

# Dc corona discharges in CO<sub>2</sub>–air and CO–air mixtures for various electrode materials

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Received 6 November 1997, in final form 13 March 1998

**Abstract.** Positive and negative dc corona discharges in CO–air and CO<sub>2</sub>–air mixtures were applied. Natural humid air was used. The step by step development with time of the formation of gas products after the action of the corona discharge was measured *in situ*. The discharge tube was situated in an IR gas cell. The IR absorption spectra were scanned from the area of the inter-electrode distance in successive time steps of the action of the discharge (about 1 min).

Measurements were performed for three combinations of electrode materials, namely Mo–stainless steel, Mo–brass and Cu–brass. Reflection IR absorption spectra from the surfaces of the electrodes used were scanned after the action of the discharge. The influence of the electrode material on the development with time of the reaction products was observed. Polymer–metal complexes with possible catalytic activity are formed on the surfaces of electrodes. From measurements it resulted that the discharge processes consist of simultaneously acting volume processes of plasmochemical nature (probably initiated by electrons) and electrocatalytic surface processes on electrodes (probably initiated by photons).

## 1. Introduction

Corona discharges are usually realized in non-uniform gaps such as wire–cylinder and point–to–plane gaps and are operated with dc, ac or pulsed power supplies. Corona discharges have been used from the beginning of this century in precipitation and ozonizer techniques and later as a source of charged particles, especially electrons, for the initiation of chemical reactions. One of the most important uses of corona discharges is their use in electrostatic precipitators [1].

Corona discharges are very suitable for removal of various compounds such as SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>x</sub> and hydrocarbons (VOC) from exhausts [2–8]. Usually the ‘carrier gas’ for these compounds is the natural air (with 350 ppm CO<sub>2</sub> and about 4% water vapour), synthetic air without CO<sub>2</sub> and H<sub>2</sub>O or combustion exhaust (with 2–15% CO<sub>2</sub> and about the same amount of water vapour as CO<sub>2</sub>).

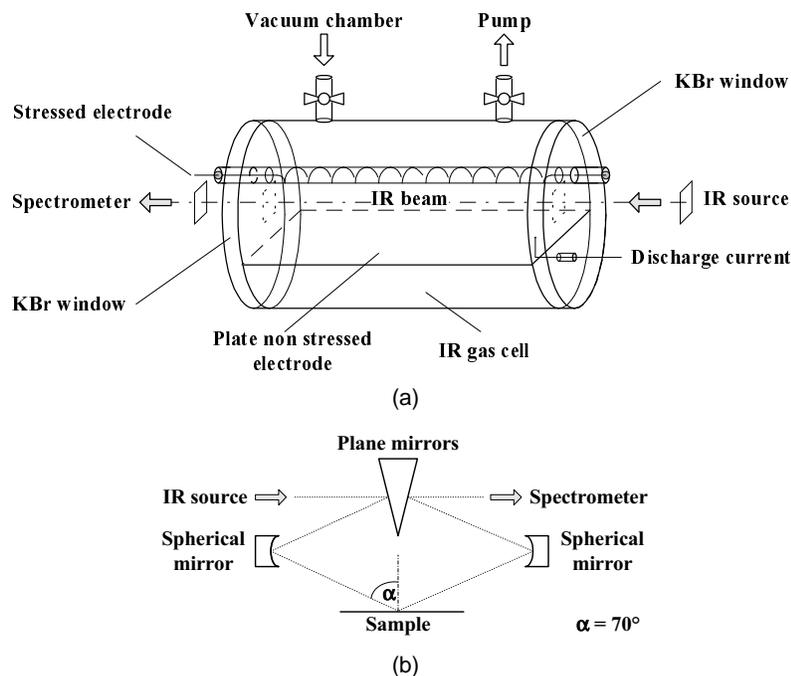
It is of vital interest to control not only emissions of NO<sub>x</sub> and SO<sub>2</sub>, which are the major causes of acid rain, but also emissions of CO<sub>2</sub> (30 Gt per year, 60% of all greenhouse gases), CH<sub>x</sub> and N<sub>2</sub>O, which may lead to global warming of the atmosphere (the greenhouse effect). The CO<sub>2</sub> level in the atmosphere must not increase above 400 ppm (by volume), the present level is 350 ppm (by volume). To attain this it is necessary to reduce the present level of emission of CO<sub>2</sub> by at least 10% [9]. Many industrial nations made commitments at the 1992

Rio summit to stabilize CO<sub>2</sub> emissions at the level of 1990 by the year 2000. The UN’s Intergovernmental Panel on Climate Change recommends a 50% reduction of global CO<sub>2</sub> emissions within the next 50 years.

An important source of CO<sub>2</sub> is traffic (12 Gt per year). The methods based on a corona discharge used for removal of various compounds from internal combustion engines usually have an effect also on carbon dioxide. The influences of various corona discharges on diesel and Otto engine exhausts were published in [10, 29, 36–38].

Investigation of CO<sub>2</sub> decomposition processes in corona discharges in the mixture of CO<sub>2</sub> with air, including homogeneous and heterogeneous processes on the surfaces inside the discharge tubes, are of great interest. Very good results were obtained in a pulsed corona discharge in the presence of granular ferroelectric matter. The volume and surface reactions were studied [4, 11–13, 28]. Many authors are still interested in dc corona discharges. The problem of conversion of CO<sub>2</sub> to CO in dc corona discharges of both polarities was studied in [10, 14–16, 24, 26].

