-plate matrix and silver paste applied at the PST-MLCs electrode terminals to connect all MLCs in parallel. A polyolefin hose was used to encapsulate the AER and minimize dead volume, simplifying as much as possible the overall design. Polyurethane foam was eventually applied after to improve thermal insulation. This prototype produced a temperature span of 13 K after 2000 s of operation for an applied voltage of 600 V \((E = 160 \text{kV cm}^{-1})\). This result, which entails a regeneration factor of 6, remains today the maximum temperature span ever observed in an EC cooler. An extra AER, made of eight columns and four rows of 1 mm thick PST–MLCs and a resistive wire at the cold side, was built to collect cooling power values reaching 12 W kg\(^{-1}\) (of electrocaloric material) for a temperature span of 0 K. The same numerical modeling was adjusted to predict the performances of this AER. This model foresees that, by thinning the MLCs down to 0.2 mm, by utilizing water as heat transfer fluid and by utilizing better ordered PST in the MLCs activated close to their current breakdown field (ECE of 5.5 K at 29 \(\text{V mm}^{-1}\)),\(^{[80]}\) a maximum temperature span of almost 50 K and a maximum cooling power of 850 W kg\(^{-1}\) (of active EC material) should be obtained. This outcome is similar to Kitanovski’s model, stressing out the importance of utilizing water as a heat transfer fluid and increasing the sample breakdown field so that higher EC effects can be safely applied. Thinning down the active layers, breakdown electric field decreases with thickness, extending annealing time, and industrial optimization of samples fabrication are parameters susceptible to increase further breakdown electric field.

### 4.4. Leibniz Universität Hannover Prototypes

The last European fluid-based EC cooler to be described was developed by Blumenthal and Raatz in 2018 (Figure 5f).\(^{[80]}\) The authors presented a new AER based on PMN-8PT MLCs with the aim to produce a small-scale desktop cooling device, robust, reliable, and able to display a temperature span larger than 1 K. Their approach was based on the well-known V-Model—a standard tool in engineering systems and software development—in which the classification of device types, influencing factors and numerical simulation methods are integrated altogether to identify favorable geometrical and operating parameters. The PMN-8PT MLCs samples were 10 × 8 × 0.45 mm\(^3\), with 47 \(\mu\text{m}\) thick inner ceramic plates. They were fabricated in IKTS Fraunhofer. The AER parallel plate matrix consisted of 3 columns × 5 rows, structured with 3D-printed supports and housing. Even though the ideal fluid spacing derived by their model was 0.19 mm, a larger one (0.3 mm) was experimentally introduced to diminish the effect of uneven plates, fragile electrical joints, and electrical shorts due to enclosed air bubbles. The fluid was dielectric silicone oil. To increase the device’s practical lifetime, the cooler was operated only at low electric fields \(E = 32 \text{ kV cm}^{-1}\). At this applied field, the material showed an ECE of 0.39 K and the device a maximum temperature span of 1.12 K after optimization (cycle frequency of 0.3 Hz and 80\% of fluid displaced). This corresponds to a regeneration factor of 3, in agreement with previous works based on the same principle and utilizing similar materials.\(^{[42,43]}\) The authors emphasized as well that after more than 2000 h of operation, the device was still able to operate without any failures, proving its robustness.

### 4.5. United Technologies Research Center Prototypes

In the last years, the United Technologies Research Center has been developing fluid-based EC devices for both cooling and heating purposes. The project, founded by the U.S. Department of Energy’s Office of Energy Efficiency and Renewable Energy (EERE), has not been published in peer-review journals, but a summary report is available online describing their progress and results.\(^{[82]}\) In this document, Annapragada et al. showed that their heat pump was based on inexpensive polymer EC materials able to display a \(\Delta T_{\text{od}} = 8.9 \text{ K} \) at 43 °C and close to their breakdown field (1500 kV cm\(^{-1}\)). Under such conditions, their device was able to cool ambient air by 8.4 °C (the hot side did not change its temperature because of a hot bath). However, this temperature span of 8.4 °C could not be maintained because the high electric field led to electric breakdown in some of their samples. Unfortunately, more details on the experimental parameters and geometric dimensions were not disclosed.

### 5. Solid-Based Electrocaloric Coolers

Hereunder are described all electrocaloric coolers based on solid elements. Table 2 and Figure 6 summarize their performance and designs.

#### 5.1. University of California Prototypes

After the discovery of serendipity EC effects in commercial BaTiO\(_3\)-based MLCs,\(^{[59]}\) the department of mechanical and aerospace engineering of University of California designed a solid-state refrigerator based on these same samples. The device consisted of a single stage, formed by one BTO MLC, oscillating between a heat source and a heat sink thanks to the action of a motorized z-stage, as depicted in Figure 6a. The key element of their work was switchable liquid-based thermal interfaces, which permitted fast and reliable heat transfer between the EC MLC and the source/sink. These thermal interfaces were formed by dispensing glycerin droplets onto previously patterned hydrophilic islands (diameter < 1 mm) on the backside of the heater and the top surface of the heat sink. A constant Joule-heating current kept the heater temperature at 27 °C, while the heat sink was maintained at 25.7 °C (they did not mention how). For an applied frequency of 0.3 Hz and an electric field of 300 kV cm\(^{-1}\) (which induced an EC effect in the BTO MLC of 0.5 K), the temperature of the heater was cooled down by 1 K (26 °C). Considering that 15 mW...
of Joule-heating was applied at the heater and that the mass of 1 single BTO MLC is around 0.1 g, we can deduce a cooling power of 160 W kg⁻¹ of EC material. The authors explained that their experimental results were supported by a 1D numerical model, though the latter was not displayed.

