

THE INFLUENCE OF WATER VAPOUR AND TEMPERATURE ON DEPLETION OF CARBON MONOXIDE IN D.C. CORONA DISCHARGE

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The plasmochemical and/or electrocatalytical reactions of carbon monoxide with water vapour were studied. Dc corona discharge of both polarities at room temperature and temperatures enhanced up to 70°C was applied at pressures close to atmospheric.

The reaction products were analysed by IR absorption spectrometry. The main products in the gas phase were CO₂ and CH₄. The reactions are influenced by the formation of a catalytically active surface layer on electrodes. The composition of this layer depends on the polarity of electrode.

Introduction

Corona discharge is usually realised in a non-uniform gap such as a wire-cylinder or a point-to-plane and is operated with dc, ac or pulsed power supply. Various metal electrodes with or without dielectric or ferroelectric material between the electrodes are applied.

Carbon monoxide CO is a toxic pollutant introduced into the Earth's atmosphere in significant quantities. In the nature there exist various removal mechanisms. The two most important are based on the reaction with radical -OH, the first in the lower stratosphere due to UV radiation and the second using the enzymatic activity of bacteria *Methanobactericum formicum* inside the earth in the presence of water [1].

The most important exhaust sources from the point of view of CO emissions are internal combustion engine and energy producing fossil fuel combustion systems. In both the cases CO is in the mixture with water vapour and carbon dioxide. The temperature of flue gases at the place of the exhaust pipe where it is possible to install some removal equipment is at the average about 80°C.

In the last few years we have made a group of measurements with various sources of exhaust where the concentration of CO does not exceed 12 vol.% in dynamic regime. We have tried to control the concentration of CO and also other compounds (NO, NO₂, SO₂, CO₂, aromatic compounds, aerosols, submicron particles) [2].

From the performed measurements the influence of a non-stressed electrode surface can be seen. The electrode surface material was modified due to the action of discharge. Water condensed on the surface modified the formed layer. This induced our study of the CO with water mixture at high concentrations of both components in static discharge operation regime and with various materials of non-stressed electrodes. Gained results are presented in the following paper.

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Experimental

Two most important processes involved in CO removal are based on the reaction with radical -OH . That is why it is necessary to test the reaction of CO with water vapour in the discharge system. To study such a process we have introduced water vapour into the discharge gap using various methods. In this work we have tested evaporation of water in relation to the applied temperature.

In our earlier results we have found out that the removal processes using discharges comprise two simultaneously acting effects:

- volume processes of plasmachemical nature probably initiated by electrons,
- electrocatalytic surface processes on electrodes probably initiated by photons.

To test these two aspects of our system, i.e. the influence of water and discharge on one side and the influence of electrode material on the other, we have used the following two discharge systems:

Coaxial discharge system — Fig. 1 — was applied to study the influence of water vapour pressure (ratio of water to carbon monoxide).

The discharge chamber is build from a steel cylinder with radius 12.5 mm as a non-stressed electrode with Mo wire of radius 0.1 mm as a stressed electrode. The length of the discharge tube was 100 cm.

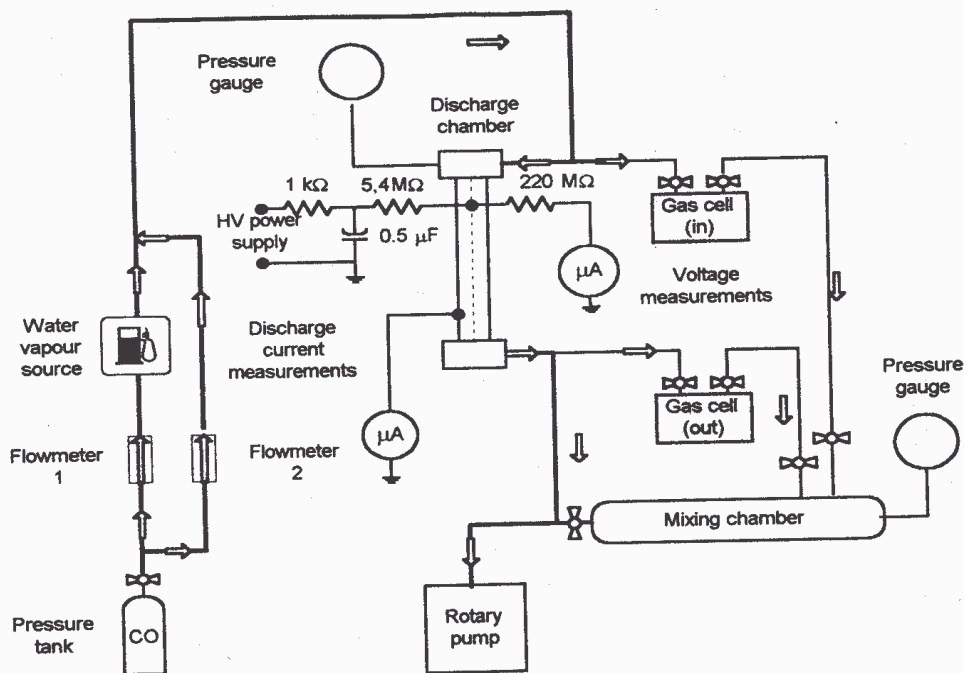


Fig. 1. Coaxial discharge system together with vacuum and electric scheme.

The vacuum apparatus connected with 1 m long discharge tube enabled heating of the system up to 80°C. Pressure between the atmospheric one and that of about 100 Pa was possible to measure with the installed membrane vacuumometer. Overview of the discharge system, inclusive the vacuum part and electric scheme is in Fig. 1.

