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Content

Electron induced fluorescence of H_2 continuum

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We report our current experimental results regarding electron induced H_2 continuum radiation of the $a^3\Sigma_g^+ \rightarrow b^3\Sigma_u^+$ transition in the spectral range of 180 – 900 nm at near-threshold electron impact energies, measured at the electron induced fluorescence (EIF) experiment. In contrast to earlier studies, present measurements indicate that H_2 continuum radiation is detectable above 500 nm.
The EIF apparatus is described in detail in [4]. The core of the experiment are crossed molecular and electron beams. Heated tungsten hairpin filament and a trochoidal electron monochromator (TEM) are used to create the electron beam with electron current of a few hundred nA and with electron kinetic energy ranging from 5 to 100 eV. Photon emission is measured using an optical system comprising of Cornerstone 260 grating monochromator and a cooled Hamamatsu R3896 PMT tube, with spectral range from 180 to 900 nm. Typical signal intensities are in $10^0 – 10^1$ order of magnitude. Spectral sensitivity calibration is performed using tungsten filament emission, taking grey body radiation model for wavelengths above 500 nm and using known H_2 continuum radiation shape for wavelengths above 200 nm [5].
Fluorescence spectra of H_2 were taken first in 180 – 500 nm spectral range (Fig. 1) and then in 420 – 900 nm range, while using an optical filter with 420 nm cut-off wavelength to rule out higher order grating diffractions (Fig. 2). Traces of electron source filament radiation in the 500 – 700 nm region were measured and subtracted from the H_2 spectrum. Distinct spectral features, such as the continuum maximum and Fulcher bands were visible. Uniqueness of these spectra lies in observation of the continuum radiation up to 900 nm, which is much higher than the commonly reported 500 nm limit. To prove the origin of the longer wavelength radiation is in the $a^3\Sigma_g^+ \rightarrow b^3\Sigma_u^+$ transition, we have measured relative EECS of H_2 continuum at 670 nm and 900 nm and compared their shape and thresholds to relative EECS measured at 230 nm (Fig. 3).

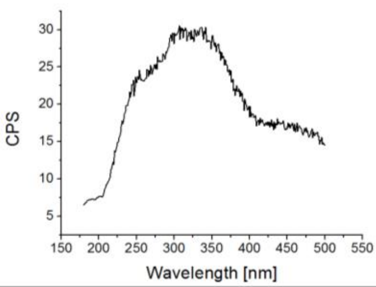

Fig 1: H_2 180 – 500 nm.

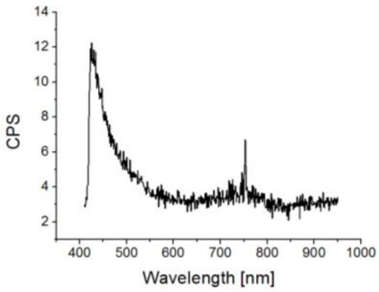

Fig 2: H_2 180 – 500 nm.

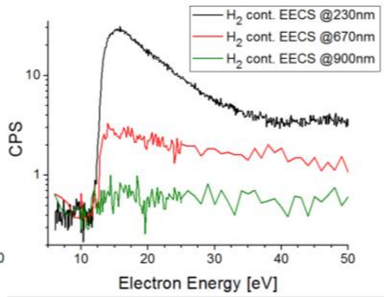

Fig3: H_2 EECSs.

Acknowledgements
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References
[1] B. P. Lavrov et al. 1999 *Phys. Rev. E* **59** 3526
[2] M. Ajello, D. E. Shemansky 1993 *ApJ* **407** 820
[3] H. M. James et al. 1939 *Phys. Rev.* **55** 184
[4] M. Danko et al. 2013 *J. Phys. B* **46** 045203
[5] G. K. James et al. 1998 *J. Geophys. Res.* **103** 2011

Application of diaphragm discharge for acrylic acid deposition on polypropylene non-woven for adhesion improvement

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Polypropylene non-woven textile (PPNT) treatment via plasma generated by diaphragm water-based acrylic acid (AAc) solution discharge was studied in order to improve the PPNT adhesion. For plasma generation a high voltage (~25 kV) thyratron with frequency of 100 Hz and microdischarge duration in order of ns was applied. The exposure time for 3 mm long diaphragm and speed of PPNT movement through it was determined as 3.5 s. The concentration of AAc in water was 5, 10, 20 and 30% that corresponded to conductivity of solution 1.85, 2.39, 2.11 and 1.7 mS/cm, respectively. Treated PPNT strip was cut in half, one half was 2-times washed in distilled water and the second half was kept unwashed. Then the samples were dried at 60 °C for 20 min. Ageing effect after 8 days was investigated, too.

In general, within error bars the strike-through time was shorter for unwashed than for washed samples and it decreased with increasing percentage of AAc in water. The unwashed samples treated in 10, 20 and 30% AAc solution achieved strike-through time ~3 s ± 0.5 s, which is the standard time for absorbent pad. However, the 30% AAc water solution treated and washed PPNT exhibited longer strike-through time than PPNT treated in 20% AAc, and the same applied to both, washed and unwashed samples of PPNT treated in 30% AAc water solution and stored 8 days. This could be due to quicker polymerization of AAc at higher concentrations and probable cloaking of pores in the textile.

The FTIR measurements showed formation of C=O, C-O and -OH functional groups on PPNT surface that indicates presence of AAc on treated PPNT. Amount of these functional groups increased with increasing AAc concentration in solution. On the washed samples the C=O, C-O and -OH functional groups were found only on 30% AAc treated sample. On aged samples the results of FTIR measurements were the same.

The peel test showed that all PPNT samples treated in AAc solution by diaphragm discharge had better adhesion than PPNT treated only in distilled water. The unwashed samples treated at given AAc concentration could withstand higher load than the same washed samples. The best adhesion was achieved for unwashed sample treated in 5% AAc water solution, where the adhesion was improved to average load 8.9 N/m from the reference sample value of 3.8 N/m. During this measurement the adhesion force pulled PP threads out of the sample. The best adhesion was probably caused by formation of thinner AAc layer comparing to the other samples, where the deposited AAc layer was consisting of Aac layer with higher thickness.

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Frequency response of microdischarges in argon

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This paper contains results of the experimental and theoretical studies on electrical breakdown characteristics direct current argon microdischarges for the gaps between 1 µm and 100 µm. The breakdown voltage curves and Volt-Ampere characteristics proved to be a fertile basis for studies of discharges in microgaps. The breakdown phenomena have been discussed in terms of field emission of electrons from the cathode. The obtained results are in a good agreement with the theoretical predictions which state that Townsend phenomenology breaks down when field emission becomes the key mechanism leading to the breakdown Space charge effects are also estimated and distinction between Fowler-Nordheim field emission and space charge limited current density is analyzed. The effective yields estimated from the measured breakdown voltage curves, confirm that the secondary electron emission due to high electric field generated in microgaps depends primarily on the electric field leading directly to the violation of the Paschen's law.