5.2. Penn State University Prototypes

In 2013, Zhang’s group from Penn State presented the first solid-based regenerator. This device consisted of 0.25 mm thick rectangular EC modules that were sandwiched in between four 0.5 mm thick stainless-steel plates (Figure 6b). The inner structure of these EC modules was made of 24 PVDF 8 μm thick films (similar to MLCs), with gold sputtered electrodes. Glued thin silver wires were then connected to them to carry electric current. Ultimately, the films were glued on top of each other with epoxy resin, forming a 1 μm layer in between the films. The overall EC module showed 2.5 K of adiabatic temperature change at 35 °C under an electric field of 1000 kV cm⁻¹, which differs from the more than 20 K of temperature change that thinner films of the same PVDF displayed under 1600 kV cm⁻¹. According to the authors, the reason for that was the amount of inactive mass (electrodes, wires, glues, resins, etc.) that the EC module englobes. The resulting device followed then the principle of passive regeneration, in which the EC modules were moved back and forth through the stainless steel plates synchronically with the activation and deactivation of the EC effect. As a result, a maximum temperature span of 6.6 K was measured between the ends of the stainless-steel plates at a frequency of 1 Hz and an electric field of 1000 kV cm⁻¹, which corresponds to a regeneration factor of 2.6.

A second solid–solid EC device from Zhang’s group was proposed in 2017, utilizing commercial Y5V ceramic MLCs. The device consisted of a novel regenerative design formed by two adjacent rings (Figure 6c), each constituted of 12 trapezoid-like shaped MLCs (named EC elements in the figure, with the bases of these trapezoids being 12 and 5 mm, the height 5 mm and the thickness 0.46 mm), that was inspired in previous modeling works (see section 6). Fixed heat exchangers were placed at the ring ends representing the hot side (red colored, where heat is rejected) and the cold side (blue colored, where heat is absorbed). To accomplish solid to solid regeneration, 1) the two rings are rotated in opposite direction and 2) the electric field is only applied in the regions where the EC elements rotate from the fixed hot heat exchanger to the fixed cold heat exchanger (highlighted semicircle in the figure). Since the rotation direction is different for each ring, these highlighted areas become complementary to each other, as depicted by the right image of Figure 6c. Such samples displayed an EC effect of 0.9 K at 200 V (E = 165 kV cm⁻¹), and the maximum temperature difference between the hot and cold heat exchangers measured was 2 K at a rotation speed of 5 rounds per minute.

5.3. Palo Alto Research Center Prototypes

Schwartz’s group in the Palo Alto Research Center (PARC) has been developing solid-based EC coolers since 2015. In their first prototype, a heat-switch-based electrocaloric cooler utilizing commercial BTO-based MLCs was presented (Figure 6d). The active part of the device consisted of a 4 × 5 BTO MLC array (labeled EC module in the figure), with each BTO MLC being 3.3 × 1.9 × 2.6 mm³. Bespoke heat switches were placed in between the EC module to pump heat from a source (a resistor heater on the top of the structure) to a sink (copper block at the very bottom). To change the conductance of the heat switch from a high to a low value, the match and mismatch of patterned grooved silicon parts (blue elements in the figure) was attempted by displacing a hook that was attached to an actuator, as depicted by the figure. As a result, the BTO MLCs were set in thermal contact either with sink or source, depending on the position the actuator was found in. In the figure, thermal contact is set between the BTO MLCs and the heat sink (copper block), as the blue elements (heat switch) matching describe. At an applied electric field of 277 kV cm⁻¹ and a temperature change in the EC module of 0.5 K, such a cooler was able to build a maximum temperature difference between heat source and sink of 0.3 K. This value is understandable since neither regeneration nor multistaging was performed to enlarge its temperature span. When activating the heater, a maximum cooling power of 36 mW was observed at 0 K temperature span (q_c = 19 W kg⁻¹). In addition,
Figure 6. Solid-based EC prototypes. a) First EC solid-based prototype by Jia et al., from University of California, where BTO MLCs oscillate between a heat source and a heat sink thanks to the action of a motorized z-stage. Adapted with permission.[60] Copyright 2012, AIP. b) Penn State solid–solid heat regenerator. PVDF plates moved in an oscillatory manner through stainless steel plates. The system is based on passive regeneration and reached a $T_{\text{span}}$ of 6.6 K. Adapted with permission.[76] Copyright 2013, AIP. c) Penn State rotatory EC prototype based on commercial trapezoid-like shaped BTO MLCs with cascading principles. Adapted with permission.[63] Copyright 2017, AIP. d) PARC’s EC cooler with heat switches, based on commercial BTO MLCs and a lateral actuator that activated (and deactivated) alternatively the heat path between the BTO MLCs and the heat sink or the heat source. Adapted with permission.[61] Copyright 2015, AIP. e) PARC’s second cooler based on PST MLCs and cascading principles. The device reached a temperature span of 5.5 K with only 9 MLCs. Adapted with permission.[12] Copyright 2020, AAAS. f) LIST and University of Cambridge’s cooler, so-called the “slapping machine,” based on commercial BTO MLC. The implementation of energy recovery allowed the COP to be improved by almost a factor of 3.[23] g) Pei’s first prototype, from the University of California, based on PVDF MLCs and electrostatic actuation. The implementation of energy recovery allowed the COP to be improved by almost a factor of 3. h) Pei’s multistaged prototype, based on their previous design, with 4-staged EC polymers. The device exhibited a temperature span of 8.7 K and a cooling power of 990 W kg$^{-1}$. Adapted with permission.[13] Copyright 2020, Springer Nature. i) University of Ljubljana’s cantilever EC prototype made with PMN-PT.[97] More details about these prototypes can be consulted in Table 2.
the device showed a robust and reliable performance by being able to operate >10 h without failure.

