# PLASMA-LIQUID SYSTEM WITH ROTATIONAL GLIDING DISCHARGE WITH LIQUID ELECTRODE

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Plasma-liquid system based on rotational gliding discharge with one liquid electrode was developed. Emission spectra of plasma of rotational gliding discharge with one liquid electrode were investigated. Discovered effective mechanism of controlling non-isothermal level of plasma in dynamic plasma-liquid systems. Major mechanism of expulsion of metal anode material from plasma-liquid systems with rotational discharges was shown.

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## INTRODUCTION

The problem of energy efficiency of plasma technologies is connected with a fact that plasma generation employs the most expensive energy–electricity. Therefore, a possible way to solve this problem can lie in embedding of plasma technologies into the traditional chemical technologies. Plasma has been effectively injected into the reaction chamber. Chemical processes must be managed with help of plasma, which plays a catalyst role. For this reasons the primary aim of plasma chemistry is research and development of new plasma systems that are able to generate non-equilibrium plasma at high pressure and at the same time have high service time and energy efficiency.

Atmospheric pressure plasmas can be created by various types of discharges: transverse arc [1-3]; gliding arc [4-7] and rotational gliding arc [8-15]. Unlike the gliding arc [4-7], the transverse arc [1-3] has a fixed length of discharge column, but shorter service time. The rotational gliding arcs [8-15] subdivide into rotational gliding arcs with longitudinal motion [8-11] and rotational gliding arcs without longitudinal motion [12-15] of discharge column. Rotational gliding arcs with longitudinal motion [8-11] aren’t sufficiently stable. Stabilization of high pressure discharge in powerful plasmatrons is attained by vortex flow of gas [16]. The rotational gliding arc without longitudinal motion have fixed discharge column, unlike the gliding arc [4-11], and longer lifetime, unlike the transverse arc [1-3]. In the low-powered high pressure discharges the reverse vortex flow “tornado” type can be used for the space stabilization [17]. Recently, a dynamic plasma-liquid system with DC discharge in reverse vortex gas flow of tornado type with a liquid electrode was investigated [18-21]. Plasma-liquid system with rotational gliding discharge with one liquid electrode (LE) is a prototype of rotational gliding arc with solid-state electrodes [12-15], but with some modifications, which are interesting for plasma technology. The peculiarity of plasma-liquid systems usage for plasmas generation is that they do not require pre-gasification of liquid. In this regard, the research and development of plasma-liquid systems with rotational gliding discharge with one liquid electrode for application in energy technologies is an urgent task. It is not only important to be able to generate non-equilibrium plasma but also to have ways of controlling its properties and increasing or decreasing its equilibrium when needed. Comparing to classical gas discharges, plasma-liquid systems with vortex gas flow have a set of additional factors that influence energy properties of plasma. It is important to study influence of these factors on non-equilibrium of plasma in dynamic plasma-liquid systems.

## 1. EXPERIMENTAL SET-UP

Schematic of plasma-liquid system with rotational gliding discharge with one liquid electrode was shown in the previous paper [22]. Direct current power supply provides voltage between electrodes up to 7 kV. During experiments, system was working using air as supplied gas and distilled water as liquid. System was tested in two discharge modes: “solid” cathode (SC) mode and “liquid” cathode (LC) mode. Plasma torch appeared outside the system after a gas layer breakdown between the electrodes, its length dependant on discharge mode and gas flow rate. Discharge in both SC and LC modes leads to various electrochemical processes or electrolysis of water to be precise. Water contained tiny bubbles of molecular oxygen $O_2$ during discharge in SC mode and molecular hydrogen $H_2$ during discharge in LC mode. In both modes, bubbles left water volume through surface at the area of water-plasma interface.

Emission spectroscopy was used as main method for plasma diagnostics. Spectral device for emission spectra registration contained optical fibre and S-150-2-3648 USB spectrometer. This spectrometer is able to register wavelengths from 200 to 1000 nm. Electron temperature $T_e^*$ of atomic hydrogen H was obtained by using method of relative intensities on two intensity line/multiplets $H_\alpha$ (656.3 nm) and $H_\beta$ (486.1 nm). Electron temperature of atomic oxygen O was obtained from Boltzmann diagrams based on three most intensive multiplets (777.2, 844.6, 926.6 nm). Rotational $T_r^*$ and vibrational $T_v^*$ temperatures of hydroxyl were obtained by comparing experimental emission spectra with those calculated by SPECAIR software [23]. Hydroxyl band OH (A-X) was modelled based on previously calculated electron temperature of atomic oxygen O. Rotational and vibrational temperatures for the model were entered inside SPECAIR software [23].

