ELECTROCHEMICAL PROBE OF SINGLE CAVITATIONAL BUBBLE

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Abstract

The change of a current in an electrochemical cell together with dynamics and light emission of a single cavitational bubble induced in focusing shock wave near to the disk anode with a diameter of 0.6 mm in NaCl solution is investigated experimentally. It is shown that the maximum jump of a current takes place at the moment of a bubble collapse. Five possible explanations are discussed without reaching a satisfactory conclusion.

Introduction

The combined action of ultrasonic cavitation and electrolysis results in expansion of range of application of electrochemistry for metal nanoparticles production [1] and realization of nuclear reactions of synthesis [2]. The action of cavitation is distributed to the increase of an electrochemical current due to stirring of electrolytes [3], erosion and purification of electrodes [4], the local increase of temperature and pressure at the moment of a collapse of bubbles [5] and additional electrokinetic effects [6], connected with various phases of bubble oscillations. It can result in the change of electrolysis current [7-9]. Non-homogeneity of cavitation excludes a direct correlation of the phase of bubble oscillations (expansion, collapse) with the electrolysis current, therefore, the reason of transit events in cavitation in a cell is not obvious a priori.

In the work, the results of observation of electrokinetic processes induced by a single cavitational bubble on a surface of the electrode are presented.

Materials and methods

An electrochemical cell with the disk anode and reference electrode combined with a generator of spherically focused acoustic pulse was used [10].

The anode was made from a copper wire ПЭВ-2 with a diameter of 0.6 mm with varnish isolation. Its end was a perpendicular cut-off after steel blade and it could move in three mutually perpendicular directions. The plane of the anode was placed parallel to a focal plane of the generator. The cell was filled by NaCl solution with a concentration of 25 g/liter (resistance of the cell to an alternating current R_0 = 0.3-0.8 kOhm). An electric feeding of the cell was applied from a battery U_b = 4.5 V. A combination of potentials and materials of electrodes with used solution prevented allocation of gas bubbled products of electrolysis on the anode. To measure current through the cell the shunt R_{sh} = 120 Ohm was used. The period of current relaxation time after the switching on the feed was T_{rel} = 0.2 s. The gauge was established on the axis of transducer to achieve the maximal amplitude of a signal in a compression phase of initial shock wave [10].

The focal distance of transducer of the generator was F = 55 mm. In the focus, the pressure pulse consisted of compression phase with an amplitude of 70 MPa and, following it, rarefaction phase having amplitude of -20 MPa [11]. In the phase of rarefaction, the electrolyte (salt solution) could cavitate with the formation of bubbles at an end face of the electrode and cloud of bubbles in the bulk of liquid. In our case, the cavitation on the border electrode/electrolyte occurred both with switched on and switched off source of voltage with probability equal to unit. As the amplitude of negative phase of the focused pulse depends on a distance up to the source, the maximal radius of bubbles could be changed by moving the anode from the focus.

Photographing of cavitation processes was carried out using a digital camera SensiCam Fast Shutter (PCO, Kelheim, Germany) with xenon flash lamp ИСШ-400 (duration is 1 us). The pressure was measured by turmalin gauge (size of a crystal is 0.7x0.7x0.1 mm^3, sensitivity is ~10 mV/MPa) located at the same distance from transducer as electrochemical gauge but 5-6 mm displaced from an axis. Light emission of a bubble was registered with the help of photomultiplier tube (PMT) ФЭУ-35 (spectral range is 300-600 nm, anode resistance is 75 Ohm).

The signals are stored with the help of digital oscilloscope TDS 210 (Tektronix, 8 bits) on the personal computer. The time was counted from the point of the beginning of discharge in the high current pulse generator. The noise from the discharge is registered practically in all signals in time interval from 0 to ~20 us.

Results

Electrochemical current

In passing of acoustic pulse through electrolytic cell, several pulses of a current are observed (Fig. 1). The pulse A is time correspondent to the action of the compression phase of initial pulse with t_A = F/c = 37 us (c is a speed of sound in solution). Its rise time was 0.2 us, and fall time, ~1 us, is equal to the

duration of compression pulse [10, 11]. The following pulses of current O, K1, K2 are present with 300-700 us delay depending on the probe position.

