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Pyroelectric conversion cycle of vinylidene fluoride-trifluoroethylene copolymer

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Copolymers of vinylidene fluoride-trifluoroethylene P(VDF-TrFE) exhibit large piezoelectric and pyroelectric effects. In addition to the most common application of the pyroelectric effect (radiant detection) it is possible to convert heat directly into electrical energy by pyroelectric conversion. This study reports the first pyroelectric conversion cycle to be measured for the copolymer P(VDF-TrFE). It is found that standard isothermal D - E hysteresis loop measurements are not necessarily accurate predictors of pyroelectric conversion performance for this material. Conduction effects are found to obscure the observation of conversion cycles in most cases for the presently available materials. In spite of these difficulties, a conversion cycle was measured whose output electric energy density was 30 mJ/cm^3 . The output density is 15 times larger than any other polymer previously measured.

I. INTRODUCTION

The pyroelectric effect is the flow of charge to and from the surfaces of a material resulting from a change in temperature.¹ This effect may be used for the conversion of heat directly into electrical energy. In spite of its apparent lack of promise in the early 1960s this approach to energy conversion has been revived by recent advances. Some researchers are now suggesting that this type of conversion may be more efficient than previously believed.^{2,3} In addition, in the past couple of years, pyroelectric generators have been built which produce more than four orders of magnitude greater power than the devices of 20 years ago.⁴⁻⁶

Some of the work in the early 1960s centered on pyroelectric conversion in space. Experiments by Beam, Fry, and Russel^{7,8} were not encouraging primarily because of the particular choice of thermal-electrical cycle and the lack of pyroelectric material with high-performance characteristics. In a theoretical study done in 1965 Margosian⁹ summarized:

"With currently known materials, this generator is too heavy to be of interest for electric propulsion. As a source of auxiliary power it is comparable, at best, to solar cells in weight. If materials with substantially better characteristics than those considered are found, competitive performance as a power source might be possible."

The copolymer of the present study, vinylidene fluoride-trifluoroethylene [P(VDF-TrFE)], is expected to fulfill that promise. Section II describes the pyroelectric conversion cycle. Subsequent sections detail the first observation of such cycles P(VDF-TrFE).

II. PYROELECTRIC CONVERSION CYCLE

A pyroelectric converter is a form of heat engine which directly transforms heat energy into electrical energy. The thermodynamics of the pyroelectric converter are analogous to the more familiar steam engine with pressure-volume mechanical work replaced by voltage-charge electrical output. In addition to operating as a generator of electrical energy from heat, a pyroelectric converter may be "run backwards" to provide either heat pumping or refrigeration. In refrigeration,

the electrocaloric effect, which is analogous to the widely known magnetocaloric effect, can operate in a manner similar to adiabatic demagnetization cooling. Before describing the proposed pyroelectric conversion experiments an introduction to the basic thermodynamic cycle (from the electrical-energy-producing point of view) will be helpful.

The electrical energy production cycle may be described in terms of the charge-voltage behavior of a ferroelectric (FE) material. Figure 1 illustrates, at various temperatures, the charge-voltage (displacement versus applied electric field) behavior of a ferroelectric material which may be utilized for pyroelectric conversion. Notice that the displacement is not a single-valued function of the applied electric field. The displacement depends in a hysteretic way upon the applied field. The remanent displacement (which is the focus of this investigation) is the amount of displacement which remains when the externally applied voltage is reduced to zero.

For any cyclic process an area on a charge-voltage diagram represents an electrical work since

$$W = \oint V dq, \quad (1)$$

where W = electrical work, V = voltage, and q = charge. The direction of the path (clockwise or counterclockwise) determines whether electrical energy is produced or dissipated. A familiar example is the hysteretic heating of a ferroelectric element. Every time that the voltage applied to a ferroelectric sample is cycled isothermally, an amount of electrical energy (equal to the hysteresis loop area) is dissipated as heat. In this case the loop is cycled in the counterclockwise sense, as indicated by the arrows in Fig. 1.

The pyroelectric generator exploits the fact that, by removing the isothermal constraint, it is possible to reverse the direction in which the loop is cycled. The loop may be cycled in a clockwise sense, thus resulting in the production of electrical energy from heat.

