Activation of phase boundary and current-generating processes in plasma-electrochemical systems

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Annotation. This paper reviews and presents the principles for implementing a microplasma fuel cell. Conducting work in this direction can in the long run ensure the creation of low-temperature fuel cells that operate without the use of expensive catalysts, ion-separation membranes and are capable of quickly reaching the operating mode.

1. Introduction
One of the most important scientific and technical problems in our days is the development of effective ways of converting the chemical energy of fuel into electrical energy. Devices for direct conversion of these types of energy received the name "Fuel cells" (FC). The market for fuel cells used as autonomous power sources is developing dynamically and, according to forecasts from Price Waterhouse-Coopers, by 2020 its volume will reach $1.7 trillion. [1]. The existing devices today have a number of significant drawbacks, among which, first of all, a long exit to the working mode and shutdown of work should be highlighted.

Current-forming oxidation of fuel without the participation of catalysts can take place only at high temperatures, but this is a serious obstacle in the process of operation and the creation of fuel cells in a particular version. We have proposed to localize high-density energy in nanolayers directly at the interface between the fuel and electrolyte in an electrochemical system to activate the process of fuel oxidation. Localization of high-density energy in the surface layer can be achieved by applying ultra-short pulses of polarizing voltage, which allow high-density currents to flow through the interface. In this case, the effect of the occurrence of microplasma discharges is visually observed. The flow of the discharge leads to a significant increase in temperature in the breakdown channel and its surrounding areas; a low-temperature plasma is formed, in which high-temperature reactions take place, leading to both intense oxidation of the fuel and synthesis of the oxidant.

2. Theoretical modelling
Let us consider in more detail the process of localization of energy at the interface between solid fuel and liquid electrolyte when imposing pulses of polarizing voltage above 100 V. In the mode combining the pulsed nature of the process and the region of high polarization voltages, the process is non-equilibrium, and, accordingly, its description is not shown correct, while in these conditions all possible electrochemical reactions are thermodynamically resolved. Due to this, at the initial moment of time there is an intense loss of charge carriers in the near-electrode region, and a barrier layer with thickness δ is formed. The value of δ corresponds to the size of the diffusion layer, since under the described conditions diffusion and migration are the factors that limit the speed of the electrochemical
process. Due to the pulsed nature of current transmission, heat exchange and convective transfer can be neglected.

Thus, the speed of electrode processes is determined by the gradient of concentrations at the interface:

\[ I = -z \cdot F \cdot D_{\text{ef}} \cdot S \cdot \frac{\partial N}{\partial x}, \]  

(1)

where \( z \) - the number of electrons involved in the electrode reaction; \( F \) - Faraday constant; \( D_{\text{ef}} \) - effective diffusion coefficient; \( S \) - the area of the interface electrode - electrolyte solution.

We will write the expression for the voltage drop in the electrode layer:

\[ U = I \cdot R = -z \cdot F \cdot D_{\text{ef}} \cdot S \cdot \frac{\partial C}{\partial x} \int_{0}^{\delta} \rho(t, C, U) dx, \]  

(2)

where \( \rho \) - resistivity of the barrier layer; \( t \) - current passing time.

Then the instantaneous density of energy localized in the barrier layer:

\[ Q(x) = U \cdot I = I^2 \cdot R = \left[ -z \cdot F \cdot D_{\text{ef}} \cdot S \cdot \frac{\partial N}{\partial x} \right]^2 \int_{0}^{\delta} \rho(t, C, U) dx. \]  

(3)

The solution describing the concentration distributions in the near-electrode layer, taking into account the boundary and initial conditions, was found in [2]:

\[ C(x, t) = (C_0 - C_s) \cdot \text{erf} \left( \frac{x}{2 \sqrt{D_{\text{ji}} \cdot t}} \right) + C_s, \]  

(4)

where \( C_s \) is the concentration of ions on the electrode surface; \( C_0 \) is the concentration of ions in the solution.

The distribution of the current passing through the near-electrode area is determined by the ratio:

\[ i = -z \cdot F \cdot D_{\text{sp}} \cdot \frac{\partial C}{\partial x} = -0.5 z \cdot F \cdot D_{\text{ef}} \cdot 0.5 \cdot (C_0 - C_s) \cdot \text{erfc} \left( \frac{x}{2 \sqrt{D_{\text{ji}} \cdot t}} \right). \]  

(5)

To calculate specific values of the energy density in the near-electrode layer, we will take the following conditions: electrolyte - potassium chloride solution, \( C_0 = 1 \text{ mol/l} \), \( D_{\text{ef}} = 10^{-5} \text{ cm}^2/\text{s} \), \( C_s = 0.0001 \text{ mol/l} \), electrical conductivity coefficient in the near electrode layer is \( K_1 = 0.7397 \text{ l/(Ohm·cm·mol)} \).

