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## ON THE DISCOVERY OF THERMOELECTRICITY BY VOLTA

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*The results of historical research proving the discovery of thermoelectricity by Volta are given. Physical conditions for observation by Volta of the origination of thermoelectric effect are described. The observations by Volta are confirmed by reproduction of his experiments.*

### Introduction

It is common knowledge that thermoelectricity today has become an important line of scientific and technical progress essentially responsible for success in such vital domains of mankind development as space and military technique, electronics, radio engineering, fiber optic communication, computer technique, infrared technique, metrology, medicine, household equipment, etc.

Impressive is progress of thermoelectricity in outer space. For instance, the universally known fantastic achievement in the exploration of far planets of solar system realized by "Voyager" spacecrafts would not be possible without thermoelectricity. Two thermogenerators of amazing reliability and long service life powered these spacecrafts for more than 20 years, having completely afforded the research programs scheduled.

Similar unique examples when thermoelectric products have no alternative are numerous.

At the present time space technologies are coming back to the Earth. They gain widespread acceptance for creation of equipment improving the comfort and quality of human life. It is beyond question that the efficiency of thermoelectric power conversion will be steadily increasing, hence the fields of application of thermoelectricity will expand, too.

Due to the unquestionable progress in thermoelectricity it becomes more and more interesting to clarify what scientific discoveries formed the basis for this line and who was the pioneer in thermoelectricity?

### 1. The role of Seebeck in the discovery of thermoelectricity

It is generally recognized that thermoelectricity dates back to discovery of thermoelectromotive forces by Seebeck in 1821. Therefore, at present this effect bears his name. It has been also universally accepted that the onset of thermoelectricity is related to the name of Seebeck.

However, with a more detailed insight into the history of discovery of thermoelectricity a peculiar picture is beginning to emerge.

It was established that, in fact, German scientist Seebeck studied magnetic field of the Earth. Seebeck's experiments consisted in the following. He used two heterogeneous materials shaped as wire or rods of bismuth or antimony and copper, brought them into contact and heated on one side (Fig. 1).

As a result, he observed the origination of magnetic field that was registered by the deviation of magnetic needle. From this experiment Seebeck concluded that "temperature difference at contact

points of metal circuit is the source of releasing magnetism, the reason for magnetic actions" [1].

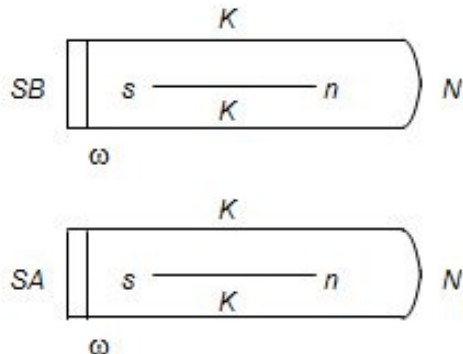


Fig.1. Scheme of Seebeck's experiments [1].  
A – antimonide plate; B – bismuth plate;  
K – copper wire; sn – magnetic needle; w – heat

In the process, the value and direction of action on magnetic needle depended on the degree of heating and the material of which the circuit under study was made. Seebeck called this effect thermomagnetism. Seebeck believed that this phenomenon provides the best explanation for the origination of the Earth: he related magnetic properties of the Earth to the effect of temperature difference between the poles and the equator in different parts of the Earth's crust.

A report on the Seebeck's research was published as late as 1825 in the proceedings of Berlin Academy of Sciences [1]. However, physicists from many countries were familiarized with the new effect as far back as 1823 from the brief communication by

Oersted [2]. Besides, in the same year, Oersted at the meeting of French Academy of Sciences devoted to the results of investigations he performed jointly with Fourier delivered a report published later in scientific collection [3], beginning with the words: "I have the honour to demonstrate to the Assembly wonderful experiments owing to which Seebeck proved that electric current can be generated in the circuit formed solely by solid conductors, with violation of temperature equilibrium only". Oersted showed that the effect discovered by Seebeck is of electric, not magnetic nature, and lies in the origination of electric current in closed circuit of heterogeneous conducting materials when contact points have different temperatures. Hence followed another, more precise name of this effect proposed by Oersted — "thermoelectricity", that became firmly established in physics [4, 5].

Thus, it can be asserted that discovery of thermoelectricity on the basis of Seebeck's experiments can be assigned to Oersted who gave correct explanation of these experiments, rather than to Seebeck himself.

Therefore, it becomes particularly interesting who in fact is the pioneer in thermoelectricity; Seebeck or Oersted?

However, history of science gives quite unexpected answer to this question — thermoelectricity was discovered by Italian scientist Alessandro Volta.

