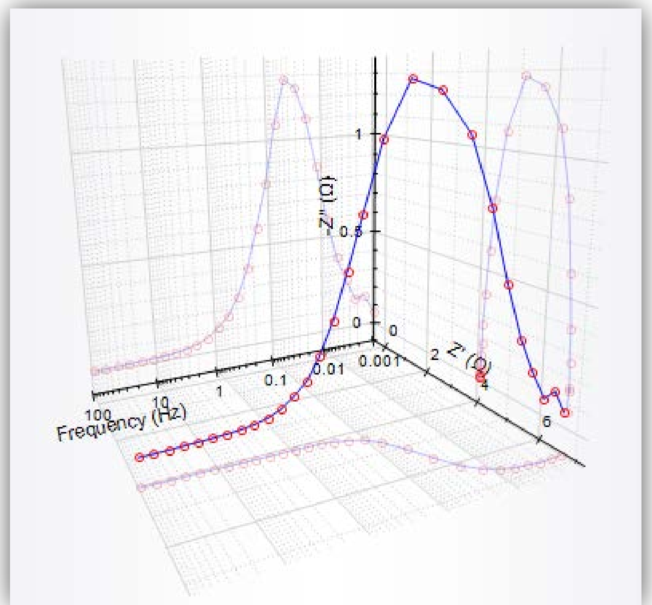
Purdue University Seminar
- 10th June 2014 -

Impedance spectroscopy methods applied to thermoelectric materials and devices



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Outline

1. Introduction
2. Impedance spectroscopy fundamentals
3. Theoretical background
4. Experimental validation
5. Physical meaning
6. Acknowledgements

1. Introduction

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

Application	**Waste heat**
Electrical consumption in our houses from power plants	60% during generation 8 – 15% in transport and transformation **~70% Total losses**
In transportation (cars)	40% of energy generated 30% used to cool the engine **70% Total losses** (+CO_2 emissions)

Thermoelectrics have the ability to **convert temperature differences** into **electricity,** i. e., obtain power from wasted heat.

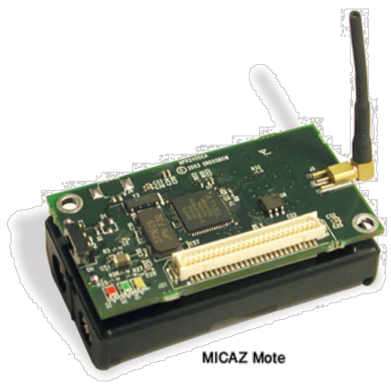
They are called to have a **role in the improvement of the efficiency of** the current **energy system** by harvesting wasted heat.

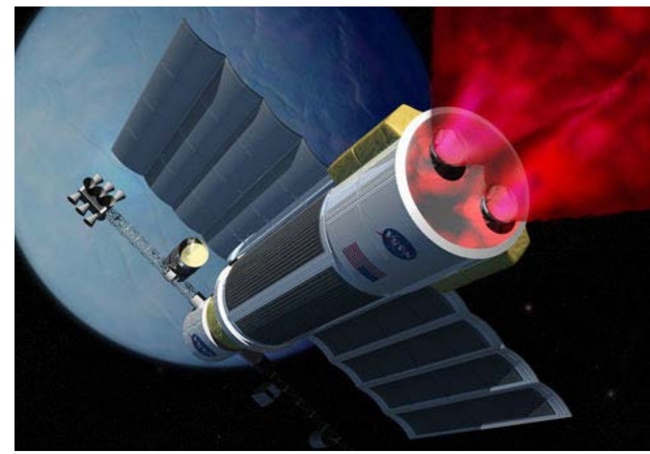
M. Martín-González, O.Caballero-Calero, P. Díaz-Chao, Renewable and Sustainable Energy Reviews 24 (2013) 288.
"Nanoengineering thermoelectrics for 21st century:Energy harvesting and other trends in the field"

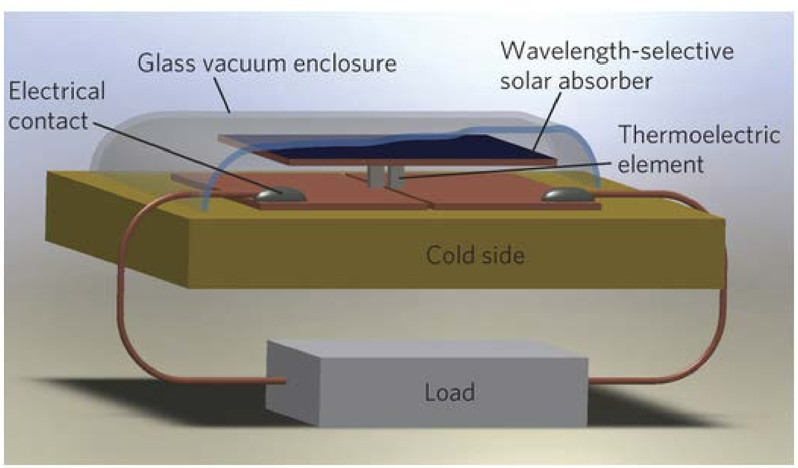
1. Introduction

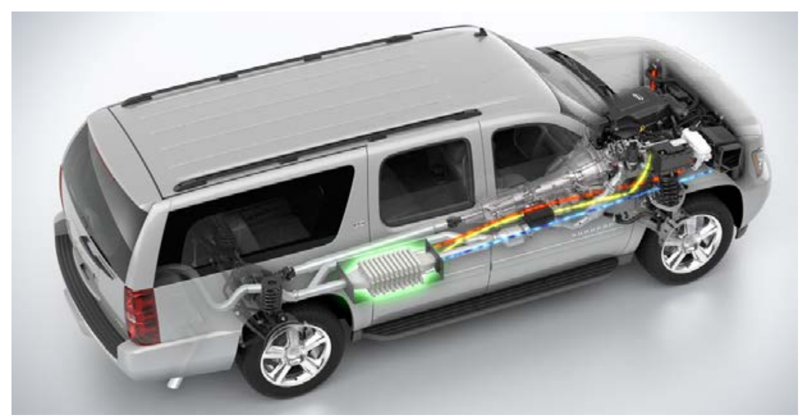
Applications

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:

$$\eta = \frac{P_{max}}{Q_{in}} = \frac{(T_H - T_C)}{T_H} \frac{\sqrt{1+Z\overline{T}} - 1}{\sqrt{1+Z\overline{T}} + T_H / T_C}$$

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

Seebeck coefficient

Electrical conductivity

$$ZT = \frac{S^2 \sigma}{\lambda} T$$

Thermal conductivity

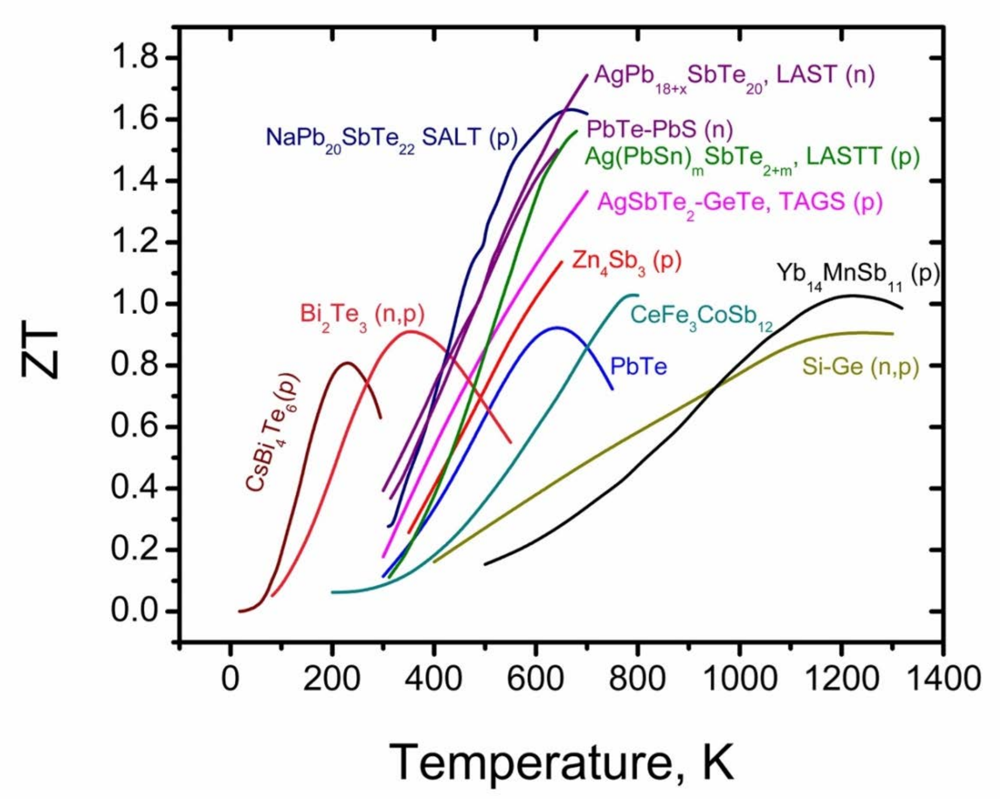
- High S provides higher open-circuit voltage (charge separation)
- High σ provides higher currents
- Low λ provides higher ΔT

Properties interrelated, difficult to achieve efficient materials

1. Introduction

Materials

Thermoelectric materials are typically **highly-doped semiconductors**. A lot of materials are being explored (silicies, skutterudites, oxides, SiGe, Bi_2Te_3, conducting polymers, etc.)