Shown in Fig. 2 is an overlay of the charge-voltage characteristics of a ferroelectric at two different temperatures. Figure 2 also shows how clockwise cycling may be achieved when operating between these two temperatures. Starting in

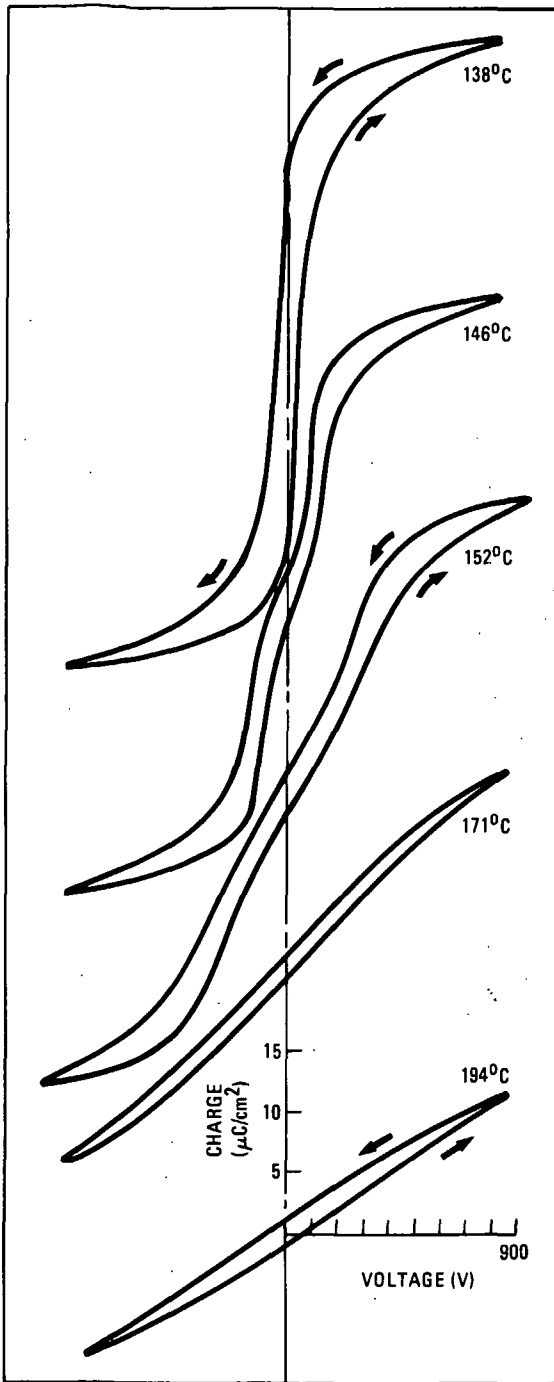


FIG. 1. Charge (displacement) vs. applied voltage (electric field) for various temperatures of 0.025-cm-thick $\text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.68}, \text{Sn}_{0.25}, \text{Ti}_{0.07})_{0.98}\text{O}_3$.

the upper-right-hand corner at high voltage and low temperature, the FE is discharged as it is heated. After reaching a high temperature, the FE is further discharged by reducing the externally applied voltage. The FE is then recharged at low voltage while cooling. After reaching low temperature, the FE is further recharged by increasing the externally applied voltage. Thus, the electrical cycle may be executed in a clockwise manner—opposite to the hysteretic loop direction—in which an amount of electrical energy,

$$\oint V dq = \text{shaded area of Fig. 2}, \quad (2)$$

may be produced. This cycle is an electrical analog of the Ericsson heat engine cycle.