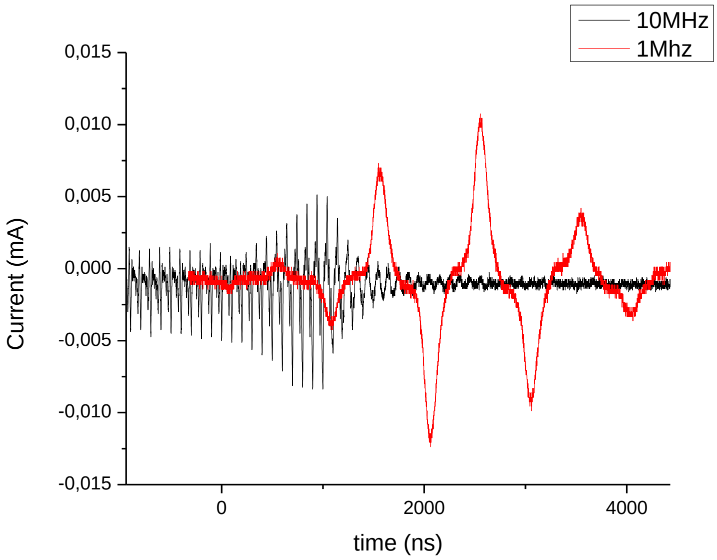

Fig. 1: Comparison of current waveforms of 10MHz and 1MHz Argon discharge

Experimental data are supported by the theoretical predictions that suggest departure from the scaling law and a flattening of the Paschen curves at higher pressures. The obtained results may provide better understanding of the breakdown phenomena in microgaps. A discharge region similar to arc at the pressure of around 200 Torr has been observed.

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Atmospheric pressure low-temperature plasma for calcination of ceramic nanofibers

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Inorganic ceramic fibers (Al_2O_3, SiO_2, TiO_2, ZnO, etc.) are one of the most studied materials in the submicron region. They are usually prepared by thermal calcination of composite metal-organic fibers [1]. The basis of these composite fibers is the carrier polymer material - *base polymer* and *precursor* serving as a source of inorganic material. Composite organometallic fibers are prepared from this "cocktail" using standard spinning techniques (electrospinning, forcespinning, chemical spinning) [2]. Then, the composite fibers are transformed to ceramics by heat treatment in the process of *thermal calcination*. Thermal calcination is used for removing the organic base polymer by the preparation of inorganic submicron fibers. It proceeds at high temperature (500-1000°C) for several hours (5-10 hrs). Due to the high temperature approach and long treatment times, conventional thermal calcination needed by the processing of inorganic submicron fibers is significantly time- and energy-consuming process. High temperature also limits preparation of submicron fibers from many materials.

Recent research is focused on the searching for the procedures to prepare inorganic fibers by simpler, low temperature and economic way. The use of plasma is one of the potential alternatives [3]. Plasma technologies are successfully replacing a number of processes in many fields of industry. With a large number of parameters by which the properties of plasma can be customized for a required purpose, it is an ideal tool for the removal of the organic polymer at room temperature in a relatively short time [4,5].

In this work we study the plasma assisted calcination of various types of submicron composite fibers by using Diffuse Coplanar Surface Barrier Discharge (DCSBD) [6,7]. The effect of plasma on the composite fibers comprising two types of polymers and several types of precursors prepared by two different spinning techniques (electrospinning and forcespinning), was examined in terms of the organic polymer removal using several of surface diagnostic techniques (FTIR, EDX, XPS). The influence of plasma on the morphology of the fibers was investigated by SEM and X-ray diffraction (XRD). The samples were also studied using the CHNS analysis to determine the total carbon in a sample and thermogravimetric analysis to investigate the changes in the thermal degradation of organic material.

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References

[1] K. Starbova, D. Petrov, N. Starbov, and V. Lovchinov, *Ceram. Int.*, **38**, 4645–4651 (2012).

[2] K. Sarkar, C. Gomez, S. Zambrano, M. Ramirez, E. De Hoyos, H. Vasquez, and K. Lozano, *Mater. Today*, **13**, 12–14 (2010).

[3] Y. Li, P. Kuai, P. Huo, and C. jun Liu, *Mater. Lett.*, **63**, 188–190 (2009).

[4] P. Baroch, J. Hieda, N. Saito, and O. Takai, *Thin Solid Films*, **515**, 4905–4908 (2007).

[5] H. Wang, H. Tang, J. He, and Q. Wang, *Mater. Res. Bull.*, **44**, 1676–1680 (2009).

[6] M. Černák, D. Kováčik, J. Ráhel', P. St'ahel, A. Zahoranová, J. Kubincová, A. Tóth, and L. Černáková, *Plasma Phys. Control. Fusion*, **53**, 124031 (2011).

[7] V. Medvecká, D. Kováčik, A. Zahoranová, and M. Černák, *Appl. Surf. Sci.*, **428**, 609–615 (2018).

Fluorescence of hydrogen induced by monoenergetic electrons

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Hydrogen is the simplest molecule and at the same time its importance in different fields of science and technology is very high. This gas is used in many applications of low and high temperature plasma physics as well. Therefore, there is a great interest in the spectrum of this gas. The spectra of molecular hydrogen are studied from beginning of the 20th century [1, 2]. The spectrum is very rich containing more than 3000 rotational lines. The excitation and dissociative excitation of H_2 by electron impact started early [3], followed by studies Lyman and Balmer's emission studies [4], Fulcher bands [5], VUV continua studies [6] and UV-NIR spectra of H_2 to mentions just several of the large number of studies. In this work we present the results concerning the electron impact excitation and dissociative excitation of hydrogen molecule. We present the emission spectra induced by 50 eV monochromatic electrons in the spectral range 200 - 700 nm. For several emission lines we present excitation curves with determined threshold values.

Nearly monoenergetic electrons form a beam in trochoidal electron monochromator. The effusive molecular beam and the electron beams collide in the collision chamber producing excited molecules and atoms emitting photons. These photons are analysed using Czerny-Turner optical monochromator and later detected by Hamamatsu photomultiplier working in photon-counting regime.

