

PERSPECTIVE

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# New approach to waste-heat energy harvesting: pyroelectric energy conversion

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## Abstract

Harvesting waste heat for useful purposes is an essential component of improving the efficiency of primary energy utilization. Today, approaches such as pyroelectric energy conversion are receiving renewed interest for their ability to turn wasted energy back into useful energy. From this perspective, the need for these approaches, the basic mechanisms and processes underlying their operation, and the material and device requirements behind pyroelectric energy conversion are reviewed, and the potential for advances in this area is also discussed.

Power generation processes are plagued by inefficiencies and reject approximately two-thirds of the primary energy produced as waste heat<sup>1</sup>. A significant portion of this waste is low-grade heat (generally below 100–230 °C), which is both ubiquitous and underutilized. The recovery of this waste heat for energy generation, however, is limited due to the poor efficiency of energy harvesting systems working with small temperature differentials that are well below the fundamental Carnot limit. Solid-state approaches to harvest this energy, like thermoelectrics<sup>2</sup>, are generally limited by their relatively low figures of merit (FoM) for energy conversion below 100 °C. Vapor-based organic Rankine cycles (ORC) have been demonstrated to be cost effective at a large scale but become cost prohibitive at low powers due to turbine inefficiency<sup>3</sup>. In turn, research is driven by a need to develop techniques that convert low-grade waste heat with high fractions of Carnot efficiency<sup>4,5</sup>. Here, we discuss an approach to do just that—pyroelectric energy conversion (PEC).

Pyroelectrics constitute a class of noncentrosymmetric polar crystals that exhibit an inherent coupling between

electrical polarization  $P$  and temperature  $T$ , such that a change in temperature results in a change in the electric dipole moment or a pyroelectric effect (PE) (Fig. 1a), which is quantitatively described by the pyroelectric coefficient,  $\pi = \left(\frac{\partial P}{\partial T}\right)$ . Since the PE manifests as a temperature-dependent change in the surface-charge density, PEs can also be generated via the temperature-dependence of the dielectric permittivity, thermally induced strain in piezoelectric materials<sup>6</sup>, and flexoelectric effects<sup>7</sup> from thermal gradients in all materials. Ferroelectrics are a subset of pyroelectrics that can switch polarization under an applied electric-field and exhibit some of the largest PEs near their phase-transition temperatures, thus often forming the basis of modern PEC devices.

Unlike thermoelectrics that utilize a spatial-temperature gradient, PEC requires a temporal variation in temperature  $\left(\frac{\partial T}{\partial t}\right)$ , making PEC highly desirable in instances where temperature gradients are either difficult to establish or the temperature of the heat source is fluctuating. These temperature changes result in a pyroelectric current  $i_p = \pi A \frac{dT}{dt}$ , where  $A$  is the area of the device, which means performance scales with the area, not the volume, of a material. This fact leads to a number of potential advantages for thin-film-based devices and thus motivates our focus on materials at such geometries here. To actually harvest waste heat, a PEC device mimics a