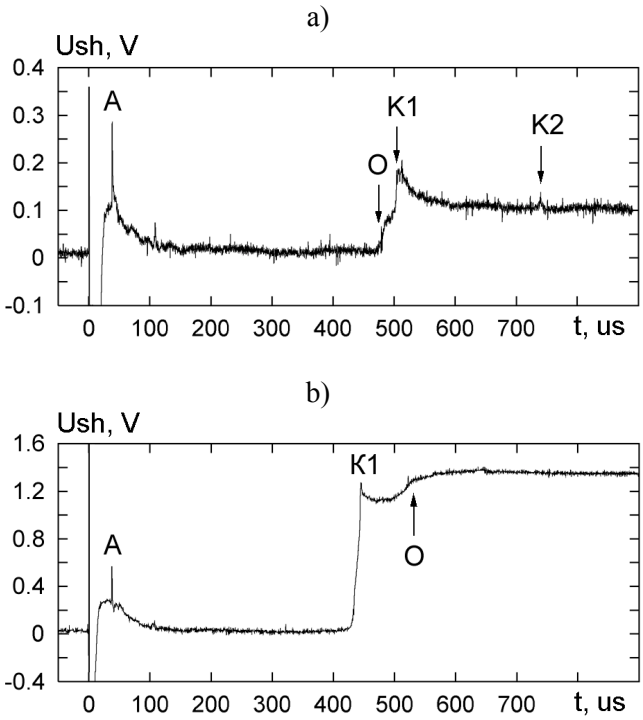

Figure 1: Voltage from the shunt of electrolytic cell, a) $T_{K1} > T_O$, b) $T_{K1} < T_O$.

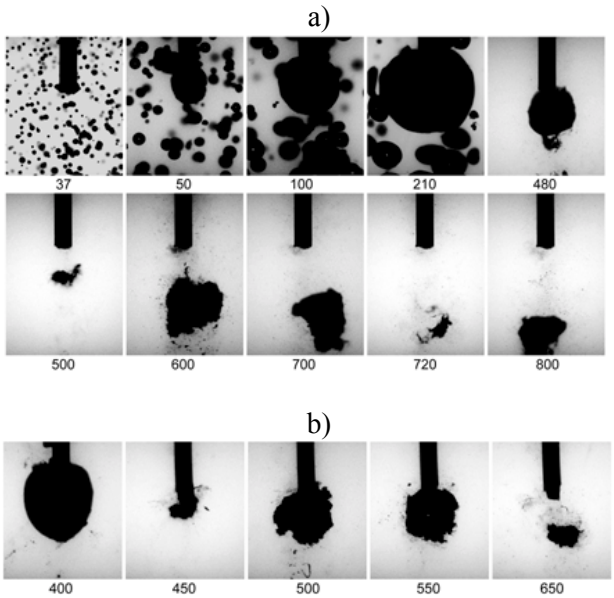

Figure 2: Dynamics of bubbles photographed with the help of a microsecond flash lamp. a) frames 1 and 5-8 - $T_{K1} > T_O$, frames 2-4 - $T_{K1} < T_O$; b) $T_{K1} < T_O$. The numbers represent time in microseconds.

Bubble dynamics

With pressure less than -10 MPa in a tensile phase in the focus of transducer, the cavitation, whose photos in the different moments of time are shown in Fig. 2, is observed. As a result of coalescence, at an end face of the electrode one bubble grows; its maximal radius is equal to about 3.0 mm, it exceeds the diameter of electrode 5 times and it exceeds the radius of the neighboring bubbles more than 2 times.

Further dynamics of the bubble at an end face of the electrode is similar to that described in [12] for the case of laser inception of cavitation. Depending on the intensity of cavitation the collapse of the bubble occurs near to the electrode (Fig. 2a) or at its end face (Fig. 2b) at the instant t_{K1}. In settled water the number of cavitational bubbles is less, and the collapse of the bubble occurs on the electrode (Fig. 2b). In this case instead of current jumps O and K1 one pulse of the current K1 (Fig. 1b) was observed. Here, its amplitude has increased 6-8 times reaching the greatest possible value $U_{K1} = U_b R_{sh} / (R_{sh} + R_0) =$ 1.2 V. Subsequent decrease of the current, which proceeds up to detachment of the bubble at the instant t0, is caused by an interruption of an electrical circuit by the bubble, which has rebounded after a collapse (frames 3 and 4 in Fig. 2b). On the last frame, after the detachment of the bubble, the result of cavitational erosion of the electrode (as a result of series of repeated experiments) is seen. It results in the increase of electrode surface and reduction of resistance R_0 of the cell.

