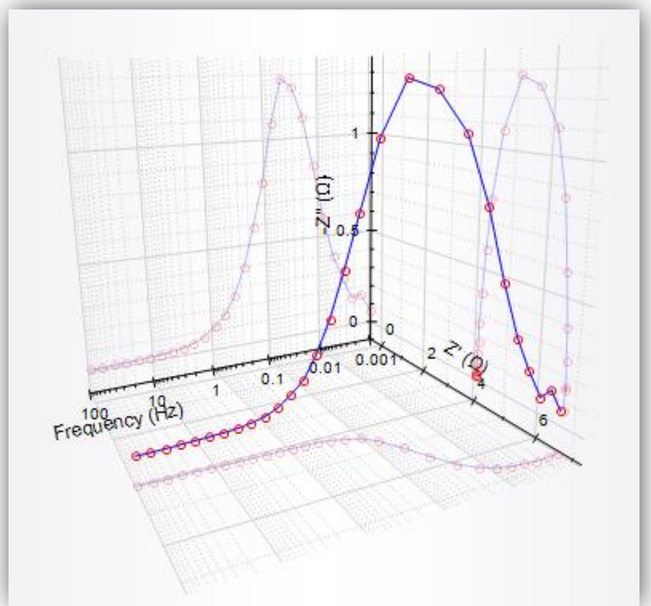
Thermoelectric Network Workshop
- Loughborough University, 14th April 2015 -

Measurement of thermoelectric properties by means of impedance spectroscopy



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Outline

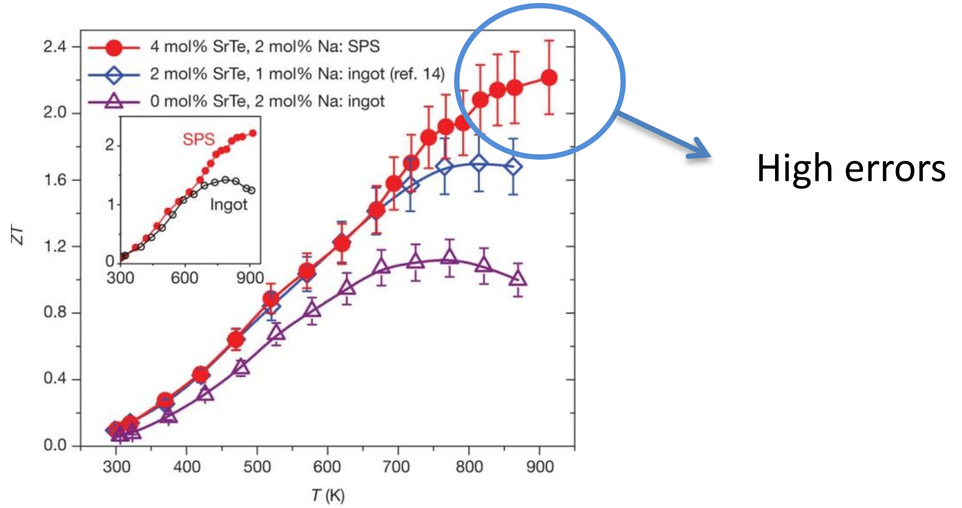
1. Introduction
2. Impedance spectroscopy fundamentals
3. Theoretical background and validation
4. Acknowledgements

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.



K Biswas et al. Nature **489**, 414-418 (2012)

- **Thermal conductivity** is **difficult** to measure and involves very expensive equipments.

1. Introduction

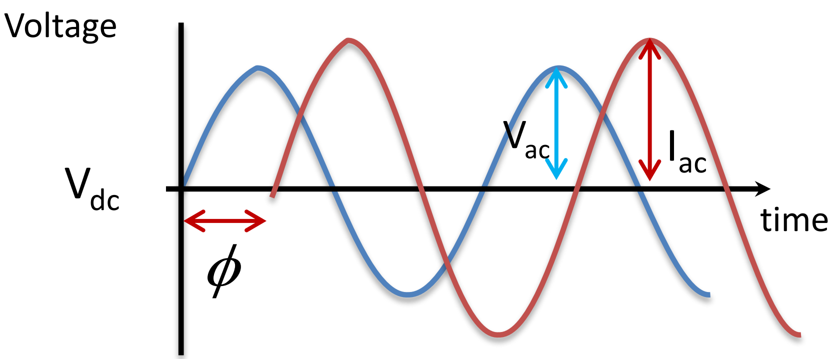
Why exploring impedance?

