Correct Measurement of Seebeck Coefficient & Resistivity

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23,000 students of which
4,500 are in masters and
2,700 are in doctorate programs.

METU hosts over 1,500 international students from nearly 80 different countries.

METU actively took part in and managed many Med-Campus, MEDA, COST, Eureka, NASA, NATO, NSF, UN, World Bank, Jean Monnet, INCO, EUMEDIS, 6th and 7th Framework, Erasmus Mundus ECW, Leonardo and Socrates projects.
Basic Research Topics in Our Laboratory
Surface Science Research Laboratory (SSRL)
Metallurgical & Material Engineering Department

+ Thermoelectrics
  × Synthesis, Structural and Electrical Characterizations

+ Dye-sensitized solar cell (DSSC, DSC or DYSC)
  × Some Synthesis, Characterizations, Modulating

+ Piezoelectric –thin film
  × Synthesis, Structural & Ferro-electrical Characterizations,
After studying eath magnetisim he called this invention as thermomagnetism **1825**.

The priority of Volta in the discovery of thermoelectric effect of EMF generation due to temperature difference.

First, A. Volta carried out purposeful experiments, with a view to discover thermoelectromotive forces arising under the influence of temperature difference.

Volta invented 27 year earlier (Volta wrote to professor of physics in Royal University of Turino abbot Anton Maria Vassali three letters entitled “A new paper on the animal electricity”)

German physicists I. Ritter (1798) and I. Sveiger (1810)

• **Introduction**
  - World Energy Needs
  - Working Principles of Thermoelectric Devices

• **Thermoelectric Effect – Figure of Merit**

• **Thermoelectric Materials**

• **Electrical Characterizations**
  - Resistivity, and Seebeck Coefficient

• **Conclusion**
Thermoelectric materials can convert electrical energy into a temperature gradient as well as thermal energy into electrical energy.

Thermoelectric (TE) materials have unique position for dual electrical generation on one side and cooling/heating on the other side.

Power generation is achieved by applying a temperature difference between two ends of the TE material, while cooling or heating is obtained by applying electrical current.
Working Principle of Thermoelectric Devices

Converting heat energy to the electrical energy directly is called Seebeck Effect or vice versa Peltier Effect.

Figure 1. Schematic view of Seebeck Effect
Working Principle of Thermoelectric Devices

Thermoelectricity is the direct conversion of temperature differences to electric voltage and vice versa.

Figure 2. Schematic view of Peltier Effect
Figure of Merit (ZT)

\[ ZT = \frac{S^2 T}{K_T \rho} = \frac{S^2 \sigma T}{K_L + K_e} \]

- Thermopower
- Temperature
- Electrical Conductivity
- Electronic Thermal Conductivity
- Lattice Thermal Conductivity
- Thermal Conductivity
- Electrical Resistivity
Waste Energy Recovery

Figure 3. Typical energy split in gasoline internal combustion engines.

CO₂ emissions of 140 g CO₂/km or lower

Transform huge amounts of waste energy to electrical energy
(Recover and effectively utilize the waste energy)

BMW has won an ÖkoGlobe award.

BMW Group Wins Award For Thermoelectric Generator

http://green.autoblog.com/
Comparison of TE Materials

**Figure 4.** Thermoelectric Materials for Heat-to-Electricity Direct Energy Conversion

Ref. Michitaka Ohtaki, Micro Review, Faculty of Engineering Sciences, Kyushu University
Thermocouples

- By using the Thermocouple Law of Intermediate Metals and making some simple assumptions, you will find that the measured voltage depends on the thermocouple type, thermocouple voltage, and the cold-junction temperature.
- The measured voltage is independent of the composition of the measurement leads and the cold junctions, J2 and J3.
- According to the Thermocouple Law of Intermediate Metals inserting any type of wire into a thermocouple circuit has no influence on the output as long as both ends of that wire are the same temperature, or isothermal.

Junctions J2 and J4 are the same type (copper-constantan). Because both are in the isothermal region, J2 and J4 are also the same temperature.

