Study of Plasma Induced Chemistry by DC Discharges Above Water Surface in $CO_2/N_2/H_2O$ Mixture

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Abstract.

The chemistry induced by atmospheric pressure DC discharges above a water surface in $CO_2/N_2/H_2O$ mixtures was investigated. The gaseous mixtures studied represent a model prebiotic atmosphere of the Earth.

The most remarkable changes in the chemical composition of the treated gas were the decomposition of CO_2 and the production of CO. The concentration of CO increased logarithmically with the increasing input energy density and an increasing initial concentration of CO_2 in the gas. The highest achieved concentration of CO was 4.0 ± 0.6 vol. %.

The production of CO was crucial for the synthesis of organic species, since reactions of CO with some reactive species generated in the plasma, e. g. H• or N• radicals, were probably the starting point in this synthesis. The presence of organic species (including the tentative identification of some amino acids) was demonstrated by the analysis of solid and liquid samples by high-performance liquid chromatography, infrared absorption spectroscopy and proton-transfer-reaction mass spectrometry. Formation of organic species in a completely inorganic $CO_2/N_2/H_2O$ atmosphere is a significant finding for the theory of the origins of life.

Keywords: non-thermal plasma, organic synthesis, origins of life

1. Introduction

The theory of the evolution of life is based on the possibility of the synthesis of organic compounds by abiotic processes from inorganic species. Possible energy sources for these processes include UV radiation, electric discharges, shock waves, radioactivity, cosmic rays, solar wind, volcanoes, and hydrothermal vents (Miller, 1992). The first experimental support for the evolution theory came from Miller and Urey's famous experiment in the 1950s (Miller, 1953). They subjected methane, hydrogen, ammonia and water to an electric discharge and detected products like HCN, aldehydes, ketones and the ammonia in liquid water, where the amino acids were synthesized via HCN polymerization reactions (Miller, 1955):

$$RCHO + NH_3 + HCN \;\rightarrow\; RCH(NH_2)CN + H_2O \qquad (1)$$

$$RCH(NH_2)CN + 2\ H_2O \;\rightarrow\; RCH(NH_2)COOH + NH_3 \qquad (2)$$

Nevertheless, according to current geochemical knowledge, the atmosphere relevant for the chemical evolution of life had a different composition. It was formed by the volcanic out-gassing of the Earth and its major components were N_2, CO_2, and H_2O (Rubey, 1955; Sigvaldason and Elisson, 1968). Thus, Miller's experiments were repeated under varying conditions, with different composition of gases and various energy sources. A review on this topic was recently presented by Rode (1999).

Schlesinger and Miller (1983) reported that carbon yields of amino acids generated by the action of a spark discharge from CH_4-N_2-H_2O, and CO_2-N_2-H_2O were 1 % and 0.0006 %, respectively. It was thus suggested that a strongly reducing atmosphere would have been required for the origin of life, which is contrary to the conclusions drawn from atmospheric modeling. Kasting and Brown (1998) suggested that a CO_2-N_2-H_2O atmosphere containing tens to hundreds of ppm of CH_4 might have existed. Such amounts of CH_4 could have produced a small amount of HCN (the production rate was estimated to have been 10^8 $cm^{-2}s^{-1}$). However, according to Miyakawa et al. (2002a), biologically important molecules might not have been synthesized sufficiently via HCN polymerization with such a low production rate of HCN, unless portions of the Earth were frozen. As an alternative possibility, they suggested a CO-N_2-H_2O atmosphere and a high energy source (2.5–3.0 MeV protons) (Miyakawa et al., 2002b).

Based on these results, the chemical evolution of life would seem to be impossible in CO_2-N_2-H_2O mixtures with only small admixtures of CO and CH_4. However, in work with a different context, Morvova et al. (1998; 2000) reported the synthesis of various organic compounds by the plasma discharge treatment of various exhaust gases with the major components N_2, CO_2 and H_2O. A novel mechanism of synthesis of amino acids involving the NCO• radical, the HNCO species and a catalytic effect of copper electrodes was suggested. The production of NCO• radical was suggested to proceed via reactions of excited N_2 and CO_2 species. This mechanism therefore does not require the presence of CO or CH_4 in the gas, though their treated exhaust gases contained other minor admixtures, such as CO, nitrogen oxides (NO_x), O_2, and volatile organic compounds (VOCs). These species, despite their low concentrations, can significantly influence the discharge induced chemistry. Moreover, some of these admixtures were most probably not present in the prebiotic atmosphere. We repeated these experiments in a simplified system, with a discharge above a water surface in the mixture of pure N_2 and CO_2. We focused on the gas phase chemistry, but we also present results from the analysis of liquid samples here.

