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# Electrochemical discharges—Discovery and early applications

Rolf Wüthrich [a,*,1], Philippe Mandin [b,1]

[a] Department of Mechanical and Industrial Engineering, Concordia University, 1455 de Maisonneuve Blvd. West, Montreal, Quebec, H3G 1M8, Canada
[b] Laboratoire d'Electrochimie et de Chimie Analytique, UMR CNRS 7575, ENSCP, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

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ABSTRACT

Electrochemical discharge phenomenon, as well known as plasma electrolysis, electrode effects or contact glow discharge electrolysis, was first described in literature more than 150 years ago. Today this effect is studied only in quite specialised applications. This was not always the case. During the 19th century and early 20th century, electrochemical discharges were intensively studied and a broad spectrum of applications, ranging from X-ray imaging to wireless telegraphy, was developed. This communication retraces this early history of electrochemical discharges by highlighting the interesting electrochemical effects and applications linked to them. The paper ends by shortly mentioning today's applications of electrochemical discharges which are in the field of micro-machining, surface engineering, nanotechnology and waste water treatment.



## 1. Introduction

Electrochemical discharges are known since more than 150 years. They are often termed in literature as anode or cathode effects depending on which electrode the phenomena takes place. Other used terminologies are electrode effects or plasma electrolysis. Experimentally, they are observed after the breakdown of electrolysis as the terminal voltage of an electrochemical cell is increased. The same behaviour is observed if the current is increased in a galvanostatic cell. While these effects appear as an unwanted behaviour in electrolysis (the famous anode effect in the Hall–Héroult process for example [1]), they are desired in contact glow discharge electrolysis (CGDE) [2], in micro-machining by spark assisted chemical engraving (SACE) [3] and surface treatment by plasma electrolysis [5].

Today, mainly the works of Kellogg [4] and Hickling and Ingram [6,7] (in the middle of last century) are known. But electrochemical discharges were used before in a large number of practical applications ranging from wireless telegraphy to medical imaging. Most of these applications are today more or less forgotten. The aim of the present contribution is to trace the early history of the discovery and first applications of electrochemical discharges. The paper will restrict this historical review to electrochemical discharges happening in an aqueous electrolyte. The authors hope as well to promote the knowledge about this phenomenon, which is still largely unknown, even in specialised research community.

## 2. Discovery

The first description of the electrochemical discharges can be attributed to the French physicists Hippolyte Fizeau (1819–1896) and Léon Foucault (1819–1868) [8]. The motivation of their research was to obtain more insights in the nature of light and the formation of light spectra, one of the great research objects of the 19th century. The interesting point is that at the end of their paper, where they compared spectra emitted by various light sources, the authors mentioned a light source obtained during electrolytic water decomposition with two thin platinum wires. This short note was the first description in literature of a phenomenon which is today called electrochemical discharges. Foucault and Fizeau were most probably not the first having observed electrochemical discharges. According to [9], this effect was described in experiments of water decomposition made with static electricity as early as in 1789. However, Foucault and Fizeau can be considered as the discoverer of electrochemical discharges as they were the first to associate them with electrical discharges.

The publication of Fizeau and Foucault will become an inspiration for the work of several researchers (mainly in France) on the subject, some of whose will be translated in German by the Annalen der Physik and in English by the Journal of the Franklin Institute. It was probably Sir William Robert Grove (1811–1896), the inventor of the fuel-cell, who promoted the phenomenon in

* Corresponding author.
*E-mail address:* wuthrich@encs.concordia.ca (R. Wüthrich).
[1] ISE member.

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the English scientific community [10]. With the avenue of more stable and powerful power sources, quantitative studies became possible as the one from Jules Violle (1841–1923) and Michel Chassagny (1865–1918) published in 1889 [11]. Let us follow their work.

The two French scientists used two thin platinum wires (1.6 mm and 4.5 mm in diameter) dipped into sulphuric acid. By applying a constant voltage between the wires, Violle and Chassagny decomposed water into hydrogen and oxygen. However, when they used a voltage higher than 32 V, they could observe a new effect: the thinner platinum wire became surrounded by a gas film in which discharges took place. Violle and Chassagny studied the influence of the geometry and electrode polarisation on the phenomenon and concluded that the electrochemical discharges take place only above a critical voltage. They noted as well that the gas film appeared always on the thinner of the two wires and observed that discharges are harder to obtain in case the thinner wire is an anode (more than 50 V are needed in this case). During their study, they were, as many other researchers, fascinated by the light emitted during the process.

A large number of communications reporting research works about this new phenomenon were published in the second half of the 19th century. Most studies related to the electrochemical discharges dealt with the observation of the spectrum of the emitted light and the heat produced by them. This is understandable if we recall that the middle of the 19th century was a time where significant research was done on the fundamental understanding of light and the formation of its spectra. But the physics behind the electrochemical discharges was questioned as well. It appeared since the very beginning that the observed light and the abrupt decrease in current have their origin in a gas film built around an electrode, which was termed the *active electrode* [12]. Studies of the emitted light spectra allowed concluding that the chemical composition of the gas must be a mixture of hydrogen with components from the electrolyte (such as sodium for example) and the electrode itself (like platinum or silver). The mechanism leading to the formation of the gas film was, however, much more debated. This intense discussion will lead to new discoveries.

