Research of oscillatory processes in electrolyte medium

D L Kirko
National Research Nuclear University MEPhI (MEPhI), 31 Kashirskoe shosse, Moscow, 115409, Russia

E-mail: dlkirko@mephi.ru

Abstract. This paper presents a study of the main characteristics of the discharge in electrolyte. It presents the current and voltage characteristics of the discharge. It includes the description of the most important parameters of the oscillatory discharges within the frequency range 1 kHz–140 MHz. It presents an investigation into the possibility of adding fine-grained powder to the electrolyte solution. It contains the description of the electro technical characteristics of these modes of the device. It also contains a study of the high-frequency oscillations in an electric circuit and a chart of the spectrum of such oscillations. Finally, it discusses the possible explanation for the occurrence of the discussed oscillatory processes.

1. Introduction
A discharge in an electrolyte causes light emission near the electrodes and convective fluid streams. Such discharges may be created directly in the fluid medium or above its surface [1, 2]. A piece of surface of electrolyte may function as one of the electrodes. The scope of such discharge application is connected with the ways of metal surface modification to possibly create ceramic-like finishes [3-6]. During the discharges, strong oscillations may be witnessed [6-8]. We have studied the effect of the electrolyte composition on the electro technical parameters of the discharges [8]. For the purpose of this study, we added fine-grained substances to electrolyte.

2. Electro technical characteristics of the discharge in electrolyte
Cylindrical chambers V=100-250 cm³ made of plexiglass we used to create a discharge (figure 1). During the tests, electrolyte created with the addition of the sodium carbonate (Na₂CO₃) or potassium hydroxide (KOH) was put in a chamber. For cathodes, we used tungsten or titanium rods (diameter 2–3 mm), for anodes we used stainless steel or molybdenum plates (thickness 0.2-0.5 mm). The discharge was powered using a biphasic rectifier (voltage 0-250 V, frequency 100 Hz). Right at the surface of the cathode there is the catholyte area of the discharge, which emits the most intense light. This area is surrounded by the middle plasma area, which is surrounded by the vapor and gas cover.

Let us investigate the trends of the discharge formation in electrolyte. For the experiments, the concentration of the sodium carbonate (Na₂CO₃) was within the range C=0.01-1 M or m=1.06-106 g per 10³ cm³ of distilled water. The experiments resulted in obtaining the current-voltage characteristics (CVC) of the discharge for various concentrations of the working medium. Let us see the CVC for the sodium carbonate at C=0.5 M (figure 2a). The initial part of the trend is mostly linear. In the point (1) the discharge is ignited and plasma appears. The most typical color of the discharge is yellow-red. The catholyte area (7) that surrounds the cathode is 1-2 mm. This area has the highest radiance capacity and temperature. Plasma temperature in this area had been already measured and was T=2800±200 K.
in the working mode of the discharge, at current \( I \approx 1.2 \) A. The catholyte area is surrounded by the middle plasma area (8), with dimensions 1.5-2.0 cm. Due to higher resistance the characteristic then shows a curve (part 1-2). Then the discharge builds up and the trend is again linear (part 2-3). This part of CVC is the main working range. At the part 3-4 the current gradually decreases and the discharge gradually fades (point 4).

![Experimental setup](image)

**Figure 1.** Experimental setup: 1 – enclosure, 2 – electrolyte, 3 – cathode, 4 – ceramic tube, 5 – anode, 6 – power source, 7 – near cathode area of the discharge, 8 – middle area, 9 – magnetic probe, 10 – spectrum analyzer.

![Current-voltage characteristic](image)

**Figure 2.** The current-voltage characteristic of the discharge is a) sodium carbonate (\( C = 0.5 \)), b) potassium hydroxide (\( C = 0.5 \)).

The shape of CVC is influenced by the concentration of the substance in the solution [8]. We also studied the connection between the ignition voltage and the substance concentration. The general trend is that the ignition voltage grows when the concentration is reduced. CVC for potassium hydroxide at \( C = 0.5 \) is shown at figure 2b. This connection dependence has its peculiar characteristics. The general CVC trend’s shape is similar to hysteresis.

