Relaxor Ferroelectric Polymer Based Electrotexile
for Thermal Management of Soldiers with Protective Gears

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Synthetic Multifunctional Materials (SMFM)

Point of Contact

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A. Executive summary

Recent experimental evidence and basic material considerations indicate the existence of large electrocaloric effect in the multifunctional relaxor ferroelectric polymers. We propose to develop a novel class of electrotextiles for thermal management based on the multifunctionality of this newly developed ferroelectric polymers -- the large electrocaloric effect to change the entropy of the system, the large actuation capability to move the heat, and dependence of the dielectric constant on temperature as temperature sensors. In addition, we propose a novel concept of combining the electrocaloric effect of the relaxor ferroelectric polymer with the micro-heat-transfer process used in the thermoacoustic engine to develop an electrotextile cooling system, that transfers heat from the cold end to the hot end through a polymer fiber or ribbon. The synthetic multifunctional material (SMFM) technology developed in this program is directed towards DoD applications, such as the thermal management (cooling) of soldiers in battlefield wearing biologic and chemical gears. The flexible electrotextile can be easily integrated into the biologic and chemical gears. By using a dielectric material as the refrigerant, the applied field will not produce extra-heat during the operation which could lead to high efficiency. The development of such a multifunctional material system for thermal management will also have great impact on many military and high-tech applications such as on-chip cooling. In reverse, this SMFM technology may also be used for the thermal energy harvesting.

The proposed effort is planned as a forty-eight (48) month program with two phases. Phase I effort, with a duration of 18 months, will focus on material development and exploration of novel design concepts for electrotextile cooling systems. Phase II, with a duration of 30 months, will integrate the resulting technologies into an electrotextile cooling system for the thermal management of soldiers in battlefields.

A Consortium has been established to accomplish these goals. There are four team members participating in Phase I:

- The Pennsylvania State University
- Massachusetts Institute of Technology
- University of Massachusetts at Dartmouth
- Institut Franco-Allemand de Recherches de Saint-Louis (ISL) of France

Dr. Qiming Zhang of Penn State is a leading researcher in US in the electroactive materials and their related devices. He was the first to conceive the idea of exploiting molecular conformation change in PVDF based ferroelectric polymers to realize large electrostrictive strain. More recently, based on molecular consideration, he also proposed and demonstrated fully functional polymers, exhibiting very high dielectric constant (~1000) and electromechanical strain. He will be responsible for materials development and material integration with electrotextile cooling device. Dr. J.L. Smith and Dr. J.G. Brisson of the Cryogenic Engineering Laboratory at the Massachusetts Institute of Technology have developed and worked on many new types of refrigeration systems and power systems including Stirling refrigeration, superfluid Joule-Thomson refrigeration and superconducting power generators. They will spearhead the effort for developing a self-consistent thermodynamic analysis for the proposed cycles as well as predicting and characterizing the performance of the devices developed as part of this effort. Dr. Calvert is a recognized leading researcher in smart textiles, embedding of ferroelectric polymer sensors in composites and freeform fabrication of many materials. He will be responsible for developing the electrotextile using the relaxor ferroelectric polymers. In this program, the composition of the relaxor ferroelectric polymer will be varied in order to optimize the properties related to the room temperature refrigeration. The synthesizing of these relaxor ferroelectric polymers at different compositions will be carried out by Dr. Francois Bauer. Dr. Bauer is the director of research in the field of ferroelectric polymers and piezoelectric materials at Institut Franco-Allemand de Recherches de Saint-Louis (ISL), France. He has made many important contributions to the ferroelectric based materials and devices. His group has recently developed a unique capability for synthesis of the relaxor ferroelectric terpolymer, to
be used in this project. They can now routinely synthesize these polymers in relatively large batch (2 kg/batch), that makes it possible for these polymers to be used for the prototype devices and scaling up to large quantity device production. In the phase II of the program, we will also address the issues of large scale fabrication of the electrotextile cooling system, the integration with the DoD applications, and the electric driving circuits for energy recovery. QorTek, a research and development company specializing in micro-devices, flexible electronic substrates, and high power, high efficiency drives for reactive loads, will join the program in Phase II. QorTek brings the expertise of power electronics and flexible electronics to the energy recovery electric driving systems, to recycle 95% to 99% of reactive power.

B. Technical Section

B. 1. Introduction

Military and other high technology systems are in general systems of complex integration of parts in the thousands-to-millions count range. The development and utilization of Synthetic Multifunctional Materials (SMFM) which are a class of novel materials designed and processed to provide multiple performance capabilities in a single material can result in drastic weight reduction, higher level of performance, great flexibility in design, reduction in complexity in manufacture, maintenance and repair, and improvement in reliability of these systems.