J. R. Sootsman et al. Angew. Chem. Int. Ed. 48 (2009) 8616. New and Old Concepts in Thermoelectric Materials

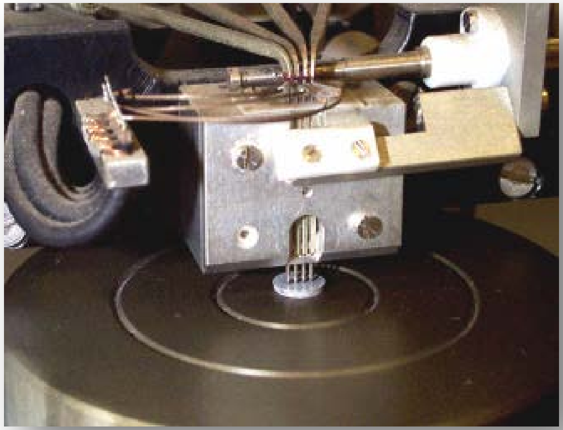
1. Introduction

The task of characterisation

It requires measuring the **variation with T of 3 parameters**: *S, σ and λ*

- 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, *σ* and *λ* 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 coeffcient)

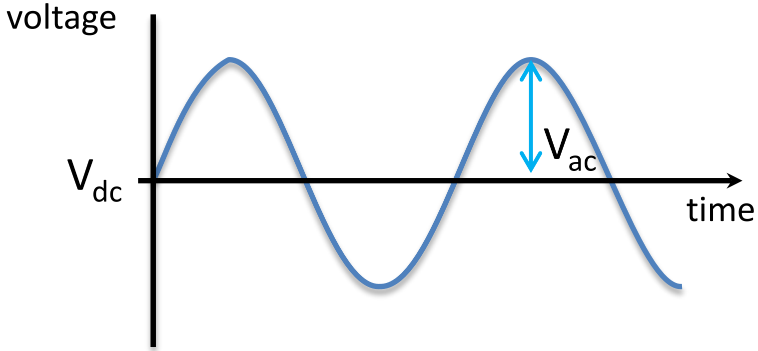


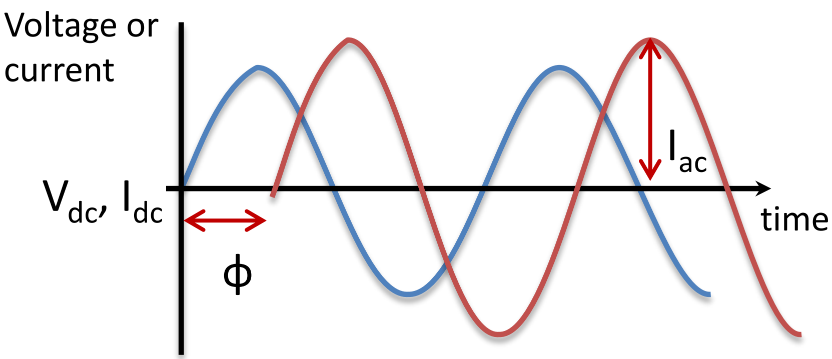
4-probe (electrical resistivity, sheet resistance)

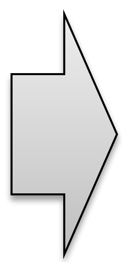
2. Impedance spectroscopy fundamentals

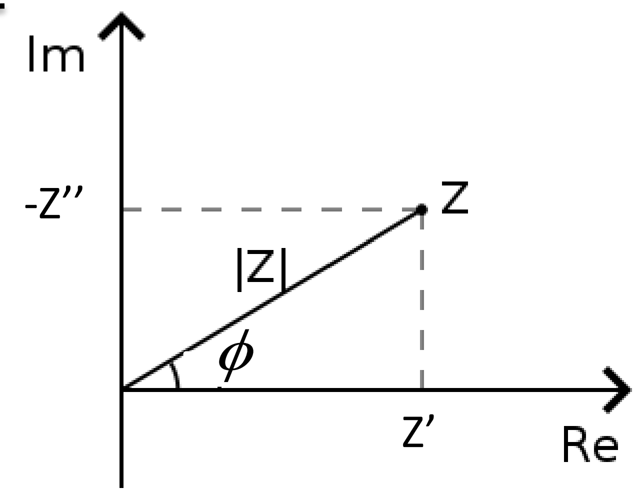
Impedance spectroscopy

- 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)









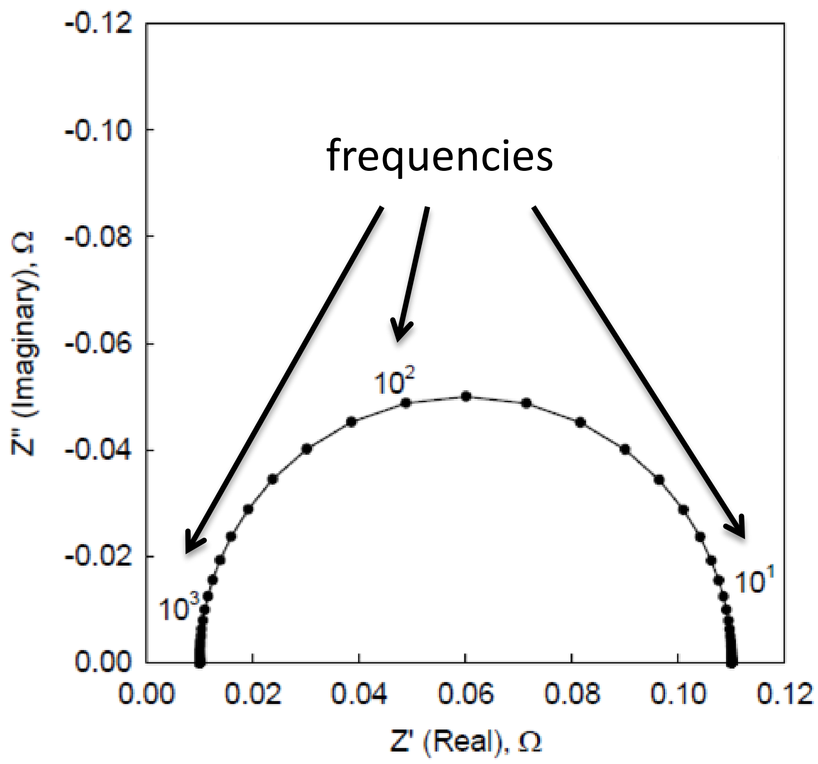
$$|Z| = \sqrt{Z'^2 + Z''^2} = \frac{V_{ac}}{I_{ac}}$$

$$\phi = arc\ \tan\left(\frac{Z''}{Z'}\right)$$

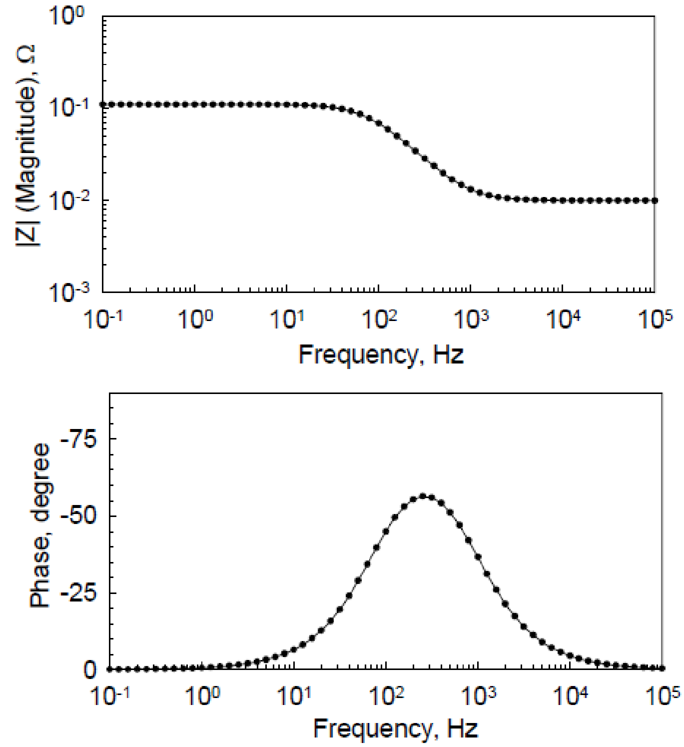
2. Impedance spectroscopy fundamentals

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



Impedance spectrum (Nyquist plot)



