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A New Non-destructive Method of Alternative Determination of the Thermoelectric Cell Efficiency

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1. Introduction

Original thermoelectric generators with diesel burners that used to power radio stations (in areas separated from the distribution grid) were replaced by transistors, but thermoelectric cells are widely used in space research even nowadays They are used especially in solar thermoelectric converters (most often from Ge-Si alloy) suitable for operation at high temperatures and when exposed to radiation. Photoelectric cells, when compared to thermoelectric cells, age very quickly due to high temperature and radiation. That is why they are the most current nuclear thermoelectric generators heated by radioactive sources with isotopes (most often

^{90}Sr and ^{238}Pu), known for their independence, reliability and long-term functionality [1–8]. Thermoelectric cells are, even after nearly 100 years after the invention of the first thermoelectric phenomena, still modern alternative energy sources, not only from ecological but also from economic perspective. The main objective of the effort studying the material and construction properties of thermoelectric cells is to increase their existing relatively low efficiency (15%; [4]).

2. Theoretical part

Thermoelectric cell is defined as a series connection of the same type of thermocouples. The total voltage is the sum of the partial voltages of the individual thermocouples. A semiconductor thermocouple consists of two semiconductor posts with different type of conductivity. At one end, the two posts are conductively connected by a soldered metal bridge. Conductors are soldered, again using metal bridges; to the second ends of both posts in order to connect the thermocouples into the electrical circuit [3]. There are well-known thermoelectric phenomena taking place simultaneously in the thermocouple: Seebeck, Peltier, Thomson and Benedick effect. When connecting the thermoelectric cell into a circuit with an external electrical source, the Peltier effect is preferentially applied and the electric energy is used for cooling, respectively, when reversing the external electric source, for heating. When connecting the thermoelectric cell into a circuit with an external heat source, the Seebeck effect is preferably applied, and thermal energy is used for direct conversion into electric energy [5].The efficiency η (2) of the partial thermoelectric couple or thermoelectric cell is typically evaluated using temperatures T_1 of the warmer end of the thermocouple (bridge - thermoelectric cell wall), temperature T_2 of the colder end of the thermocouple (bridge - thermoelectric cell wall), their temperature difference ΔT and the parameter of thermoelectric efficiency (quality factor) Z [K^{-1}] (1). The Z parameter can be measured from the material constants, namely from the Seebeck coefficient of the thermoelectric voltage α [V·K^{-1}], specific electrical conductivity σ [S·m^{-1}] and specific thermal conductivity λ [W·m^{-1}·K^{-1}].

$$Z = \frac{\sigma \cdot \alpha^2}{\lambda} \tag{1}$$

$$\eta = \frac{T_1 - T_2}{T_1} \cdot \frac{\sqrt{1 + 0.5 \cdot Z \cdot (T_1 - T_2)} - 1}{\sqrt{1 + 0.5 \cdot Z \cdot (T_1 - T_2)} + \frac{T_2}{T_1}} \tag{2}$$

The first factor in equation (2) expresses the thermodynamic efficiency of the reversible heat source, the second one reflects the reduction in thermodynamic efficiency due to irreversible losses caused by thermal conductivity and the release of Joule heating on the cell resistance (or more accurately, the total resistance of both of its posts) [6]. The amount of consumed current therefore depends on the material properties of the thermoelectric cell, its construction, and also of the temperature difference. Practically, we heat one side of the thermoelectric cell by putting it closer to the heat source, while the other side has more or less the ambient (air) temperature and its temperature will, at most, slightly increase owing to the overall heating.

