## CONCERNING SHOCK POLARIZATION OF WATER

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The electric signals produced by passage of a shock wave through a metal—water—metal system are investigated. It is found that shock loading produces a dc emf that depends on the nature of the electrode metal. The nature of the electric signal is related to the potential difference between the shock-loaded and unloaded metal electrodes. The shape of the electric signal, which consists of two characteristic peaks, may be attributed to variation of the impedance of the experimental setup during shock loading.

## INTRODUCTION

T was indicated in<sup>[1]</sup> that when a shock wave passes through a thin layer of water placed between two metallic electrodes, an electric signal is produced. This signal consists of two current pulses, one produced at the instant when the shock wave merges at the interface of the working electrode, and the other when the shock wave front (SWF) reaches the comparison electrode. In analogy with electric signals produced when polar dielectrics are loaded, it was assumed that the electric signal in the case of water is due to rotation of the dipole molecules on the SWF. In<sup>[2,3]</sup>, the resultant electric signal was also ascribed a pure polarization character.

Shock loading of a metal—electrolyte—metal system revealed experimentally a dependence of the electric signal on the properties of the interface<sup>[4]</sup>. The electromotive force (emf) producing the electric current was attributed to the potential difference between the shock-loaded and unloaded metallic electrodes. Water in the ordinary state is a weak electrolyte, but after shock loading its dissociation constant increases appreciably<sup>[5,6]</sup> and at a pressure 10 GN/m<sup>2</sup> the electric conductivity of water approaches that of strong acids  $(10^{-1} \text{ ohm}^{-1} \text{ cm}^{-1})$ . Therefore for metal—water—metal systems one could also expect an emf to be produced as a result of the change in the potential of the shockloaded electrode.

If the distance between the working electrode and the comparison electrode is much smaller than the length of the shock wave, then the pressure and the temperature on the surface of the working electrode can be regarded as constant during the time of passage of the wave between the electrodes. Assuming that the emf depends on the pressure and temperature of the working electrode, we can assume that in this case, as in shock polarization of dielectrics, which relax rapidly on the SWF<sup>[7]</sup>, the emf producing the electric signal will be constant. Starting from these premises, the magnitude of the electric signal for water should depend on the nature of the metal of the working electrode, and its waveform should be governed by the change in the impedance of the experimental setup during the process of shock loading.

## FORMULATION OF PROBLEM

Let us obtain the dependence of the electric current in the circuit on the time during the course of shock loading of a metal-water-metal system. Figure 1 shows the equivalent electric circuit realized in the shock-loading process. The circuit parameters with subscripts 1 and 2 pertain to the regions of the working electrode and the comparison electrode, which are separated by the SWF. The instant of loading of the working electrode corresponds on the circuit to the closing of the switch M. The solution for an analogous particular problem without allowance for the conductivity of the substance ahead of the SWF ( $R_2 = \infty$ ) was considered in<sup>[7]</sup>.

Assuming that the dielectric constant  $(\epsilon_1)$  and the resistivity  $(\rho_1)$  behind the SWF do not change in time, the electric current in the process of shock loading of the experimental setup (Fig. 2) can be described by a system of linear differential equations

$$i_{1}' + \Theta_{1} \frac{di_{1}'}{dt} = i_{2}' + \Theta_{2} \frac{di_{2}'}{dt}, \quad \frac{\Theta_{1}L}{S\sigma} \frac{t}{T} i_{1}'$$

$$- \frac{\Theta_{2}L}{S} \left(1 - \frac{t}{T}\right) i_{2}' + R \left(i_{2}' + \Theta_{2} \frac{di_{2}'}{dt}\right) = E_{0},$$
(1)

where

+

 $\Theta_1 = R_1 c_1 = \text{const},$  $\Theta_2 = R_2 c_2 = \text{const},$  $\sigma = D / (D - u),$ 

D is the shock-wave velocity, u the velocity of the working electrode, t the running time coordinate, T = l/D the time required for the shock wave to cover the distance L between electrodes, S the area of the electrodes, and  $\rho_1$  and  $\rho_2$  the resistivities of the loaded and unloaded water.

If  $R \gg \rho_1 L/S$ , which is the case in our experiments (R = 75 ohm and according to the data of<sup>[6]</sup>  $\rho_1 L/S$  = 1 ohm), with allowance for the initial conditions

$$\dot{i_2}'|_{t=0} = 0, \quad i|_{t=0} = 0$$

the solution of (1) can be written in the form

$$I = \frac{E_0}{R} \left[ 1 - \frac{b}{T} \left( 1 - \frac{t}{T} \right) \exp \left( -a \frac{t}{T} + \frac{b}{2} \frac{t^2}{T^2} \right) \right] \times \int_0^t \exp \left( a \frac{\zeta}{T} - \frac{b}{2} \frac{\zeta^2}{T^2} \right) d\zeta \right],$$
(2)

where

$$a = \frac{T}{\Theta_2} \frac{\rho_2 L}{SR} + \frac{T}{\Theta_2}, \qquad b = \frac{\rho_2 L}{SR} \frac{T}{\Theta_2}, \qquad I = \frac{i}{E_0/R}.$$

The time dependence of the electric current in the external circuit in the interval from 0 to T, calculated from this formula, is shown in Fig. 3 (curve 1). At the instant when the emf is turned on, a sharp surge of electric current is observed in the circuit, owing to the capacitive susceptance of experimental setup. As the capacitance becomes charged, the current decreases, but it rises subsequently because of the decrease of the active resistance and capacitive reactance of the substance ahead of the SWF.