Gas cell corona discharge tube suitable for materials studies — Fig. 2. The discharge system comprises the wire plane electrode configuration made from various electrode materials (the stressed electrode was the wire of 0.2 mm in diameter wound on a glass tube; the non-stressed electrode was the plane

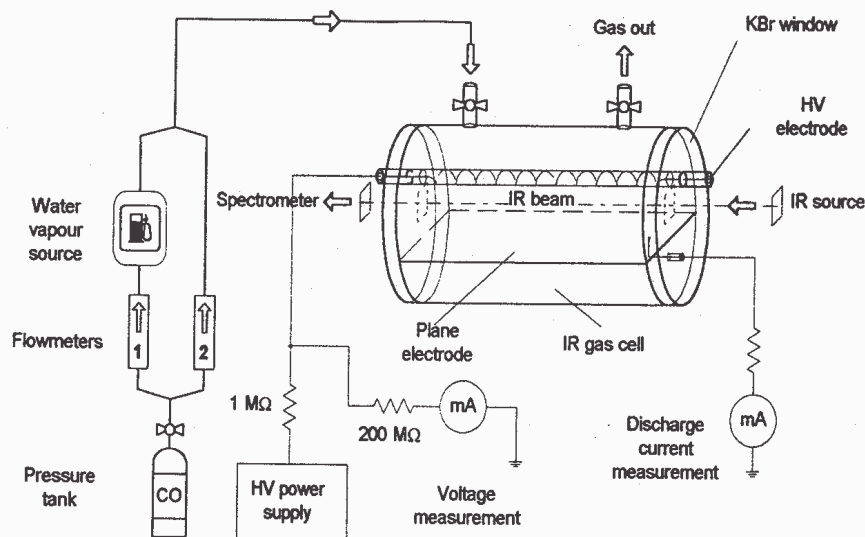


Fig. 2. Gas cell corona discharge tube suitable for materials studies together with vacuum and electric scheme.

35 × 100 mm², the inter electrode distance was 11 mm). The discharge tube was situated in the IR absorption gas cell so that the electrodes were parallel with the optical axis of the gas cell.

The small vacuum system connected with the wire-gas cell discharge tube enables to introduce various gases, working in the defined gas mixture at atmospheric pressure (but it is impossible to measure the pressure value).

Table 1. Material of electrodes.

Central stressed electrode	Plane non-stressed electrode
molybdenum	molybdenum
stainless steel	stainless steel
copper	copper
brass	brass

The main advantage of the system is the possibility of electrode material variation; step by step analysis of gas composition and both electrode surface analyses.

The measurements in the gas cell discharge tube gives us a possibility to determine the influence of electrode material on corona discharge affected chemical changes. All measurements were made parallel to the measurements in the cylindrical discharge tube. The material we used for electrodes is given in Table 1.

Type of discharge

A spontaneously pulsing d.c. electric discharge with a "brush-like" streamer to spark type of current pulses supplied by the dc HV source was used. The individual sparks appeared regularly together with corona discharge. The discharge operates in corona geometry, but some physical properties correspond to the high-pressure glow discharge. The cathode and anode spots are fully developed in the near electrode region. The discharge has strongly shining channels migrating quickly along the stressed electrode.

In the electric circuit the high voltage source PGK of Bauer was used with possible applied voltage up to 70 kV and maximal current up to 10 mA. Voltage and current were measured. The electric schema is seen from both Figs. 1 and 2.

For each discharge condition the current-voltage characteristic and onset voltage were measured and calculated. As the formed surface spots and layer on the non-stressed electrode are of semiconducting nature, the potential of this electrode from the discharge side is not identical with the earth potential and has the value of few volts due to the nature, polarity and thickness of the surface layer. Due to this electrocatalytic effects appeared.

Diagnostics

The infrared absorption spectrometry as a powerful method for identification of various materials in gas, liquid and solid phase was used for analysis. Carbon dioxide and carbon monoxide are compounds with intensive infrared absorption bands. Due to the action of electrical plasma various plasmochemical reactions take place. The final reaction products and intermediate ones are in many cases

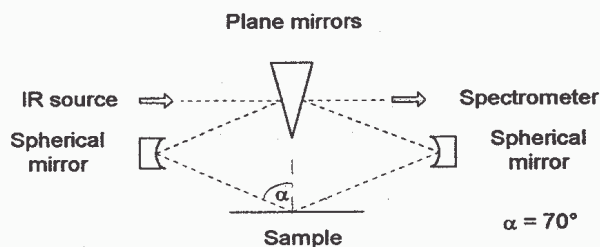


Fig. 3. IR reflection equipment.

unknown. The infrared spectroscopy is a very suitable method for its analysis. We have used various IR techniques. The gases were analysed in the 10 cm gas cell with KBr or KRS5 windows of similar construction as the gas cell discharge tube described in Fig. 2.

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 together pulverised in the vibration mill. The mixture is then pressed under pressure (5–22) MPa to the metal ring and by this way the pellet is formed. From the pellet the spectra are scanned.

The electrode surface from the discharge system in Fig. 2 was analysed using reflection spectra. The reflection depends on the wave number, angle of incidence, index of refraction and absorption features of the sample. The used device allows measuring the reflection spectra at 20° and 70° angles of incidence. Most of the spectra were measured with 70° angle as it is seen from Fig. 3.

Results and discussion

We have made a lot of earlier work scoped to studies of chemical processes in CO with H₂, N₂, O₂, air, CO₂ and H₂O in dc corona discharge of both polarities at room temperature in the coaxial discharge system [3]. As in each of this system surface processes seem to play an important role, we have built up a special gas cell discharge tube suitable for studies of surface "electrocatalytic" heterogeneous processes. The gas cell discharge tube gives the possibility to study "in situ" step by step time development of chemical process inside the discharge zone but only at atmospheric pressure and room temperature. In the following paper we have used a part of possibilities given by these two systems. All temperature depending measurements (variation of water vapour to carbon monoxide ratio) were made in the coaxial system. All measurements scoped to surface studies were made in the gas cell discharge tube.