If the given thermoelectric cell is made of material that the user is not perfectly familiar with, the exact determination of the material parameters is really difficult. In addition to the accurate electrical measuring instruments themselves, especially voltmeter with a very high internal resistance, the realizable determination of the *Z* parameter requires a special apparatus for measuring the Seebeck coefficient of thermoelectric voltage [7], a special apparatus for measuring the specific electrical conductivity using a 2-probe or a 4-probe method [7], and a special apparatus to measure the specific C-value using Ioffe´s method [7]. These measurements are also associated with the destruction of the thermoelectric cell into subsamples. Apart from this procedure for measurements of the *Z* parameter, there is also the so called „method ΔT_{max}" (the method of maximum temperature difference between warm and cold junction), but it is feasible only with a special, relatively expensive apparatus. This apparatus consists of a drained container with the sample and a measured thermocouple. By plunging a massive suspension bar into the thermostat, you can change the temperature of the environment, so it is possible to measure simultaneously the *Z* parameter and its temperature dependence [6].

An alternative, relatively simple and experimentally undemanding method of evaluating the thermoelectric efficiency of a thermoelectric cell made of unknown materials is a method evaluating its "static" properties when comparing the two basic thermoelectric processes. This method requires precise experimental procedure:

1. the temperatures of both walls and, at the same time, the size of Seebeck thermal voltage $U_{S,}$, which arises as a result of the temperature difference between the thermoelectric cell walls, are measured (in an open electrical circuit) when one wall of the thermoelectric cell is heated using an external source of heat;
2. the temperatures of both walls and, at the same time, the thermoelectric voltage U_{TEB}, that was induced by the flowing current (the thermoelectric cell current produces heat and, simultaneously, also causes the temperature difference between its walls) are measured (in a closed electrical circuit) when the thermoelectric cell is heated by the electric current from an external electric source.

In principle, the newly designed method tries to uncover how the passage of electric current changes the voltage of the thermoelectric cell, in comparison with the measured voltage of the same thermoelectric cell the current does not flow through. The comparisons can be made only when the mean temperatures of the thermoelectric cell correspond with each other. The mean temperature T_S is an arithmetic average between the temperatures T_1, T_2 of both thermoelectric cell walls. From a mathematical point of view, it is a functional dependence U_{TEB} (U_S) expressed by functional dependencies of U_{TEB} (T_S), U_S (T_S). When we express the ratio of both voltages U_{TEB}/U_S related to the given mean temperature of the T_S, this value can be conventionally described as material efficiency ε_Z. It is therefore a value that can be assigned to parameter Z (preferably averaged for all the points in the equidistant time intervals of the performed measurement, or at least for guidance for the so called "working point"). The generally valid equivalent of material parameter Z of ternary alloys and the newly designed material efficiency ε_Z can be declared only after multiply repeated measurements of many kinds of thermoelectric cells are carried out (thermoelectric cells from different materials and identified by reliably known, i.e. given by the manufacturer, parameters Z).

The theoretical calculation of the Z parameter must, however, be looked upon with certain tolerance. This material "constant" changes not only according to the actual temperature, but also according to the eventual depreciation of the given thermoelectric cell in time. Due to a long-term or excessive thermal stress, the value of the Z parameter changes significantly (even by order). In case of ternary alloys, the excessive thermal stresses means, for example, such a temperature difference between the thermoelectric cell walls when the temperature of the heated wall is more than three times higher than the temperature of the reverse wall, away from the heat source or when $T_1 > 3\ T_2$ condition is valid during heating by a current from an external power source. Measuring its internal resistance can serve as fast and reliable information on the proper functioning of thermoelectric cell in technical practice. For example, Peltier cell made of ternary alloys have internal resistance in the order of tens of mΩ which, depending on admissible heating, shows only relatively slight increase (not by orders). However, in case of presence of a cold joint, the thermoelectric cells show quickly fluctuating internal resistance at zero and constant temperature difference between the walls, with the value in the orders of tens up to hundreds of Ω or, in case of destruction of the thermoelectric cell (in extreme case of overheating), the value of internal resistance is in the order of millions of Ω.

3. Experimental part

Accurate determination of the efficiency η of thermoelectric cell made of unknown material, respectively of its Z material parameter, is a matter of precise electrical measurement, the measurement of voltage, current and temperatures of the thermoelectric cell walls in fine, equidistant time intervals. It is advisable to use a computer to model the interdependencies of the measured variables and to control this procedure.

