Impedance spectroscopy methods applied to thermoelectric materials and devices

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Outline

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3. Theoretical background
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Most of the energy produced in our society is lost as heat. Two examples:

<table>
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<th>Application</th>
<th>Waste heat</th>
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<tbody>
<tr>
<td>Electrical consumption in our houses from power plants</td>
<td>60% during generation, 8 – 15% in transport and transformation, ~70% Total losses</td>
</tr>
<tr>
<td>In transportation (cars)</td>
<td>40% of energy generated, 30% used to cool the engine, 70% Total losses (+CO₂ emissions)</td>
</tr>
</tbody>
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Thermoelectrics have the ability to convert temperature differences into electricity, i.e., obtain power from wasted heat.

They are called to have a role in the improvement of the efficiency of the current energy system by harvesting wasted heat.

1. Introduction

**Applications**

Industries (furnace waste heat), Aerospace (radioisotope), Wireless sensors (ambient heat), Vehicles (exhaust heat), Solar Energy (TE solar devices)
1. Introduction

*The figure of merit (Z)*

The efficiency of a thermoelectric material is given by:

\[
\eta = \frac{P_{\text{max}}}{Q_{\text{in}}} = \frac{(T_H - T_C)}{T_H} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_H / T_C}
\]

*ZT* is the figure of merit and indicates **how efficient is a thermoelectric material.**

- High *S* provides higher open-circuit voltage (charge separation)
- High *\(\sigma\)* provides higher currents
- Low *\(\lambda\)* provides higher *\(\Delta T\)*

**Properties interrelated, difficult to achieve efficient materials**
1. Introduction

**Materials**

Thermoelectric materials are typically **highly-doped semiconductors**. A lot of materials are being explored (silicides, skutterudites, oxides, SiGe, Bi$_2$Te$_3$, conducting polymers, etc.)

![Graph showing ZT vs Temperature for various materials](image)

1. Introduction

The task of characterisation

It requires measuring the variation with T of 3 parameters: $S$, $\sigma$ and $\lambda$

• Usually 3 different equipments are required.
• A variety of home-made techniques are frequently used, no standard methods are followed.
• $ZT$ is usually obtained from the measurement of $S$, $\sigma$ and $\lambda$ and collects the errors of all these 3 measurements.
• Thermal conductivity is difficult to measure and involves very expensive equipments.

Home-made hot-probe (Seebeck coefficient) 4-probe (electrical resistivity, sheet resistance)
2. Impedance spectroscopy fundamentals

**Impedance spectroscopy**

- A **small amplitude** sinusoidal voltage wave of certain frequency is applied.
- The system responds with a current wave proportional to the voltage that can be shifted in time (phase).

\[
|Z| = \sqrt{Z'^2 + Z''^2} = \frac{V_{ac}}{I_{ac}}
\]

\[
\phi = \arctan\left(\frac{Z''}{Z'}\right)
\]
2. Impedance spectroscopy fundamentals

The impedance spectrum

$Z$ is obtained for a range of frequencies (1 MHz to 10 mHz), obtaining one point in the spectrum per each frequency.
2. Impedance spectroscopy fundamentals

**Equivalent circuits**

The impedance results can be modelled by means of equivalent circuits:

$$Z = R$$
2. Impedance spectroscopy fundamentals

**Equivalent circuits**

\[ Z = R + \frac{1}{j\omega C} \]
2. Impedance spectroscopy fundamentals

**Equivalent circuits**

\[ Z = R_1 + \frac{R_2}{1 + j\omega CR_2} \]

\[ \omega_{\text{max}} = \frac{1}{R_2 C} \]

- \( R_1 = 100 \, \Omega \)
- \( R_2 = 400 \, \Omega \)
2. Impedance spectroscopy fundamentals

**Impedance spectroscopy use**

Is a very powerful **characterisation technique** used in a lot of fields:

- solar cells
- batteries
- fuel cells
- supercapacitors
- corrosion

It allows **separation** and **direct determination** of different **processes** occurring in the devices and under actual **operating conditions**:

- Electron/hole transport
- Lifetime, Recombination
- Charge transfer reactions
- Accumulation of charge
- Diffusion of ions ...

2. Impedance spectroscopy fundamentals

**Impedance spectroscopy in thermoelectrics (I)**

In the thermoelectric field it has **hardly been explored**

The work by **Downey et al.** relates the impedance response with equivalent thermal circuits. Reported a **Resistance** \( R_1 = 2.56 \, \Omega \) and **Capacitance** \( C_1 = 1.72 \, \text{F} \) **in parallel** as the main feature of the thermoelectric response.