For studying conversion of CO<sub>2</sub> to CO it is very important to know the amounts of positive and negative ions present in the inter-electrode area of the discharge. However, most of the measurements (mass spectrometric) are performed for reduced pressures. From these the most frequent ion at reduced pressures is CO<sub>3</sub><sup>–</sup>. With rising pressure the concentration of CO<sub>4</sub><sup>–</sup> ions increases and, after the pressure of 4 kPa (30 Torr), these ions begin to



**Figure 1.** (a) The gas cell corona discharge tube and (b) a schematic diagram of the IR reflection equipment.

dominate. The concentration of cluster ions also rises with increasing pressure. For the negative corona discharge the dominate ions were  $O^-$ ,  $CO_3^-$  and  $CO_4^-$ , and those for the positive one were  $HCO_2^+$ ,  $CO_2^+$  and  $H^+[H_2O]_n$  [18, 19]. In the presence of water vapour the surface reactions are very important and lead to the formation of  $H_2CO_3$  [20].

The objective of the present work is to describe

(i) the step by step development with time of the decrease in  $CO_2$  and CO decrease using IR absorption spectrometry;

(ii) the formation of gas products containing stable-NCO radicals and  $-COO^-$  and  $NH_2^+$  ions; and

(iii) the corona discharge's self-produced surface catalytic activity of various electrode materials.

## 2. The experimental set-up and procedure

The experimental apparatus used for *in situ* laboratory measurements and for step by step monitoring of the development with time of product formation consists of

(i) the gas cell corona discharge tube described in figure 1,

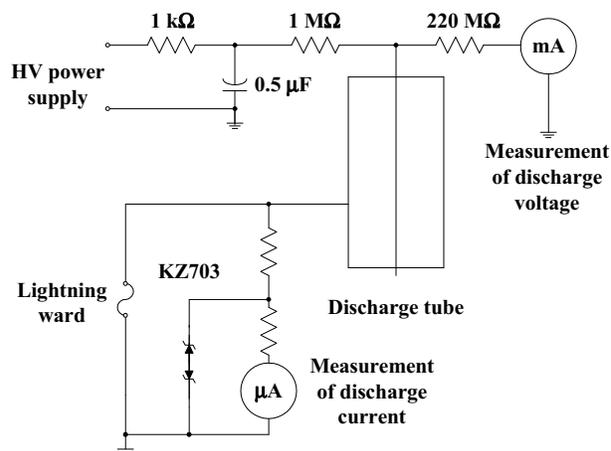
(ii) the electrical circuit described in figure 2,

(iii) a gas inlet system and

(iv) auxiliary devices (an IR absorption spectrometer Specord M 80 from Carl Zeiss, an IR gas cell of length 10 cm, reflection equipment, ATR equipment and equipment for the KBr pellet technique).

### 2.1. The gas cell corona discharge tube

The discharge tubes used were of wire–plane configuration with various electrode materials. The stressed electrode



**Figure 2.** The electrical circuit of the apparatus used.

**Table 1.** Combinations of electrodes.

Central stressed electrode	Plane non-stressed electrode
Molybdenum	Stainless steel
Molybdenum	Brass
Copper	Brass

was wire of 0.2 mm diameter wound on a glass tube. The non-stressed electrode was a 35 mm × 100 mm plane. To determine the influence of the electrode material on the corona-discharge-affected chemical changes we have used the combination of electrodes in table 1.

The inter-electrode distance was 11 mm. The discharge tube was situated in an IR absorption gas cell so that the

electrodes were parallel to the optical axis of the gas cell, figure 1. This gave the possibility of scanning *in situ* IR absorption spectra from the drift region of the corona discharge along the discharge tube. The IR reflection absorption spectra of the non-stressed plane electrode and IR absorption spectra of deposits on the stressed electrode could also be scanned after the completion of measurements and opening of the discharge tube.

## 2.2. The electrical circuit of the apparatus

The electrical circuit used is illustrated in figure 2. Two direct-current (positive and negative, 50 Hz rectified by use of a diode) Baur PGK70 high-voltage power sources with 500 W power output, voltage range 0.5–70 kV and maximal current 30 mA were used. The high-voltage dc signal after filtration by a 1 k $\Omega$  serially connected resistance and a 0.5  $\mu$ F parallel connected capacitance was connected to the stressed electrode. The applied voltage was measured by using a milli-ammeter connected via the 200 M $\Omega$  resistor to the ground. The current was measured directly from the non-stressed electrode by using a micro-ammeter, protected by a lightning ward and two Zener diodes.

## 2.3. IR absorption spectrometry

Infrared absorption spectrometry, which is powerful method for identification of various materials in gas, liquid and solid phases, was used for analysis. Carbon dioxide and carbon monoxide are compounds with intense infrared absorption bands. Owing to the action of the electrical plasma, various plasmachemical reactions take place. The final reaction products and intermediates are in many cases unknown. The infrared method is very suitable for their analysis. For analysis we have used various IR techniques and catalogues of IR spectra [40–44] for interpretation.

The gases were analysed in a 10 cm gas cell with KBr or KRS5 windows of similar construction to the gas cell discharge tube described in figure 1. Liquid samples were analysed using the ATR technique with crystals made of KRS5 or Ge, angle of incidence 45° and 60°, sample thicknesses in the range 1.5–5 mm and the crystal length 35 mm.

For solid samples the KBr pellet technique was used. The sample is mixed with the KBr powder in the ratio approximately 0.2–1:100 and they are pulverized together in the vibration mill. The mixture is then pressed under a pressure of 5–22 MPa to the metal ring and in this way the pellet is formed. Spectra from the pellet are scanned.