2. Experimental Set-Ups and Methods

We performed a series of discharge experiments in $CO_2/N_2/H_2O$ mixtures, with N_2 and CO_2 supplied from pressure tanks. Water was directly present in the discharge chamber: the low voltage (LV) planar copper electrode was submersed. Experiments were carried out in the continual regime with gas flows from 0.2 to 0.7 L/min at room temperature. The concentration of CO_2 (c_{CO_2}) in the input gas varied from 0 to 100 vol. %. The concentration of water vapor in the gas phase was around 2 vol. %, since the saturated water vapor pressure at room temperature is approximately 2200 Pa.

Besides the short-term experiments focused on gas phase chemistry, we also performed three long-term measurements, during which ultra pure water (suitable for HPLC analysis, Fluka Chemie AG, Germany) remained in the discharge chamber for three weeks. The discharge was on for about eight hours per day, when the discharge was off, the chamber was closed. To exclude any possible influence of impurities, blank samples were taken from the discharge chamber before each long-term experiment, one day after the chamber was cleaned and filled with ultra pure water.

A copper wire with diameter of 0.3 mm, coiled up on glass tube with a diameter of 6 mm, was used as a high voltage (HV) electrode. The inter-electrode distance was 10 mm. The distance between the HV electrode and the water surface was approximately 6 mm. The decrease of water amount due to its evaporation was minimized, because the input gases from pressure tanks (N_2, and CO_2) were moisturized in gas-bubblers. The electrodes were installed in a standard gas cell used for an acquisition of gas samples for the analysis by Infrared (IR) absorption spectroscopy, having a shape of a glass tube with two valves for gas inlet and outlet, the length of 100 mm, and the inner volume of 100 ml. The sides of the discharge chamber were enclosed by Teflon windows with openings for electrodes.

In order to generate the electric discharge, we employed a 1.4 kW DC power supply, BAUR PGK 70, delivering up to 70 kV and 20 mA, together with an external capacitor of 0.5 μF, and a ballast resistor of 3.9 MΩ, as shown in Figure 1. Typical average discharge current in our experiments varied from 0.4 to 2.3 mA. In this range, and with the used electric setup, the discharge can operate in two regimes, named according to their properties 'High Pressure Glow Discharge' (HPGD) and 'Spontaneously Pulsing Transition Discharge' (SPTD) (Machala et al., 2000). Both regimes work in both polarities, we only used positive polarity in these experiments. The discharge regime depends also on the gas composition, properties of the electrodes, and the distance of HV wire electrode from the water surface. Higher inter-electrode distance and higher gas flow rate favor the SPTD regime, whereas the higher concentration of CO_2 favors the HPGD regime.

2.1. Applied Analytical Techniques

The IR absorption spectroscopy was used as a main analytical technique in this work. We used a double beam spectrometer Specord M 80 working in the range of 4000–200 cm^{-1} for the detection and quantitative analysis of CO_2, CO and NO_x species in gaseous samples, as well as for the analysis of deposits formed on the surface of the LV electrode (KBr pellet technique). The concentrations of CO_2 and CO were calculated from the obtained spectra by using Lambert-Beer law.

