Predicting performance of thermal-electrical cycles in pyroelectric power generation

Masaaki Baba1,2,3, Masahiro Ejima1, Ichiro Murayama2, Tatsuo Fukuda3, Hirohisa Tanaka4, Tohru Sekino5, Yoonho Kim2, Noboru Yamada1, and Masatoshi Takeda1

1Department of Mechanical Engineering, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan
2Research Institute of Car and Life-style, Daihatsu Motor Co., Ltd., 1-2 Yoshimoto Tanunishiru, Kurume, Fukuoka 839-1206, Japan
3Materials Sciences Research Centre, Japan Atomic Energy Agency, 1-1-1, Kouto, Sayo, Hyogo, 679-5148, Japan
4Kwansei Gakuin University, 2-1 Gakuen, Sanda, Hyogo, 669-1337, Japan
5The Institute of Scientific and Industrial Research (ISIR), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka, 567-0047, Japan

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A method is proposed to predict the power generation performance of a pyroelectric generator (PEG) for waste-heat recovery systems in which an external electric field is applied to a ferroelectric material in synchrony with rapid temperature changes. The net generated energy density \(N_D\) of the PEG at any temperature and electric field is predicted for two thermal-electrical cycles (including the Olsen cycle). This is done by approximating the dependence of the polarization density on temperature and electric field using hysteresis loop measurements. The difference between the predicted and measured values of \(N_D\) was less than 15\%. This method could be used to screen promising candidate materials for PEGs.

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1. Introduction

Waste-heat recovery systems (WHRSs) have received considerable attention because of their environmental and energy-saving benefits. The Rankine cycle1) and thermo-electric power generation2,3) are frequently used in WHRSs that target constant-temperature exhaust heat. However, some kinds of exhaust heat fluctuate with time. In particular, the temperature of exhaust from a car is greatly changed by acceleration and deceleration.4–6) Therefore, a power generation technology suitable for variable-temperature exhaust heat is necessary to realize an efficient WHRS for vehicles. Ferroelectrics and other pyroelectric materials show great potential for such an application.

Pyroelectric materials generate electrical power by polarization variation synchronised with temperature variation.7–11) However, a pyroelectric generator (PEG) using only temperature variation has a low conversion efficiency,12) and is thus difficult to use in a WHRS. Attention has therefore been focused on thermal-electrical (T–E) cycles using pyroelectric materials. In this technique, an electric field is applied synchronously with the temperature variation, realizing a thermodynamic cycle.5–6,13–17) The T–E cycle can improve the conversion efficiency of a PEG by using the hysteretic characteristics of pyroelectric materials.

Figure 1 shows the Olsen T–E cycle10,13,18–27) and a novel T–E cycle (Kim’s cycle) proposed by Kim et al.4–5) The Olsen cycle consists of two isothermal processes [Fig. 1(a): \(\text{I} \rightarrow 2, 3 \rightarrow 4\)] and two isoelectric-field processes [Fig. 1(a): \(2 \rightarrow 3, 4 \rightarrow 1\)], as shown in Fig. 1(a). In other words, an electric field is applied (removed) in the isothermal process between 1 and 2 (3 and 4), and heating (cooling) is performed in the isoelectric-field process between 2 and 3 (4 and 1). The area enclosed by the clockwise loop 1–2–3–4 is the net generated energy density, \(N_D\). The Olsen cycle can increase \(N_D\) several hundred-fold compared to power generation without the externally applied electric field, and the exergy efficiency theoretically reaches 50%.23) Kim’s cycle is a T–E cycle that consists of an isoelectric-field process [Fig. 1(b): \(4 \rightarrow 1\)], a constant polarization process [Fig. 1(b): \(1 \rightarrow 2, 3 \rightarrow 4\)], and two isothermal processes [Fig. 1(b): \(1 \rightarrow 2, 3 \rightarrow 4\)], as shown in Fig. 1(b). The constant polarization process is realized by electrical insulation between the pyroelectric material and a load at heating (between 2 and 3’) process. In this process, the electric field is increased to the \(E_k\) value based on the electro-thermodynamic equation: \(\frac{dD}{dt} = \varepsilon \frac{dE}{dt} + pd\theta/dt\), where \(D\), \(E\), \(\theta\), \(c\), \(t\), and \(p\) are the polarization density, electric field, temperature, dielectric permittivity, time, and pyroelectric coefficient, respectively.4–6) This cycle can produce a higher \(N_D\) than the Olsen cycle under similar operating conditions.

