Role of Streamers and Bubbles in the Plasma Assisted Production of Hydrogen

L. Bardos[1,2] and H. Baránková[1,2]

[1] *Uppsala University, Angstrom Laboratory, Uppsala, Sweden*

[2] *BB Plasma Design AB, Uppsala, Sweden*

The 9 ns 9 kV negative pulses with repetition frequency between 7 and 15 kHz applied in water solutions with 35% alcohol were found very efficient for production of the synthesis gas (H_2 + CO) with up to about 65% of H_2. The delivered average power was as low as about 10 W and the energy consumption was less than 10 kWh/kgH_2. Three alcohols were tested, ethanol (C_2H_5OH), methanol (CH_3OH) and isopropanol (C_3H_8O). Because of different H/C ratio in individual alcohols, in ethanol H/C = 3, in methanol H/C = 4 and in the isopropanol H/C ≈ 2.67, it was expected that the highest hydrogen content could be produced in methanol.

Main parts of the reactor used were described elsewhere [1-3]. Two basic arrangements of the submerged pulsing electrode were tested, the coplanar and coaxial ones. The schematics of these arrangements are shown in Fig. 1 together with pictures of the generated plasma. The figure shows also the gas flows produced from ethanol-based electrolyte, detected by the rotameter. The higher flow was produced when the coaxial electrode arrangement was used.

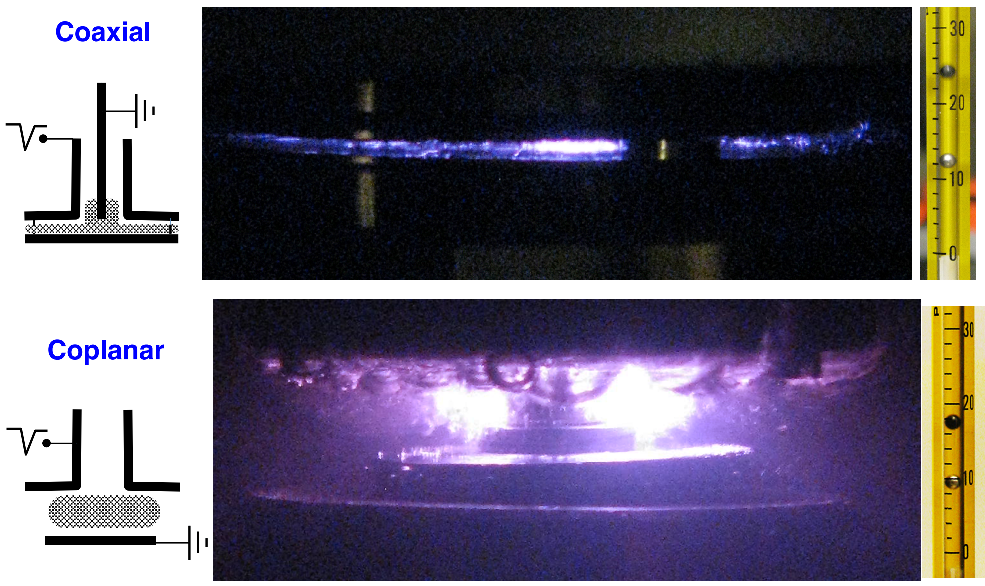

Fig. 1 Coaxial and coplanar arrangement of the pulsing electrode with pictures of the plasma in ethanol-water electrolyte. The rotameter confirms larger gas flow from the coaxial arrangement.

After optimization of the process the current pulse on the oscilloscope has always shown a large number of sharp spikes about 0.3 nm, as can be seen in Fig. 2. Then the discharge becomes flickering and noisy, which is characteristic for streamer discharges. Note that similar conditions for maximum generation of the synthesis gas were needed for all three tested alcohols.

