
PLASMA
CHEMISTRY

Theoretical Simulation of the State of an Interface between Two Liquid Phases on High-Voltage Polarization and Microplasma Discharge Excitation

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Received April 15, 2004

Abstract—As a result of solving boundary problems, theoretical studies were performed that made it possible to reveal the reason for and the feasibility of excitation of microplasma discharges at an interface between two liquid phases by high-voltage polarization. The models proposed explain the formation of a barrier layer due to concentration changes near the interface on passing current through the interface under potentiostatic and galvanostatic conditions and the appearance of a field strength that suffices to excite microplasma discharges.

Microplasma processes in electrolyte solutions induced by the high-voltage polarization of an interface are transient nonequilibrium processes accompanied by plasma microdischarges, luminescence, and ionization. These processes are the subject matter of high energy chemistry [1].

Techniques for microplasma discharge excitation at the electrode–solution interface are well known. As a rule, these techniques are used for applying ceramic oxide coatings. Theoretical and technological problems of the high-voltage polarization of solid electrodes were considered in sufficient detail [2–4].

Electrochemical and microplasma processes at the interface between two liquid phases represent a fundamentally new problem in electrochemistry [5]. To our knowledge, there are no published data regarding the conditions required for the appearance and occurrence of a microplasma process at a liquid–liquid interface.

In this work, we report the results of theoretical studies, which allowed us to clarify the reason for and the feasibility of excitation of microplasma discharges at the interface between two liquid phases by high-voltage polarization.

THEORETICAL

It was found both theoretically and experimentally that at least three conditions should be fulfilled for the excitation of microplasma processes at a liquid–liquid interface.

One of these conditions is that the voltage drop at the interface between liquid phases should be sufficient for interface polarization and for the occurrence of electrochemical reactions at this interface.

The voltage applied to this electrochemical system can be represented as follows:

$$U = U_o + U_w + IR_o + IR_w + U_E, \quad (1)$$

where U_o is the electrode polarization in the organic phase, U_w is the electrode polarization in the aqueous phase, IR_o is the voltage drop in the organic phase, IR_w is the voltage drop in the aqueous phase, and U_E is the polarization of the interface between two immiscible liquids.

If electrode polarizations U_o and U_w are low (the case of electrodes with a large surface area) and the electrodes are arranged near the interface between liquids, the main voltage drop from a power source is localized at the interface between two liquid phases.

The evidence for the electrochemical polarization of an interface is its motion. This is explained by the fact that interfacial tension changes with an increase in the driving voltage across electrodes placed in different phases and, thus, leads to interface motion; correspondingly, interface polarization takes place as shown in [6].

The second condition necessary for the appearance of a microplasma process is the existence of a barrier layer, i.e., the layer of a material that is inherently present or is formed at the interface and exhibits a high resistance. For the barrier layer to be formed there must be chemical or electrochemical reactions occurring at the interface. These reactions cause the depletion of the layer in ions that enter the chemical or electrochemical reactions or the enrichment of the layer near the interface due to the accumulation of reaction products. These concentration changes lead to the generation of the barrier layer and, hence, make the excitation of microplasma processes feasible at an interface between two liquid phases.

It was found experimentally that the high-voltage polarization of the interface between two liquid phases resulted in the motion of the interface and the occurrence of chemical and electrochemical reactions at both the electrodes and the interface between the liquid phases. The concentrations of reactants near the interface changed as a result of these reactions.

The third condition is that the strength of the electric field produced at the interface by electric current should be higher than the electric strength of the interface. The electric field strength at the interface was determined from the polarizing voltage and the barrier-layer thickness, which was equal to 0.001–0.01 cm. As the thickness of the barrier layer we took the thickness of a diffusion layer in which concentration changes for reacting ions responsible for the properties and resistance of the barrier layer occur [6].

Thus, as found both theoretically and experimentally, the electric field strength at which microplasma discharges appear in electrochemical systems is equal to 10^5 – 10^7 V/cm.

The electric field strength at the interface between two immiscible liquids is determined by the relationship

$$\frac{\partial U}{\partial x} = \frac{\partial(IR)}{\partial x} = R \frac{\partial I}{\partial x} + I \frac{\partial R}{\partial x}, \quad (2)$$

where U is the polarizing voltage, I is the current, and R is the resistance. With consideration for the interfacial area S and the dependence of the resistance of solution on its concentration

$$I = iS, \quad (3)$$

$$R = \int_0^x \frac{dl}{S k c(l)}, \quad (4)$$

where k is the coefficient of proportionality, $r = \frac{1}{k c(x)}$.