In order to design a PEG for vehicles, it is necessary to understand the power generation characteristics of pyroelectric materials. The \(N_D\) of T–E cycles depends on material properties, temperature variation (maximum temperature, minimum temperature, and frequency), and electric field. It is thus necessary to conduct many power generation experiments under various temperature and electric field conditions to obtain the power generation characteristics of a material. A less empirical \(N_D\) prediction method is therefore needed.20,25,26)

Both physical models25,26) and hysteresis loops in the \(D – E\) plane20) (the only kind of hysteresis loops discussed in this paper) have been used in past attempts to predict \(N_D\). By measuring the hysteresis loops of a pyroelectric material, \(N_D\) can be obtained by simply calculating the area of the loop, without any power generation experiments. However, this method can only be used at temperatures where a hysteresis loop has been measured. On the other hand, using a physical model makes it possible to predict the theoretical value of \(N_D\) using known material properties such as the pyroelectric and piezoelectric coefficients. However, such models assume that these properties can be linearly approximated and can
therefore be applied only in the range where the polarization density depends linearly on the electric field and temperature. Therefore, both methods have limited temperature and voltage ranges. Moreover, published semi-theoretical performance predictions disagree with the experimental results, probably because hysteretic energy loss was not taken into account. Olsen et al. noted that hysteresis loss is non-negligible in $N_D$ predictions, and they calculated this loss by measuring the partial hysteresis using a unipolar electric field.20) The purpose of the present study is to establish a more precise $N_D$ prediction method for the Olsen cycle and Kim’s cycle at any temperature and electric field within the measurement range of the hysteresis loop, taking hysteresis loss into account. Material properties are approximated as polynomial functions of temperature and electric field. Hysteresis loops are measured using bipolar and unipolar electric fields, and formulas to estimate $N_D$ for the T–E cycles using the measurement results are derived. The results obtained by this method are compared to the empirical $N_D$ from power generation experiments.

2. Methods

2.1. Polarization density–electric field loop measurement
The $N_D$ prediction formula derived in the next section requires information from hysteresis loop measurements. Such measurements are common in material development.28–30 Figure 2 shows our experimental setup, consisting of a heater, silicone oil bath, Sawyer–Tower circuit, and pyroelectric material. Hysteresis loops of the sample were measured in the silicone oil bath using the Sawyer–Tower circuit. The silicone oil was heated by the heater. $D$ and $E$ were calculated from the measured voltage according to the standard equations:

\[ D = \frac{C V_c}{A}, \quad (1) \]
\[ E = \frac{V_E}{w}, \quad (2) \]

where $C$ is the capacitance of capacitor in the Sawyer–Tower circuit, $V_c$ the voltage across the capacitor, $A$ the electrode area of the sample, $V_E$ the voltage across the resistance, and $w$ the thickness of the sample. Table I summarizes the measurement conditions and physical properties of the sample, which was made of a commercially available ferroelectric, Pb(Zr, Ti)O$_3$ (Material no. C-9, Fuji Ceramics Corporation, Japan). The sample temperature was measured by a thermocouple (type K). The measurements were carried out at every 10 °C from 50 °C to 190 °C. In this study, both a bipolar electric field (−20 < $E$ < 20 kV cm$^{-1}$) and a unipolar electric field (0 < $E$ < 20 kV cm$^{-1}$) were applied to estimate hysteresis loss. Figure 3 shows the hysteresis loops measured at 80 °C and 150 °C under bipolar and unipolar electric field conditions. The hysteresis loss is the area enclosed by the partial hysteresis loop measured under the unipolar condition.

2.2. Derivation of prediction formula
Figure 4 shows the measured partial hysteresis loops and the semi-theoretical T–E cycles. The lower curve $D(\theta, E)$ and $E(\theta)$ were fitted by polynomial functions of $\theta$.