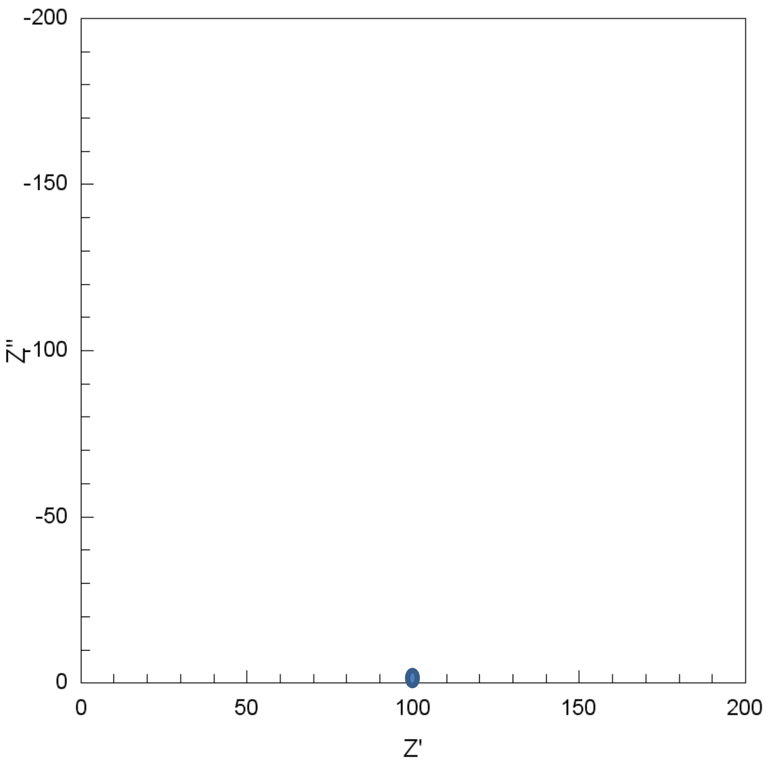
Parameters vs frequency (Bode plots)

