Applied Plasma Chemistry – New Practical Exercises

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Abstract
Three new practical exercises oriented on the application of plasma chemical processes are presented. Two exercises for the special practical course are focused on the study of processes in the DC diaphragm discharge in a water solution. The first measurement is the hydrogen peroxide generation, the second part of the task studies destruction of the chosen organic dyes. The third exercise is focused on the plasma treatment of polymers by the surface discharge. The treated and untreated samples are characterised by the surface energy evaluation from the contact angles of 3 different testing liquids with the measured sample. Each of these works can be completed within a relatively short period of 150 minutes.

Keywords: discharge in liquids, diaphragm discharge, practical exercises, surface discharge, plasma treatment, surface energy, contact angle.

1. Introduction
Plasma chemistry is a comparatively new scientific discipline that has became a part of university curricula relatively recently. The discipline can be studied from two rather different points of view. The plasmachemistry courses for physicists are naturally focused on the basic phenomena in plasmas, the courses for chemists focus more on the use of plasma as an instrument for demonstrating various processes. In both of these conceptions, the problem of modern plasmachemical technologies plays only a minor role, although a huge increase of plasmachemical technologies has been observed during the last years. Practical exercises complementing the lectures at universities are normally focused on the basic processes and basic phenomena (studies of DC glow discharge etc.) and on some plasma diagnostic methods. At technical universities, practical exercises are usually in the form of plasma technology demonstrations without an active participation of students.

The curricula at our university include a course in applied low temperature plasma physics and chemistry, where students can obtain the basic information about a theoretical description of plasmas and later about some plasmachemical technologies. Four years ago we prepared a special practical course focused on the applications of low temperature plasma processes [1]. This contribution presents two new practical exercises. Both of them share the main characteristics of the other exercises, the expenses connected with them are reasonable and the degree of their safety gives students a possibility to carry them on. Finally, the experimental plasma devices used in the practical course are simultaneously used also during the work on the students’ master and doctoral theses. This in return makes possible the continual enlargement and improvement of the exercises.

2. Diaphragm discharge in liquids

Experimental
A special batch discharge reactor is used in the experiments [2]. It consists of two chambers with one planar electrode in each part. Electrodes are arranged in the distance of 2 cm from the diaphragm. A small pinhole (initially of 0.25 mm) is located in the centre of the dielectric diaphragm. Processes investigated in this discharge are influenced by the material of the dielectric diaphragm and the high voltage electrodes, too. The most convenient material for the diaphragm is PET with the thickness of about 0.2 mm, stainless steel electrodes are suitable for the experiments [3]. The DC non-pulsed voltage source (from 1.3 kV to 1.6 kV) is used to create the discharge [2]. To ensure the homogeneous conditions in the whole volume of liquid, a mixing system is placed in the reactor. Due to the considerable heating of the reactor by the discharge and to prevent the hydrogen peroxide from destruction, two cooling boxes with ice are installed in both parts of the reactor. In the case of organic dyes, the cooling system is not necessary.
**Results and Discussion**

The experimental studies showed that hydrogen peroxide molecules are one of the main active species for the other processes in the liquid phase [4]. Therefore they are measured also in this practical exercise as a quantitative parameter of the discharge.

The demineralised water containing suitable electrolyte (NaCl, Na₂HPO₄) was used to obtain the defined initial conductivity of the solution (optimal 300-700 µS·cm⁻¹).

The mechanism of hydrogen peroxide generation by the electric discharge in water is not simple, because the process is a series of subsequent chemical reactions. Partially it was described in [3]. The active species (especially radicals) are produced by the discharge, they can react together to create molecules or they can react with other compounds present in the liquid medium and cause their decomposition. However, we can express the overall reaction of hydrogen peroxide creation by the following equation [5]:

\[
2 \text{H}_2\text{O} \xrightarrow{\text{dich}} \text{H}_2\text{O}_2 + \text{H}_2.
\]

The rate constant of this reaction is \( k_{\text{per}} \). Due to the constant water concentration, the reaction is regarded as a zero-order reaction. Thus the final expression for the peroxide concentration is:

\[
c_{\text{per}, t} = k_{\text{per}} \cdot t,
\]

so it increases linearly in time.

The colorimetrical method was used for the hydrogen peroxide determination. The selective titanium reagent in sulphuric acid reacted with H₂O₂ and gave a yellow complex with the maximum absorbance at 407 nm. The hydrogen peroxide concentration in the sample was directly proportional to the absorbance value. This exercise was more suitable for students of chemistry due to the special chemical reagent used in experiments.

The second exercise focused on the organic dyes decomposition by the discharge could be more suitable for students of physics. Different organic dyes in solid phase, varied in colour and structure, and of the defined quantity were solved in demineralised water. The list of suitable dyes with their absorbance maximum is shown in Table 1. These dyes were quite fast decomposed by the discharge and thus this effect was also clearly seen visually. For example, the dye Methylene Blue was not convenient for this experiment because its degradation took more time and its decolorisation was not visible without a photometer.

