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Microwave plasma membrane reactor for the decomposition of CO_2

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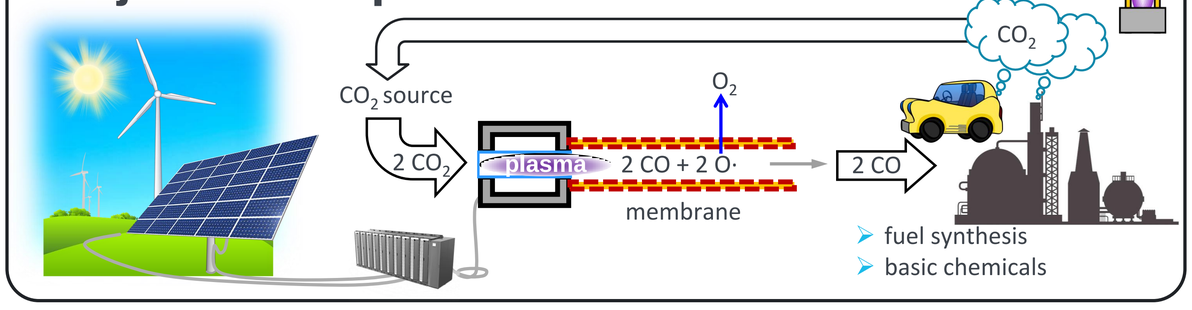
Microwave Plasma Reactor for CO_2 Decomposition

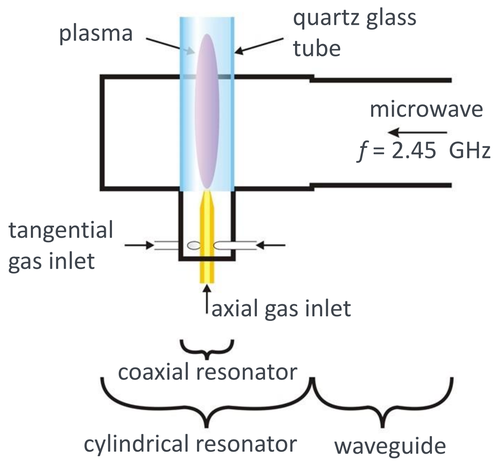
Introduction

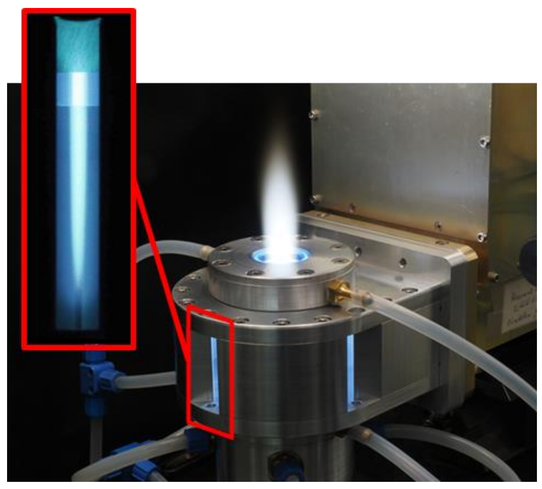
Since electricity from renewable sources of energy is subject to fluctuations, energy storageon demand plays a crucial role to create a reliable grid system. One promising approach towards energy storage is a plasma assisted CO_2 gas conversion into CO and O powered by renewable energy. By separation of the oxygen via a perovskite membrane bundle the remaining CO gas can be utilized for the conversion into syngas or higher hydrocarbons. Hence, a zero emission carbon cycle can be established. On the basis of technological requirements for a microwave plasma unit for CO_2 conversion an oxygen-permeation membrane plasma reactor has been developed.