\( R_1 \) and \( C_1 \) relate with the **thermal capacitance** and **thermal resistance** of the module respectively.

2. Impedance spectroscopy fundamentals

*Impedance spectroscopy in thermoelectrics (II)*

In two papers from Giaretto et al., a physical and mathematical description in the context of a **thermal impedance** is provided. They developed a method to **accurately** evaluate the **ZT** in modules.

A. De Marchi, V. Giaretto, Review of Scientific Instruments, 82 (2011) 34901
A. De Marchi, V. Giaretto, Review of Scientific Instruments, 82 (2011) 104904

**Motivation for our research**

Literature reported is mainly **focused on** the calculation of **ZT** and despite of the previous studies impedance is **not used** as a characterization tool by the thermoelectric community.

In this seminar I will present our research to try to advance this method, focused on:

- The **theoretical models** for **electrical impedance**
- Analysis of results in the **complex plane**
- Exploitation as a method able to provide **complete TE characterisation** and **quantify** the **losses** of the system
3. Theoretical background

**Considerations**

- **Thermoelectric element** with certain area $A$ and length $L$ contacted by **metallic contacts** of length $L_M$.
- **Adiabatic conditions** (no heat exchanged with surroundings).
- All thermal and TE **parameters independent on temperature**.
- System is **initially at thermal equilibrium** with temperature $T_i$.
- **Joule effect** is neglected.

\[(T - T_i) = \Delta T\]
\[d(\Delta T) = dT\]

(Blue line indicates T profile of n-type thermoelement at a certain moment in time under an applied positive current)
3. Theoretical background

**Impedance function**

\[ V = IR + S[T(L) - T(0)] \]
\[ Z(t) = \frac{V}{I} = R + \frac{S[T(L) - T(0)]}{I} \]

Time domain \((t)\)

\[ \mathcal{L}\{\Delta T\} = \theta \quad \mathcal{L}\{I\} = i_0 \]
\[ T(L) - T(0) \to -2\theta(0) \]

Frequency domain \((j\omega)\)

\[ Z(j\omega) = R - \frac{S2\theta(0)}{i_0} \]

To know the impedance function we **need to know the T difference** at \(x=0\) as a function of frequency.

\(R=\)ohmic resistance, \(\omega=2\pi f, f\) is the frequency, \(j=\sqrt{-1}\)
3. Theoretical background

1. Heat equation with no contact influence

Very thin contact considered \((L_M \to 0)\)

In the thermoelectric material:

\[
\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha_{TE}} \frac{\partial T}{\partial t}
\]

at \(0<x<L\)

Boundary conditions:

\[
-\frac{\pi I}{A} + \lambda_{TE} \left( \frac{\partial T}{\partial x} \right)_0 = 0 \quad \text{at } x=0 \text{ (adiabatic)}
\]

\[
T(L/2,t) = T_i \quad \text{at } x=L/2 \text{ (heat sink)}
\]

\(\alpha_{TE}=\)thermal diffusivity, \(\lambda_{TE}=\)thermal conductivity
3. Theoretical background

1. Heat equations with no contact influence

Equations converted to the frequency domain

In the time domain (t):

\[
\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha_{TE}} \frac{\partial T}{\partial t} \\
- \frac{\pi_0 I_0}{A} + \lambda_{TE} \left( \frac{\partial T}{\partial x} \right)_0 = 0 \\
T(L/2, t) = T_i
\]

at 0<x<L, at x=0, at x=L/2

In the frequency domain (j\omega):

\[
\frac{d(\Delta T)}{dt} = \Delta T \\
\mathcal{L}\{\Delta T\} = \theta \\
\frac{\partial^2 \theta}{\partial x^2} = \frac{j \omega}{\alpha_{TE}} \theta \\
- \frac{\pi_0 i_0}{A} + \lambda_{TE} \left( \frac{\partial \theta}{\partial x} \right)_0 = 0 \\
\theta(L/2, \omega) = 0
\]
3. Theoretical background

1. Heat equations with no contact influence

Solution to the differential equation

\[ \frac{\partial^2 \theta}{\partial x^2} - \frac{j \omega}{\alpha_{TE}} \theta = 0 \]

at \( 0 < x < L \)

\[ \omega_{TE} = \frac{\alpha_{TE}}{(L/2)^2} \]