Measurements at room temperature

By using the bubbler at room temperature it is possible to reach maximal partial pressure of H₂O about 2.5 kPa. The used partial pressure of CO was (40–50) kPa, i.e., ratio CO:H₂O was about 20:1. We have found out the influence of actual pressure to be much smaller than the influence of actual CO concentration. As it is hardly possible to maintain water vapour pressure, we have used in all measurement CO pressure between (35–60) kPa. The ratio between CO and H₂O was an important parameter, which is important stoichiometric information. All these measurements were made on the coaxial system described in the experimental part and in Fig. 1.

Under these circumstances the formation of gas reaction products is very low. Only about (1–2)% of CO₂ and the same amount of CH₄ were formed in both positive and negative polarity of discharge (Fig. 4).

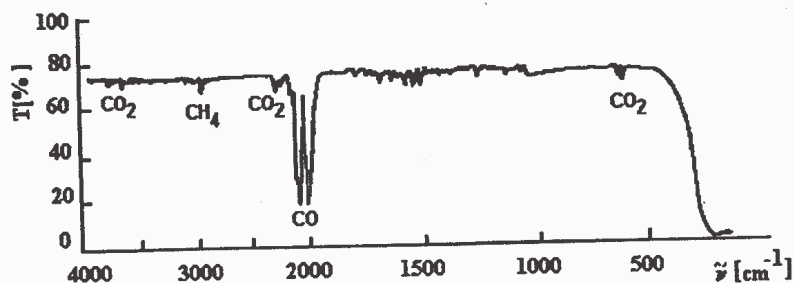


Fig. 4. IR absorption spectra of gas products from the mixture of CO+H₂O with ratio 20:1 and total pressure of 47.5 kPa after the action of positive corona discharge.

The plasma chemistry of the corona discharge is rather difficult, especially because of acting at atmospheric pressure. This caused the high ratio of great clusters in the drift region of the discharge near the non-stressed electrode. The ionisation processes occurred especially in the ionisation zone near the stressed electrode. The ionisation energy of possible ions (positive: CO⁺, C⁺, C₂O⁺, C₃O₂⁺, CO₂⁺, H₃O⁺, CHO⁺, CHO₂⁺, and its clusters with CO, CO₂ and H₂O or negative: O⁻, O₂⁻, O₃⁻, CO₃⁻, CO₄⁻, H⁻, OH⁻, and its clusters with CO, CO₂ and H₂O varies between 6 and 14 eV.

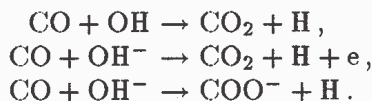
The average energy applied in the positive or negative corona discharge by electron impact is between 2 and 6 eV due to discharge current. The ions are formed after manifold repeated impacts which is possible under atmospheric pressure. That is the reason of low ionisation degree in corona discharge.

But this does not explain, rather it is against, the high effectivity of corona discharge to some plasmachemical processes, which were published and measured by many laboratories.

We suppose the electrocatalytical effect of the non-stressed electrode due to the enhanced value of relative permittivity in the surface layer of this electrode. The water layer on the surface has relative permittivity of 84. Formed products enhanced the relative permittivity of the surface. The several types of metal oxides and metal organic compounds, which are formed on the surface of the electrode have also an enhanced value of relative permittivity, especially when the water is built in the surface layer. Specific situation is in the case of ferroelectric materials. The ionisation potential on the surface of the electrode is lower than the ionisation potential in the volume of gas in the ratio 1 to square of relative permittivity [4]. The necessary energy comes from the recrystallisation process inside the solid. The electric wind continually transports the neutral gas to the electrode surface. This leads to an enhanced concentration of charged species near the non-stressed electrode.

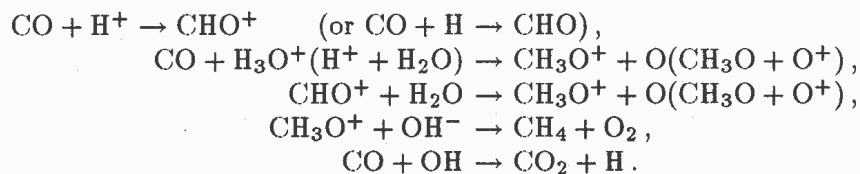
According to the possibility of recrystallisation energy use (in the case of enhanced relative permittivity) the dissociation of H₂O in the near electrode area can take place also when H₂O is in the ground state H₂O → H + OH. Then the probable reactions with CO which can lead to the obtained gas products, are, in

the near anode area:

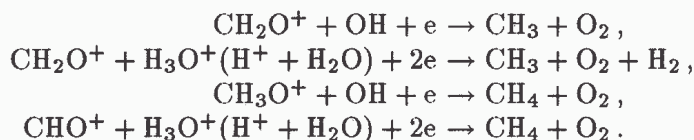


The main product from the near anode area is CO_2 , i.e., oxidative surrounding dominates.

The probable reactions in volume are:



The probable reactions in the near cathode area are:



The main product from the near cathode area is CH_4 molecular oxygen and hydrogen, i.e., reductive surrounding dominates. Molecular oxygen is usually set free and introduces further reactions. The only evidence of the great probability of these reactions (coming out from dissociation and dissociate ionisation of H_2O on the surface) is the fact that the main products CO_2 and CH_4 occurred in practically equal amounts.

