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# Hollow cathode and hybrid atmospheric plasma sources*

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*Abstract*: Generation and features of the radio frequency (RF) hollow cathode discharge (HCD) are compared for the atmospheric and moderate pressures. The atmospheric-pressure plasma systems, fused hollow cathode (FHC) and hybrid hollow electrode-activated discharge (H-HEAD), are described. Examples of applications where both FHC and H-HEAD have already been employed are given, and potentials for new processes are discussed.

*Keywords*: fused hollow cathode; cold atmospheric plasma; hybrid plasma; air plasma; gas conversion.

## INTRODUCTION: ATMOSPHERIC-PRESSURE PLASMA SOURCES

For generation of cold atmospheric plasma, power must be delivered selectively to electrons so that electrons will attain high energy while the gas temperature remains low despite high collision frequency. This nonequilibrium can be reached, for example, by using high generation frequencies, by short-pulse generation, or by suppression of ohmic currents by dielectrics. In molecular gases, instabilities causing discharge contraction into a contracted arc (e.g., thermal instability) must be leveled off.

New concepts of fused hollow cathode (FHC) and hybrid hollow electrode-activated discharge (H-HEAD) cold atmospheric plasma sources based on these principles are introduced.

## FUSED HOLLOW CATHODE (FHC) COLD ATMOSPHERIC PLASMA SOURCE

In hollow cathodes, the pendulum motion of fast electrons between the opposite space-charge sheaths or cathode falls at the cathode walls is responsible for forming the population of high-energy electrons. Therefore, the hollow cathode is a nonequilibrium source from its principle. The concept of the radio frequency (RF) hollow cathode, the RF hollow cathode plasma jet (RHCPJ) in a coaxial arrangement, for activation of gas and for deposition of films was patented in 1985 [1].

The hollow cathode effect, i.e., "large increase of current density with reduced cathode separation", exists only at certain combinations of hollow cathode dimensions and gas pressures. As the space-charge sheath thickness is inversely proportional to the gas pressure [2], the cathode dimensions must be reduced with the increasing pressure. The single RF hollow cathode ignition and operation were successfully tested at atmospheric pressure, with gas flowing through the cathode, for monoatomic and mo-

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lecular gases [3,4]. The V–I characteristics of RF hollow cathodes measured at atmospheric pressure show similar shapes as V–I characteristics measured at moderate pressures [5–7].

In Fig. 1, a comparison of peak-to-peak voltages $V_{pp}$ vs. RF power curves in monoatomic gases for the RHCPJs is shown, both for atmospheric and moderate pressures. The hollow cathodes for atmospheric and reduced pressures are of different dimensions, with inner diameters of 400 µm and 3 mm, from stainless steel and titanium, respectively, and the curves feature different monoatomic gases, neon and argon. Both curves show very clearly an increase of the voltage in the predischarge mode and a steep voltage drop with the hollow cathode discharge (HCD) ignition. The atmospheric-pressure curve exhibits higher voltages compared to the moderated-pressure curve. This reflects the Paschen breakdown curve, i.e., higher voltages needed for the breakdown (predischarge) and subsequent breakdown between the space-charge sheath and plasma. Figure 2 shows absolute values of self-bias voltages vs. RF power for the same hollow cathodes. The self-bias voltage values are lower for the atmospheric-pressure HCD, which could be explained by building the self-bias across a much thinner space-charge sheath.

Emission spectra are a sensitive diagnostics of the difference between the HCD and “normal” glow discharge [8]. In the 320–380 nm region, we observed $Ne^+$ emission lines typical for the HCD, when the inner diameter of the cathode was 400 µm. These lines were not present when the diameter exceeded 800 µm, i.e., when the dimension is not suitable for the neon HCD at atmospheric pressure. The condition of the inner surface at the cathode outlet indicates penetration of the discharge approximately 2 mm up into the 400-µm-diameter tube or slit. A similar depth/diameter ratio of about 5 is observed both in moderate- and low-pressure HCDs.

