Supplementary Materials

Section S1. Gas Analyses with Mass Spectrometer

The evolved gases from the cathode were analysed in a mass spectrometer RGA-100 (Pfeifer). In case of solid cathode (Headspace gases from catholyte compartment were collected and analysed from a gas syringe. Gas flow by the GDE were collected into gasbag for further analysis. Results were normalized vs total consumed CO_2 and total amount of detected products represented in results table. Quadrupole Mass Spectrometers are gas-specific instruments, the fragmentation pattern may lead to spectral overlap (Figure S1).

Calibration. To minimize the effort for calibration, gas mixtures which contain several components in a chemical inert carrier gas typically are used. The precondition is that there is no overlap between the components contained in the mixture. We used GASCO 602 Calibration Gas 1%CO, 1%CO_2, 1%CH_4, 1% C_2H_6, 1%C_2H_4, 1%C_2H_2 in N_2 (w%). Automatically one then gets the sensitivity of the components relative to the carrier gas and the cracking pattern of each component.

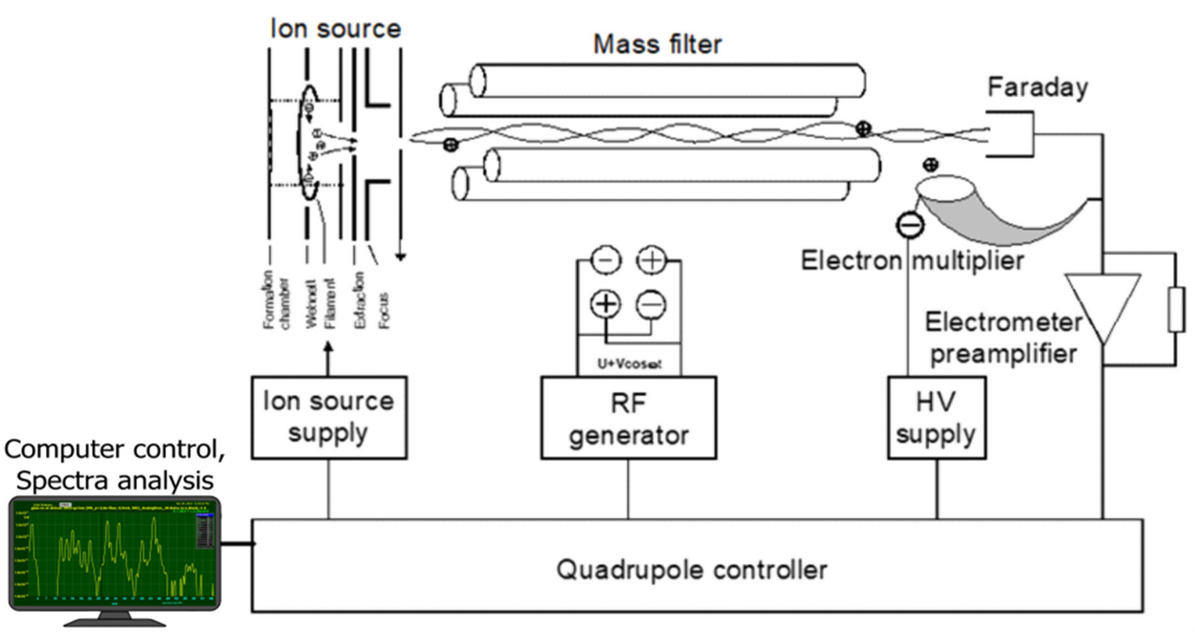


Figure S1. Functional units of Quadrupole Mass-Spectrometer and spectra obtained (PPT from „Measurement of Gas Concentrations by Mass Spectrometers“ Günter Peter, Bled April 2012).

When there is a multi-gas mixture, the spectra of each of the gas molecules and their ionized fragments give a very complex spectrum combination (model spectrum in the Figure S2) that can only be deciphered by an experienced specialist using a computer program library. Some of the mass spectra of gases that we are interested can be seen in Figure S3.