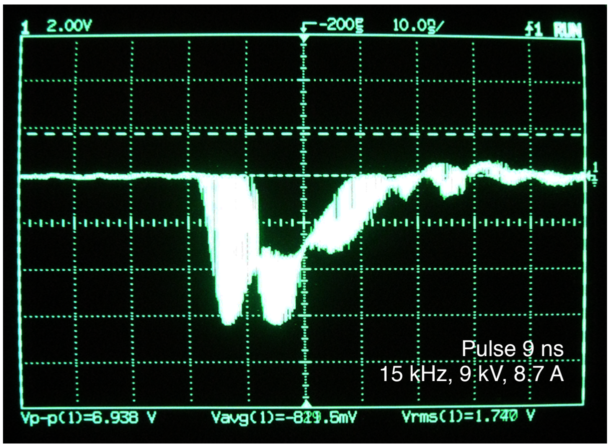

Fig. 2 Pulse current with multiple "spikes" at maximum production of gas. In this regime the discharge forms multiple streamers and becomes noisy.

As expected, the contents of hydrogen in the produced synthesis gas measured by HY-Alerta^{TM}500 detector was highest in case of water with methanol, see Fig. 3.

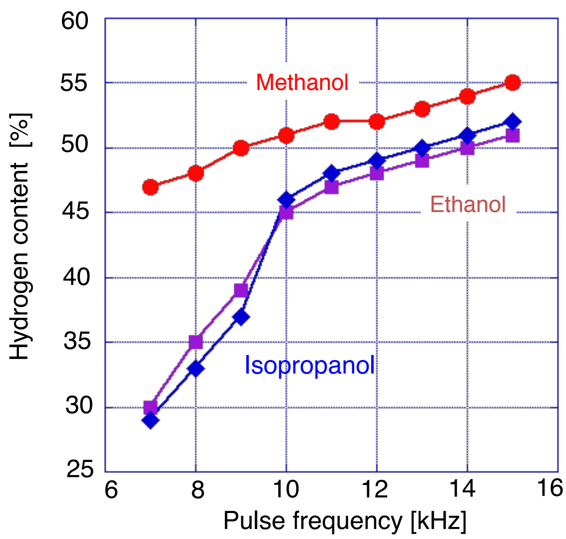

Fig. 3 Hydrogen contents in synthesis gas generated at growing pulse repetition frequency from three different alcohols in water.

The methanol-based electrolytes proved about 25% higher production efficiency than the ethanol and isopropanol ones. The energy consumption in best regimes from methanol in water was as low as about 4.5 kWh/kgH_2.

According to [4] the plasmas generated by nanosecond pulses form streamers, which propagate when the electric field is of the order of about 10^7 V/m (10 kV/mm). Indeed, in all three alcohol-based electrolytes the used 9 kV pulses were able to ignite the discharge. The streamers in liquids generate various sizes of gas bubbles as it is evident on photographs in Fig. 1. A more "open" coplanar electrode clearly demonstrates both, a typical streamer "cloud" at negative pulsing electrode and a number of produced bubbles around. In the coaxial arrangement the most bubbles are produced inside.

A "suspicion" on possible role of nanobubbles during streamer production of synthesis gas was reported in [3]. Nanobubbles are ultrafine gas-containing cavities with sizes typically between 50 and 500 nm. They differ from larger bubbles and they can affect basic characteristics of liquids. Besides of high gas pressure inside nanobubbles their extraordinary property is their metastability. According to [5], when the bubble is sufficiently small already upon its formation, the dissolving process cannot begin and the bubble remains small for very long time. A simple digital USB microscope with enlargements up to 2000x identified small bubbles attached to the reactor window. An example in Fig. 4 shows bubble sizes down to about 10 µm, but all backgrounds of the taken pictures were always like "powdery".