The model of the atmospheric-pressure hollow cathode sheath was developed [9], taking into account secondary and fast electrons on the top of slow electrons and ions in the sheath equations. Results show that the sheath potential penetrates further into the plasma, i.e., the space-charge sheath thickness expands compared with the model, accounting only for slow electrons.

Further development of the model has been done [10], including collisions between different particles. Time has also been added to the model, making it possible to study the time evolution of the RF

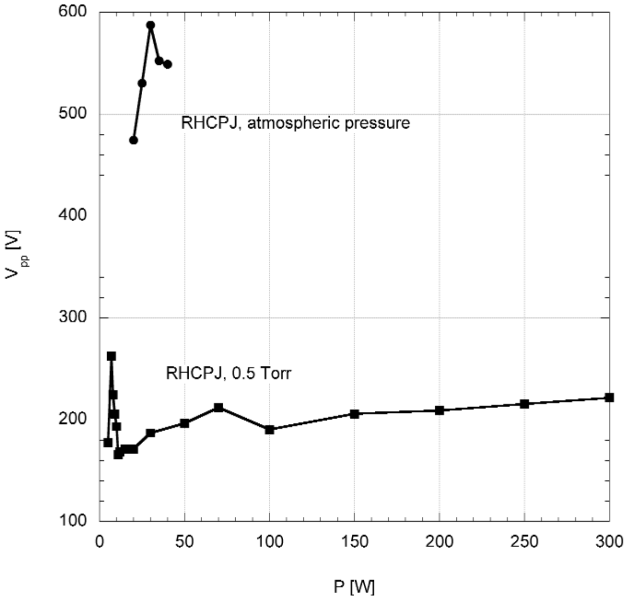

**Fig. 1** $V_{pp}$ vs. RF power as measured for the RHCPJ at atmospheric and moderate pressures (0.5 Torr), respectively. Ne and Ar flows of 100 sccm.

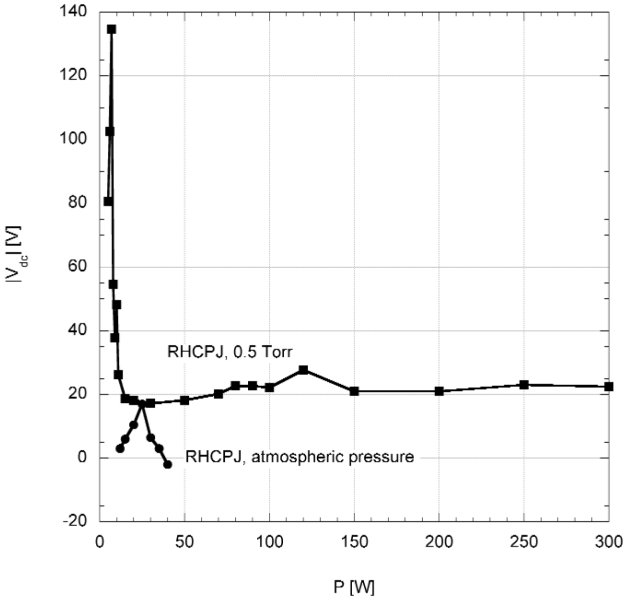

**Fig. 2** Self-bias voltage voltage vs. RF power as measured for the RHCPJ at atmospheric and moderate pressures (0.5 Torr), respectively. Ne and Ar flows of 100 sccm.

sheath. The ion density stays more or less constant over time, while the electron density oscillates back and forth, always with a maximum at the ion density. The effect of expanding sheath thickness with including secondary and fast electrons becomes more marked at lower pressures. The results are in a good agreement with experimental results over the moderate to atmospheric pressure range.