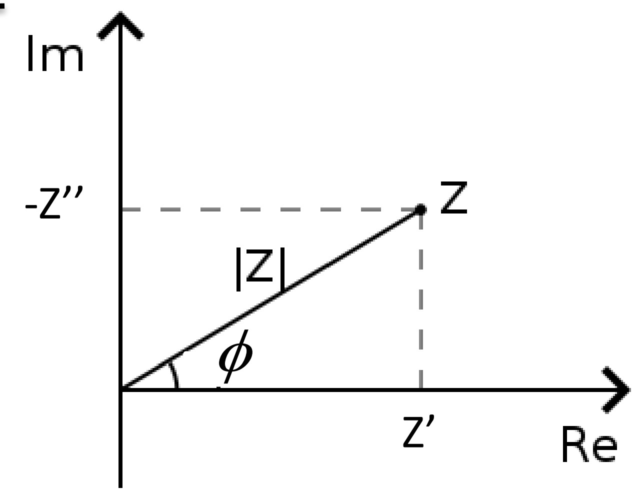
- It is **widely used** in a lot of different fields (solar cells, fuel cells, corrosion, supercapacitors, biosensors, etc.).
- Powerful and very **reliable equipment** are **available in the market**.
- It allows the **separation** of the **physical processes** occurring in a device.
- It can be used under **actual operating conditions**.

2. Impedance spectroscopy fundamentals

Perturbation and system response

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





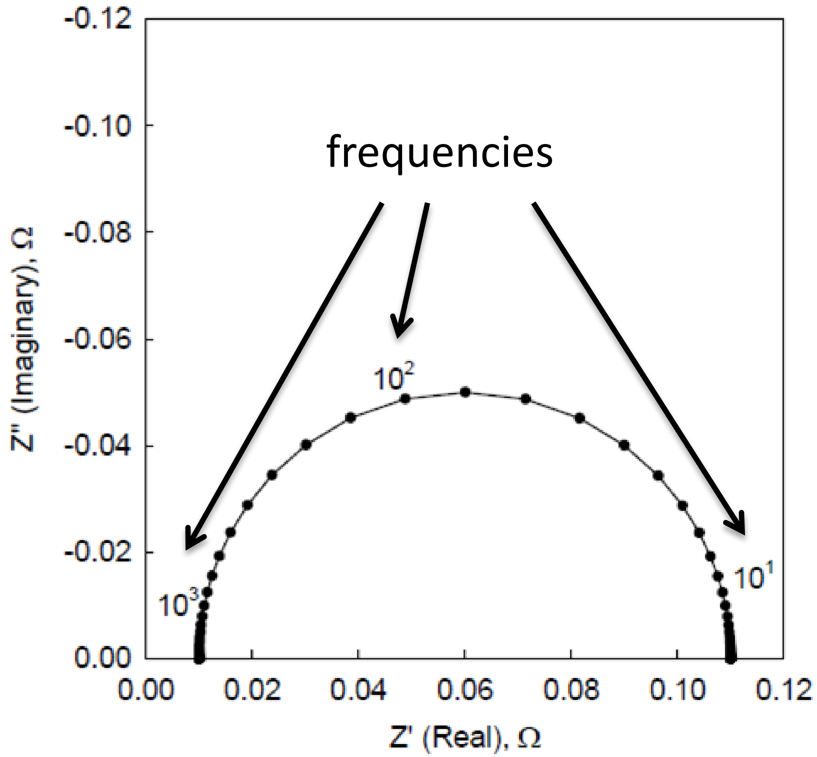
$$\frac{V_{ac}}{I_{ac}} = |Z| = \sqrt{Z'^2 + Z''^2}$$