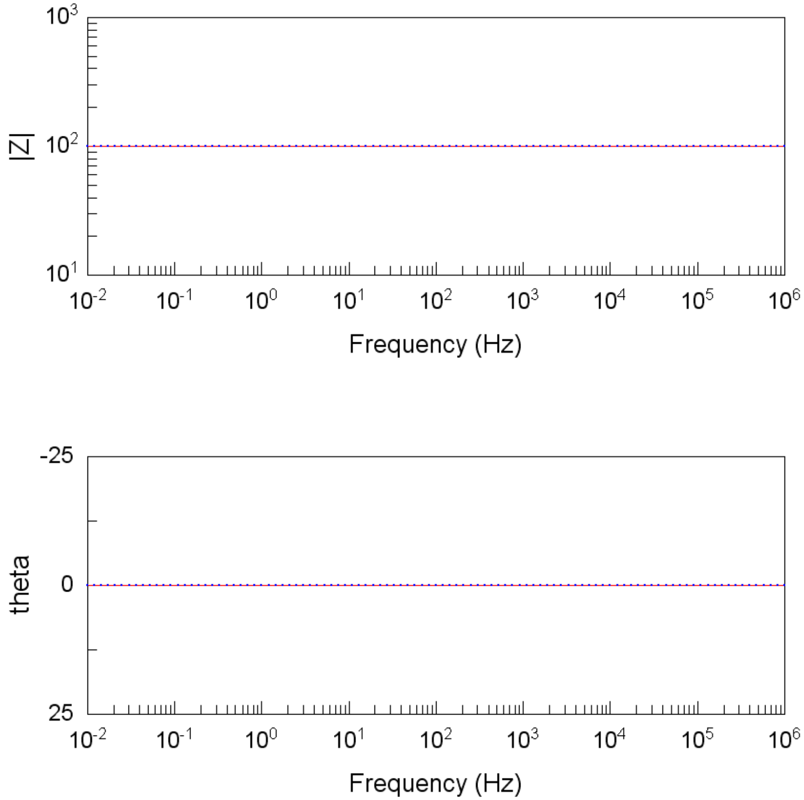
2. Impedance spectroscopy fundamentals

Equivalent circuits

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

$$Z = R$$

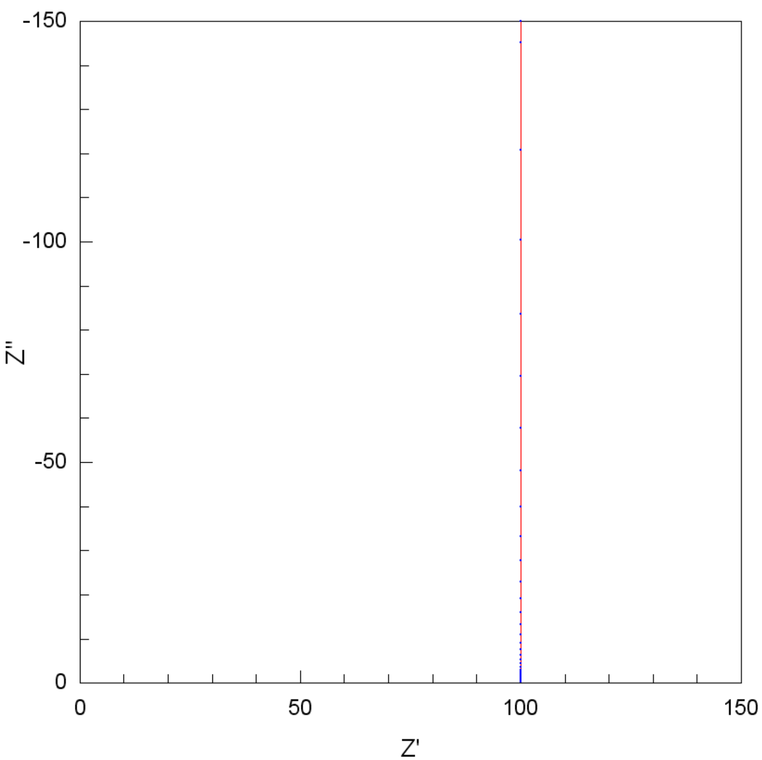


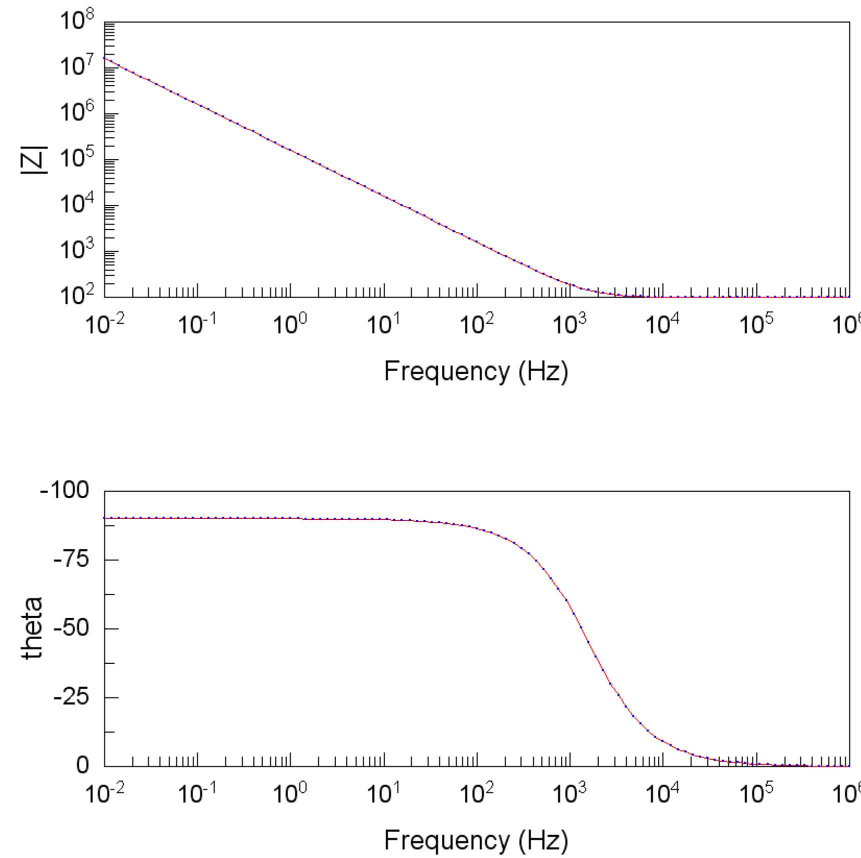


2. Impedance spectroscopy fundamentals

Equivalent circuits

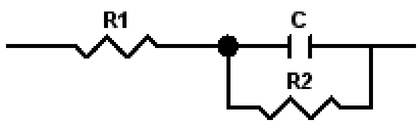
$$Z = R + \frac{1}{j\omega C}$$



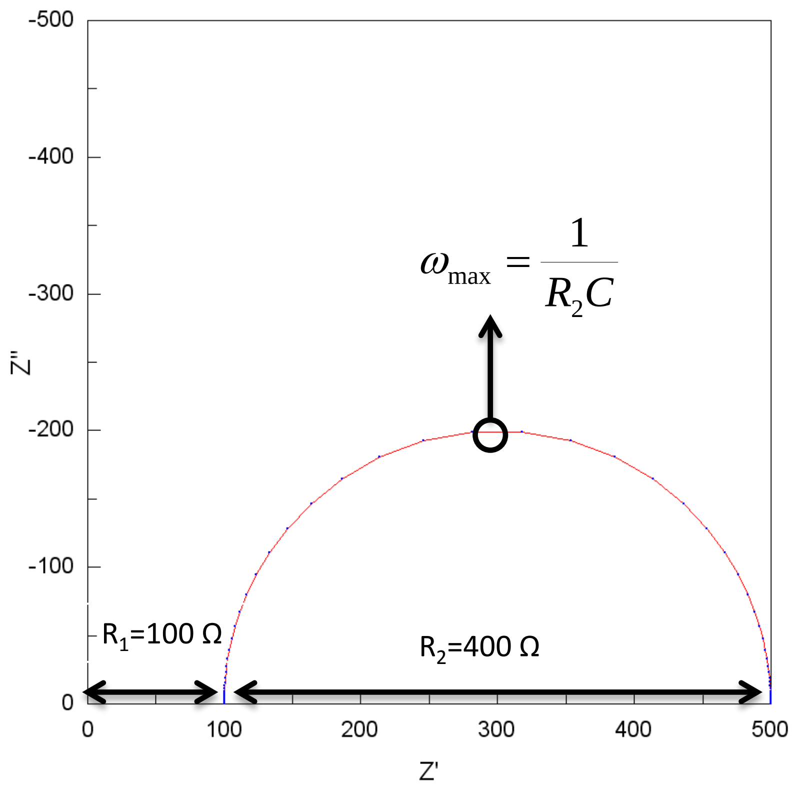


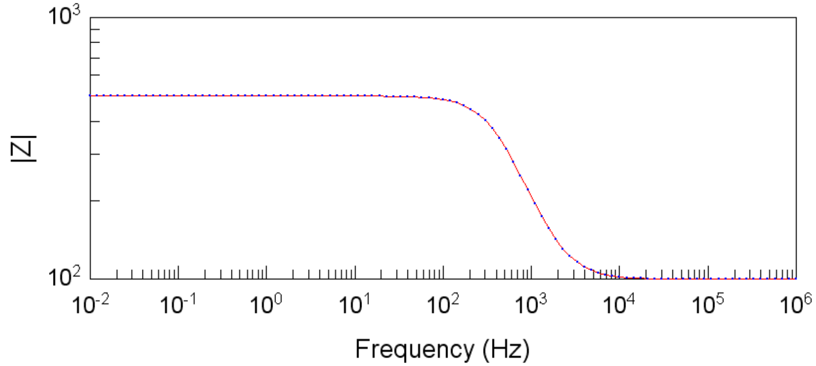
2. Impedance spectroscopy fundamentals

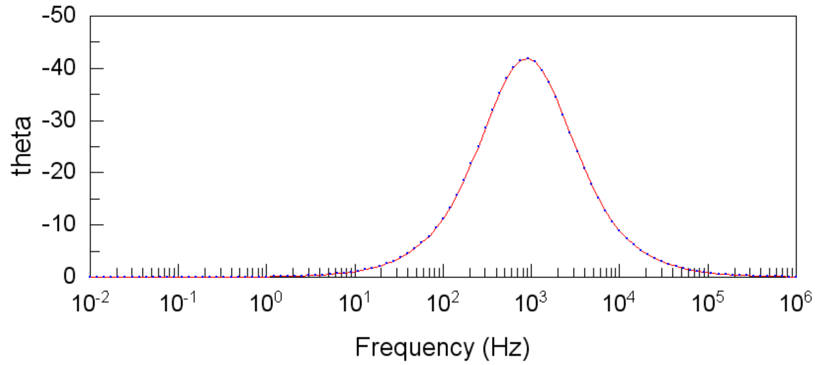
Equivalent circuits



$$Z = R_1 + \frac{R_2}{1 + j\omega C R_2}$$







2. Impedance spectroscopy fundamentals

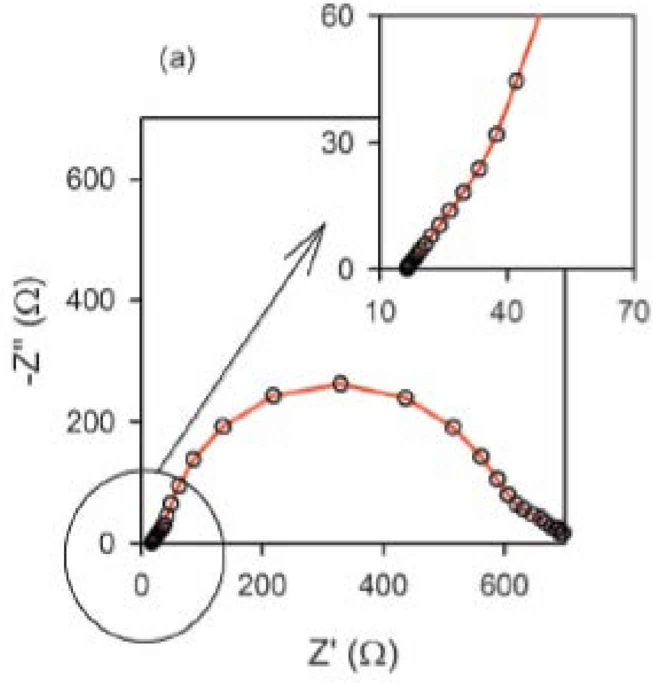
Impedance spectroscopy use

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 …

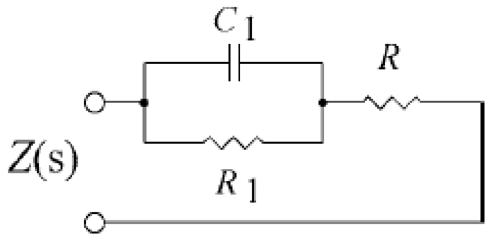


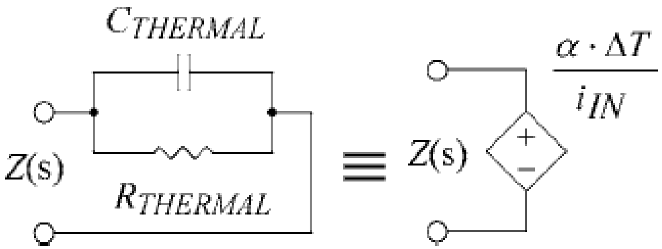
Impedance results for a dye-sensitised solar cell. Fabregat-Santiago et al. ChemPhysChem 13 (2011) 9083

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 Ω) and **Capacitance** (C_1=1.72 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.