### 3. Oscillatory processes of discharge in electrolyte

This part of the study was to compare the frequency dependencies of the oscillations with a discharge in electrolyte to similar dependencies with added crystalline powders in electrolyte. For this reason the
most typical parameters for the sodium carbonate working medium at $C=0.5$ concentration were
selected. Discharge current pulses are repeated at 100 Hz. An individual pulse is a damped sinusoid
with $\sim 1.1$ ms cycle, number of cycles $n=2-3$ (figure 3a). High frequency oscillations are seen in
the beginning of the first cycle of current. Electric oscillations were studied using magnetic probes and
Tektronix TDS 2024B oscilloscope. Measurements results were processed using the Origin program.
Magnetic probes were designed as small coils (diameter 2-3 mm, 50-180 loops in the coil, wire
diameter 0.1 mm), protected by enclosures from the electrolyte. Probes (9) were placed in the
electrolyte at different distance from the discharge, or were located outside the chamber (figure 1). Measurements allowed us to reveal the most intensive frequencies of the self-oscillations of the discharge current. During the experiments we have observed the following rather intensive oscillations at the listed frequencies: $(41\pm2)$ kHz, $(265\pm13)$ kHz, $(6.4\pm0.4)$ MHz, $(11.5\pm0.5)$ MHz, $(17.1\pm0.7)$ MHz, $(34\pm2)$ MHz, $(47\pm2)$ MHz. The spectrum of the high-frequency oscillations of the discharge is given in figure 3b.

![Figure 3](image)

**Figure 3.** Oscillatory processes of discharge: a) oscillogram of a separate discharge current pulse b) spectrum of the high-frequency oscillations of the discharge.

Let us see the most well-known plasma frequencies for the discharge in electrolyte. For a typical
value of the electron concentration in plasma $n_e=4.2\cdot10^{15}$ cm$^{-3}$ [8] the frequency of plasma is
$\omega_{pe}=\left(4\pi n_e e^2/m_e\right)^{1/2}=3.6\cdot10^{12}$ s$^{-1}$. Considering the field of current for the magnetic field value $B=200$ Gs the ion-cyclotron and the electron-cyclotron frequencies are, correspondingly: $\omega_{pi}=eB/m_i=1.92\cdot10^6$ s$^{-1}$ и $\omega_{pe}=eB/m_e=3.52\cdot10^9$ s$^{-1}$. Considering these frequency values, all the frequencies recorded in the experiments may correspond to the ion-cyclotron and the electron-cyclotron plasma waves [9].

4. **Investigation of the effect of adding crystalline powders in the electrolyte**

Taking into consideration the experiments for studying the discharge in electrolyte, it was valuable to study the possibility of adding various substances in the fluid and see how they affect the system parameters. In this regard, experiments for measuring the potentials on an electrolytic cell in the presence of fine-grained powders were of particular interest [11]. In this aspect, we conducted experiments, placing fine-grained powdered crystalline substances in the electrolyte. For the experiments we used a cylindrical aluminium vessel (1) (figure 4), volume (0.1-0.5)$\cdot10^3$ cm$^3$, diameter 40-80 mm, into which we placed the examined substance, the fine-grained powdered calcite CaCO$_3$ (grain size 2-10 $\mu$m). In order to create the necessary conditions, this calcite substance was impregnated with electrolyte prepared from the distilled water with added sodium containing substances (sodium carbonate Na$_2$CO$_3$, solution concentration $C=0.3-0.7$ M). A metal electrode rod (4) (copper, diameter 3-4 mm) was installed vertically in the vessel and was one of the electrodes, the
second one was the aluminium electrode. Electrode (4) was firmly fixed at a preset distance from the vessel bottom using a holder. Voltage and current were measured with a microvoltmeter (exactness $\Delta U=\pm 1 \mu V, \Delta I=\pm 0.1 \mu A$).

![Electrolytic cell diagram](image)

**Figure 4.** Electrolytic cell diagram: 1 – metal vessel, 2 – external vessel, 3 – studied substance, 4 – central electrode.

During the experiments, we registered negative potential on the aluminium vessel (1) (figure 4) and positive potential on the central copper electrode (4). Let us express the dependencies for the voltage and current in the system from the thickness of the calcite $h_1$ and the depth of the electrode immersion $h_2$ (figure 5).

![Graphs](image)

**Figure 5.** Electro technical measurements at the electrolytic cell: a) voltage dependence from the calcite layer thickness (electrode immersion depth: 1 – $h_2=5$ mm, 2 – $h_2=10$ mm, 3 – $h_2=15$ mm), b) current dependence from the load applied (calcite layer thickness is $h_1=30$ mm, electrode immersion depth: 1 – $h_2=5$ mm, 2 – $h_2=10$ mm, 3 – $h_2=15$ mm).

As for the dependence from the thickness of the substance layer in the vessel (figure 5a), we first saw growth, and then there was a tendency for saturation. This can possibly be connected with the higher volume of the substance used and the number of the current carriers in the process.

To measure the current running through the examined substance during the short circuit, an ammeter was connected directly to the electrolytic cell electrodes (figure 4). A typical current-time dependence includes an exponential decline with the time constant $t_o \approx 8.5$ s from the initial current value $I_o$ to the final current value $I_f$. All the current values specified thereon are the final ones.