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

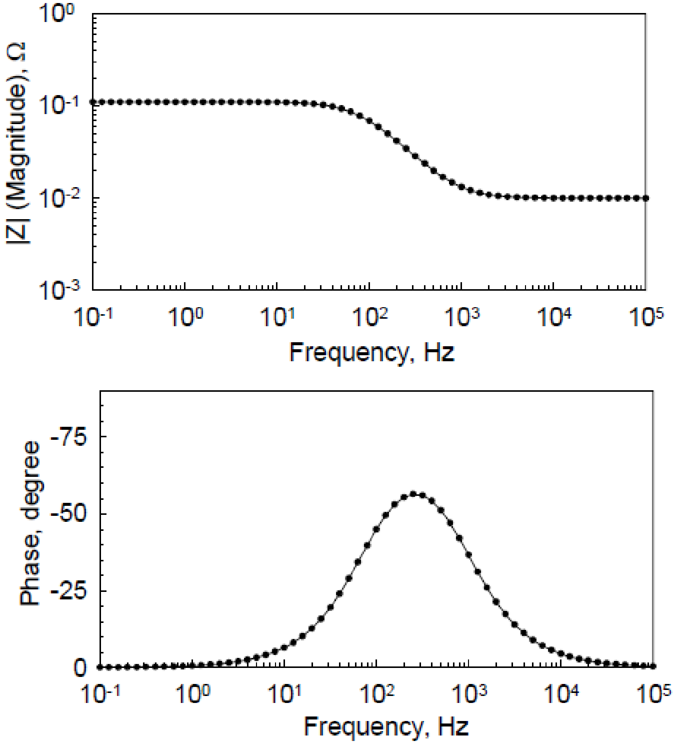
2. Impedance spectroscopy fundamentals

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



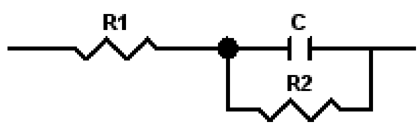
Impedance spectrum (Nyquist plot)



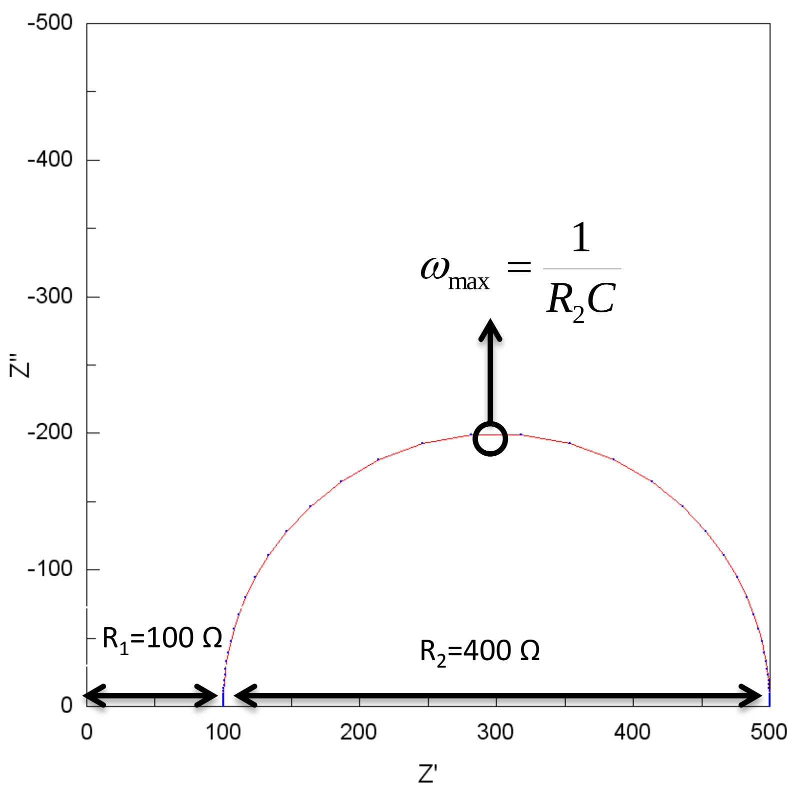
Parameters vs frequency (Bode plots)

