

The spectroscopic study of a glow discharge generated between pin electrode and water in open air atmosphere

P. Jamroz, W. Zyrnicki

Analytical Chemistry Group, Chemistry Department, Wrocław University of Technology,
Wyb. Wyspińskiego 27, 50-370 Wrocław, Poland

Abstract: The discharge generated between solid electrode and water (working as cathode) was investigated by optical emission spectroscopy. The spectral characteristics of the discharge was examined. High energy species were identified in plasma. The emission intensities of main species were measured versus various experimental parameters. The rotational, vibrational and excitation temperatures were determined and compared for the selected experimental parameters. Additionally, the ion to atom ratio and the electron number density were measured. Plasma processes and plasma non-equilibrium phenomena were discussed. The analytical performance of the plasma source was investigated for selected metals (Zn and Cu) dissolved in water.

Keywords: plasma diagnostics, optical emission spectroscopy, atmospheric pressure glow discharge

1. Introduction

The study of the atmospheric pressure glow discharge (APGD), generated between water and solid electrode, is of a great importance due to their potential application in analytical spectrometry as well as surface and environmental protection engineering [1-4]. This kind of discharge, sometimes called: electrolyte cathode glow discharge (ELCAD) or glow discharge electrolysis (GDE), was applied to determine the concentrations of metals [1,5]. GDE was also employed to modify the surface of materials [2], for purification of water [3] and for the plasma sterilization [3].

Understanding the chemistry and mechanism of plasma processes, occurring in plasma source, requires knowledge of concentrations of species and their energy distributions under various experimental conditions [6]. Optical emission spectroscopy (OES), due to non-invasive character, was often applied for investigation of behaviour of active species as well as determination of plasma (excitation, vibrational and rotational) temperatures.

The spectroscopic characterization of glow discharge operated in open air atmosphere is the main objective of the work. Plasma parameters, such as: excitation, vibrational and rotational temperatures, were determined and compared. In addition, the analytical performance of the plasma source was also investigated.

2. Experimental setup

The atmospheric pressure glow discharge was generated in small Pyrex – glass reactor (diameter 30 mm, total height 70 mm) between solid electrode (anode) and water (working as cathode) in open air atmosphere (see

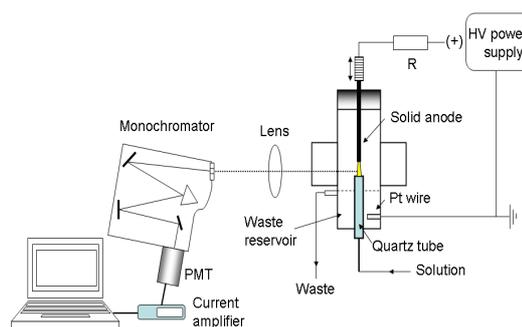


Fig.1 The experimental setup

Fig.1). A high – voltage power supply (max. power 200Watt) was used. To stabilize the discharge current a 1k Ω or 20k Ω ballast resistor between the molybdenum anode (outer diameter 2 mm) and positive output of high – voltage power supply were applied. The discharge current and voltage were: 10 – 60 mA and 700 – 1700 V, respectively. The distance between the solid anode and water surface was maintained by micrometer screw attached to the anode with the precision of 0.1 mm. The gap between electrodes was changed from 0.5 mm to 5 mm. The liquid sample was introduced into the plasma zone by quartz tube, with inner diameter 5 mm, using a peristaltic pump (range of flow rates from 0.65 to 3.2 ml min⁻¹). The grounded platinum wire was used as an electrical contact with the waste solution in reactor reservoir. The solution overflows from quartz tube served as an electrical connection between solution in reservoir and the discharge zone. The water solutions were acidified with hydrochloric, acetic or nitric acid in order

to improve the conductivity.

Emission intensities were measured near the water cathode. The discharge was imaged with an achromatic quartz lens ($f=80$) onto the entrance slit of JY 320 TRIAX scanning monochromator (resolution: 0.04 nm for diffraction grating with 1200 grooves mm^{-1}). A Hamamatsu R-928 photomultiplier biased at -700 V, with current amplifier (JY SpecAcq2 system) was employed as detection system. The SpectraMax/32 software was applied for the data processing. The spectral response of photomultiplier was calibrated by means of CL2 halogen lamp (Protection Engineering Ltd.) with the radiation certificate in the 250 – 800 nm spectra region.

