PRACTICAL EXERCISES IN APPLIED PLASMA CHEMISTRY

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Abstract

The contribution presents our results obtained when we were solving one of the basic problems in teaching plasma chemistry. We prepared a special practical course focused on applied physical and chemical processes in low temperature plasma. We present the results of the first practical works as well as some of the works being prepared at present. Finally, suggestions concerning further works of this kind are presented. Works focused on other technologies can be added as a result of international co-operation. Our course is as safe, complex, cheap and clear to students as possible.

1. Introduction

Plasma chemistry is a relatively new scientific discipline that 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. 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. Usually, the practical exercises complement the lectures. The practical exercises 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
the technical universities, the practical exercises are usually in the form of plasma technology demonstrations without active participation of the students.

The study programs at our university contain a course in applied low temperature plasma physics and chemistry where students can obtain the basic information about the theoretical description of plasmas and later on about some plasmachemical technologies. This conception raises a serious problem how to present the modern plasmachemical technologies to our students because there is only a small chance to see the technologies in specialized laboratories or in industry except during excursions. Besides the presentation of some technologies on video during the lectures [1], we prepared a special practical course focused on the applications of low temperature plasma processes.

The exercises include various technologies, such as surface treatment, thin layer deposition or decomposition of molecules and also some basic tasks, such as calibration of the measuring devices and characterization of the final products. Plasma diagnostics and fundamentals of vacuum physics that are not included in any other course at our university are included in our course as well. The diagnostic methods use the apparatus available in our laboratories, so the students can obtain also information about other devices. Finally, most of the experimental plasma devices used in the practical course can be used also during the work on the students' master and doctoral thesis. This in return allows the continual enlargement and improvement of the exercises.

The interesting point of experimental plasma devices used in our course is that these apparatuses are mostly very cheap and also safe to be used by the students. Some basic ideas of our course are clarified in the following two paragraphs presenting two of our exercises. The survey of other exercises, including the planned ones, is given below.

2. The ozone generation

The ozone generation in the low temperature plasma is one of the most instructive exercises. The students can observe the discharge plasma and the concentration of the generated ozone can be estimated by both UV light absorption and iodometric titration methods. The generated ozone can be used as oxidiser in other chemical processes.
Figure 1: Simplified scheme of the experimental set up. 1 – oxygen bomb; 2 – rotameter; 3 – ozonizer; 4 – UV absorption measuring unit; 5 – KI double bubbler. Details can be found in the text.

The plasma part of the experimental device given in Fig. 1 is the ozonizer. We used the coaxial configuration with metallic inner cylinder of 27 mm in diameter, the outer graphite electrode is as a surface layer on a Pyrex glass tube (the inner diameter of 30 mm). The total length of the ozonizer is 40 cm, its active part being 30 cm long. The power supply constructed in our laboratory uses the car-starting coil gives the voltage amplitude of 10 kV at the frequency of 50 Hz. The input power supply current can be continuously varied between 16 and 34 mA. Due to the use of high voltage, the ozonizer itself is installed in the centre of a Perspex box (10 x 10 x 50 cm). The power regulation is at the low voltage part, therefore it can be placed outside this box.

The ozone can be generated from both the air and oxygen. To regulate the gas flow we used non-calibrated rotameter for flows up to 1 Sl/min. The rotameter calibration is the first of the students’ tasks.

The determination of the amount of the generated ozone can be done by two different methods – by UV light absorption (in our case it is being tested at present) and by iodometric titration. The ozone absorption has a wide band in the range of 200 – 300 nm with the maximum at about 250 nm [2]. Due to this fact, the best source of UV light is a low-pressure mercury lamp coupled with an interference filter passable at the mercury line of 253 nm. The silicon UV sensitive photodiode with an appropriate amplifier and an AD converter can be used as a light detector. Of course, the ozone detection unit is not calibrated. The iodometric
titration method is used to calibrate the detection unit. This method is based on the following reaction:

\[ 2 \text{KI} + \text{O}_3 + \text{H}_2\text{O} \rightarrow \text{I}_2 + 2 \text{KOH} + \text{O}_2. \]

We use a 0.2 M KI solution. The HCl 2 M solution is added in the amount of 10 ml/100 ml of KI solution. Titration is done by a 0.05 M Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} solution. 1 ml of 0.05 M Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} solution is equal to 0.6 mg of ozone [3].

In our case, the generated ozone bubbles in the KI trap for 5 minutes if the generation is done from oxygen or for 10 minutes if the generation is done from air. We use 100 ml of KI solution. The second trap is added mostly for security, only about 1% of generated ozone is destroyed in it. After ozone generation the standard titration is completed and the amount of the generated ozone can be established.

In conclusion, the students must themselves calibrate the rotameter and the ozone detection unit. Then they can measure the dependencies of ozone generation on the discharge current as well as on the gas flow rate for both gases (oxygen and air). An example obtained from the students’ laboratory record is given in Fig. 2.

![Graph showing ozone generation as a function of gas flow rate for three power supply currents.](image)

**Figure 2:** The ozone generation as a function of gas flow rate for three power supply currents.

3. **The local surface treatment of polymers using the plasma pencil**

This practical work is based on use of our patented type of small plasma jet known as a plasma pencil [4, 5]. The surface treatment of polymers is a relatively well-known plasma chemical process and a lot of information can be found in bibliography, for example in [6]. The scheme is given in Fig. 3.

