Relationship Between the Material Properties and Pyroelectric-Generating Performance of PZTs

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In pyroelectric applications, the general figures of merit (FOMs) have been applied and reported near room temperature. We derived the modified FOMs in considering our electro-thermodynamic cycle for the usage environment of automotive applications. The relationship between the material properties and generating performance of PZTs was investigated at various temperatures. The $F_D$ was suggested from $F_D$, a FOM for a pyroelectric sensor, based on the modified pyroelectric coefficient ($\overline{p}$); $\overline{p} \cdot \Delta T$ was calculated by the change in the spontaneous polarization ($P_S$) according to a given temperature variation during one cycle; $\Delta P_S/\Delta T (T_{max} - T_{min})$. It was indicated that the $F_D$ could be effective as a FOM for the pyroelectric generating performance and the dielectric loss ($\tan \delta$) significantly affected the generating performance in addition to $\overline{p}$ under high-temperature and electric-field conditions. Furthermore, of the PZTs tested, the C-91 sample which showed the highest generating performance resulted in a generated energy of 1.3 mW cm$^{-3}$ in the engine dynamometer assessment. This is 13 times greater than the generated energy reported in a previous study of C-6 (0.1 mW cm$^{-3}$).[1]

How much wasted heat exists, and how can we utilize it as renewable energy? These questions have been explored in automotive applications. Recently, there has been increasing interest in thermoelectric generation as an energy-regeneration technology because of the increasing concerns about environmental pollution and commitments to a low-carbon society. Therefore, to improve the fuel efficiency (energy saving) of automobiles, in this study, we focus on exhaust losses (exhaust gas), which account for approximately 30% of the gasoline energy, which is equal to the driving energy,[2] and developed an exhaust energy-regeneration technology based on thermoelectric generation.

According to a given temperature variation during generating cycle:

$$\Delta P_S/\Delta T (T_{max} - T_{min})$$

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In pyroelectric applications, general figures of merit (FOMs) have been applied and reported near room temperature. We derived modified FOMs for the usage environment of automotive applications by considering an electro-thermodynamic cycle. The relationship between the material properties and the generating performance of lead zirconate titanates (PZTs) was investigated at various temperatures. A general FOM $F_D$ for a pyroelectric sensor, quantifying the electrical noise caused by thermal energy (Johnson noise) was modified and suggested as $F_D$ by using $\overline{p}$ instead of pyroelectric coefficient ($p$). $\overline{p}$ was calculated from the change in the spontaneous polarization ($P_S$) according to a given temperature variation during generating cycle:

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In the context of exhaust energy regeneration, the majority of researchers assume that the thermoelectric generating system, which harnesses the Seebeck effect based on a spatial temperature gradient, is the most effective method for converting waste heat from exhaust gas into electricity.[13–20] The performance of materials based on the Seebeck effect is represented by the dimensionless figure of merit (FOM)

$$ZT = S^2 \sigma T \kappa^{-1}$$  \hspace{1cm} (2)

where S is the Seebeck coefficient, $\sigma$ is the electrical conductivity, T is the absolute temperature, and $\kappa$ is the thermal conductivity. Thus, the material requires conflicting properties of high electrical conductivity and low thermal conductivity. In addition, the temperature of both the cold and hot heat sources will always be required to be constant in terms of generating efficiency. However, the temperature of the exhaust gas from an automobile is unstable due to the inherent cycle of an internal combustion engine (intake $\rightarrow$ compression $\rightarrow$ explosion $\rightarrow$ exhaust). Moreover, it varies temporally according to the driving conditions, such as the acceleration and deceleration, which causes the engine rotation speed to fluctuate. In an automobile with a small engine, the engine’s rotational speed changes considerably, and the temperature change of the exhaust gas is more active. Therefore, in a compact vehicle, the thermal energy of the exhaust gas with temporal temperature variations negatively affects the use of the conventional thermoelectric-generation principle.

On the other hand, such temporal temperature variations can be an advantage for another application, the pyroelectric effect, which can also directly convert heat into electricity.[9–12] To date, considerable effort has been devoted to investigating the pyroelectric effect to develop a useful renewable energy source based on theoretical investigations, materials, and systems.[13–18] In the 1980s, Olsen et al. reported on an electrothermodynamic cycle (Olsen cycle) using the pyroelectric effect and an external electric field,[19,20] which can be described by a loop of electric displacement, $D$, versus the electric field, E ($D$–$E$ loop). The area denotes an energy density ($N_D$, theoretical generating potential), and a power density ($P_D = N_D E$) can also be evaluated.[13–20] However, despite these trials, this cycle has not yet been established in reality due to the difficulty of obtaining alternating high and low isothermal temperature periods.[13–20]

