Dimensionless figure of merit and its efficiency estimation for transient response of thermoelectric module based on impedance spectroscopy

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It is well known that thermoelectric materials such as bismuth–telluride (BiTe) can convert temperature differences into electricity directly.1–3 In applications, numerous thermoelectric elements are assembled to efficiently control the heat flow into a thermoelectric module, which is called a Π-shaped thermoelectric module and comprises not only thermoelectric elements but also metal electrodes, binders such as conventional solder, and isolation plates with a high thermal conductivity. According to the theory of impedance spectroscopy,4–6 RC approximation can be introduced to estimate the performance of the module in the frequency domain when the total cross-sectional area of all the elements is nearly equal to that of all the electrodes.7–9 Because the commercial thermoelectric module is typically tightly integrated to enhance the performance of power generation, this condition is generally satisfied. Upon applying the RC approximation, the impedance Z of the module is given as9,10

\[
Z = R_{\text{ohm}} + R_{\text{mod}} \left( 1 - j(\omega/\omega_{\text{mod}}) \right) \left( 1 + (\omega/\omega_{\text{mod}}) \right)^{-1}, \tag{1}
\]

where \( R_{\text{ohm}} \) is the non-recovery term of the thermoelectric phenomenon, which is called the ohmic resistance of the element in the module and includes the contact resistance. \( R_{\text{mod}} \) is the impedance produced at a certain angular frequency \( \omega \), and \( \omega_{\text{mod}} \) is the representative angular frequency for the module, which depends on the characteristics of the thermoelectric element used. The latter is ideally expressed as7–9,10

\[
\omega_{\text{mod}} = \frac{\alpha_{\text{TE}}}{(L_{\text{TE}}/2)^2},
\]

where \( \alpha_{\text{TE}} \) and \( L_{\text{TE}} \) are the thermal diffusivity and length of the elements, respectively. According to the theory, the impedance \( R_{\text{mod}} \) represents the electricity recovered from the temperature difference using the module. Equation (1) implies that by applying the RC approximation, the thermoelectric module can be represented by an equivalent electric circuit involving two resistors and a capacitor, as shown in the inset of Fig. 1. The real part in the second term of the right-hand side of Eq. (1) is related to the generation of direct electric power from the temperature difference, and the imaginary part produces an impulse delay owing to the existence of the capacitance component derived from the heat capacity of the module. Here, the dimensionless figure of merit of the module in the steady-state condition is expressed as

\[
z_{0}T = \frac{R_{\text{mod}}}{R_{\text{ohm}}} = \frac{R_{\text{mod}} + R_{\text{ohm}}}{R_{\text{ohm}}} - 1,
\]

using the product of the figure of merit \( z_{0} \) under the steady-state condition and the temperature \( T \).1–3,9,13 This notation is identical to that of the Harman method based on the steady-state condition because the resistances \( R_{\text{mod}} + R_{\text{ohm}} \) and \( R_{\text{ohm}} \) correspond to the real part of the direct (\( R_{\text{DC}} \)) and alternative (\( R_{\text{AC}} \)) resistance, respectively.9,11–13 It has been shown that the figure of merit depends on the input heat angular frequency \( \omega \) based on the theory of impedance spectroscopy5–9 and not just the Seebeck coefficient, resistivity, and thermal conductivity. Therefore, the notation should be modified from Eq. (1) to \( z_{0}T \); i.e.,

\[
z_{0}T = \frac{R_{\text{mod}}}{R_{\text{ohm}}} \left[ \frac{1}{1 + (\omega/\omega_{\text{mod}})^2} \right],
\]

when the input heat angular frequency is \( \omega \) and the real part in Eq. (1) is utilized. It is shown that \( z_{0}T \) at \( \omega = 0 \) should be equal to \( z_{0}T \). Here, the normalized dimensionless figure of merit \( zT_{N} \) is defined as

\[
zT_{N}(\omega, \omega_{\text{mod}}) = \frac{z_{0}T}{z_{0}T} = \frac{1}{1 + (\omega/\omega_{\text{mod}})^2}, \tag{2}
\]
which is a function of the input heat angular frequency \( \omega \) and the representative angular frequency \( \omega_{\text{mod}} \). \( z_T \) is expressed as the ratio of dimensionless figure of merit at a certain angular frequency \( \omega \) to that at steady state (\( \omega = 0 \)).