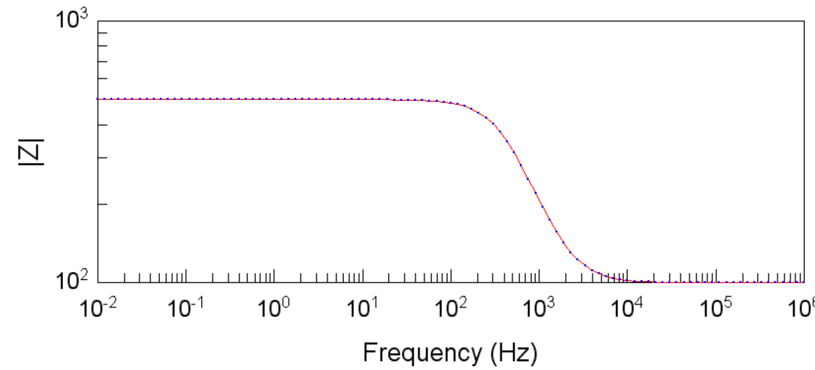
2. Impedance spectroscopy fundamentals

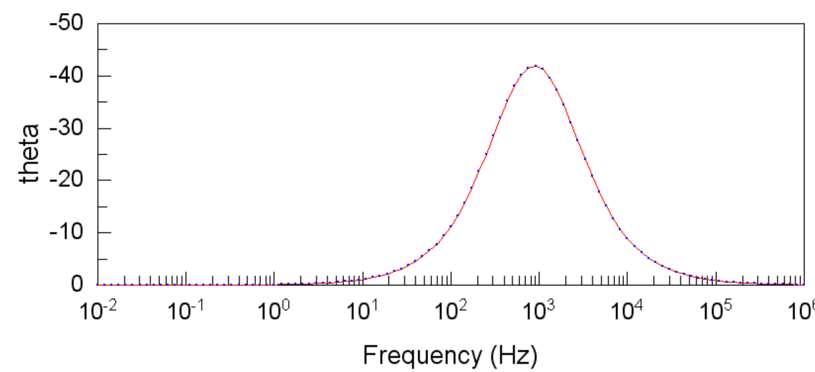
Equivalent circuits



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



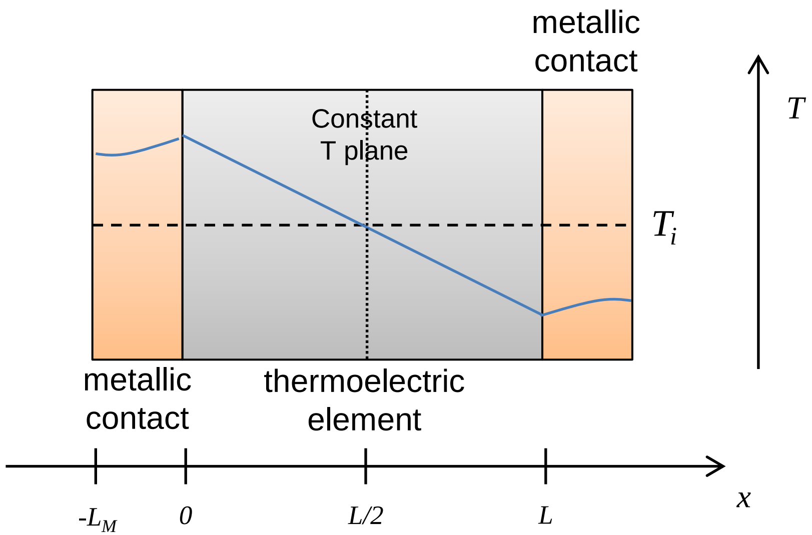




3. Theoretical background and validation

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** at temperature T_i.
- **Joule effect** is **neglected** both in the bulk and at the junctions.



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

3. Theoretical background and validation

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)

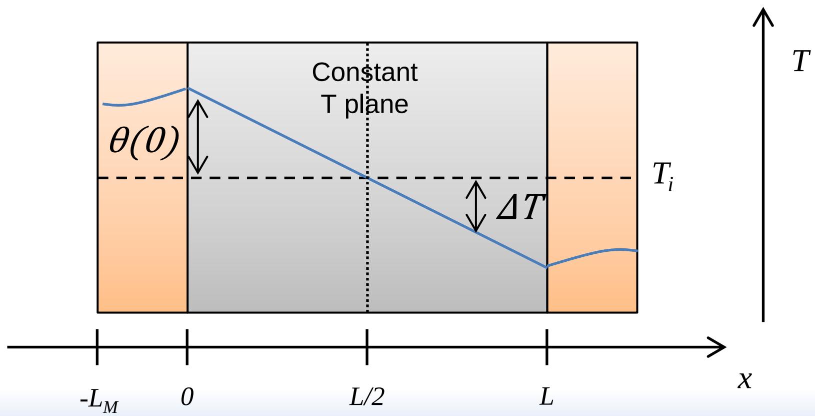
$\mathcal{L}\{\Delta T\} = \theta \quad \mathcal{L}\{I\} = i_0$

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

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

frequency domain (*jω*)

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



V=V(0)-V(L), *R*=total ohmic resistance, *ω=2πf*, *f* is the frequency, $j = \sqrt{-1}$

3. Theoretical background and validation

1. No contact influence approximation

Very thin contact considered ($L_M \rightarrow 0$)

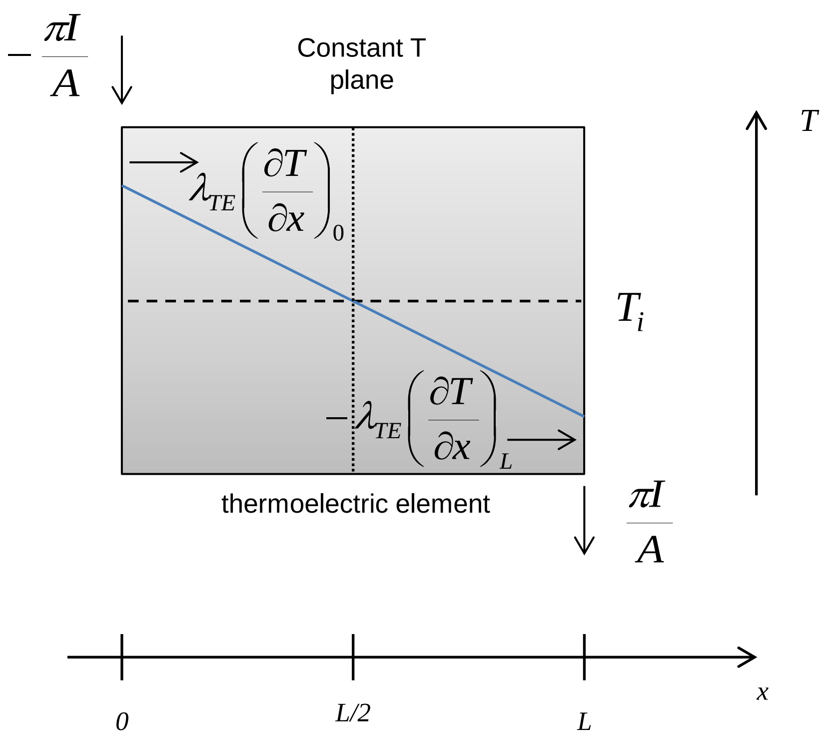
In the thermoelectric material:

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha_{TE}} \frac{\partial T}{\partial t} \quad \text{at } 0<x<L$$

Boundary conditions:

$$-\frac{S T_0 I_0}{A} + \lambda_{TE}\left(\frac{\partial T}{\partial x}\right)_0 = 0 \quad \text{at } x=0 \text{ (adiabatic)}$$

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



α_{TE}=thermal diffusivity, λ_{TE}=thermal conductivity, π=ST=Peltier coefficient

3. Theoretical background and validation

1. No contact influence approximation

$$Z(j\omega) = R + R_{TE}\left(\frac{j\omega}{\omega_{TE}}\right)^{-0.5}\tanh\left\{\left(\frac{j\omega}{\omega_{TE}}\right)^{0.5}\right\}$$

Constant T Warburg (W_{CT})

$$R_{TE} = \frac{S^2 T_i L}{\lambda_{TE} A}$$

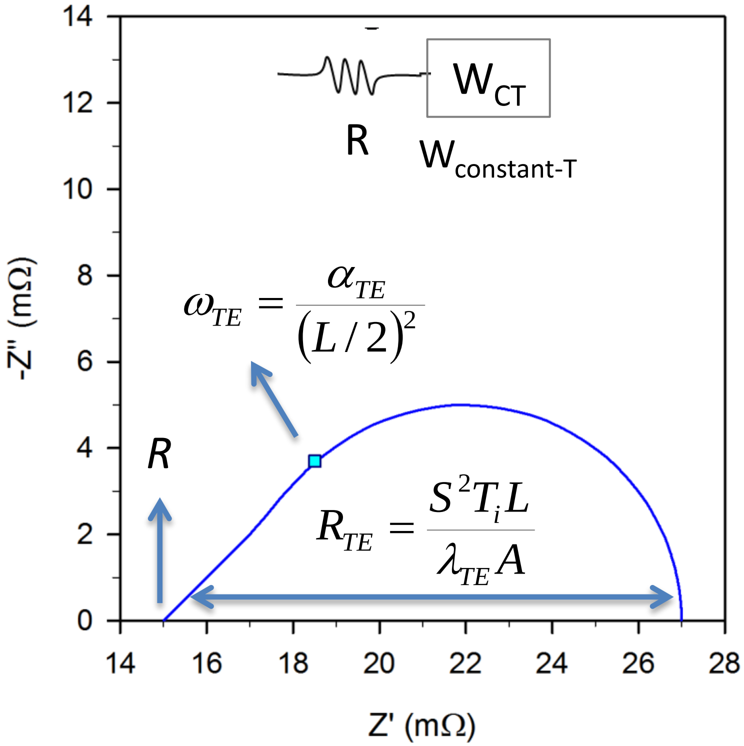
Thermoelectric resistance

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

Characteristic frequency of thermal diffusion

$$C_{TE} = \frac{1}{R_{TE}\omega_{TE}} = \frac{dC_p AL}{4S^2 T_i}$$

Thermoelectric capacitance



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

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

S=Seebeck coefficient, α_{TE}=thermal diffusivity, λ_{TE}=thermal conductivity, *d*=mass density, C_p=Specific heat