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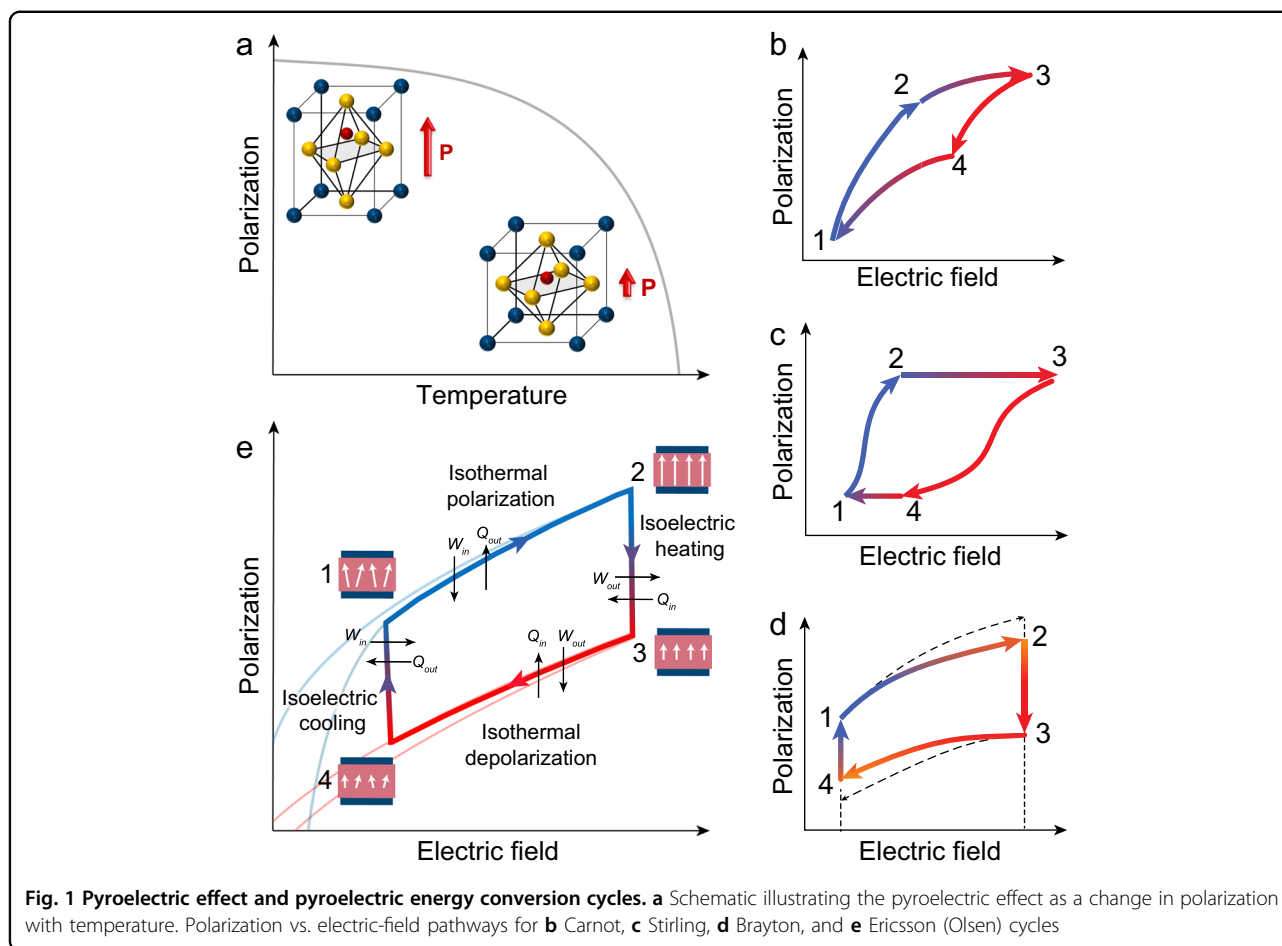
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thermodynamic heat engine. The polarization is analogous to the volume, and the electric-field is analogous to the pressure of the working fluid. A variety of thermodynamic cycles<sup>8</sup> have been proposed for PEC and are distinguished by their polarization vs. electric-field (*P*–*E*) pathways. While it is possible to envision a Carnot cycle (i.e., two adiabatic (2 → 3, 4 → 1) and two isothermal (1 → 2, 3 → 4) processes, Fig. 1b), realization of adiabatic processing in a ferroelectric is difficult, making these cycles impractical. Stirling (i.e., two isodisplacement (2 → 3, 4 → 1) and two isothermal (1 → 2, 3 → 4) processes, Fig. 1c), Brayton (i.e., two isoelectric (2 → 3, 4 → 1) and two adiabatic (1 → 2, 3 → 4) processes, Fig. 1d), and Ericsson (or Olsen) cycles (i.e., two isothermal and isoelectric processes, Fig. 1e), are used in various situations depending on the sample geometry and heat source<sup>8,9</sup>. The Olsen cycle has been most widely employed and has been demonstrated to produce some of the highest PEC efficiencies, defined as:<sup>10</sup>

$$\eta = \frac{\oint EdP}{\int_{T_L}^{T_H} C(T)dT + Q_{ECE}} \cong \frac{\oint EdP}{\int_{T_L}^{T_H} C(T)dT} \quad (1)$$

where *C*(*T*) is the heat capacity, *T<sub>H</sub>* (*T<sub>L</sub>*) is the temperature for the heat source (heat sink),  $\oint EdP$  is the net electrical work done (*W<sub>E</sub>*), and *Q<sub>ECE</sub>* is the electrocaloric work. Since the vibrational entropy change (associated with the heat capacity) is typically much larger than the dipolar entropy change, the electrocaloric work can be ignored in the denominator of Eq. (1), which represents the heat input. The FoM for PEC<sup>11</sup> is thus  $FoM_{PEC} = \frac{\pi^2 T}{C \epsilon_0 \epsilon_r}$ ; therefore, a large PEC efficiency requires independently enhancing  $\pi$  and reducing dielectric permittivity  $\epsilon_r$ .