It should be noted that loading of the working electrode and the entrance of the SWF into the water occur not instantaneously, but within a certain time determined by the curvature and inclinations of the SWF. The smooth increase of the electric signal at the instant of shock loading of the working electrode can then be explained in two ways. First, if the emf producing the electric signal appears on the SWF as a result of polarization of the water, then as the front leaves the working electrode the signal increases because of the increase in the number of oriented dipoles. Second, if the emf on the shock-loaded point of the electrode is due to the change of the polarization of the interface, then a charging of the electric double layer on the unloaded part of the surface should occur, and this can give rise to a corresponding change of the current in the measuring circuit.

Let us assume for simplicity that the effective emfE which appears in the external circuit depends linearly



FIG. 1. Equivalent circuit of experimental setup.  $E_0$ -emf produced at the instant of loading of the working electrode;  $i_1$ ,  $i_1'$ -current through the capacitance and resistance of the shock-loaded portion of the substance;  $i_2$  and  $i_2'$ -current through the capacitance and resistance of the unloaded portion of the substance;  $R_1$  and  $R_2$ -ohmic resistances of the shock-loaded and unloaded parts of the substance;  $c_1$  and  $c_2$ -capacitances of the shock-loaded and unloaded parts of the substance; R-resistance of the measuring device; M-switch closed at the instant when the working electrode is loaded; i-current through the measuring instrument.



FIG. 2. Experimental setup used for the study of shock polarization of water: 1-working (shock-loaded) electrode; 2-water, 3-comparison electrode, 4-glass cover, 5-screen. The arrows show the direction of the shock wave.



FIG. 3. Experimental and calculated dependences of the electric current in the measuring circuit, reduced to dimensionless coordinates: 1– curve calculated without allowance for the SWF curvature  $(T/\Theta_2 = 0.2; \rho_2 L/SR = 100); 2$ -curve calculated with allowance for the SWF curvature  $(T/\Theta_2 = 0.2; \rho_2 L/SR = 100; t_0/T = 0.2); 2'$ -experimental oscillogram  $(T/\Theta_2 \approx 0.2; \rho_2 L/SR \approx 100; t_0/T \approx 0.2); 3$ -curve calculated with allowance for the SWF curvature  $(T/\Theta_2 \approx 0.2; \rho_2 L/SR \approx 100; t_0/T \approx 0.2); 3$ -curve calculated with allowance for the SWF curvature  $(T/\Theta_2 \approx 0.2; \rho_2 L/SR \approx 100; t_0/T \approx 0.2); 3$ -curve calculated with allowance for the SWF curvature  $(T/\Theta_2 \approx 0.2; \rho_2 L/SR \approx 2; t_0/T \approx 0.2).$ 

on the time up to the instant  $t_0$  of total loading of the working electrode:

$$E(t) = E_0 kT / T, \qquad (3)$$

where k is a certain proportionality coefficient. Substituting (3) in place of the right-hand side of (1) and solving the resultant system in analogy with Eqs. (1), we obtain an expression for the current

$$I = \frac{kE_0}{R} \left[ \frac{t}{T} - \frac{b}{T} \left( 1 - \frac{t}{T} \right) \exp\left( -a \frac{t}{T} + \frac{b}{2} \frac{t^2}{T^2} \right) \\ \times \int_0^t \frac{\zeta}{T} \exp\left( a \frac{\zeta}{T} - \frac{b\zeta^2}{2T^2} \right) d\zeta \right],$$
(4)

which is valid in the time interval  $0 \le t/T \le t_0/T$ . The curve calculated from this formula for the current in the external circuit in the case of loading of the metal—water—metal system appears as curve 2 in Fig. 3 together with the experimental oscillogram 2', both in dimensionless coordinates.