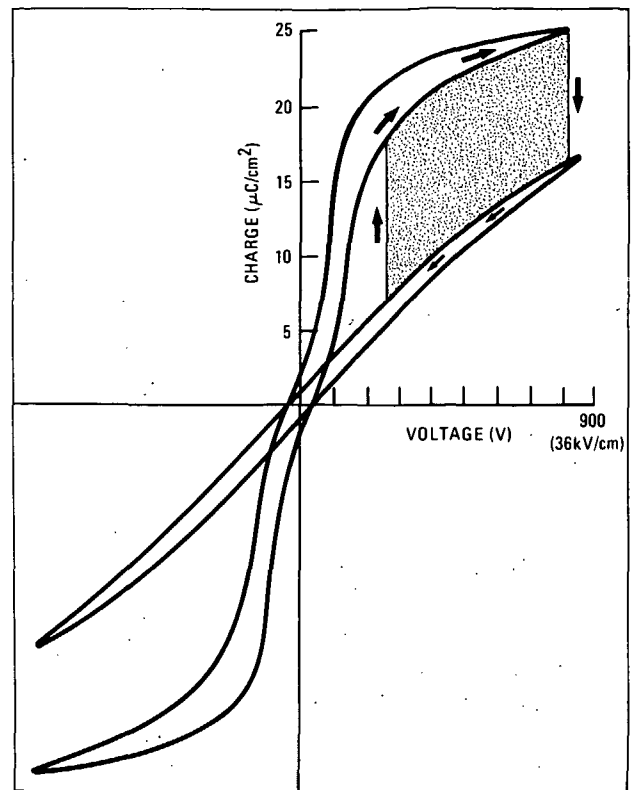


FIG. 2. Electrical energy production cycle may be realized by appropriately phased changes in temperature and applied electric field. The shaded area is equal to the electrical energy per cycle which may be produced by $\text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.68}, \text{Sn}_{0.25}, \text{Ti}_{0.07})_{0.98}\text{O}_3$.

The spontaneous polarization is of key importance because it sets the scale for the amount of displacement change which is achievable in a conversion cycle. Along with the dielectric strength, the remanent polarization determines the order of magnitude of the amount of electric work which may be produced in a thermodynamic cycle.

The data shown in Figs. 1 and 2 correspond to measurements on a ceramic of lead zirconate modified with tin and titanium (PZST). The discovery of this material, with its unusually good pyroelectric properties, allowed the recent upsurge in the development of pyroelectric conversion.⁴⁻⁶

Now, however, an even more attractive pyroelectric material is appearing. Japanese workers¹⁰⁻¹⁴ have reported the first polymer, P(VDF-TrFE), shown to have an observable ferroelectric to paraelectric transition. Such a transition is necessary for a highly active thermodynamic medium for use in pyroconversion.

Thermodynamically, the copolymer is impressive. P(VDF-TrFE) has a transition similar to that shown for the ceramic PZST in Fig. 1 with a few important differences. One difference is that the transition (ferroelectric to paraelectric) occurs at a lower temperature. Much more importantly though, the dielectric strength of the copolymer is presently 25 times greater than that of the ceramic. Since the electrical output energy density of the pyroelectric converter scales as the product of the electric field and the spontaneous polarization, the higher dielectric strength of the copolymer represents a very important improvement. The present dielectric strength of commercial capacitor grade homopolymer P(VDF) is yet another five times greater (5 MV/cm). It

is expected that the copolymer dielectric strength may, with proper processing, achieve comparable strength.

It is helpful to estimate the electrical output energy density which is possible using this new copolymer material. Since electrical output energy density is equal to the product of displacement density times electric field (corresponding to the area in Fig. 2), the scale of this density is (for the copolymer) 25 J/cm^3 ($5 \mu\text{C/cm}^2 \times 5 \text{ MV/cm}$). Actual cycles do not utilize the complete energy density calculated this way and are smaller by a factor of 3 or 4. Thus it is estimated that P(VDF-TrFE) may produce an impressive 7 J/cm^3 per cycle once its dielectric strength is improved to that of capacitor grade P(VDF). This would represent a 35-fold improvement in energy density as compared with the ceramic (PZST).

III. EXPERIMENT

Resins of vinylidene fluoride-trifluoroethylene copolymer were supplied by Daikin Kogyo Co., Ltd. The copolymer film samples were prepared by pressing the resin powder between two hot (190°C), smooth, and flat nickel platens to form thin ($30\text{--}70 \mu\text{m}$) sheets. In early work the dielectric strength in the polymer of interest at 90°C was roughly 600 kV/cm . Later in this investigation, extended-duration (12 h plus) vacuum (50 mTorr) bakeout of residual monomer and other impurities at 140°C improved both the dielectric strength and the resistivity. The films were not mechanically stretched to orient polymer chains. Aluminum electrodes 2.5 or 5.0 cm^2 of overlap area were evaporated onto the films. Electrical leads were attached by silver epoxy to the overhanging tabs of the aluminum electrodes.