Project concept



Modular plasma torch





- narrowband coaxial resonator for plasma ignition; radius: 15 mm, height: 80 mm
- broadband cylindrical resonator for the plasma operation; radius: 50 mm
- allows self-ignition in atmospheric pressure and generates a contact free plasma
- parameter range: microwave power $P \approx 0.6$-2 kW; gas flow $V \approx$ 1-100 l/min

FEM-simulations of the plasma torch

Modeling of the electric field distribution inside the resonator

The electromagnetic wave equation is given by:

$$\nabla \times \left(\frac{1}{\mu}\nabla \times \vec{E}\right) - k_0^2 \varepsilon \vec{E} = 0$$

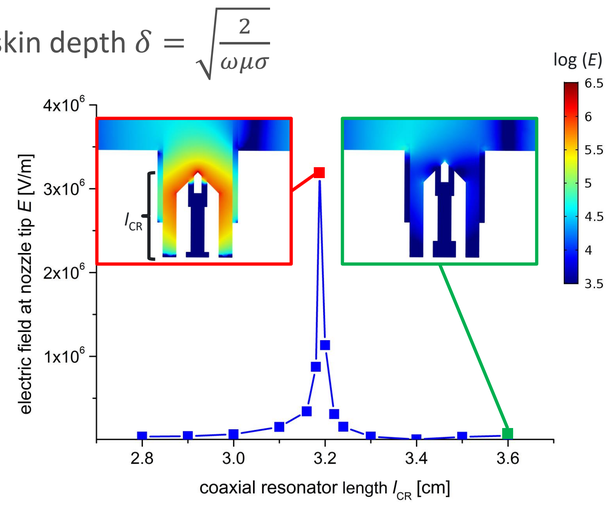
permeability $\mu = \mu_0 \mu_r$
permittivity $\varepsilon = \varepsilon_0 \varepsilon_r$
wavenumber $k_0 = \omega\sqrt{\varepsilon_0 \mu_0}$

- impedance boundary condition with skin depth $\delta = \sqrt{\frac{2}{\omega \mu \sigma}}$

Results

Matching of microwave wavelength λ and coaxial resonator length l_{CR}

- resonance condition: $l_{CR} = \lambda/4$
- high electric field for $l_{CR} \approx 3.2$ cm $\approx \lambda/4$
- plasma ignition at the nozzle tip of the coaxial resonator; operation in the cylindrical resonator
  → detached plasma



Modeling of the cold gas flow inside the quartz glass tube

The basis for the simulation are the Navier-Stokes-Equations:

equation of continuity

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0$$

conservation of momentum

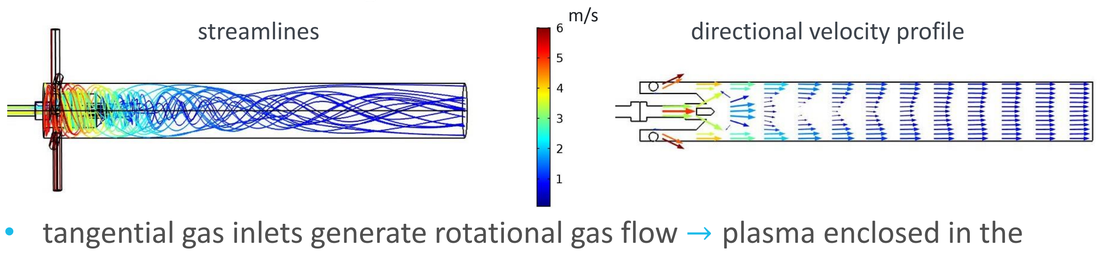
$$\rho \frac{\partial \vec{v}}{\partial t} + \rho(\vec{v} \cdot \nabla)\vec{v} = \nabla \cdot (-p\mathbf{I} + \tau) + \vec{\mathbf{F}}$$

ρ = density, $\vec{v}$ = velocity, $\boldsymbol{I}$ = unity tensor, τ = friction tensor, $\vec{\boldsymbol{F}}$ = body force density

