

Effect of Thermal Cycling on Commercial Thermoelectric Modules

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ABSTRACT

The large temperature gradients experienced by thermoelectric modules induce significant thermal stresses which eventually lead to device failure. The impact of thermal cycling on a commercial thermoelectric module is investigated through characterization of the electrical properties. In this work, we measure the evolution of the thermoelectric and electrical properties with thermal cycling. One side of the thermoelectric module is cycled between 30°C and 160°C every 3 minutes while the other side is held at ~20°C. The thermoelectric figure of merit, $Z_{TE}\bar{T}$, and electrical resistivity are measured after every 1000 cycles. The measured $Z_{TE}\bar{T}$ value is compared using both a modified Harman method and an electrical measurement technique analyzed with an electrical circuit model. In addition, the change in output power and resistivity with cycling are reported. This study provides insight into characterization methods for thermoelectric modules and quantifies reliability characteristics of thermoelectric modules.

KEY WORDS: thermoelectric modules, thermoelectric figure of merit, thermal cycling

NOMENCLATURE

ΔT	temperature difference across the module (K)
G_m	effective thermal conductance (W/K)
I_a	applied current (A)
I_O	current output (A)
k	thermal conductivity (W/m/K)
R_l	load resistance (Ω)
R_m	effective resistance of TE (Ω)
$\bar{T}$	average temperature (K)
TE	thermoelectric module or device
S_m	effective Seebeck coefficient (V/K)
s	Laplace domain variable ($\sigma + j\omega$)
V_O	voltage output (V)
Z_M	impedance of thermoelectric module
$Z_{TE}\bar{T}$	thermoelectric figure of merit for module

Greek symbols

ρ	density (Mg/m ³)
σ	real part of Laplace variable
θ	phase of impedance (rad)
ν	Poisson ration
ω	angular frequency, imaginary part of Laplace variable

Subscripts

a	applied
C	cold side
e	Ohmic

H	hot side
l	load
m	module
o	output
th	thermal

INTRODUCTION

Thermoelectric (TE) devices have been widely investigated for direct energy conversion and electricity generation from waste heat sources as well as scalable, solid state refrigeration [1]. A large temperature gradient across the TE module is required for significant power generation, and this temperature gradient leads to significant thermal stress. The performance of TE modules degrades with thermal cycling as the constituent materials and interfaces are exposed to large temperature gradients[2-5].

Hatzikraniotis *et al.* [3] found that thermal cycling significantly affected the performance of a thermoelectric generator. After cycling up to a hot side temperature (T_H) of 200°C for 6000 cycles, the maximum power output of TE and EMF, measured by monitoring the module voltage and current during the reliability test, dropped by 14% and 3.3%, respectively. Additionally, Z-meter and AC impedance measurements indicated electrical resistance increased by ~16%, while the Seebeck coefficient decreased by 3.8%. The degradation in performance and ultimate device failure were attributed to formation of cracks, as well as inter-diffusion of metal solder into the p- or n-type blocks. In addition, Saber *et al.* [6] conducted a reliability test at a significantly higher cycling temperature of $T_H \sim 700^\circ\text{C}$ on Skutterudite-based thermoelectric uncouples both with and without a metallic sublimation suppression coating. In the study, the uncoated samples were significantly degraded after 1000 hours compared to those with the metallic sublimation suppression coating, as measured by the rapid change in the n- and p-leg electrical resistances and the Seebeck coefficient.

Using a continuum simulation technique, Hori *et al.* [4] revealed tensile stresses on TE module up to 142.6 TPa when the temperatures on hot side and cold side are 180°C and 30°C, respectively. This stress, caused by thermal expansion mismatch of TE elements and metal contacts, led to degradation of the power output resulting in TE failure within 400 cycles. In addition, Barako *et al.* [7] found that through cycling the current applied though TE module microcracks formed at the interface between the connecting metal and the thermoelectric element and non-uniformity of temperature distribution as seen in figure 1. The TE module oscillates between +146°C and -20°C for 45000 cycles until failure. Compared to the condition of a TE before thermal cycling, the Seebeck coefficient remains stable, the thermal conductivity increases ~20% and the electrical resistance decreases by a