The measurements were carried out using thermoelectric cell consisting of 4 thermocouples, made of ternary alloys (specifically, the alloy of bismuth telluride and selenide $Bi_2Te_3 - Bi_2Se_3$, conductivity type N, bismuth telluride and antimony $Bi_2Te_3 - Sb_2Te_3$ conductivity type P), connected by a copper bridge. The selected thermoelectric cell was fitted with a cooler (it was glued with epoxy to one of its walls), stored in a calorimetric vessel (the external glass container was isolated by a layer of air from the internal metal one) with a thermally non-conductive lid and with an opening for thermistor contact thermometer probe. Water was chosen as the internal vessel bath (at higher temperatures, the hole in the lid served as continuous vapours escape). The accuracy of the continuously used measuring instruments varied from 0.01% (MIT 330 voltmeter) to 2.5% (thermistor contact thermometer PU 520).Two differential equations causing voltage in the thermoelectric circuit were theoretically developed ("rougher" and "softer" flow, see Fig. 1) and their solution was compared with the empirical data. It was based on the data measured in 2 steps of the given proposed method experimental procedure. These facts were converted from a tabular form into a graphical one and the chart structure was compared with the presented equations (4), (6) as matching (close conformity).

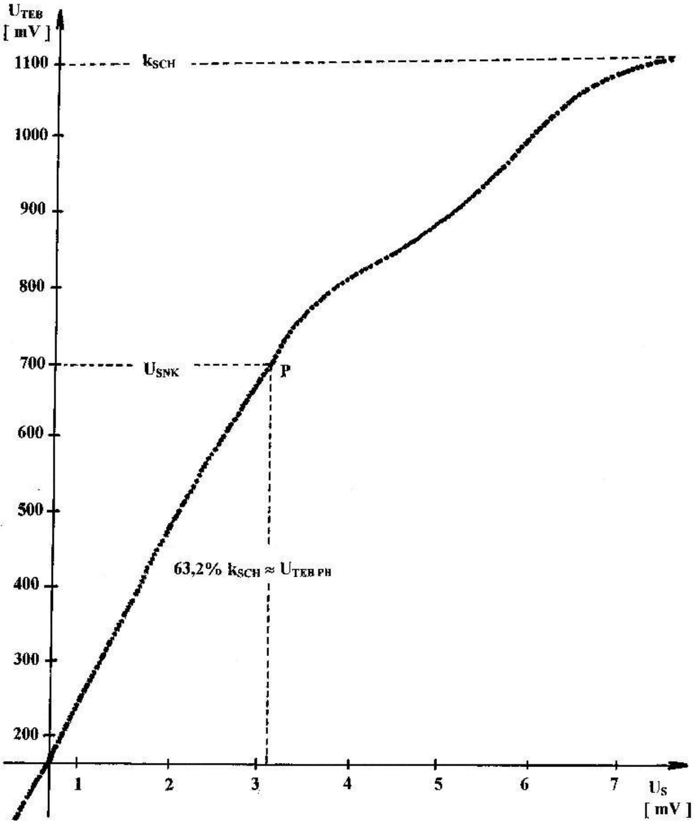

Fig. 1. Dependence of thermoelectric cell voltage U_{TEB} on its Seebeck voltage U_S
Rys. 1. Zależność napięcia termoelektrycznego U_{TEB} komórek od napięcia Seebeck'a U_S

Notes to Fig. 1:

1. Static characteristic constant k_{SCH}
    1.1 can be evaluated by reading from the trend curve, according to the line which makes the asymptote of the transition curve and determines the stagnation of development, namely $k_{SCH} \cong 1.1\text{V}$ (with reference to a detailed graphic course);
    1.2 can be evaluated by calculating the mathematical model, (i.e. according to the solution of differential equation of the 1st order), which is performed gradually by calculating all the taken measurements of points with experimentally obtained coordinates [U_S, U_{TEB}], followed by calculating the average value of all the results, namely $k_{SCH} \cong 1.0928$ V; (referring to the physical relationship of the corresponding mathematical formula).
    1.3 can be evaluated by a calculation according to the mathematical model, (i.e. according to the solution of differential equation of the 1st order), which means calculating the measurement of the working point P with experimentally obtained coordinates [U_S, U_{TEB}], namely $k_{SCH} \cong 1.1074\text{V}$(with reference to the detailed measurement tables).
2. Working point P and Seebeck voltage constant U_{SNK}
    U_{SNK} can be determined from the graphical dependence U_{TEB} (U_S) with comparable values of T_S, using working point P. This working point can be found as a point with the y-coordinate corresponding to 63.2 % of k_{SCH} value, namely $U_{TEBP} \cong 0.700$ V, while its x-coordinate is just the searched value U_{SNK}, namely $U_{SNK} \cong 0.0031$ V.