The experimental measurement involves the thermodynamic cycling of the pyroelectric copolymer. The type of cycle which was described in Sec. II requires that a specimen of pyroelectric polymer be subjected to both thermal and electrical oscillations. The experimental apparatus (a similar device has been described previously⁵) which performs the simultaneous variation of these two parameters therefore consists of two major systems. One system controls the electrical behavior of the test polymer, the other system manages the heat flow. Consider first the system which imposes the necessary temperature oscillations on the specimen.

A schematic view of the experimental apparatus is shown in Fig. 3. The key element of the experiment is the spiral stack in which the copolymer specimen is placed. As shown from the top in Fig. 4, the spiral is wound around a central support rod. The spiral consists of alternate layers of plastic sheet and nylon separator screen. Wrapped into the spiral stack is the copolymer specimen. The nylon separator screen allows heat-exchange fluid (a high-dielectric-strength silicone oil) to flow over the surface of the plastic sheet and the specimen. The heat-exchange fluid is pumped by a piston which is in the cylinder below the stack. A temperature gradient is imposed upon the fluid by the heater which resides in the top of the stack and the cooler (heat exchanger) which sits below the stack. Since the fluid is hotter in its top portion and cooler in its lower portion, the net result of pumping the fluid up and down through the stack is that the specimen temperature is forced to oscillate.

The piston position is changed by a stepping motor. The

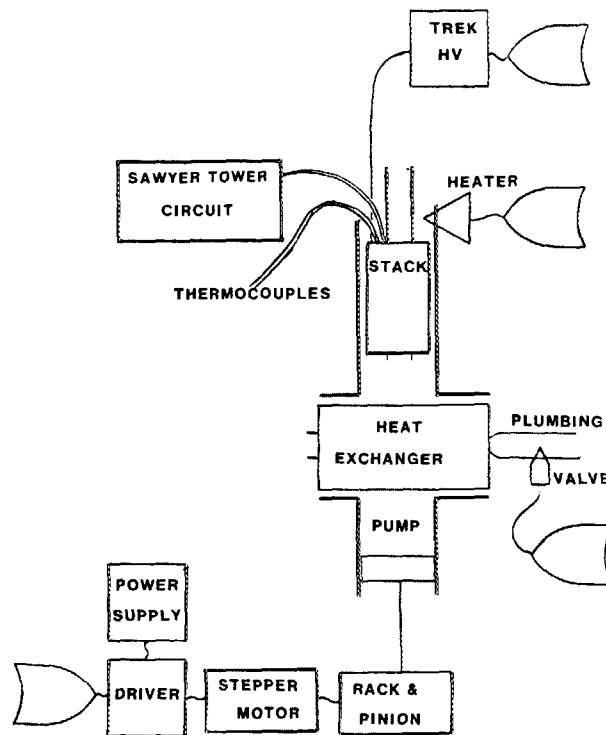


FIG. 3. Schematic of experimental apparatus in which temperature and electric field of pyroelectric conversion materials are cycled.

stepping motor is physically linked to the piston via a rack and pinion gear, and the stepping motor is controlled by a microprocessor. The maximum displacement of the piston is approximately 10 cm , which corresponds to 4000 steps of the stepping motor. The pumping cycle period is typically in the range of $2\text{--}10 \text{ s}$.

The input heat to the apparatus comes from an electrical heater in the form of a stainless-steel band which is wound into the spiral stack. The heater power (1300-W max-

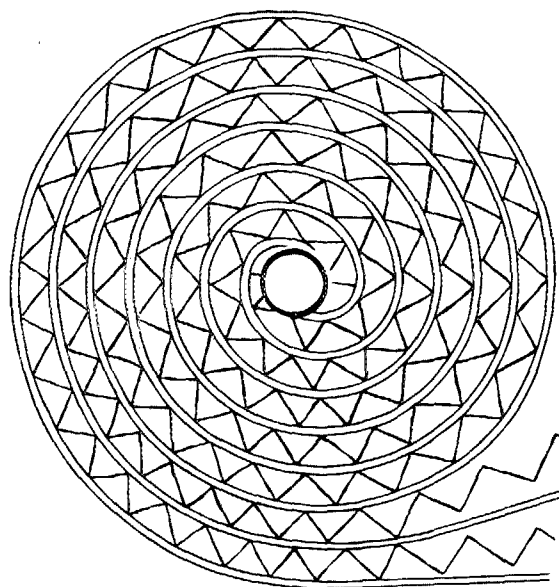


FIG. 4. Top view of the stack shown in Fig. 3. The spiral consists of alternate layers of plastic sheet and nylon separator screen. The copolymer specimen is wrapped into the stack.