Characteristic frequency

\[ \theta(x, j \omega) = C_1 \sinh \left( \frac{x}{L_H} \left( \frac{j \omega}{\omega_{TE}} \right)^{0.5} \right) + C_2 \cosh \left( \frac{x}{L_H} \left( \frac{j \omega}{\omega_{TE}} \right)^{0.5} \right) \]

\[ \frac{\partial \theta}{\partial x}(x, j \omega) = \frac{1}{L_H} \left( \frac{j \omega}{\omega_{TE}} \right)^{0.5} \left\{ C_1 \cosh \left( \frac{x}{L_H} \left( \frac{j \omega}{\omega_{TE}} \right)^{0.5} \right) + C_2 \sinh \left( \frac{x}{L_H} \left( \frac{j \omega}{\omega_{TE}} \right)^{0.5} \right) \right\} \]

After applying the boundary conditions:

\[ \theta(0) = -\frac{\pi_0 i_0 L_H}{\lambda_{TE} A} \left( \frac{j \omega}{\omega_{TE}} \right)^{-0.5} \tanh \left( \left( \frac{j \omega}{\omega_{TE}} \right)^{0.5} \right) \]
3. Theoretical background

1. Heat equation with no contact influence

The impedance function after using \( T(x=0) \approx T_i \) and \( \pi_0 = S T_i \) is given by:

\[
Z(j \omega) = R + \frac{S^2 T_i L}{\lambda_{TE} A} \left( \frac{j \omega}{\omega_{TE}} \right)^{-0.5} \tanh \left\{ \left( \frac{j \omega}{\omega_{TE}} \right)^{0.5} \right\}
\]

- at \( \omega >> \omega_{TE} \)
  
  \[
  Z = R + \frac{S^2 T_i L}{\lambda_{TE} A} \left( \frac{j \omega}{\omega_{TE}} \right)^{-0.5}
  \]  
  (1-slope, Warburg)

- at \( \omega << \omega_{TE} \) and \( R=0 \)
  
  \[
  Z^{-1} = \frac{1}{R_{TE}} + \frac{1}{3 \, R_{TE} \omega_{TE}}
  \]  
  (semicircle)

It can provide all thermal constants if \( S \) is known

(simulation for Bi\(_2\)Te\(_3\) element 1 mm\(^2\) area and 1.5 mm length)
2. Heat equation with contact influence

Heat conduction and absorption by the metallic contacts have to be considered.

In the metal:

\[
\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha_M} \frac{\partial T}{\partial t}
\]

at \(-L_M<x<0\)

Boundary conditions:

\[
-\frac{\pi I}{A} - \lambda_M \left( \frac{\partial T}{\partial x} \right)_{0,M} + \lambda_{TE} \left( \frac{\partial T}{\partial x} \right)_{0,TE} = 0 \quad \text{at } x=0
\]

\[
\left( \frac{\partial T}{\partial x} \right)_{-L_M} = 0 \quad \text{at } x=-L_M \text{ (adiabatic)}
\]

\[
T(0)_M = T(0)_{TE} \quad \text{at } x=0 \text{ (T continuity)}
\]

\(\alpha_M=\text{thermal diffusivity, } \lambda_M=\text{thermal conductivity}\)
3. Theoretical background

2. Heat equations with contact influence

Solution to the differential equations

\[ \theta(0) = -\frac{\pi_0 i_0}{A} \left( \frac{1}{Z_{th,TE}^{-1} + Z_{th,M}^{-1}} \right) \]

\[ Z_{th} = \text{Thermal impedance} \]

\[ Z_{th,TE} = \frac{L/2}{\lambda_{TE}} \left( \frac{j\omega}{\omega_{TE}} \right)^{-0.5} \text{tanh}\left( \left( \frac{j\omega}{\omega_{TE}} \right)^{0.5} \right) \]

\[ Z_{th,M} = \frac{L_M}{\lambda_M} \left( \frac{j\omega}{\omega_M} \right)^{-0.5} \text{coth}\left( \left( \frac{j\omega}{\omega_M} \right)^{0.5} \right) \]

\[ \omega_M = \frac{\alpha_M}{(L_M)^2} \]

Characteristic frequency in the metal

Impedance function given by

\[ Z = R + \frac{2S^2 T_i}{A} \left( \frac{1}{Z_{th,TE}^{-1} + Z_{th,M}^{-1}} \right) \]
3. Theoretical background

2. Heat equation with contact influence

The impedance function assuming no heat conduction in TE element $\lambda_{TE} \approx 0$

$$Z = R + \frac{2S^2 T_i}{A} \frac{L_M}{\lambda_M} \left( \frac{j \omega}{\omega_M} \right)^{-0.5} \coth \left\{ \left( \frac{j \omega}{\omega_M} \right)^{0.5} \right\}$$

- at $\omega >> \omega_M$ and $R=0$

$$Z = \frac{2S^2 T_i}{A} \frac{L_M}{\lambda_M} \left( \frac{j \omega}{\omega_M} \right)^{-0.5}$$