In 1894, the French researcher E. Lagrange and P. Hoho made a series of studies about the gas film formation. They were probably the first to not only focus on the gas film but rather the various steps leading to its formation. Their observations can be summarised as follows. For low cell terminal voltages, water is decomposed in hydrogen and oxygen and the current increases proportionally to the voltage. Starting from a critical voltage, electrolysis becomes unstable. Very large bubbles are produced and the electrolyte seems to boil locally. The current is fluctuating and some lightening can be observed. Lagrange and Hoho called this phase the unstable period (*période instable* in French). For higher voltages, the phenomenon becomes more stable. Bright lightening can be observed. During their studies, Lagrange and Hoho described as well a practical application of the electrochemical discharges for welding and hardening of metals [12]. But a real breakthrough from the application point of view will come 5 years later.

The physicist Arthur Wehnelt (1871–1944), who came across the work of Lagrange and Hoho, repeated their experiments. The very regular noise produced when the active electrode was brought in the vicinity of a metal plate intrigued the German scientist. After several experiments, he was able to master the effect and to use it for a practical application in form of a high frequency current interrupter. In 1899 he published in the Annalen der Physik his paper "Ein elektrolytischer Stromunterbrecher" (An electrolytic interrupter) presenting a new device which will later be called the Wehnelt interrupter [13]. In 1905, Wehnelt will be awarded the John Scott Medal by the Franklin Institute for its invention [14].

## 3. The electrolytic current interrupter

### 3.1. Invention and main applications

The publication in 1899 by Wehnelt on his current-interrupter gave a new turn to the research about electrochemical discharges. For the first time a technological application was developed based on the electrochemical discharge phenomenon. The same year, Wehnelt's invention was commercialised by several companies (for example in Germany by Ferdinand Ernecke and Siemens & Halske [13] and in France by Armagnat-Carpentier [15]). The device, with a wide range of applications, became rapidly popular and widely used.

Wehnelt first conducted experiments using two dissimilar sized electrodes dipped into sulphuric acid. The smaller electrode (the active electrode) was a platinum wire, the larger one was made of lead. He rapidly identified the need to enclose the active electrode into a glass tube in order to have a well-defined geometry and avoid projection of the electrolyte during the experiment. In order to study in more details the discharge activity and to verify his idea that the phenomenon taking place on the active electrode is acting as an interrupter, Wehnelt used an external circuit consisting of a capacitor and an induction coil[2] (see Fig. 1). During his experiments, Wehnelt found that this apparatus (which he named electrolytic interrupter; *Elektrolytischer Unterbrecher* in German) can be used as a current interrupter. The frequency of interruption can be controlled by the external circuit, in particular by the inductance of the induction coil, resulting in high frequencies for low values of the inductance. The researcher showed that 1000–2000 interruptions per second can be achieved. Best results were obtained if the active electrode is polarised as anode. With these high interruption numbers, together with the induction coil, it became possible to produce high voltages from a low voltage source.

Wehnelt's current interrupter became very popular and a direct competitor to the Rühmkorff coil, a device that most of us still knows from physics lessons at secondary school. But compared to Rühmkorff's coil, Wehnelt's electrolytic interrupter could provide higher interruption numbers and worked in general more reliably. The applications were numerous and several patents were deposited during the beginning of last century. The device was used for the production of electrical arcs in connection with an induction coil with application in many fields, among others in the study of electrical conduction of gases. Another utilisation was as current rectifier, an application of electrochemical discharges which was actually first proposed, about 30 years earlier in France by Bouchotte [16] and Alexandre Edmond Becquerel (1820–1891) [17]. The current interrupter played as well a significant role in the development of wireless telegraphy because of its capability to generate high frequency interruptions, an application first suggested by Jacques-Arsène D'Arsonval (1851–1940) when he presented Wehnelt's device to the *Académie des Sciences* in Paris [18]. In 1903 the Canadian inventor Reginald Aubrey Fressenden (1866–1932) patented a wireless telegraphy receiver based on Wehnelt's device. Wehnelt's interrupter became as well a key component in early X-ray imaging devices. This application was of course connected to a large medical market. More and more companies started to build electrolytic interrupters (Fig. 2). Many laboratories all over the world did own such devices. In various discoveries in physics,

[2] The induction coil (or spark coil) was a device made of two concentric coils winded around a common iron core. The current was supplied to the primary coil with lower number of windings. The secondary coil, with large number of windings, was connected to two electrodes between which it was possible to have an electrical discharge. In today's language an induction coil would be called a high voltage transformer.