![Figure 1](image1.png)

(a) Olsen cycle. (b) Kim’s cycle. For each cycle, figures show (left) electric field/polarization density diagram, and (right) variation of temperature and electric field with time. $N_D$: net generated energy density.

![Figure 2](image2.png)

Fig. 2. (Color online) Experimental setup for hysteresis loop measurement using a Sawyer–Tower circuit.

![Figure 3](image3.png)

Fig. 3. Hysteresis loops measured at 80 °C and 150 °C under bipolar and unipolar electric field conditions. The hysteresis loss is the area enclosed by the partial hysteresis loop measured under the unipolar condition.

![Figure 4](image4.png)

Fig. 4. Measured partial hysteresis loops and the semi-theoretical T–E cycles. The lower curve $D(\theta, E)$ and $E(\theta)$ were fitted by polynomial functions of $\theta$.

| Physical properties of the Pb(Zr, Ti)O$_3$ sample and measurement conditions of hysteresis loop measurement. |
|---|
| Physical properties of the sample |
| Curie temperature °C | 130 |
| Density $10^3$ kg m$^{-3}$ | 7.75 |
| Pyroelectric coefficient $\mu C$ cm$^{-2}$ K$^{-1}$ | 0.098 |
| (50 °C) | |
| Remanent polarization $\mu C$ cm$^{-2}$ (Room temperature RT) | 25 |
| Coercive field kV cm$^{-1}$ (RT) | 7.0 |
| Measurement conditions |
| Temperature °C | 50–190 |
| Electric field waveform | Sine wave |
| Electric field (bipolar) kV cm$^{-1}$ | –20–20 |
| (unipolar) kV cm$^{-1}$ | 0–20 |
| Frequency (bipolar) Hz | 0.05 |
| (unipolar) Hz | 0.1 |
upper curve $D_u(\theta, E)$ of the partial hysteresis loops (where $\theta$ is temperature) were used for the calculation of $N_D$. $D_l(\theta, E)$ and $D_u(\theta, E)$ correspond to the electric field application (point 1 to 2) and removal (point 3 to 4) processes of the T–E cycle, respectively. For example, for $\theta_{\text{high}} = 150 \, ^\circ\text{C}$ and $\theta_{\text{low}} = 80 \, ^\circ\text{C}$, the semi-theoretical $N_D$ is calculated using $D_l(\theta = 80 \, ^\circ\text{C}, E)$ and $D_u(\theta = 150 \, ^\circ\text{C}, E)$.

$D_u(\theta, E)$ and $D_l(\theta, E)$ were obtained from the measured hysteresis loops. First, the partial hysteresis loops measured at each temperature $\theta$ were approximated by cubic polynomials in $E$, as follows:

$$D_l(\theta, E) = a_l(\theta)E^3 + b_l(\theta)E^2 + c_l(\theta)E + d_l(\theta),$$

$$D_u(\theta, E) = a_u(\theta)E^3 + b_u(\theta)E^2 + c_u(\theta)E + d_u(\theta).$$

The coefficients of determination for all approximate functions were more than 0.99.

Next, the coefficients $a_l(\theta)$, $b_l(\theta)$, $c_l(\theta)$, $d_l(\theta)$, $a_u(\theta)$, $b_u(\theta)$, $c_u(\theta)$, and $d_u(\theta)$ in Eqs. (3) and (4) were approximated by quartic polynomials in $\theta$. Figure 5 shows the coefficients $[a_l(\theta), b_l(\theta), c_l(\theta)$, and $d_l(\theta)]$ at each temperature and their best-fit curves. Near the Curie temperature, the physical properties of a pyroelectric material change drastically with temperature, so in the fitting we divided the temperature range for the approximation function into two ranges at the discontinuity point. The dividing points were 100 °C and 110 °C for Eqs. (3) and (4), respectively. The coefficients of determination for all approximate functions were over 0.98. After these approximations, $D_l(\theta, E)$, $D_u(\theta, E)$ can be calculated at any $E$ and $\theta$ within the ranges of the hysteresis loop measurement.