The FHC cold atmospheric plasma source is based on simultaneous generation of multiple RF-HCDs in an integrated open structure with flowing gas [11]. Figure 3 shows a schematic diagram of the system. The operational stability of the FHC systems is excellent, the discharges are homogeneous and do not exhibit streamers. The power consumption for noble gases is of the order of 0.1 W per 1 cm$^2$ of the active electrode area. The RF powers to ignite and sustain the discharge are comparable for the FHC and single hollow cathode at atmospheric pressure. Impedances measured by the RF impedance probe are slightly lower for the FHC system due to parallel operation of multiple discharges. The FHC systems allow generation of cold plasma in both monoatomic and molecular gases [4,12]. A uniform non-equilibrium discharge, for example, in nitrogen was generated over the area of 2.25 cm$^2$.

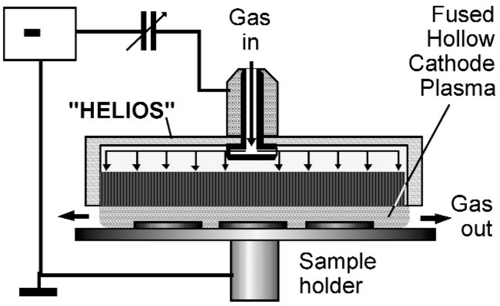

**Fig. 3** Schematic sketch of the FHC with integrated open structure and flowing gas.

Atmospheric-pressure plasma sources based on the hollow cathodes exhibit a high activation degree of species. The FHC with its modular concept has been successfully used for surface treatment, activation, and cleaning of temperature-sensitive materials at ambient atmosphere [13].

The FHC concept, with aerodynamic stabilization, was successfully proved for the gas conversion applications. 100 % conversion of $NO_x$ in nitrogen was achieved using both the RF and pulsed DC generations, for gas flows as high as 20 l/min. The photograph in Fig. 4 shows the aerodynamically stabilized RF-generated HCD in the $NO_x$–$N_2$ mixture. Figure 5 shows the concentrations of NO, $NO_2$, and $N_2O$ in the $NO_x$–$N_2$ mixture, treated by aerodynamically stabilized hollow cathode system, vs. pulse repetition frequency, for the short-pulse generation. The average delivered power is approximately 4 W at 2 500 Hz. The short-pulse generation enables measurements along very fine increments of power to follow the conversion action evolution. The conversion kinetics is being studied in more complex systems of air-based gas mixtures.

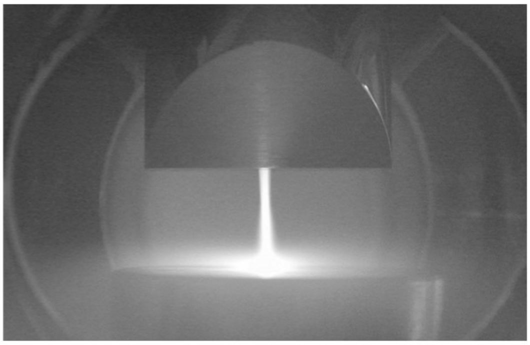

**Fig. 4** Photograph from the aerodynamically stabilized HCD in $NO_x$–$N_2$.

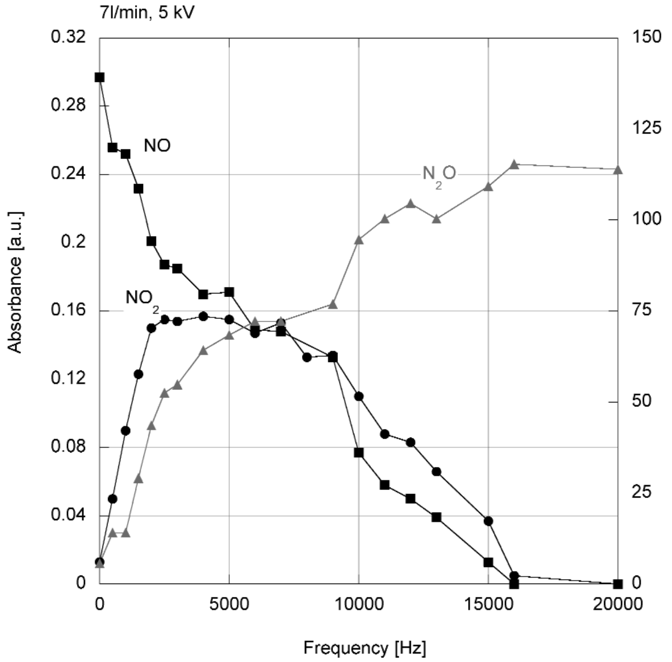

**Fig. 5** Atmospheric plasma conversion of $NO_x$ in $N_2$. Aerodynamically stabilized FHC, short-pulse generation. Concentrations of NO, $NO_2$, and $N_2O$ vs. repetition frequency. Gas flow of 7 l/min.