(1-slope, Warburg)

- at $\omega << \omega_M$ and $R=0$

$$Z = \frac{1}{3} R_M + \frac{R_M \omega_M}{j \omega}$$

(vertical line)

(simulation for Cu contact with 1 mm² area and 0.2 mm length)
3. Theoretical background

2. Heat equation with contact influence

The complete impedance function is given by:

\[
Z = R + \frac{2S^2T_i}{A} \left( \frac{1}{Z_{th,TE}^{-1} + Z_{th,M}^{-1}} \right)
\]

At steady-state (\(\omega \to 0\)), the real impedance is:

\[
R_{dc} = R + R_{TE}
\]

Quantify all the losses of the system

(simulation for 1 mm\(^2\) and 1.5 mm length Bi\(_2\)Te\(_3\) thermoelement contacted with Cu contacts 0.2 mm length)
4. Experimental validation

**Impedance spectroscopy**

- An *impedance analyser* equipment (potentiostat) was used.

- The sample is suspended by **Cu probes** to provide adiabatic conditions and a thin **contact** is formed with **Ag paint**.
4. Experimental validation

**Bi₂Te₃** thermoelement (1.4 x 1.4 mm², 1.6 mm length)

Parameter calculation using S=175 µV/K (hot-probe)

\[
\lambda_{TE} = \frac{S^2T_iL}{R_{TE}A} = 1.27 \text{ W/mK}
\]

\[
\alpha_{TE} = \frac{(L/2)^2}{\omega_{TE}} = 0.013 \text{ cm}^2/s
\]

\[
C_{pTE} = \frac{\lambda_{TE}}{d\alpha_{TE}} = 0.13 \text{ J/gK}
\]

\[
\sigma = \frac{L}{RA} = 96.67 \text{ S/cm}
\]

\[
ZT = \frac{R_{TE}}{R}
\]

It can provide all thermal constants in a ~5 min measurement if S is known.

Low since contains wires and contact resistances.
4. Experimental validation

\(\text{Bi}_2\text{Te}_3\) thermoelement with Cu/ceramic contacts

- **Cu effect** can be neglected (very small thickness) and ceramic is 1 mm thick.
- In agreement with shape predicted.
- High frequency part is noisy due to \(\mu\Omega\) variations, close to equipment limitation.
- Not possible to fit to equivalent circuit.
- Improvement can be gained by increasing ceramic thickness or using lower thermal conductivity contacts.

(Impedance spectrum from 100 to 0.01 Hz)
4. Experimental validation

**Thermoelectric module (254 legs, 1 x 1 mm², 1.5 mm length)**

\[
Z(t) = R + 254 \frac{S[T(L) - T(0)]}{I}
\]

\[
Z(j\omega) = R + 254 \frac{2S^2 T_i}{A} \left( \frac{1}{Z_{th,TE}^{-1} + Z_{th,M}^{-1}} \right)
\]

- \( R_C = 254 \frac{2S^2 T_i L_C}{\lambda_C A} = 149 \text{ m}\Omega \)
- \( S = 191.5 \mu\text{V/K} \)
- \( \lambda_C = 30 \text{ W/mK} \)
- \( R_{TE} = 254 \frac{S^2 T_i L}{\lambda_{TE} A} = 2.585 \text{ \Omega} \)
- \( \lambda_{TE} = 1.60 \text{ W/mK} \)
- \( R = 254 \frac{L}{\sigma A} = 4.29 \text{ \Omega} \)
- \( \sigma = 888 \text{ S/cm} \)

Complete characterisation is achieved

J. García-Cañadas, G. Min, Impedance spectroscopy models for the complete characterization of thermoelectric materials, *J. Appl. Phys.* (Submitted)
The thermoelement at steady state

For a thermoelement (same assumptions) but now considering Joule effect, the solution to the steady-state heat balance equation at the cold side is given by:

\[
0 = \frac{\pi I}{A} + \frac{\lambda}{L} (T_H - T_C) + \frac{1}{2} \frac{I^2 R}{A}
\]

\[
(T_H - T_C) = \frac{-L}{\lambda A} \left( \pi I + \frac{1}{2} I^2 R \right)
\]

\[
V_S = S(T_C - T_H) = \frac{SL}{\lambda A} \left( \pi I + \frac{1}{2} I^2 R \right)
\]
5. Physical meaning

**Thermoelectric resistance**

We define a thermoelectric resistance as

\[ R_{TE} = \frac{V_s}{I} \quad \rightarrow \quad R_{TE} = \frac{SL}{\lambda A} \left( ST + \frac{1}{2} IR \right) \]