Using the RC approximation, the dimensionless figure of merit can be easily analyzed by varying the temperature for transient response. It is assumed that the input heat angular frequency \( \omega \) is completely fixed by that of the heat source. This implies that the heat capacity of the thermoelectric module is significantly smaller than that of the source. Let us consider the transient response when there is a certain temperature difference at \( t = 0 \) (hot side: \( T_h \), cold side: \( T_c \)) and the difference completely disappears at the characteristic time \( t = \tau \) (hot side: \( T_h \), cold side: \( T_c \)). Figure 1 shows five different temperature profiles \((n = 1 \text{ to } 5)\) that demonstrate the relationship between the time \( t \) and the normalized temperature difference \( \Delta T(t, \tau) = [T_h(t) - T_c(t)]/\Delta T_0 \), where \( \Delta T_0 = T_h(0) - T_c(0) \) is the initial temperature difference at \( t = 0 \) for \( \tau = 1 \text{ s} \). For example, \( \Delta T(1, \tau) \) has a constant initial temperature difference at \( t = 0 \), and the difference decreases linearly with time. Finally, the temperature difference between the hot and cold sides decreases to 0 at \( t = \tau \) s.

Because each transient response has a representative angular frequency distribution, the distribution can be revealed by Fourier cosine transformation using the Fourier cosine amplitude \( F_{c,n}(\omega, \tau) = \sqrt{2/\pi} \int_0^{\infty} \Delta T_n(t, \tau) \cos \omega t \, dt \) for each temperature profile \( \Delta T_n(t, \tau) \). \( F_{c,n}(\omega, \tau) \) takes a positive or negative value from \( \omega = 0 \) to \( \infty \); therefore, the normalized distribution of the input heat angular frequency in the frequency domain \( g_n(\omega, \tau) \) is expressed as

\[
g_n(\omega, \tau) \, d\omega = \frac{|F_{c,n}(\omega, \tau)| \, d\omega}{\int_0^{\infty} |F_{c,n}(\omega, \tau)| \, d\omega}.
\]

This means that \( g_n(\omega, \tau) \, d\omega \) is proportional to a certain angular frequency \( \omega \), and \( \int_0^{\infty} g_n(\omega, \tau) \, d\omega = 1 \). The inset of Fig. 1 shows the input heat angular frequency dependence of \( g_n(\omega, \tau) \) for \( \tau = 1 \text{ s} \). The component of \( g_n(\omega, \tau) \) rapidly decreases as \( \omega \) increases. For example, \( g_1(\omega, \tau) \) and \( g_5(\omega, \tau) \) are approximately 0.318 and 0.127, respectively, at \( \omega = 0 \). Moreover, the dominant component of the angular frequency is less than approximately 6 rad/s, corresponding to \( 2\pi/\tau = 2\pi/\tau \) at \( \tau = 1 \text{ s} \).

Because the thermoelectric module acts as a low-pass filter in the equivalent circuit shown in the inset of Fig. 1, the magnitude of \( g_n(\omega, \tau) \, d\omega \), which is less than the representative angular frequency \( \omega_{\text{mod}} \), significantly affects the energy conversion and its efficiency. It is expected that the component of an input heat angular frequency far higher than \( \omega_{\text{mod}} \) would be somewhat neglected. We consider a simple case to estimate the dimensionless figure of merit and its efficiency for the transient response. We assume that the figure of merit \( z \) is inversely proportional to the temperature \( T \) \((z \propto 1/T)\), which means that the dimensionless figure of merit \( z_T \) has no temperature dependence. According to Eqs. (2) and (3), the effective dimensionless figure of merit \( z_T \) in the transient response is expressed as

\[
z_T(\omega, \omega_{\text{mod}}) = \int_0^{\infty} z_T(\omega, \omega_{\text{mod}}) g_n(\omega, \tau) \, d\omega.
\]

\( z_T(\omega, \omega_{\text{mod}}) \) is determined by the frequency-domain performance of the module used, particularly with regard to the thermal diffusivity and the length of the thermoelectric element in the module. On the other hand, the temperature variation, \( g_n(\omega, \tau) \) \( d\omega \), depends on the characteristics of the heat source. Although the effective dimensionless figure of merit \( z_{T_{\text{eff}},n} \) is determined by two completely different and independent factors \( (\omega_{\text{mod}} \text{ and } \tau) \), \( z_{T_{\text{eff}},n} \) can be described by using the dimensionless parameter \( \omega_{\text{mod}} \). Figure 2 shows the \( \omega_{\text{mod}} \) dependence of \( z_{T_{\text{eff}},n} \). \( z_{T_{\text{eff}},n} \) is close to zero for \( \omega_{\text{mod}} < 0.1 \) and increases with \( \omega_{\text{mod}} \) for any temperature variation. Finally, \( z_{T_{\text{eff}},n} \) nearly reaches 1.0 at \( \omega_{\text{mod}} > 10 \). This tendency is almost the same regardless of the temperature variation shown in Fig. 2 but depends strongly on the component of \( g_n(0, \tau) \). A far higher \( z_{T_{\text{eff}},n} \) at a certain \( \omega_{\text{mod}} \) necessitates a larger \( g_n(0, \tau) \) because the time constant of the circuit shown in the inset of Fig. 1 is determined by \( \omega_{\text{mod}} \), which is low compared with the electric circuit. The typical value of \( \omega_{\text{mod}} \) is on the order of 1 rad/s for a thermal diffusivity of \( \alpha = 1 \times 10^{-6} \text{ m}^2/\text{s} \) and a length of \( L = 1 \text{ mm} \), which are representative values for commercial thermoelectric modules using BiTe elements.\(^{10,14,15}\) The upper vertical axis in Fig. 2 shows the characteristic time \( \tau \) required to achieve a certain normalized dimensionless figure of merit \( z_{T_{\text{eff}},n} \) for \( \omega_{\text{mod}} = 1.0 \text{ rad/s} \) as a representative value. According to rough estimation, the effective dimensionless figure of merit, \( z_{T_{\text{eff}},n} \), weakly depends on the function of the temperature profiles.