## HYBRID HOLLOW ELECTRODE-ACTIVATED DISCHARGE

The concepts of the RHCPF and microwave antenna (MWA) [14] were combined into one common system, H-HEAD source. The H-HEAD source provides a very efficient control of plasma parameters by both microwave and hollow cathode (RF or pulsed DC) generation powers. The source with a simple cylindrical electrode terminated by a gas nozzle combines the MWA plasma with the hollow cathode plasma generated inside the gas nozzle [15]. A simple schematic sketch of the source is shown in Fig. 6.

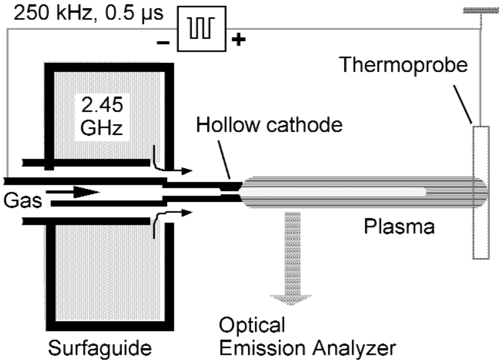

**Fig. 6** Schematic diagram of the H-HEAD source.

The H-HEAD cold atmospheric plasma source, capable of generating plasma plumes in ambient air more than 15 cm long, enables treatment of 3-d and complex geometry objects even at very low gas flows. The H-HEAD source does not require stabilization by helium.

Metal particles released from the hollow cathode outlet can be carried by the flowing plasma to the substrate as far as several cm from the cathode. For example, using a titanium nozzle, the titanium oxide film was analyzed on the silicon substrate placed at the distance of 2 cm from the nozzle, in the ambient atmosphere. This finding indicates an interesting possibility to use the H-HEAD source for combined atmospheric plasma vapor deposition (PVD) and plasma-enhanced chemical vapor deposition (PE-CVD) regimes.

The H-HEAD source was first tested with monoatomic gases. Generation of stable long plumes of cold atmospheric plasma in molecular gases, in nitrogen, and in air has been successfully performed recently. The H-HEAD source is capable of generating up to 10-cm-long plumes in air at microwave powers below 500 W and at air flow rates as low as 100 sccm. Corresponding flow rates in nitrogen plasma are even less than 80 sccm. The discharges in air and nitrogen have similar shapes and are comparable with corresponding plasma columns in argon.

Optical emission spectra of air and nitrogen columns revealed the presence of molecular bands and atomic lines of nitrogen and oxygen, respectively, and a possibility of a controlled release of metal particles from the hollow cathode. At the microwave power between 200 and 300 W and at gas flow rates between 100 and 300 sccm, the vibrational temperatures of nitrogen molecules, determined from the second positive system of the $N_2$ molecules, reached values between 3000 and 6000 K. Corresponding temperatures measured at thermally insulated steel probe 1 cm from the hollow cathode were below 600 °C.

The shapes of atomic oxygen emission intensities vs. the microwave power in the air and nitrogen H-HEAD discharges, respectively, exhibit similarities to the temperatures at the thermoprobe vs. microwave power curves [16].

Moderate substrate temperatures enabled growth of diamond grains without simultaneous graphitization. Nanocluster diamond was grown in ambient air at steel substrates using air plasma interacting with the air + ethanol mixture [17,18]. Oxygen-containing plasma enhances the quality of diamond, etching away diamond-like carbon (DLC) and graphitic phases.