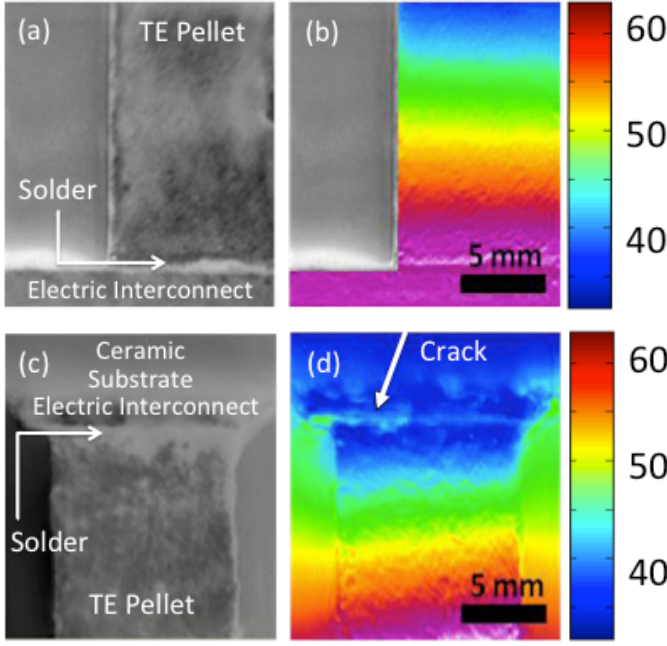


Figure 1. (a) Optical and (b) infrared image for a thermoelectric pellet before internally generated thermal cycling. (c) Optical and (d) infrared image for a thermoelectric pellet after 45,000 cycles. Courtesy of Barako *et al.* [7].

factor of ~ 30 . As a result, the $Z_{TE}\bar{T}$ of the sample module drops to $\sim 3\%$ of the original value, and the change in $Z_{TE}\bar{T}$ and electrical resistance of the TE module over thermal cycling has degraded with same trajectory.

The performance of TE modules is generally characterized by the power output and conversion efficiency. Several methods have been developed to characterize the thermoelectric figure of merit, $Z_{TE}\bar{T}$, a key metric of thermoelectric efficiency [1,8-11]. To characterize $Z_{TE}\bar{T}$, two types of methods are commonly used: transient characterization (*i.e.* the Harman method) and frequency response measurements [8,9].

In this work, the evolution of the TE module performance with thermal cycling is reported. The hot side of the thermoelectric module is cycled between 30 and 160°C every 3 minutes while the cold side is held at $\sim 20^\circ\text{C}$. In order to evaluate the efficiency of the module, $Z_{TE}\bar{T}$ is measured every 1000 cycles using both the Harman method and an electrical measurement technique analyzed with an RC one-port model. The electrical resistance and power output of the module are also evaluated.

EXPERIMENTAL SETUP

Thermal Cycling

In this work, we analyze a commercial thermoelectric module (Ferrotec 9500/127/060 B), consisting of 127 np thermoelectric junctions. The dimension of a TE module is 39.7mm x 39.7mm x 4.16mm, and the thermoelectric elements are Bi_2Te_3 -based alloys. As shown in figure 2(a), the hot side of the TE module being measured (“sample module”) is heated with two thermoelectric devices (“drive modules”) in series. The drive TE modules are attached to the sample module with a heat spreader. Chilled water heat exchangers,