A.D. Downey, T.P. Hogan, B. Cook, Review of Scientific Instruments, 78 (2007) 93904

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

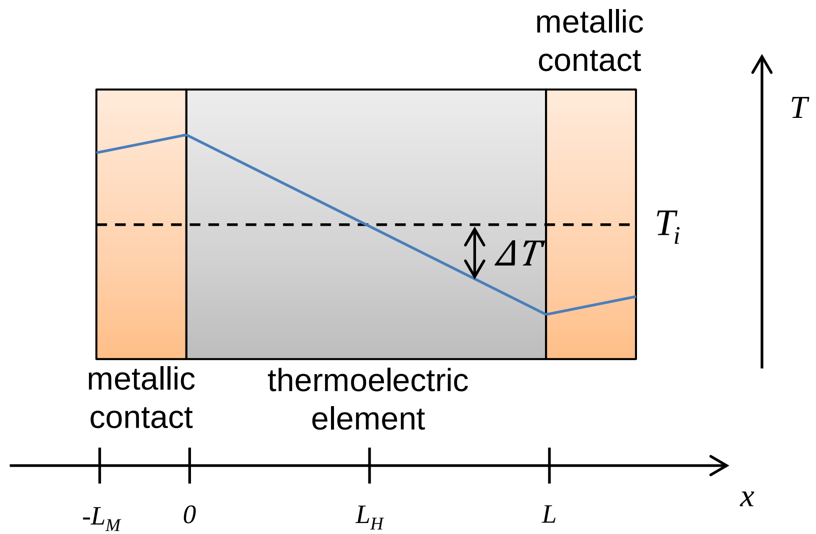
3. Theoretical background

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)

$\mathcal{L}\{\Delta T\} = \theta \quad \mathcal{L}\{I\} = i_0$

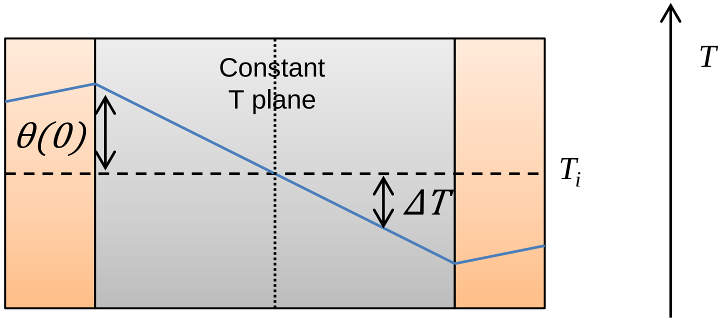
$T(L) - T(0) \rightarrow -2\theta(0)$

$$Z(j\omega) = R - \frac{S\,2\theta(0)}{i_0}$$

frequency domain ($j\omega$)

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

Solve heat equation



R=ohmic resistance, *ω=2πf*, *f* is the frequency, $j=\sqrt{-1}$

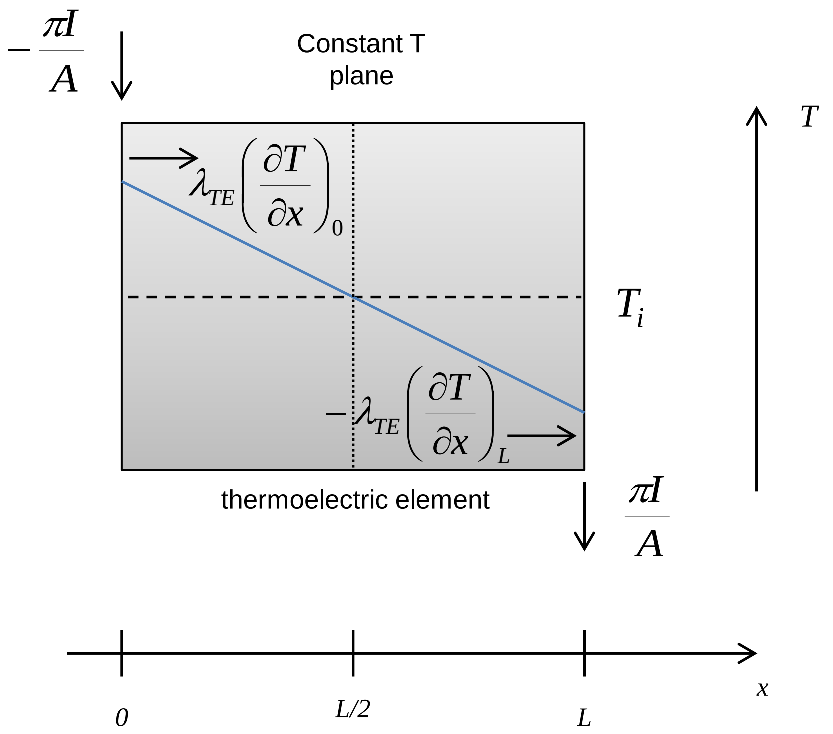
3. Theoretical background

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:

$$-\frac{\pi_0 I_0}{A} + \lambda_{TE}\left(\frac{\partial T}{\partial x}\right)_0 = 0$$ at x=0 (adiabatic)

$$T(L/2, t) = T_i$$ at x=L/2 (heat sink)

α_{TE}=thermal diffusivity, λ_{TE}=thermal conductivity

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3. Theoretical background

1. Heat equations with no contact influence

Equations converted to the frequency domain

time domain (t)			frequency domain ($j\omega$)
$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha_{TE}} \frac{\partial T}{\partial t}$$	at 0<x<L	$d(\Delta T) = dT$ → $\mathcal{L}\{\Delta T\} = \theta$	$$\frac{\partial^2 \theta}{\partial x^2} = \frac{j\omega}{\alpha_{TE}} \theta$$
$$-\frac{\pi_0 I_0}{A} + \lambda_{TE}\left(\frac{\partial T}{\partial x}\right)_0 = 0$$	at x=0	$\mathcal{L}\{I\} = i$ →	$$-\frac{\pi_0 i_0}{A} + \lambda_{TE}\left(\frac{\partial \theta}{\partial x}\right)_0 = 0$$
$$T(L/2, t) = T_i$$	at x=L/2	→	$$\theta(L/2, \omega) = 0$$

3. Theoretical background

1. Heat equations with no contact influence

Solution to the differential equation

$$\frac{\partial^2\theta}{\partial x^2} - \frac{j\omega}{\alpha_{TE}}\theta = 0 \qquad \text{at } 0<x<L$$

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

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 $\pi_0 = ST_i$ is given by:

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

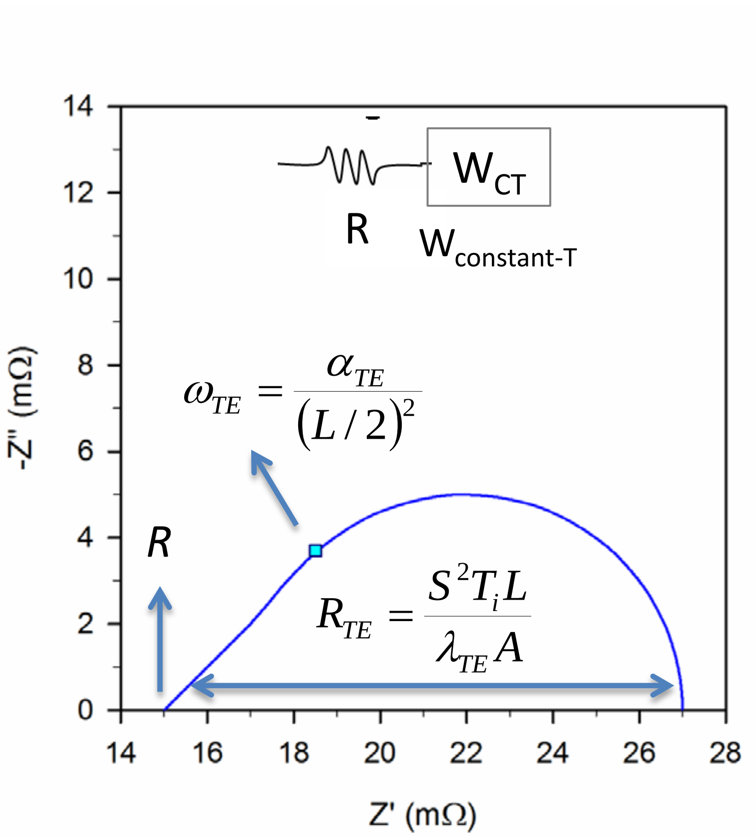
- at $\omega >> \omega_{TE}$

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

- at $\omega << \omega_{TE}$ and R=0

$$Z^{-1} = \frac{1}{R_{TE}} + \frac{1}{3}\frac{j\omega}{R_{TE}\omega_{TE}} \quad \text{(semicircle)}$$

It can provide **all thermal constants**
If *S* is known



(simulation for Bi_2Te_3 element 1 mm^2 area and 1.5 mm length)