With the aim to improve the temperature span of their device, the same group presented in 2020 a new device based on the cascading principle (Figure 6e).\textsuperscript{[12]} This time, the EC material were PST MLCs from Murata (each 10.4 \( \times \) 7.2 \( \times \) 0.9 mm\(^3\)) that showed an EC effect of 2.5 \( k\) at the applied electric field \( E = 108 \text{ kV cm}^{-1}\). The design of the cooler consisted of two rows of PST MLCs, thermally coupled, so that heat could be easily transferred from one to the other. The top row had 5 PST MLCs and the bottom one had 4. In addition, the latter contained aluminum plate-fin heat sinks (hot end, yellow square) and left side (cold end, gray square) to facilitate achieving stable temperatures at the right side. A miniature fan was placed at the hot side to ease the release of heat when reporting on cooling power. In the figure, the PST MLCs are represented either by black squares (meaning that no field is applied) or red squares (a field is being applied). To pump heat from the source to the sink, the PST MLCs were moved laterally relative to one another as the polarizing electric field was switched. At the applied field of 108 kV cm\(^{-1}\), a maximum temperature difference between sink and source of 5.2 \( k\) was measured at no-load conditions for a frequency of 0.15 Hz (to maximize the temperature span, hot and cold ends were fully insulated and the fan in the hot side removed). Even though the prototype's temperature span did not cross the 10 \( k\) barrier, it is rather impressive to see that such performance was only achieved with 4.5 \( g\) of EC material (9 PST MLCs of thickness 0.9 mm). Evidently, higher temperature spans could be easily achieved by inserting more PST MLCs in the row. To report cooling power values, an electric heater was attached to the cold end and the fan was activated so that the temperature of the sink (hot side) was maintained near ambient temperature. Under these conditions, the corresponding maximum cooling power (temperature span = 0 \( K\) measured was 85 mW. According to the authors, the PST MLCs used were not optimized for such design. Hence, fabricating PST MLCs with the same form factor as the previously used commercial BTO MLC and orienting the electrode plates parallel to the heat transfer direction should substantially improve the performance.\textsuperscript{[12]} Finally, a COP/COP\(_{\text{Carnot}}\) of 20% was reported from a linearized efficiency model derived in the paper. When considering Brayton cycles, this efficiency was reduced to 11.5\% (if 95\% of charge is assumed to be recovered) or 15.5\% (if 98\% of the charge is recovered instead). Their calculations excluded the mechanical work required to move the reciprocating system, which was considered negligible because it is orders of magnitude smaller than the other work contributions. The authors finalized the article mentioning that “Our estimate of the COP/COP\(_{\text{Carnot}}\) of the current design (...) shows that up to 56.4\% may be achievable with the existing PST material. These values could make our system competitive with vapor compression cooling”.

5.4. Luxembourg Institute of Science and Technology and University of Cambridge Prototypes

In 2018, Defay’s group in Luxembourg Institute of Science and Technology developed a solid-to-solid-based EC device with the collaboration of the University of Cambridge. Although the main goal of the device was to enhance the overall device efficiency by recovering the charge employed in the EC effect, it is also another example of solid–solid EC prototype.\textsuperscript{[23]} The device, which is sketched in Figure 6f, consisted of two plates, each containing 12 commercially BTO-based MLCs, that oscillated alternately in between two copper heat sinks and a copper heat load thanks to the action of a motor (slapping machine). In such scenario, the load could only be cooled by 0.26 k, whereas the temperature of the heat sinks (\( T_s \)) remained to be the starting temperature because each sink was sufficiently massive.\textsuperscript{[23]} The reasons behind such low temperature difference were 1) heat regeneration was not implemented and 2) the MLCs used exhibited a low EC effect (0.3 k at 70 V). The authors measured 113 mJ of heat being pumped each half cycle, which corresponds to a cooling power of 12.7 W kg\(^{-1}\) (here we have considered that each plate had a total mass of 0.68 g and that the period was 26.46 s (13.23 s each half cycle)). After including and electric circuit to recover the charge by transferring it from two capacitors that operated in antiphase, the measured COP of the device increased almost a factor of three, from 2.9 to 8.4.