From Fig. 5 we can see a more steep progress of real current-voltage characteristics comparing to the computed one (from the Townsend equation for coaxial geometry). The value of relative permittivity was calculated from the ratio of measured and calculated current-voltage characteristics for each point. The average value was also calculated. The relative permittivity of all gases present in the volume of the discharge tube does not differ very much from the relative permittivity of air. The possible explanation for the growth of relative permittivity of real discharge comparing to the computed one is in properties of surface products formed on the non-stressed electrode. It is necessary to say that the gained values are not the real relative permittivities of the layer/spots on the electrode, because the thickness of the layer is variable according to its position on the electrode surface.

From the enhanced value of relative permittivity we can see that the surface processes in discharge play a more important role on the anode and less important on the cathode. The similar result comes out from the measured IR reflection spectra of surface products on the corresponding electrodes.

The IR reflection spectra were made for various materials of the non-stressed electrode in the gas cell discharge tube. From the FIR region of these spectra, where the metal oxide type and the character of metal organic bond is seen, we can

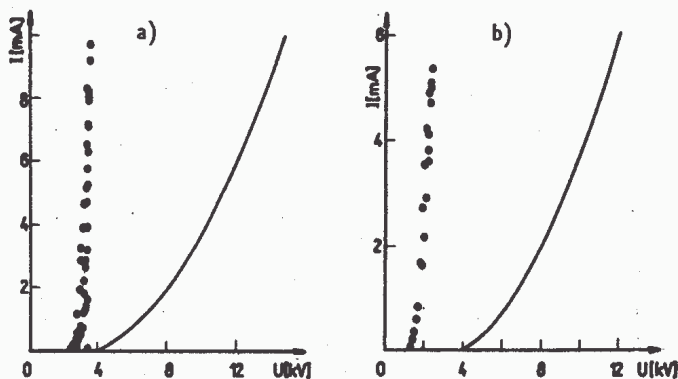
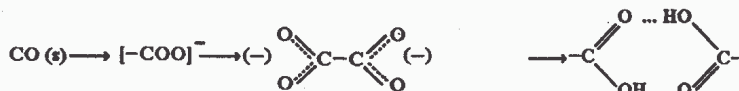


Fig. 5. The current-voltage characteristics of negative (a) and positive (b) corona discharge at room temperature and pressure 56 kPa and 53 kPa, respectively. The full line is the calculated characteristic and the points are measured values of the characteristic. The calculated average value of relative permittivity is 11.5 and 1.56, respectively.

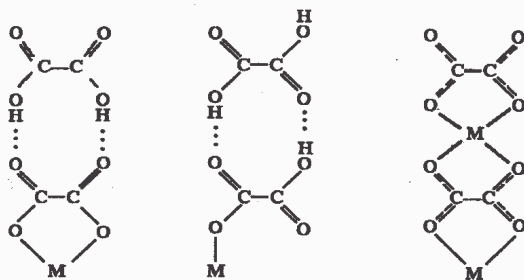
estimate the thickness of the surface spots and/or layer which is usually smaller than 10 μm.

In the atmosphere of CO without discharge the adsorption on the surface of the electrodes take place. In the IR reflection spectra of CO adsorbed on the surface the rotational structure of CO bands known from the gas spectra disappears [5]. When the chemisorption occurs, mono and poly nuclear metal carbonyls are formed on the surface (in IR reflection spectra bands with lower wave numbers are seen) [5,6].

On the non-stressed electrode, especially when it is the anode the conversion of the adsorbed CO to CO₂ in the form of carboxylate ion COO⁻ as an intermediate appears. Carboxylate ion COO⁻ very quickly dimerizes to stable the cyclic dimer. In the presence of water various dicarboxylic and hydroxy acids are formed as it is seen in the picture.



Surface oxides make possible to bond formed compounds to the surface.



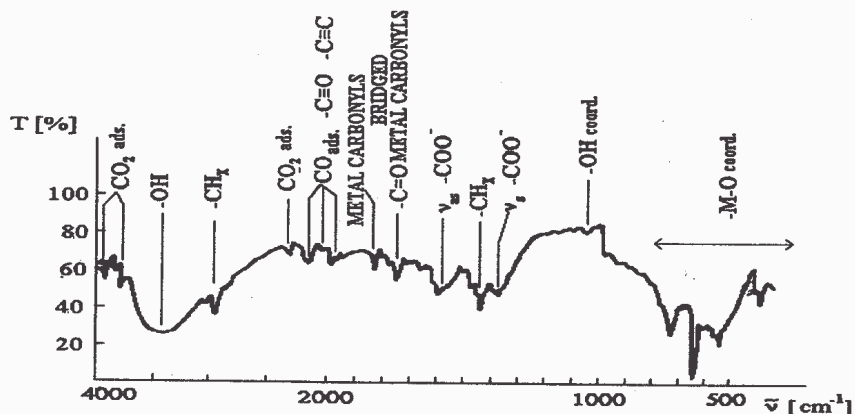


Fig. 6. The IR absorption reflection spectrum of the non-stressed electrode-anode after the application of negative corona discharge at room temperature in mixture of CO+H₂O, ratio 18:1 and pressure 47.5 kPa.

The proposed structures overcome from the qualitative analysis of the gained IR absorption surface reflection spectra of the non-stressed electrode from the gas cell discharge tube after the corona discharge action.

In the case of negative corona discharge the spectrum is shown in Fig. 6 and in the case of positive corona discharge the spectrum is plotted in Fig. 7.