The electrode's surface was analysed using reflection spectra. The reflection depends on the wavenumber, angle of incidence, refractive index and absorption features of the sample. The device used allows one to measure the reflection spectra at 20° and 70° angles of incidence. Most of the spectra were measured with 70° angle, as shown in figure 1(b).

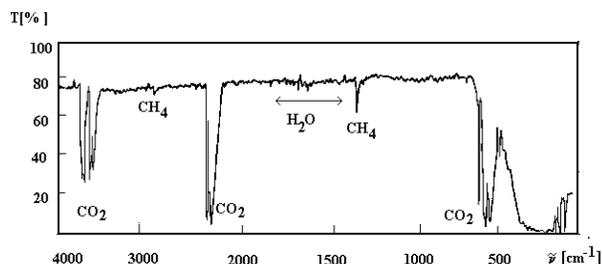


Figure 3. The IR absorption spectrum of CO<sub>2</sub>.

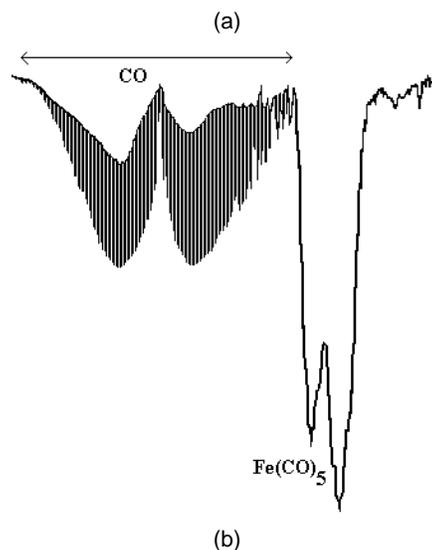
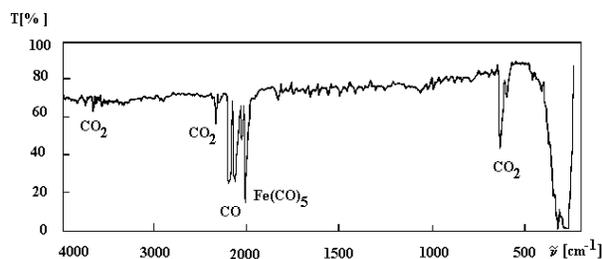


Figure 4. (a) The IR absorption spectrum of CO. (b) Detail of the IR absorption spectrum of CO.

## 2.4. Gases applied

The CO<sub>2</sub> gas used was of technical grade, contaminated mostly by CH<sub>4</sub> and H<sub>2</sub>O, 3.5% together. The IR absorption spectrum of it is in figure 3. The main IR absorption bands of CO<sub>2</sub> are at 670 cm<sup>-1</sup> (the deformation vibration band), 2350 cm<sup>-1</sup> (the  $\nu_s$  stretching vibration) and 3700–3800 cm<sup>-1</sup> (the cumulative stretching band).

The CO gas used was Matheson with 5% of impurities. The contaminants were Fe(CO)<sub>5</sub>, which is always present in the pressure tanks with CO to an amount of about 4%, CO<sub>2</sub>, about 1%, and H<sub>2</sub>O, only traces. The IR absorption spectrum of CO with contaminants is in figure 4(a). CO bands are typical vibration–rotational with the maxima of P and R bands at 2169 and 2115 cm<sup>-1</sup> (figure 4(b)).

The applied air was not dry. It contained, similarly to natural air, up to 4% of water vapour.

## 2.5. Measurement procedures

In a gas cell discharge tube we have performed step by step measurements of the development with time of gas phase products and intermediates formed by a discharge in the introduced gas mixture. The infrared spectra from the area of the inter-electrode distance were scanned *in situ*. The studied gas mixture was introduced into the evacuated gas cell–discharge tube as shown in figure 1. The IR spectrum of the introduced gas was scanned. Then the discharge was applied for a defined time and the spectrum was scanned again. This procedure we reiterated until no more changes in composition of the gas took place.

For the introduced CO<sub>2</sub>–air mixture the changes of gas product concentration (CO<sub>2</sub> and CO) were studied in time steps 0, 1.5, 3, 4.5, 6 and 16 min. For the introduced CO–air mixture the changes of gas product concentration (CO<sub>2</sub> and CO) were studied in time steps 0, 1, 2, 3 and 4 min. Both positive and negative polarities of the discharge were applied.

After completion of gas phase measurements the non-stressed plate electrode was removed from the gas cell discharge tube and the reflection IR absorption spectrum of it was scanned. From this spectrum it was possible to identify the solid and liquid products on this electrode. The liquid products were additionally analysed by the ATR technique.

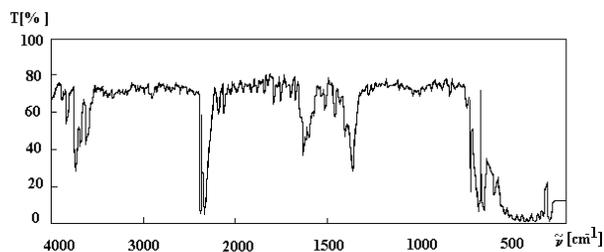
During the time of discharge actions considerable changes of gas composition take place. So it was impossible to measure current–voltage characteristics. However, the actual values of the current and voltage were measured and processed in the PC. The applied voltage during the action of the glow corona was about 11 kV and the discharge current was in the range 40–60  $\mu$ A. When the concentration of CO was high the discharge had a typical glow character. With an enhanced CO<sub>2</sub> concentration the typical glow corona action alternated with a streamer-like spontaneously pulsing discharge with currents up to 300  $\mu$ A connected with the fall of the voltage to about 1–2 kV.