Results

Balanced combination of tangential and axial inflow velocities

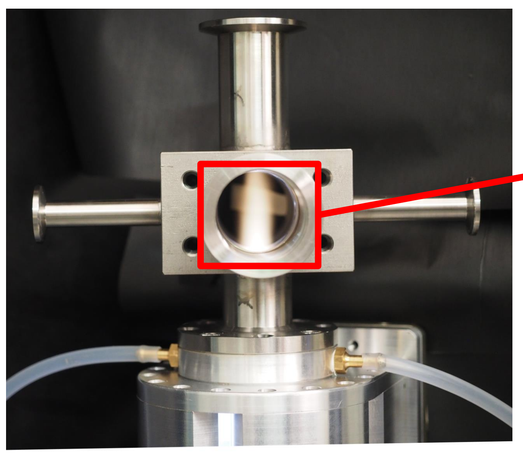
streamlines



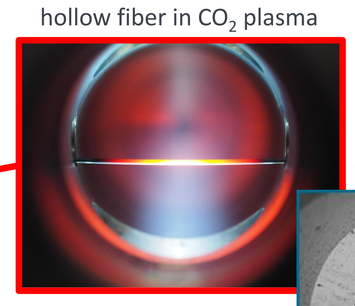
directional velocity profile

- tangential gas inlets generate rotational gas flow → plasma enclosed in the center of the glass tube → contact-free plasma operation
- axial gas inlet prevents back flow of the gas → stabilization of the plasma

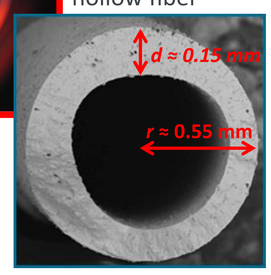
Oxygen-permeation membrane reactor



hollow fiber in CO_2 plasma



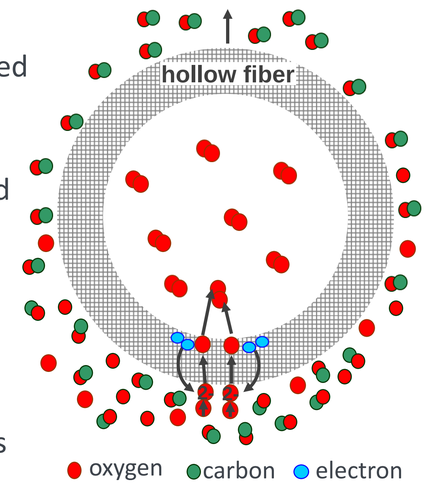
hollow fiber



- the reactor can easily be flange mounted on top of the plasma torch
- incorporates a gland sealing for the hollow fiber membrane as well as access points for spectroscopic investigations

Hollow fiber membrane in CO_2 plasma

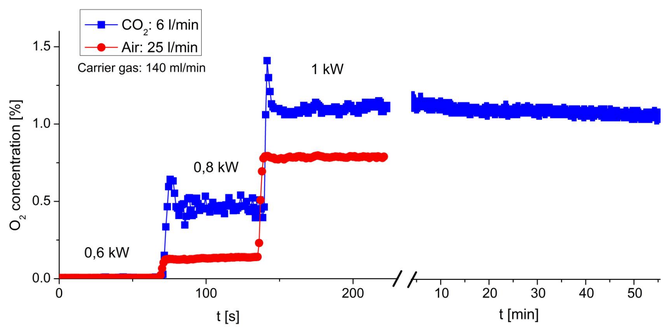
- CO_2 dissociates into CO and atomic oxygen
- the oxygen is reduced to O^{2-} by absorption of two electrons from the perovskite grid, and is incorporated into the grid
- by diffusion the oxygen ions reach the inner surface of the hollow fiber with lower chemical potential and release their electrons to form atomic oxygen
- after recombination to O_2 and desorption from the inner perovskite surface the oxygen molecules are carried to an oxygen detector by a carrier gas
- **aim:** implementation of a membrane bundle
  → increasing the separation of the oxygen molecules
  → higher purity of CO gas