## 2. RESULTS AND DISCUSSION

Fig. 1 shows the voltage-current characteristics of discharge in “solid” cathode mode (see Fig. 1,a) and "liquid" cathode mode (Fig. 1,b). In SC mode without airflow electrical current was increasing but voltage stayed constant. Increase in airflow leads to increase of minimal current needed to sustain discharge. Voltage-current characteristics of rotational gliding discharge with one liquid electrode working in SC mode are substantially different from those of rotational gliding arc with two metal electrodes [15]. Three factors usually define a behaviour of voltage-current characteristics: airflow rate, discharge current value and distance between liquid and metal electrodes. Airflow rate has direct influence on interaction between plasma and gas, its increase leads to higher discharge voltage. Higher flow rate also generates higher water cone, therefore decreasing distance between electrodes and lowering discharge voltage. At the same time, high discharge current causes destruction of the water cone.

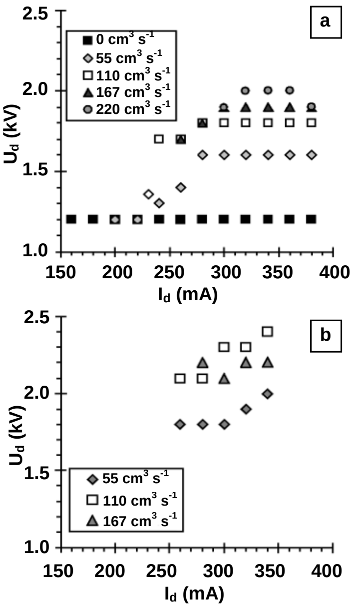

*Fig. 1. Voltage-current characteristics of rotational gliding discharge with one liquid electrode in SC (a) and LC (b) modes*

There is no water cone and distance between electrodes does not change without an airflow. It means that changes in current have no influence on discharge voltage. When airflow appears and discharge current is low, the discharge voltage increases because water cone generated at these conditions decreases distance between electrodes. Further increase of current with a set airflow rate leads to destruction of liquid cone. At the same time, voltage is rising until destruction of a liquid cone.

In LC mode (see Fig. 1,b) discharge was less stable. Airflow range in the system was from 25 to 200 cm$^3$•s$^{-1}$. Discharge current ranged from 250 to 350 mA, which is narrower than in SC mode. Comparison of discharges with the same airflow rate and discharge current in both modes shows that in LC mode voltage is higher. The reasons for higher discharge voltage probably lie in some properties of electron emission from water surface. Behaviour of voltage-current characteristics in dependence on airflow rate is the same in both modes but in LC mode it is less intensive.

Fig. 2 shows typical emission spectra of plasma in gap between electrodes in SC and LC modes. Distance between liquid and upper flange is 5 mm, discharge current is 360 mA and airflow rate is 167 cm$^3$·s$^{-1}$. Optical fibre captured light from the middle of a gap between water surface and upper metal electrode (z = 2.5 mm). Both emission spectra are normalized on the intensity of light at 283 nm wavelength. Main components of plasma in the gap between electrodes in both modes are atomic oxygen O, atomic hydrogen H and hydroxyl OH. In SC mode material of metal electrode is absent from plasma of the gap between electrodes. In SC mode (black curve), intensity of atomic hydrogen lines and oxygen multiplets is lower than in LC mode (grey curve). In addition, resonance lines of Cu appeared in plasma spectrum emitted from inside the chamber during LC mode. Copper is a material of upper electrode, which works as anode during LC mode. This means that anode dissolution is the main mechanism of expulsion of metal electrode material. Despite metal electrode not being submerged in liquid, it nevertheless can be covered with liquid (water) film. Emission spectra do not contain any traces of bottom flange material, which is made from stainless steel and works as anode during SC mode. This is due to so-called electrode passivation during these modes. Electrode passivation is possible for some materials that in special conditions do not undergo anode dissolution.