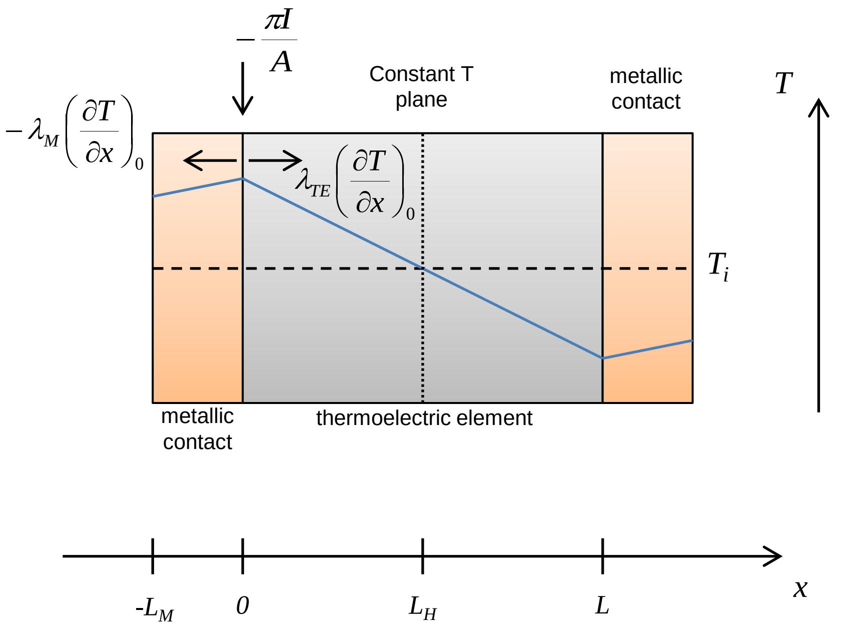
3. Theoretical background

2. Heat equation with contact influence

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

In the metal:

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha_M}\frac{\partial T}{\partial t} \quad \text{at } -L_M<x<0$$



Boundary conditions:

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

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

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

α_M=thermal diffusivity, λ_M=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}=Thermal impedance

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

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

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

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 $\lambda_{TE}\approx 0$

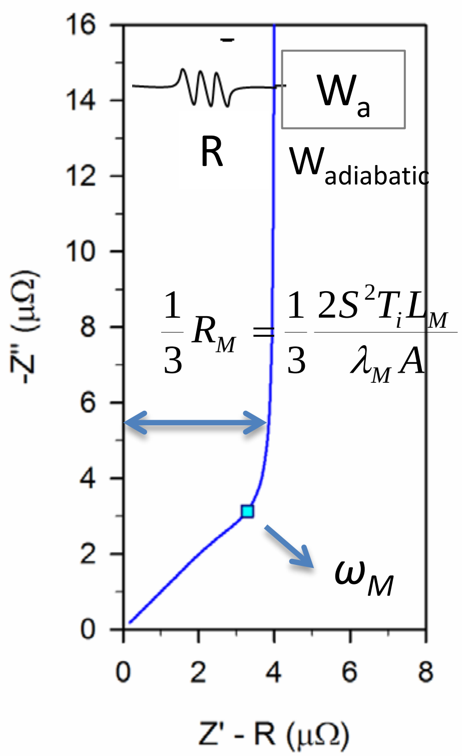
$$Z = R + \frac{2S^2T_i}{A}\frac{L_M}{\lambda_M}\left(\frac{j\omega}{\omega_M}\right)^{-0.5}\coth\left\{\left(\frac{j\omega}{\omega_M}\right)^{0.5}\right\}$$

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

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

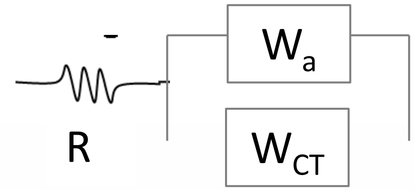


(simulation for Cu contact with 1 mm^2 area and 0.2 mm length)

3. Theoretical background

2. Heat equation with contact influence

The complete impedance function is given by:

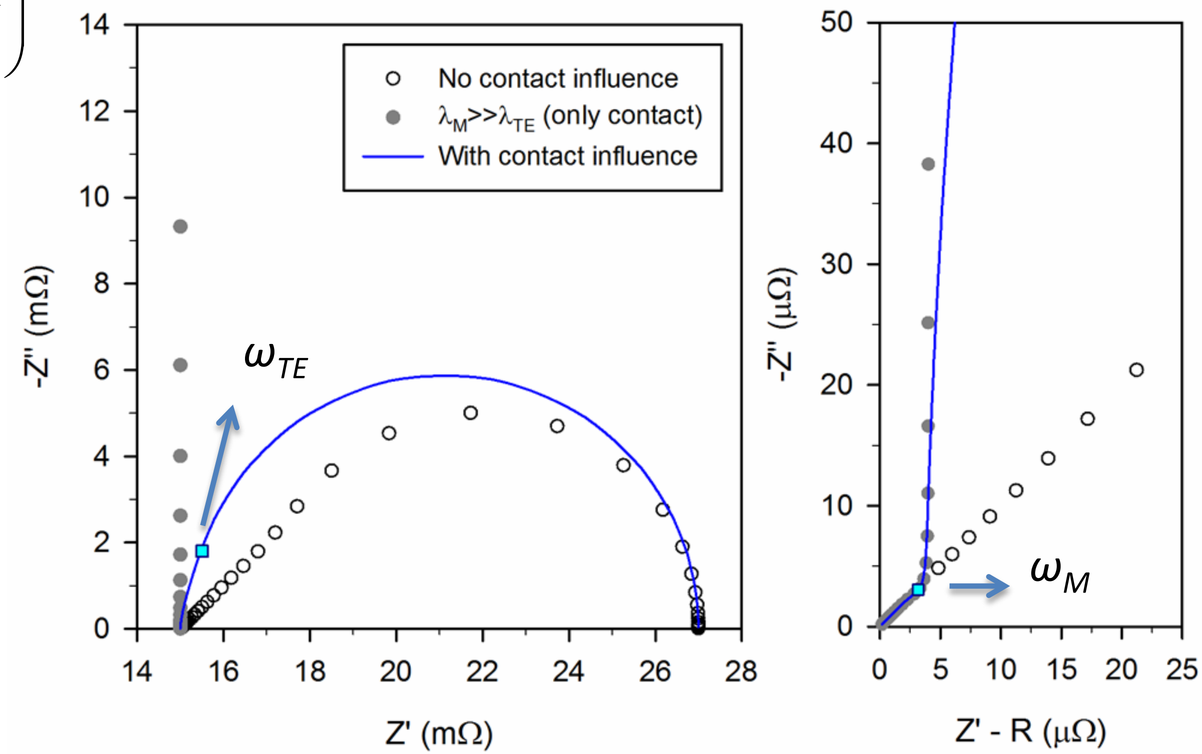


$$Z = R + \frac{2S^2 T_i}{A}\left(\frac{1}{Z_{th,TE}^{-1} + Z_{th,M}^{-1}}\right)$$

At steady-state (ω → 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_2Te_3 thermoelement contacted with Cu contacts 0.2 mm length)

4. Experimental validation

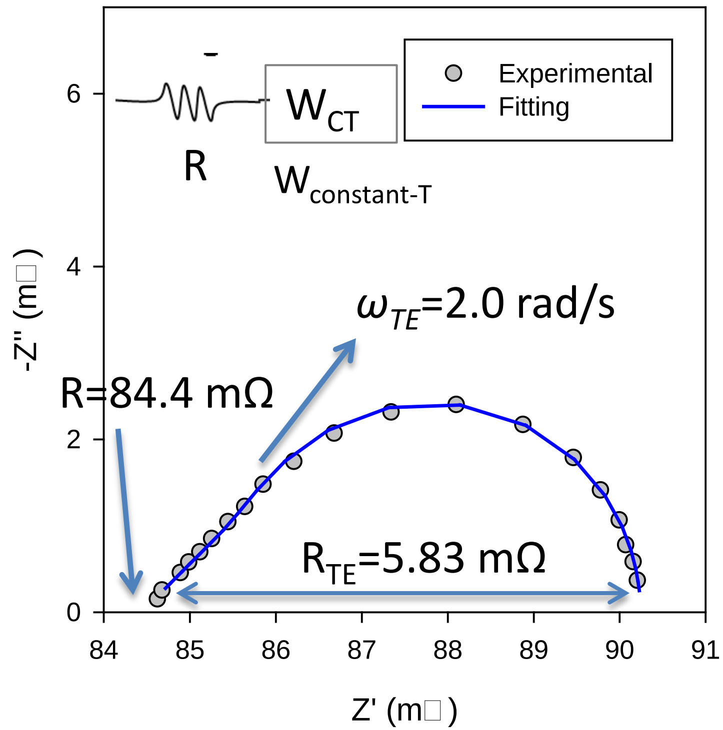
Impedance spectroscopy

• 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

Bi_2Te_3 thermoelement (1.4 x 1.4 mm^2, 1.6 mm length)