Liquid samples were analyzed by high performance liquid chromatography (HPLC), and by proton-transfer-reaction mass spectrometry (PTR-MS). The HPLC is a very rapid and sensitive method for the separation of amino acids, peptides, and protein substances. Our samples were derivatized according to Waters AccQTag method for amino acids. The same procedure was used to derivatize the standard amino acids. The resulting solutions were analyzed by reversed phase HPLC on an Agilent 1100 system. The eluent was a mixture of two solvents. Solvent A consisted of 140 mM sodium acetate in water with 17 mM TEA, titrated to pH 5.05 with phosphoric acid and filtered through a 0.2 μm hydrophilized polypropylene GHP membrane (Pall Gelman) before use. Solvent B was 60 % acetonitrile (super gradient grade for HPLC) in the ultra pure water. The analysis was performed using the following conditions (all segments linear):

gradient 1: 0 min 0 % B, 0.5 min 2 % B, 15 min 7 % B, 19 min 13 % B, 33 min 32 % B, 34 min 100 % B, 39 min 100 % B, 40 min 0 % B, stop time 50 min

gradient 2: 0 min 0 % B, 0.5 min 5 % B, 15 min 10 % B, 19 min 16 % B, 33 min 37 % B, 34 min 100 % B, 39 min 100 % B, 40 min 0 % B, stop time 50 min

The PTR-MS technique was developed several years ago at the Institute of Ion Physics, University of Innsbruck, for the purpose of online monitoring of VOCs with concentrations in the range from pptv to ppmv (Hansel et al., 1995). It is based on proton-transfer reactions, and H_3O^+ is used as a primary reactant ion. This ion is very suitable for the analysis of VOCs, because the most common of them have larger proton affinities than water, and their reactions with H_3O^+ often lead to no fragmentation. On the other hand, other air components, such as N_2 and O_2, have proton affinities lower than water and the H_3O^+ ions do not react with them. Thus, air can be used directly as a buffer gas. PTR-MS was also applied for the analysis of gas phase products near the channel of spark discharge in $N_2/CO_2/H_2O$ mixture (Mikoviny et al., 2005). Indirectly, this technique can be also used for the analysis of liquid samples. In our case, we bubbled an inert gas through our samples and analyzed its composition (so-called head space measurements).

The disadvantage of PTR-MS is that due to the absence of fragmentation, several VOCs can lead to the production of ions with the same mass (mass of the parent molecule plus one). The identification of peaks in the PTR-MS spectrum of complicated gas mixtures is therefore very difficult. However, the list of possible species is limited by constraints resulting from our experimental conditions and limitations of head space method. For example, we may detect only volatile organic compounds with proton affinity higher than water, which are stable and soluble in water. We may exclude highly soluble carboxylic acids, which cannot be stripped from the water into the gas phase and would thus not be measurable by this method (Plankensteiner et al., 2007). On the other hand, highly volatile species would be flushed out from the reactor already during the experiments.

3. Results

3.1. Analysis of Liquid Samples

The average current during the first two long-term experiments was around 1 mA (SPTD) and the energy input density (E_d) was around 500 J/L. The concentration of CO_2 varied from 3 to 60 vol. %, with an average value around 25 %. In the third experiment, we used only CO_2 as an input gas for the first two weeks, and then we gradually increased the concentration of N_2. The average current was around 2 mA (HPGD), though the value of E_d remained around 500 J/L.

The water from the discharge chamber after three weeks of experiments contained dispersed particles, which were most probably identical with substances covering the surface of the LV electrode. We flushed these deposits from the LV electrode with ultra pure water and analyzed them by HPLC and IR spectroscopy. We found that several amino acids had retention times consistent with the retention times of some peaks of unknown compounds from the first two samples in case of both gradients applied (glycine and serine in the first sample and glycine, proline and valine in the second sample). The concentration of these amino acids would be in the order of μM. However, there were most probably no amino acids in the third sample. This was expected, since during the third experiment, we mostly used only CO_2 as the input gas and there was not enough nitrogen. No coincidences of retention times with amino acids were found in blank samples either.

