Historical Corner Column

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Foreword

This issue presents a paper by Antonio Savini, Emeritus Professor at the University of Pavia, Italy, and Chair of the History activity Committee of the IEEE Italy Section. The paper originated at the time that was getting close to the anniversary of the discovery of thermoelectricity, credited to Thomas Johan Seebeck, Estonian scientist, in 1821. What is less widely known is that such credit is incorrect, since it has been recently proven that thermoelectricity was indeed first observed and reported by Alessandro Volta in 1787 [1] (based on previous investigations in Italian, dating to 2005). In this paper, Antonio Savini makes this point for the benefit of our wide community.

Reference

1. L. Anatychuk, J. Stockholm, G. Pastorino, "On the Discovery of Thermoelectricity by A. Volta," Proc. of the 8th European Conference on Thermoelectrics, Como, Italy, 2010, pp. 15-18.

The Early Experiments of Alessandro Volta and the Seebeck Effect

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Abstract

The early history of thermoelectricity is briefly reviewed, starting from the pioneering observations made by Alessandro Volta up to the work of Thomas J. Seebeck, to whom the effect of electric current generated by the difference of temperature in a metal chain is attributed.

1. Pioneering Observations Made by Alessandro Volta on Thermoelectricity

Stimulated by the booklet "De Viribus electricitatis in motu muscolari commentarius" by L. Galvani (1791), presented to him by B. Carminati, Professor of Anatomy at the University of Pavia, in 1792 Alessandro Volta started

Figure 1a. Luigi Galvani [Bologna, Italy, September 9, 1737 – Bologna, Italy, December 4, 1798].

Figure 1b. Alessandro Volta [Como, Italy, February 18, 1745 – Como, Italy, March 5, 1827].

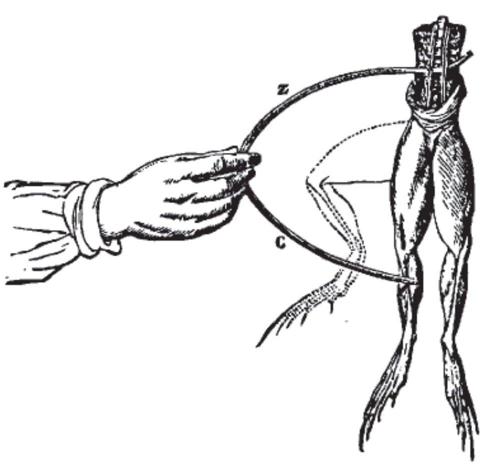

Figure 1c. Frog's legs used as a galvanoscope by both Galvani and Volta.

to investigate the so-called "animal electricity" using metallic arcs and frogs (Figure 1). He gradually came to the realization that the source of electricity was not in frogs (animal electricity) but in metals (metallic electricity), whereas frogs were merely "animal electrometers." He described his studies in many papers, and finally in a letter addressed to Anton Mario Vassalli, Professor at the University of Torino, on February 10, 1794 (Nuova Memoria sull'elettricità animale del Sig. Don Alessandro Volta) [1]:

> "Che pensa Ella della pretesa Elettricità Animale? Per me sono convinto da un pezzo che tutta l'azione procede originariamente dai metalli combacianti un corpo umido qualunque, o l'acqua stessa; in virtù del quale combaciamento viene spinto avanti il fluido elettrico in esso corpo umido od acqua dai metalli medesimi, da quale più da quale meno (più di tutti dal Zinco, meno quasi di tutti dall'Argento); onde indotta una comunicazione non interrotta di acconci conduttori è tratto esso fluido in un continuo giro...."

> "What do You think of the supposed Animal Electricity? I have been long convinced that all action is originated by metals in contact with any wet body or water itself; thanks to this contact the electric fluid is pushed forward to the wet body or water by metals themselves, more by some of them, less by others (more than others by Zinc, less than almost all others by Silver); then, having established a non-interrupted contact of suitable conductors, such a fluid is induced to a continuous circulation...." (translation from the original Italian)

As a result of a number of experiments using various material with differences at their ends (internal structure, thermal treatment, heat), in the same letter he described, as a side effect observed, what we can define as the first experiment of thermoelectricity:

"...Fatto dunque un arco di un grosso filo di ferro, crudo ed elastico, provava se intingendo i suoi due capi ne' due bicchieri d'acqua in cui pescava una rana puntualmente e di fresco preparata,...mi riuscisse di farla convellere e saltare....