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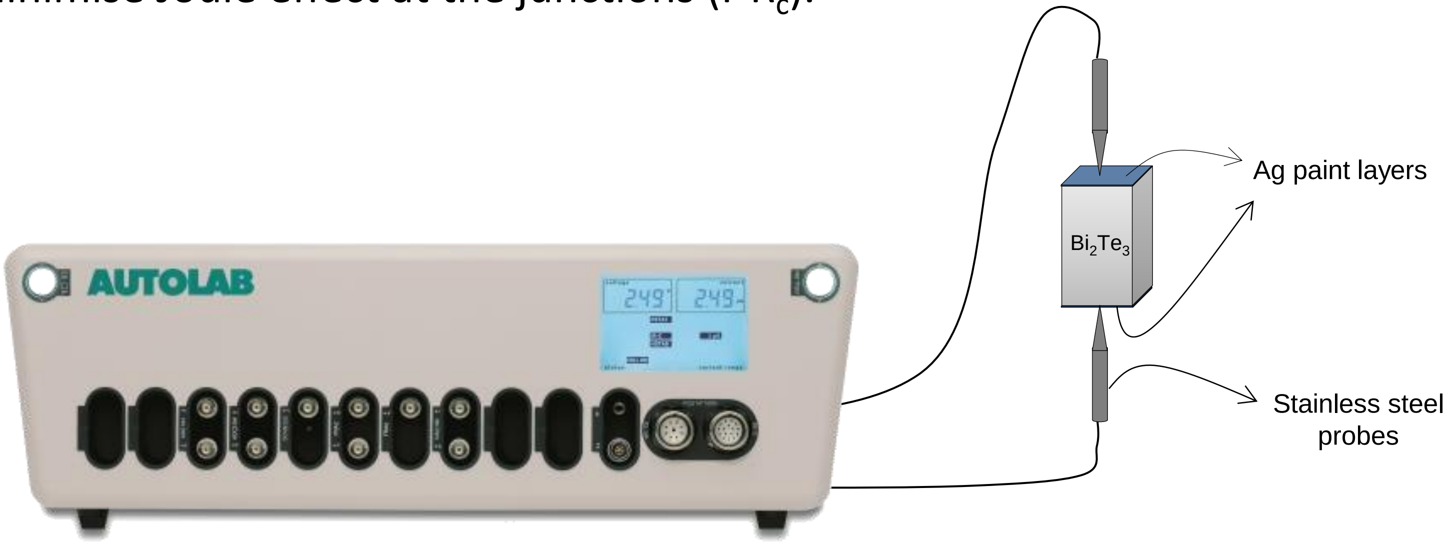
3. Theoretical background and validation

Experimental validation

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

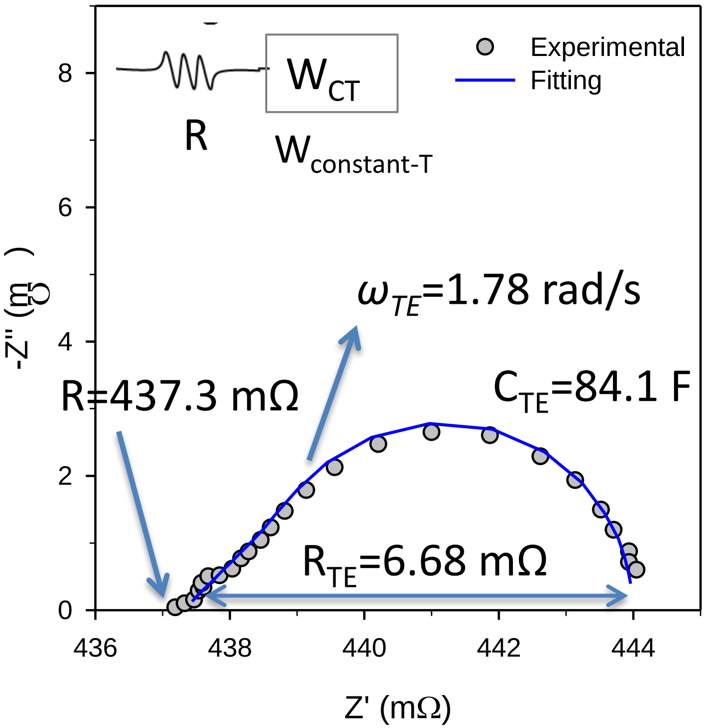
- The sample is suspended using thin **probes of a low thermal conductivity material** (Stainless Steel) to provide adiabatic conditions and reduce the cold finger effect.

- A thin **contact** is formed with **Ag paint**. Low contact resistance R_c should be achieved to minimise Joule effect at the junctions (I^2R_c).