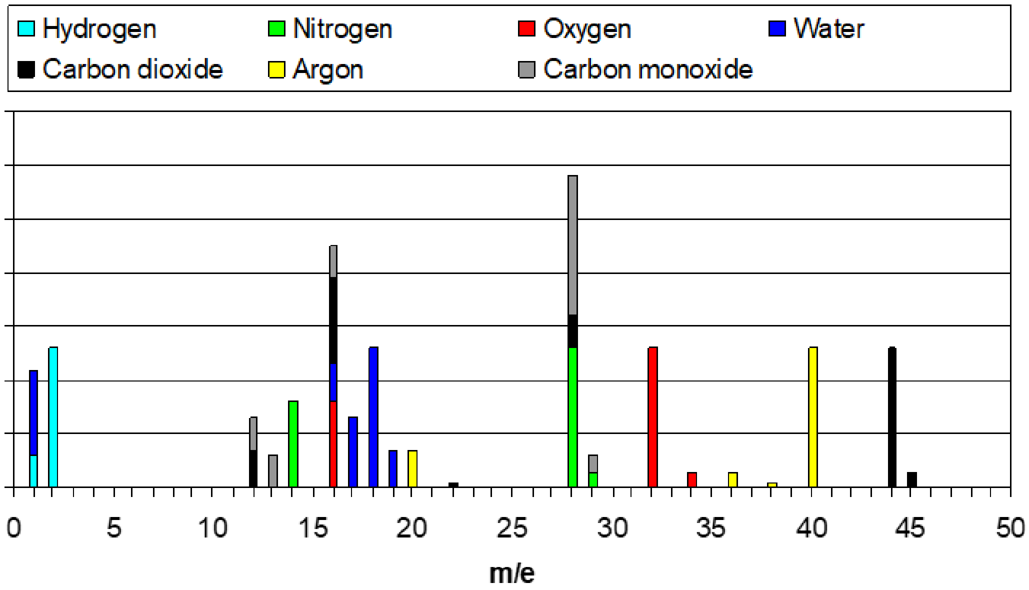
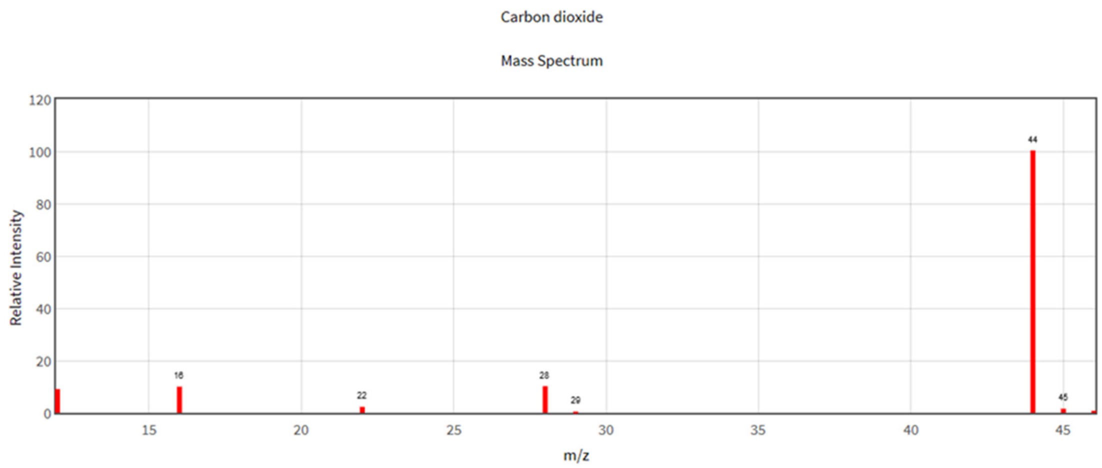
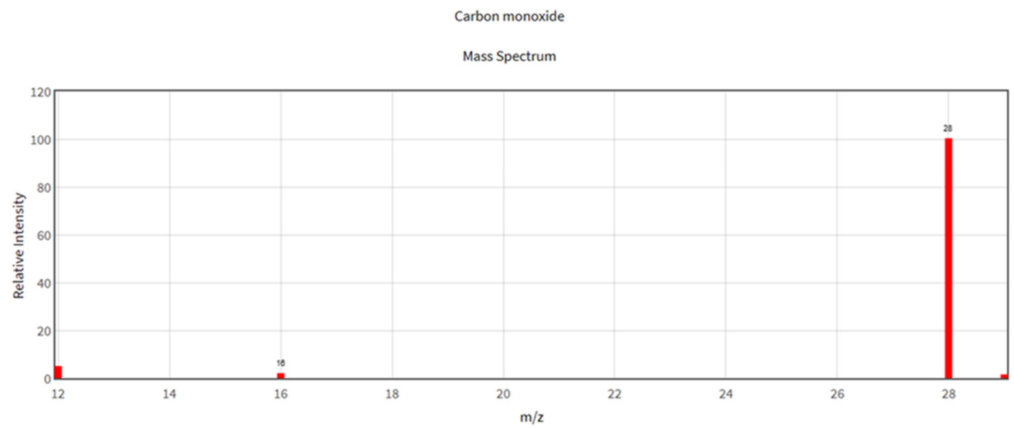