## EXPERIMENTAL RESULTS AND THEIR DISCUSSION

The experimental setup (Fig. 2) constitutes two identical metallic electrodes between which doubly distilled water with conductivity not higher than  $10^{-6}$ ohm<sup>-1</sup> cm<sup>-1</sup> was poured. The electrode surfaces were mirror-polished prior to the experiment and cleaned of surface-active substances with calcium hydroxide, which was subsequently washed off with doubly distilled water. The dynamic loading of the apparatus was by means of a shock wave of  $10-12 \mu$  sec duration, obtained by detonation of an explosive. So that the change of the electrode material would not cause a change in the shock-wave pressure, the working electrode was applied in the form of a thin foil (0.1 mm) to a screen which was always made of aluminum. For the Cuwater-Cu and Al-water-Al systems we also used a massive working electrode of copper or aluminum, respectively. In these cases, the shock-wave pressure was maintained constant by special choice of the explosive and of its density. A typical oscillogram of the electric current is shown in Fig. 4b. The electric signals in the case of the massive working electrode



FIG. 4. Typical oscillograms of the electric signal produced by loading the experimental setup (Fig. 2): a-R = 75 ohm, L = 4 mm; b-R = 30 kilohm, L = 3 mm. Both oscillograms were obtained with a comparison electrode having an area 1 cm<sup>2</sup> and with water having a conductivity  $10^{-6}$  ohm<sup>-1</sup> cm<sup>-1</sup>.  $t_1$ -instant of loading of the working electrode;  $t_2$ -instant of loading of the comparison electrode.

did not differ from the signals obtained by using a thin copper foil applied to an aluminum screen.

The first current peak varies from experiment to experiment, but it has a tendency to decrease with increasing distance between electrodes. It should be noted that in none of the experiments did the first peak exceed the value of the electric signal produced when the shock wave approached the comparison electrode. The depth of the dip between the peaks depends substantially on the electrode area  $(1-9 \text{ cm}^2)$ , and its duration depends on the distance between electrodes (2-4 mm), the magnitude of the second peak remaining constant within the limits of experimental error  $(\pm 20\%)$ .

The experimental time dependence of the electric current and that calculated from formula (4) at  $\rho_2 L/SR$  = 100 and  $T/\Theta_2 = 0.2$  are shown in Fig. 3.

We see that after the first peak the calculated curve agrees satisfactorily with the experimental one. However, the shape and magnitude of the first peak on the calculated curve differ from those on the experimental one. The discrepancy can be attributed to the inaccuracy of the assumption that E(t) depends linearly on the time.

It was of interest to demonstrate experimentally that the emf after complete loading of the working electrode remains unchanged during the course of registration of the electric signal. By decreasing the ratio of the resistance of the experimental setup to the resistance of the recording device ( $\rho_2 L/SR$ ), we succeeded in obtaining an electric signal having a waveform close to rectangular (Fig. 4a). The corresponding theoretical curve is shown in Fig. 3.

The similarity between the experimental and calculated curves is evidence that the assumption  $E_0$ = const is correct. In addition, it can be concluded that the electric signal produced when the shock wave approaches the comparison electrode would be close to the emf.

It follows from all the foregoing that the waveform of the electric signal can be attributed to changes in the internal resitance of the experimental setup, and does not reflect the nature of the emf producing the electric signal.

To ascertain whether the electric signal is produced by the mechanism of polarization of the polar dielectrics or whether it is due to the change in the potential of the shock-loaded electrode, we obtained electric signals for metal—water—metal systems in which the metals were copper, nickel, tin, lead, and aluminum. To reduce the influence of the fact that the dynamic loading was not one-dimensional and to register a quantity close to the emf, the resistance R of the recording device was increased to 10 kilohms.

It turned out that the electric signal depends on the nature of the metal and, for example, for the systems Cu-water-Cu and Al-water-Al it differs by 0.5 V at a shock-wave pressure 10 GN/m<sup>2</sup>. To verify that such a difference is not accidental, we performed experiments on the aforementioned systems without a cathode follower (R = 75 ohm) and using massive electrodes. The electric signals are compared at the values of the second peaks. The values obtained were  $0.12 \pm 0.03$  and  $0.6 \pm 0.07$  V for copper and aluminum electrodes at a SWF pressure in water 9 GN/m<sup>2</sup>.

The dependence of the electric signal on the nature of the metal of the electrodes cannot be explained from the point of view of polarization of the substance on the SWF, and it is therefore necessary to take into account the electrochemical contribution to the resultant emf. Similar cases can also occur for other weak electrolytes or substances that become electrolytes after shock loading.

<sup>1</sup>R. T. Eichelberger and G. E. Hauver, In: Les ondes de détonation, Paris, 1961, p. 361.

<sup>2</sup>Ya. B. Zel'dovich, Zh. Eksp. Teor. Fiz. 53, 237 (1967) |Sov. Phys.-JETP 26, 159 (1968)].

<sup>3</sup>Y. Horie, Brit. J. Appl. Phys. 1, 2 (1968).

<sup>4</sup>O. N. Breusov, A. N. Dremin, V. N. Kochnev, O. K. Rozanov, and V. V. Yakushev, Élektrokhimiya 5, 719 (1969).

<sup>5</sup>A. A. Brish, M. S. Tarasov, and V. A. Tsukerman, Zh. Eksp. Teor. Fiz. 38, 122 (1960) [Sov. Phys.-JETP 11, 89 (1960)].

<sup>6</sup>S. D. Hamman and M. Linton, Trans. Farad. Soc., 62, (8), 2234, 1966).

<sup>7</sup>A. F. Ivanov and E. Z. Novitskii, Prikl. Mat. Teor. Fiz. 5, 104 (1966).

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