Table 1: List of organic dyes suitable for the experiment.

<table>
<thead>
<tr>
<th>Organic dye</th>
<th>Type</th>
<th>Colour</th>
<th>Absorbance maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescein</td>
<td>fluorone</td>
<td>yellow</td>
<td>484 nm</td>
</tr>
<tr>
<td>Saturn Red L4B</td>
<td>azo-dye</td>
<td>red</td>
<td>506 nm</td>
</tr>
<tr>
<td>Azorubin</td>
<td>azo-dye</td>
<td>red</td>
<td>516 nm</td>
</tr>
<tr>
<td>Evans Blue</td>
<td>disazo-dye</td>
<td>blue</td>
<td>592 nm</td>
</tr>
<tr>
<td>Malachite Green</td>
<td>triarylmethane</td>
<td>green</td>
<td>621 nm</td>
</tr>
</tbody>
</table>

Chemical active species (especially radicals) produced by the discharge caused the decomposition of organic dyes dissolved in water. This process was visible directly through the decolourisation of the dye [6]. Therefore the degradation can be clearly and simply observed by photometry. The main absorption peaks of these dyes are relatively broad and no significant peaks of the discharge products were observed around the absorbance maxima listed in the Table 1. Due to this fact, the photometer can be replaced by a simple photodiode detector equipped with an interference filter transparent around the absorbance maximum of the selected dye.

Figure 1 shows the H₂O₂ concentration increase during the discharge in water. The production of hydrogen peroxide had almost a linear character in time and it was highly dependent on the discharge polarity. The generation was more significant in the positive discharge. The hydrogen peroxide amount became about 1 mmol·l⁻¹, i.e. approximately 34 g·l⁻¹. The second process, degradation of organic dye dissolved in water, is presented in Fig. 2. Water solution of the dye Azorubin was treated for 100 minutes by the discharge. The concentration decrease was more significant in the negative polarity, when the concentration became nearly zero already after 40 minutes of the experiment. Therefore the experimental time for the practical exercises can be
shorter, e.g. about only half an hour. The evaluation of the dye decrease was approximately exponential in both discharge polarities. In the case of positive discharge, the final concentration became about 30 % after 100 minutes.

Fig. 1: Production of hydrogen peroxide by the diaphragm discharge in a water solution (146 W, 5 mM NaCl, 500 µS·cm⁻¹).

Fig. 2: Concentration decrease of the dye Azorubin during the discharge treatment (146 W, 5 mM NaCl, 500 µS·cm⁻¹).

During the experiments, the changes in both conductivity and pH were observed. Results of these measurements are given in Figs. 3 and 4. The solution conductivity increased in both discharge polarities (Fig. 3). A higher enhancement was observed in the negative discharge (i.e. in the part of the reactor with the anode). This effect can be explained by the production of chemical species by the discharge and by metallic traces involved NEROZUMIM from electrodes by the electrolysis. Fig. 3 also compares two water solutions – electrolyte NaCl (left) and Saturn Red dye with NaCl (right). The relative increase in conductivity was higher in the pure electrolyte and the difference between the two polarities was also more significant in this solution.

Fig. 3: Change in conductivity during the discharge treatment in a water solution of the electrolyte NaCl (left) and in a water solution of the same electrolyte with the dissolved organic dye (right); 117 W, 4 mM NaCl, Saturn Red dye (12 mg l⁻¹).
Fig. 4 demonstrates the obtained results of pH measurements in both solutions, pure electrolyte (left) and Saturn Red dye with NaCl (right). The time evaluation had similar character in both experiments. While in the positive discharge the pH increased from approximately 6 to almost 10, in the opposite polarity, it had a decreasing tendency (from 6 to less than 4). In the solution with the dissolved dye, the difference in pH was more significant.

3. Treatment of polymers by the surface discharge

Experimental
The surface modification of the polymers is at present one of the most emerging plasma technologies. Industrial applications prefer the treatment in low temperature plasma at an atmospheric pressure. The surface barrier discharge and diffuse coplanar discharge are very suitable for this purpose.

A special plasma reactor based on the surface barrier discharge [7] was developed for this application (see Fig. 5). The surface discharge is the non-equilibrium plasma supplied by the high DC voltage with the operation frequency of 7 kHz. The reactor was constructed in order to prevent students from being injured by the high
voltage, therefore the plasma chamber is mounted with a power supply and the electrode is placed under a glass cylinder. Moreover, the device is portable (30x30x35cm). The discharge chamber can be evacuated before the plasma treatment and then filled with pure gases or various gas mixtures. The reactor is constructed only for laboratory tests therefore the treated samples are restricted to the maximal dimensions of 10x10cm. In the real industrial application it is possible to shape the treating unit for a continuous treatment of materials with the width of even more than 1 m. The treatment time can vary from a few seconds up to 20 min, but the electrode and power supply need cooling. The treatment time longer than one minute is not necessary during the exercises (see below) therefore the supplementary cooling is not integrated in the reactor.