Figure S2. Origin of lines (peaks) in mass spectra (model from [1]).

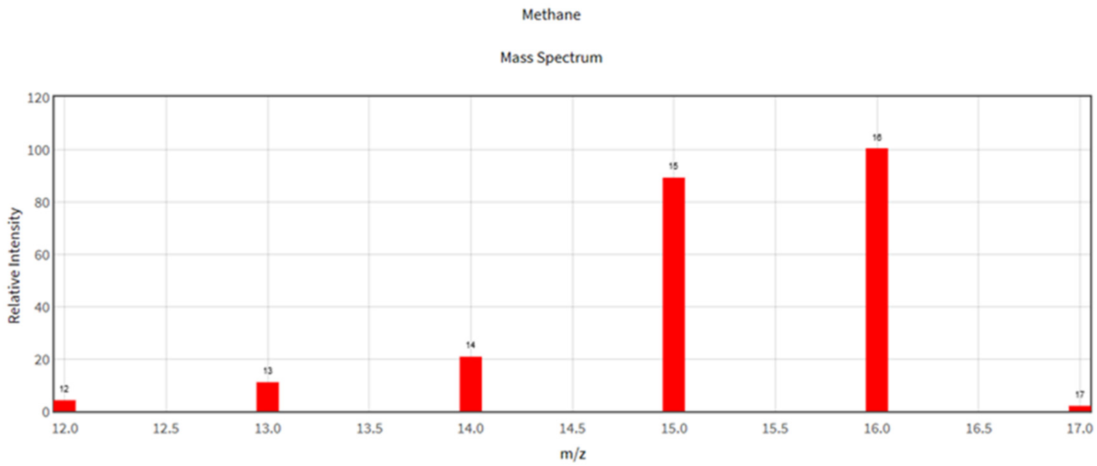
(1) CO_2 Carbon dioxide



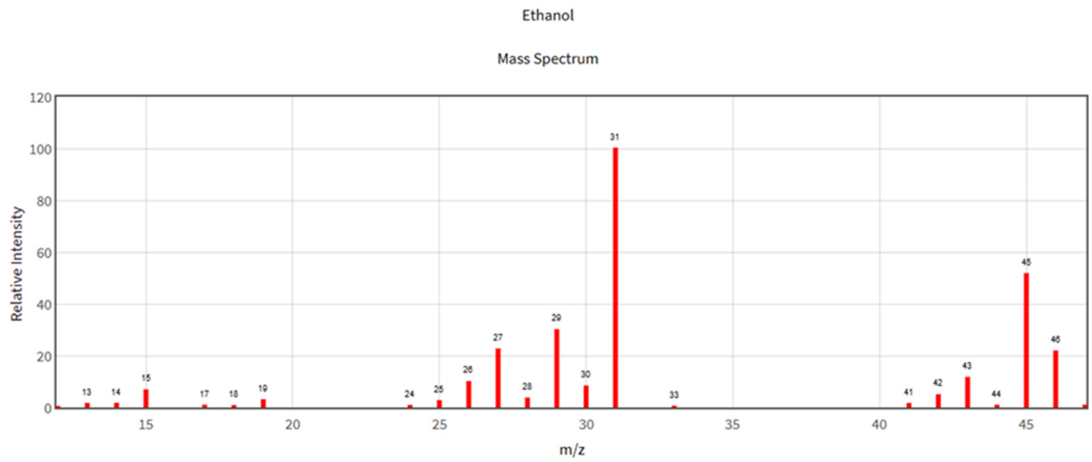
(2) CO Carbon monoxide



(3) CH_4 Methane



(4) C_2H_5OH Ethanol



(5) C_2H_4 Ethylene

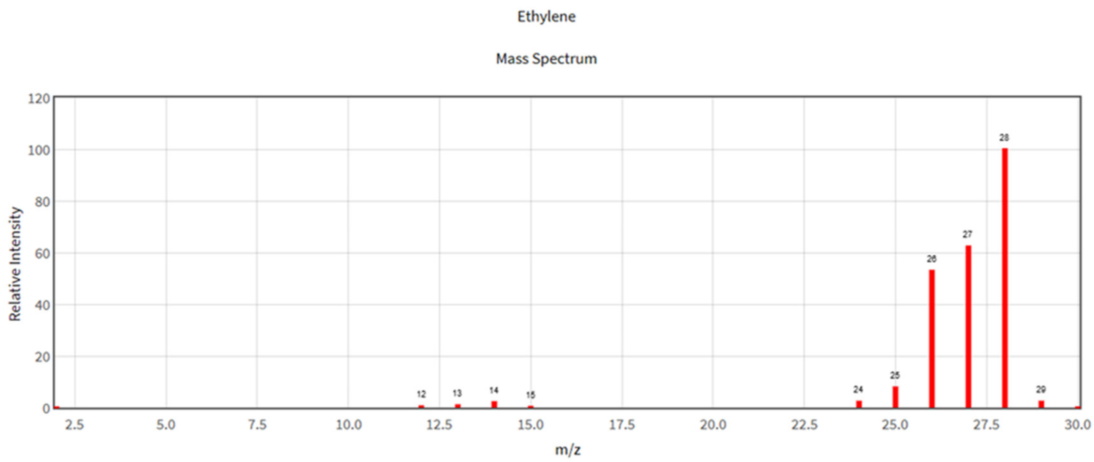


Figure S3. Some of the mass spectra of gases that we are interested (NIST Chemistry Web Book (https://webbook.nist.gov/chemistry).

In our measurements we used Pfeiffer Vacuum RGA-100 quadrupole mass spectrometer to analyse gaseous products from cathode compartment in electrolysis cell. Medical syringe was used to take gases from cathode compartment. RGA 100 instrument connected with PCT Pro2000 hydrogen adsorption system was used to measure mass spectra of gaseous products from electrolysis. One experiment were ethylene was detected in electrolyse products is described below.

Experimental spectra and analyse

GDL/N-GGS/Cu@Cu_2O catalyst catode obtained step by step – Cu@Cu_2O catalyst layer is coated on GDL/N-GSS substrate with electrochemical pulse deposition in 1.25M $CuSO_4$. Tests done in stationary electrolyte cell with 1M $KHCO_3$ electrolyte with 150 mA/cm^2 during 60 min (gas sampling time – 30 min, CO_2 flow 20 ml/min from backside of cathode) showed the presence of ethylene in concentration 2.8 vol% (FE~27% for both C_2H_4 and H_2 – Figure S4).