After separate peaks the current tends to the initial value with time constant, which has appeared to be approximately equal to T_{rel}.

Light emission

For the definition of relative collapse moment and current peak the light emission from the cell and pressure near to the electrode were registered. A PMT signal together with current one is shown in Fig. 3 on the same time scale. As it is seen from the figure, the light emission from the bubble occurs simultaneously with the maximal value of the current at the instant t_{K1}.

Shock wave emission

With the change of z from 0 up to 25 mm the period of the first pulsation of a bubble $T_1 = T_{K1} - T_A$ has decreased from 470 to 210 us, however, the amplitude of the peak K1 has not practically changed (to an accuracy of 10%). For example, for z = 15 mm T_1 has decreased to 275 us (Fig. 4b), the amplitude of the current has been 0.25 V, as in the case for z = 0 mm (Fig. 3b). The gauge of pressure registers an initial wave at the instant t_A, and just as in [12] it registers a shock wave from the bubble collapse (Fig. 4). In the latter case, the delay of the pulse to the collapse is about 4 us. The relation of periods of the second and the first pulsations of the bubble T_2/T_1 depends on liquid properties and was about 0.5.

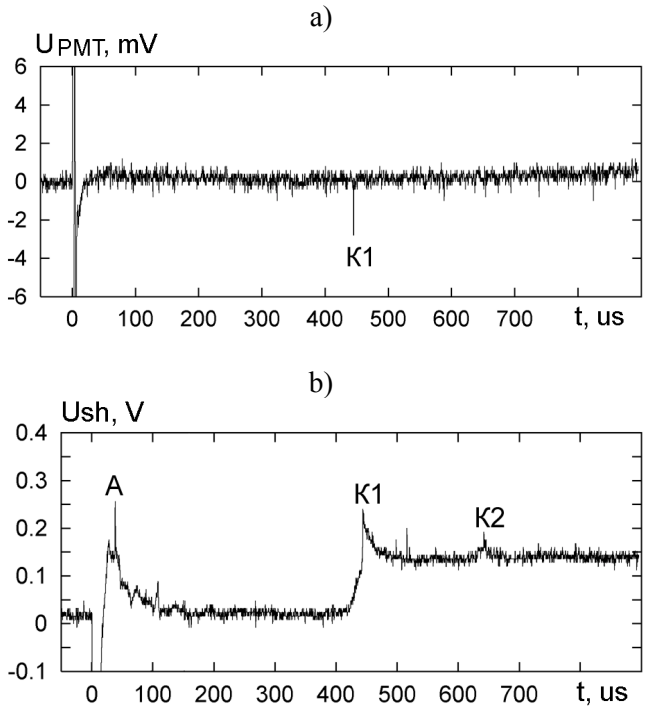

Figure 3: Comparison of simultaneous records of light emission in the cell (a) and electrolytic current (b). The anode is placed in focus (z = 0).