Ref. National Instruments: Thermocouples
Temperature Measurement

Thermocouple reference tables are generated with the reference junction held at 0 °C, therefore, to determine the temperature at the thermocouple junction we can start with Equation 2 shown below, where \( V_{\text{MEAS}} \) is the voltage measured by the data acquisition device, and \( V_{TC} (T_{TC} - T_{ref}) \) is the Seebeck voltage created by the difference between \( T_{TC} \) (the temperature at the thermocouple junction) and \( T_{ref} \) (the temperature at the reference junction):

**Equation 2:** \( V_{\text{MEAS}} = V_{TC} (T_{TC} - T_{ref}) \)

We can rewrite Equation 2 as shown in Equation 3 where \( V_{TC} (T_{TC}) \) is the voltage measured by the thermocouple assuming a reference junction temperature of 0 °C, and \( V_{TC} (T_{ref}) \) is the voltage that would be generated by the same thermocouple at the current reference temperature assuming a reference junction of 0 °C:

**Equation 3:** \( V_{\text{MEAS}} = V_{TC} (T_{TC}) - V_{TC} (T_{ref}) \)

**Equation 4:** \( V_{TC} (T_{TC}) = V_{\text{MEAS}} + V_{TC} (T_{ref}) \)

In Equation 4, the computed voltage of the thermocouple assumes a reference junction of 0 °C. Therefore, by measuring \( V_{\text{MEAS}} \) and \( T_{ref} \), and knowing the voltage-to-temperature relationship of the thermocouple, we can determine the temperature at the primary junction of the thermocouple.

Ref. National Insturments: Thermocouples
**Temperature Measurement**

<table>
<thead>
<tr>
<th>TYPE E</th>
<th>TYPE J</th>
<th>TYPE K</th>
<th>TYPE R</th>
<th>TYPE S</th>
<th>TYPE T</th>
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<tr>
<td>Nickel-10% Chromium(+)</td>
<td>Iron(+)</td>
<td>Nickel-10% Chromium(+)</td>
<td>Platinum-13% Rhodium(+)</td>
<td>Platinum-10% Rhodium(+)</td>
<td>Copper(+)</td>
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<tr>
<td>Versus Constantan(-)</td>
<td>Versus Constantan(-)</td>
<td>Versus Nickel-5%(-) (Aluminum Silicon)</td>
<td>Versus Platinum(-)</td>
<td>Versus Platinum(-)</td>
<td>Versus Constantan(-)</td>
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<tr>
<td>-100°C to 1000°C</td>
<td>0°C to 1370°C</td>
<td>0°C to 1000°C</td>
<td>0°C to 1750°C</td>
<td>-160°C to 400°C</td>
<td></td>
</tr>
<tr>
<td>± 0.5°C</td>
<td>± 0.7°C</td>
<td>± 0.5°C</td>
<td>± 1°C</td>
<td>± 0.5°C</td>
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</tr>
<tr>
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<td>0.927763167</td>
<td>0.10060910</td>
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<td>0.263632917</td>
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<td>0.10060910</td>
</tr>
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<td>179075.491</td>
<td>169526.5150</td>
<td>25727.94369</td>
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</table>

**TEMPERATURE CONVERSION EQUATION:**

\[ T = a_0 + a_1x + a_2x^2 + \ldots + a_nx^n \]

**NESTED POLYNOMIAL FORM:**

\[ T = a_0 + x(a_1 + x(a_2 + x(a_3 + x(a_4 + a_5x)))) \]

(5th order)

where \(x\) is in Volts, \(T\) is in °C

**NBS POLYNOMIAL COEFFICIENTS**

Voltage Measurement

Figure 5. Theoretical limits of voltage measurements

The axial-flow technique (two-probe), the temperature difference and the electric potential are measured on the probes which are in direct contact with the ends of the specimen (Goldsmid and Tritt).

The potentiometric arrangement (or four-probe), the temperature difference and the voltage difference are measured at two points on the sample (or inserted within the sample) equidistant from the hot and cold sinks and on the axis parallel to the thermal gradient.

To maintain accuracy, the diameter of each temperature/voltage probe must be much smaller than the effective distance between them. There is some debate as to which method provides the most accurate determination of temperature and voltage difference at the same points.

Wood (Rev. Sci. Instrum., 1985, 56, 719) compared the results of thermocouples pressed on the ends of a sample with those obtained by inserting them in holes drilled in the sample. For the temperature and the material evaluated, the results were consistent within the measurement uncertainty.
Electrical Characterization

- Contact issue

**Figure 6.** Detailed types of contacts
Considering the diversity of research materials in both geometry and contact resistance, the potentiometric arrangement may benefit longer, lower cross-sectional area specimens, while the axial-flow arrangement may benefit shorter or disk-shaped specimens, provided the thermal resistance of the sample is larger than the thermal resistance of the contact interface. Thus, a versatile and flexible apparatus would not only enable comparative measurements on materials with different contact resistances, thermal conductivities, and heat capacities, but also expand the practical range of sample geometries.

The primary requirements for “good” Seebeck coefficient measurements are:

- The spatially synchronous measurement of voltage and temperature, that is, the voltage and temperature must be measured at the same location and at the same time;
- Probes in very good thermal and electrical contact with the specimen; and
- The acquisition of low voltages (microvolts) with minimal extraneous contributions.