Fig. 3 shows image of rotational gliding discharge during SC mode (see Fig. 3,a) and LC mode (see Fig. 3,b) at the same airflow rate (167 cm$^3$·s$^{-1}$) and discharge current (340 mA). Height of plasma torch in SC mode can go up to 150 mm along z-axis and in LC mode up to 50 mm. Video shows a difference in discharge channel diameter $d$ (volume that emits light) between SC and LC mode. For SC mode $d \approx 1.2 \pm 0.2$ cm and current density is $j_d \approx 0.3 \pm 0.1$ A·cm$^{-2}$. For LC mode with same airflow and current, $d \approx 3.3 \pm 0.2$ cm and current density is $j_d \approx 0.04 \pm 0.005$ A·cm$^{-2}$. During LC mode current density is on order of magnitude higher than in SC mode. In both modes current density is lower than in traditional arc discharges where $j_d \approx 1$ A·cm$^{-2}$. Voltage-current characteristics are also different from that of traditional arc discharges. There is no material of metal electrode in SC mode emission spectra. Due to this circumstances rotational gliding discharge with one liquid electrode cannot be classified as arc-type discharge.

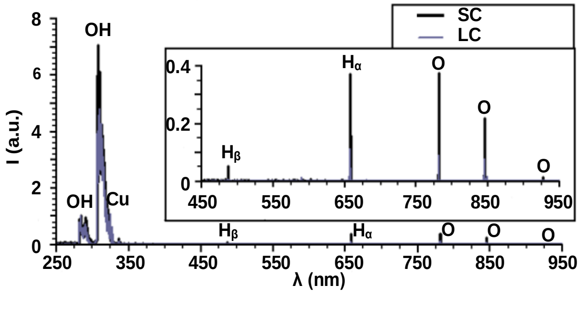

*Fig. 2. Typical emission spectra of plasma in the gap between electrodes in SC (black) and LC (grey) modes*

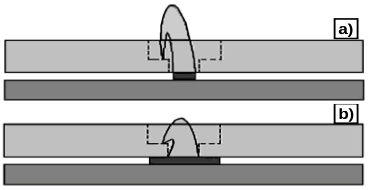

*Fig. 3. Schematic image of discharge plasma channel in SC (a) and LC (b) modes*

Fig. 4 shows typical emission spectra of plasma outside the system (z = 30 mm) and inside the system (z = 2.5 mm) in SC mode. Both spectra are normalized based on intensity at $\lambda_N$ = 309 nm wavelength. In a gap between electrodes, base plasma components are atomic oxygen O, atomic hydrogen H and hydroxyl OH. Plasma torch primarily contains hydroxyl OH and copper Cu. There are no evidence of hydrogen and oxygen in emission spectra of the torch. Copper is material of a cathode.

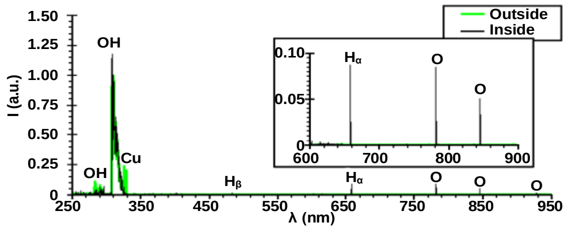

*Fig. 4. Typical emission spectra of plasma in SC mode. Discharge current is 360 mA, voltage is 2 kV, airflow rate is 220* $cm^3 \cdot s^{-1}$

Fig. 5 shows axial distribution of electron $T_e^*$, vibrational $T_v^*$ and rotational $T_r^*$ temperatures of plasma components in the gap between electrodes and in plasma torch. Emission spectra was registered on line of sight parallel to water surface and upper flange in SC (see Fig. 5,a) and LC (see Fig. 5,b) modes. Due to non-transparency of upper flange, there is a dead zone in spectral measurement. At z ≥ 35 mm difference between $T_v^*$(OH) and $T_r^*$(OH) temperatures in plasma torch is 700 K in SC mode and 600 K in LC mode. The reason of $T_r^*$(OH) in plasma torch being decreased in comparison to $T_v^*$(OH) can be due to adiabatic expansion. Plasma in the torch is non-isothermal. In SC mode there is a difference between $T_v^*$(OH) and $T_r^*$(OH) ($T_v^*(OH) > T_r^*(OH)$) near water surface (z = 0 mm), however near the upper flange (z = 5 mm) they have the same value, with $T_r^*$(OH) rising while $T_v^*$(OH) stays constant. In LC mode $T_v^*(OH) = T_r^*(OH)$ both near water surface (z = 0 mm) and at the upper flange (z = 5 mm). Additionally, in both modes $T_v^*$(OH) of plasma inside the gap between electrodes has the same value. Electric discharge is accompanied by water electrolysis. In LC mode, this leads to generation of bubbles of molecular hydrogen near surface of the bottom flange. Bubbles come out from the liquid at the water-plasma interface and hydrogen in them reacts with air, leading to full hydrogen oxidation reaction at the water surface (z = 0 mm). This causes an appearance of exothermal reactions in the system. Exothermal reactions increase thermal energy of heavy particles and rotational temperature of plasma components. In SC mode, bubbles are filled with molecular oxygen, which is why there are no exothermal reactions and no additional thermal energy near the water surface (z = 0 mm), however at z = 5 mm rotational temperature $T_r^*$(OH) is already equal to $T_v^*$(OH). Exothermal reactions had same influence on rotational temperature $T_r^*$(OH) during conversion of hydrocarbon fuels into syngas [20, 21, 24]. During ethanol-to-syngas partial oxidation reforming with an excess of oxidiser rotational and vibrational temperatures of hydroxyl were equal ($T_v^*(OH) = T_r^*(OH)$) [21, 24]. Adding even small amounts of inhibitor gas ($CO_2$) to oxidiser [21] led to decrease in $T_r^*$(OH) while $T_v^*$(OH) was unaltered. This makes it possible to control the non-isothermal (non-equilibrium) level of plasma, decreasing it with exothermal reactions and increasing by suppressing these reactions with inhibitor gas.