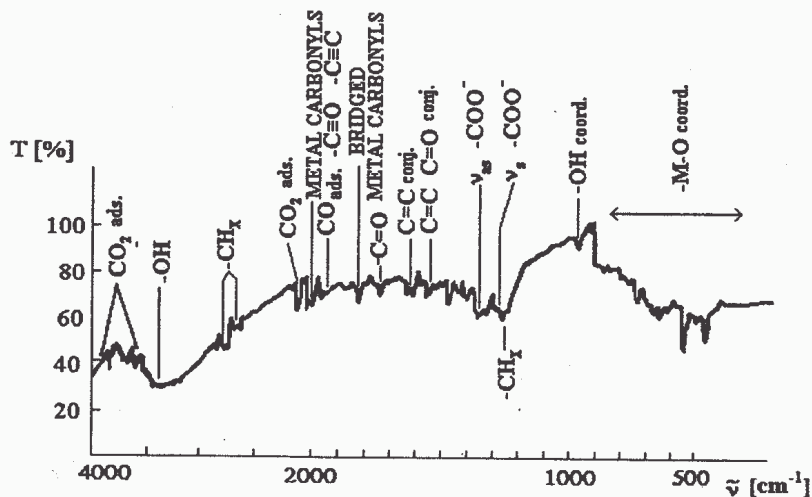


Fig. 7. The IR absorption reflection spectrum of the non-stressed electrode-cathode after the application of positive corona discharge at room temperature in mixture CO + H₂O ratio 19:1 and pressure 50 kPa.

In the IR absorption spectra the main absorption bands are carboxylate ion COO^- and its dimer $\nu_s = (1380-1440) \text{ cm}^{-1}$, $\nu_{as} = (1560-1600) \text{ cm}^{-1}$, the co-ordinated metal oxide bands M_xO_y at 360, 440, 490, 540, 585 cm^{-1} (for the brass metal surface), the $-\text{OH}$ band of hydroxo-complexes at $(3400-3600) \text{ cm}^{-1}$ and $(950-1000) \text{ cm}^{-1}$, CO and CO_2 adsorbed on the surface $(2000-2400) \text{ cm}^{-1}$, metal carbonyl bands $(1800-2000) \text{ cm}^{-1}$. The richest spectrum especially in the far infrared region was observed for the brass non-stressed electrode surface. That was the reason why I have used it as an example spectrum. From the absorption bands in FIR region it overcomes the presence of CuO , Cu_2O , ZnO , co-ordinated compound built on CuO_2 and ZnO_2 containing as ligand dicarboxylic acid and/or hydroxy acid [7,9].

The colour of the surface layer on the low voltage electrode was (for brass) from red-brown to violet (Cu_2O), somewhere matt white (complex dicarboxylic acids) or matt grey-black (CuO) due to the nature of the surface layer. By use of other materials as a non-stressed electrode (stainless steel, Mo) the gained spectra are very similar to that in Figs. 6 and 7 in the middle infrared region. For stainless steel only metal carbonyl bands of $\text{Fe}(\text{CO})_5$, $\text{Ni}(\text{CO})_4$, $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$ are more intensive than for copper and brass. The main difference can be seen in the far infrared region, where for stainless steel there are present the bands of Fe_2O_3 , Fe_3O_4 , NiO , triacetate of Fe and diacetate of Ni due to the bands at 330, 380, 420, 470, 560 and 770 cm^{-1} . But the bands are not so separated as it is in the case of brass. For Mo non-stressed electrode surface only the bands of MoO_2 , MoO_3 and $\text{Mo}(\text{CO})_6$ on the wave numbers 230, 370, 440, 590 and 680 cm^{-1} are present. From spectra of non-stressed electrode surfaces for all used materials it comes out that due to the action of the discharge in $\text{CO} + \text{H}_2\text{O}$ mixture the surface layer is formed on the non-stressed electrode for both polarities of the discharge, which has the domains (probable organo metallic) with enhanced relative dielectric permittivity. I suppose that this could cause the electrocatalytic behaviour. It seems to be necessary to prove the crystal lattice of the surface layer in future.

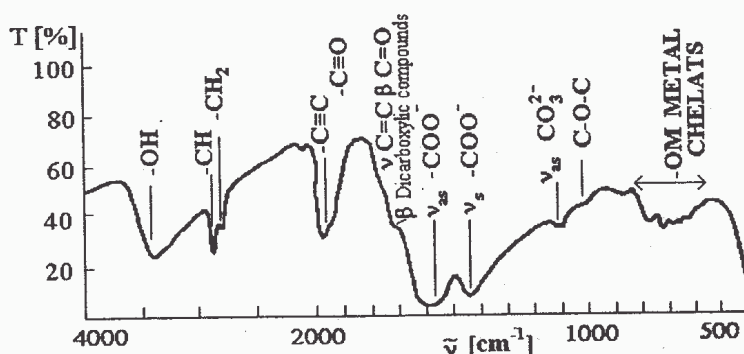
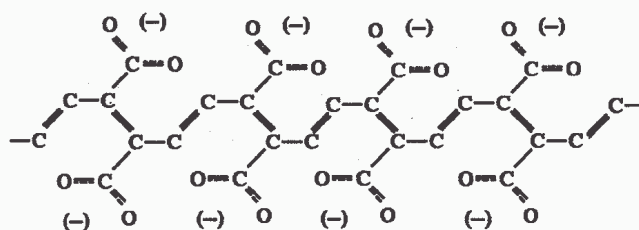


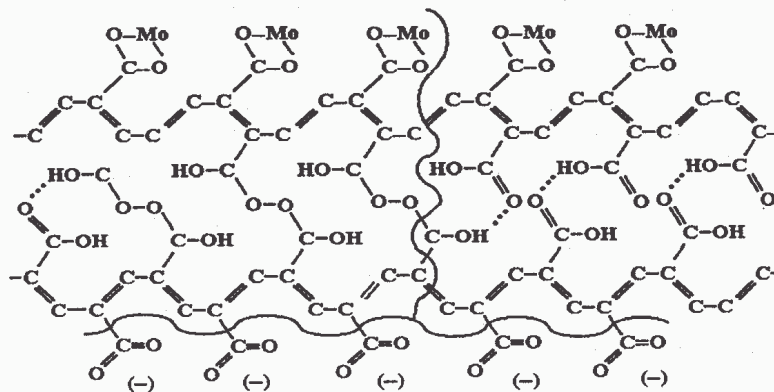
Fig. 8. The IR absorption spectrum of the surface layer on the stressed central electrode-anode formed after the action of positive corona discharge at room temperature in $\text{CO} + \text{H}_2\text{O}$ mixture, ratio 19:1 and total pressure 50 kPa.

