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Theodor von Grotthuss' Contribution to Electrochemistry

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ABSTRACT

Freiherr Christian Johann Dietrich Theodor von Grotthuss (1785-1822) lived and worked in Lithuania. Inspired by Volta's pile he proposed the first theory of water electrolysis, which was published in 1805 in Rome. Michael Faraday acknowledged T. Grotthuss for this theory in his further investigations of electrolysis processes. Having studied in Germany and France Grotthuss brought science to province by establishing his laboratory in Gedučiai village in his mother's real estate. Lithuanian scientists are proud that life of Theodor von Grotthuss was related to this country. Many events to remember this prominent scientist are organised in Vilnius and other places. His works and example provided a good basis for further development of electrochemical science in Lithuania. Grotthuss insights into the mechanism of proton transport still are of great relevance to such areas of modern science as membrane biochemistry, energy conversion and storage.

Contents

1. Introduction

Science of electrochemistry started to develop at the end of the 18th and the beginning of 19th centuries. In 1791 Luigi Galvani (1737-1798) published his theory on electrical nature in muscular motion as an essay "De Viribus Electricitatis in Motu Musculari Commentarius (Commentary on the Effect of Electricity on Muscular Motion)", where he described the experimental results of almost 30 years of investigations [1]. One of the first significant breakthroughs in electrochemistry was the invention of the prototype of modern electrical batteries by Alessandro Volta (1745-1827) in 1799, which was called Volta's pile [2]. This discovery was inspired by the research of L. Galvani.

Later on, Sir Humphry Davy (1778-1829) of the Royal Institution in London was one of the most important experimenters with the new voltaic battery. He found out that the production of electricity by the voltaic pile depended on the chemical reactions, what Volta had not suspected. Davy used current supplied by the pile to separate compounds into their constituents, discovering several new elements. In 1806 he proposed an electrical theory of chemical affinity: since electrical current overcame the normal force that held elements together in compounds, he argued, this force must be electrical in nature [2]. Davy's student, Michael Faraday (1791-1867), studied the relationship between electricity and magnetism. In the course of his research he invented the first electric motor in 1821 and the first dynamo in 1831. His two fundamental laws of electrochemistry, published in 1834, predict how much product results from passing a certain amount of current through a chemical

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compound or its solution, a process that he named "electrolysis." [2].

Although Faraday was the first to introduce the term "electrolysis", the description of the phenomenon and the first theory was proposed by Theodor Grotthuss (1785-1822). He gave Volta's pile a particular importance in his further investigations of the new invention. For Grotthuss it was not just a generator of galvanic phenomena, not well understood up till that time, but also a model of a real "electropolar" system that existed in nature and that manifested itself through this newly created artefact. He published his theory in 1805 (more detailed version in 1806) in the memoir entitled "Sur la décomposition de l'eau et des corps qu'elle tient en dissolution à l'aide de l'électricité galvanique" (Theory of decomposition of liquids by electrical currents) [3]. The present paper discusses the contribution this German scientist made to development of electrochemistry. His ideas could have been worthy of a Nobel Prize if such had existed at that time.

1.1. Brief biographical sketch

Freiherr Christian Johann Dietrich Theodor von Grotthuss (Fig. 1) was born on January 20, 1785 in Leipzig (Germany) in the aristocratic family of Kurlandian (Latvia) landlord. Theodor dedicated his life to science and chose a solitary lifestyle. Except for five years (1803–1808) devoted to studies and research in Western Europe (Leipzig, Naples, Rome, Paris) and some time in St. Petersburg in 1812, he spent the rest of his life at his mother's estate in Gedučiai (Geddutz) village, Lithuania [4]. At the time Grotthuss studied in Europe, chemistry became the most popular subject at the Vilnius University, the main institution of higher education in Lithuania. Prominent scholar Jedrzei Sniadecki (1768–1838) worked as a professor of chemistry at the Vilnius University. It is unfortunate, however, that such a talented student as Theodor Grotthuss did not study in this prestigious Lithuanian school.

Fig. 1. Theodor von Grotthuss (portrait by unknown artist, Bauska museum, Latvia). Zeitgenössische Abbildung.

Fig. 2. House where Theodor von Grotthuss was living in his mother's real estate in Gedučiai, Lithuania. Most probably, the laboratory was set up here.

In Paris, T. Grotthuss attended lectures of famous scientists and so he learned about Volta's pile. Joseph Louis Gay-Lussac (1778-1850) introduced Theodor von Grotthuss to experimental science [5]. After his studies abroad, T. Grotthuss returned home in 1808 to continue his scientific work. He built a home laboratory where he carried out chemical and physical experiments. It is supposed that the laboratory was located in the building shown in the photo in Fig. 2. The same year T. Grotthuss was elected as a corresponding member of the Academy of Sciences and Arts of Turin. In 1811, the last time he was known to leave home, Theodor Grotthuss left for Russia for half a year where he stayed in St. Petersburg [4]. Despite his eager correspondence with the scientific community to take a position of Professor at the University of Dorpat (Tartu), his candidature was not accepted. The reason of the rejection was most probably related to the fact, that he had studied abroad ignoring the prohibition by Russian Empire, which considered that studies abroad can "contaminate" people with ideas of revolution [6,7]. In 1814, he was elected a corresponding member of the Munich Academy of Sciences. Some time later, he also became a member of Kurland Literature and Art Society [4,6].

In March 1822, at the age of 37 Grotthuss committed suicide as a consequence of depression caused by health problems [8].

2. Grotthuss' contribution to development of electrochemical science

2.1. Grotthuss' theory of electrolysis

The article published by T. von Grotthuss in 1805 in Rome consisted of two chapters: the first one described effects of "galvanic electricity", whereas the second was on water decomposition by "galvanic electricity". The drawings in the paper were made by hand of Grotthuss himself [5] (the example is given in Fig. 3). T. Grotthuss studies on the electrical decomposition of water gave a specific importance to Volta's pile. According to his explanation, which is known as the first theory of electrolysis today, nature's foundation is based on electrical type polar opposites, what he called the elementary molecules [9]. Grotthuss proposed in his theory that the process of water decomposition and the transfer of "action" occur along the lines or chains that are formed by molecules (Fig. 3). Since these molecules are carriers of both kinds of "electricity", they are polarized accordingly between the opposite electrodes of the battery. In the place where the molecular chain touches the electrodes, the water molecules split separating themselves into parts. Hydrogen appears at the negative electrode, while oxygen is