The values of k vary from 0.05 to 0.015 $\Omega \text{ cm l g}^{-1}$. They were calculated from data on the specific conductivity of NaOH, KOH, NaCl, and NaF solutions [7]. Then, Eq. (2) is simplified:

$$-E = \frac{dU}{dx} = i \frac{d}{dx} \left[\int_0^l \frac{dl}{k c(l)} \right] + \int_0^l \frac{dl}{k c(x)} \frac{di}{dx}. \quad (5)$$

If the current density is independent of distance, the electric field strength is defined by the expression

$$-E = \frac{dU}{dx} = i \frac{1}{k c(x)}. \quad (6)$$

As a result of solving boundary problems for linear semiinfinite diffusion under stationary conditions in potentiostatic and galvanostatic regimes with taking into account the motion of the interface between liquid

phases, we obtained equations for the bulk concentrations of reacting ions with the use of the Laplace transform.

In this model, the interface motion was taken into consideration through the linear velocity V of a liquid flow. Since a liquid exhibits internal friction (viscosity), we assume that the mixing rate V_0 has a maximum values at an interface and linearly decreases with distance from the interface to the depth of solution.

$$c(x) = c_0 - \frac{c_0 - c_s}{1 - \operatorname{erf}\left[\frac{-V_0}{2aD}\right]} + \frac{(c_0 - c_s) \operatorname{erf}\left[\frac{-V_0 + ax}{\sqrt{2aD}}\right]}{1 - \operatorname{erf}\left[\frac{-V_0}{\sqrt{2aD}}\right]}, \quad (7)$$

$$c(x) = c_0 + \frac{i}{S z F D} \sqrt{\frac{D \pi}{2a}} \exp\left[\frac{V_0^2}{2aD}\right] + \frac{-i}{S z F D} \sqrt{\frac{D \pi}{2a}} \exp\left[\frac{V_0^2}{2aD}\right] \operatorname{erf}\left[\frac{-V_0 + ax}{2aD}\right]. \quad (8)$$

Substituting Eqs. (7) and (8) for the concentrations of reacting ions under potentiostatic and galvanostatic conditions in Eq. (6) for the electric field strength, we obtain that the electric field intensity is determined by Eqs. (9) and (10) for potentiostatic and galvanostatic conditions, respectively:

$$-E = z F D \sqrt{a} \frac{(c_0 - c_s) \exp\left(\frac{(V_0 - ax)^2}{2aD}\right)}{\sqrt{D} \left(1 + \operatorname{erf}\left(\frac{V_0}{\sqrt{2aD}}\right)\right)} \sqrt{\frac{2}{D}} \quad (9)$$

$$\times \left[k \left(c_0 - \frac{c_0 - c_s}{1 - \operatorname{erf}\left[\frac{-V_0}{2aD}\right]} + \frac{(c_0 - c_s) \operatorname{erf}\left[\frac{-V_0 + ax}{\sqrt{2aD}}\right]}{1 - \operatorname{erf}\left[\frac{-V_0}{\sqrt{2aD}}\right]} \right)^{-1} \right],$$

$$-E = \frac{i}{k} \left\{ c_0 + \frac{i}{S z F D} \sqrt{\frac{D \pi}{2a}} \exp\left[\frac{V_0^2}{2aD}\right] + \frac{-i}{S z F D} \sqrt{\frac{D \pi}{2a}} \exp\left[\frac{V_0^2}{2aD}\right] \operatorname{erf}\left[\frac{-V_0 + ax}{2aD}\right] \right\}. \quad (10)$$

Let us analyze the resulting equations. Figure 1 illustrates the dependence of the electric field strength under potentiostatic conditions (Eq. (9)) on distance from the interface between two liquid phases and on surface concentration c_s , provided that the bulk concentration of ions c_0 is equal to 1 g/ml, the diffusion coefficient is $D = 1 \times 10^{-5} \text{ cm}^2/\text{s}$, the bulk concentration of ions near the interface c_s varies from $0.01 c_0$ to $0.1 c_0$, $k = 0.015 \Omega \text{ cm l g}^{-1}$, $a = 0.01 \text{ s}^{-1}$, and $V_0 = 0.0001 \text{ cm/s}$.