The experimental measurements have two modes: i) spectrum mode at fixed electron energy and ii) excitation curve mode at wavelength set to a particular emission line or band and the electron energy is increased from in 0.1 eV steps. Hydrogen spectrum was detected at the electron energy of 50 eV. In the spectrum the Balmer's series lines (H_α - H_ζ) and Fulcher systems ($\alpha - \delta$) were identified. Apart from them the continuum H_2 ($a^3\Sigma^+_g \rightarrow b^3\Sigma^+_u$) was identified as well. The excitation curves were measured at the wavelengths corresponding to the Balmer's series lines. At this wavelength the continuum and Balmer's line are superimposed and the continuum excitation curve measured at different wavelength had to be subtracted to determine the H_α threshold.

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References

[1] O.W.Richardson, T.B. Rymer: Proc. R. Soc. Lond. A **147**, pp 24 (1934)
[2] H.G. Gale, G.S. Monk, K.O. Lee: The Astrophysical Journal **2**, pp 89 (1928)
[3] P. M. S. Blackett and J. Franck: Z. Physik **34**, pp 389 (1925)
[4] D. A. Vroom, F. J. De Heer: J. Chem. Phys. **50**, pp 580 (1969)
[5] G.R. Möhlmann, F.J. De Heer: Chem. Phys. Lett. **43**, pp 240 (1976)
[6] H. Abgraall, E. Roueff, X. Liu, D.E. Schemansky: Astrophys. J. **481**, pp 557 (1997)
[7] A. Aguilar, J. M. Ajello, R.S. Mangina, G. K. James, H. Abgrall, E. Roueff: Astrophys. J. Suppl. Ser. **177**, pp 388 (2008)

Inactivation of fungal contamination on nuts by cold atmospheric pressure plasma

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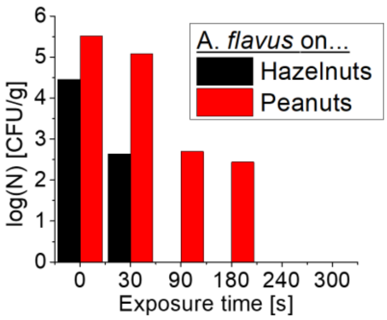
The low-temperature (LT) non-equilibrium plasma is the prospective alternative to high temperature or chemical processes for application in medicine, biotechnology, food industry and agriculture for bio-decontamination, increase of biocompatibility or other surface modification of biological and non-biological material [1–3]. Nuts are important commodity in human nutrition. Since the effect of plasma on the decontamination of surface of various kind of nuts is widely studied issue [4,5], the impact of plasma on the quality, surface properties, biological compounds and ageing effect of nuts has not been studied in detail.

In our work, we analysed the influence of cold atmospheric pressure plasma generated by Diffuse Coplanar Surface Barrier Discharge (DCSBD) [6] on the properties of hazelnuts (*Corylus avellana*) and peanuts (*Arachis hypogaea*) depending on exposure time of samples in plasma. DCSBD generates non-thermal macroscopically homogeneous diffuse plasma in ambient air and it was successfully used for decontamination of wheat, black peppercorn or almonds [7–9].

The changes in chemical bonds on the surface and inside the samples were measured by Attenuated Total Reflectance Fourier Transform Spectroscopy (ATR-FTIR) immediately after plasma treatment and after 1 and 3 months after storage. The influence of plasma on morphology of nuts was observed by Scanning Electron Microscope (SEM). The antioxidant effect was evaluated by different assays for the analysis of antiradical activity and reducing ability of antioxidants presented in nuts. Since hazelnuts and peanuts are food with high content of fat qualitative parameters of oil were also studied.



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References:

[1] S. Cheruthazhekatt *et al.*, *Journal of Applied Biomedicine*, **8** (2010), 55.
[2] G. Fridman et al., Plasma Processes and Polymers, **5** (2008), 503.
[3] K. Shimizu, H. Fukunaga, M. Blajan, *Current Applied Physics*, **14** (2014).
[4] P. Basaran, N. Basaran-Akgul, L. Oksuz, *Food Microbiology*, **25** (2008), 626.
[5] B.G. Dasan, M. Mutlu, I.H. Boyaci, *International Journal of Food Microbiology*, **216** (2016), 50.
[6] M. Černák et al., Plasma Physics and Controlled Fusion, **53** (2011), 124031.
[7] A. Zahoranová et al., Plasma Chemistry and Plasma Processing, **36** (2016), 397.
[8] S. Mošovská *et al.*, *Food Research International*, **106** (2018), 862.
[9] C. Hertwig et al., Innovative Food Science and Emerging Technologies, **44** (2017), 242.

Mechanism of corona discharge (CD) atmospheric pressure chemical ionization (APCI) with and without NH_3 dopant studied by ion mobility spectrometry combined with mass spectrometry

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We have studied atmospheric pressure chemical ionization (APCI) mechanism of 2-nonanone, cyclopentanone, acetophenone, pyridine, and di-tert-butyl pyridine (DTBP) by IMS combined with orthogonal acceleration time-of-flight mass spectrometry (TOF-oaTOFMS). The IMS and MS spectra were recorded after APCI ionization in zero air gas with and without NH_3 dopant ($NH_4^+.(H_2O)_n$ n=0,1 and $H_3O^+.(H_2O)_n$, n=2,3 reactant ions, respectively). The MS spectra showed that, in the absence of dopant, ionization of all compounds proceeds via proton transfer from $H_3O^+.(H_2O)_n$, whereas in the presence of NH_3 dopant (with $NH_4^+.(H_2O)$ reactant ion) two different ionization processes occur i) protonation for molecules with proton affinities (PA) higher than that of NH_3, ii) NH_4^+ attachment, for molecules with lower proton affinity. We have studied ionization of acetamide, which is a model molecule with two proton acceptor sites. Ionization with $H_3O^+.(H_2O)_n$ leads to more complex IMS and MS spectra. Addition of NH_3 dopant results selectively in NH_4^+ attachment to more basic site (O atom) and consequently substantial simplification of IMS and MS spectra.[1-3]