The PTR-MS analysis of liquid samples from the three long-term experiments confirmed the presence of organic species as well. The list of detected ions with average counts per second (CPS) after the extraction of background counts, their sum formulas, and possible species from which they were formed are viewed in Table I. The PTR-MS spectra obtained from individual samples were different from each other, but they were in a good agreement in major features. Almost all major peaks were present in all three samples (masses 32, 41, 42, 45, 46, 59, 62, and 71). Two additional strong peaks appeared only in the third sample (masses 33 and 47) and two peaks were strong only in the second sample (masses 55 and 73). However, masses 55 and 73 can be most probably attributed to the water cluster ions $(H_2O)_2.H_3O^+$ and $(H_2O)_3.H_3O^+$. There is therefore no principal difference between the first two samples. What concerns the additional peaks in the third sample, masses 33 and 47 can be most probably attributed to the methanol and ethanol, respectively. Other organic species which can be identified from the obtained spectra are most likely acetaldehyde (mass 45) and nitromethane (mass 62). Mass 32 can be attributed to O_2^+ ion. Thus, similar to masses 55 and 73, it is not listed in Table I.

3.2. Solid Deposits on the LV Electrode

Figure 2 shows example of the obtained IR spectra (from the second long-term experiment) of solid deposits flushed from the LV electrode. The spectra from the other two samples were again not identical, similar to PTR-MS spectra, but the main absorption bands (850 - 450, 1500 - 1200, 1700 - 1550, and traces of CH_x around 3000 cm^{-1}) were present in all of them. The identified compounds in solid products were copper oxides (CuO, Cu_2O), ions of inorganic salts (HCO_3^-, CO_3^{2-}), and organic compounds. The most probable organic species are carboxylic acids and their amide derivates.

The water solutions of these solid samples were also tested by HPLC for the presence of amino acids. Results from this analysis are very similar to results from the HPLC analysis of liquid samples. The consistency of retention times with peaks in these samples in both gradients was found for serine and glycine (1^{st} sample), and for proline and valine (2^{nd} sample).

3.3. Analysis of Gas Samples

We monitored the changes of the composition of the treated gas in different experimental conditions by comparing IR spectra of gas samples taken before and after the discharge reactor. Occasionally we observed traces of NO_x in samples taken after the reactor, but usually we only observed the decrease of the CO_2 concentration and the production of CO. We found that the efficiency of the decomposition of CO_2 and the production of CO depended on two parameters: energy density E_d and the composition of the treated gas (i. e. the ratio CO_2/N_2).

At a constant value of E_d, the concentration of CO (c_{CO}) and the decomposition of CO_2 increased with the increasing CO_2/N_2 ratio (Figure 3). The growth of c_{CO} was logarithmic-like. A similar growth of c_{CO} was observed when the concentration of CO_2 in the input gas remained constant and the value of E_d increased (Figure 4), regardless whether the increase of E_d was achieved by raising the power input, or by lowering the gas flow rate. The highest achieved concentration of CO was 4.0 ± 0.6 vol. % in pure CO_2 at $E_d \approx 700$ J/L.

The absolute amount of decomposed CO_2 molecules also increased with increasing c_{CO_2} in the input gas (logarithmic-like growth similar to the growth of c_{CO}). Based on the changes of concentrations of CO and CO_2 calculated from the obtained IR spectra, the amount of removed CO_2 molecules was equal to the number of produced CO species, within the experimental error (Figure 3). As a result, the relative CO_2 removal ($deCO_2$) decreased with increasing input concentration of CO_2 (Figure 5). The amount of the energy required to remove one molecule of CO_2 (E_{deCO_2}) therefore also decreased exponentially with increasing c_{CO_2}, and then it remained almost constant, 42 ± 12 eV, for $c_{CO_2} > 25$ vol. % (Figure 5).

The accuracy of the obtained results was decreased by the condensation of water vapors on IR windows of cells used for gas sampling. Moreover, the accuracy of our results from calculations of CO_2 removal efficiency could be influenced also by the presence of liquid water in the discharge chamber. CO_2 from the gas phase dissolves in water where it forms carbonic acid (H_2CO_3), which dissociates to carbonate (HCO_3^-) and bicarbonate (CO_3^{2-}) ions. As was already mentioned, their presence in the solid products formed on the electrodes was indicated also by

IR spectra. However, H_2CO_3 is only a weak acid and the water in the reactor was only slightly acidic (pH ≈ 5.5) after the experiments. The majority of dissolved CO_2 remains in the aquated form: CO_2(aq). The concentration of CO_2(aq) depends on c_{CO_2} in the gas above the water surface. Thus, any changes of c_{CO_2} in the input gas led to the establishment of a new equilibrium between concentrations of CO_2 in liquid and gas phase. For example, we detected CO_2 in the gas samples taken after the discharge chamber even several minutes after c_{CO_2} was set to zero. However, the volume of the used discharge chamber was small and new equilibrium was achieved within several minutes.