5.5. University of California Prototypes-Pei’s group

Pei’s group in the University of California presented in 2017 an EC prototype that did not require the circulation of a fluid nor the presence of extra solid elements to pump heat.\textsuperscript{[64]} Instead, they made use of electrostatic interaction to quickly move a flexible EC element between a heat source and a heat sink, as the two images in Figure 6g display. The EC element (EC polymer in the figure) consisted of two 30 \( \mu\)m thick PVDF layers of area 7 \( \times\) 3 cm\(^2\) sandwiched in between electrodes (active area of 5 \( \times\) 2 cm\(^2\)), with one side clamped at the heat sink and the other at the heat source. When the field is applied, electrostatic interaction brings the film in contact to the heat sink (top image in Figure 6g). When the field is removed, the film remains in contact with the heat source thanks to its flexibility (bottom image in Figure 6g). By doing this, almost the entire surface of the EC polymer stack is successfully put in thermal contact with either the sink or the source. Hence, heat flow and cooling power are maximized. At the applied field of 667 kV cm\(^{-1}\) (2000 V), such a device was able to reach a cooling power of 2800 W kg\(^{-1}\) (=150 times higher than previous works) and a measured COP of 13 without recuperating the energy in the depolarization process (the electric work was measured with an oscilloscope). Considering that the temperature span was 1.4 \( K\), this supposes a COP/COP\(_{\text{Carnot}}\) ratio of 6.1\%. When the aluminum heat sink and heat source were replaced by carbon nanotube-coated polyethylene terephthalate (PET) films (thickness of 100 mm), the temperature span increased to 2.8 \( K\)\textsuperscript{[64]} although the values of cooling power and COP were not reported in this case.

In 2020, an upgraded version of this work was presented.\textsuperscript{[33]} The authors developed a cascaded EC cooler with the aim to increase the temperature span of their previous device. In addition, the authors also integrated energy recovery to enhance the overall efficiency. The device consisted of four units of EC polymer stacks with the same electrostatic actuation described above, placed one on top of the other (Figure 6h), with a heat
flux sensor attached between the heat source and the EC polymer laminate. When attempting to measure the maximum cooling power \( (T_{\text{span}} = 0) \), a fin cooler was attached to the heat source, while a thick Aluminum block (6.3 mm) played the role of heat sink. On the other hand, when attempting to measure the maximum temperature span \( (T_{\text{span}} = 0) \), the loads were removed, and the bottom steel shim electrodes were replaced with thermally less conductive PET films. To pump heat from the source to the sink 1) adjacent EC polymer stacks were operated in an antiphase manner (in the figure, field applied to the EC polymer stacks in red, and not applied to the ones in blue, and vice versa), 2) the system oscillated between the two states shown in the images in Figure 6h. Furthermore, with this antiphase operation, charge could be transferred from one EC unit to the adjacent one, permitting the efficiency to be enhanced as shown previously.[23] By doing so, the authors managed to recover up to 70% of the electric work, reducing it from 29.2 to 8.76 mW cm\(^{-2}\). For an electric field applied of 600 kV cm\(^{-1}\) \((V = 3000 \text{ V})\), each EC unit displayed an adiabatic temperature change of 3.0 K, and the device showed a maximum temperature difference (no load conditions) between the heat sink and the heat source of 8.7 K. This result is remarkable considering that only four layers of PVDF with a total EC mass of 0.92 g were used (here we assume that each polymer stack has the same mass of 0.23 g reported in their previous work).[64] After obtaining a good agreement between experimental data and simulations, their model predicted temperature spans of respectively 12 and 14 K for six- and eight-layer prototypes. Returning to the four-layer device, a maximum cooling power of 90 mW cm\(^{-2}\) \((2140 \text{ W kg}^{-1})\), considering a total polymer stack area of 21.6 cm\(^2\) from their previous work,[64] was measured at 0 K temperature span, and the corresponding COP was 10.4. For a temperature span of 2.7 K, the cooling power was 78.5 mW cm\(^{-2}\) \((1850 \text{ W kg}^{-1})\) and the COP 9.0 \((\text{COP}/\text{COP}_{\text{Carnot}} 8\%)\). A numerical modeling based on real device operation scenarios showed that the COP/\text{COP}_{\text{Carnot}} ratio peaked at 12% for a temperature span of 6 K and a COP of 6. In comparison, their simulations showed a maximum COP/\text{COP}_{\text{Carnot}} of 3.8% for the unit device, different than the 6% reported in their previous work.[64] In all COP calculations, the authors assumed a charge recovery of \( \approx 70\% \) (as measured beforehand).