Ferroelectric materials are intrinsically multifunctional and have found a broad range of applications. However, the low responses in traditional ferroelectric materials limit the performance of these devices and systems. As has been observed in many ferroelectric materials, by operating near the instability regions such as ferroelectric-paraelectric (F-P) transitions, many of these responses can be significantly enhanced. On the other hand, phase transition occurs over a narrow temperature range and, in most cases, involves large hysteresis, preventing these enhanced responses from practical and general applications.

We propose to develop a multifunctional electrotextile based on the newly developed relaxor ferroelectric polymers, the terpolymers of P(VDF-TrFE-CFE). This new class of ferroelectric polymers was developed from the normal ferroelectric PVDF polymer by employing proper defect modifications that eliminate detrimental effects associated with a normal first order F-P transition while maintaining high material responses. This class of electroactive polymers, in recent years, has been demonstrated to have many unique and superb properties compared to other polymers. The terpolymer exhibits high electrostrictive strain (>7% strain) with relatively high modulus (>0.3GPa). The high room temperature dielectric constant (~ 50, the highest among all the known polymers), high induced polarization (~ 0.1 C/cm²), and high electric breakdown field (>400 MV/m) lead to very high volume efficiency for the electric energy storage operated under high voltage (~ 10 J/cm³). The large entropy change associated with the polarization change in the material also makes it unique as a ferroelectric material which will be exploited in this project for the electrotextile cooling systems.

Specifically, we seek to develop an electrotextile cooling system using flexible ribbons based on the multifunctionality of the relaxor ferroelectric polymer – the large electrocaloric effect to change the entropy of the system, the large actuation capability to transport the heat, the self-temperature sensing using the temperature dependence of the dielectric constant, and that the relaxor ferroelectric polymer ribbons (see figure 1) can be woven into a textile. The goal of this proposed effort
is to develop an electrotextile cooling system suitable for the thermal management of soldiers in battlefield wearing chemical-biological protective gears (see figure 2). In the proposed cooling system, the relaxore ferroelectric polymer ribbons will be woven into a textile, while performing various functions to achieving high efficiency cooling. For such an application, the electrotextile should be able to pump 300 watts between 50 °C and 20 °C, which, as will be shown in this proposal, is achievable. The successful development of this innovative approach will also have great impact on the solid state refrigeration technology, which will have a wide range of applications including on-chip cooling, temperature regulation of bio-chips, and other high-tech applications.

It is also interesting to make a comparison with the traditional thermoelectric cooling device (a solid state cooler) based on Peltier effect. Due to the large DC current required to remove the heat, large amount of extra-heat is generated in the device. For example, using the typical COP (coefficient of performance) of 0.4 to 0.7, pumping 1 watt heat from the cold end will generate 2.4 watts to 3.5 watts of heat at the hot end. That means that there is extra-heat of 1.4 watts to 2.5 watts input from the driving electric circuit to the cooling device, undesirable for many military and high-tech applications. In contrast, the operation of the proposed electrotextile cooling system is based on a dielectric material and the applied electric field will not generate much heat (except the dielectric loss which is orders of magnitude smaller than the DC current heating in the Peltier devices) during the operation.

**B. 2. Large electrocaloric effect in the multifunctional relaxor ferroelectric polymers**

Electrocaloric effect, which is the electric field induced temperature change in a dielectric material, has been investigated in the past. It has been shown that the electrocaloric effect in lead-scandium tantalate ceramic (PST) can produce an adiabatic temperature change of 1.3-1.5 °C, the best value obtained to date in inorganic materials. The basic principle of the electrocaloric effect is illustrated schematically in figure 3. Application of an electric field to a dielectric material induces ordering of the polarization (entropy reduction), which leads to heating or the ejection of heat from the material. In the reverse process, removing the applied electric field lowers the ordering of the polarization (entropy increase), which leads cooling or absorbing heat from the surrounding. A material with a large electrocaloric effect, that is, a large entropy change induced by electric field, is required to achieve an effective solid state electric cooling device. Because the origin of the field induced entropy change is due to the change of dipoles (polarization), there are advantageous to working with ferroelectric materials, which provide most effective coupling between the applied field and polarization change. In addition, in order to induce large polarization change, it is necessary to operate the device based on ferroelectric materials in a temperature...
region just above a ferroelectric (polarization ordered phase)-paraelectric (polarization disordered phase) (F-P) transition where an electric field induced F-P phase change can result in a large polarization change and consequently large entropy change. Indeed, relatively large electrocaloric effect has been observed in ferroelectric materials and the early investigations in PST ceramics have indicated that it is in the F-P temperature region that an adiabatic temperature change of 1.5 °C, induced by external electric field, was observed.\textsuperscript{4}