...Or dunque trovato, con saggiarne molti, uno di tali archi di ferro, che non facesse nulla neppur da principio, ed altre volte aspettato che fosse indebolita la rana, e resa non più eccitabile da uno di quegli altri valevoli sulle prime a commuoverla (il che succede ben presto), tuffava nell'acqua bollente un capo di tal arco per qualche mezzo minuto, indi trattato fuori e senza dargli tempo di raffreddarsi, ritornava all'esperienza sopra i due bicchieri di acqua fresca: ed ecco che la rana a bagno si convelleva; e ciò anche due, tre, quattro volte ripetendo la prova; finché raffreddata per tali immersioni più o meno durevoli e ripetute...ritornava codesto arco inetto del tutto ad eccitare le convulsioni dell'animale...."

"…So, taken an arc of a thick iron wire, coarse and flexible, I tried to put its two ends into two glasses of water where two parts of a frog recently and conveniently prepared were immersed in order to observe contractions and jumping of the frog….

…After many e trials I took one of such iron arcs that had not reacted since the beginning and in other time after waiting that the frog became weak and no more sensitive to other arcs that first had been able to affect it (which soon happened), I immersed one end of the arc into boiling water for some half a minute then after removing it from there without letting it to cool down, I repeated the experiment with the two glasses of cold water; suddenly the frog started contracting; this happened two, three, four times until the arc, returned cold after repeated immersions, became unable of

Figure 2a. Johan Wilhelm Ritter [Samitz, Poland, December 16, 1776 – Munich, Germany, January 23, 1810].

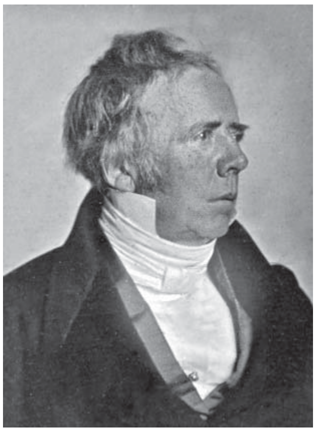

Figure 2b. Hans Christian Oersted (Rudkoebing, Denmark, August 4, 1777 – Copenhagen, Denmark, March 9, 1851).

Figure 2c. Thomas Johann Seebeck [Tallinn, Estonia, April 9, 1770 – Berlin, Germany, December 10, 1831]

exciting the animal's contractions…" (translation from the original Italian)

As Volta himself pointed out, the thermoelectric effect can be observed in an arc made of a single metal provided the material has some inhomogeneities between the ends. The effect is more pronounced if one uses a bimetallic arc.

It can be remarked that Volta just detected the phenomenon by rough instruments (frog, his own tongue), and did not perform detailed measurements of the phenomenon.

In all his investigations, Alessandro Volta was guided by the feeling that metals are motors of electricity. Throughout all the 1780s, he made experiments with conductors of different species, being convinced that an electromotive force (tension) originated from the contact of different conductors. Eventually in 1800, he communicated the invention of the artificial electric organ (the electric battery or pile): for the first time, a generator of continuous flux of electric charges was available.

Soon after the invention, scientists everywhere started to build and use batteries in order to investigate the effects of electric current. Johann W. Ritter, a German physicist, was among them. In 1801, he too observed thermoelectric currents (Figure 2).

2. Seebeck's Experiments

In 1820, Hans C. Oersted (Figure 2), when lecturing in electricity and magnetism at the University of Copenhagen, demonstrated the magnetic effect of electric current: a current flowing in a wire was able to deviate a magnetic needle placed nearby.

Attracted by Oersted's discovery, Thomas Johann Seebeck (Figure 2), an Estonian scientist and a member of the Berlin Academy, when studying magnetism on Earth, performed various experiments. In one of these, he connected two pieces of different metals in a circuit with a winding, over which he placed a magnetic needle. After heating one of the metals, he observed the deflection of the magnetic needle [2]:

12. Eine Wismuthscheibe wurde mit den beiden Enden einer Kupferspirale in Beruhnung gebracht, unter die geschlossen Kette eine Kalte unt auf dieselbe eine uber Lampe erwarmte Kupferscheibe gelegt. Es erfolge sopleich einer Declination, und dazu eine viel lebhaftere als bei den fruheren Versuchen. Die Magnetnodel innerhalb der Spirale machte eine Bewegung von 50° bis 60° und blieb bei 17° stehen,....

12. A bismuth disk was placed in contact with the ends of a copper winding and a copper disk was located under the closed chain; the copper disk was warmed over a lamp. A sudden deviation of the magnetic needle was observed, much more remarkable than the previous times. The needle within the winding rotated from 50° to 60° and remained at 17°....(translation from the original German)

In 1821, he reported this experiment to the Berlin Academy:

Aus meinen Untersuchungen uber den Magnetismus der galvanischen Ketten in den Abhandlungen der Konigl. Akademie von 1820-1821 S. 289-346 hatte sich ergeben, dafs die Intensitaet des Magnetismus dieser ketten in geradem Verhaltnifs zu der Energie der durch den feuchten Leiter begrundeten chemischen Action stehe,....