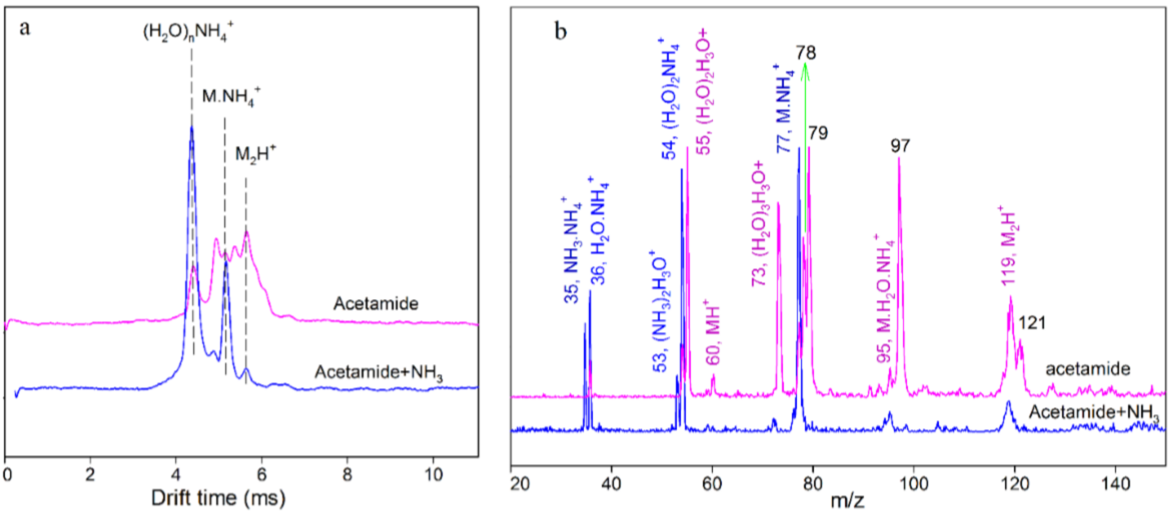

Fig. 1 Comparison of the (a) IMS and (b) MS spectra of acetamide with and without NH3 dopant.

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References

[1] V. Ilbeigi, M. Sabo, Y. Valadbeigi, S. Matejcik and M. Tabrizchi, J. Chromatogr. A 2016, 1459, 145–151.

[2] R. G. Ewing, G. A. Eiceman, C. S. Harden and J. A. Stone, Int. Journal. Mass Spectrom. 2006, 255–256, 76–85.

[3] M. Sabo and S. Matejcik, Anal. Chem. 2012, 84, 5327–5334

Ion mobility spectrometry monitoring of phthalate isomers

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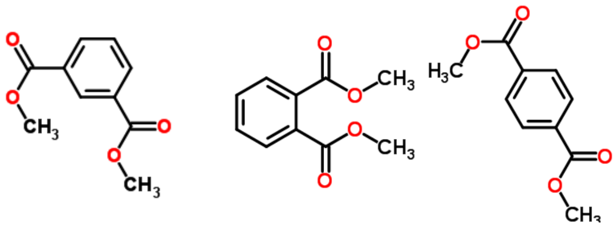
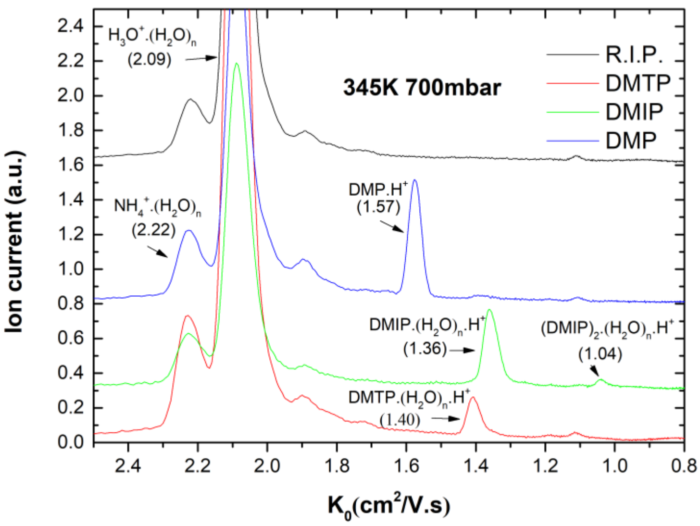
In this work we present the separation of the isomers of DMP in positive polarity IMS in combination with APCI ion source based on corona discharge. The differences in ion mobility spectra of the isomers were significant, and larger as expected from geometry differences of the isomers. IMS offers detection of low concentraton of vapours in air with high sensitivity combined with fast response time and sufficient spectral resolution and therefore is suitable for online monitoring of these compounds. In present work Dimethyl phthalate (DMP) Dimethyl isophthalate (DMIP) and Dimethyl terephthalate (DMTP) vapours mixed with ambient air at atmospheric pressure were investigated.





IMS spectrum of DMP isomers at temperature 345K and gas pressure 700mbar.

The displayed spectra were measured at relative low concentration, for this reason dimers peaks were observed only for the DMIP molecule, which has a stronger affinity to build clusters. At elevated drift gas temperature of 72C, all three isomers have been detected. APCI of these molecules results in the formation of the monomer ion peaks with reduced ion mobility of 1.57 $cm^2V^{-1}s^{-1}$ (DMP), 1.36 $cm^2V^{-1}s^{-1}$ (DMIP) and 1.40 $cm^2V^{-1}s^{-1}$ (DMTP).

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Electrical breakdown in water: The statistical study

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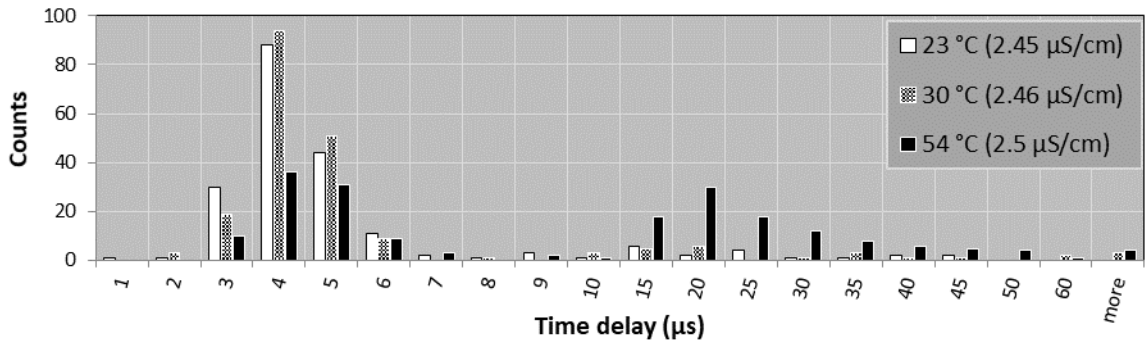
Electrical discharges are nowadays a subject of a wide interest of many scientific groups [1]. They are also used in lot of environmental and medical applications as a source of a dense non-equilibrium plasma, which contains many active species, UV-radiation and shockwaves [2, 3]. However, there is still no comprehensive theory describing breakdown mechanisms and effects of various parameters.
In this work, we have focused on the fundamental research of breakdown time-delay. Time-delay distribution may carry useful information about dielectric strength of the water, initiation mechanism or streamer speed. Experimental measurements were made for low energy pulses (up to 0.5 J) in water with low conductivity. We have evaluated effect of water conductivity and temperature on time-delay of breakdown. We have found out that effect of these parameters cannot be generalized for initiation of microsecond and super-microsecond electrical breakdown. We assumed there is possibility to statistically resolve time-delay of breakdown into statistical delay and formative time by exponentially modified Gaussian distribution.