3. Theoretical background and validation

$p\text{-}Bi_2Te_3$ thermoelement (1.4 x 1.4 mm², 1.6 mm length)



(Impedance spectrum from 300 to 0.05 Hz)

Parameter calculation using S=195 μV/K (hot-probe)

$$\lambda_{TE} = \frac{S^2 T_i L}{R_{TE} A} = 1.37\ W/m\ K$$

$$\alpha_{TE} = \frac{(L/2)^2}{\omega_{TE}} = 3.6\text{x}10^{-3}\ cm^2/s$$

$$C_{pTE} = \frac{\lambda_{TE}}{d\alpha_{TE}} = 0.45\ J/gK$$

Literature values*
1.50 W/m K
3.7x10^{-3} cm²/s
0.54 J/gK

It can provide **all thermal constants** in a ≈5 min measurement **If S is known**. **No thermocouples used** to measure T differences.

d=7.53 g/cm³, (*) Data from Custom Thermoelectric manufacturer

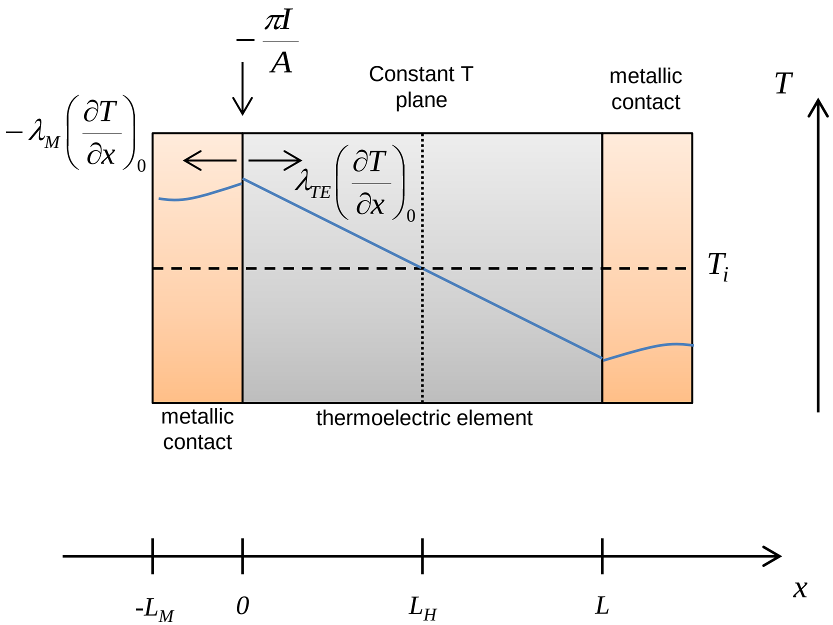
3. Theoretical background and validation

2. Heat equations 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:

$$-\frac{ST_0I}{A} - \lambda_M\left(\frac{\partial T}{\partial x}\right)_{0,M} + \lambda_{TE}\left(\frac{\partial T}{\partial x}\right)_{0,TE} = 0 \quad \text{at } x=0$$

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

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

α_M=thermal diffusivity of metal, λ_M=thermal conductivity of metal

3. Theoretical background and validation

2. Heat equations with contact influence

$$Z = R + \left(\frac{1}{Z_{W_{CT}}^{-1} + Z_{Wa}^{-1}} \right)$$

$$Z_{Wa} = R_C \left(\frac{j\omega}{\omega_C} \right)^{-0.5} \coth\left\{ \left(\frac{j\omega}{\omega_C} \right)^{0.5} \right\}$$

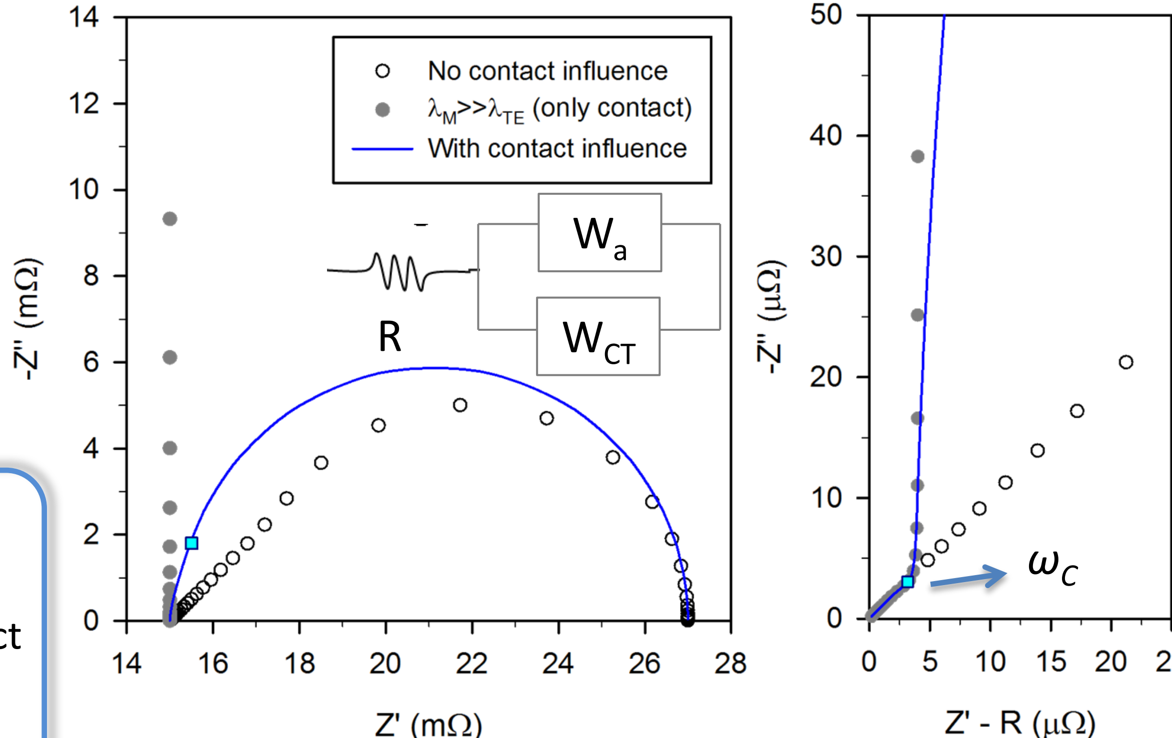
Adiabatic Warburg (W_a)