To minimize this source of uncertainties, we used only samples where we expected equilibrium conditions for the calculation of CO_2 removal efficiency. Together with other sources of uncertainties, we estimate that calculated concentrations and removal efficiencies can be characterized with errors up to 25%.

4. Discussion

4.1. GAS PHASE CHEMISTRY

High energy electrons accelerated by an electric field are the key initiating factors in low-temperature plasma chemistry. The inelastic electron-impact reactions can lead to the formation of radicals, ions or excited species, which can in the next step initiate secondary chemical reactions, leading to the formation of stable products. In the studied gas mixture, high energy electrons can dissociate all three present species:

$$CO_2 + e \rightarrow CO + O\bullet + e \tag{3}$$

$$H_2O + e \rightarrow OH\bullet + H\bullet + e \tag{4}$$

$$N_2 + e \rightarrow 2N\bullet + e \tag{5}$$

Reaction 5 is much slower than the reactions (3) and (4) (Hokazono et al., 1991). Thus, the most significant gas phase reactions are related to the decomposition of CO_2 to CO and its backward oxidation to CO_2 by OH• radical:

$$CO + OH\bullet \rightarrow CO_2 + H\bullet \tag{6}$$

This reaction (Eq. 6) is considered to be the most important reaction for CO_2 regeneration from CO in humid mixtures (Hokazono et al., 1991). Two competitive processes, decomposition and regeneration of CO_2, had the strongest influence on the concentration of CO at the output. It is obvious, that the rate of CO_2 decomposition should increase due to either increasing input energy, or increasing concentration of CO_2 in input gas. However, E_d must have similar influence also on the production of OH• radicals, and the rate of Eq. (6) depends on the product of CO and OH• species. As a result, the increase of CO concentration also enhanced the backward CO_2 regeneration reactions. This negative feedback effect can perhaps explain the observed quasi-logarithmic behavior of CO concentration as a function of either increasing input energy, or increasing concentration of CO_2 in the input gas. This effect is also probably responsible for an approximately constant value of E_{deCO_2} for $c_{CO_2} > 25$ vol. %.

4.2. Synthesis of Organic Species

We suppose that the CO produced by dissociation of CO_2 was also crucial for the synthesis of organic species we detected. For example, the average concentration of CO_2 and thus also the concentration of CO were higher during the third long-term experiment and also the corresponding PTR-MS spectrum was richer than the spectra from the first two experiments. We assume that there are two major reaction pathways which could lead to the synthesis of the detected organic species and/or their precursors, and CO plays an important role in both these mechanisms. The first is the CO hydrogenation to CH_xO species, which was also observed during our previous experiments in CO/H_2O mixture (Morvova, 1999). The second process is nitrogen fixation and the formation of a bond between C and N (production of HCN and/or HNCO species detected by Mikoviny et al., 2005 and by Schlesinger and Miller, 1983).

The hydrogenation of CO is initiated by its reactions with H• and H_2, leading to the production of HCO• and CH_2O species, respectively. At atmospheric pressure and room temperature, these reactions are slower by two orders of magnitude than the reaction of CO with OH• radical (Hokazono et al., 1991). Moreover, formaldehyde (CH_2O), which is probably one of the most important intermediates leading to the synthesis of detected organic species, can be converted back to CO and CO_2 in the plasma (Hensel et al., 2003). Reactions leading to the fixation of nitrogen and the formation of species with CN group from CO are most probably even slower, having thus almost no influence on the concentration of CO. This is in agreement with our experimental finding that the amount of produced CO molecules is equal to the total number of decomposed CO_2 molecules, within the range of experimental error.