Effect of water temperature on time delay. *Every plot consists of 200 measurements. Conditions: electrode spacing 0.5 mm, voltage 5 kV, conductivity 2.5 µS/cm, flow rate 0.8 lit/min, switching frequency 1/3 Hz.*

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References

[1] Bruggeman P. and Leys C.. ‘Non-thermal plasmas in and in contact with liquids‘, *Journal of Physics D: Applied Physics*,vol. 42, no. 5, pp. 053001, 2009.

[2] Akiyama H., ‘Streamer Discharges in Liquids and their Applications’, *IEEE Trans. Dielectr. Electr. Insul.*, vol. 7, no. 5, pp. 647–652, 2000.

[3] S. Xiao, R. P. Joshi, J. F. Kolb, and K. H. Schoenbach, “Nanosecond, electrical triggering of water switches,” *IEEE Trans. Dielectr. Electr. Insul.*, vol. 16, no. 4, pp. 1066–1075, 2009.

[4] K. M. Bhatta, “Electrohydraulic lithotripsy,” 5,152,768, 1992.

[5] C. M. Brablec A., Slavicek P., Stahel P., Cizmar T., Trunec D., Simor M., “Underwater pulse electrical diaphragm discharges for surface treatment of fibrous polymeric materials,” *Czech. J. Phys*, vol. 52, no. Suppl. D, pp. D491–D499, 2002.

Examination of dielectric water discharge behavior

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Electrical discharges in or in contact with water have been frequently aim of study for last few decades. Discharges in (or in contact with) water are source of pressure shockwaves, UV emission, and many active species (Bruggeman, 2009). They have found application in engineering, medical, environmental and many other applications (Akiyama, 2000). In this work we presented two types of the discharges occurring under the same conditions in very low conductive water. Their preliminary electrical and spectroscopic measurements, energy effectivity evaluation and optimization and plasma activated water analysis. Contaminated alfalfa seeds and lentils were treated by the plasma activated water with visible, but still unsatisfactory, decontamination effect.
Examined discharges were generated by positive pulsed HV source up to 40 kV on sharped metallic rod electrode, slightly submerged into water. Grounded electrode was placed around the perimeter of water container bottom. First type of discharges occurs on the water lever spreading from HV electrode, maximizing charge draining surface of the water level, generated air plasma reacts with water producing, HNO_3, NH_3 another other metastable and radicals. The second type occurred under the water on the sharp wedge-shaped end of HV electrode and have partial volume discharges properties. Partial volume discharges (PVD) occurred with time-delay 20 to 200 µs, generates mostly water radicals like OH, H_2O_2, H_3O^+. Preventing both discharges occurring at the same time, by the insulating stressed part of electrode, allowed us to study the both breakdowns separately fig. 1. Time-delay investigation have outlined possible energy efficiency optimization of PVD for further application research. Temporary inability to drain electrical charge from electrode or plasma channel showed to be crucial for surface discharge. PVD also showed up as preferring low conductivity water.

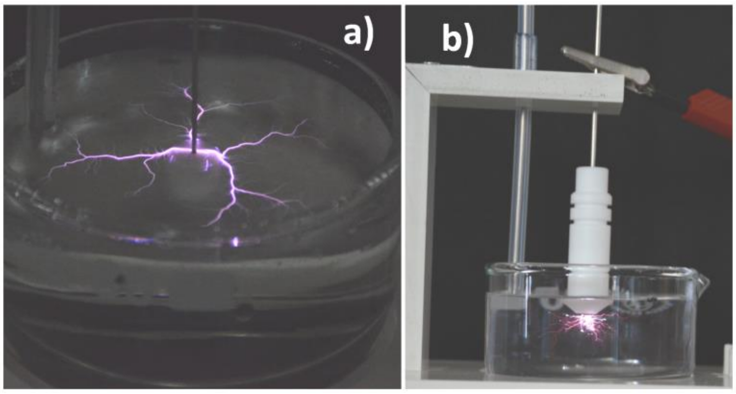

Figure 1. Dielectric surface discharge a) and partial volume discharge b)

Acknowledgement
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References

Akiyama H., ‘Streamer Discharges in Liquids and their Applications’, *IEEE Trans. Dielectr. Electr. Insul.*, vol. 7, no. 5, pp. 647–652, 2000.
Bruggeman P. and Leys C.. ‘Non-thermal plasmas in and in contact with liquids‘, *Journal of Physics D: Applied Physics*,vol. 42, no. 5, pp. 053001, 2009.

Electron impact excitation of gases relevant for Titan atmosphere

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In the recent history the Titan is of great interest within the scientific community. One of the reasons is the composition of its atmosphere resembling the early Earth atmosphere. The Cassini space mission to Saturn with its Huygens probe aimed at the Titan provided wealth of data on the composition of its atmosphere. As the optical emission spectroscopy is one of the most important methods of investigating the atmosphere the availability of precise and reliable data on molecular spectra and cross-sections is crucial. The electron induced fluorescence is a method that can provide such data. It is a tool to study the electronic states of the molecules by observing emission from the molecules or their fragments after impact of mono-energetic electrons. Electrons with well-defined energy collide with molecules and excite their electronic, vibrational and rotational states. Unlike photon excitation, the electron impact allows us to study also optically forbidden excited states and their subsequent radiative decay to lower states. Using the crossed-beams apparatus it is possible to measure emission spectra at selected electron energy, or the excitation curves for selected spectral line or band. In this way it is possible to study the excited states of the molecules, emission from these states and the efficiency of the overall process as a function of the energy of the exciting electrons.

In this work we focus on investigating the spectra of methane and nitrogen, the main constituents of the Titan's atmosphere. For nitrogen we present the emission spectrum of nitrogen second positive system where we were able to identify lines corresponding to 25 transitions. It is an improvement in comparison to former studies where 10 lines have been identified. We have measured emission spectra of nitrogen in range 280-440 nm initiated by impact of electrons with 14 eV energy.

For methane we have measured emission spectra of methane in range 180-700 nm initiated by impact of electrons with 30, 50 and 80 eV energies. We also measured relative emission cross sections for different dissociative excitation processes including hydrogen lines of Balmer series, CH(A-X, B-X and C-X) transitions and C line, and identified their threshold energies.