Recently, Pei’s group has proposed self-actuating EC fibers as a new potential kind of cooling device.[85] The fibers are composed of spray-coated PVDF on a conductive fiber that acts as core electrode. The outer electrode is obtained by coaxially coating single-walled carbon nanotubes on PVDF surface to keep the fiber flexible. After this process, the resulting EC fibers had a diameter of around 160 µm and were 8 cm long. The interesting feature of this kind of object (for which an ECE of 0.7 K has been reported at 1000 kV cm\(^{-1}\)) is its self-actuation effect, allowing it to commute between two different places, i.e., a heat source and a heat sink, without diminishing the EC performance. More interestingly, this avoids the use of any other additional driving mechanisms, such as pumps, motors or moving stages. Although the idea is still embryonic and unripe, these self-actuating EC fibers let envision the first ever active cooler in a thin fiber form factor, as the authors quoted.

5.6. Jožef Stefan Institute Prototypes

Based on previous theoretical studies utilizing finite-element modeling,[86] a cascade of two cantilevers made of bulk PMN/ Pt/PMN (Figure 6i) was presented by Barbara Malic’s group in 2021.[87] Similarly to Pei’s work, the system takes advantage of the electromechanical effect to bend the samples upon application of an electric field and establishes this way the required thermal contact to pump heat according to the cascading principle. Although previous simulations predicted a temperature span of 12.6 K in a 15-stage system (the EC effect of their samples was of 1.2 K, entailing a regeneration factor of more than 10),[86] the presented 2-stage experimental cascade exhibited a maximum temperature span of 0.05 K at 45 kV cm\(^{-1}\) and frequency of 1 Hz, which was found to be the optimal. At this applied field, the cantilever underwent an ECE of 0.5 K so that a regeneration factor of 0.1 was deduced. The authors explained that the difference between theory and experiment was caused by poor thermal contacts induced by surface roughness and bending radius of the cantilever, and by the limited frequency of 1 Hz, which was found to be optimum above 50 Hz in the modeling studies. Another important consideration that the modeling showed is that, under realistic conditions, a certain critical amount of active EC mass is needed to overcome the losses to the environment, implying that a device made only of 2 stages would never be enough. This issue is recurring in EC prototypes, where the desire to develop low-scale and miniaturized devices pushes them to be as small as possible.

6. Numerical Models

In this section, some of the numerical modelings on EC coolers are reviewed for completeness. They include both fluid and solid based. Note that some of these models[11-13,43,76,86] have been already disclosed in previous sections and hence are not described hereunder.

6.1. Fluid-Based EC Models

In 2014, Guo et al.[88] presented a 3D model of a fluid-based microscale AER utilizing finite elements (COMSOL Multiphysics software) (Figure 7). The AER parallel-plate matrix was 2 mm long and 1.25 mm wide, containing 5 x 10 µm thick plates made of PVDF (spaced 50 µm thanks to SU-8 spacers) and the heat transfer fluid HT-70. The motion of the fluid was carried out thanks to two diaphragms placed at the ends of the AER that were actuated electrostatically in an antiphase fashion. The temperature span of the device was externally imposed by defining the temperature of the cold and hot side so that the corresponding cooling power could be measured. For a given temperature span of 15 K and operating the device at a frequency of 20 Hz, the model reported a cooling power density (space-averaged heat flow on the cold end cross-section of the AER) of 3 W cm\(^{-2}\) and a COP/\text{COP}_{\text{Carnot}} of 31%. The authors mentioned as well that “the time lag between the electric field and the diaphragm motion was found to play an important role,” and that higher applied electric fields should lead the model to higher temperature spans and cooling power densities.
In 2021, a model of a fluid-based rotatory electrocaloric cooler using finite element software (ANSYS 18) was presented by Shi et al.\[89\] with the aim to demonstrate a large cooling capacity. The operation of such a system is sketched in Figure 8, where rotary in plane movement of a cylinder containing the EC material P(VDF-TrFE-CFE) is coupled with continuous unidirectional out of plane flow of a heat transfer fluid (HT-70) through the EC material and pipes. The simulated cylinder (with an inner diameter of 40 mm, outer diameter of 110 mm, and height of 200 mm) is divided into 12 even parts, and the EC material structured in 0.45 mm plates. The volume of the EC material in each EC unit is 170 cm$^3$, giving rise to a total EC mass of 3.6 kg. In this model, the EC effect was simulated with positive and negative heat pulses and adiabatic conditions were assumed at the exterior walls to thermally insulate the material from the environment. A cooling power of 290 W was calculated when the device was operated at a temperature span of 10 K and cycle period of 10 s. The COP under these conditions was of 5.5. Moreover, the authors observed that both cooling power and COP increase linearly with the applied electric field if the temperature span is maintained constant. As expected, shorter cycle periods largely increased the total cooling power, and after properly tuning the operational parameters, a maximum cooling power of 1730 W was reported. This envisions the possibility of designing EC devices able to operate in the kilowatt range.

Shortly after, the same team presented a complementary outcome of their rotatory electrocaloric refrigeration device.\[90\] This time, the target was to come up with compact and efficient devices for cooling applications where size and weight are the main priority. Hence, the rotary EC cylinder had an inner diameter of 4 mm, an outer diameter of 11.1 mm, and a height of 50 mm, and was evenly divided into two parts. Each of these parts contained 36 EC sheets (0.1 mm thick) and the fluid slits were set to 0.1 mm. In this work, the operation of different heat transfer fluids (water, HT-70, and silicone oil) was studied as well. Their results showed that when water is utilized, cooling power and COP are maximized, reporting a maximum cooling power of 9.89 W cm$^{-3}$ and a COP of 10.5 for a temperature span of 10 K. Interestingly, the lowest temperature of the cold-side heat exchanger was extracted when using silicone oil as the heat transfer fluid. This work suggests that, depending on the application needs, a different choice should be made to optimize performance, prioritizing water for higher cooling power demands, and silicone oil for colder temperatures at the cold side.