## CONCLUSIONS

The RF hollow cathode atmospheric-pressure discharge exhibits similar ignition and performance features as the moderate pressure RF-HCD; e.g., the V–I characteristics and peak-to-peak and self-bias voltage vs. power dependences, characterizing transitions between individual operation modes. However, the values of $V_{pp}$ and thresholds for ignition of the discharge and of self-bias voltages across the space-charge sheath depend on the gas pressure.

Experimental results are in good agreement with the model of the atmospheric-pressure hollow cathode sheath, which takes into account secondary and fast electrons.

The FHC cold atmospheric plasma source based on unifying the RF-HCDs generated simultaneously in the integrated open structure is extremely suitable for scale-up and flexible for different large-area applications. Uniquely low power consumption enables surface treatment of temperature-sensitive materials. The source has been successfully employed for gas conversion. Conversion kinetics is studied for RF and short DC pulse generations in different gas mixtures.

The H-HEAD atmospheric plasma source, combining hollow cathode and microwave plasmas, provides a very efficient control of plasma parameters and enables treatment of 3-d objects, even at very low gas flows. The H-HEAD is capable of generating over 15-cm-long noble gas plasma plumes in open air and up to 10-cm-long plasma plumes at less than 150 sccm of air or nitrogen flowing in open air. The transport of material from the electrode was observed at a sufficient hollow cathode plasma power. Nanocluster diamond was synthesized in ambient air at steel substrates using air plasma interacting with the air + ethanol mixture.

## ACKNOWLEDGMENTS

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## REFERENCES

1. L. Bardos, J. Musil, V. Dusek, J. Vyskocil. Czech Patent PV 4407-85.
2. J. Perrin, P. R. Cabarrocas, B. Allain, J.-M. Friedt. *Jpn. J. Appl. Phys.* **27**, 2041 (1988).
3. H. Baránková, L. Bardos. *Appl. Phys. Lett.* **76**, 285 (2000).
4. H. Baránková, L. Bardos. *Surf. Coat. Technol.* **163–164**, 649 (2003).
5. H. Baránková, L. Bardos. *Surf. Coat. Technol.* **120–121**, 704 (1999).
6. H. Baránková, L. Bardos. *Vacuum* **80**, 688 (2006).
7. H. Baránková. In *Proc. The Joint Int. Meeting of the Electrochemical Society and the Int. Soc. of Electrochemistry*, Paris, 1997, Vol. 97-30, p. 348, Electrochemical Society (1998).
8. J. W. Frame, D. J. Wheeler, T. A. DeTemple, J. G. Eden. *Appl. Phys. Lett.* **71**, 1165 (1997).
9. D. Söderström, H. Baránková, L. Bardos. *IEEE Trans. Plasma Sci.* **35**, 522 (2007).
10. D. Söderström, H. Baránková, L. Bardos. *Int. Vacuum Congress (IVC-17)*, Stockholm, 2–6 July 2007, paper PSTFO2-Or1.
11. H. Baránková, L. Bardos. Swedish patents 9901527/3 and 0000167/7, PCT/SE00/00791, U.S. Patent 6,238,629; 6,524,538.
12. H. Baránková, L. Bardos. *Galvanotechnik* **95**, 2244 (2004).
13. H. Baránková, L. Bardos. *Surf. Coat. Technol.* **174 –175**, 63 (2003).

14. L. Bardos, H. Baránková, S. Berg. *J. Vac. Sci. Technol., A* **14**, 474 (1996).
15. L. Bardos, H. Baránková. Swedish patent 9904295-4, PCT/SE00/02315, EP 1 236 381.
16. H. Baránková, L. Bardos, D. Söderström. *J. Vac. Sci. Technol., A* **24**, 1410 (2006).
17. H. Baránková, L. Bardos, D. Söderström, L.-E. Gustavsson. In *49th Annual Technical Conference Proceedings*, p. 41, Society of Vacuum Coaters, Albuquerque, NM (2006).
18. L. Bardos, H. Baránková. *Plasma Process. Polym.* **4**, 511 (2007).