imum) is controlled by sensing the temperature in the heater with a thermocouple, feeding the information to a digital controller, and then switching on and off the heater current with a solid-state relay. Heat is extracted from the apparatus by the heat exchanger which is cooled by tap water. Control of the cooling power of the heat exchanger is analogous to control of the heater. In the cooling heat exchanger case, however, the opening and closing of the solenoid valve on the cooling water line is used to control the temperature of the cooler. The maximum temperature which may be produced at the specimen is about 90 °C with the present design.

The electrical system contains two primary components. One system controls the voltage of the copolymer specimen. It also coordinates the timing of voltage changes with the thermal conditions of the specimen. Meanwhile the other electrical system measures the pyroelectric cycle of the specimen. The electrical measurement system will be described first.

The charge-voltage behavior of the pyroelectric conversion cycle of the specimen is measured with an uncompensated Sawyer–Tower circuit.^{15–17} A relatively large (19.6 μF) capacitor is used to integrate the charge so as to minimize the error induced in the voltage measurement (due to the small voltage drop across this integrating capacitor). Simultaneous readings of both charge and voltage of the specimen are recorded on a storage oscilloscope.

In order to achieve the electrical analog of an Ericsson cycle, certain control and coordination of the thermal and electrical oscillations must be obtained. To produce the Ericsson thermodynamic cycle, it is necessary to change the applied voltage on the specimen whenever the specimen's temperature reaches either a maximum or a minimum. At low pumping frequency, the extremal temperatures occur at the high and low points of the fluid-pumping stroke. Therefore, the coordination between temperature and applied voltage may be accomplished by ensuring the voltage ramp-ups and voltage ramp-downs occur at the ends of the fluid-pumping stroke. The computer receives signals from the pump's stepping motor microprocessor so that it knows when to send out a command to change the voltage on the specimen. The computer controls the output of a 10-kV bipolar power supply via a digital-to-analog converter.

Once the specimen is in place and all of the thermal and electrical cycling conditions have been provided, the actual measurement is straightforward. The experiment consists of the measuring the charge-voltage behavior of the specimen as a function of thermal and electrical cycling limits.

IV. RESULTS

Before beginning the power cycle experiments a number of standard isothermal hysteresis curves were measured at 2 Hz. Figure 5 is representative of the earliest of such measurements on P(VDF-TrFE) which is 73% VDF. Several curves were measured on specimens held within the thermal cycling apparatus under isothermal conditions achieved by stopping the fluid-pumping piston during the measurement of the hysteresis cycle. The hysteresis cycles so measured were essentially identical to other hysteresis cycles which were measured in a standard isothermal oil bath ar-

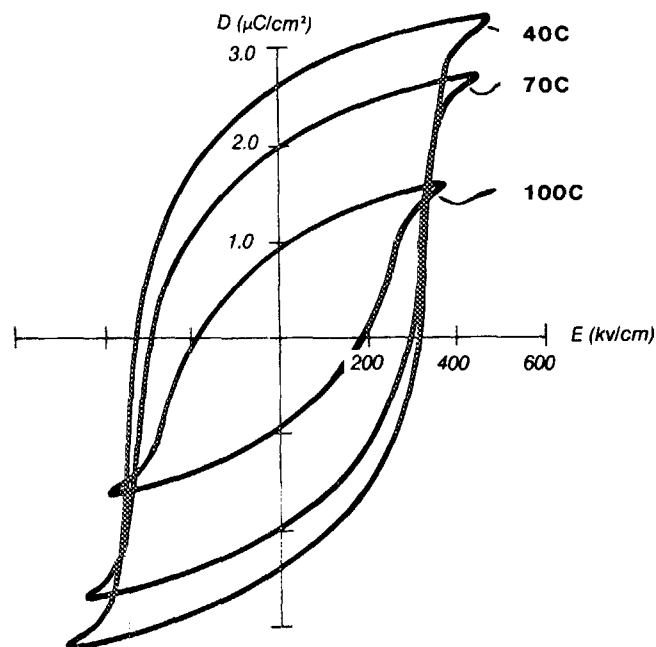


FIG. 5. Displacement vs electric field (D - E) hysteresis loops for P(VDF-TrFE), which is 73% VDF, at 40, 70, and 100 °C.

rangement.¹⁴ The cycles in Fig. 5 were made on materials for which bakeout procedures had not been performed.