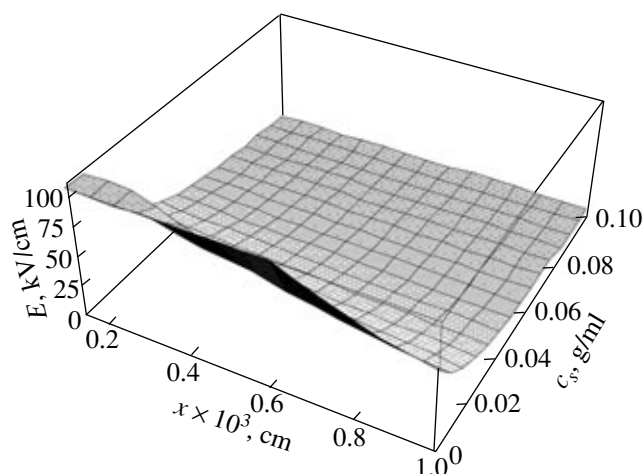


Fig. 1. Dependence of the electric field strength on the surface concentration of reacting ions and on the distance to the interface at $c_0 = 1 \text{ g/ml}$, $D = 1 \times 10^{-5} \text{ cm}^2/\text{s}$, $c_s = (0.01-0.1)c_0$, $k = 0.015 \text{ } \Omega \text{ cm l g}^{-1} \text{ (NaCl)}$, $a = 0.01 \text{ s}^{-1}$, and $V_0 = 0.0001 \text{ cm/s}$.

The maximum electric field strength was observed at the interface on depletion of an interfacial liquid layer in reacting ions and on the formation of a barrier layer due to this depletion.

The dependence of the electric field strength on the distance and interface velocity is of particular interest. Since the velocity of the interface exhibits a minimum at the initial point in time, pulse potentiostatic conditions should be used for reaching a breakdown.

The electric field strength increases with decreasing velocity of the interface (Fig. 2) and with decreasing distance to the interface. The maximum value of the field strength was as high as 10^5 – 10^6 V/cm , which was sufficient for the breakdown of the barrier layer formed.

Let us analyze the behavior of the electric field strength under galvanostatic conditions. The mathematical analysis of changes in the concentration of reacting ions under galvanostatic conditions (Eq. (8)) demonstrates that there is a decrease (depletion) in concentration of reacting ions near the interface on the high-voltage polarization of the interface between liquids; i.e., the shorter the distance to the interface, the lower the concentration. As the velocity of the liquid increases, the region of low reactant concentrations extends to wider liquid layers near the interface.

Figure 3 illustrates the graphical analysis of the electric field strength near the interface as a function of the velocity of the liquid and the distance from the interface. According to these data, the field strength increases with a decrease in the interface velocity and with an increase in the distance from the interface. In this case, a field maximum occurs in the bulk of solution near the interface, not at the interface, which is also confirmed by data in Fig. 4.

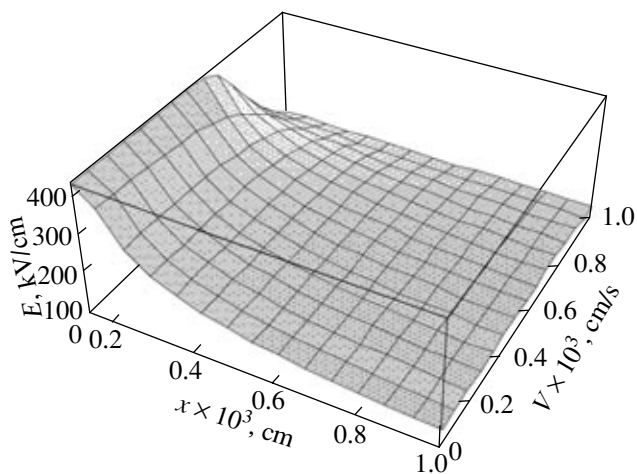


Fig. 2. Dependence of the electric field strength on the distance to the interface and on the interface velocity. $c_0 = 1 \text{ g/ml}$; $D = 1 \times 10^{-5} \text{ cm}^2/\text{s}$; $c_s = 0.0001 \text{ g/ml}$; $k = 0.015 \text{ } \Omega \text{ cm l g}^{-1} \text{ (NaCl)}$; and $a = 0.01 \text{ s}^{-1}$.

Figure 5 shows the results of calculations of the electric field strength as a function of current density and the viscosity of the liquid, which is indirectly characterized by coefficient a (the higher the viscosity of the liquid, the smaller the coefficient a).

The higher the current density and the lower the viscosity of the liquid (i.e., the greater the coefficient a), the higher the electric field strength. The maximum value of field strength decreases with an increase in viscosity.