As typical examples, we focus on the temperature variation of \( \Delta T(1, \tau) \) and \( \Delta T(3, \tau) \). We previously reported the representative angular frequency in air according to the measurement of the thermal diffusivity by an infrared camera for the element parts \( (\omega_{\text{mod}}, \text{TE}: 3.01 \text{ rad/s}) \) and impedance spectroscopy \( (\omega_{\text{mod}}: 0.629 \text{ rad/s}) \) for the commercial BiTe thermoelectric module.\(^{10}\) The difference is due to the influence of the heat capacity of the electrodes, binders, and isolation plates in the actual application. The analysis of the effective dimensionless figure of merit applies to these values. Figure 3 shows the characteristic time dependence of the effective dimensionless figure of merit for the temperature variations \( \Delta T(1, \tau) \) and \( \Delta T(3, \tau) \), obtained using realistic
values of $\omega_{\text{mod,TE}}$ and $\omega_{\text{mod}}$. If the contribution of only the thermoelectric element parts is considered ($\omega_{\text{mod,TE}}$), a higher $\zeta_T$ can be achieved at a significantly smaller time $\tau$ than expected; however, $\omega_{\text{mod}}$ measured via impedance spectroscopy is far smaller than that of the element parts ($\omega_{\text{mod}} < \omega_{\text{mod,TE}}$). Therefore, the calculated $\zeta_T$ curve is shifted to a higher characteristic time. As an example, we consider the condition at $\Delta T_1$ and $\Delta T_2$ using $\omega_{\text{mod,TE}}$ are 0.528 and 1.66 s, respectively. On the other hand, the required characteristic times $\tau_{0.5}$ for $\Delta T_1$ and $\Delta T_2$ using $\omega_1$ are 2.56 and 7.88 s, respectively, as expected from the magnitude of $g_0(0, \tau)$, given that $\zeta_T(\omega_{\text{mod}}, \tau) < \zeta_T(\omega_{\text{mod,TE}}, \tau)$ generally. A characteristic time one order greater is required to obtain $\zeta_T > 0.9$. If the characteristic time $\tau$ exceeds $10^3$ s, the performance of the thermoelectric module is identical to that under the steady-state condition. The insets of Fig. 3 show the representative angular frequency $\omega_{\text{mod}}$ and characteristic time $\tau$ dependence of the effective dimensionless figures of merit $\zeta_{T,\text{eff,1}}$ and $\zeta_{T,\text{eff,5}}$, respectively.

As the effective dimensionless figure of merit $\zeta_{T,\text{eff,1}}$ is estimated for the transient response, the efficiency of the thermoelectric conversion $\eta$ can be calculated as

$$\eta_{\text{fi}}(T_h, T_c, \omega_{\text{mod}}, \tau) = \frac{T_h - T_c}{T_h} \times \sqrt{\frac{1 + \zeta_{T,\text{eff,1}}(\omega_{\text{mod}}, \tau)}{1 + \zeta_{T,\text{eff,1}}(\omega_{\text{mod}}, \tau) + T_c/T_h}}.$$  

Figure 4 shows the calculated efficiency $\eta_{\text{fi}}$ for $\Delta T_1(t, \tau)$ in Fig. 1 for a varying hot-side temperature $T_h$ and fixed cold-side temperature of $T_c = 300$ K, assuming no temperature dependence of $\zeta_{T,\text{eff,1}}$ and $\zeta_{T,\text{eff,5}} = 1.0$. For example, the efficiency is 8.2% for a temperature difference of 200 K ($T_h = 500$ K) in the steady-state condition ($\tau \approx \infty$), and the efficiency gradually decreases with a decrease in the characteristic time for $\tau > 10$ s, as shown in the inset of Fig. 4. In the region of $\tau < 10$ s, the efficiency decreases drastically. Then, the reduction of the efficiency might occur in $\tau < 10$ s at $\omega_{\text{mod}} = 0.629$ rad/s. The difference in the efficiency between the steady-state condition (~8.2%) and $\tau = 10$ s (~7.3%) is <1% at $T_h = 500$ K, as shown in Fig. 4. Of course, the estimated efficiency is far lower than that in the steady-state condition — less than 3% at $\tau = 1$ s; however, the characteristic time is too low for cooling from $T_h = 500$ to 300 K in 1 s, owing to the heat capacity of the heat source and module.