Martin, Tritt, and Uher J. Appl. Phys. 108, 121101 2010
Methods of TE Voltage Measurement

- Measurement of the Seebeck voltage requires the open circuit condition $J=0$ (where $J$ is the electrical current density), such that the junctions are isothermal and the electrochemical potential is continuous.

- In the Harman method (or Z meter), the ohmic voltage is measured under both isothermal and adiabatic conditions, such that $J \neq 0$ and the temperature difference forms due to the induced Peltier effect at the contacts.

- **Differential Method – DC Method**
  - The steady-state condition
  - The quasi-steady-state condition

- **Integral Method – DC Method**

- **3 ω - AC Method**

C. A. Domenicali, Rev. Mod. Phys., 1954, 26, 237
Methods of TE Voltage Measurement

**Differential Method (Small $\Delta T$)**

\[
\frac{\Delta V_{ab}}{\Delta T} = S_{ab}(T_o) + \Delta S_{ab}(T_o)
\]

**Integral Method (Large $\Delta T$)**

\[
S_{ab}(T_2) = S_b(T_2) - S_a(T_2) = \frac{dV_{ab}(T_1,T_2)}{dT_2}
\]

Direct Measurement

**Curve fitting is necessary**
- Walking polynomial
- Spline fit
- Global least-squares fits of varying order
- Orthogonal coefficient decrease
- F-test
Bidwell then measured the Seebeck coefficient and resistivity of germanium rods
2.4 cm long between 191 and 675 °C

Martin, Tritt, and Uher J. Appl. Phys. **108**, 121101
2010
Methods of TE Voltage Measurement

by Burkov and the other by Zhou and Uher provide detailed descriptions of the apparatus and instrumentation suggested for high temperature implementation of the differential steady-state method.

Methods of TE Voltage Measurement


Martin, Tritt, and Uher J. Appl. Phys. 108, 121101
2010
Methods of TE Voltage Measurement


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Resistance Measurements

- Wire – for example mercury probe, MEMS
- Film – for example mercury probe, MEMS
- Bulk – four probe method is advised
Eliminate Thermoelectric Voltage Effects

Ways to Reduce Thermoelectric Voltages

- Construct test circuits using the same materials for interconnects.
- Minimize temperature gradients within the test circuit.
- Allow the test equipment to warm up.
- Use an offset compensation method.

Use the Current Reversal Method to Eliminate Voltage Offsets ($V_{EMF}$)

Measurement with Positive Polarity

$$V_{\text{EMF}} = V_{\text{pos}} + IR$$

Measurement with Negative Polarity

$$V_{\text{EMF}} = V_{\text{neg}} - IR$$

Thermoelectric voltages are generated when dissimilar metals (Metal A and Metal B) in the circuit are at different temperatures (T1 and T2).

Ref. Keithley.com
Film Resistance

- 3-point spreading resistance measurements
Mercury Probe Resistance Measurement

2 Probe Resistance Measurement

http://www.mdc4cv.com/mercuryprobe.htm
Resistivity Measurement of a Single Wire

Fig. 1. Four nanomanipulators with probes installed for manipulation inside an SEM.

Fig. 2. Visual recognition of probes and nanowires from SEM visual feedback. (a) Four probes and nanowires. (b) Probes and nanowires are recognized from image processing.

Fig. 7. Manual operation often causes probe tip damage and sometimes inadvertently severs a nanowire.
Correction tests

Fig. 10. Four probes landing on target positions for four-point probe measurement.

Fig. 11. Four-probe measurement results of a nanowire. (a) $I-V$ data of a nanowire with regard to different separations between the two inner probes. (b) Separation-resistance relationship.
The measurement of bulk resistivity is similar to that of sheet resistivity except that a resistivity in cm$^{-3}$ is reported using the wafer thickness, $t$:

$$\rho = \frac{\pi}{\ln(2)} t \left( \frac{V}{I} \right) = 4.523 t \left( \frac{V}{I} \right)$$

Where $t$ is the layer/wafer thickness in cm.

The simple formula above works for when the wafer thickness less than half the probe spacing ($t < s/2$) (Schroder). For thicker samples the formula becomes:

$$\rho = \frac{V}{I} \frac{\pi t}{\ln \left( \frac{\sinh \left( \frac{t}{s} \right)}{\sinh \left( \frac{t}{2s} \right)} \right)}$$

Where $s$ is the probe spacing.

Ref. Jandel.com
4 probe contact with silver paint – at low temp
Conclusion

- The importance of thermal and voltage contacts
- Very careful design and implementation
- Wiring
- The measurement capability of devices
- Different measurement atmosphere for different materials
- Simultaneous measurement of TE voltage and temperature
Thank you for kind attention