## 3. Measurements and discussion of results

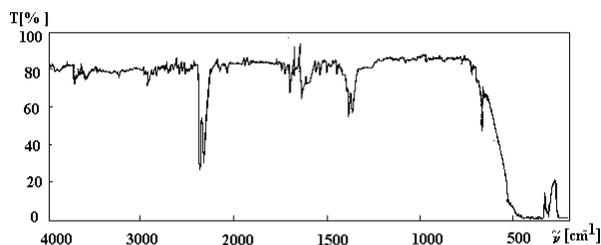
### 3.1. Products created by the action of a discharge in volume

The greatest difference from the point of view of gas composition is that between gas products in positive polarity with electrode materials Mo and stainless steel (figure 5) and negative polarity with electrode materials copper and brass (figure 6). This can be seen from IR absorption spectra. The detailed interpretation of the spectra will be given in section 3.1.2.

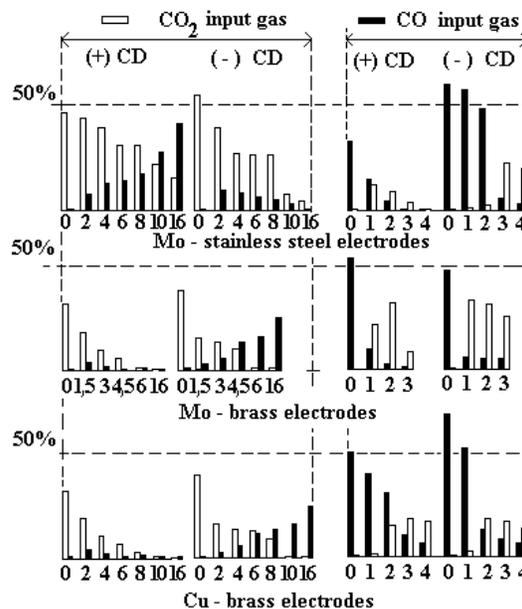
**3.1.1. Main gas components.** The relative concentrations of CO<sub>2</sub> and CO in percentages of the input concentration for both polarities of a dc corona discharge are shown in figure 7. The time steps used in measurements were 0, 1.5, 3, 4.5, 6 and 16 min for the discharge when a CO<sub>2</sub>–air mixture was introduced and 0, 1, 2, 3 and 4 min for the discharge when a CO–air mixture was introduced. Mo–stainless steel, Mo–brass and Cu–brass electrodes were used.



**Figure 5.** Gas products after the action of a positive dc corona discharge for the Mo–stainless steel combination of electrodes.

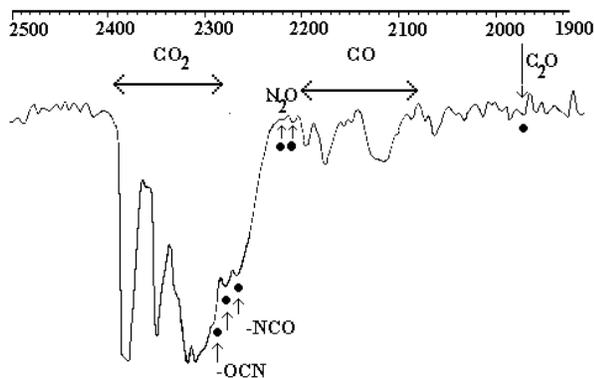


**Figure 6.** Gas products after the action of a negative dc corona discharge action for the copper–brass combination of electrodes.

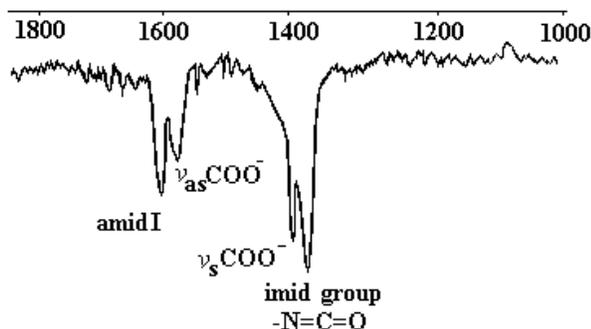


**Figure 7.** The relative changes in concentration of CO<sub>2</sub> and CO as percentages of the input concentration for both polarities of the dc corona discharge and with Mo–stainless steel, Mo–brass and Cu–brass combinations of materials used for the electrodes.

**3.1.2. Minority gas components.** Very important information from measurements is the spectroscopic evidence about formation of stable –NCO intermediate radicals. This radical is formed during the decomposition of CO<sub>2</sub> and/or from CO when activated nitrogen is present in the gas mixture. The IR absorption bands of the –NCO radical in the gas phase are at 2270 and 2290  $\text{cm}^{-1}$ . The presence of this radical in the gas after a discharge can be seen from the detailed IR absorption spectrum in figure 8.



**Figure 8.** Detail of the IR absorption spectrum after the action of a dc corona discharge, in which evidence for the existence of  $-NCO$  radicals,  $N_2O$  and  $C_2O$  in the gas phase can be seen.