Figure 6 shows the room-temperature hysteresis loop for a specimen which had been processed with the careful bakeout procedure. The dielectric strength was increased to about 1 MV/cm. An important secondary effect of the increase in the electric field limit is that the electric displacement was also increased.

In spite of the resistivity increase which was achieved by the bakeout procedure, the measured "power cycles" were extremely distorted from the ideal (expected) cycles by conduction.

It is helpful to review what was expected in these cycle measurements. The expected displacement change (implied by Fig. 5) was about 1.5 μC/cm². Furthermore, this displacement change was anticipated to be much greater than the amount of charge conducted through the copolymer specimen during the cycling period. The charge per unit area conducted through the copolymer, q_c , is given by

$$q_c = \int_0^\tau J(E, T) dt \sim J(E_{\max}, T_{\max}) \tau = E \tau / \rho(E_{\max}, T_{\max}), \quad (4)$$

where J is the conduction current per unit area, ρ is the bulk electrical resistivity, and both J and ρ are functions of electric field E and temperature T . The conduction charge was expected to be about 0.12 μC/cm² (assuming $\rho = 10^{13} \Omega \text{ cm}$, $E = 4 \times 10^5 \text{ V/cm}$, $\tau = 3 \text{ s}$). Thus the displacement charge was expected to be about ten times larger than the conduction charge.

As it turns out, the temperature dependence indicated by Fig. 5 may be dominated by quasi-irreversible changes similar to those reported recently by Davis *et al.*¹⁸ and Olsen *et al.*¹⁹ The quasi-irreversible behavior stems from the appreciable conductivity at elevated temperatures which in the presence of electric fields leads to greatly reduced displace-

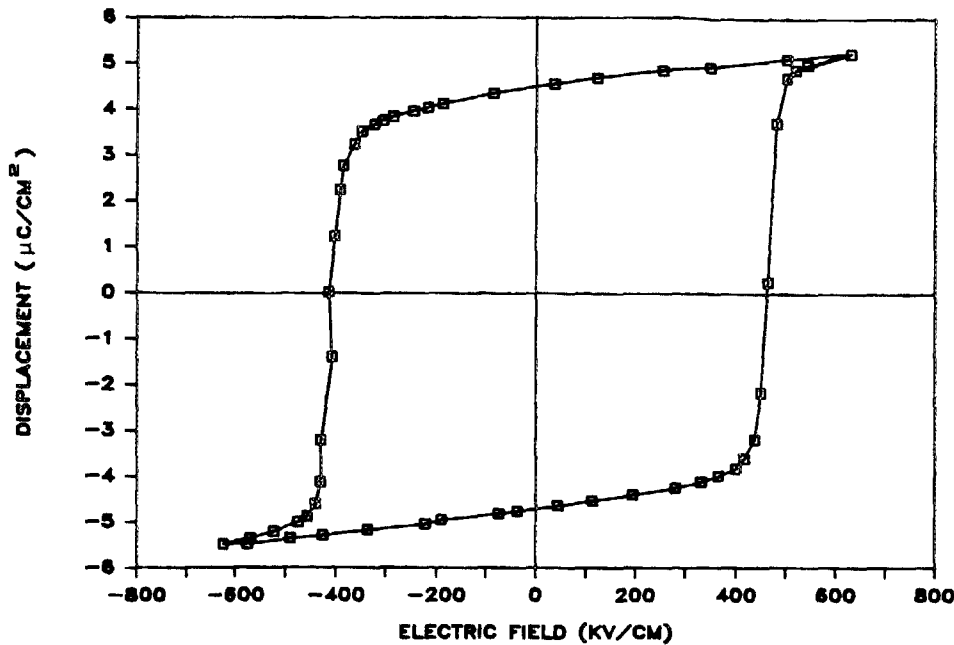


FIG. 6. Displacement vs electric field (D - E) hysteresis loop for P(VDF-TrFE), which is 73% VDF, at 27 °C. This specimen had been processed with the bakeout procedure described in the text.

ment. The phenomenon is described as quasi-irreversible because as Davis *et al.* reported after heating the copolymer above the ferroelectric to paraelectric transition temperature, the room-temperature hysteresis (displacement) can be restored.