From my research on the magnetism of the galvanic chains in the Proceedings of the Royal Academy of 1820-1821 p. 289-346 it has been concluded that the intensity of magnetism of these chains is in direct relation with the energy of the wet conductor based on the chemical action....(translation from the original German)

Seebeck emphasized the connection between heat and magnetism, a sort of thermos-magnetism. Actually, now one knows that the difference of temperature of the two metals produces an electromotive force that is responsible for the circulation of electric current, and eventually for the deviation of the magnetic needle.

In 1823, Oested himself reported Seebeck's discovery, and proposed to call it "thermoelectricity" [3]:

M. Seebeck, member de l'Acadèmie de Berlin, a découvert q'on peut établir un circuit électrique dans le metaux sans l'interposition d'aucun liquid. On établit le courant dans le circuit en troblant l'èquilibre de temperature. L'appareil pour faire voir cette action est fort simple: on peut le composer de deux arcs de mètaux diffèrences, par exemple, de cuivre et de bismuth soudès ensemble aux deux bouts, en sort qu'ils fassent en tout un circle....

Pour étanblir le courant, on chauffe l'anneau à l'un des deux endroits ou se touchent le deux metaux....

On ne peut dècouvrir ces courans électiques que par l'auguille aimantèe, sur laquelle ils exercent une influence très sensible il foudra sans doute dèsormais distinguer cette nouvelle classe de circuit électiques par une dènomination significative, et comme telle je propose l'expression de «circuits thermo-électriques» ou peut-etre «thermélectriques»: en meme temps ou pourrait distinguer le circuit galvanique par le nom circuit hydro-électrique ...."

Mr. Seebeck, a member of the Berlin Academy, has discovered that an electrical circuit can be established in materials without the interposition of any liquid. We establish the current in the circuit by adjusting the temperature equilibrium. The device to show this action is very simple: it can be composed of two arcs of different metals, for example, copper and bismuth welded together at the two ends, so that they make a whole circle....

To generate the current, we heat the ring in one of the two places where the two metals touch....

We can only discover these electric currents by the magnetic needle, over which they exert a very sensitive influence. It will undoubtedly be clear from now on to distinguish this new class of electric circuits by a significant denomination, and as such I propose the expression of «thermo-electric circuits» or perhaps «thermelectrics»: at the same time one could distinguish the galvanic circuit by the «name hydro-electric circuit»....

The discovery of thermoelectricity is normally attributed to T. J. Seebeck, while the original and fundamental observation made by Alessandro Volta is forgotten. However, in recent times the International Thermoelectric Academy recognized Alessandro Volta as the early discoverer of the thermoelectric effect [4]. As evidence of this, in 2005 a memorial plaque was therefore dedicated in Como, the birth place of Alessandro Volta.

3. Conclusion

In 2021, we will celebrate the two-hundredth anniversary of Seebeck's discovery. In this respect, it is necessary to remark that after him, investigations on thermoelectricity have not stopped and, in particular, in 1834 Jean-Charles A. Peltier, a French scientist, described the reverse effect, i.e. the cooling of a junction as electric current flows through it.

Even in recent times, scientists and technologists are studying new materials, including nano-engineered materials, in order to check the possibility of generating small voltages thanks to small differences in temperature, and also in the microscopic world [5, 6]. Harnessing wasted heat in the inorganic as well in the organic world is the main purpose of these investigations in progress.

4. References

1. A. Volta, "Nuova memoria sull'elettricità animale 1794-95" in *Le Opere di Alessandro Volta*, ed. naz. Vol. I, Hoepli, Milano, 1918, pp. 168-220.

2. T. J. Seebeck, "Magnetische Polarisation der Metalle und Erze durch Temperature-Differenz" in *Abhandlungen der Koniglichen Akademie der Wissenshsften zu Berlin aus den Jahren* 1822-23, p. 265.

3. C. Oersted, "Nouvelles experiences de M. Seebeck sur les actions èlectromagnetiques, *Annales de Chimie et de Physique*, 2nd series, 1823, pp. 199-201.

4. L. Anatychuk, J. Stockhom, and G. Pastorino, "On the Discovery of Thermoelectricity by A. Volta," Proc. 8th European Conference on Thermoelectrics, Como, 2010, pp. 115-18.

5. K. Uchida et al., "Observation of the Spin Seebeck Effect," *Nature*, **455**, 2008, pp. 778-781.

6. H. Kojima et al., "Universality of the Giant Seebeck Effect in Organic Small Molecules," *J. Materials Chemistry Frontiers*, **7**, 2018, pp. 1276-1283.