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The mass spectrometry of electron attachment to gas-phase and clusters of octafluorocyclobutane

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Last few years a great effort of Electron Plasma Processes Laboratories (EPPL) at the Comenius University in Bratislava has been applied to understand the elementary processes of low-energy electron interactions with precursor molecules relevant to nano-technology [1-5]. We have studied several precursors available for deposition of Fe, Co, Cu, Zn, Ni, Si or W layers. Most recently the gas-phase experiments were upgraded to cluster measurements to reveal the behavior electron attachment of a c-C_4F_8 precursor in larger environment. Our gas phase DEA measurements on c-C_4F_8 were compared with Harland and Thynne [6], with good agreement of the F^-, F_2^-, CF_2^-, CF_3^- and $C_3F_5^-$ cross sections, however on a larger energy range from 0 – 18 eV. New cross sections were obtained for DEA products $C_2F_3^-$, $C_2F_5^-$, c-$C_4F_7^-$ and for the molecular ion c-$C_4F_8^-$ with a strong resonance at ~0 eV. In the cluster environment we have detected core exited resonances as well for the molecular ion which were not observed in the gas phase, these resonances became more significant with increasing size of the (c-$C_4F_8)_nC_4F_8^-$ cluster size. These are the dominant products of electron attachment of the c-C_4F_8 cluster spectrum, other significant products are formed via competitive reactions, formation of F^- and (c-$C_4F_8)_nF^-$ vs c-$C_4F_7^-$ and (c-$C_4F_8)_n$c-$C_4F_7^-$. Here the dominant resonance above 4 eV measured in the gas phase is strongly suppressed with the clusters. New ions have been observed in the monomolecular part of the cluster spectrum contrary to the gas phase spectrum of DEA to c-C_4F_8, namely $C_2F_4^-$, $C_3F_6^-$ and c-$C_4F_6^-$.

Acknowledgments

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References

[1] Lacko, M., Papp, P., Szymanska, I.B., Szlyk, E, and Matejčík, Š.; Beilstein J. Nanotechnol. 9, 384, 2018

[2] Lengyel, J., Papp, P., Matejčík, Š., Kočišek, J., Fárnik, M., and Fedor, J.; Beilstein J. Nanotechnol. 8, 2200, 2017

[3] Lacko, M., Papp, P., Wnorowski, K., and Matejčík, Š.; Eur. Phys. J. D 69, 84, 2015

[4] Engmann, S., Stano, M., Papp, P., Brunger, M. J., Matejčík, and Š., Ogólfsson, O.; J. Chem. Phys. 138, 044305, 2013

[5] Papp, P., Engmann, S., Kučera, M., Stano, M., Matejčík, and Š., Ogólfsson, O.; Int. J. Mass. Spectrom. 356, 24, 2013

[6] Harland, P.W., and Thynne, J.C.J.; Int. J. Mass Spectrom. Ion Phys. 10, 11, 1972/73

Non-radioactive electron gun operating at atmospheric pressure

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Recently, electron guns with nanomembrane vacuum-atmosphere interface (window) of 300 nm thickness were reported, applicable for transport of keV electrons from vacuum to atmosphere [1-3]. Such electron sources are suitable replacements for radioactive ion sources based on β radiation and could be applied for Atmospheric Pressure Ionization (API) in Mass Spectrometry (MS) and Ion Mobility Spectrometry (IMS) or other analytical methods at atmospheric pressure (fluorescence) [4].

In this work we present results of recent studies involving absolute measurements of electron currents after transition through very thin Si_3N_4 membrane as a function of initial kinetic energy of electrons E_i.

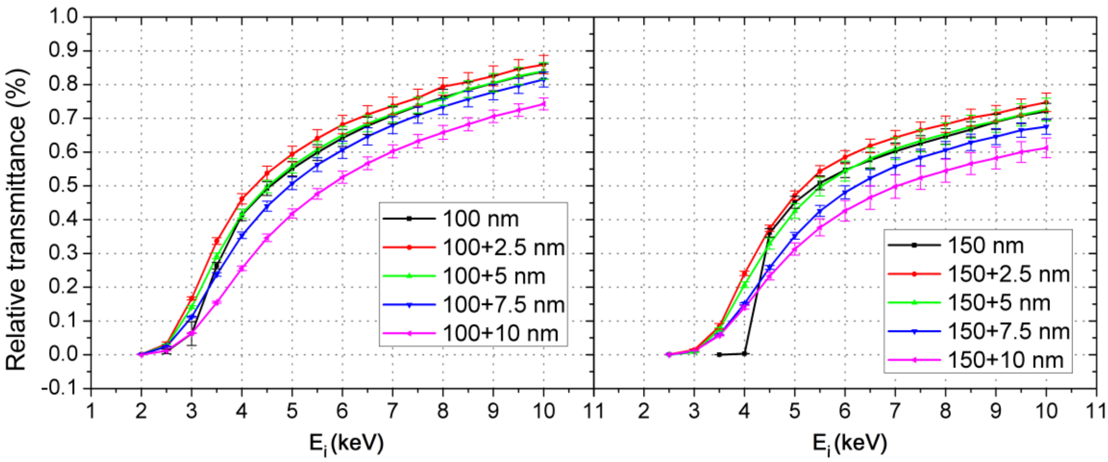

Figure 1: The relative electron transmittances of Si_3N_4 membranes with thicknesses of 100 (left) and 150 nm (right). The thicknesses of gold films are written after the plus signs in both legends.

Figure 1 presents the relative transmittances of electrons for all investigated membranes. The relative transmittances were calculated as a ratio of the absolute transmission current of the investigated membrane to the reference current of the square aperture at given E_i. We have prepared gold plated membranes with thicknesses of the gold films of 2.5, 5, 7.5 and 10 nm for both 100 and 150 nm membranes. The figure indicates that the deposited 2.5 nm gold film improves the electron transmittances of both types of membranes.

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References

[1] F. Gunzer et al. 2010 Int. J. Ion Mobil. Spec. 13 9-16.
[2] P. Cochems et al. 2012 Int. J. Ion Mobil. Spec. 15 223-229.
[3] P. Cochems et al. 2009 Sens. Actuators A: Phys. 206 165-170.
[4] A. Ulrich et al. 2009 Eur. Phys. J. Appl. Phys. 47 22815.

Porous polypropylene membranes grafted by polyacrylic acid applied as separators in alkaline water electrolysis cell

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Connection of alkaline water electrolysers with intermittent renewable energy sources like wind power or photovoltaics in power-to-gas applications sets high requirements on inter-electrode separator. In order to operate safely even at low current density, permeation of the produced hydrogen and oxygen gases through the separator must be minimized [1]. To achieve this, high wettability of separator membrane by the electrolyte is necessary. Today, the state of the art separators are composites of polymers and inorganic fillers, where polymer provides mechanical support, while the filler enhances wettability [2]. However, to achieve required wettability, high content of mineral filler is necessary, resulting in weakened mechanical strength.