In the case of the central stressed electrode the high surface temperature, more than $(400-500)^{\circ}\text{C}$, can be expected. This leads to degradation of the surface layer. The poly-conjugated carbon-carbon and carbon-oxygen systems are formed. In the IR absorption spectra the new bands in the region $(1600-1720)\text{ cm}^{-1}$ due to $\nu\text{ C}=\text{C}$ and $\nu\text{ C}=\text{C}, \text{C}=\text{O}$ conjugated in cis and trans forms appeared. The spectra were gained using halide disc technique. The corresponding IR absorption spectra for the positive corona discharge are shown in Fig. 8 and for the negative corona discharge in Fig. 9.

In the case of the positive central stressed electrode-anode (practically the whole electrode was covered with the layer) the depth of the layer was more than $10\text{ }\mu\text{m}$ and the colour was dark brown or black. From IR spectra, where the most significant bands are $(1600-1720)\text{ cm}^{-1}$ corresponding to $\nu\text{ C}=\text{C}$ and $\nu\text{ C}=\text{C}, \text{C}=\text{O}$ conjugated, carboxylate ion COO^- and its dimer ν_s $(1380-1440)\text{ cm}^{-1}$, ν_{as} $(1560-1600)\text{ cm}^{-1}$, the following structure can be proposed:

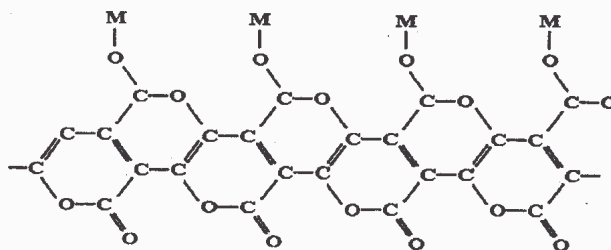


The air humidity influences the surface product so that it creates induced cross-linking of the suggested structure as it is seen from the following figure:



The connection of the suggested structure to the metal surface is realised through the MoO_2 structure (the $510, 560, 610,$ and 660 cm^{-1} bands).

In the case of the negative central stressed electrode-cathode only small spots scattered on the electrode were seen, the colour was also dark brown or black. From the IR spectra, where the most significant bands are $(1600-1720)\text{ cm}^{-1}$ corresponding to $\nu\text{ C}=\text{C}$ and $\nu\text{ C}=\text{C}, \text{C}=\text{O}$ conjugated (all two bands for carboxylate ion are negligible, but the ether band of $\text{C}-\text{O}-\text{C}$ at 1060 cm^{-1} corresponding to the heterocyclic lactone ring is very strong) the following structure can be proposed:



The connection of the suggested structure to the metal surface is realised through the MoO structure (460 cm^{-1} band).

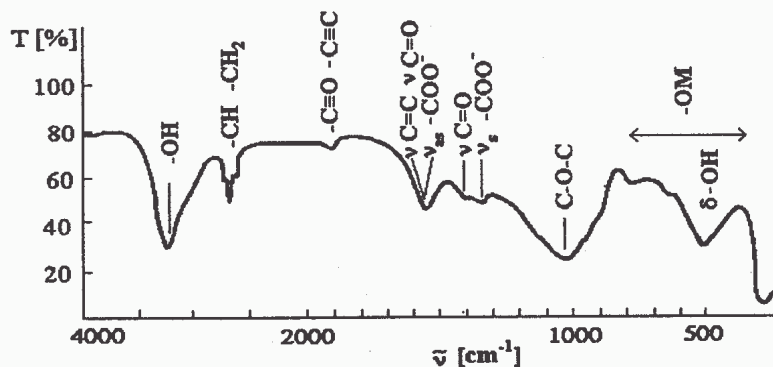


Fig. 9. The IR absorption spectrum of the surface layer on the stressed central electrode-cathode formed after the action of the negative corona discharge at room temperature in CO + H₂O mixture, ratio 18:1 and total pressure 47.5 kPa.

The structure of the material on the stressed electrode has many similarities with the thermal polymer of C₃O₂ [10–12] as it is possible to see from certain bands in infrared absorption spectra in the solid phase. But the spectrum of monomer malone acid anhydride C₃O₂ in the gas phase was not observed.

The interpretation of IR spectra and the construction of possible structures from the observed spectra was made with the help of literature [5–12].

Measurements at temperature about 70°C

The aim of enhanced temperature measurements was to make reaction CO+H₂O in ratio close to 1:1. To enhance the water vapour concentration we have heated the system up to 70°. The measurements at enhanced temperatures were made in the coaxial system, which is possible to heat up to 80° in static regime. The relation between the saturated water vapour pressure and the temperature is in Fig. 10.

At 70°C we should gain up to 70 kPa of water vapour, but in a real apparatus we can reach maximally 33 kPa because of losses on various surfaces. The water vapour pressure creates a lot of problems with realising of the same conditions (total pressure and partial pressure of components) in positive and negative corona discharges.