It matches the impedance function at steady-state when Joule effect is neglected:

\[
Z(\omega) = \frac{S^2T_iL}{\lambda_{TE} A} \left( \frac{j\omega}{\omega_{TE}} \right)^{-0.5} \tanh \left\{ \left( \frac{j\omega}{\omega_{TE}} \right)^{0.5} \right\} \quad \rightarrow \quad Z(\omega = 0) = \frac{S^2T_iL}{\lambda_{TE} A}
\]
5. Physical meaning

**Thermoelectric resistance**

**t≈0, no T difference**

The **applied voltage** generates a **drift current** given by the ohmic resistance \((R)\) of the system.

**At steady-state**

Due to **Peltier a T difference** appears and carriers redistribute generating the opposed **Seebeck voltage**.

\[ R_{TE} \] accounts for the losses of the system introduced by the thermoelectric effects.
5. Physical meaning

**Thermoelectric capacitance**

Can be defined using the Seebeck voltage definition \((dV_S = Sd(T_H - T_C))\)

\[
C_{TE} = I \frac{dt}{dV_S} = \frac{I}{S} \left( \frac{d(T_H - T_C)}{dt} \right)^{-1}
\]

Using the definition of the **thermal diffusivity** \(\alpha = \frac{\lambda}{\rho C_p}\)

and inserting \(\lambda\) and \(C_p\) from the heat conduction \((dQ/Adt = -\lambda dT/dx)\) and specific heat \((C_p = dQ/\rho ALdT)\) definitions respectively

\[
dt = \frac{-L}{\alpha} \, dx \quad \Rightarrow \quad C_{TE} = \frac{-IL}{S\alpha} \left( \frac{d(T_H - T_C)}{dx} \right)^{-1}
\]

Finally, since \(d(T_H - T_C) = -2dT_c\), and using the heat balance at the cold side we obtain:

\[
\left( \frac{dT}{dx} \right)^{-1}_L = \frac{\lambda A}{I\pi}
\]

\[
C_{TE} = \frac{\rho C_p AL}{2S^2 T}
\]
5. Physical meaning

**Thermoelectric capacitance**

\[
C_{TE} = \frac{\rho C_p A L}{2 S^2 T}
\]

It also appears in the impedance function:

\[
Z(j\omega) = \frac{S^2 T_i L}{\lambda_{TE} A} \left( \frac{j\omega}{\omega_{TE}} \right)^{-0.5} \tanh \left\{ \left( \frac{j\omega}{\omega_{TE}} \right)^{0.5} \right\} \]

\[
\omega_{TE} = \frac{\alpha_{TE}}{(L/2)^2}
\]

For a p-type leg (1.4 x 1.4 mm\(^2\) and 1.6 mm length)

\[
C_{TE} = \frac{1}{R_{TE} \omega_{TE}}
\]

\[
C_{TE} = \frac{1}{5.83m\Omega \ 2 \text{rad} / \text{s}} = 86 \ F
\]

Far from electrical capacitance
5. Physical meaning

Thermoelectric capacitance

The $C_{TE}$ gives information about the charge separation (reorganisation) process and the Seebeck current appearing in the system.

$$C_{TE} = I \frac{dt}{dV_S} = \frac{I}{S} \left( \frac{d(T_H - T_C)}{dt} \right)^{-1}$$

$$C_{TE} = \frac{\rho c_p A L}{2S^2 T}$$

The physical origin is not well understood yet.
5. Physical meaning

**Time constant (τ)**

From the impedance analysis:

\[
R_{TE} = \frac{S^2 L}{\lambda A} T
\]

\[
C_{TE} = \frac{\rho C_p A L}{4 S^2 T}
\]

\[
τ = R_{TE} C_{TE} = \frac{(L / 2)^2}{\alpha}
\]

Related with time that heat flow takes to diffuse in the thermoelement

It can also be directly obtained from \(ω_{TE}\)

\[
τ = \frac{1}{ω_{TE}}
\]

Summary and future work

**Summary**

- Theoretical models for electrical impedance have been presented and analysed in the complex plane.
- Experimental validation has been provided, showing that complete characterisation of the materials can be obtained.
- In addition, the different contributions to the losses in the system can be separated and quantified.
- The physical meaning of parameters obtained from the impedance ($R_{TE}$, $C_{TE}$ and $\tau$) has been analysed.

**Future work**

- Develop theoretical models for characterisation under operating conditions (include Joule effect, heat inputs, heat sinks, convection, etc.).
- Further understanding of the thermoelectric capacitance.
- Apply method to nanostructured materials and thin films.
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