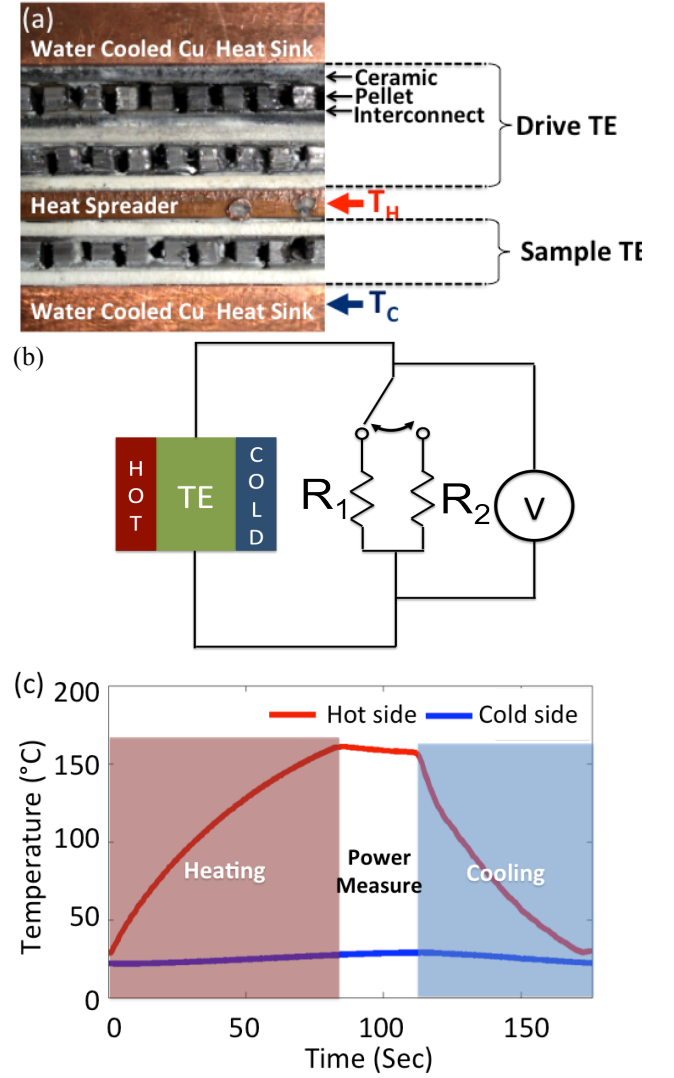


Figure 2. (a) Thermal cycling configuration examined in this work. The sample TE module is sandwiched between a heat spreader and water cooling block. The hot side of the sample TE module is heated with two drive TE modules connected in series. The cold side of the first drive TE module is also cooled by a chilled-water heat exchanger. The temperatures of the hot and cold sides of the sample TE module are indicated by locations marked T_H and T_C . (b) The circuit for power measurement. The temperatures in hot and cold sides and voltage for R_1 and R_2 are measured. R_1 and R_2 are $47\ \Omega$ and $1\text{k}\Omega$, respectively. (c) Thermal cycling profile. The hot side temperature (red line) is cycled between 30°C and 160°C , while the cold side temperature (blue line) remains at $\sim 20^\circ\text{C}$. The temperature is slightly changed due to the delay in thermal response while measuring power, and its averaged value is used for the result.

attached to both sides of the stack of thermoelectric modules, serve as thermal reservoirs and maintain the cold side of the sample module at $\sim 20^\circ\text{C}$ throughout thermal cycling, which allows to improve cycling efficiency. In order to reduce the thermal contact resistance between the components, all

contacting surfaces were coated with thermal grease (Omegatherm 201).

During thermal cycling, the hot side temperature is measured at the heat spreader block and the cold side temperature is measured at the water-cooling block. All temperatures are measured using K-type thermocouples placed in holes drilled in the copper pieces and are recorded with LabVIEW using an SCXI-1102 isothermal data acquisition board. The measured temperature difference across the two copper blocks is almost constant during power measurements. However, the temperature difference across the sample TE module itself will be slightly reduced due to contact resistances between the copper and the TE module.

As shown in Figure 2(b), the hot side of sample TE module is cycled between 30°C and 160°C over 180 seconds and the cold side temperature is held at 20°C with water-cooling. Thermoelectric and electrical properties are measured before thermal cycling and after every 1000 cycles.

Property Measurements

The maximum efficiency of thermoelectric module is analytically calculated, and the formula for the efficiency is expressed in [1]:

$$\eta_{\max} = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + Z_{TE}\bar{T}} - 1}{\sqrt{1 + Z_{TE}\bar{T}} + \frac{T_C}{T_H}}, \quad (1)$$

The efficiency of the TE module can be determined by characterizing the figure of merit, $Z_{TE}\bar{T}$. In this work, we use a modified Harman method and a frequency dependent characterization technique (analyzed with a one-port RC model) to characterize $Z_{TE}\bar{T}$ of the module [8,9].

Harman method. A modified Harman method measures the effective module figure of merit and electrical resistance of the sample TE module. A 5 mA DC current is sourced through the thermoelectric module until the system reaches thermal equilibrium. This current is low enough to create a small temperature gradient without providing significant Joule heating. The total measured voltage across the module consists of an Ohmic component, V_e , and a thermal voltage, V_{th} , due to the Seebeck effect. When the current source is turned off (at ~35 sec in Figure 3(b)), the Ohmic voltage component instantaneously ceases, but the temperature gradient is temporarily maintained across the module owing to its heat capacity. The slower voltage decay, evident in Figure 3(b), corresponds to the voltage generated by the Seebeck effect. The effective device figure of merit is calculated with:

$$Z_{TE}\bar{T} = \frac{V_{th}}{V_e}, \quad (2)$$

where $\bar{T}$ is the average temperature. From the Ohmic component of the measured voltage and the applied current, I_a , the module electrical resistance, R_m , is calculated simply using Ohm's Law. For this method to be accurate, the system must reach steady-state before the current flow is stopped, 1-D conduction must dominate the sample, and the temperature increase due to the applied current must be small [8]. As shown in figure 2(b), the system reaches steady state before the current source is stopped. Each individual pellet of the TE