The prediction formula based on $D_l(\theta, E)$, $D_u(\theta, E)$ is derived under the following assumptions: I. Material temperature is uniform; II. Leakage current is zero; III. The secondary pyroelectric coefficient is zero. (The secondary pyroelectric coefficient corresponds to the piezoelectric contribution due to thermal expansion; it is much smaller than the primary pyroelectric coefficient, which corresponds to change in crystal dipole moment.)

The semi-theoretical net generated energy density of the Olsen cycle, $N_{D,\text{Ot}}$, is then
where $E_{\text{high}}$, $\theta_{\text{low}}$, and $\theta_{\text{high}}$ are the applied electric field, minimum temperature, and maximum temperature of the T–E cycle, respectively. The semi-theoretical net generated energy density of Kim’s cycle, $N_{D,Kt}$, is

$$N_{D,Kt} = \int_{E=0}^{E_{\text{high}}} D_{\Delta}(\theta_{\text{low}}, E)dE - \int_{E=0}^{E_{\text{high}}} D_{\Delta}(\theta_{\text{high}}, E)dE,$$

where $E_{\text{high}}$ is the electric field at the point 3’ in Kim’s cycle. $E_{\text{high}}$ is calculated from the following relation:

$$D_{\Delta}(\theta_{\text{high}}, E_{\text{high}}) = D_{\Delta}(\theta_{\text{low}}, E_{\text{high}}).$$

2.3. Power generation experiment

Figure 6 shows the experimental setup of the power generation experiment. It consists of two infrared radiation (IR) heaters, two IR thermometers, a “diode and two switches” (DSW) harvesting circuit, and the pyroelectric material. To realize the square-wave temperature variation shown in Fig. 6, the temperatures measured by the IR thermometers were fed back to the IR heaters. The temperature variation frequency was 0.02 Hz, and the temperature difference ($\theta_{\text{high}} - \theta_{\text{low}}$) was 40 °C. The DSW harvesting circuit can measure the net generating power of Kim’s cycle, and can also measure $E$ and $D$. In the Olsen cycle case, the switches in the DSW circuit were kept conductive at all times; in the Kim’s cycle case, the switches were turned on or off as needed. The electric field was applied and removed synchronously with the temperature variation; the $E_{\text{high}}$ values were 8.2 and 12.3 kV cm$^{-1}$. $D$ was calculated from the capacitance and voltage of the capacitor that was connected in series to the pyroelectric material. $N_{D}$ was obtained by integrating the measured T–E cycle in the $D$–$E$ diagram.

3. Results and discussion

Figure 7 shows the directly measured net generated energy density of the Olsen cycle, $N_{D,Om}$, and the directly measured net generated energy density of Kim’s cycle, $N_{D,Km}$, along with the corresponding semi-theoretical values ($N_{D,Ot}$ and $N_{D,Kt}$), for various $\theta_{\text{high}}$ and $E_{\text{high}}$. Maximum $N_{D,Om}$ and $N_{D,Km}$ were obtained at $E_{\text{high}} = 12.3$ kV cm$^{-1}$, $\theta_{\text{high}} = 140$ °C. In this condition, the $N_{D,Km}$ is 1.55 times larger than the $N_{D,Om}$, showing that Kim’s cycle realized more efficient power generation than the Olsen cycle. By controlling the switch of the DSW circuit, Kim’s cycle can produce $N_{D,Km}$ that is larger than $N_{D,Om}$, as shown in Fig. 1.4,5)

Figure 7(a) shows the experimental results for power generation in the Olsen cycle case, together with the calculated results. The calculated values, $N_{D,Ot}$, are comparatively close to $N_{D,Om}$. Therefore, the present method can accurately predict the power generation performance of pyroelectric materials. However, the temperature dependences of the calculated and measured $N_{D}$ differ somewhat.
Maximum $N_{D,\text{Om}}$ was obtained at $\theta_{\text{high}} = 129^\circ \text{C}$, $132^\circ \text{C}$ for $E_{\text{high}} = 8.2, 12.3$, respectively, while maximum $N_{D,\text{Om}}$ was obtained at $\theta_{\text{high}} = 140^\circ \text{C}$ for both values of $E_{\text{high}}$. The predicted temperature at which the maximum power density is obtained is approximately $10^\circ \text{C}$ lower than the experimental result. The reason for this difference may be the drastic change in the material properties near the Curie temperature ($130^\circ \text{C}$).