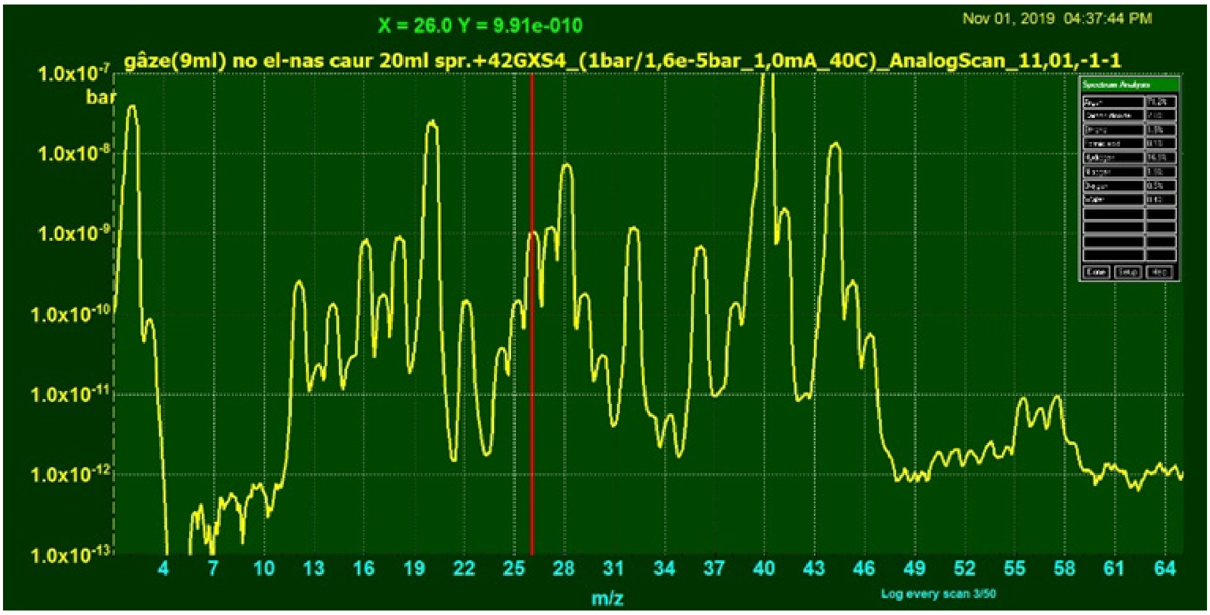


Figure S4. Mass spectra of electrolysis products from backside of cathode.

The table on the right upper corner of Figure S4 shows a table in which the operator selects the gases for a specific sample. As shown in Figure S4 there are some monochromatic peaks that are determined only by specific compound in a given gas mixture (such as 2 - hydrogen, 44 - CO_2, 40 – argon, triplet 25-26-27 for ethylene); then put them in the table right away, the rest components should be guessed from experimental conditions. The precision of the table depends on the exact choice of the gases in the table.

Section S2. Faraday Efficiency Calculations from Mass Spectra Analysis

By defining FE as a charge that has gone to the formation of a particular gas against the total charge past between electrodes, we can write:

$$FE = \frac{Q_i}{Q_\Sigma} \tag{1}$$

Were Q_i is multiplication between the charge of electron, number of electrons necessary to create particular molecule N, and the number of these molecules k:

$$Q_i = e \cdot N \cdot k \tag{2}$$

The number of molecules by the amount of substance is bound by the Avogadro number:

$$n_i = \frac{N}{N_A} \rightarrow N = n_i \cdot N_A \tag{3}$$

We are taking volume V of electrolysis gas with syringe and at room temperature and pressure there are n_Σ moles of gas:

$$n_{\Sigma} = \frac{pV}{RT} \quad (4)$$

From mass spectra we can obtain partial pressures of particular gas expressed from equation of ideal gases as percentage composition $n_{\%}$. Thereby amount of gas substance in volume will be:

$$n_i = n_{\%} \cdot n_{\Sigma} \quad (5)$$

From Equations (2)–(5), we can obtain number of electrons necessary to produce amount of particular gas in electrolysis cell:

$$N = n_{\%} \cdot \frac{pV}{RT} \cdot N_A \quad (6)$$

The Faraday Efficiency FE can be obtained combining (6) with (2) and inserting in definition of FE (1):

$$FE = \frac{e \cdot n_{\%} \cdot \frac{pV}{RT} \cdot N_A \cdot k}{Q_{\Sigma}} \quad (7)$$

Two constants can be combined in new one Faraday constant $F = e \cdot N_A$, therefore equation (7) can be rewritten as:

$$FE = \frac{F \cdot n_{\%} \cdot \frac{pV}{RT} \cdot k}{Q_{\Sigma}} \quad (8)$$

The following example shows the measured concentrations and calculated FE values - Table S1.

Table S1. Gaseous components from electrocatalyst cathode carbon paper/GSS/Cu after 1 h electrolysis (error in FE calculations estimated at least 25% of value).

No	Gas	Number of Electrons	Amount of Gas, vol%	Concentration of Gas Substance, ppm	Faraday Efficiency, %
1	H_2	2	22.9	228,900	68.4%
2	CO	2	1.95	19,500	9.3%
3	C_2H_4	12	0.4	4400	7.9%
4	HCOOH	4	0.3	3000	2.9%
			Summary:		**88,478%**

In the analyzed sample, most of the volume was occupied by CO_2 released from the saturated electrolyte. In the Faraday efficiency calculation, it was assumed that of the 4 gases generated in the electrolysis (100 vol%) the part of formic acid remained in the electrolyte in liquid form. Analysis of electrolysis products in the electrolyte was not performed. Formic acid has relatively high evaporation rate from water solutions, but most substance is left in electrolyte, therefore summary FE of particular experiment is below 100%.