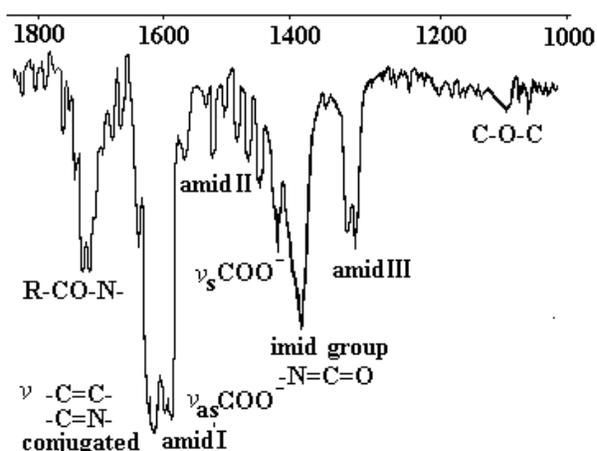


**Figure 9.** Detail of the IR absorption spectrum after the action of the negative corona discharge with copper and brass electrodes.

Because the  $-NCO$  radical is surface sensitive it forms organometallic compounds on the non-stressed electrode. Some of these compounds are known to influence the decomposition processes of  $CO_2$ ,  $CO$  and  $NO$  gases. These surface products are based on  $OC-NCO$  and  $ON-NCO$  structural groups [32]. When these solid products with participation of the  $-NCO$  group in their structure are formed the wavenumbers of  $-NCO$  bands in IR absorption spectra are shifted to 2170 and 2215  $cm^{-1}$  [33]. A part of the solid products can be decomposed due to electron bombardment and further cross linking. These processes are associated with the formation of small amounts of  $N_2O$  with absorption bands at 2220 and 2240  $cm^{-1}$  and  $C_2O$  with absorption bands at 1950  $cm^{-1}$ , as can be seen from figure 8.

In all mixtures containing  $CO$  and  $CO_2$  the carboxylate ion  $-COO^-$  is formed after the action of the discharge. This ion is present especially in surface products and for a negative polarity of the corona discharge as can be seen from figure 9. Also the carboxylate ion is very important for further production of organometallic complexes on the surfaces of electrodes.

$C$ ,  $C_2O$  ( $C+CO$ ) and finally  $C_3O_2$  ( $C_2O+CO$ ) are formed by the  $CO$  decomposition processes.  $C_3O_2$  named malonic acid anhydride, is a monomer which polymerizes differently for various polarities of the discharge. Created



**Figure 10.** Detail of the IR absorption spectrum after the action of the positive corona discharge with molybdenum and stainless steel electrodes.

polymers are described in our previous work [16, 21]. For a positive polarity of the discharge the presence of malonic acid anhydride leads to a great increase in intensity of the broad band at 1650  $cm^{-1}$  due to the conjugated  $-C=C-$  bond, as can be seen from figure 10.

Some of the intermediate products are similar to those proposed by Maezono and Chang [26] ( $C$ ,  $C_2O$ ,  $NCO$  and  $CO_3$ ), but the final gas products that we have identified from IR absorption spectra are different. The main reason for this is the electrode material used. As we can see from figure 9, with a negative polarity of the discharge in the case of copper or brass electrodes the solid product is formed from gas products or intermediates. Owing to this the pressure of gas products permanently decreases, there is not equilibrium in the gas phase and the final efficiencies of  $CO$  and  $CO_2$  removal processes increase. The final gas phase products (figure 9) contain the amino group and carboxylate ion,  $[NH_2-COO]^-$ . This is the radical of the unstable carbonic acid amide, but existing in a great variety of derivatives in the form of *negative ions*.

For the positive discharge polarity the gas products are based on the *positive ion*  $[NH_2-CO]^+$ , giving further amides and amino acids. This ion differ only by one oxygen from the previous one (for negative polarity), but give very different IR spectra. Typical is the presence of carbonyl and the amide III band and the absence of carboxylate ion bands, as can be seen from figure 10.

In the case of the stainless steel electrode the surface products are created very slowly. This leads to the development of a reaction equilibrium and limits the efficiency of removal of  $CO$  and  $CO_2$ . Owing to this the concentration of all intermediates is high.

### 3.2. The influence of the electrode material on the step by step development with time of products formed in the gas phase

The individual measurements of  $CO$  and  $CO_2$  with air at atmospheric pressure were made for a longer period of time. That is why there are various differences in applied

**Table 2.** The step by step development with time of products for Mo and stainless steel electrodes.

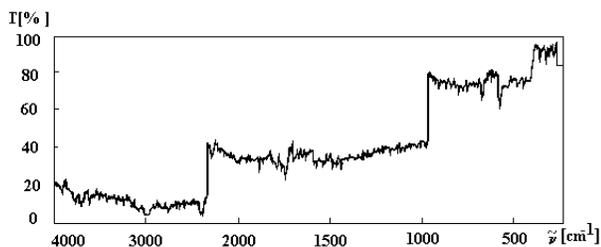
Introduced gas CO <sub>2</sub> –air mixture		Introduced gas CO–air mixture	
Positive polarity, 47.5% CO <sub>2</sub>	Negative polarity, 55.7% CO <sub>2</sub>	Positive polarity, 34.3% CO	Negative polarity, 55% CO
After 4.5 min CO 11.7% maximum CO <sub>2</sub> 33.3% After 16 min Formation of –NCO radical and –COO <sup>–</sup> ion CO <sub>2</sub> 15.7% The surface reaction products are not bonded with the metal of the electrode	After 1.5 min CO 9.5% maximum CO <sub>2</sub> 40.5% After 6 min Formation of –NCO radical After 16 min CO <sub>2</sub> 14.6% The surface reaction products are not bonded with the metal of the electrode	After 1 min CO <sub>2</sub> 12.3% maximum Formation of –NCO radical, –COO <sup>–</sup> ion and carbonyl –CO After 3 min CO decreases to zero CO <sub>2</sub> decrease to 5.3% The surface reaction products are not bonded with the metal of the electrode	After 4 min CO decrease continually but not linear down to 4.1% CO <sub>2</sub> increase continually but not linear up to 21.5% The production of new gas products is very weak. The surface reaction product is not formed