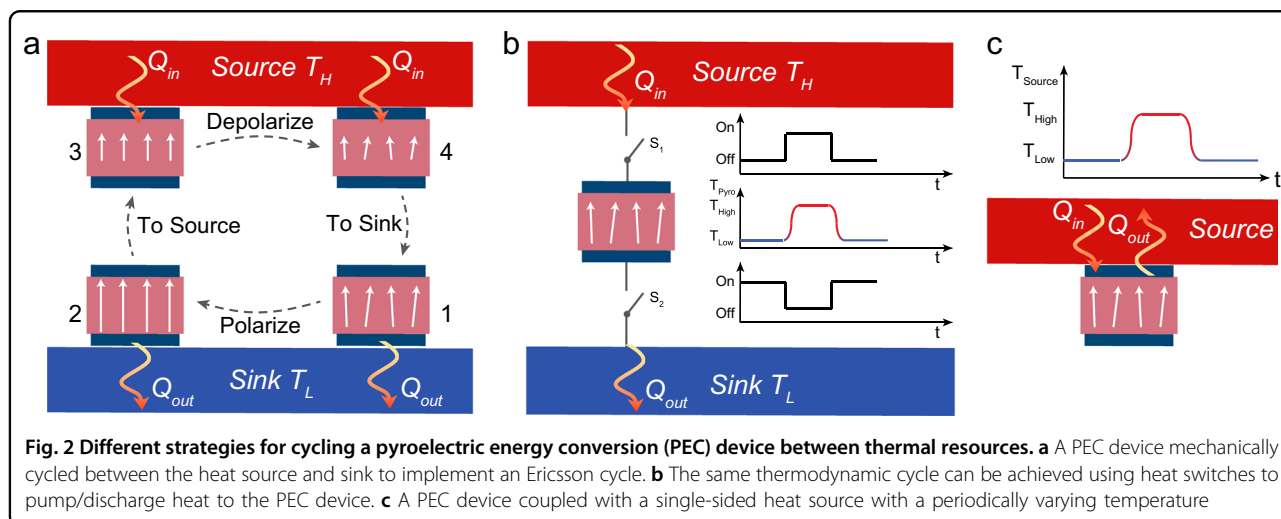
The second-order derivatives of the free energy typically diverge in the vicinity of phase transitions; thus, positioning the material at the brink of a ferroelectric-to-paraelectric phase-transition (Curie temperature, *T<sub>C</sub>*) serves as a route to enhance the intrinsic  $\pi$ . Consequently, considerable effort has focused on tuning *T<sub>C</sub>* via the chemistry<sup>12</sup>, hydrostatic pressure<sup>13</sup>, or epitaxial strain<sup>14</sup> in the case of thin films. In addition, transitions between various ferroelectric phases can result in polarization rotation (e.g., in proximity to a morphotropic phase boundary) that can result in divergence of the surface-charge density. The order of these phase transitions is important. First-order transitions, despite having a steep

change in the polarization with respect to temperature (large  $\pi$ ), are associated with a wasteful temperature hysteresis that limits the operating temperature regime. Second-order transitions (usually the case under a large electric-field and for clamped thin films) circumvent thermal hysteresis but are associated with a relatively smaller magnitude of  $\pi$ , leaving the ultimate choice of material (first- vs. second-order) to be jointly optimized with the operating temperature range. The increase in the dielectric constant and specific heat around the phase-transition can reduce the overall benefit of any increase in intrinsic  $\pi$ , as seen in the equation for the  $FoM_{PEC}$ . Increasing the power density of the device often necessitates the application of high electric fields that also tend to dampen first-order transitions. Direct measurements of the PE have also shown a reduction in the PEC at low electric fields for polydomain thin films and that non-intrinsic effects can have the same order of magnitude as intrinsic effects<sup>15,16</sup>.

Temperature perturbations change the polar structure/order not only at a unit-cell level (i.e., the *intrinsic* response) but also at a mesoscopic level (e.g., domain structures). Prior work on polydomain ferroelectric thin films has shown that the temperature-dependent motion of ferroelastic domains can result in enhancements to the PE via so-called *extrinsic* contributions<sup>17</sup>. In turn, research is focused on identifying systems with large structural phase instabilities and engineering novel domain structures that respond dramatically to temperature. For example, temperature-induced competition between various classical ferroelectric and toroidal polar-vortex phases in  $PbTiO_3/SrTiO_3$  superlattices<sup>18</sup> and mixed-phase hierarchical domain structures in tetragonal  $PbZr_{1-x}Ti_xO_3$ <sup>19</sup> offer exciting opportunities to enhance extrinsic contributions. Thin films are also mechanically clamped to their substrate, and the thermal expansion

mismatch between the film and the substrate results in *secondary* contributions to the PE, which are mediated by piezoelectricity. Unlike the intrinsic contribution, the secondary contribution may be either negative or positive, enhancing the PE in the former and suppressing it in the latter case<sup>17</sup>. Accordingly, the use of “unclamped” microfabricated or free-standing architectures could offer new possibilities for a large  $\pi$  and PEC.