Aprea et al. have carried out several models of EC devices. They are all based on 2D representations of active regenerators. In 2016, a publication was presented studying the impact of different EC materials on the AER performance.\[91\] In 2017, a new AER model was presented based on the multicaloric material PbTiO$_3$, which is both electrocaloric (EC) and elastocaloric.
The authors operated the cooler at different fluid-flow rates while keeping the frequency and temperature span constant, showing that the highest COP could be obtained when the PbTiO$_3$ underwent exclusively eC effects. On the other hand, operating the device so that both elastocalorics and electrocaloric effects of PbTiO$_3$ are combined increased the cooling power by around 65% with respect to the single electrocaloric or elastocaloric operation. In 2018, the performances of different caloric materials, including EC materials such as P(VDF-TrFE-CFE)/BST polymer, 0.93PMN-0.07PT thin films, Pb$_{0.97}$La$_{0.02}$(Zr$_{0.75}$Sn$_{0.18}$Ti$_{0.07}$)O$_3$ or Pb$_{0.8}$Ba$_{0.2}$ZrO$_3$ were studied and compared.$^{[93,94]}$ In 2019, they completed the study by analyzing the influence of novel heat transfer fluids such as Al$_2$O$_3$–water nanofluids.$^{[95]}$ The authors concluded that with this kind of fluids the caloric coolers could notably improve their performance.

### 6.2. Solid-Based EC Models

A numerical modeling of a rotatory EC prototype was presented in 2015 by Zhang’s team based on finite element simulations. The system consisted of two EC rings (outer diameter 20 mm, inner diameter 2 mm) placed one on top of the other with 16 EC elements each as shown in Figure 9a. The material of the EC elements was poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) (P(VDF-TrFE-CFE)) terpolymer with $k = 0.2$ W m$^{-1}$ K$^{-1}$, $\rho = 1500$ J Kg$^{-1}$ K$^{-1}$, and $\rho = 1800$ kg m$^{-3}$ that were kept constant with respect to the temperature in the simulations. Note that, contrary to other systems, the device did not utilize any external heat transfer substance to regenerate heat. Instead, 1) the 2 EC rings were rotated coaxially with the same speed but in opposite directions and 2) the electric field was applied only to half of the EC elements in the ring, as shown in the figure. Note that the regions where the electric field is applied in the top and bottom rings are complementary to each other, so that heat is always transferred between the EC rings. Also, the rotation of the two EC rings is done in a stepwise fashion meaning that the two EC rings rotate by a certain angle (given by the number of EC elements in the ring, $N_e$) so that EC elements in the top and bottom rings are vertically aligned. After each rotation step, the two rings remain still for some time to allow heat to be transferred. After that, the two rings undergo another rotation step, and so on and so forth. The predicted temperature span is plotted as a function of the EC temperature change in Figure 9b showing that a regeneration factor ($\Delta T_{\text{span}}/\Delta T_{\text{EC}}$) of 10 is expected when the EC rings are discretized down to 20 elements. Further simulations reported a cooling power density of 37 W cm$^{-3}$ for a temperature span of 20 K and a COP/COP Carnot of 57%. The authors attempted an experimental version of this device in 2018 (see Section 5) utilizing BaTiO$_3$-based multilayer capacitor ceramics as the EC working material.$^{[63]}$ Under an electric field of 165 kV cm$^{-1}$ (200 V), these EC samples showed an EC magnitude of 0.9 K, and a maximum $T_{\text{span}}$ of 2 K was experimentally measured at a rotation speed of 5 rounds per minute.

In 2015, Smullin et al.$^{[96]}$ presented a model for a heat-switch-based heat pump utilizing EC multilayer capacitors (MLCs). Given a target temperature span and cooling power as well as the size of the MLCs and heat switches, their model was able to predict the amount of the needed EC mass, heat switch area, and number of samples required to be stacked in series.

Other analytical and numerical models of EC devices can be consulted elsewhere.$^{[97–100]}$

### 6.3. Hints, Guidelines, and Conclusions

This work summarized the performance and design of all EC coolers proposed to date with the aim to condensate the different works and efforts in one single catalog. Second, we have sorted the EC coolers in two main categories: those based on the circulation of an external fluid and those that utilize exclusively solid elements. In addition, some numerical models of EC devices have been revised as well for completeness.