In a previous study, we presented a novel electro-thermo-dynamic cycle based on a temporal temperature variation to obtain a practical net energy from the exhaust gas of a automobile.[1] The most representative pyroelectric and piezoelectric material, Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (PZT, Fuji ceramics), was used. The temperature variation was considered as a simple sinusoidal wave based on imaging of the temperature fluctuation of the exhaust gas (Figure S1, Supporting Information). An external electric field, which corresponds to the temperature variation, was applied to the material (Figure S1). As a result, the $D$–$E$ loop of the new cycle resulted in a 1.9-fold larger area and 1.3-fold larger practical net energy than that produced by the Olsen cycle with the same input energy.[1] Furthermore, a net generated energy of 0.1 mW cm$^{-3}$ was obtained for the duration of the official standard test for light-duty vehicles in Japan (JC08) with a real engine.[1] The proposed new cycle indicated the possibility for real-world applications.

To realize the practical use of our cycle, the energy generation must be further improved, which may be possible by selecting and designing new materials with a high generating performance. FOMs are generally used for applications in energy harvesting ($F_E$, $k^2$)[11,12,21–24] and pyroelectric sensing ($F_V$, $F_D$, $F_O$).[9,12,21–25] $F_O$ and $k^2$ represent how much and how efficiently a pyroelectric material converts thermal energy into electrical energy. $F_V$, $F_D$ and $F_O$ denote the generation of maximum voltage, current, and noise for a given power input, respectively. In the reports relating to these FOMs the temperature dependence is not mentioned in detail because the usage environment of these applications is generally near room temperature.[9,12,21–25] In this study, the required material properties for higher generating performances were investigated based on the study of the relationship between material properties, which affect the FOM, and the pyroelectric generating performance. So our cycle was developed for applications using temperature variations near the Curie temperature ($T_C$), whereby the temperature dependence of all material properties that affect the FOM were measured at various temperatures individually (in the range of 50 °C to above the $T_C$); including the pyroelectric coefficient ($p$), relative dielectric constant ($\varepsilon_r$), dielectric loss (tan$\delta$), specific heat ($C_p$), and density ($\rho$).

The PZTs used in this study, their material properties, and their $F_E$ and $F_D$ at the minimum temperature (50 °C) are

| Sample | Type | $\rho$ ([nC cm$^{-2}$K$^{-1}$]) | $\varepsilon_r$ | tan$\delta$ (%) | $C_p$ ([J g$^{-1}$K$^{-1}$]) | $\rho$ ([x10$^5$ kg m$^{-3}$]) | $T_C$ [°C] | $F_E$ ([J m$^{-3}$K$^{-2}$]) | $F_D$ ([Pa$^{1/2}$]) |
|--------|------|-----------------------------|---------------|----------------|-----------------------------|-----------------------------|---------|-----------------------------|-----------------------------|
| C-9    | Soft | 91.5                        | 7233          | 3.7            | 0.34                        | 7.75                        | 130     | 1.31E + 11                  | 7.13E – 06                  |
| C-91   | Soft | 74.4                        | 3899          | 3.1            | 0.35                        | 7.75                        | 165     | 1.60E + 11                  | 8.38E – 06                  |
| C-82   | Soft | 46.2                        | 2582          | 1.8            | 0.36                        | 7.50                        | 195     | 9.34E + 10                  | 8.44E – 06                  |
| C-6$^a$| Soft | 53.1                        | 1652          | 1.5            | 0.34                        | 7.65                        | 295     | 1.93E + 11                  | 1.38E – 05                  |
| C-3    | Hard | 55.4                        | 427           | 0.6            | 0.35                        | 7.60                        | 270     | 8.12E + 11                  | 4.37E – 05                  |
| C-2    | Hard | 56.1                        | 1069          | 0.3            | 0.35                        | 7.60                        | 300     | 3.33E + 11                  | 3.96E – 05                  |
| C-213  | Hard | 58.7                        | 1328          | 0.5            | 0.34                        | 7.70                        | 345     | 2.93E + 11                  | 2.92E – 05                  |

$^a$basis sample used (C-6) from a previous study.[1]

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summarized in Table 1. As a representative of the samples, the data for the C-91 sample is shown in Figure 1 (all other data is compiled in Figure S2 of the Supporting Information). The maximum values (i.e., their peaks) of any of the material properties were observed around the $T_C$.