$$R_C = 2\frac{S^2 T_i L_C}{\lambda_C A}$$

Thermoelectric resistance from contact

$$\omega_C = \frac{\alpha_C}{(L_C)^2}$$

Characteristic frequency of thermal diffusion at the contact

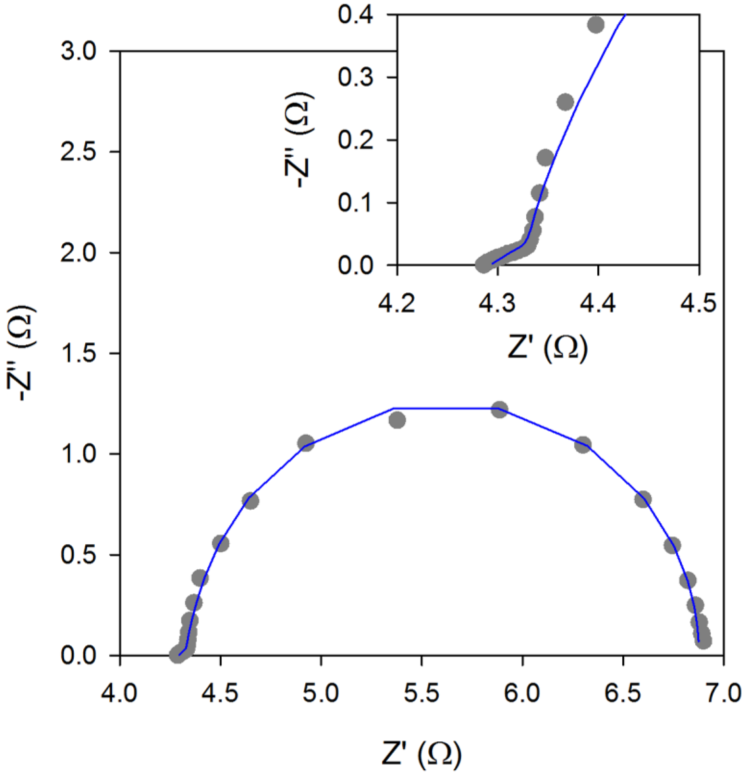


(simulation for 1 mm^2 and 1.5 mm length Bi_2Te_3 thermoelement contacted with Cu contacts 0.2 mm length)

α_C=thermal diffusivity of contact, λ_C=thermal conductivity of contact

3. Theoretical background and validation

<u>*Thermoelectric module (252 legs, 1 x 1 mm^2, 1.5 mm length)*</u>



(Impedance spectrum from 1,000 to 0.01 Hz)

$$Z(j\omega) = R + 252\left(\frac{1}{Z_{Wa}^{-1} + Z_{W_{CT}}^{-1}}\right)$$

$$R_C = 252\frac{2S^2T_iL_C}{\lambda_C A} = 149\ m\Omega$$

λ_C=30 W/mK

S=193.5 µV/K

$$R_{TE} = 252\frac{S^2T_iL}{\lambda_{TE} A} = 2.585\ \Omega$$

λ_{TE}=1.62 W/mK

$$Z_{eff}T = \frac{R_{TE}}{R} = \frac{252S^2T_iL}{\left(R_p + \frac{252L}{\sigma A}\right)\lambda_{TE}A}$$

$Z_{eff}T$=0.60

Complete module characterisation is achieved

J. García-Cañadas, G. Min, Impedance spectroscopy models for the complete characterization of thermoelectric materials, ***J. Appl. Phys.*** *116* (2014) 174510

4. Acknowledgements

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- Moving to **Universitat Jaume I** in Castellón (Spain) in September 2015 -

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