The compounds tentatively identified as amino acids were most probably formed in the liquid phase from dissolved HCN, RCHO and NH_3 species by reactions identical or similar to those proposed by Miller (1955). Based on the analysis of preliminary blank samples, we believe we can exclude the possibility that the amino acids were of external origin. On the other hand, we cannot exclude the possibility that HCN, RCHO and NH_3 species might have their origin in other hydrocarbon impurities, which could be present in the input gas. For example, minor hydrocarbon impurities can lead to the production of $CN\bullet$ species in plasma generated in N_2 (Foltin et al., 2006). Thus, we assume that even small amounts of hydrocarbons (HCs) may enhance the synthesis of amino acids, since they can serve as a source for the production of HCN and RCHO species.

4.3. SUMMARY

The electric discharges lead to the establishment of quasi-equilibrium concentration of CO in the $N_2/CO_2/H_2O$ mixture. We suppose that the production of CO by the decomposition of CO_2 was crucial for the further synthesis of organic species in our experiments. A similar effect should also be expected to occur in the prebiotic atmosphere, although we are not able to estimate the average CO concentration there. However, for the plasma chemistry a relatively high concentration of CO in the discharge channel is relevant. Despite this fact, reaction pathways leading to the production of organic species from CO are not very efficient and the organic species produced, as well as their intermediates, can be oxidized back to CO and CO_2 both in gaseous and liquid phase. As a result, even during our experiments where we achieved relatively high final CO concentrations (up to 4 vol. %), the concentration of organic species found in the liquid phase was very low.

We cannot estimate the overall efficiency (or yields) of the conversion of CO_2 to hydrocarbons (HCs), since we worked in a flow regime. After three weeks of the discharge action we already probably had achieved equilibrium between the production and removal of detected HCs. Moreover, the calculation of yields would be in our case complicated by the incorporation of organic compounds in the solid products deposited on the copper electrode. This process can be also considered as a sink of HCs, or on the contrary, it could serve as a protection for the synthesized HCs for their further utilization in chemical evolution.

5. Conclusions

We investigated the synthesis of organic species and the decomposition of CO_2 in $CO_2/N_2/H_2O$ mixtures, under the action of electric discharges operating above a water surface. The decomposition of CO_2 was accompanied by the production of CO. The highest concentration of CO reached was 4.0 ± 0.6 vol. % ($E_d \approx 700$ J/L, 100 % of CO_2 in the input gas), and the amount of CO produced was equal to the total number of decomposed CO_2 molecules, within the range of the experimental error.

The synthesis of organic species was indicated by analysis of solid and liquid samples. Based on IR absorption spectroscopy, the most probable organic species are carboxylic acids and their amide derivates. The PTR-MS analysis showed the presence of several other VOCs, the most probable being acetaldehyde, methanol, ethanol, or nitromethane. In addition, some peaks in the HPLC analyses seemed to indicate the possible presence of several amino acids (including serine and glycine), which we expect to be able to confirm in future work. The synthesis of amino acids from inorganic $N_2/CO_2/H_2O$ mixture is clearly of significance for origins of life. We assume that the concentration of the CO produced was crucial to the synthesis of the organic species detected. However, the efficiency of the processes involved is low and we cannot yet completely exclude the possible influence of minor hydrocarbon impurities on the synthesis of the detected species. Such an effect, of course, might also have been significant in the atmosphere of primitive Earth.

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Table I. Results from the PTR-MS analysis of liquid samples.

Mass	**Counts per second** Sample 1	 2	 3	**Possible** **ions**	**Possible parent molecules**
33	50	36	109	CH_5O^+	methanol
				$N_2H_5^+$	hydrazine
41	107	101	91	$C_3H_5^+$	fragments from propanal or butanal
42	81	220	450	$C_3H_6^+$	products of fragmentation
				$C_2H_4N^+$	acetonitrile
45	307	931	234	$C_2H_5O^+$	acetaldehyde
46	41	235	505	$C_2H_6O^+$	products of fragmentation
				$C_2H_8N^+$	ethylamine, dimethylamine
				CH_4NO^+	formamide
47	4	1	138	$C_2H_7O^+$	ethanol
				$CH_3O_2^+$	formic acid
59	850	560	830	$C_3H_7O^+$	propanal, acetone, ...
				$C_2H_7N_2^+$	acetamidine, (E)-dimethyldiazene
62	202	117	115	$CH_4NO_2^+$	nitromethane, methyl nitrate
				$C_2H_8NO^+$	ethanolamine, N-methoxy-N-methylamine
71	34	68	202	$C_4H_7O^+$	2-methylpropenal, cyclobutanone, ...
				$C_5H_{11}^+$	2-methyl-2-butene, pentene
				$C_3H_7N_2^+$	dimethylcyanamide, 3-aminopropionitrile, ...