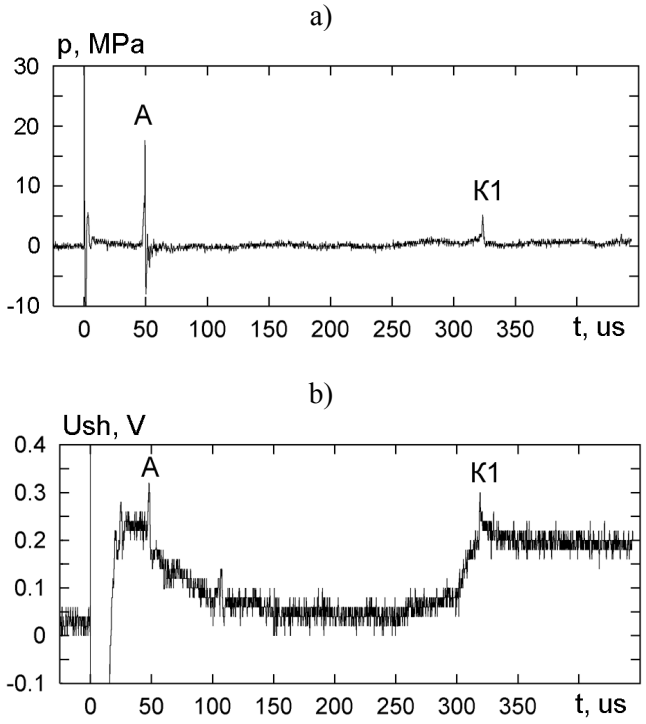

Figure 4: Simultaneous record of pressure near to the anode (a) and electrolytic current (b). The anode is on an axis with z = 15 mm.

Discussion

Thus, the offered method of cavitation inception with the help of shock wave focusing has allowed us to produce a single bubble on the electrode and to compare phases of its oscillations and translation motion with the change of a current in an electrolytic cell. The single bubble is formed from merged tiny bubbles growing on an end face of the electrode. Its maximal radius and, hence, reserved potential energy and period of oscillation surpass similar parameters for bubbles in the bulk of liquid.

The peaks of current are time correspondent to 1) shock wave front, 2) detachment of a bubble from the electrode, 3) collapse of a bubble. The amplitude of peak of current owing to the detachment of the bubble considerably surpasses the same parameter for a shock wave with the amplitude of 70 MPa irrespective of the collapse site.

Obviously, the switch-off of the current by the cavitational bubble and then the action on the electrode by flows around collapsing bubble results in instability of a double electrical layer (DEL). With the expansion of the bubble the size of an active surface of the electrode decreases, and thus, the current decreases. Reaching the maximal size, the bubble completely blocks the surface of the electrode, which appears in rarefied gas inside the bubble. Therefore the electrical circuit becomes broken off, DEL on the electrode disappears. The positive jump of the current arises with restoration of the electrical circuit as a result of either collapse or detachment of the bubble from the electrode. Then the current tends to the equilibrium value as DEL is formed [13].

The peak of current accompanying the second collapse of the bubble far from the electrode can be caused by

(i) shock wave from the bubble collapse in manner like compression in the primary wave acts [14],
(ii) intensification of inflow of reagents into diffusive area of DEL because of increased stirring of electrolytes in hydrodynamic flows around the collapsing bubble,
(iii) electrokinetic potential induced in liquid by a flow around the bubble [14],
(iv) radio frequency electromagnetic pulses due to alternative dipole momentum of unstable jets in the bubble [7],
(v) resistance of the bubble to the electric current near to the anode.

From these possibilities we should rule out (v), because in additional experiment we were not able to detect a significant deviation of R_0, with a dielectric ball with the same diameter near the anode at a distance equal to the diameter of the ball. For (iv) both polarities - positive and negative - of pulse are expected in contrast to the experimental observations. With (ii) and (iii) we cannot explain the duration of existing current pulse (the velocity in liquid flow near the electrode reaches maximum when the bubble radius is around 0.6 of its maximum), additionally (ii) should be also eliminated by the previous stirring

during the first collapse. Furthermore, in [14] the potential due to pressure disturbance (i) is expected to be higher than Debye vibration potential (iii). However, for (i) there no significant pressure pulse with similar shape recorded at that instant and, hence, the reason is not clear.

Conclusions

Using cavitation inception in focusing shock wave we were able to separate in time noise signals from high pulse current machine and from cavitation which occurs later than pressure disturbance arrives in the focus. It makes possible to measure potentials as low as millivolts without using any additional technique.

Positive electric pulses are observed in the cell circuit accompanying 1) primary shock wave, 2) first bubble collapse, and 3) second collapse. When pulse (1) can be used to measure velocity of compression waves in electrolytes, pulse (2) characterizes rarefaction component of the primary wave. The relation of time interval between peaks (2) and (3) to interval between (1) and (2) depends on liquid properties. All tree sorts of pulses seem to be corresponding to pressure variations near to anode.

Cavitation on electrodes can be used in electrochemical technologies to increase the speed of reaction and clear the surface of electrodes.

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