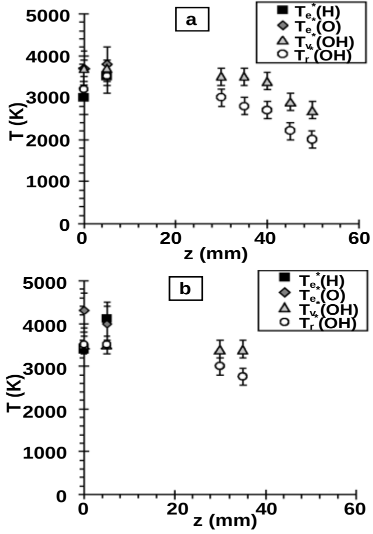

*Fig. 5. Axial distribution of temperatures of plasma torch components in SC (a) and LC (b) modes*

In earlier work, it was shown that it is possible to decrease non-equilibrium level of plasma with help of exothermal reactions [24]. However, it left open questions concerning increase of plasma non-equilibrium level when exothermal reactions are already taking place. This problem can be solved now by adding inhibitor gas that suppresses exothermal reactions. Plasma-liquid systems with rotational discharges and with liquid aerosols are promising direction for further research. Addition of aerosol to rotational gliding arc with solid electrodes can give it advantages of plasma-liquid systems with one liquid electrode.

## CONCLUSIONS

The plasma-liquid system based on rotational gliding discharge with one liquid electrode for the first time was developed. When compared to existing discharges, rotational gliding discharge with one liquid electrode has operating mode with low electrode erosion, which can be used in creation of plasma generators with long service life. Anode dissolution is major mechanism of expulsion of metal anode material from plasma-liquid systems with rotational discharges. Choosing a combination of electrode materials and operational modes that results in electrode passivation can solve the problem of anode dissolution.

Effective mechanism of controlling non-isothermal level of plasma in dynamic plasma-liquid systems was discovered: the non-isothermal level of plasma can be lowered by increasing the rate of exothermal chemical reactions and raised by suppressing exothermal chemical reactions (via introduction of inhibitory gas).

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## ПЛАЗМЕННО-ЖИДКОСТНАЯ СИСТЕМА С ВРАЩАТЕЛЬНЫМ СКОЛЬЗЯЩИМ РАЗРЯДОМ С ЖИДКИМ ЭЛЕКТРОДОМ

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Разработана плазменно-жидкостная система, в основе которой лежит вращательный скользящий разряд с одним жидким электродом. Исследованы спектры излучения плазмы вращательного скользящего разряда с одним жидким электродом. Обнаружен эффективный механизм контроля уровня неизотермичности плазмы в динамических плазменно-жидкостных системах. Показан основной механизм выноса материала металлического анода в плазменно-жидкостной системе с вращательным скользящим разрядом.

## ПЛАЗМОВО-РІДИННА СИСТЕМА З ОБЕРТАЛЬНИМ КОВЗНИМ РОЗРЯДОМ З РІДКИМ ЕЛЕКТРОДОМ

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Розроблено плазмово-рідинну систему, в основі якої лежить обертальний ковзний розряд з одним рідким електродом. Досліджено спектри випромінювання плазми обертального ковзного розряду з одним рідким електродом. Виявлено ефективний механізм контролю рівня неізотермічності плазми в динамічних плазмово-рідинних системах. Показано основний механізм виносу матеріалу металевого аноду в плазмово-рідинній системі з обертальним ковзним розрядом.