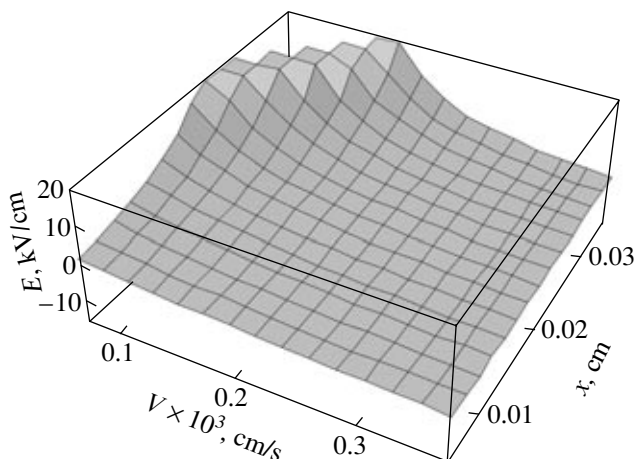


Fig. 3. Dependence of the electric field strength on the distance to the interface between two liquid phases and on the interface velocity. Calculation conditions: $c_0 = 1 \text{ g/ml}$; $D = 1 \times 10^{-5} \text{ cm}^2/\text{s}$; $i = 100 \text{ A/cm}^2$; $S = 1 \text{ cm}^2$; $F = 96500$; $Z = 2$; $a = 0.01$; and $k = 0.015$.

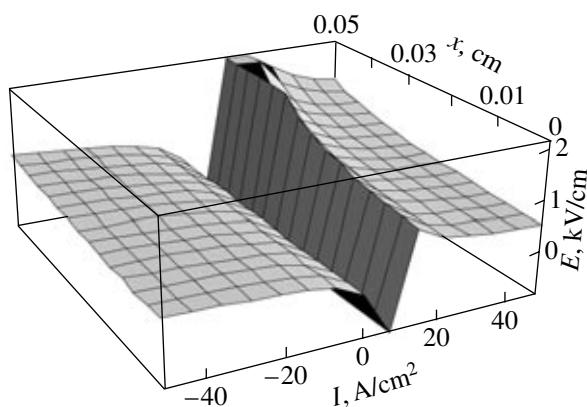


Fig. 4. Dependence of the electric field strength on current density and distance to the interface. Calculation conditions: $c_0 = 1$ g/ml; $D = 1 \times 10^{-5}$ cm²/s; $S = 1$ cm²; $F = 96500$; $Z = 2$; $a = 0.01$; $k = 0.015$; and $V_0 = 0.0005$ cm/s.

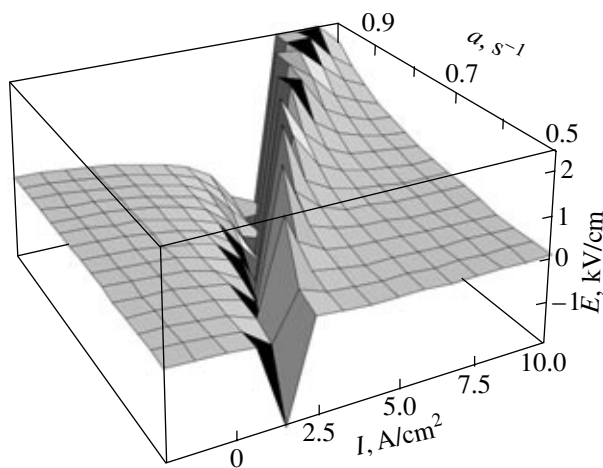


Fig. 5. Dependence of the electric field strength on current density and the viscosity of liquid. Calculation conditions: $c_0 = 1$ g/ml; $D = 1 \times 10^{-5}$ cm²/s; $S = 1$ cm²; $F = 96500$; $Z = 2$; $k = 0.015$; and $V_0 = 0.0005$ cm/s.

As the velocity of the interface increases, the region with a high electric field strength occupies progressively thicker layers near the interface. As the viscosity increases (with a decrease in a), the high field strength extends to wider layers of the liquid.

The electric field strength at the interface is much different from that in solution.

CONCLUSIONS

Theoretical models were proposed and equations were derived for the electric field strength at the interface between two liquid phases under potentiostatic and galvanostatic conditions. These models explain the formation of a barrier layer under potentiostatic and galvanostatic conditions during high-voltage polarization of the interface between two liquid phases as a result of concentration changes near this interface on passing current through the interface. The barrier layer and the high-voltage polarization of the interface between two liquid phases create conditions for the appearance of electric field strength sufficient for the excitation of microplasma discharges. Under potentiostatic conditions, the maximum electric field strength appears at the interface between the two liquid phases. Under galvanostatic conditions, the maximum field strength, which is sufficient for the excitation of microplasma discharges, is in the bulk of solution near the interface, rather than at the interface between the two liquid phases, as found by calculations and in experiments.

In summary, the reasons behind the excitation of microplasma processes at the interface between two liquid phases on the high-voltage polarization of this interface were theoretically substantiated.

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