„Rougher" description of dependence $U_{TEB}(U_S)$, convenient for relatively lower mean temperature values T_S (i.e. up to working point P, see fig. 1), can be characterised using a linear equation of the 1st order:

$$U_{SNK} \cdot \frac{dU_{TEB}}{dU_S} + U_{TEB} = k_{SCH} \tag{3}$$

Solution (3) is represented by a „trend curve"

$$U_{TEB} = k_{SCH} \cdot \left(1 - e^{-\frac{U_S}{U_{SNK}}} \right) \tag{4}$$

„Softer“ description of dependence $U_{TEB}(U_S)$, convenient for relatively higher mean temperature values T_S (above working point P, see fig. 1), can be characterised using a linear equation of the 2nd order:

$$n \cdot \frac{d^2 U_{TEB}}{dU_S^2} + U_{SNK} \cdot \frac{dU_{TEB}}{dU_S} + U_{TEB} = k_{SCH} \tag{5}$$

With regard to the issue of the non-linear behaviour of the studied dependence U_{TEB} (U_S) in the "inflection point" area and the issue of the influence of thermal inertia and a higher thermal heating of semiconductor material of the thermoelectric cell, it is necessary to implement a more accurate approximation. Seebeck coefficient of thermoelectric voltage, specific electrical conductivity and specific C-value are slightly temperature dependent, especially in a wider temperature range, owing to (1) the Z parameter is slightly temperature dependent as well. In more accurate terms of the studied dependence U_{TEB} (U_S), there is also the “unknown” coefficient n, in addition to the above-mentioned physical quantities. This coefficient must be specified using solution (5) so as to achieve other relevant contexts. Solution (5) is represented by "oscillations"

$$U_{TEB} = k_{SCH} \pm \sqrt{\frac{n^2 \cdot U_{SNK}^2 \cdot k_{SCH}^2}{4n - U_{SNK}^2} + k_{SCH}^2 \cdot n^2} \cdot e^{-\frac{U_{SNK} . U_S}{2n}} \cdot S \tag{6}$$

where coefficient $S = \sin\left(\frac{\sqrt{4n - U_{SNK}^2}}{2n} \cdot U_S + arctg \frac{\sqrt{4n - U_{SNK}^2}}{U_{SNK}} \right)$.

If we use the experimentally acquired data in this solution (according to Table 1), i.e. the mutually corresponding values U_{TEB}, U_S and, following the previous steps of the described procedure, the numerical values of the established constants k_{SCH}, U_{SNK}, we are going to find out that the sought coefficient n of the studied linear differential equation of the 2nd order is not constant, but varies linearly, surprisingly accurately, depending on the pre-established variables k_{SCH} and U_{TEB}

$$n = -\frac{1}{k_{SCH}} \cdot U_{TEB} + 1 \tag{7}$$

Table1. Presentation of the selected measurement results of $U_{TEB}(T_S)$, $U_S(T_S)$, calculations of k_{SCH} values according to the model (solution of a differential equation of the 1st order), and calculation of the n coefficient values according to the model (solution of a differential equation of the 2nd order)

Tabela 1. Prezentacja wybranych wyników pomiarów $U_{TEB}(T_S)$, $U_S(T_S)$, obliczenia wartości k_{SCH} według modelu (rozwiązanie równania różniczkowego 1. rzędu) oraz wyliczenie współczynnika n wartości zgodnie z modelem (rozwiązanie równania różniczkowego 2. rzędu)