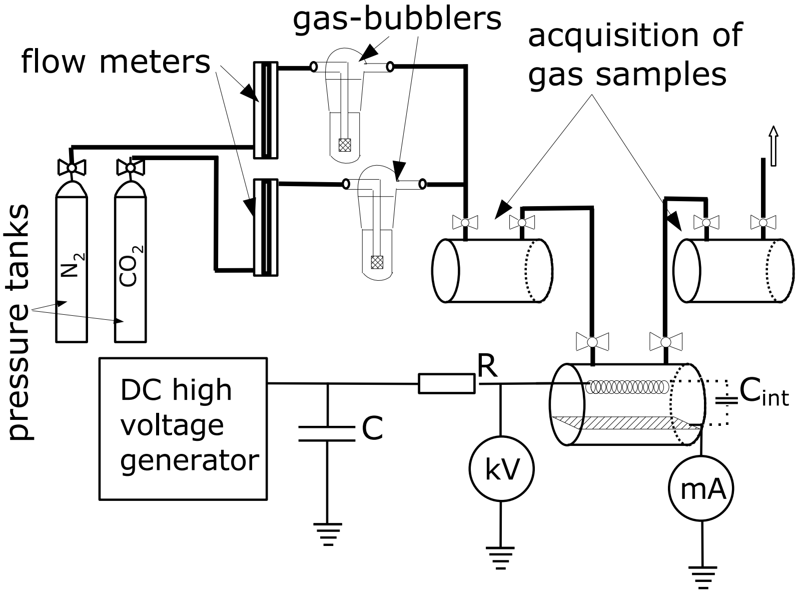

Figure 1. Simplified scheme of used experimental set-up

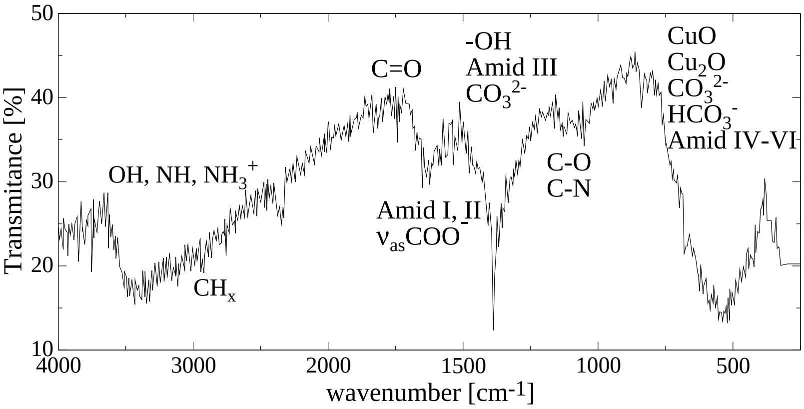

Figure 2. IR spectrum of solid deposit on LV electrode

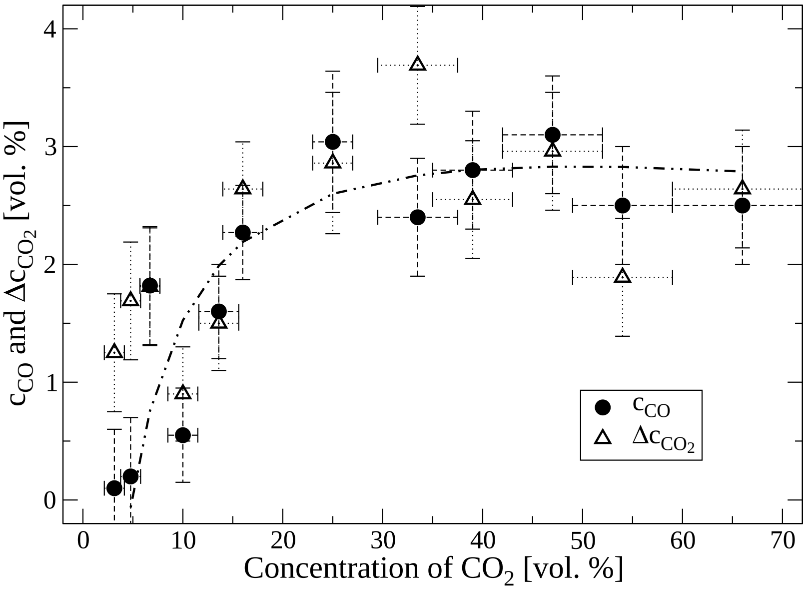

Figure 3. Production of CO and absolute decomposition of CO_2 (ΔCO_2) as functions of c_{CO_2} at $E_d \approx 550$ J/L.