We will write the expression describing the distribution of the energy density:

\[ q(x, t) = \frac{0.25 z^2 \cdot F^2 \cdot D_{\text{sp}} \cdot (C_0 - C_s)^2 \cdot \text{erfc} \left( \frac{x}{2 \sqrt{D_{\text{ji}} \cdot t}} \right)^2}{K \cdot (C_0 - C_s) \cdot \text{erf} \left( \frac{x}{2 \sqrt{D_{\text{ji}} \cdot t}} \right) + C_s}. \]  

(6)

The graphical distribution of energy density in the electrode layer is shown in figure 1.

An analysis of the above dependence allows one to speak of an increase in the values of localized energy as it approaches the phase interface. The values of localized energies themselves significantly
exceed the energy of a chemical bond, for example, in a water molecule ($E_b = 497.02 \text{ kJ/mol}$) [3]. Under these conditions, ionization of the electrode space will occur due to the breaking of chemical bonds, and the plasma process will occur. Maximum energy localization is reached in the near-nanolayer up to 200 nm thick.

![Graph showing energy density distribution](image)

**Figure 1.** The distribution of energy density.

In the breakdown zone of a microplasma process, temperatures up to several thousand degrees [4] can be achieved, which removes kinetic restrictions for starting the process of oxidizing fuel in the form of, for example, metal or carbon.

Thus, when imposing pulses of polarizing voltage in the electrochemical system, electrochemical reactions are carried out and plasma-chemical processes are initiated that occur spontaneously. These processes include current-forming chemical oxidation of fuels. In the near-electrode space activated by the plasma process there are oxygen ions. Fuel, such as graphite, interacts with them in the form of current-forming reactions:

$$C + 2O^{2-} \rightarrow CO_2 + 4e^-.$$

3. **Materials and methods**

For direct measurements based on analogue-to-digital converters, a semi-automatic measuring system is used, which provides a time-coordinated measurement of the electrical parameters of rapid pulsed electrochemical processes. A detailed description of this system is given in [5, 6].

The system allows measurements of electrical parameters and automated construction of current-voltage characteristics (figure 2) of microplasma processes, both for each individual voltage pulse and for an array of pulses.

![Graph showing cyclic current-voltage dependence](image)

**Figure 2.** Cyclic current-voltage dependence ($I_1$ is the current of the activating part of the pulse, $I_2$ is the current obtained after the termination of the activating effect).
For the measurement and removal of parameters of current-generating processes, we used an electrochemical cell, which includes series-connected and placed in the case - a cathode, an electrolyte and an anode-fuel. The anode-fuel was titanium alloy VT1-0, both electrodes are placed in an aqueous solution of electrolytes.

4. Results and discussions

Figure 3 shows the current-voltage dependences obtained during a single voltage pulse in a plasma electrochemical system.

![Figure 3](image)

Figure 3. Cyclic voltammograms (1 - in KOH solution, 2 - in KCl solution).

The given dependences were used to calculate the expended (ascending part) and released (descending part) energy. Obtained data being integrated on the amount of energy expended and received are given in table 1.

| Electrode/Electrolyte Material | The amount of energy expended, W | The amount of energy received, W | The amount of energy released, W |
|-------------------------------|---------------------------------|---------------------------------|---------------------------------|
| BT1-0 / KOH solution          | 0.00356                         | 0.00659                         | 0.008547                        |
| BT1-0 / KCl solution          | 0.00389                         | 0.00748                         | 0.003629                        |

Thus, a theoretical analysis of the dependences of the energy localization process at the solid-fuel liquid electrolyte phase interface showed that when impulses of a polarizing voltage are applied in an electrochemical system, electrochemical reactions take place and plasma-chemical processes are initiated that occur spontaneously. It was established experimentally that using the activation of the fuel-electrolyte interface by a high-voltage voltage pulse with the occurrence of electrochemical and plasma-chemical processes leading to an oxidizer at the interface, it is possible to obtain electrical energy.

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