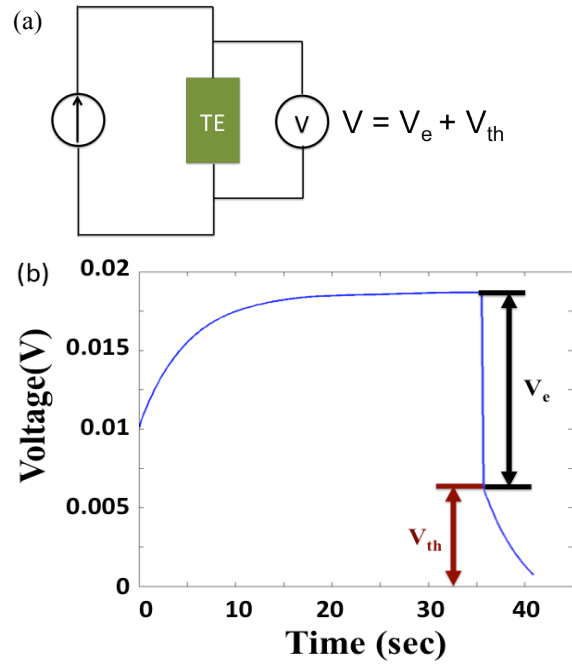


Figure 3. (a) Circuit for the Harman method. The voltage across the sample TE module is measured while constant current is applied. Once the voltage reaches steady-state, the current source is stopped and the voltage decay characterizes the module $Z_{TE}\bar{T}$. (b) Measured voltage trace for the sample TE module from the Harman method. V_e and V_{th} are the voltages due to electrical resistance of TE and due to the Seebeck effect, respectively.

module has a small Biot number, less than 0.1, and thus conduction along the sample is dominant. Finally, the temperature increase across the TE is calculated to be less than 0.2K from the measured thermal voltage and nominal Seebeck coefficient from Ferrotec [12].

Frequency-Dependent Electrical Measurement & RC One-Port Model. The frequency-dependent impedance of the thermoelectric module is measured in order to estimate the thermoelectric figure of merit. A sinusoidal current passes through the thermoelectric module in series with 47Ω resistor that is comparable to the intrinsic resistance of TE (see Figure 4 (a)). The voltages across the module, V_{TE} , and across the separate resistor, V_R , are measured with a lock-in amplifier, and the impedance of TE is calculated with the amplitude and phase (θ) of these two voltage signals. The magnitude and phase of the impedance of the module (Z_m) are expressed in equation (3) and (4), respectively:

$$|Z_m| = R \frac{V_R}{V_{TE}}, \quad \text{and} \quad (3)$$

$$\angle Z_m = \theta_{TE} - \theta_R. \quad (4)$$

When the AC current is applied to the thermoelectric module, the time scales of the thermal and electrical responses are critical. At low frequency, a temperature gradient is generated across the module each cycle of the current source. Thus, both

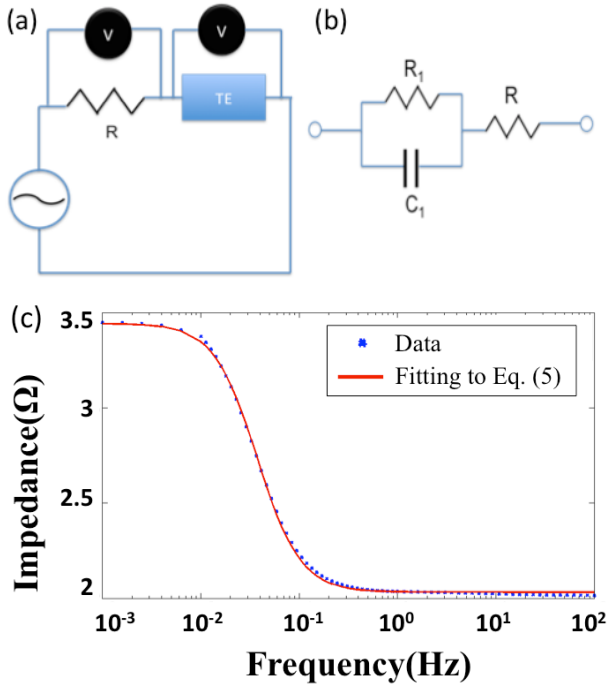


Figure 4. (a) Experimental circuit for the frequency-dependent measurement ($R = 47\Omega$). (b) RC one-port model. The thermoelectric module is modeled with the equivalent electrical circuit composed of two resistors and a capacitor. (c) Measured (points) and modeled (red line) frequency response of thermoelectric module.

the Seebeck effect voltage and the Ohmic voltage drop contribute to the measured voltage signal and impedance. But at high frequencies, the thermal diffusion depth is small and the voltage signal is primarily from the Ohmic component.