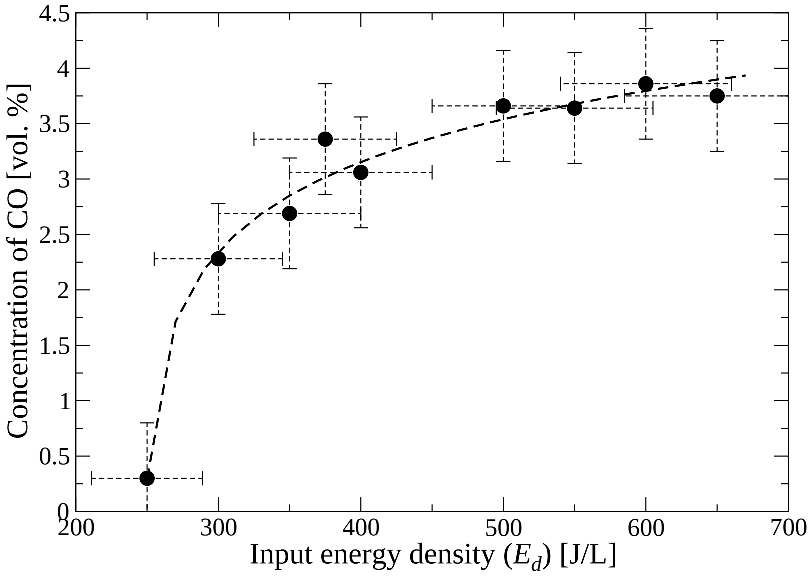

Figure 4. Production of CO as a function of input energy density (E_d) in CO_2/H_2O mixture.

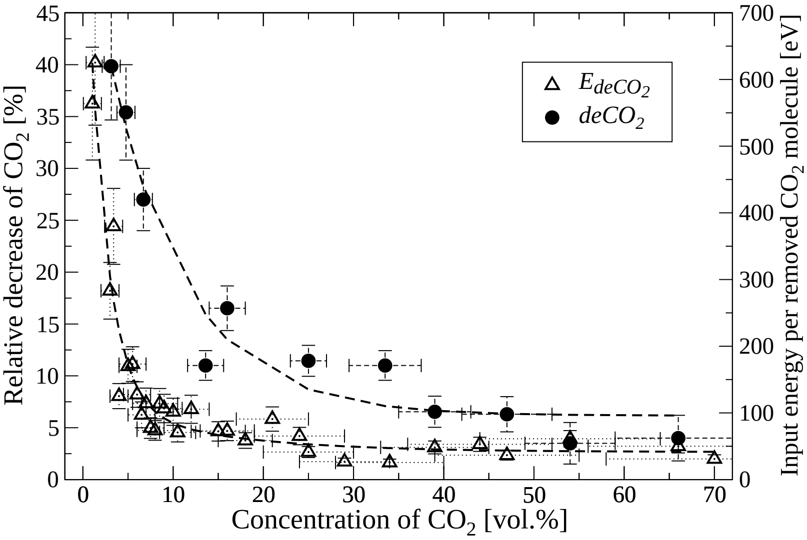

Figure 5. Relative removal of $CO_2(deCO_2)$ at $E_d \approx 550$ J/L, and input energy required to remove 1 CO_2 molecule (E_{deCO_2}) as functions of c_{CO_2}.