Therefore, the reversible component of the temperature dependence of the displacement change is likely to be overestimated by the data of Fig. 5. Preliminary measurements of the reversible component²⁰ indicate that it is about $0.15 \mu\text{C}/\text{cm}^2$, i.e., a factor-of-10 smaller than suggested by Fig. 5.

In addition to the smaller than expected displacement changes, the resistivity was observed to be less than $10^{13} \Omega \text{ cm}$ in most specimens at the temperatures of interest for pyroelectric cycling. A detailed study of both the high-field

resistivity and of the reversible displacement changes will be presented elsewhere.²⁰

To summarize then, the highly distorted power cycles resulted from displacement changes (ten times smaller than expected) which were obscured by conduction.

In spite of the problems which were encountered, it was possible to measure modest pyroelectric power cycles as shown in Fig. 7. The cycle of Fig. 7 still suffers from a substantial amount of drift which is due to conduction of charge through the bulk of the copolymer specimen. The points 1-7 indicate consecutive times in the cycle. In the vertical line 2-3, the conduction process adds to the apparent displacement change. By contrast, in the vertical line 4-5, conduction diminishes the apparent displacement change. The conducted

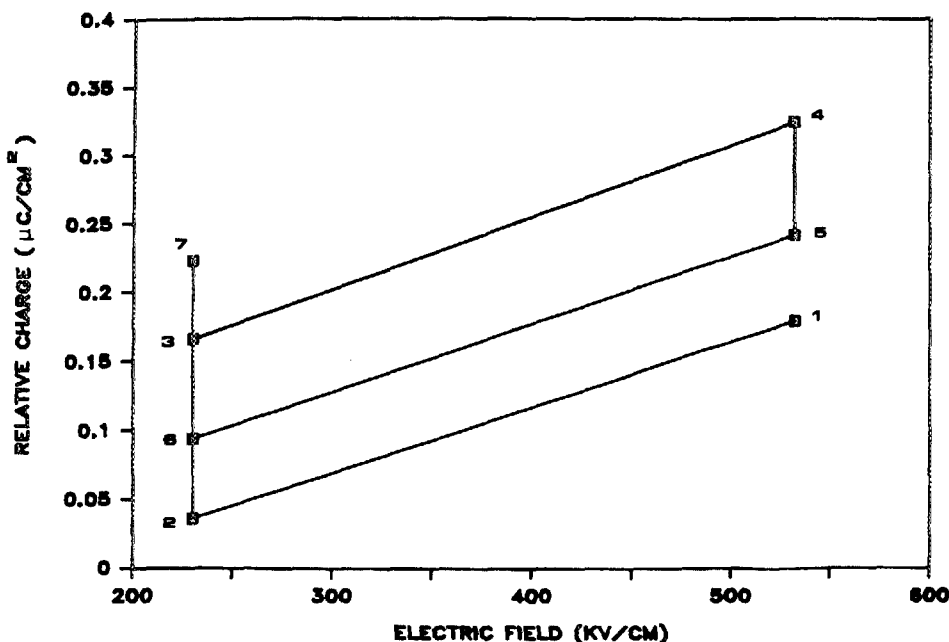


FIG. 7. A modest pyroelectric conversion cycle. The cycle suffers from drift due to conduction of charge through the bulk of the specimen. The copolymer is 73% VDF. The temperature limits of the 12.6-s period cycle are 23 and 67 °C.

charge at high electric field is larger than it is at low field. For all fields the effect of conduction is to make the cycles drift upward in Fig. 7. The size of the reversible displacement was at least $0.1 \mu\text{C}/\text{cm}^2$ according to the high-field line 4-5 and less than $0.18 \mu\text{C}/\text{cm}^2$ according to the low-field line 2-3. This is in agreement with displacement change measurements taken at fixed field.²⁰ The electrical output energy density demonstrated by Fig. 7 is about 30 mJ/cc per cycle. This output is about an order of magnitude smaller than that demonstrated for the ceramic material PZST.²¹

V. DISCUSSION

Previous to the present study, three main relationships between standard isothermal hysteresis loops and pyroelectric energy conversion cycles appeared to be valid. The relationships were: (1) the temperature dependence of isothermal loops could be used to estimate the pyroelectric cycle behavior; (2) the hysteretic loss of the pyroconversion cycle would be overestimated by the hysteresis loops; and (3) the minimum field required for repoling in the pyroelectric cycle would be overestimated by the hysteresis loops.