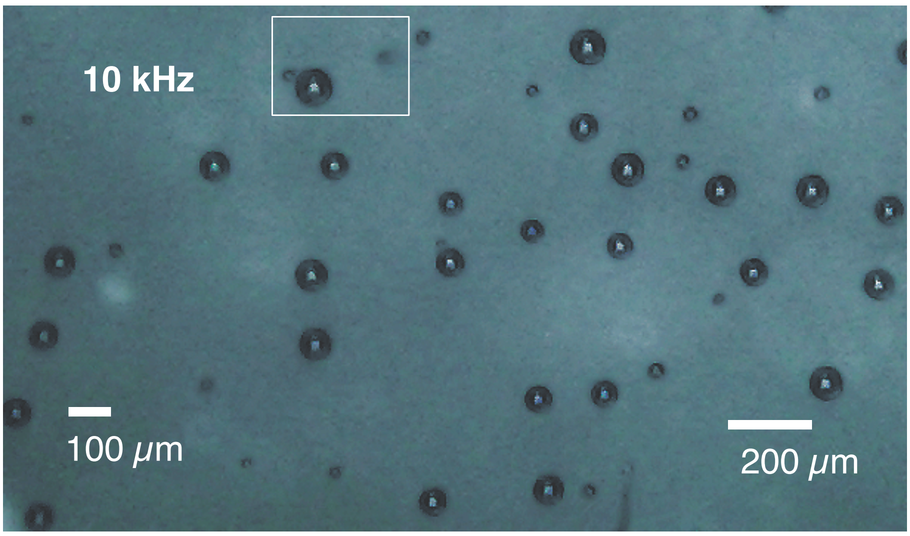

Fig. 4 Microscopic bubbles attached to the reactor window during 10 kHz pulsing in water with 35 % of isopropanol.

The character of nanobubbles in water were described in [6] in submerged "pin-to-plate" arrangement during 100 μs rectangular pulses -3.5 to -5.5 kV on a sharp end of the negative electrode by using a high-speed camera with a microscope focused to the gas channels along streamers. A very important quantity is high gas pressure in small bubbles (it is inversely proportional to the bubble diameter). This is because the increased pressure means increased concentration of dissolved gases, which could reduce the energy needed for breaking the chemical bonds and accelerate chemical reactions.

By simple digital enlargement of small rectangular area noted in Fig. 4 one can confirm the presence of smaller bubbles even with submicron diameters. A clearer evidence of submicron nanobubbles will require better optical equipment. However, surprisingly high efficiency and low energy consumption in the processes powered by high-voltage nanosecond pulses, importance of streamers, as well as rapid restarts of the process even after several days of pausing, indicate important assistance of active nanobubbles. It is also to be noted that the used electrolytes were always clean after tests, without any small solid particles.

It is possible to conclude that the field of generation and role of micro- and nano-bubbles in submerged short-pulsed discharges is still quite new and it may bring new approaches also to other plasma assisted processes.

Acknowledgment

The authors are very grateful to the J. Gust. Richert Foundation in Sweden for generous financial support of this research.

References

[1] L. Bardos, H. Baránková and A. Bardos: "Production of Hydrogen-Rich Synthesis Gas by Pulsed Atmospheric Plasma Submerged in Mixture of Water with Ethanol"; Plasma Chem. Plasma Proc. **37** (2017) 115-123.

[2] H. Baránková, L. Bardos and A. Bardos: "Non-Conventional Atmospheric Pressure Plasma Sources for Production of Hydrogen"; MRS Advances **3** (18) (2018), 921-929.

[3] L. Bardos and H. Baránková: "Possible Role of Nanobubbles in the Pulsed Plasma Production of Hydrogen"; International Journal of Hydrogen Energy **97** (2025) 581-584.

[4] E. Jüngling, K. Grosse, and A. von Keudell: " Propagation of nanosecond plasmas in liquids - Streamer velocities and streamer lengths"; J. Vac. Sci. Technol. A **40** (4) (2022) 043003-1 - 043003-11; doi: 10.1116/6.0001669.

[5] T. Vehmas and L. Makkonen: "Metastable nanobubbles"; ACS Omega **6** (2021) 8021-8027.

[6] T. Sato, T. Nakatani, T. Miyahara, S. Ochiai, M. Oizumi, H. Fujita and T. Miyazaki: "Study on Formation of Plasma Nanobubbles in Water"; Journal of Physics: Conference Series **656** (2015) 012036.