The plasma is produced in a hollow massive metallic electrode by RF (13.54 MHz) power supply of 0 – 800 W. The plasma jet interacts (perpendicularly or under any other angle) with the polymer surface. The sample can be continuously shifted under the plasma jet to achieve a relative homogeneity of the surface treatment. Air, nitrogen or argon can be used
as the buffer gases and various additives can be used, too. This allows a great variety of the discharge conditions and thus the effects of the plasma surface treatment can be specific for each of the students.

The plasma treatment can be characterised by the measurement of the changes of the surface energy. This energy can be calculated from the contact angle of various liquids with the treated and untreated polymer sample. There are many methods how to complete this calculation; in our practical exercises we use the Extended Fowkes model [7]. Due to the fact that the surface treatment by a plasma pencil is local, only the students can characterise also the homogeneity of the treated samples. In our laboratory we use a commercial device for the measurement of the contact angle (Kruss), but for the laboratory practical exercises of the students a simpler configuration described below can be used.

![Diagram](image)

**Figure 3:** The scheme of the surface treatment of polymers using plasma pencil. 1 – RF power supply (13.54 MHz, 0 – 800 W); 2 – adapting unit; 3 – xy micrometer feed sample holder (table); 4 – reacting gases reservoir; 5 – plasma pencil.

A wide laser beam has been used to project the small liquid drop created at the polymer surface by microburette on the screen. This screen is equipped with an angular scale that allows reading the contact angle of the drop. Of course, the accuracy of this method is in order of a few degrees but the surface changes are so obvious that this simple method is sufficient for the observation.

In conclusion, the students can observe in this exercise the real plasma jet in various gas mixtures. They can study the surface energy changes for various polymeric materials by the means of plasma. The homogeneity of the local treatment of the polymer surface can be studied, too.

4. A survey of the practical exercises
The presented exercises cover technologies the most frequently used in practice. Since there is no special course in plasma physics and plasma diagnostics held at the university, the first two works are focused on this field.

**Exercises taking place at present**

- **Calibration of pressure gauges**
  Calibration of Pirani gauge at two different operating temperatures; calibrations of an ionizing gauge in two different gases.

- **Optical emission spectroscopy**
  Identification of radiative particles – atoms and molecules; calculation of the rotational temperature (using the simulated spectrum because we do not have a spectrometer with a sufficiently sensitive detector); estimation of vibrational distribution or, if possible, the calculation of vibrational temperature. This work is done using two different DC discharge lamps. Study of the high voltage and influence of the slit width on the signal intensity and on the spectra resolution.

- **Ozone generation in the silent discharge in air and pure oxygen**
  All the details are given above in section 2.

- **Plaschemical modification of polymer surface energy**
  The full description of the exercise was presented in section 3.

- **Radio-frequency discharge at low pressure**
  Measuring of the efficiency of RF power absorption in the inductively coupled discharge. Observation of the absorption efficiency as a function of the pressure.

- **Transport phenomena in diluted gases**
  Measuring of the vacuum leakage, setup of the pressure and gas flow in the plasma reactor. This exercise will be in the near future probably omitted due to an implementation of new, better exercises focused more on chemistry and technology.

- **Electron spin resonance spectroscopy**
  At present this exercise includes only the basic measurements by a very old ESR spectrometer (made in 1958). From the next year the following one will replace this exercise.

**Exercises in preparation**

- **Generation of radicals at the polymeric surface**
  Treatment of a thin polymeric foil using the barrier discharge. The radical generation can be observed immediately ex situ by ESR spectroscopy.

- **Wettability measurements of plasma treated synthetic polymer multicord sewing threads**
  Polymer samples will be treated by the barrier discharge; the wettability changes will be characterized by the methods described in [8].

- **DC diaphragm discharge in liquids**
  Study of plasma chemical reactions in the liquid phase; generation of peroxides and their applications to the decomposition of organic molecules. The work is based on results the reached at the Institute of Plasma Physics in Prague [9, 10].

**Other possible practical exercises**

- **Decomposition of organic pollutants in a gliding arc discharge**
- **A thin film deposition in the RF discharge and its characterization by IR spectroscopy**
- **Deposition of a thin film at the atmospheric pressure**
• Plasma spraying using plasma pencil or another plasma micro jet
5. Conclusions

We have prepared a special practical course focused on applied low temperature plasma physical and chemical processes. We present the results of the first practical exercises as well as a survey of some exercises that are in preparation now. The exercises include various technologies, such as a surface treatment, a thin layer deposition, a decomposition of molecules; the exercises are connected with some basic problems, such as the calibration of measuring devices and the characterization of final products. Plasma diagnostics and fundamentals of vacuum physics that are not included in any other course at our university are included, too. The plasmatic part of the exercises is mostly very cheap and thus the device can be simply installed anywhere. The diagnostic methods presented above are based on the apparatus available to us and they can be replaced by other methods. More experimental exercises will be added during the next years to cover other interesting technologies.

We think the knowledge of the university graduates is not sufficient in the field of practice plasmachemistry. The international interaction and a new practical course can significantly increase the quality and adaptability of graduates in technological practice. Thus the acceleration and the progress in plasmachemical technology applications can be reached in the near future.

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References