3. Results and discussion

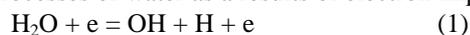
3.1. Emission spectra

3.1.1. The emission spectra for water with the addition of acids.

The spectra of atmospheric pressure glow discharges were measured in the range from 200 to 800 nm wavelength. Firstly, the distilled water acidified by hydrochloric acid were applied. Numerous bands of nitrogen (belonging to the $C^3\Pi_u-B^3\Pi_g$ system) and strong bands of $A^2\Sigma-X^2\Pi$ OH (bands at 281.1 nm and 306.4 nm) were detected (Fig. 2). Additionally, the $A^3\Pi_g-X^3\Sigma^-$ (0-0) NH bandhead at 336.0 nm, partially overlapped by the strong (0-0) $C^3\Pi_u-B^3\Pi_g$ band of N_2 with the bandhead at 337.13 nm was also noticed. Two lines of hydrogen: strong $H\alpha$ at 656.28 nm and weak $H\beta$ at 486.13 nm were observed. The next line of H (i.e. $H\gamma$) at 434.05 was not clearly identified due to the overlapping by the $C^3\Pi_u-B^3\Pi_g$ (0-4) band of N_2 at 434.36 nm. The atomic line of oxygen (O I) was noted at 777.20 nm. Numerous weak bands of NO (γ system) were also identified in the region from 200 nm to 280 nm (bandhead at 271.32; 258.75; 247.11; 236.33; 226.28; 214.86; 204.7 nm). The presence of NO is probably due to the chemical reaction of nitrogen molecules with oxygen (O, O*, O₂).

Comparable emission spectra were observed for solutions containing nitric acid or mixture of hydrochloric and acetic acids. Emission spectra of CN, CH, CO, CO⁺, C and other carbon species have not been detected. It indicates that the decomposition degree of acetic acid was very low and much lower than for water. Additionally, the introduction of acetic acid to the discharge zone cause fall of the emission intensities coming from OH, N₂ and H species in comparison with hydrochloric acid.

The main source of OH and H is the decomposition processes of water as a results of electron impact:



The excited states of nitrogen N₂(C) are produced from

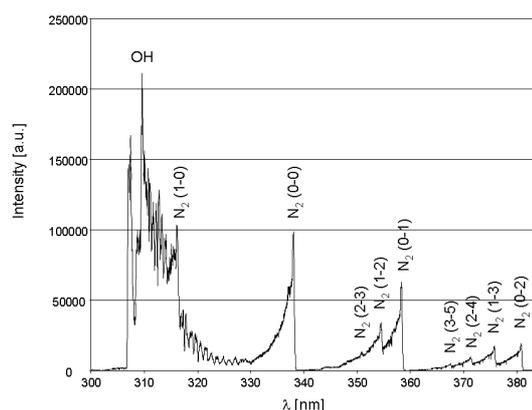
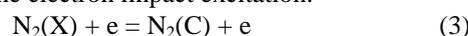


Fig.2 The emission spectra in the region from 300 to 385 nm.

the electron impact excitation:



The emission intensities of the following species: OH (at 306.36 nm), H (at 656.28 nm), N₂ (at 380.2 nm), O (at 777.2 nm) were chosen to monitor the behaviour of active plasma components versus the flow rate of solutions acidified by HCl, gap between anode and cathode and concentration of HCl in solutions. The change of flow rate of solution from 0.65 to 3.2 ml min^{-1} and the concentration of HCl (from 0.01M to 1M) led to increase in the emission intensities of OH, H, O and N₂.

The emission intensities of main species were also monitored as a function of gap between the cathode and anode. The distance between solid anode and water surface (working as cathode) were changed from 0.5 mm to 5 mm. Generally, the maximum values of emission intensities of OH, N₂ and H were found for the gap equal 3.5 mm. This value of gap was applied in all experiment.

Table 1 The most characteristics lines of metals excited in the discharge

Element	Wavelength[nm]	Excitation energy [eV]
Cu	324.75 (Cu I)	3.82
	327.40 (Cu I)	3.78
K	766.49 (K I)	1.62
	769.89 (K I)	1.61
Mg	285.21 (Mg I)	4.34
	279.55 (Mg II)	4.43, E _{ion} =7.64
Mn	279.48 (Mn I)	4.43
	279.83 (Mn I)	4.43
Zn	213.86 (Zn I)	5.80
	481.05 (Zn I)	6.66

3.1.2. The emission spectra for water with the addition of metal ions.

One-element and multi-element water solutions were analyzed. The solutions of metals were acidified by addition of hydrochloric acid. Neutral atom spectra were dominating in the glow discharge (see e.g. Fig.3). Only for the magnesium two ionic lines (Mg II at 279.55 nm

and 280.27 nm) could be measured with relatively high intensity. The most characteristics lines of Cu, K, Mg, Mn and Zn observed here as well as their excitation energies, are listed in the Table 1. Generally the atmospheric pressure glow discharge is much more limited in comparison to ICP or MIP source. The atomic line intensities depended significantly on the experimental conditions, i.e. concentrations of acid and metals, current of discharge, sample intake, electrode gap.