## 2. Activity of Alessandro Volta in physics and electricity

Alessandro Volta was born on 18.02.1745 in a little town of Como in the North of Italy. Material well-being of the family allowed his parents to give him good education. Teaching of A. Volta was entrusted to Elizabeth Pedralio di Brunito. Her husband who was a skilled craftsman of physical devices, especially measuring instruments, aroused in the boy's soul a love for physics – the domain that later became dear to him [6].

The second half of XVIII century was characterized by enhanced interest of scientific circles and the general public in electricity. It was the time when the first electrostatic machines were

constructed, Leyden jar and other electric devices were invented.

Volta did not pass by these events either. At the age of 18 he came to conclusion that some electrical phenomena are attributable to Newton's law of universal gravitation. Volta wrote of his ideas to known at that time French scientist abbot Jean Antoin Nollais and received an approving answer. Inspired by this support and recognition, Volta developed further his research on electricity. In particular, he found a new way for electric charge excitation using the phenomenon of electrostatic induction.

Beside electricity, A. Volta, professor of experimental physics in Como, member of Zurich physical organization, professor of physics in Pavia, was engaged in research on chemistry and physiology. He also contributed to the study of atmospheric electricity [6].

Volta invented electrophorus, sensitive electroscope, eudiometer; discovered contact electromotive forces between two metals, as well as between metal and electrolyte. He established electromotive series for metals, introduced a concept of electron and ion conductors. Volta expressed the ideas of conservation of energy, studied electrophysiological effects in organs and tissues of human and animal, and, what is most important, he created a pile called after his name Voltaic pile the first source of direct electric current.

Alessandro Volta entered the history of science as a famous physicist and physiologist, a pioneer of genius in electric current investigation. It is common knowledge that the unit of electrical voltage ~ one Volt- was called after his name.

### 3. Discovery of thermoelectricity by Alessandro Volta

However, little is known to scientific community that the name of Alessandro Volta is also related to discovery of thermoelectricity.

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

In his book "Geschichte der Physik" M. Laue [7] indicated that in the early periods of physics development scientists used to declare and describe their discoveries either in the books or letters to other scientists. Such was the case with Volta's experiments that resulted in the discovery of thermoelectricity.

In 1794 — 1795 A. 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» [8].

In the first of these three letters Volta describes the following experiment:

«So, having bent an arc from 3 thick iron wire (Fig. 2), coarse and flexible, and having immersed its both ends into two glasses with water where carefully as-prepared frog was placed in such a way that its hind legs were in one glass, and its V back or spine (if spine alone was left) in the other glass, I managed to make it contract and jump.

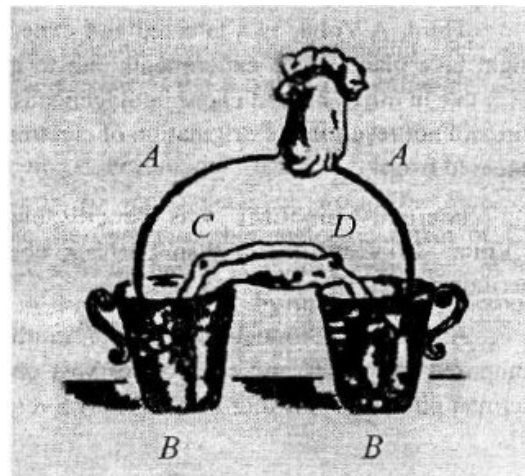


Fig .2. Scheme of Volta's experiment that resulted in the discovery of thermoelectricity.  
A –metal (iron) arc, B –glasses with water,  
C and D – frog parts placed in glasses with water.

And, indeed, I succeeded to achieve it only several times, i.e. twice, three or four times, and after a lapse of several minutes I could not do it anymore. I must also say that some of the various iron arcs that I used produced no effect from the very beginning. The same happened with some silver and brass arcs that I found to be ineffective at each attempt. Thus, there are all grounds to think that experiments with these unfit arcs failed because at their both ends they were absolutely equal in hardening and in every particular, hence identical, which was not the case with the others. So, here we seem to observe a rare phenomenon, i.e. genuine total similarity in every respect. *And so, having tried many arcs and found one of them — of iron, that was ineffective from the very beginning, and in other cases waiting for the frog to become weak and non longer immune to that of the other arcs that were able to affect it from the very beginning (which happened fairly soon), I immersed for a mere 30 seconds the end of such arc into boiling water, removed it and allowing no time for it to cool down, resumed the experiment with two glasses of cold water. It was then that the frog in the water started contracting, and it happened even two, three, four times on repeating the experiment till one end of the iron previously immersed into hot water did not cool down due to such more or less durable re-immersions or due to rather long stay in the air, and the arc again became totally incapable of causing the animal convulsions».*

The analysis of the description of this experiment makes possible the following important conclusions.

First, A. Volta carried out purposeful experiments, with a view to discover thermoelectromotive forces arising under the influence of temperature difference. Therein lies the difference between the experiments carried out by A. Volta and Seebeck who denied the electrical nature of thermomagnetic effect he discovered.