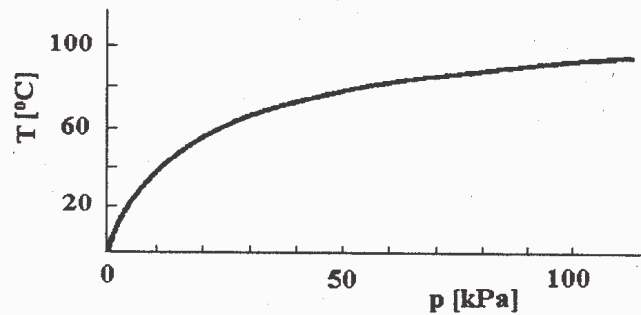


Fig. 10. The dependence between saturated water vapour pressure and temperature.

This fact was also the reason why the applied total pressure was strongly depending on the pressure of water vapour that we reach in an individual measurement. This property of water introduced into the system makes this method very unfavourable for the future applications.

For both positive and negative corona discharges the current-voltage characteristics were measured and calculated. The value of relative permittivity was calculated from the ratio of measured and calculated current-voltage characteristics for each point in a similar way as in the case of room temperature measurements. The average value of relative permittivity was also calculated. The current-voltage characteristics for negative corona discharge are displayed in Fig. 11a and for positive corona discharge in Fig. 11b.

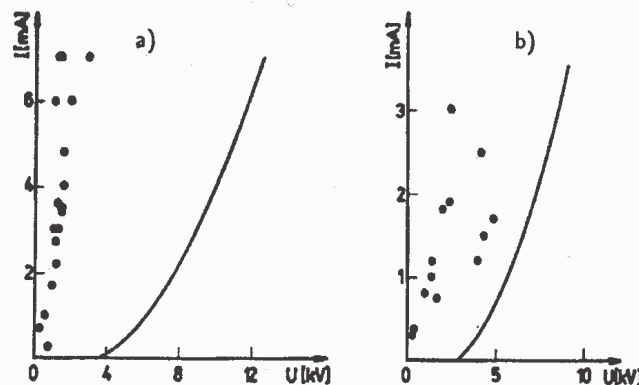


Fig. 11. The current-voltage characteristics of negative (a) and positive (b) corona discharge at the temperature of 70°C and the pressure of 53 kPa and 34.6 kPa, respectively. The full line is the calculated characteristic and the points are the measured values of the characteristic. The calculated average value of relative permittivity is 45.9 and 17.7, respectively.

In the case of negative corona discharge the components were introduced to the pressures 30.7 kPa (CO) and 22.7 kPa (H₂O) which represent 57.5% of CO and 42.5% of H₂O in the mixture and ratio CO:H₂O = 1:0.74. The negative corona discharge was applied for about 25 minutes. After the action of discharge the gas sample was introduced to the evacuated IR gas cell (H₂O was eliminated during introducing to the cell as the KBr windows were used in the gas cell) and IR absorption spectrum was scanned. It is shown in Fig. 12.

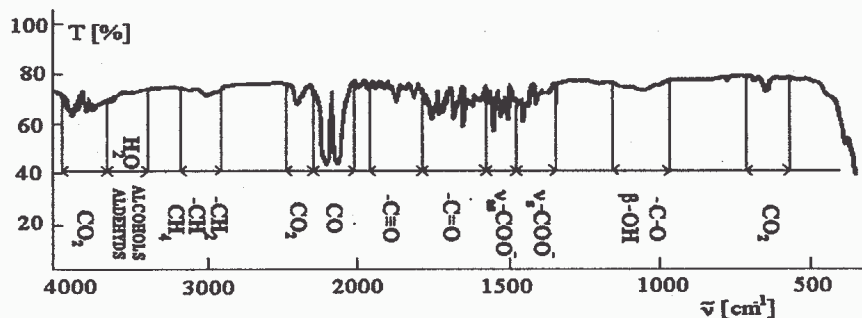


Fig. 12. The IR absorption spectrum of gas products after the action of negative corona discharge in CO+H₂O, mixture ratio 1:0.74 at temperature about 70°C and total pressure 53.4 kPa.

In IR absorption spectrum the following compounds and structural groups can be seen: CO (2020–2260 cm⁻¹); CO₂ (670, 2240–2400 cm⁻¹); CH₄ (2920–3180, central peak 3018 cm⁻¹); HCOH, CH₃COH (–C=O: 1740 cm⁻¹, –CH_x: 2850–2920 cm⁻¹); CH₃OH (3685 cm⁻¹, C–O(H): 1100–1200 cm⁻¹); HCOOH, CH₃COOH, carboxylate ion and its cyclic dimer [COO⁻]₂ (1420 cm⁻¹, 1580 cm⁻¹).

After the action of discharge the following changes of the mixture composition occurred:

- CO decreased from 30.7 kPa to 19.7 kPa (i.e. from 57.5% to 36.9%);
- H₂O was hold approximately at the same pressure level (by continual introducing into discharge) during the discharge action (the value was 22.7 kPa, i.e. 42.5%);
- CO₂ was formed during the discharge action but its final pressure was only 1.7 kPa (i.e. 3.2%);
- CH₄ was formed and its final pressure was 1.5 kPa (i.e. 2.8%);
- all other gas and liquid products were formed up to 2.5 kPa (i.e. 4.6%);
- the pressure decrease observed during the corona discharge action was 5.3 kPa (i.e. 10%) due to the formation of solid and liquid products on the electrodes.

The efficiency of CO decrease in the negative corona discharge at 70°C, the total pressure of 53.7 kPa and ratio CO:H₂O = 1 : 0.74 was 35.8%.

In the case of positive corona discharge the components were introduced to the pressures 16 kPa (CO) and 18.7 kPa (H₂O) which represents 46.1% of CO and 53.9% of H₂O in the mixture and ratio CO:H₂O = 1:1.17.