Compared to ferroelectric ceramic materials, polymers offer a much higher entropy change in the transformation between the ferroelectric and paraelectric phases. This can be understood by considering the basic molecular structure. In ceramic materials, the small ionic displacement in the lattice associated with the F-P transition generates very small entropy change in the lattice. For example, the heat of F-P transition for a very strong order-disorder ceramic system (triglycine sulphate, TGS) is 2 J/g, and for BaTiO\textsubscript{3} it is 0.93 J/g.\textsuperscript{6} On the other hand, the disordering of the dipoles in the ferroelectric polymers can result in a large entropy change. As shown in figure 4, for the poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) copolymer, the heat of F-P transition is more than 20 J/g (~24 J/g or entropy change of 64 J/(kgK)). (In figure 4, the peak at 150 °C is the melting and the lower temperature peak is the F-P transition). The effect can also be compared with recent reported “giant” magnetocaloric effect at near room temperature where the corresponding heat extraction due to the induced magnetic transition is about 5.4 J/g (or entropy change of 20 J/kgK), much smaller than the ferroelectric polymer.\textsuperscript{7} The magnetocaloric effect has been used in low temperature refrigeration. Recently, there is a great deal of effort and interest in developing room temperature cooling devices based on the “giant” magnetocaloric effect in several magnetic alloys.\textsuperscript{7,8}

Although the F-P transition can generate large entropy change, there are several factors that must be considered in the material selection. One of these is the temperature of the transition. For the P(VDF-TrFE) copolymer, this transition occurs at a temperature much higher than room temperature (>60 °C). In addition, the hysteresis associated with transition will cause dielectric heating and will reduce the efficiency of the electrocaloric effect. Small hysteresis and room temperature operation prompted investigation of ceramic PST system as well as other relaxor ferroelectric ceramics in the past for the electrocaloric effect in the ferroelectric materials and indeed these materials exhibited relatively good performance among all ceramic materials.

Recently, we demonstrated that, by defect modification, P(VDF-TrFE) copolymer can be converted to a relaxor ferroelectric which eliminated the polarization hysteresis (dielectric heating) associated with the change of polarization (see figure 5) and moved the dielectric constant peak to room temperature.\textsuperscript{1,3} This provides a unique opportunity to exploit the large entropy change in the ferroelectric polymers for the solid state electric cooling devices. We propose to take advantage of this opportunity and investigate the electrocaloric effect in the relaxor ferroelectric PVDF polymer. In a recent simple experiment, where a thin film (30 μm thick, 1 cm x 2 cm area) of the relaxor ferroelectric PVDF was placed in ambient atmosphere and a thermocouple was placed on the film surface (isolated by a thin insulating sheet), under an external electric field excursion, a temperature change of 0.7 °C was observed—both heating and cooling with increasing and decreasing electric field. The adiabatic film temperature change should be
much larger than 0.7 °C since the measurement was not conducted under adiabatic condition. This result demonstrates the existence of large electrocaloric effect in the relaxor ferroelectric polymer, which is consistent with the large heat of transition between the dipolar-ordered and disordered phases as shown in figure 4.

Another unique feature of this relaxor ferroelectric polymer is the large electrostrictive strain, which can be induced by external electric fields. As shown in figure 6, an electrostrictive strain of more than -7% can be induced along the thickness direction. For the transverse strain, the transverse strain depends on the film processing condition. For unstretched films, the transverse strain is 3% and for the uniaxially stretched films, the strain along the stretching direction is 5% under 150 V/μm and in the direction perpendicular to stretching, the strain is very small. In the proposed solid state cooling system, the electrocaloric effect and the electrostrictive strain will be combined to generate entropy transport and refrigeration.

In addition to these functionalities, the polymeric material also offer other advantages. For example, the polymers can be easily made into fibers or ribbons to form textiles which will be made use of in this program to develop an electrotextile cooling system.

### B. 3. Design considerations for the proposed electrotextile cooling systems

One key component of a cooling device is the transportation of entropy from the cold end to the hot end. The objective is to transport entropy from one temperature level to another temperature level in a reversible manner, that is, to transport the entropy without generating any additional entropy in the process. This requires a substance whose entropy depends on some property other than temperature. In the multifunctional material system, this substance is the ferroelectric relaxor polymer, which entropy can be changed by external electric field. All steady state converters must be cyclic since the entropy carrying substance is not consumed. In a practical device, the irreversible leaking of entropy down the temperature gradient by conduction and various losses can generate extra-entropies. In this program, these considerations will be integrated to the material development and material system design to realize a high efficiency electrotextile cooling system.