Second, the origination of thermoelectromotive forces was discovered by A. Volta directly, in contrast to Seebeck who observed magnetic action of thermoelectric current excited by thermoelectromotive forces in closed circuit.

Third, A. Volta, as a talented and experienced experimenter, first excluded the distortions that might take place in his experiments due to galvanic EMF caused by heterogeneity of metal wires. With this in mind, he first chose homogeneous arcs that in the absence of temperature difference in the wire did not result in the origination of electromotive forces even in such a primitive EMF indicator as prepared frog.

Fourth, thermoEMF was directly observed by A. Volta 27 years earlier than Seebeck observed the thermomagnetic effect.

A similar thermoelectric effect in the circuits composed by metals and electrolytes was observed by German physicists I. Ritter (1798) and I. Sveiger (1810) [9].

Thus, the experiments performed and their analysis allow unambiguous assertion that origination of electromotive forces under the influence of temperature difference was first observed by Volta well before Seebeck and the priority of pioneer in thermoelectricity belongs precisely to Volta (Fig. 3). Moreover, we know the date and time of description of thermoelectric effect by Volta in his first letter to abbot Vassali ~ February 10, 1794, that can be taken as the date of discovery of

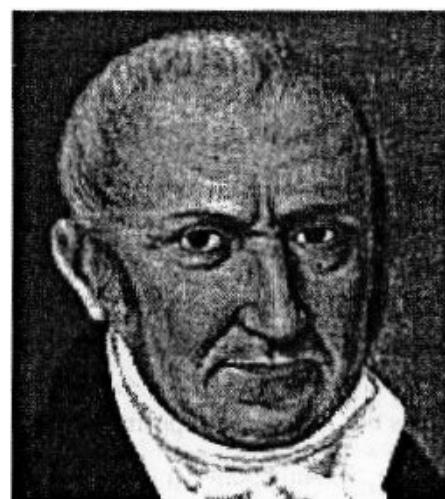


Fig. 3. Pioneer in thermoelectricity – Alessandro Volta

thermoelectricity.

In 2003, at Thermoelectric Department of Chernivtsi National University, Kushnir R.I. who made her diploma paper "Research on the Discovery of Thermoelectricity by Volta» [10] based on the above descriptions by Volta reproduced his experiments for the observation of thermoelectromotive forces (Fig. 4). The experiments reproduced to the maximum the conditions described by Volta. Naturally, instead of a frog, a high—sensitive digital voltmeter with resolution  $10^{-7}\text{V}$  was used. Thermoelectromotive forces with characteristics that coincided with the descriptions by Volta were observed.

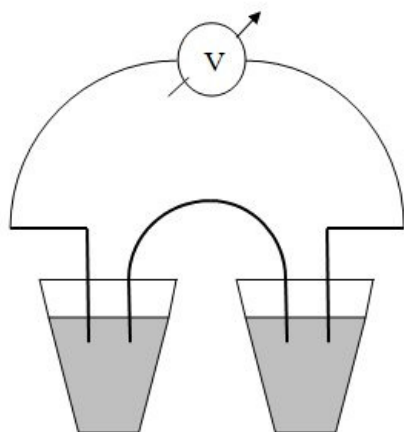


Fig. 4. Reproduction of Volta's experiment in diploma paper by R. Kushnir [10].

Volta's priority in the discovery of thermoelectricity was also marked in 1950 by Mario Gliozzi in his book "Storia del Pensiero Fisico" [5]. Discovery of thermoelectricity by Volta was also emphasized in [11].

The fact of discovery of thermoelectricity by Volta was also described in the book by A.A. Buryak and N.B. Karpova "Essays of Thermoelectricity Development", 1988 [12].

In 1992 the newsletter «Thermoelectric News», No.2 of Inter—Republic Research Society of Thermoelectricians published the paper [14] «Seebeck or Volta?», where the attention was also drawn to the priority of Alessandro Volta in the discovery of thermoelectricity. In 1994 the paper of the same title was published in "Journal of Thermoelectricity" on the occasion of two hundredth anniversary of discovery of thermoelectricity by Volta [14].

Thus, a combination of the foregoing facts gives sufficient grounds to recognize that the history of thermoelectricity dates back to experiments carried out by Volta.

The present paper was reported to XI International Forum on Thermoelectricity that gave grounds to the International Thermoelectric Academy to recommend to world thermoelectric community to recognize Italian scientist Volta as the discoverer of thermoelectric effect of EMF generation under the influence of temperature difference, as well as to apply to government of Italy with a proposal to immortalize Volta as the pioneer in thermoelectricity by installing the memorial plaque in his homeland.

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\* Interrepublic Research Society of Thermoelectricians was created in 1993 and liquidated due to foundation of International Thermoelectric Academy.