Up to now, fluid-based EC prototypes have shown the best performances in terms of temperature spans and regeneration factors, proving that temperature differences larger than 10 K are

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**Figure 9.** a) Sketch of a modeled rotatory EC cooler. The device consists of 2 rings, each containing 16 EC elements (T1–T16 for ring on the top, and B1–B16 for ring on the bottom) and 4 heat exchangers (at T1 and B1, where heat is rejected, and at T9 B9 here heat is absorbed). The electric field $E$ is applied only to half of each ring in complementary regions, i.e., wherever the field is applied on the top ring, it is not in the bottom ring, and vice versa. b) Temperature span $\Delta T_{\text{span}}$ predicted by the model as a function of the EC effect $\Delta T_{\text{EC}}$ for different number of EC elements $N_e$ in each ring. Adapted with permission.$^{[84]}$ Copyright 2014, AIP.
This kind of prototypes remain still today the handiest ones because their principle is well known, thermal contacts are maximized by default and their structure is easier and simpler to implement. In addition, the resulting coolers are robust, what makes their industrial development more plausible. On the other hand, cooling powers in fluid-based prototypes have been scarcely reported, and those who did, did not show competitive figures. The reason is mainly due the dielectric fluids in use, exhibiting poor thermal properties that limit heat transfer. The utilization of water instead (which requires electric insulation of the EC samples and connections) is key to raise these values and reach performances in the same order than MC and EC fluid-based devices, where cooling powers around 100–1000 W kg⁻¹ of caloric material have already been reported. In addition, thinner and more regularly shaped EC samples should enhance heat transfer, allowing for higher cycle frequencies and minimizing the contributions of parasitic heat losses. Similarly, prototypes’ efficiency in fluid-based prototypes has not been investigated yet and magnitudes such as COP and COP/COP Carnot have not been reported. The disadvantages of fluid-based prototypes are 1) the volume of inactive heat transfer fluid lowers performance and requires the presence of a pump, 2) higher cycle frequencies, which require large flow rates, are challenging to deploy because of the fluidic nature and potential turbulences, which promotes degradation of the temperature gradient. Despite these limitations, there is enough evidence to consider that fluid-based prototypes have still room for improvement, and that their performances have not reached yet their limit.

Although nine solid-based prototypes have already been presented, they remain a less common and known type in the caloric materials field. Their performances in terms of temperature span have not been as impressive as the best fluid-based, with none of them crossing yet the 10 K barrier (though 8.7 K has been recently reported). However, the amount of active mass used in these works has been exceptionally low (cf., Table 2) and higher temperature spans are soon expected if researchers make it possible to stack more stages in their prototypes. On the other hand, the lack of a fluidic media has permitted conducting more accurate and reliable analysis on cooling power (and thus efficiency), reporting up to 2800 W kg⁻¹ of EC material and COPs ≈ 10 (COP Carnot ≈ 10%). These numbers are equivalent to the ones displayed by the best EC and MC coolers. Of particular interest are the multistage and cascading designs, which seem to be the most adequate working principle for solid-based devices because they do not require any external element to pump heat and the activation mechanisms have negligible power consumptions. While these approaches are unique and very promising, the engineering of their designs is complex and delicate, and there are still some limiting factors that should further be improved such as the high thermal resistance typically seen in solid–solid interfaces due to poor thermal contact. A solution to that are flexible surfaces bounded by electrostatic attraction, as PVDF can provide, but even in these cases heat transfer remains limited by the low thermal conductivity of EC materials. Higher thermal conductivities should enable employing higher cycle frequencies and lowering the contributions of parasitic heat losses. At the same time, the latter can be reduced by developing better insulation, such as vacuum surroundings. To increase cooling power, thicker samples could be needed, although this implies higher applied voltages (if multilayers samples are not contemplated) and degradation of heat exchange.

Common to both fluid and solid-based devices, enlarging the active thermal mass of the EC prototypes, increasing their breakdown field for higher applied fields, or just developing new EC materials with more pronounced EC effects would infer an enhancement of the overall prototype’s performance in all directions. Finally, fatigue-life of EC samples needs to be addressed so that future EC coolers can stand the number of cycles that practical cooling applications require (∼10⁶ cycles). In these regards, Fulanović et al. shown in 2017 that common EC material Pb(Mg₁/₃Nb₂/₃)O₃ (PMN-10PT) in the form of multilayer capacitors could be a good candidate, exhibiting almost no degradation of the EC effect (less than 1%) after 10⁶ unipolar cycles at the electric field change of 110 kV cm⁻¹. Similar findings were reported by Del Duca et al. in 0.9Pb(Mg₁/₃Nb₂/₃)O₃−0.1PbTiO₃ (PMN-10PT) bulk relaxor ferroelectric although the authors mentioned as well that some of their samples underwent premature failure and hence further improvements are required. Interestingly, Bradesko et al. showed in 2019 that the degradation of the EC properties could be related to an increase of grain boundary conductance caused by the electric-field-induced-phase-transition. According to the authors, this is a new fatigue mechanism that “provides the first guidelines for the integration of high-performance relaxors into cooling devices”.

To conclude, it is often discussed whether the reported COPs include all meaningful power contributions extrinsic to the EC effect (as motors, pistons, pumps, etc.) or not. At the stage that EC cooling is found today, we believe that counting exclusively the EC effect power should be enough to foresee the potential of the technology in terms of its energy efficiency and whether it is plausible or not to envision systems like this in the market in the coming years. However, reporting COP with all kinds of power contributions as well is interesting because it would help having a better picture and provide the readership with a fairer comparison between the different working principles, kinds of prototypes and caloric families, since different instrumentation and machinery have been used for each case. Thus, we encourage coming works to provide the two kinds of COP values.