Measurement	T_S [°C; K]	U_{TEB} [V]	U_S [V]	k_{SCH}	n
1	24.50; 297.5	0.200000	0.000900	0.793721	0.818182
2	27.50; 300.5	0.355000	0.001500	0.925426	0.677273
3	30.50; 303.5	0.480000	0.002000	1.009629	0.563638
4	36.00; 309.0	0.700000	0.003100	1.107384	0.363641
5	40.50; 313.5	0.810000	0.003900	1.131607	0.263643
6	45.50; 318.5	0.880000	0.004800	1.117589	0.200010
7	51.50; 324.5	1.010000	0.006000	1.180395	0.081836

For $U_{TEB} = 0$ V, $n = 1$. For limit voltage $U_{TEB} = k_{SCH}$, $n = 0$. It can be assumed that after detailed measurement of the voltage interval around the working point P, we can realistically predict further voltage flow of the thermoelectric cell, without the necessity to expose it to heat load up to its maximum allowable voltage. It is a practical need, in particular with regard to the sensitivity of semiconductor materials to long-term and excessive thermal stresses.

4. Results and discussions

The transfer of the measured data from a spreadsheet processor into a graph was followed by an analysis and interpretation of the results:

1. study and work description of the voltage dependencies, i.e.:
   - introduction of the limit voltage UTEB as a maximum voltage to which the voltage of the thermoelectric cell can grow in real terms, i.e. k_{SCH} static characteristics constant,

   - introduction of the so-called working point P of the flow, the x-value U_S of which corresponds to the Seebeck voltage constant (i.e. U_{SNK}) and the y-value U_{TEB} of which is, in line with the theory, equal to 63.2% of k_{SCH} value (i.e. U_{TEBP}) of thermoelectric cell voltage in working point P,
2. estimate of the voltage dependencies course and its mathematical description using a differential equation,
3. solution of the established differential equation,
4. reverse verification check, whether the measured data really correspond with the proposed model of the given differential equation solution.

5. Conclusion

The paper deals with the method of determining the material efficiency ε_Z (equal to material parameter Z) of thermoelectric cells, in order to determine the thermoelectric cell efficiency. In principle, it is focused on determining the functional dependence U_{TEB} (U_S), i.e. the U_{TEB} voltage of thermoelectric cell heated by the flowing current to voltage U_S of the same thermoelectric cell heated by an external heat source, at comparable mean temperatures T_S of the thermoelectric cell. The voltage flow U_{TEB} (U_S) is interpreted as a presented graph, whose development corresponds to two solutions of the linear differential equations. The material efficiency ε_Z of the thermoelectric cell can be achieved on the basis of comparison of both functional dependencies $U_{TEB}(T_S)$ and $U_S(T_S)$ in such a way, that the ratio of both given voltages is applied in the corresponding mean temperature T_S. Especially semiconductor materials are sensitive to excessive heat load. The benefits of the proposed method are the simplicity of its design, material and technical availability, non-destructive measurements and sufficiently accurate determination of the eventual actual thermoelectric cell amortization. Increasing this efficiency (through material research and design innovations) represents a key follow-up objective of the study of the thermoelectric cell properties.

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Nowe nieinwazyjne metody alternatywnego określania wydajności komórek termoelektrycznych

Streszczenie

Celem pracy jest badanie współczesnych alternatywnych źródeł energii, tj. komórek termoelektrycznych. Sprawność ogniw termoelektrycznych podczas bezpośredniej zamiany ciepła odpadowego na energię elektryczną jest zazwyczaj oceniana za pomocą komórek termoelektrycznych uwzględniając temperaturę ściany, różnicę temperatur pomiędzy ścianami termoelektrycznych komórkowych i parametru materiałowego *Z*. W artykule przedstawiono alternatywną nieinwazyjną metodę określania efektywności ogniwa termoelektrycznego za pomocą oceny wyników porównawczych pomiarów elektrycznych.