As noted, PEC requires the implementation of thermodynamic cycles using a solid-state device. These devices are generally structured around a pyroelectric capacitor with auxiliary structures dedicated to thermal/electrical management. The active material in a PEC device is coupled to electrical and thermal waveforms, resulting in *charge*  $\rightarrow$  *heat*  $\rightarrow$  *discharge*  $\rightarrow$  *cool* cycles that produce electric work. For any cycle (Fig. 1b–e), electric-field cycling with a large magnitude is readily achieved in thin-film devices and is mainly limited by the charge-discharge electrical losses, which scale with the cycle frequency, loss tangent, dielectric constant, and DC electrical losses<sup>20</sup>. Producing temperature oscillations, however, presents a more interesting challenge. This results in PEC devices falling broadly into two categories based on the nature of the thermal resources available: those that induce periodic heating from two static temperature reservoirs (Fig. 2a, b) and those that couple to a single, time-varying heat source (Fig. 2c). In both cases, the PEC device can be optimized for maximal efficiency, energy density, or power density. Application of large electric fields leads to high-energy densities and efficiencies<sup>21</sup> that are always limited by  $\eta_{Carnot}$ . The power density, however, is governed by the combined electrical and thermal-time constant,  $\tau$ , of the PEC device, where the maximum power  $P_{max} = W_E f_{max} = W_E / \tau$  and  $f_{max}$  is the maximum cycling frequency. The thermal-time constant can be much larger than the electrical-time constant



and is, therefore, the limiting factor in achieving a large power density. Neglecting contact resistance between the heat source and the PEC device,  $\tau_{thermal} = L^2/\alpha$ , where  $L$  and  $\alpha$  are the thickness and thermal diffusivity of the device, respectively. It follows that  $P_{max} = W_E/\tau_{thermal} \propto 1/L^2$  and thus thin-film devices<sup>21</sup> inherently have a better power density than bulk devices<sup>22</sup>. This was demonstrated recently, where thin-film relaxor ferroelectrics<sup>21</sup> achieved a power density that is 3 orders of magnitude larger than that of bulk versions<sup>22</sup> despite having an energy density that is only one order of magnitude larger. Looking forward, it appears that thin-film geometries are promising for future PEC device design.

Despite advances in the energy and power densities, much needs to be done to enhance the efficiency of the PEC process. The high specific heat of pyroelectric materials results in more heat energy absorbed than electrical dipolar energy gained. Although the lattice always dominates PEC conversion physics, regenerative schemes employing multi-staged heat reservoirs have been proposed to reduce the total heat input and thus increase efficiency<sup>10</sup>. This device, however, must operate quasistatically; thus, the power density (and utility) suffers. Instead of seeking reversible devices, investigators have, therefore, focused on different energy harvesting cycles (e.g., Ericsson and Brayton) to maximize performance. Recent efforts have, however, moved even further by considering, for example, hybrid cycles. In this spirit, combined piezo/pyroelectric devices have demonstrated larger maximum output voltages<sup>23–25</sup>, and others have even fabricated thin films capable of harvesting solar, thermal, and mechanical energies<sup>26</sup>. Combined ferro-/antiferroelectric cycles have been realized in a single device, taking advantage of the bidirectional nature of the pyroelectric coefficient in these materials<sup>20</sup>. These hybrid generators aim to increase device performance by integrating systems to maximize the extractable energy between two temperature extrema. Within the conventional PEC approach, there are several opportunities for improving performance. At a bare minimum, there is a need for a targeted design of materials tailored to a specific waste-heat source. Beyond this, it is possible to minimize heat losses to auxiliary structures (e.g., through the use of free-standing films) or to combine corresponding effects arising from pyromagnetism (via multi-ferroic and magnetoelectric materials) to enhance overall performance.

Ultimately, the development of modern PEC materials and devices is poised for a renaissance. Advances in our ability to accurately measure materials<sup>27</sup>, focus on the design of high-performance pyroelectrics, and production of nanoscale device structures offer unprecedented access to innovation. These developments enable further investment in a burgeoning field, the formation of a robust

research community, and a sustained research effort like that seen in thermoelectrics. Today marks the beginning of a time of great development for pyroelectric materials and their application in the field of PEC.

#### Acknowledgements

We acknowledge the support of the Army Research Office under grant W911NF-14-1-0104; the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award Number DE-SC-0012375 and the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-AC02-05-CH11231 (Materials Project program KC23MP); and the National Science Foundation under grants CMMI-1434147, DMR-1451219, OISE-1545907, DMR-1608938, DMR-1708615, and DGE-1752814.

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#### Conflict of interest

The authors declare that they have no conflict of interest.

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Received: 27 August 2018 Revised: 8 February 2019 Accepted: 7 March 2019

Published online: 07 June 2019

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