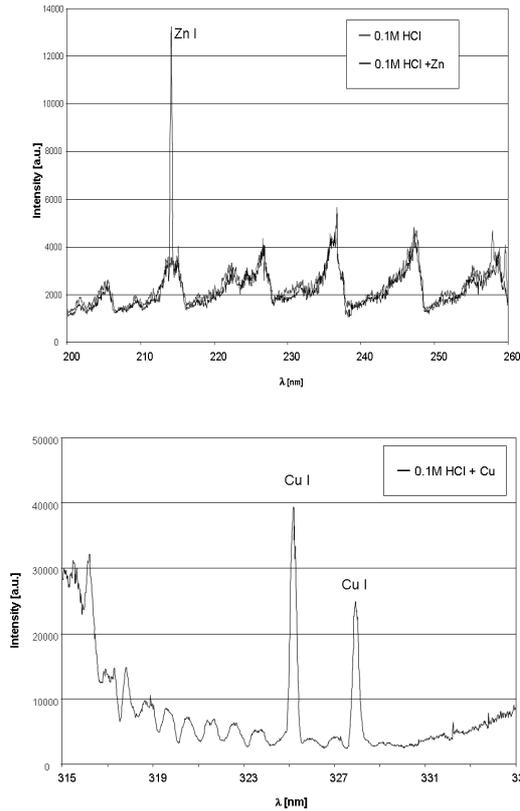


Fig.3 The emission spectra of solution of HCl spiked with a) 10 ppm Zn and b) 10 ppm Cu

3.2. Plasma diagnostics

Optical temperatures are very important parameters for description of energy distributions. The temperature determination from different species permits a characterization of plasma non-equilibrium phenomena and investigation of various plasma processes. The H excitation, N₂ vibrational and OH rotational temperatures were determined here and compared.

The electron excitation temperature was determined using the two line intensity ratio method:

$$\frac{I_1}{I_2} = \left(\frac{g_1 A_1 \lambda_2}{g_2 A_2 \lambda_1} \right) * \exp\left(-\frac{E_1 - E_2}{kT_{exc}} \right) \quad (4)$$

where: I is the emission intensity of line, g – statistical weight, A - transition probability, λ - wavelength of light, E – energy of the upper levels, k – Boltzmann constant.

The two lines of hydrogen: Hα and Hβ, with the energies 12.1 eV and 12.8 eV, respectively, were applied.

The vibrational temperature (T_{vib}) of N₂ was calculated from the relation:

$$\ln\left(\frac{I_{v',v''}}{q_{v',v''} \nu_{v',v''}^4} \right) = C - \frac{G(v')}{kT_{vib}} \quad (5)$$

where: I_{v',v''} – intensity of the vibrational band, q_{v',v''} - the Franck – Condon factor, ν - the transition frequency, G(v') - the vibrational energy of the upper state, v – the vibrational quantum number, C - constant.

The four bands of the C³Π_u-B³Π_g system of N₂, i.e. (3-5); (2-4); (1-3); (0-2), were used. The all band head intensities were measured considering the background corrections, separately for each band. The molecular constants and Franck - Condon factors have been taken from [7,8]. The distribution of the analyzed vibrational levels of N₂ was found to follow Boltzmann law as shown in Fig.4.

To determine the OH rotational temperature, simulated and measured spectra of the (A-X) band of OH at 306.0 nm were compared for various rotational and vibrational temperatures. LIFBASE [9] program was applied for the generation of the simulated spectra of OH.

The uncertainties of the temperature values were evaluated to be: ~ 15 %, ~ 2-10% and ~ 10%, respectively for the excitation, vibrational and rotational temperatures.

The excitation temperature of H and vibrational temperature of N₂ were varied from 3800 K to 4100 K and from 3400 K to 4600 K, respectively. The H excitation and N₂ vibrational temperatures, measured here, were consistent, i.e. T_{exc}(H)≈T_{vib}(N₂), considering the temperature uncertainties. The OH rotational temperature was ~ 3000K. The difference between excitation and rotational temperatures indicated that generated plasma was far from equilibrium state.

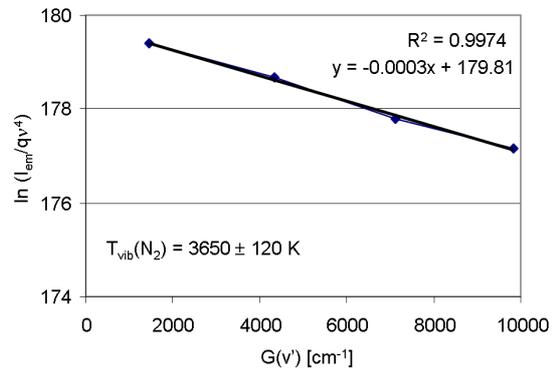


Fig.4 The Boltzmann plot for vibrational levels of N₂

The ion to atom ratio for Mg (MgII/MgI) was determined to be about 0.02. Assuming the mean value of electron temperature ~4000 K, the electron number density (N_e) was determined from Boltzmann – Saha

equation [10]. The average value of $N_e = 3.2 \cdot 10^{12} \text{ cm}^{-3}$ was found for the current 20 mA (pH=1, solution containing HCl and metals dissolved in water). Similar value of electron number density was reported by Mezei and Cserfalvi for the ELCAD source [11].