(Impedance spectrum from 70 to 0.04 Hz)

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

$$\lambda_{TE} = \frac{S^2 T_i L}{R_{TE} A} = 1.27 \ W/mK$$

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

$$C_{pTE} = \frac{\lambda_{TE}}{d\alpha_{TE}} = 0.13 \ J/gK$$

$$\sigma = \frac{L}{RA} = 96.67 \ S/cm$$

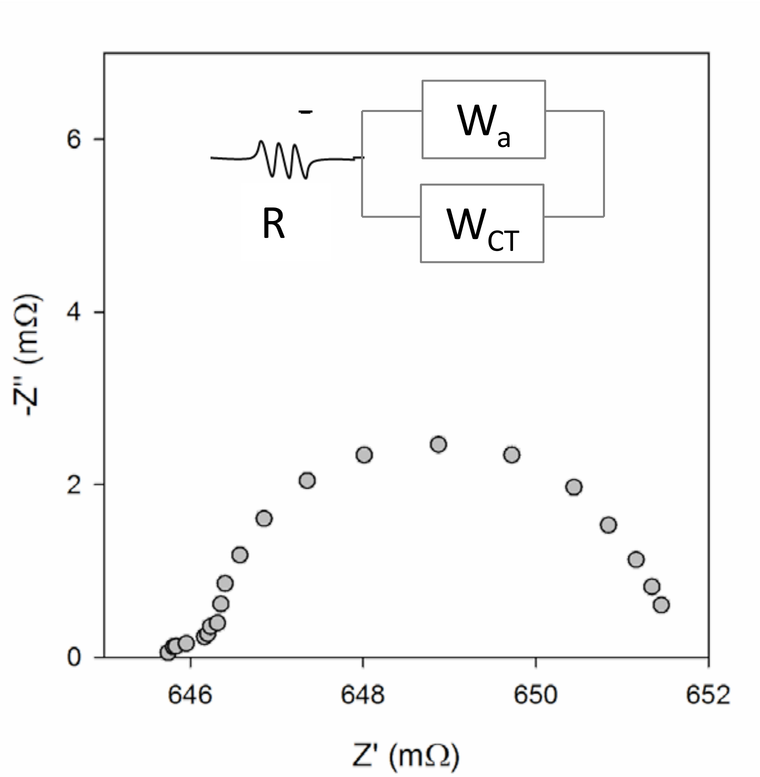
→ Low since contains wires and contact resistances

$$ZT = \frac{R_{TE}}{R}$$

It can provide **all thermal constants** in a ~5 min measurement **If S is known**

4. Experimental validation

Bi$_2$Te$_3$ thermoelement with Cu/ceramic contacts



(Impedance spectrum from 100 to 0.01 Hz)

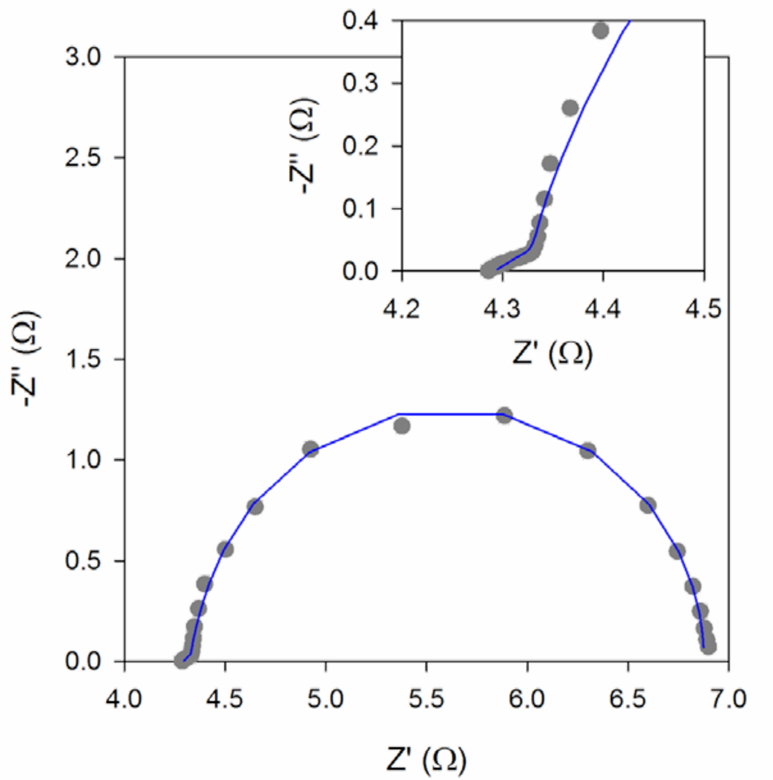
- **Cu effect** can be **neglected** (very small thickness) and ceramic is 1 mm thick.
- **In agreement** with shape predicted.
- **High frequency part** is noisy due to ***μΩ*** variations, close to **equipment limitation**.
- Not possible to fit to equivalent circuit.
- Improvement can be gained by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

4. Experimental validation

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

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

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



(Impedance spectrum from 1000 to 0.01 Hz)

$$R_C = 254\frac{2S^2T_iL_C}{\lambda_C A} = 149\ m\Omega$$

λ_C=30 W/mK

S=191.5 µV/K

$$R_{TE} = 254\frac{S^2T_iL}{\lambda_{TE} A} = 2.585\ \Omega$$

λ_{TE}=1.60 W/mK

$$R = 254\frac{L}{\sigma A} = 4.29\ \Omega$$

σ=888 S/cm

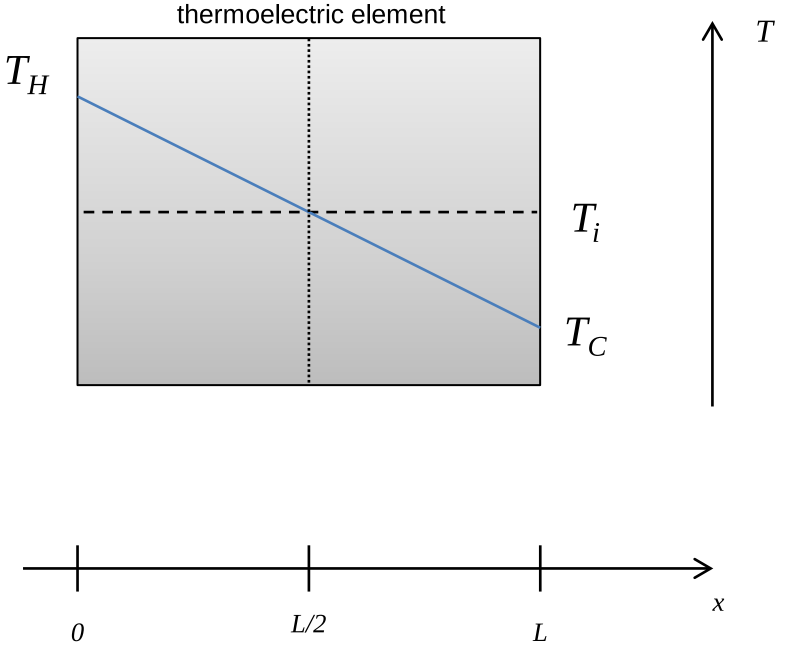
Complete characterisation is achieved

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

5. Physical meaning

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:



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

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

$$V_S = S\left(T_C - T_H\right) = \frac{SL}{\lambda A}\left(\pi I + \frac{1}{2} I^2 R\right)$$