In the laboratory tests, 5 PZT samples (C-9, C-91, C-82, C-3, C-2) exhibited a higher generated energy than that of C-6 (reference material used in the previous study, $W_{max} = 0.14 \text{mW cm}^{-3}$ at 180 °C), as shown in Figure 2. C-91 exhibited the highest generated energy ($W_{max} = 0.46 \text{mW cm}^{-3}$ at 180 °C). These 5 samples showed a high temperature dependency related to the $T_C$.

From these results, it can be concluded that near-room-temperature FOMs cannot predict the pyroelectric generating performance at temperatures around the $T_C$. Therefore, the material properties and FOMs should be investigated in a wide temperature range. For example, the $F_E$ and $F_D$ of C-6 ($1.93 \times 10^{11} \text{J m}^{-3} \text{K}^{-2}, 1.38 \times 10^{-5} \text{Pa}^{-1/2}$) are obviously larger than those of C-91 ($1.60 \times 10^{11} \text{J m}^{-3} \text{K}^{-2}, 8.38 \times 10^{-6} \text{Pa}^{-1/2}$) at 50 °C.

The energy-harvesting FOM, $F_E$, which represents the amount of electrical power that a pyroelectric material can harvest from a hot source,[12,21–24] was first considered as a suitable FOM for our cycle and it is defined as:

$$F_E = \frac{p^2}{\epsilon_0 \epsilon_r}$$  \hspace{1cm} (3)

where $\epsilon_0$ is the vacuum permittivity ($8.854 \times 10^{-12} \text{F m}^{-1}$). The temperature dependence of $F_E$ is depicted with the results of the laboratory tests in Figure 3a. The results of the comparison between the temperature dependence of $F_E$ and that of the generated energy could be divided into three groups. C-9, C-91, C-82, and C-3 were grouped into group A; both temperature dependence exhibited the same tendency. C-6 and C-2 were grouped into B; both exhibited a peak but at different temperature ranges. C-213 was placed in group C; $F_E$ showed a peak; however, the generated energy decreased without a peak with increasing temperature. From the results of group B and C, other significant factors aside from the material properties that affect $F_E$ were expected to have an effect on the generating performance under high temperature and electric-field conditions, even when considering measurement errors of the equipment.

Because $F_E$ showed a correlation with the generating performance only for group A, other FOMs, $F_V$, $F_I$, and $F_D$, which are
generally used to describe pyroelectric sensor, were investigated next. \( F_D \) showed the best correlation with the generating performance for all PZTs. \( F_D \), which quantifies the electrical noise caused by the thermal energy (Johnson noise) and is generally the primary source of noise in a pyroelectric infrared detector, \[9,23–25\] is defined as

\[
F_D = \frac{\rho}{\rho C_r \sqrt{\varepsilon_0 \varepsilon_r}} \tan \delta
\]  

(4)

\( F_D \) showed a good correlation with the generating performance for group A. In addition, \( F_D \) also exhibited a closer correlation for the PZTs in groups B and C than that of \( F_E \), as shown in Figure 3b. The main difference between \( F_E \) and \( F_D \) is that \( F_D \) includes \( \tan \delta \), which is defined as

\[
\tan \delta = \frac{I_c}{I_R} = (\omega CR)^{-1}
\]  

(5)

where \( I_R \), \( I_C \), \( \omega \), \( C \), and \( R \) are the resistive current, capacitive current, angular frequency \( (\omega = 2\pi f) \), capacitance, and resistance, respectively. The lower generated energy of PZTs in group B compared to those in group A could be explained by the leakage current, which is one component of \( \tan \delta \). It is thus confirmed that \( \rho \) and \( \tan \delta \) are the fundamental material properties affecting the generating performance in our cycle.

By the way, even though \( F_D \) showed a good correlation with the generating performance, both peaks did not match completely. The peak of \( F_D \) was sharp and present only in a narrow temperature range. Therefore, it was different from the broad peak of the generated energy over a wide temperature range. This can be explained because \( F_D \) is derived from \( \rho \), which is defined as the amount of charge per unit area by a 1 °C temperature variation (change in spontaneous polarization, \( dP_s/dT \))\[9,11,12\]. In contrast, the generated energy can be defined as the total amount of charge created during a certain temperature variation (from \( T_{\text{min}} \) to \( T_{\text{max}} \); 10 s per cycle). Thus, \( F_D \) should be modified including a consideration of the temperature conditions under which the generated energy was measured in our cycle. A new parameter \( F_D \) based on \( \rho \), is

\[
F_D = \frac{\rho}{\rho C_r \sqrt{\varepsilon_0 \varepsilon_r} \tan \delta} \Delta P_s / \Delta T 
\]  

(6)
In Figure 3b the temperature dependence of $F_0$ and the generated energy are also analyzed. The correlation with group B could be obtained in addition to that of group A. From Table 1 it can be seen that there were 6 PZT samples for which a $F_0$ is effective as the FOM; the exception was C-213 of Group C. Additionally, the $F_0$ are more accurate with $F$, which is derived from changes in the spontaneous polarization for a given temperature variation. From these results, the required material specifications for a high generating performance could be chosen based on the following: high $F$ and low $\varepsilon$, $\rho$, $C_p$, and $\tan\delta$.