To estimate the module figure of merit from measured frequency response, the TE module is modeled with an equivalent electrical circuit consisting of a capacitor and two resistors (shown in figure 4(b)). As shown by Downey *et al.* [9], the resistor and capacitor in parallel ($R_1 || C_1$) account for the thermal/thermoelectric effects, while the additional resistor in series (R) accounts for the electrical resistance of the TE module.

In the Laplace domain, the impedance of the system can be expressed as:

$$Z_m(s) = \frac{R(s + \omega_z)}{(s + \omega_p)}, \quad (5)$$

where ω_z is the zero frequency, ω_p is the pole frequency, and in Laplace domain, $s = \sigma + j\omega$. The critical frequencies of the equivalent circuit are extracted by fitting the frequency-dependent impedance response (see Figure 4(c)) yielding $\omega_z = 0.0557 \cdot (2\pi)$ rad/s and pole frequency, $\omega_p = 0.0329 \cdot (2\pi)$ rad/s (before thermal cycling).

Assuming one-dimensional conduction, a small temperature gradient, and steady-state conditions, the figure of merit, $Z_{TE}\bar{T}$, is evaluated using critical frequencies of the system. In this case, steady-state indicates that the amplitude of the voltage response remains constant over several cycles of

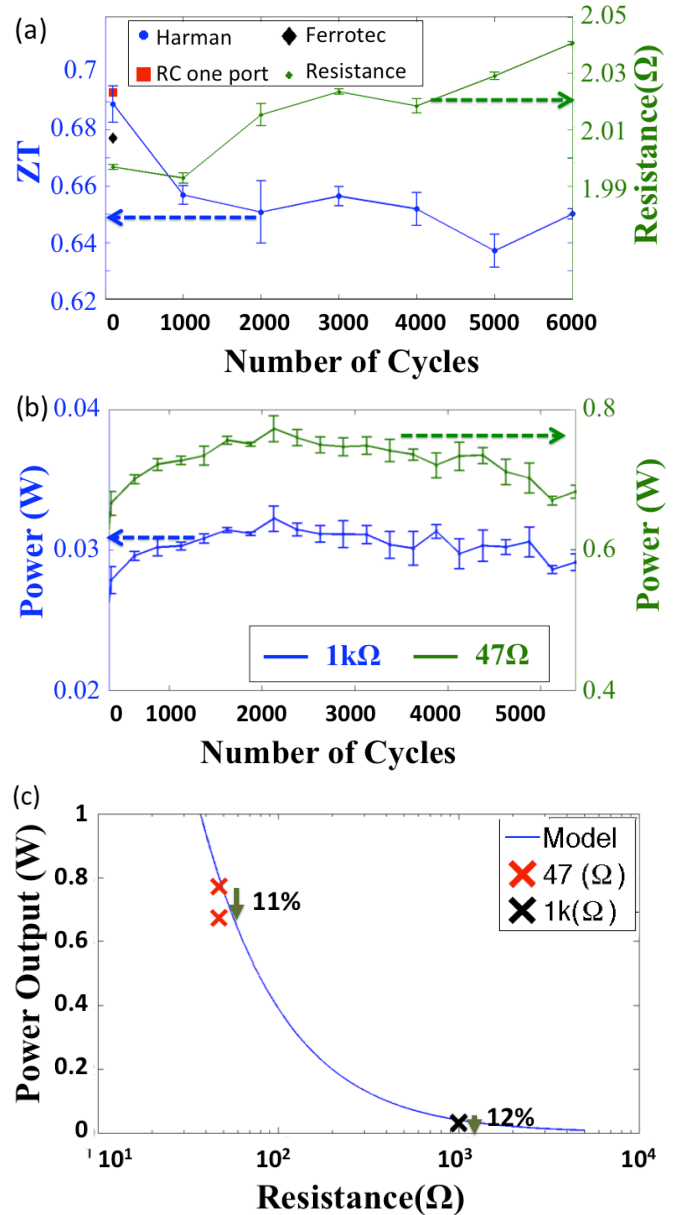


Figure 5. (a) $Z_{TE}\bar{T}$ and electrical resistance of the TE module during thermal cycling. (b) Output power of the TE module with the 47 Ω and 1k Ω load resistors. (c) Power output as a function of the load resistance. Two points for each resistance (the maximum and minimum powers) show degradation of the thermoelectric module.