In the past, several designs have been investigated for the refrigerators based on the electrocaloric effect in ferroelectric ceramics and all these designs do not possess any mechanical flexibility and can’t generate large temperature difference between the cold and hot ends (<10 °C). In this program, we will investigate several designs which make use of the polymer flexibility and easy fabrication of multilayer films for the electrotextile cooling systems.
B.3.1. We propose a novel design of an electrotextile cooling system, combining the electrocaloric effect in the ferroelectric material with the heat transport mechanism used in the thermoacoustic refrigeration. In such a design, there is essentially no macroscopic motion of any component in this solid state cooling system.

A brief review of the operating principle of the thermoacoustic cooler—which has been developed for more than 40 years and has reached relative maturity—will help explain the micro-heat transporting process in the proposed cooling system. As illustrated in figure 7, the basic unit of a thermoacoustic cooler consists of a working fluid experiencing compression and expansion in contact with a plate (a stack) that maintains a thermal gradient $\Delta T_m/L$ where $L$ is the stack length and $\Delta T_m$ is the temperature difference between the hot and cold ends ($T_H - T_C$). As the fluid is compressed and expanded, it undergoes a temperature change, as illustrated in figure 7, resulting in a heat transportation from low temperature to high temperature. When following a fluid parcel, there are four steps in this heat transportation process. (1) In the first step, the fluid is compressed and moved to the right (figure 7(a)) and the temperature of the compressed fluid is raised; (2) In the second step, if the fluid temperature is higher than the local temperature (point B) in the plate, heat $dQ_b$ will be transferred from the fluid to the plate to reach the temperature of the plate (figure 7(b)); (3) In the third step, the fluid parcel is moved to the left to the point A and is expanded which causes the lowering of the fluid temperature (figure 7(c)); And (4) In the fourth step, if the temperature of the fluid parcel is lower than the local temperature of the plate at the point A, heat $dQ_d$ will be transferred from the plate at the point A to the fluid parcel to reach equilibrium. Integration of all the fluid parcels along the plate has the net effect that the heat is transferred from the cold end of the plate to the hot end. Although for each fluid parcel, the temperature change during this cycle is small, adding all the parcels together along the plate leads to a large temperature difference between the cold and hot ends ($>50 \, ^\circ C$ can be achieved).

In the proposed electrotextile cooling system, the relaxor ferroelectric polymer will replace the fluid and we will utilize the electrocaloric effect, rather than the thermoelastic effect, to induce the temperature change in the ferroelectric polymer film. Therefore, there is no need to strain the polymer to induce temperature change and the electrocaloric effect can induce much higher temperature change. The large electromechanical effect in the relaxor ferroelectric polymer will be employed to induce the relative motion between the ferroelectric polymer layer and the plate. This novel approach has many advantages over the thermoacoustic cooling system. The basic operation principle of the proposed solid state cooling ribbons is shown in figure 8. The plate (hatched area) maintains a temperature gradient of $(T_H - T_L)/L$.

When an electric field is applied to the terpolymer film, the electrocaloric effect induces a temperature rise in the terpolymer. By following the motion and temperature change of a small volume element of the terpolymer, one can trace the 4 steps very similar to these shown in figure 7. The only difference is the temperature change in the proposed device is induced by the electrocaloric effect in the terpolymer and therefore the magnitude of temperature change can be varied independent of the strain or the

Figure 7. Illustration of the operation of a thermoacoustic cooler. The shaded plate maintains a temperature gradient. The dashed and solid squares in figures 7(b) and 7(d) illustrate the volume change of the fluid parcel due to the heat exchange with the plate. $dW$ indicates the works exchanged between the gas parcel and the surrounding.
displacement. For the terpolymer here, the adiabatic temperature change can be much more than 1 °C under a field of 100 V/µm. In addition, the relaxor terpolymer layer can be in a multilayer form which allows a temperature profile in perpendicular to the interface between the relaxor terpolymer and the plate that can be controlled by the designer. This additional degree of freedom could further improve the efficiency and performance.