In this work we evaluate performance of porous polypropylene (PP) membranes grafted by polyacrylic acid (pAAc) as inter-electrode separators in alkaline water electrolyser. This technique modifies only the very top sufrace layer of material, providing high wettability without deteorioration of mechanical properties of the PP substrate. Nonwoven PP textile of 80 g/m^2 were activated in low-pressure capacitively-coupled discharge in oxygen at 13 MHz. Graft polymerization of AAc onto activated samples was performed in aqueous solution of AAc at concentration of 20% and temperqature of 80°C. The grafted membranes were washed in 0.1 M solution of KOH, rinsed with distilled water and dried in air at 50°C. Grafting degree (GD) was determined gravimetrically.

Ageing of surface modification was examined in 30 wt. %. The study revealed major mass depletion during the very first period of ageing test and remained at level of about 1 wt. %. We assume this initial weight loss to be associated with gradual dissolution of homopolymer, possibly trapped in separator pores. Despite the transient ageing effect, the membranes remain wettable by liquid with surface tension of 103.8 mJ/m^2.

The modified membranes were applied in alkaline water electrolyser to determine their specific resistance. The measurements of ohmic overvoltage created on the membrane as a function of cell current density was realised by electrochemical probe electrodes. For PP membranes of ~ 400 µm thickness, 75 % porosity and grafting degree of 2.3 – 3.2 wt. % we obtained specific resistances ranging from 35 mΩcm^2 to 28 mΩcm^2. The purity of produced gases was analysed by self-constructed thermal conductivity detector (TCD). When operating at current densities down to 100 mA/cm^2, the concentration of oxygen in hydrogen and vice versa was less than 0.14 % and 0.10 %. These values are comparable or less than those obtained by using Zirfon^R as a state of the art separator membrane. The impurity of gases at cell current density of 200 mA/cm^2 reported by Xu et al. was about 0.41 % and 0.47 % for hydrogen and oxygen, respectively [3].

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References

[1] A. Godula-Jopek, *Hydrogen production: by electrolysis*. Weinheim, Germany: John Wiley & Sons, 2015.

[2] D. Burnat *et al.*, "Composite membranes for alkaline electrolysis based on polysulfone and mineral fillers," *J. Power Sources*, vol. 291, pp. 163–172, Sep. 2015.

[3] L. Xu, W. Li, Y. You, S. Zhang, and Y. Zhao, "Polysulfone and zirconia composite separators for alkaline water electrolysis," *Front. Chem. Sci. Eng.*, vol. 7, no. 2, pp. 154–161, Jun. 2013.

Formation of hydroperoxide functional groups on polypropylene surface by low temperature plasma treatment

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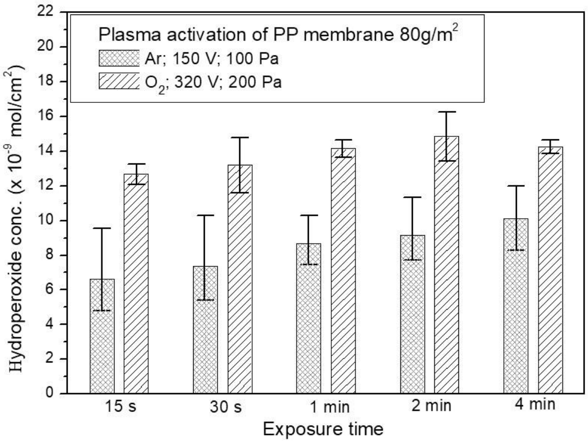
Wettability of polypropylene (PP) can be greatly improved by graft polymerization of poly-acrylic acid on its surface. In order to achieve good durability of the grafted material, the polymerization of acrylic acid (AAc) must be initiated by radicals present on the surface of the PP substrate [1].

The present work deals with optimization of plasma treatment of a PP nonwoven textile for formation of hydroperoxide functional groups. The hydroperoxides are thermally unstable and can be used as initiators of graft polymerization of AAc from a solution. The plasma treatment was done in a low-pressure RF discharge in argon or oxygen at 13 MHz. Concentration of hydroperoxides created on the polymer surface was quantified by a reaction with 2,2-Diphenyl-1-picrylhydrazyl (DPPH) [2]. DPPH is a stable free radical which selectively reacts with ·OH radicals coming from thermally-induced scissions of –OOH functional groups. As a consequence of the reaction, optical absorption spectrum of DPPH changes and the amount of DPPH consumed can be determined from Beer-Lambert law. Transmittance was measured by a spectrophotometer at $\lambda = 520$ nm. The solution used was 2x10-7 mol/ml DPPH dissolved in toluene. Glass ampoules (volume of 10 ml) with the reagent were put into an oven and kept at 70 °C for 3 h to thermally decompose hydroperoxides.

Figure shows concentrations of hydroperoxides achieved by various treatment time for both argon and oxygen plasma. It can be seen that treatment in oxygen plasma is more efficient. The hydroperoxide concentration increases with treatment time, but this increase is not very strong. Prolonged treatment may result in degradation of PP surface layer by excessive backbone cleavage, therefore short treatment time of 1 minute and less is sufficient for the surface activation.



Concentration of hydroperoxide functional groups on PP surface after plasma treatment.

Acknowledgement

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References

[1] S. Saxena, A.R. Ray, B. Gupta, Graft polymerization of acrylic acid onto polypropylene monofilament by RF plasma, J. Appl. Polym. Sci. 116 (2010) 2884–2892. doi:10.1002/app.31823.

[2] M. Suzuki, A. Kishida, H. Iwata, Y. Ikada, Graft copolymerization of acrylamide onto a polyethylene surface pretreated with glow discharge, Macromolecules. 19 (1986) 1804–1808.

Plasma assisted calcination of metal-organic ($Al(NO_3)_3$/PAN) fibers

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Recently, ceramic submicron fibers are widely studied material. Great amount of time is dedicated to development of efficient ways of production. Currently most used method of production is a two-step process consisting of spinning of metalo-organic fibers containing base polymer matrix and precursor - most commonly metallic salts or alkoxides. The second step of this method is thermal calcination. During this step, fibers are heated to high temperatures for several hours. One of alternative approaches to thermal calcination is use of non-equilibrium plasma.

The main aim of this work is to study the influence of active species in non-thermal plasma of diffuse coplanar surface barrier discharge (DCSBD) on metal-organic submicron fibers consisting of aluminium nitrate and polyacrylonitrile $Al(NO_3)_3$/PAN.