Students investigate the effect of treatment time on the surface properties of samples (polyethylene and polyester plates). Smooth materials are used for easier characterisation of the surface energy. The discharge is burning in separate rows parallel with the electrodes and thus the treatment is not homogeneous over the whole sample, if the sample is not moved through the reactor. The width of the treated rows is about 3 mm and it is sufficient for the treatment characterisation. The treatment time of both used materials is up to 60 s, a longer treatment is not recommended due to a thermal deformation of the samples that significantly decreases the treatment homogeneity.

The treated and untreated samples are characterised by the surface energy evaluation from the contact angles of 3 different testing liquids with measured sample. Surface energy evaluation is provided by the means of Surface Energy Evaluation System (SEE System) [8]. Inexpensive and fully computer-controlled setup allows to measure contact angles of various testing liquids with the sample surface and to calculate the surface energy using different models. The acid-base model was applied in our case [9, 10]. The setup is also equipped with a complete analysis of errors.

Results and discussion

The experimental results are shown in Fig. 7. It can be seen that the contact angles of the selected liquids decrease with the increase of the plasma treatment time. This effect is most remarkable in the case of distilled water, i.e. the hydrophylity of both materials increases. The main changes can be observed during the first 30 seconds, later the changes are not so high. Both figures clearly demonstrate also the problem with the surface energy estimation. The contact angles at longer treatment times are similar for the used liquids. The contact angles also have significant experimental errors that result from the inhomogeneity of the static plasma treatment. This causes the high errors in the calculated surface energies (see Table 2 below).

Fig. 7: Dependencies of the contact angle for various liquids as a function of the treatment time; left – polyethylene, right – polyester.
Table 2: Calculated surface energies of plasma treated polyethylene and polyester samples.

<table>
<thead>
<tr>
<th>Material</th>
<th>treatment time [s]</th>
<th>Total surf. energy [mJ·m⁻²]</th>
<th>Disperse component [mJ·m⁻²]</th>
<th>Polar component [mJ·m⁻²]</th>
<th>Acid component [mJ·m⁻²]</th>
<th>Basic component [mJ·m⁻²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>0</td>
<td>42.28</td>
<td>41.06</td>
<td>1.21</td>
<td>0.13</td>
<td>2.92</td>
</tr>
<tr>
<td>PE</td>
<td>15</td>
<td>45.15</td>
<td>41.26</td>
<td>3.89</td>
<td>0.30</td>
<td>12.61</td>
</tr>
<tr>
<td>PE</td>
<td>30</td>
<td>47.16</td>
<td>42.34</td>
<td>4.82</td>
<td>0.26</td>
<td>22.61</td>
</tr>
<tr>
<td>PE</td>
<td>60</td>
<td>49.57</td>
<td>42.74</td>
<td>6.82</td>
<td>0.48</td>
<td>24.34</td>
</tr>
<tr>
<td>PES</td>
<td>0</td>
<td>42.55</td>
<td>41.41</td>
<td>1.14</td>
<td>0.11</td>
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</tr>
<tr>
<td>PES</td>
<td>15</td>
<td>41.09</td>
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<tr>
<td>PES</td>
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<td>42.10</td>
<td>39.57</td>
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</tr>
<tr>
<td>PES</td>
<td>60</td>
<td>46.66</td>
<td>39.60</td>
<td>7.06</td>
<td>0.38</td>
<td>32.96</td>
</tr>
</tbody>
</table>

4. Conclusions
The practical exercises described in this contribution are a part of a special practical course focused on applied low temperature plasma-physical and plasma-chemical processes. The first exercise consists of two parts investigating the processes in the DC diaphragm discharge – hydrogen peroxide generation and organic dyes degradation. The experimental basis of this exercise is mostly very cheap, and thus the device can easily be installed anywhere. The diagnostic methods presented above are based on the apparatus available to us and they can be replaced by other methods as it was proposed.

The second exercise is focused on the treatment of polyethylene and polyester by the surface discharge. The contact angles of the selected liquids are measured as a function of treatment time up to one minute. On this basis the changes of the polymer surface energy are calculated. The whole experimental equipment is inexpensive and as safe as possible, and thus it can easily be used anywhere.

Each of the presented practical exercises can be completed within 150 minutes without any significant problems. These practical exercises show students new directions in the plasma-chemical processes and technologies. They are fully interdisciplinary, a good knowledge of both physic and chemistry is necessary. A further extension of our course is planed in the near future.

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References