5. Physical meaning

Thermoelectric resistance

We define a thermoelectric resistance as

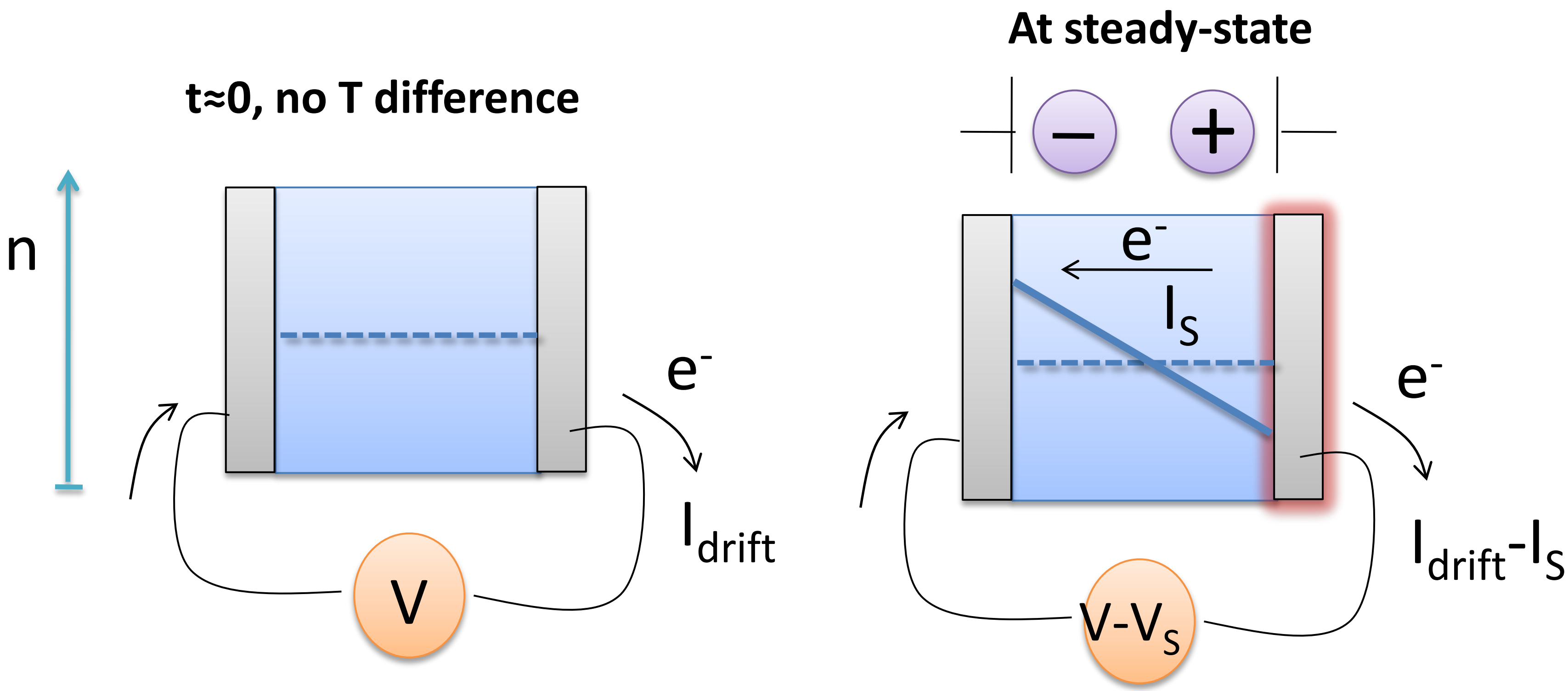
$$R_{TE} = \frac{V_S}{I} \quad \Rightarrow \quad R_{TE} = \frac{SL}{\lambda A}\left(ST + \frac{1}{2}IR\right)$$

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

$$Z(j\omega) = \frac{S^2 T_i L}{\lambda_{TE} A}\left(\frac{j\omega}{\omega_{TE}}\right)^{-0.5} \tanh\left\{\left(\frac{j\omega}{\omega_{TE}}\right)^{0.5}\right\} \quad \Rightarrow \quad Z(\omega = 0) = \frac{S^2 T_i L}{\lambda_{TE} A}$$

5. Physical meaning

Thermoelectric resistance



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

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

$$dt = \frac{-L}{\alpha}dx \longrightarrow C_{TE} = \frac{-IL}{S\alpha}\left(\frac{d(T_H - T_C)}{dx}\right)^{-1}$$

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

$$\left(\frac{dT}{dx}\right)_L^{-1} = \frac{\lambda A}{I\pi} \longrightarrow C_{TE} = \frac{\rho C_p AL}{2S^2T}$$

5. Physical meaning

Thermoelectric capacitance

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

It also appears in the impedance function:

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

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

$$\longrightarrow \quad C_{TE} = \frac{1}{R_{TE}\,\omega_{TE}}$$

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

$$C_{TE} = \frac{1}{5.83 m\Omega \;\; 2 rad/s} = 86 \;\; F$$

Far from electrical capacitance

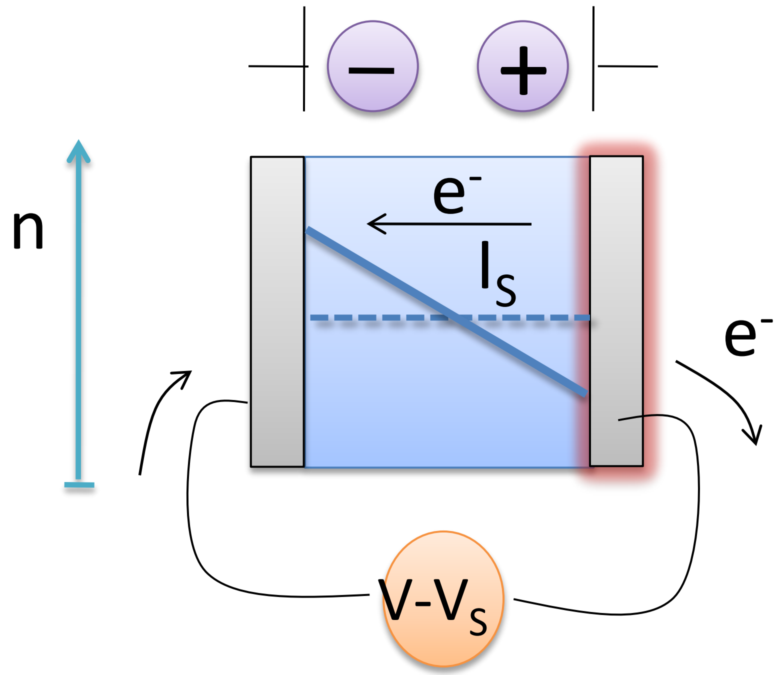
5. Physical meaning

Thermoelectric capacitance

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

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

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



The physical origin is not well understood yet

5. Physical meaning

Time constant (τ)

From the impedance analysis:

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

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

$$\tau = R_{TE} C_{TE} = \frac{(L/2)^2}{\alpha}$$

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

It can also be directly obtained from ω_{TE}

$$\tau = \frac{1}{\omega_{TE}}$$

J. García-Cañadas and G. Min. *Low frequency impedance spectroscopy analysis of thermoelectric modules.* Journal of Electronic Materials 43, 2411-2414 (2014).

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 τ)** 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.**

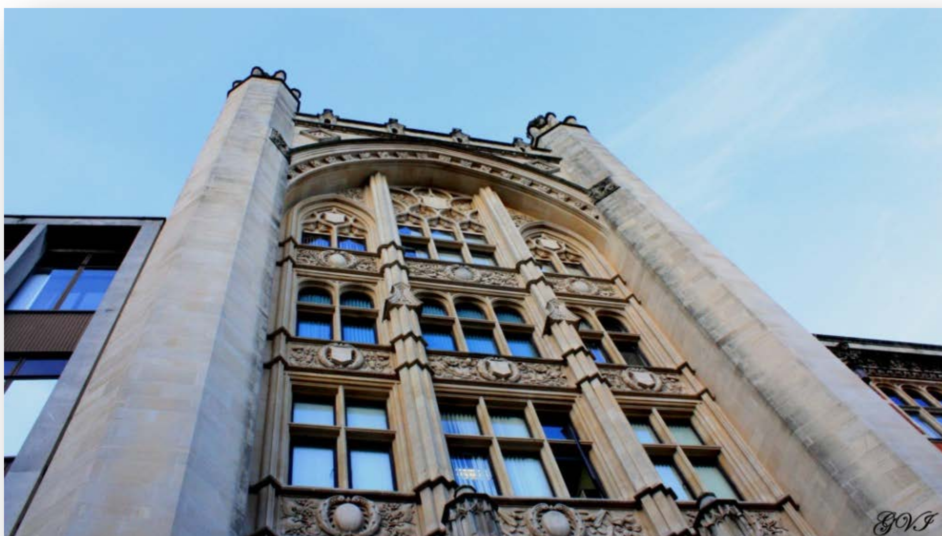
6. Acknowledgements

• **European Commission** and **European Space Agency** for financial support under Accelerated Metallurgy project (AccMet NMP4-LA-2011-263206).

• **Dr. Gao Min** for his support and contribution.

• **Dr. Upul Wijayantha** and **Dr. Matt Carnie** to allow initial experimental measurements in their labs.

• **European Thermodynamics Ltd** as module and materials provider



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