In this work, we studied the effects of plasma in dependence on the length of treatment, distance of sample from the surface of DCSBD, working gas, parameters of electric source and ambient temperature. Differences in morphology of fibers treated at different conditions were investigated by scanning electron microscope and chemical changes were studied using Fourier transform infrared spectroscopy and energy-dispersive x-ray spectroscopy. With increasing treatment time, we observed decrease of chemical bonds typical for polyacrylonitrile (Fig.1). Power supply with frequency 30 kHz and power of 600 W (source B) proved to be more efficient than power supply with frequency 15 kHz and power of 400 W (Fig. 2). Plasma generated in ambient air was comparable in effect with other working gasses (N_2, O_2, synthetic air, synthetic air with water vapors). With increased ambient temperature during plasma treatment, N_2 ratio in the sample slightly decreased. There was no observed damage on SEM images on any of the treated samples.

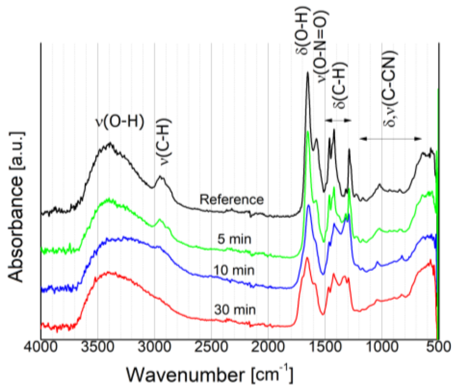

Figure 2: FTIR spectra of $Al(NO_3)_3$/PAN nanofibers after 5, 10 and 30 min plasma

Based on these results, we have chosen few samples for thermal treatment and compared the results to samples untreated by plasma, but thermally calcinated under the same conditions. We observed that samples with plasma treatment were less prone to deformation and breaking due to high heating rate (Fig.3).

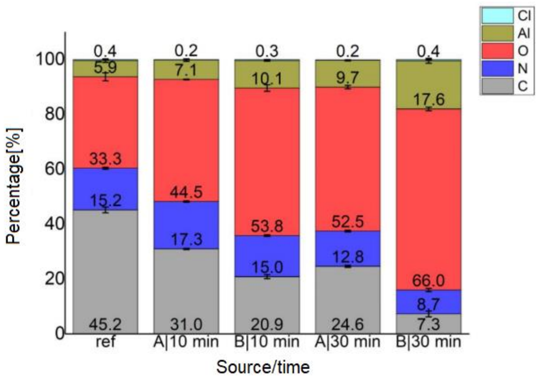

Figure 3: Percentage of mass in $Al(NO_3)_3$/PAN fibers after 10 and 30 min plasma treatment using different power supplies

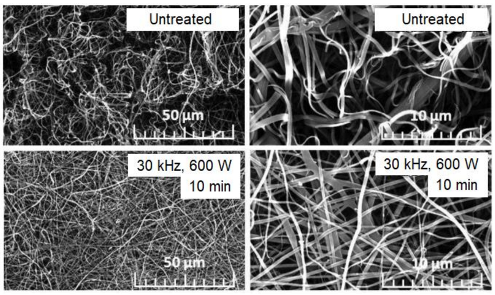

Figure 4: SEM images of untreated and plasma treated fibers after thermal calcination

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Diagnostics of low temperature plasma and of its effect on plant seeds

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In presented work we focused on the treatment of plant seeds (pea, *Pisum sativum*) using low temperature plasma (LTP). As previous works [1,2] show, plasma has a positive impact on germination, growth parameters or removal of pathogens from the seed surface. As a source of low-temperature non-equilibrium plasma we used Diffuse Coplanar Surface Barrier Discharge (DCSBD) [3] for the treatment of pea seeds. We investigated the effect of LTP generated in ambient air, nitrogen and oxygen. For better understanding the mechanisms of plasma influence on seeds, it is important to diagnostics the plasma properties in detail. For this purpose, we have determinate plasma composition and plasma temperature by Optical Emission Spectroscopy and plasma gas composition by Fourier Transform Infrared spectroscopy (FTIR). We carried out the study of the changes in chemical bonds on the seeds surface by the method of Attenuated Total Reflectance FTIR spectroscopy (Fig. 1).

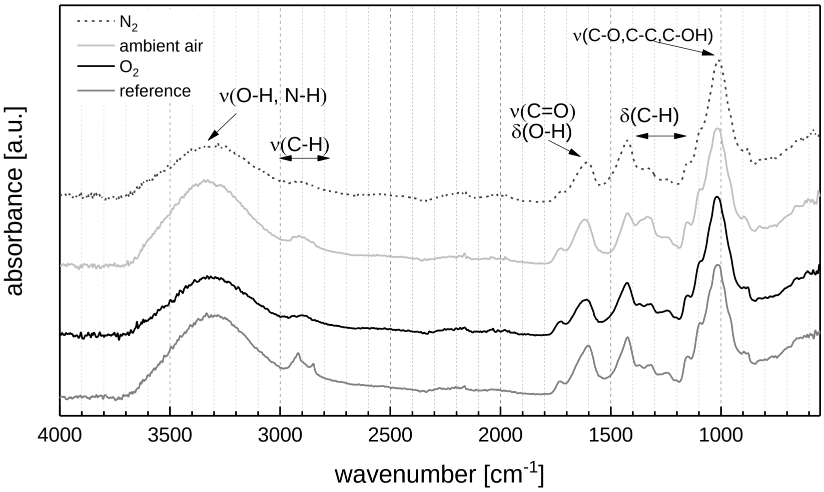

Figure 1: ATR-FTIR spectra from the pea seeds surface treated by nitrogen, oxygen and ambient air plasma in comparison with untreated sample, treatment time: 60s.

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References
[1] Henselová, M. *et al.*, Growth, anatomy and enzyme activity changes in maize roots induced by treatment of seeds with low-temperature plasma*, Biologia*, 67 (3), 490 - 497, DOI: 10.2478/s11756-012-0046-5, 2012.
[2] Zahoranová, A. *et al.*, Effect of Cold Atmospheric Pressure Plasma on the Wheat Seedlings Vigor and on the Inactivation of Microorganisms on the Seeds Surface, *Plasma Chem Plasma Process*, 36, 397–4142016.
[3] Černák, M. *et al.*, Generation of Thin Surface Plasma Layers for Atmospheric-Pressure Surface Treatments, *Contrib. Plasma Phys.*, 44 (no: 5-6), 492-495, DOI 10.1002/ctpp.200410069, 2004.