The positive corona discharge was applied for about 25 minutes. After the action of discharge the gas sample was introduced to the IR gas cell and the spectrum was scanned (Fig. 13).

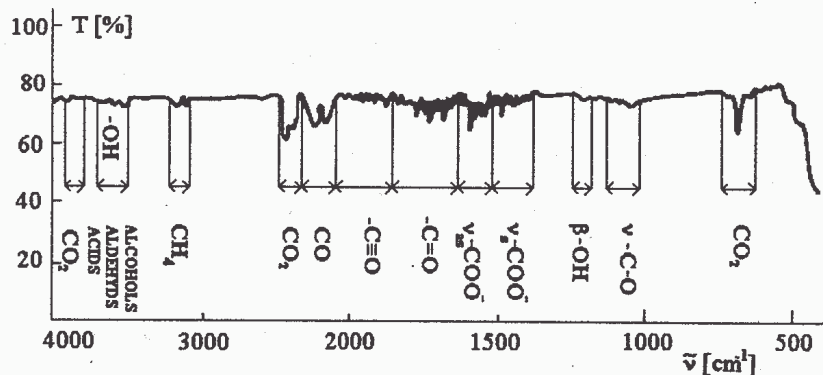


Fig. 13. The IR absorption spectrum of gas products after acting of positive corona discharge in CO+H₂O, mixture ratio 1:1.17 at temperature about 70°C and total pressure 34.7 kPa.

In the IR absorption spectrum the following compounds and structural groups can be seen: CO (2020–2260 cm⁻¹); CO₂ (670, 2240–2400 cm⁻¹); CH₄ (2920–3180, 3018 cm⁻¹); HCOH, CH₃COH (–C=O: 1740 cm⁻¹, –CH_x: 2850–2920 cm⁻¹); CH₃OH (3685 cm⁻¹); C–O(H) (1100–1200 cm⁻¹), HCOOH, CH₃COOH, [HCOO⁻]₂ (dimer) (1420 cm⁻¹, 1580 cm⁻¹).

The observed structural units were the same as in the negative corona discharge. After the positive corona discharge action the following changes of mixture composition occurred:

- CO decreased from 16 kPa to 5.3 kPa (i.e. from 46.1% to 15.4%);
- H₂O was hold approximately on the same pressure level (by continual introducing into discharge) during the discharge action (18.7 kPa, i.e. 53.9%);
- CO₂ was formed during the discharge action but its final pressure was only 1.9 kPa (i.e. 5.5%);
- CH₄ was formed and its final pressure was 0.8 kPa (i.e. 2.3%);
- all other gas and liquid products were formed up to 4 kPa (i.e. 11%);
- the pressure decrease observed during the corona discharge action was 4 kPa (i.e. 11.5%) due to the formation of solid and liquid products on the electrodes.

The efficiency of CO decrease in the positive corona discharge at 70°C and ratio CO:H₂O = 1:1.17 was 66.7%. The solid products on both stressed and non-stressed electrodes in both polarities of discharge were of the same character as in the case of room temperature.

Conclusions

From the performed measurements it is seen that in the mixture of CO with water vapour the spots and/or a layer of solid product is formed on the surfaces of electrodes. Due to the electrode polarity, the pressure of water vapour, the type and the polarity of formed particles and clusters and due to the material of metal surface the chemical composition of the surface structure is changed. One can see from the IR spectra that the linear conjugated structures are formed on the anode and hetero cyclic structures with one oxygen hetero atom on the cathode. Water preferably reacts with the structure formed on the anode. This seems to be the reason why this structure disposes with higher relative dielectric permittivity.

Formation of organo metallic structures on the metal surface leads to the change of relative dielectric permittivity of the surface and through this also in the whole discharge. The average relative dielectric permittivity of positive corona discharge at room temperature was 1.56 and rose up with temperature (water concentration) to the value of 17.7 at 70°C. The relative dielectric permittivity for the negative corona discharge at room temperature was 11.5 and rose up with temperature to the value of 45.9 at 70°C.

According to the enhanced value of relative dielectric permittivity caused by the formed surface product the ionisation potential on surface is much smaller ($1/\epsilon_r^2$ times) than it is in the discharge zone. According to the fact that the most frequent molecule on the surface is water the dissociation and ionisation of it takes place on the surface. This is the reason why the surface gains the electro catalytic activity.

The main gas products were CO₂ and CH₄. The CO₂ formed within the discharge volume is close to the anode quantitatively transformed into negative carboxylate ion. This ion then leads to the formation of surface products. Only small part of volume formed CO₂ remains in the gas phase. CO₂ which was created on the surface of the anode similarly as CH₄ formed on the cathode are both in the gas phase. The measurable values of gas CO₂ and CH₄ were reached especially in the system with enhanced temperature. The amounts of both CO₂ and CH₄ were about the same.

The partial pressure of H₂O followed the rise of temperature. More and more water molecules are transported with the electric wind to the surface, where are dissociated and/or ionised. The produced H and OH radicals (ions) are incorporated into the surface products to create dicarboxylic and hydroxy acids. Under lower temperatures dominate oxalic and malone acids, under higher temperatures tartaric and citric acids. Part of the produced H and OH ions are transported by drift again to the volume. This leads to the formation of some amounts of alcohols, aldehyds and acids in volume. Also the production of CO₂ and CH₄ increases with the rising temperature.

The most important fact coming out from the gained results is that CO₂ created due to the proposed reaction of CO with OH radical does not remain in the gas phase. CO₂ is quantitatively transformed into a solid product [13]. The process is connected with a measurable decrease of pressure and formation of intensive sound [14]. The ratio between the solid and gas product is higher in the case of the

negative polarity comparing to the positive one. Also the increase of temperature leads to the increase of gas phase products.

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