EC cooling, and caloric cooling in general, has navigated through a striking journey in recent years, achieving great advances and milestones that have caught attention. Despite these accomplishments, only further research, development, and especially support from industrial partners will tell whether real applications will come out of this, and whether these products will have the desired impact on our society and planet.

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Conflict of Interest

The authors declare no conflict of interest.
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caloric cooling, electrocaloric prototypes, heat regeneration, solid-state cooling

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[1] IEA, The future of cooling, https://www.iea.org/reports/the-future-of-cooling (accessed: May 2021).
[2] R. Radermacher, Y. Wang, Vapor Compression Heat Pumps with Refrigerant Mixtures, 1st ed., (Ed: Y. Hwang) CRC Press, 2005.
[3] A. Shakouri, Y. Zhang, IEEE Trans. Compon. Packag. Technol. 2005, 28, 65.
[4] Benefits of Leapfrogging to Superefficiency and Low Global Warming Potential Refrigerants in Room Air Conditioning, https://eta-publications.lbl.gov/sites/default/files/lbnl-1003671.pdf (accessed: December 2021).
[5] G. J. M. Velders, D. W. Fahey, J. S. Daniel, M. McFarland, S. O. Andersen, Proc. Natl. Acad. Sci. USA 2009, 106, 10949.
[6] UNIDO, Mapping the HFC phase-down, https://www.unido.org/sites/default/files/2020-04/UNIDO_brochure_HFC-Phase_Down-Complete.pdf (accessed: December 2021).

J. Tušek, K. Engelbrecht, D. Eriksen, S. Dall’Olio, J. Tušek, N. Prı́,s, Nat. Energy 2016, 1, 16134.

P. Lloberas, A. Aznar, M. Barrio, P. Negrier, C. Popescu, A. Planes, L. Maňosa, E. Stern-Taulats, A. Avramenko, N. D. Mathur, X. Moya, J. L. Tamait, Nat. Commun. 2019, 10, 1803.

B. Li, Y. Kawakita, S. Ohira-Kawamura, T. Sugahara, H. Wang, J. Wang, Y. Chen, S. I. Kawaguchi, S. Kawaguchi, K. Obara, K. Li, D. Yu, R. Mole, T. Hattori, T. Kikuchi, S. Ichiro Yano, Z. Zhang, Z. Zhang, W. Ren, S. Lin, O. Sakata, K. Nakajima, Z. Zhang, Nature 2019, 576, 506.

B. Nair, T. Usui, S. Crossley, S. Kurdi, G. G. Guzmán-Vерri, X. Moya, S. Hirose, N. D. Mathur, Nature 2019, 575, 468.

A. Torelló, P. Lhéritier, T. Usui, Y. Nouchokgwe, M. Cérard, O. Bouton, S. Hirose, E. Defay, Science 2020, 370, 125.

Y. Wang, Z. Zhang, T. Usui, M. Benedict, S. Hirose, J. Lee, J. Kalb, D. Schwartz, Science 2020, 370, 129.

Y. Meng, Z. Zhang, H. Wu, R. Wu, J. Wu, H. Wang, Q. Pei, Nat. Energy 2020, 5, 996.

X. Moya, N. D. Mathur, Science 2020, 370, 797.

X. Moya, S. Kar-Narayan, N. D. Mathur, Nat. Mater. 2014, 13, 439.

J. Shi, D. Han, Z. Li, L. Yang, S. G. Lu, Z. Zhong, J. Chen, Q. M. Zhang, X. Qian, Joule 2019, 3, 1200.

L. Maňosa, A. Planes, M. Acet, J. Mater. Chem. A 2013, 1, 4925.

S. Fähler, U. K. Rößler, O. Kastner, J. Eckert, G. Eggeler, H. Emmerich, P. Entel, S. Müller, E. Quandt, K. Albe, Adv. Eng. Mater. 2012, 14, 10.

M. Ožbolt, A. Kitanovski, J. Tušek, A. Poredoš, Int. J. Refrig. 2014, 40, 174.

A. Kumar, A. Thakre, D.-Y. Jeong, J. Ryu, J. Mater. Chem. C 2019, 7, 6836.

E. Defay, S. Crossley, S. Kar-Narayan, X. Moya, N. D. Mathur, Adv. Mater. 2013, 25, 3337.

X. Moya, E. Defay, V. Heine, N. D. Mathur, Nat. Phys. 2015, 11, 202.

E. Defay, R. Faye, G. Despesse, H. Strozyk, D. Sette, S. Crossley, X. Moya, N. D. Mathur, Nat. Commun. 2018, 9.

P. Vales-Castro, R. Faye, M. Vellvehi, Y. Nouchokgwe, X. Perpiñá, J. M. Caicedo, X. Jordà, K. Roleder, D. Kajewski, A. Perez-Tomas, E. Defay, G. Catalan, Phys. Rev. B 2021, 103, 54112.
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