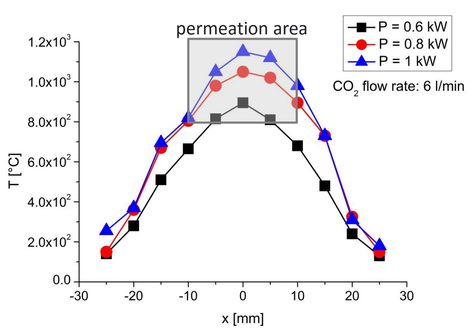
Results

Permeability of oxygen through a $La_{0.6}Ca_{0.4}Co_{0.8}Fe_{0.2}O_{3-d}$ hollow fiber in air and CO_2 plasma

oxygen permeation



temperature profile at the fiber



- oxygen concentration rises with increasing microwave power
- the temperature of the plasma at the position of the hollow fiber rises with increasing microwave power and permeation takes place for $T > 800\,^{\circ}C$
- the gas used and its flow rate influence the temperature of the plasma, which influences the permeation in addition to the oxygen partial pressure
- the maximal oxygen flux in CO_2 of 2.2 $^{ml}/_{min \cdot cm^2}$ is given for P = 1 kW

Summary

- by adjusting the coaxial resonator to the resonance frequency an ignition and stable operation of a CO_2 plasma was achieved
- adding an axial gas inlet through a jet nozzle prevents back flow of the gas
- the hollow fiber membrane shows a high stability in CO_2 plasma and the oxygen flux is of the same order of magnitude as for e.g. BCFZ membranes in air atmosphere

Outlook

Simulation

- advanced simulations with hot gas flow
- simulations including a plasma

Experiment

- investigation of the CO_2 conversion and energy efficiency
- analysis of different fiber materials

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KOPERNIKUS PROJEKTE Die Zukunft unserer Energie

Microwave plasma membrane reactor for the decomposition of CO_2

Introduction

Since electricity from renewable sources of energy is subject to fluctuations, energy storage on demand plays a crucial role to create a reliable grid system. One promising approach towards energy storage is a plasma assisted CO_2 gas conversion into CO and O powered by renewable energy. By separation of the oxygen via a perovskite membrane bundle the remaining CO gas can be utilized for the conversion into syngas or higher hydrocarbons (Figure 1). On the basis of technological requirements for a microwave plasma unit for CO_2 conversion an oxygen-permeation membrane plasma reactor has been developed. The aim of this work is on the one hand the investigation and improvement of the energy and conversion efficiency of the plasma process as well as the analysis of different ceramic membranes in order to maximize the oxygen permeation process. On the other hand the investigation of the electric field distribution and gas flow inside the plasma torch via a FEM simulation program is a powerful tool in order to optimize the configuration of the plasma torch and hence establish the most suitable operation conditions.