Making a simple specification still remains difficult, however. For example, in the case of $\varepsilon$ it should be discussed more from the view of the basic energy equation:[12]

$$E = CV^2 2^{-1} = \varepsilon SV^2 (2d)^{-1}$$  \(7\)

where $C$ is the capacitance, $V$ is the voltage, $S$ is the surface area and $d$ is the thickness. Besides, it might be also effective to consider the hysteresis characteristics of the material properties with temperature variation. Further, the material properties under applying electric field and the energy losses due to leakage current of the materials are also important. Therefore, a single FOM, which considers all of the above complicated factors, is required to develop materials with higher generating performances.

An engine dynamometer was used to evaluate the generating performance according to the official standard for light-duty vehicles in Japan (JC08).[16,27] C-91, which showed the highest power-generating energy in the laboratory test and corresponded well with the correlation of $F_0$, was chosen as the best sample. A generated energy of 1.3 mW cm$^{-3}$ was obtained, which is 13 times higher than that in a previous study of 0.1 mW cm$^{-3}$ (C-6).[13] as shown in Figure 4. $F_0$ might therefore be an extremely effective FOM for evaluating the pyroelectric generating performance with temperature variation.

In conclusion, $p$ and $\tan\delta$ were confirmed to be the fundamental material properties affecting the generating performance in our cycle. A modified FOM based on $p$ and $\tan\delta$ $F_0$ was suggested and showed a good correspondence to the pyroelectric generating performance at various temperatures. On the other hand, the existing FOMs and $F_0$ do not consider the electric field component yet, which is essential for our generating system. Thus, a novel FOM that considers the applied electric field should be proposed to aid in the development of a high-power generating material. These studies would further improve the generated energy and advance the development of the practical realization of a regenerating system.

**Experimental Section**

**Material:** The two sizes of PZT samples (Fuji ceramics, Japan) were prepared to be as small as possible based on our assessment system: one was for the laboratory test (12 mm × 17 mm × 0.5 mm, Ag electrode area: 8 mm × 13 mm), which minimized the in-plane temperature variations for the basic assessment to be able to accurately compare the measured and theoretical values, and the other sample size was for the engine dynamometer test (31 mm × 31 mm × 0.5 mm, Ag electrode area: 25 mm × 25 mm), which was installed on an automobile to perform an assessment with a real engine.

**Measuring Material Properties:** $p$ was calculated from $dP_0/dT$ where $P_0$ is defined as $i_s dt S^{-1}$, and $i_s$ and $S$ are the generating (pyroelectric) current and surface area, respectively. $i_s$ was measured using an electrometer (6517B, Keithley, accuracy: ±0.1% + 0.5 nA, ±1°C) in an electric oven with a temperature increase rate of 4°C min$^{-1}$. $\varepsilon$, $\rho$, $C_p$, and $\tan\delta$ were measured using an impedance analyzer (ZGA5920, NF Circuit Design
Bloc, accuracy: ±6%, ±1 °C in an electric oven at a measuring frequency of 1 kHz. $C_T$ was measured using a differential scanning calorimetry (DSC8500, Perkin Elmer, accuracy: ±1%, ±0.5 °C) at a temperature increase rate of 10 °C min$^{-1}$. $\rho$ was measured using an electronic balance (GR-202, A&D, accuracy: ±0.3%). In this study, the temperature dependence of $\rho$ was defined as a constant. In all measurement, the used temperature range was between 50 °C and above $T_C$. $T_C$ is referring to the catalog value of the Curie temperature from Fuji ceramics. The condition of the temperature variation was set as follows: upper limit of $T_{max} = 80 °C$–above $T_C$, temperature difference of $\Delta T = 40 °C$, and period of $f = 0.05$ Hz (time period of the temperature increase and decrease were each 10 s). An electric field of 0.2 kV mm$^{-1}$ was applied to the real sample and corresponded to the temperature variations. The electric field was varied between 0.2 and 0.8 kV mm$^{-1}$ to evaluate the generated energy. The circuit and method to measure the generated energy were the same as those of the laboratory assessment.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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