The aforementioned estimation and discussion allow the validation of the performance of the $\Pi$-shaped thermoelectric module by using it for an actual application such as the heat recovery of an automobile engine with temperature fluctuation. We guess that a conventional module can be utilized for energy recovery when the characteristic time $\tau > 10$ s. If investigation of the heat source reveals that the characteristic time $\tau$ is significantly shorter, i.e., <1 s, we must fabricate the module with a higher $\omega_{\text{mod}}$ to increase the performance of the module by using a far larger thermal diffusivity, thinner elements, or a significantly lower module heat capacity.

The five temperature profiles used in this study are associated with cooling; however, the dimensionless figure of merit and the efficiency are identical to those for heating, owing to the temperature-symmetry. When the period of the steady-state condition is far longer than that of the transient response, we guess that the consideration discussed can be neglected. On the other hand, the effective dimensionless figure of merit is considered when there are continuous large temperature variations, decreasing the performance of the module. We should realize the properties of the thermoelectric module — not only its physical properties at steady state but also the magnitude and its distribution in the frequency domain. Therefore, the concept of impedance spectroscopy is very useful for recognizing applications in which the temperature is varied using the heat source.

We estimated the effective dimensionless figure of merit for a transient response according to impedance spectroscopy by applying the RC approximation for the $\Pi$-shaped thermoelectric module. The analysis revealed that the dimensionless...
figure of merit depends on the representative angular frequency of the thermoelectric module $\omega_{\text{mod}}$ and the characteristic time $\tau$. The product of $\omega_{\text{mod}}$ and $\tau$ yields a dimensionless normalized parameter for estimation of the performance using the module, and the effective dimensionless figure of merit is given by the function $\omega_{\text{mod}} \tau$. Because the module acts as a low-pass thermal filter, a higher input angular frequency does not respond; therefore, the estimated effective dimensionless figure of merit is <1.0 when there is temperature variation. We quantitatively conclude that a far longer characteristic time (at least $\tau > 10$ s) is required for the transient response for the commercial module to achieve a higher effective dimensionless figure of merit and efficiency.

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1) G. S. Nolas, J. Sharp, and H. J. Goldsmid, *Thermoelectrics: Basic Principles and New Materials Developments* (Springer, Berlin, 2001) Chaps. 1 and 5.
2) D. M. Rowe, *CRC Handbook of Thermoelectrics* (CRC Press, Boca Raton, FL, 1995) Sects. D and E.
3) D. M. Rowe, *Thermoelectrics Handbook: Macro to Nano* (CRC Press, Boca Raton, FL, 2006) Sects. III and IV.
4) A. D. Downey, T. P. Hogan, and B. Cook, *Rev. Sci. Instrum.* 78, 093904 (2007).
5) A. De Marchi and V. Giaretto, *Rev. Sci. Instrum.* 82, 034901 (2011).
6) A. De Marchi and V. Giaretto, *Rev. Sci. Instrum.* 82, 104904 (2011).
7) J. García-Cañadas and G. Min, *J. Appl. Phys.* 116, 174510 (2014).
8) J. García-Cañadas and G. Min, *J. Electron. Mater.* 43, 2411 (2014).
9) Y. Hasegawa, R. Homma, and M. Otsuka, *J. Electron. Mater.* 45, 1886 (2016).
10) M. Otsuka, H. Terakado, R. Homma, Y. Hasegawa, Md. Zahidul Islam, G. Bastian, and A. Stuck, *Jpn. J. Appl. Phys.* 55, 126601 (2016).
11) T. C. Harman, *J. Appl. Phys.* 29, 1373 (1958).
12) T. C. Harman, J. H. Cahn, and M. J. Logan, *J. Appl. Phys.* 30, 1351 (1959).
13) H. Iwasaki, H. Morita, and Y. Hasegawa, *Jpn. J. Appl. Phys.* 47, 3576 (2008).
14) R. Homma, Y. Hasegawa, H. Terakado, H. Morita, and T. Komine, *Jpn. J. Appl. Phys.* 54, 026602 (2015).
15) M. Otsuka, R. Homma, and Y. Hasegawa, *J. Electron. Mater.* 46, 2752 (2017).