For previous pyroelectric materials, it had generally been found that the temperature dependence of standard isothermal hysteresis loops could be used as a reasonable predictor of pyroelectric cycle behavior. It has been shown previously²¹ that isothermal loops of PZST yield good estimates of the pyroelectric cycle performance of that material. In the present study it was found that presence of a quasi-irreversible displacement change can give rise to hysteresis loops whose temperature dependence is much larger (by a factor of 10) than the displacement changes which occur in the corresponding pyroelectric conversion cycles.

Bipolar (standard) hysteresis loops usually overestimate the hysteresis loss associated with a pyroconversion cycle, but the error in the ceramic PZST case was not great. For PZST, bipolar hysteresis loops estimate the loss as being 20% whereas the unipolar hysteresis loops (see Ref. 21) indicate that the loss is only 10% as large as the output energy density. In the present study, the hysteresis loops of Fig. 5 appear to indicate that hysteresis may entirely consume the pyroelectric conversion cycle. In other words, there is almost no "gap" between the hysteresis loops at two different temperatures in Fig. 5. The "gap" between the two hysteresis loops in Fig. 2 seems to form the region in which the pyroelectric cycle can be performed. As it turns out, pyroelectric cycles can be performed in spite of a lack of gap in the bipolar loops. The hysteresis loops of the copolymers exhibit very high coercive fields which overlap the gap region which would otherwise be apparent if unipolar loops were used in a manner as described previously.²¹ Thus, copolymer hysteresis loops appear to indicate that pyroconversion cycles will be wiped out by hysteretic processes. However, pyroelectric conversion cycles are possible. The bipolar hysteresis loop simply overpredicts the amount of hysteresis associated with the pyroelectric cycle. In the previous ceramic the over prediction was small. In the present copolymer case overprediction leads to a totally false implication.

The third relationship between hysteresis loops and

pyroconversion cycles is that the low-field (cooling) repoling portion of the cycles is overpredicted by the hysteresis loops. In the ceramic PZST case, the coercive field is very small (about one tenth as large as the dielectric strength) and the resulting error of the prediction is small.²¹ However, in the copolymer case, the coercive field is about half as large as the breakdown strength of the material. Hence, the error in the copolymer case may be very large. Related measurements on displacement changes indicate that significant repoling²⁰ occurs at fields as low as 100 kV/cm. Thus hysteresis loops may be of limited utility as indicators of the minimum repoling field for copolymer pyroconversion cycles.

A pair of comments on the relatively small size of the observed pyroelectric conversion cycle are in order. The cycle which was measured was far from what could be considered an optimal cycle for the copolymer. Of the copolymer ratios studied, only one (73/27) was resistive enough to permit observation of the cycle, and, unfortunately, the 73/27 material could be studied only in a temperature range substantially below its Curie point (which according to DSC measurements¹⁸ is at about 130 °C while heating). It is now well established that the largest pyroelectric conversion cycles are obtained near and above the Curie point of a given material. It is therefore expected that much larger cycles will be obtained with the copolymer once resins are available with increased resistivity (about $10^{15} \Omega \text{ cm}$) above their Curie temperatures.

Though the energy density of the present study is considered to be small for the copolymer, its magnitude still represents a very substantial increase over any previously measured polymer. The largest known measurement of any other polymer was that of Beam *et al.*⁸ in which about 2 mJ/cm³ was measured in a different type of cycle of tetrafluoroethylene-hexafluoropropylene. Therefore, the present measurement represents a 15-fold increase in the energy density observed with a polymer.

Future efforts on pyroelectric energy conversion materials should continue to stress maximizing the electrical output energy density while also requiring high resistivity.

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