Figure 7(b) shows the experimental results for power generation in the Kim’s cycle case. $N_{D,\text{Km}}$ and $N_{D,\text{Kt}}$ are close under all conditions. Moreover, the temperature dependences of the theoretical and experimental $N_{D}$ are approximately the same, as are the temperatures at which maximum $N_{D}$ is obtained.

Figure 8 shows the calculated and measured T–E cycles of the maximum $N_{D}$ condition, i.e. $E_{\text{high}} = 12.3 \text{ kV cm}^{-1}$, $\theta_{\text{high}} = 140^\circ \text{C}$. Measured T–E cycles were shifted to match the point 2 with the calculated cycles. Figure 8(a) compares the calculated and measured Olsen cycles. $N_{D,\text{Om}}$ is 10.2% smaller than $N_{D,\text{Os}}$. The curvature of the calculated Olsen cycle between points 3 and 4 also does not match the measured one. The difference of curvature in the $D$–$E$ diagram implies a difference in permittivity, which in a ferroelectric material is mainly determined by $E$ and temperature. $E$ was accurately measured by the DSW circuit and the error was small. Therefore, a possible reason for this difference is a non-uniform temperature distribution of the sample, which causes a non-uniform polarization density distribution on the sample surface. The measured temperature distribution of the sample surface indicated that the peak to average ratio in the irradiated area (20 $\times$ 15 mm) was 1.11. Therefore, the electrode area of the sample (10 $\times$ 10 mm) had a temperature distribution of approximately several degrees Celsius.

Figure 8(b) shows the calculated and measured Kim’s cycles under $E_{\text{high}} = 12.3 \text{ kV cm}^{-1}$, $\theta_{\text{high}} = 140^\circ \text{C}$, which are the same conditions as those of Fig. 8(a). $N_{D,\text{Km}}$ was 14.9% smaller than $N_{D,\text{Kt}}$. The curvature of the calculated Kim’s cycle between points 3 and 4 does not match the measured one for the same reason as in the Olsen cycle case. Furthermore, the measured $D$ decreases during the passage from 2 to 3’ in Kim’s cycle, while the predicted $D$ from 2 to 3’ is constant. The prediction formula was derived with the assumption that the leakage current is zero. In reality, however, pyroelectric materials have a finite resistance value, and a small leakage current flows out of them.21,22,24) This current caused the measured $D$ to decrease between 2 to 3’.

4. Conclusions

A method of predicting $N_{D}$ for the Olsen cycle and Kim’s cycle at any temperature and electric field within the range of the hysteresis loop was proposed. Hysteresis loops were measured by combining unipolar and bipolar electric fields to estimate hysteresis loss. Prediction formulas considering hysteresis loss were established by approximating the hysteresis loops as functions of the electric field and temperature. The resulting semi-theoretical values of $N_{D}$ were in good agreement with the measured ones: the error was less than 15% at the temperature where the maximum $N_{D}$ was obtained experimentally.

The semi-theoretical $N_{D}$ calculated by the present method differed slightly from the measured $N_{D}$ due to real-world factors such as the non-uniform temperature distribution and the leakage current of the sample. Materials with a relatively low electrical resistivity are especially prone to leakage current, which will affect the measured $N_{D}$. Nevertheless, the proposed method should be able to predict $N_{D}$ with high accuracy for most pyroelectric materials of practical interest, because the leakage current of those materials is usually small at the operating temperatures of a PEG.

This method enables us to screen promising candidate materials for PEG applications and to determine efficient conditions for power generation. Furthermore, by combining the proposed method with circuit simulation, the amount of power generated by a multi-module PEG can be predicted.

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ORCID iDs

Masaaki Baba © https://orcid.org/0000-0002-0877-7792
Noboru Yamada © https://orcid.org/0000-0003-2432-0079

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