**Table 3.** The step by step development with time of products for Mo and brass electrodes.

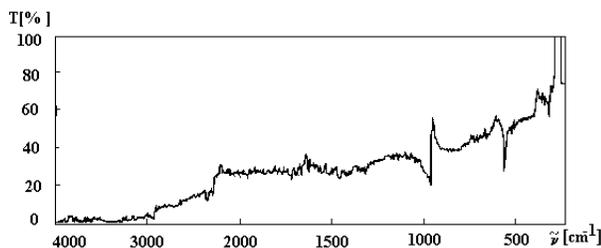
Introduced gas CO <sub>2</sub> –air mixture		Introduced gas CO–air mixture	
Positive polarity, 33.3% CO <sub>2</sub>	Negative polarity, 39.4% CO <sub>2</sub>	Positive polarity, 50.0% CO	Negative polarity, 69% CO
After 1.5 min CO 4.4% maximum CO <sub>2</sub> 19.4% After 3 min local maximum of –NCO, then a continuous rise until 16 min After 4.5 min CO <sub>2</sub> decreases to zero After 16 min CO <sub>2</sub> decreases to zero Surface reaction products are bonded to the metal of the electrode	After 1.5 min CO 4.5% maximum CO <sub>2</sub> 16.4% After 3 min CO decreases to zero After 16 min CO <sub>2</sub> decreases to zero The new gas reaction product based on –NCO radical continuously but not linearly increases. The surface reaction products are not bonded with the metal of the electrode	After 3 min CO <sub>2</sub> 19.2% maximum CO 11.3% formation of –NCO radical, –COO <sup>–</sup> ion, carbonyl –CO and amino group –NH <sub>2</sub> After 4 min CO 6.5% CO <sub>2</sub> 17.0% The surface reaction products are bonded to the metal of the electrode	After 3 min CO <sub>2</sub> 18.6% maximum CO 13.6% The CO level decreases continually down to 1.9% after 6 min CO <sub>2</sub> increases continually to 11.3% after 6 min No other gas reaction products were formed

**Table 4.** The step by step development with time of products for copper and brass electrodes.

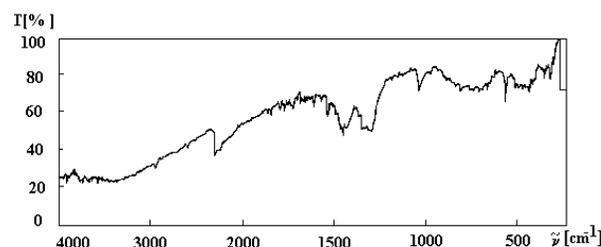
Introduced gas CO <sub>2</sub> –air mixture		Introduced gas CO–air mixture	
Positive polarity, 35% CO <sub>2</sub>	Negative polarity, 53.4% CO <sub>2</sub>	Positive polarity, 54.7% CO	Negative polarity, 49% CO
After 1.5 min CO 1.5% maximum CO <sub>2</sub> 15.6% After 4.5 min CO decreases to zero After 16 min CO <sub>2</sub> decreases to zero The new gas reaction products containing –NCO radical, –COO <sup>–</sup> ion and amino acids continuously increase until 16 min after discharge The surface reaction products containing imide and imidoester groups are bonded to the metal of the electrode	After 1.5 min CO 5% maximum CO <sub>2</sub> 33.8% After 4.5 min CO decreases to zero After 10 min CO <sub>2</sub> decreases to zero The new gas reaction product containing –NCO radical and –COO <sup>–</sup> ion continuously but not linearly increases. Surface reaction products are bonded with the metal of the electrode	After 1 min CO <sub>2</sub> 22.9% maximum CO 8.2% Formation of –NCO radical and –COO <sup>–</sup> ion, carbonyl –CO and amino –NH <sub>2</sub> groups in gas products After 3 min CO <sub>2</sub> 9.0% CO decreases to zero The surface reaction products containing imidoester and imidocarbonate groups are bonded to the metal of the electrode	After 2 min CO <sub>2</sub> 34.2% maximum CO 6.4% After 3 min CO <sub>2</sub> 26.6% CO 5.4% In reaction products, amino acids dominate. The surface reaction products had acid character and are bonded to the metal of the electrode



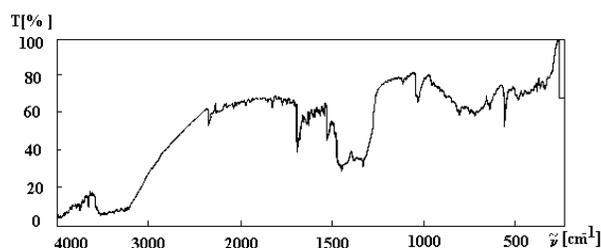
**Figure 11.** The IR absorption reflection spectrum of the stainless steel non-stressed electrode surface in the case of a positive corona discharge with electrode materials molybdenum and stainless steel and input gas  $\text{CO}_2$ .