Cathode fall (U_{cf}) was determined by the anode displacement method [1]. The 970V and 820 V values of U_{cf} were found for 20 mA and 80 mA current, respectively.

3.3. Analytical performance

The analytical performance was investigated for selected metals (Zn and Cu). The solutions of metals were acidified to pH=1 by addition of hydrochloric acid. The calibration curves are constructed for spectral lines of ZnI at 213.86 nm and Cu I at 324.75 nm by plotting the relation between the metal concentrations and their atomic line emission intensities (Fig.5).

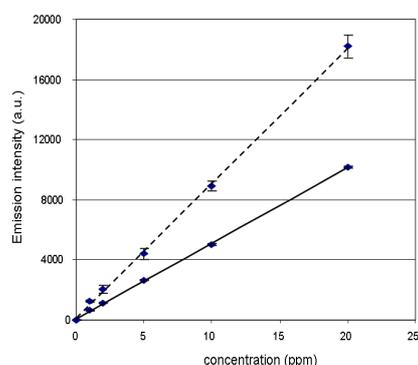


Fig.5 Linear dynamic ranges for Cu (broken line) and Zn (solid line).

The limit of detection (LOD) and limit of quantification (LOQ) were calculated by means of equations: $LOD = 3\sigma/d$ and $LOQ = 10\sigma/d$, where σ is standard deviation of the background signal (BSD) and d is the slope of the calibration curve. Twenty points of background were used for the determination of BSD. The results were presented in Table 2

Table 2 Analytical performance for lines of Zn and Cu

Element	Wavelength [nm]	LOD [ppm]	LOQ [ppm]
Zn	213.86	0.27	0.89
Cu	324.75	0.34	1.14

4. Conclusions

Atomic and molecular species were excited in plasma. The spectra of plasma were dominated by OH, N_2 , H, NH, NO and O species. Atomic lines of metals were observed. The weak ionic lines of Mg (Mg II) were found. The increase of solution flow as well as concentration of HCl

caused the growth of OH, H, O and N_2 emission intensities. The maximum emission intensities of main species were observed in the gap between solid anode and water surface equal to 3.5 mm.

The excitation and vibrational temperature varied in the range: 3800 K - 4100 K and 3400 K - 4600 K, respectively. The relation between the excitation, vibrational and rotational temperatures was as follows: $T_{exc}(H) \approx T_{vib}(N_2) > T_{rot}(OH)$. The electron number density was $3.2 \cdot 10^{12} \text{ cm}^{-3}$. The cathode falls were found at 970V and 820 V for the discharge current equal to 20 mA and 80 mA, respectively.

The very good correlations were found between the emission analytical signals of Zn and Cu and their concentrations in the range from 0 to 20 ppm.

References

- [1] T. Cserfalvi, P. Mezei, *J. Anal. At. Spectrom.* **18**, 596, (2003).
- [2] A.I. Maximov, A.V. Khlustova, *Surf. Coat. Technol.* **201**, 8782, (2007).
- [3] A. A. Ivannikov, V. M. Lelevkin, A. V. Tokarev, V. A. Yudanov, *High Energ. Chem.* **37**, 115, (2003).
- [4] Z. Machala, M. Janda, K. Hensel, I. Jedlovsky, L. Lestinska, V. Foltin, V. Martisovits, M. Morvova, *J. Mol. Spectrosc.* **243**, 194, (2007).
- [5] M.R. Webb, F.J. Andrade, G.H. Hieftje, *Anal. Chem.*, **79**, 7899, (2007).
- [6] P. Jamroz, W. Zyrnicki, *Vacuum* **82**, 651, (2008).
- [7] L. Bardos, H. Barankova, Th. Welzel, I. Dani, S. Peter, F. Richter, *J. Appl. Phys.* **90**, 1703, (2001).
- [8] P. Jamroz, W. Zyrnicki, *Eur. Phys. J. Appl. Phys.* **19**, 201, (2002).
- [9] J. Luque, D.R. Crosley, LIFBASE: Database and Spectral Simulation Program, SRI International Report MP 99-009 (1999).
- [10] J.A.C. Broekaert, *Analytical Atomic Spectrometry with Flames and Plasmas*, WILEY-VCH, Weinheim, 2002.
- [11] P. Mezei, T. Cserfalvi, *Eur. Phys. J. Appl. Phys.* **40**, 89, (2007).