A possible design for a single unit that can realize all these functions of a cooling system and be part of the electrotexile is presented in figure 9. The upper illustration of figure 9 is a three layer ribbon in which the two layers designated as Layer 2 correspond to the plates of the thermoacoustic cooler. Layer 1 is the terpolymer polymer, which is coupled to Layers 2 through high thermal conductivity lubricants which maintain good thermal conductivity between the layers. The lower illustration of figure 9 shows the electrode pattern of Layer 1, in which the middle portion generates temperature change through the electrocaloric effect. There may not be strain in this portion which can be achieved by forming a multilayer Layer 1, in which a high modulus polymer layer is included to clamp mechanically the electric field induced strain. The two small electroded areas at the two ends will generate strain under external field that cause the middle electroded portion of the Layer 1 to move with respect to Layers 2. Because of the large strain level in the ferroelectric polymer film and very small displacement needed in the relative motion between the two layers, the electroded two ends can be very small. For example, 1 mm long terpolymer film can generate 50 µm displacement at the one end if the other end is fixed (as in the case here). For the electric ribbon here, the relative motion should be less than 5 µm. Therefore, this heat transportation process here is termed as the micro-heat transfer process. With a temperature change of 0.01°C/µm polymer movement), a 1 cm long segment of ribbon can achieve 33 °C temperature difference between the hot and cold ends if the temperature

**Figure 8.** An illustration of the operation of an electrocaloric effect cooler. The terpolymer under electric field can have a temperature increase from the electrocaloric effect and a relative displacement with respect to the plate from the strain. These two quantities can be controlled independently.

**Figure 9.** Schematic illustration of one proposed design of the cooling system (a, top) a three layer ribbon with the layers 2 as the plates and the layer 1 the terpolymer film. (b, bottom) The electrode pattern on the layer 1 in which the middle large part induces the temperature change through the electrocaloric effect and the two small ends generate strain to create the relative motion of the layer 1 with respect to the plates 2. Because of the large strain, the electroded actuator area at the two ends can be very small (1 mm length can generate 50 µm maximum displacement. The proposed device needs less than 5 µm relative motion between the two layers).
gradient in the Layers 2 is 1/3 of 0.01 °C/μm.

B. 5. Proposed tasks

Phase I research:

B.5.1 Terpolymer synthesis and characterization, modeling, and optimization of the electrocaloric effect and other related properties in the relaxor ferroelectric polymers for room temperature refrigeration (Penn State, ISL, and MIT)

The electrocaloric effect in the relaxor ferroelectric polymers will be characterized in terms of the adiabatic temperature change under AC electric fields as a function of temperature. As a relaxor ferroelectric material, it is expected that the large electrocaloric effect should exist over a relatively broad temperature range, for example, from 20 °C to 60 °C, needed for the proposed applications. In an early study of the electromechanical response of the relaxor ferroelectric polymers, it has been observed that the large electrostrictive strain is nearly constant in the temperature range from 20 °C to 80 °C (see figure 14), which suggests that the electrocaloric effect can remain relatively constant in the same temperature range. For a ferroelectric polymer, it is also expected that many properties will exhibit non-linear effect which may be used to tune the electrocaloric effect. The non-linear electrocaloric effect will be evaluated as the AC applied field amplitude and DC electric bias field. Thermodynamic relations will be established for various related properties which are required in order to properly design and optimize the cooling system performance. As a dielectric material, the input electric energy to the relaxor ferroelectric polymer for the electrocaloric effect is related to the dielectric response which will influence the efficiency of the cooling devices. The dielectric and polarization response will be systematically characterized as a function of temperature, AC field amplitude, and DC bias field. The characterization will be carried out for terpolymers with different compositions (P(VDF$_x$-TrFE$_y$-CFE$_z$)$_{1-x}$) to assess how the electrocaloric effect as well as the operation temperature range are affected by the terpolymer compositions.

For the optimization of the electrocaloric effect and cooling system performance, a series of terpolymer compositions will be synthesized and characterized. Dr. Francois Bauer, who has been in collaboration with Dr. Zhang in the past several years on the terpolymers, has developed a unique capability in synthesizing relatively large quantity of PVDF based terpolymer (about 2 kg/batch and it takes about 2 days to synthesize one batch). In this program, the terpolymer synthesis will be carried out at Dr. Bauer’s group at ISL of France.

To better understand which material parameters control the electrocaloric effect in this class of polymer as well as to determine further direction on improvement in the performance of cooling system, we plan to carry out thermodynamic modeling of the electrocaloric effect in the relaxor ferroelectric polymers. The modeling work will be based on the measured results and the thermodynamic models existing for similar materials. As has been shown by several recent works on the electrocaloric effect based cooling device, modeling results can provide valuable insights on how various material processes affect the
device performance. Furthermore, we also plan to develop correlation between the material properties and cooling system performance and possible figure of merit (FOM) of the material in order to achieve high cooling performance.