**Figure 12.** The IR absorption reflection spectrum of the stainless steel non-stressed electrode surface in the case of a negative corona discharge with electrode materials molybdenum and stainless steel and input gas  $\text{CO}_2$ .

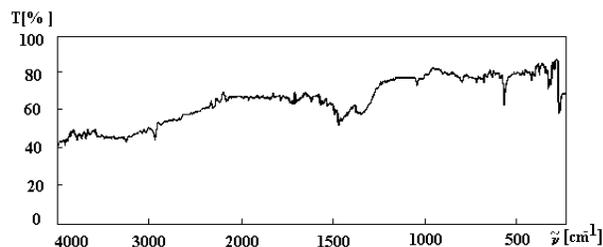


**Figure 13.** The IR absorption reflection spectrum of the brass non-stressed electrode surface in the case of a positive corona discharge with electrode materials molybdenum and brass and input gas  $\text{CO}_2$ .

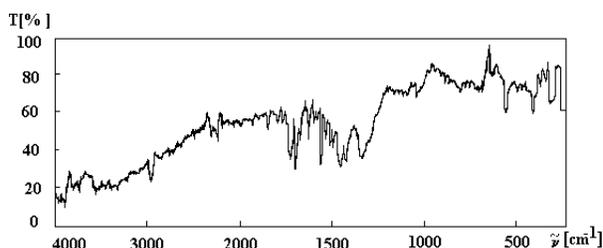


**Figure 14.** The IR absorption reflection spectrum of the brass non-stressed electrode surface in the case of a negative corona discharge with electrode materials molybdenum and brass and input gas  $\text{CO}_2$ .

parameters (input ratios between air and  $\text{CO}$  and  $\text{CO}_2$  and residence time). The measurements are performed for three combinations of materials. Owing to the method applied, it was possible to evaluate step by step the development with time of products. The concentrations of known gas



**Figure 15.** The IR absorption reflection spectrum of the brass non-stressed electrode surface in the case of a positive corona discharge with electrode materials copper and brass and input gas  $\text{CO}_2$ .



**Figure 16.** The IR absorption reflection spectrum of the brass non-stressed electrode surface in the case of a negative corona discharge with electrode materials copper and brass and input gas  $\text{CO}_2$ .

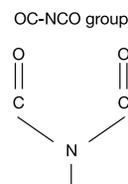
components are expressed as percentages. For products with unknown extinction coefficients we used the time of first appearance of their bands in IR spectra. To provide a more detailed overview of the described effects, we have collected results into tables 2–4 for each combination of materials.

### 3.3. Surface products

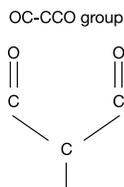
For each measurement we have analysed the surface of the non-stressed electrode. As analysing method we have used IR absorption reflection spectrometry. The reflection spectra for various materials of the non-stressed electrode, both polarities of the discharge and for  $\text{CO}_2$  input gas are in figures 11–16. The surfaces of the electrodes for  $\text{CO}$  input gas have similar characters to those in the case of  $\text{CO}_2$ , only the surface layer is fully developed in a shorter period of time.

The surface products differ with the polarity of the discharge and the material of the non-stressed electrode.

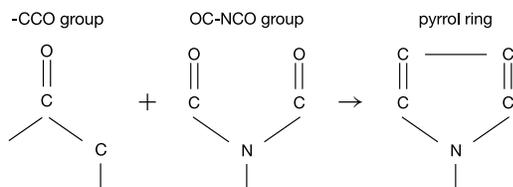
(i) For the input  $\text{CO}_2$ –air and  $\text{CO}$ –air mixtures and *negative polarity* of the discharge the surface products contain the following functional groups: the OC–NCO group in *cis* configuration, which may lead to the formation of imides



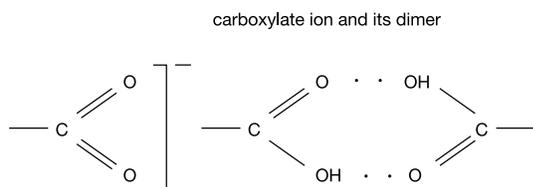
the OC-CCO groups in *cis* configuration, also known as malonic acid anhydride,



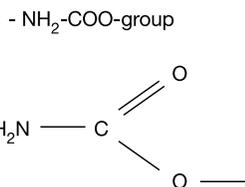
leading to the formation of chelates of  $\beta$ -dicarbonyl compounds; the -CCO group, which may create, together with OC-NCO, the pyrrole ring



the carboxylate ion  $\text{-COO}^-$  and its dimer  $(\text{-COO}^-)_2$

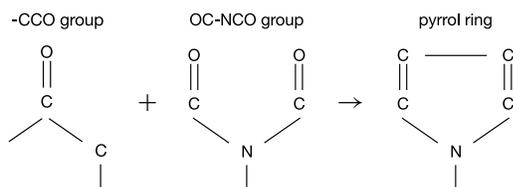


$\text{-NH}_2\text{-COO}^-$  which leads to the formation of urethanes (carbamates) and, after stabilization by polymerization, polyurethane

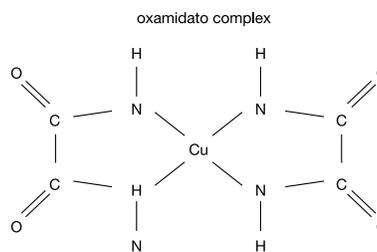


and  $(\text{HNCO})_2$  which leads to the formation of oxamidato complexes.