Microammeter resistance is $R_A \approx 1.2 \Omega$. Considering resistance the low of the microammeter, the resistance of the substance at $h_1=20$ mm for the voltage and current, correspondingly, $U=1.1 \pm 0.1$ V и
The high-frequency components of the voltage on the electrolytic cell were measured as part of the experiments. For these frequency measurements we used Tektronix TDS 2024B oscilloscope. Measurements results were processed using the Origin program. Electrolytic oscillations in a wide range of frequencies were recorded: 1 kHz – 140 MHz. In the kilohertz range the electrical oscillations were expressed as separate weak peaks: 2.4±0.3 kHz, 31±4 kHz, 97±15 kHz. More intense oscillations were observed in the megahertz range with the frequencies: 1.5±2 MHz, 11±2 MHz, 120±15 MHz. Characteristic signals in this frequency range are shown in figure 6. A tendency for the formation of wave packets has appeared for group signals.

Let us examine the substance made of powdered calcite impregnated with electrolyte, prepared based on the sodium carbonate and distilled water. Powdered calcite in its initial state has a micron-sized irregular-shaped grain structure (2-10 μm grains). The space between the grains, which works as a sort of pores (size 1–5 μm), is filled with electrolyte with sodium ions. If there is no electrolyte in the cell, there is no voltage on the electrodes. Due to this the sodium ions are a kind of connecting element to this structure. Let us assume that there is electrical conductivity in this calcite and electrolyte medium.

Currently, the metamaterials with the new unique reflective properties in the optic and high-frequency electromagnetic emission ranges are a very popular field of development [12]. These properties are connected with analyzing the phenomena in the thin micron layer on the surface of a hard body. The law of dispersion for the superficial electromagnetic waves in the electrically conductive medium is expressed as [12]:

\[ k_s \approx \frac{\omega}{c}(1+0.5\omega_\text{p0})^2, \quad \omega < \omega_\text{p0}, \quad \omega_\text{p0}=(4\pi n_e e^2/m_e)^{1/2}, \]

\( n_e \) is the concentration of electrons in the medium. For electron concentration \( n_e=10^{22} \text{ cm}^{-3} \), typical for a hard body, the plasma frequency is \( \omega_\text{p0}=5.5\cdot10^{15} \text{ s}^{-1} \). In a medium with frequencies below the plasma frequency superficial plasmon waves [12] may appear. These waves are distributed in a thin 1-50 μs outer layer of the medium. According to these assumptions, the excitation of the plasmon waves with frequencies in the range \( \nu=1 \text{ kHz}–100 \text{ MHz} \) is possible in a thin outer layer of the medium (calcite and electrolyte) or the electrode metal.

5. Conclusion
In this work we have researched the near-electrode areas of the discharge plasma in electrolyte. Voltage and current characteristics have been measured for the most important discharge modes. Main
discharge current oscillations have been recorded, and the spectrum has been plotted in the frequency range 30 kHz – 80 MHz. Ion cyclotron and electron cyclotron waves may exist in the discharge plasma in the electrolyte.

We have investigated the effect of adding crystalline powders into electrolyte to the process characteristics in this medium. Electro technical dependencies for the voltage and current for the parameters of substance in the working vessel were obtained. We have researched oscillation processes for the voltage on the electrolytic cell electrodes and have found the main oscillation frequencies in the range 1 kHz – 140 MHz. The possible processes in the outer layer of this medium, in which the plasmon waves may appear, are discussed.

References
[1] Gaisin Al F and Nasibillin R T 2011 Plasma Phys. Rep. 37 896
[2] Kayumov R R, Gaysin Al F, Son E E, Gaysin Az F and Gaysin F M 2010 Physica Scripta T142 014038
[3] Krastev D, Paunov V, Yordanov B and Lazarova V 2014 Journals of Chemical Technology and Metallurgy 49 35
[4] Du C, Cui J and Wu L, He G 2010 Materials and Manufacturing Processes 25 644
[5] Suminov I V and Epelfeld A V 2001 Pribory 9 13 (in Russian)
[6] Kanarev F M 2010 Low temperature electrolysis of water (Krasnodar: Krasnodarsk. Univ.) (in Russian)
[7] Kirko D L, Savjolov A S and Vizgalov I V 2013 Russian Phys. J. 55 1243
[8] Kirko D L 2015 Technical Physics 60 505
[9] Kroll N A and Trivelpiece A W 1973 Principles of plasma physics (New York: McGrawHill)
[10] Huddlstone R and Leonard S 1965 Plasma diagnostic techniques (New York: Academic Press)
[11] Reid M 2009 Raum & Zeit 162 76
[12] Brandt N D and Kulbachinsky V A 2007 Kvazichasticy v fizike kondensirovannogo sostojanija (M.: Fizmatlit (in Russian)