the applied current. The impedance of the thermoelectric module can equivalently be expressed in terms of the thermal diffusion time constant of the system (τ_D) and the electrical parameters of the system in Laplace domain:

$$Z_m(s) = \frac{V_e}{I_0} \cdot \frac{s + \frac{1}{\tau_D} \cdot \left(1 + \frac{V_{th}}{V_e}\right)}{s + \frac{1}{\tau_D}}. \quad (6)$$

Combining Eqs. (2), (5), and (6), the thermoelectric figure of merit can be evaluated directly from the critical frequencies as

$$Z_{TE}\bar{T} = \frac{\omega_z}{\omega_p} - 1. \quad (7)$$

Power Output

The power output of the TE module due to an applied temperature gradient is measured to evaluate the performance during thermal cycling. The sample TE module is sequentially connected to two different load resistors ($R_l = 47\Omega$ and 1000Ω). These resistors were chosen to see load dependency of TE output. For the applied temperature drop, ΔT , the effective Seebeck coefficient, S_m , and internal resistance of the module are calculated with the following equations:

$$I_o = \frac{V_o}{R_m + R_l}, \quad (8)$$

$$V_o = S_m \Delta T, \quad (9)$$

$$P_o = I_o V_o = \frac{S_m \Delta T}{R_m + R_l}. \quad (10)$$

RESULTS & DISCUSSION

The figure of merit for the thermoelectric module is evaluated in two different ways before thermal cycling: The Harman method and frequency response. As shown in table 1, ZT measured with Harman and RC one-port are within 2% of the value provided by the manufacturer, and thus the approximation applied to those methods is acceptable. Since the Harman method is faster and the results of the two methods are consistent, the Harman method is chosen for characterizing the $Z_{TE}\bar{T}$ value after thermal cycling.

As shown in Figure 5(a), the effective module figure of merit decreases ~8% with thermal cycling, while the electrical resistance of module increases only ~2%. The figure of merit is inversely proportional to its resistance:

$$Z_{TE}\bar{T} = \frac{S_m^2 \bar{T}}{R_m G_m}, \quad (11)$$

where G_m is the thermal conductance. Since the observed increase in electrical resistance does not account for the total decrease of the $Z_{TE}\bar{T}$, thermal cycling must also impact the Seebeck coefficient or the thermal conductivity. One possible explanation is that cracks within the thermoelectric couples, due to thermal cycling, impacting both electron and phonon transport [3].

As seen in Figure 5(b), the power output of the sample thermoelectric module slightly decreases with increasing

Table 1. ZT measured by different method (Before cycling)

Method	ZT
Reference [12]	0.677
Transient response (Harman)	0.6891±0.0031
Frequency response (RC one-port)	0.6932±0.0025

number of cycles. During the first 2000 cycles, the power output increases. But from 2000 to 6000 cycles, there is an 11% and 12% reduction in the output power for both load resistances (as shown in figure 5(c)) indicating that the sample TE is degrading due to thermal cycling. The power output of TE module is inversely proportional to the load resistance used for the measurement as seen in Eq. (10) and figure 5(c).

CONCLUSIONS

The performance of a TE module is investigated after repeated thermal cycling from 30°C to 160°C. After 6000 cycles, the power output is reduced by about 11%, 4000 cycles after the peak output power. With increasing number of cycling, the power output and figure of merit of thermoelectric module decrease, while the electrical resistance increases. This shows that the efficiency and the performance of the thermoelectric module are degraded due to thermal cycling. However, to fully account for the decrease in $Z_{TE}\bar{T}$, thermal cycling must also impact thermal conductivity and/or Seebeck coefficient. The measured $Z_{TE}\bar{T}$ values from two common methods for evaluating the figure of merit are investigated and agree within 2%. Moreover, both the RC one-port technique and individual property measurements (including the thermal conductivity and Seebeck coefficient) will be conducted every 10000 cycles in order to validate these techniques. Furthermore, physical change on a TE module will be observed using SEM after module failure.

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