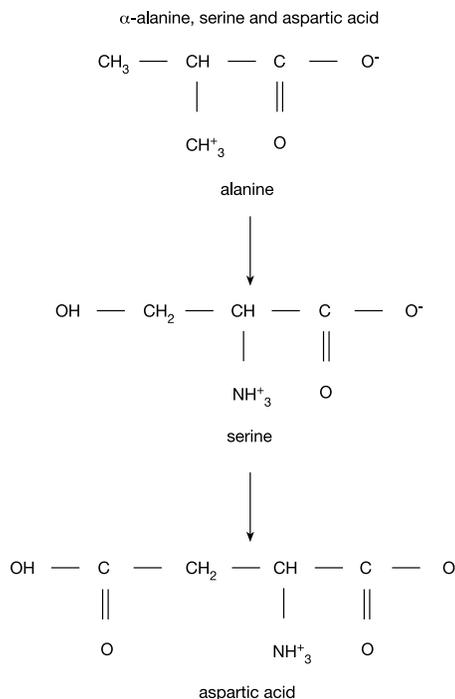
(ii) For the input  $\text{CO}_2$ -air and  $\text{CO}$ -air mixtures and *positive polarity* of the discharge the surface products contain following functional groups: the OC-NCO group in *cis* configuration, which leads later to the formation of imides. Similarly to the case with negative polarity, the pyrrole ring is created from OC-NCO and -CCO groups



$(\text{HNCO})_2$  which leads to the formation of oxamidato complexes



and  $\text{-NH}_2\text{-CO}^-$  leading the formation of amino acids, mostly  $\alpha$  alanine, serine and aspartic acids



The surface reaction products are not bonded with the metal of the non-stressed electrode for the Mo-stainless steel combination of electrodes, but are bonded to the material of the non-stressed electrode for Mo-brass and Cu-brass combinations of electrodes. For non-stressed anodes containing copper the polynuclear metal complexes formed on the electrode surface due to the action of the corona discharge act as catalysts with photochemical activity [35].

#### 4. Conclusions

The results from the studied combinations of electrodes, gas mixtures and times of action of the corona show the following.

(i) From the point of view of decreasing the concentration of  $\text{CO}_2$  the highest efficiency of removal is for a negative corona discharge with Cu and brass electrodes; the lowest efficiency of removal is for a positive corona discharge with Mo and stainless steel electrodes.

(ii) From the point of view of decreasing the concentration of  $\text{CO}$  the highest efficiency of removal is for

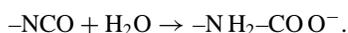
a positive corona discharge with Cu and brass electrodes; the lowest efficiency of removal is for a negative corona discharge with Mo and brass electrodes.

The discharges with electrodes made from Mo and brass in negative polarity and with electrodes of Cu and brass in positive polarity were typical, with high amounts of surface reaction products. The negative corona discharge with Mo and stainless steel electrodes acts practically without surface reaction products. The development of surface products is based on the following radicals formed by the discharge:

- (i) the NCO radical, which is changed to more complex formations such as
- (ii) OC–CCO (leading to production of chelates of  $\beta$ -dicarbonyl compounds),
- (iii) OC–NCO and ON–NCO in *cis* configuration (leading to the formation of polyimides),
- (iv) (HNCO)<sub>2</sub> (leading to the production of oxamidato complexes),
- (v) the dimer of (COO<sup>-</sup>)<sub>2</sub> (leading to the formation of acids or esters),
- (vi) –NH<sub>2</sub>–CO–, leading to the formation of amino acids (mostly  $\alpha$  alanine, serine and aspartic acids) and
- (vii) –NH<sub>2</sub>–COO–, leading to the formation of urethanes.

The necessary –NH<sub>2</sub> group is formed by the discharge in the following steps:

- (i) a change of CO<sub>2</sub> configuration from O=C=O to –COO<sup>-</sup> due to the presence of water and an electric field,
- (ii) the production of excited nitrogen by the discharge,
- (iii) incorporation of nitrogen into –COO<sup>-</sup>, exchange of oxygen with nitrogen and creation of –NCO radicals and
- (iv) reaction of –NCO radicals with H<sub>2</sub>O, formation of the –HN<sub>2</sub>–COO<sup>-</sup> functional group with a negative polarity of the discharge and –HN<sub>2</sub>–CO<sup>+</sup> with a positive polarity of the discharge:



For separation of CO<sub>2</sub> from flue gases, the following methods are used:

- (i) wet absorption of CO<sub>2</sub> in an amine or alkaline type of solvent,
- (ii) dry absorption of CO<sub>2</sub> by zeolite-packed bed filters and
- (iii) membrane separation of CO<sub>2</sub> by use of a polymer membrane.

Separated CO<sub>2</sub> will be liquefied and stored in the deep sea.

An alternative method for removal and fixation of CO<sub>2</sub> and CO could be to use corona discharges with surface active material on the electrodes in the presence of water. The method gives high efficiencies for the removal process. Although the gas intermediates (mostly amines) can be toxic, the final gas, liquid and solid products are not harmful. The method associates decomposition and activation processes in the volume of the discharge with synthesis of the final solid products on the surface of the electrodes. The activation factors for volume processes are mostly electrons, but for surface processes, with a great probability, light.

## Acknowledgments

The author wishes to express thanks to I Morva, M Kurdel, K Hensel, R Gašparík, S Strešková, E Ružinská and Z Machala for technical assistance. The discussions with Professor E Marode were a great help to me in describing more clearly the involved processes and chemical compounds. The project was partly supported by the MŠV SR in the form of grant project 1/2188/95.

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