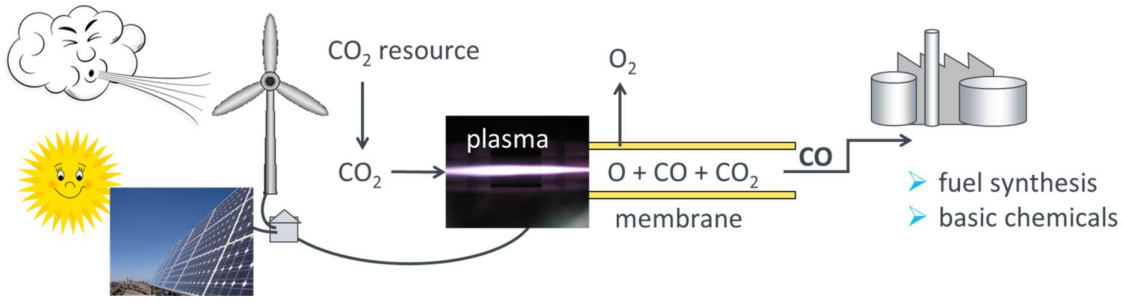

Figure 1: Schematic representation of the project concept

Microwave plasma torch

The term plasma is mostly associated with stars or fluorescent tubes. However, plasmas have found their way into many modern technological devices and are used for example in etching process in microelectronics, for the deposition of barrier or anti scratch coatings, for the decomposition of waste gases and many more. The most common plasma sources used for waste gas treatment are dielectric barrier discharges (DBD) and arc discharges but they also bear some disadvantages for example a limited electrode service life and a low efficiency for large volumes of gas especially in the case of DBDs.

For this purpose a modular microwave plasma torch has been developed, which is self igniting in atmospheric pressure and generates a contact free plasma while ensuring a stable operation for a wide range of gas throughput and microwave power. Figure 2a) shows a scheme of this plasma torch. The plasma torch consists of a cylindrical and a coaxial resonator. The microwave with a frequency of 2.45 GHz is carried via a wave guide to the resonator cavity. In the resonance condition where the length of the inner coaxial part l_{CR} is equal to the quarter wavelength of the microwave frequency λ a high electric field of more than 10^6 V/m arises at the tip of the inner conductor and the plasma is ignited. Subsequent to the ignition the plasma transitions to the cylindrical resonator where it maintains during the operation. The gas is fed into the resonator via tangential and axial gas inlets. The tangential gas inlets generate an enveloping rotational flow, which keeps the plasma in the center of the quartz glass tube. Figure 2b) shows the plasma torch in operation with air and the inset shows the contact free air plasma.

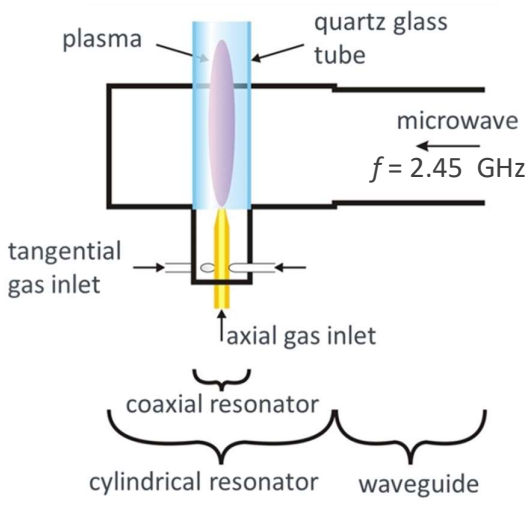

Figure 2a): Scheme of the plasma torch

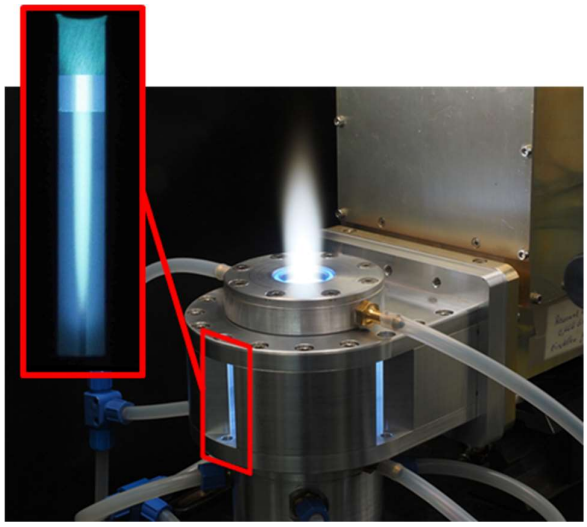

Figure 2b): Plasma torch in operation with an air plasma

FEM simulations

A FEM simulation model of the plasma torch has been developed. In Figure 3a) the simulation model and in Figure 3b) the electric field at the nozzle tip of the inner conductor in dependence of its length is shown.

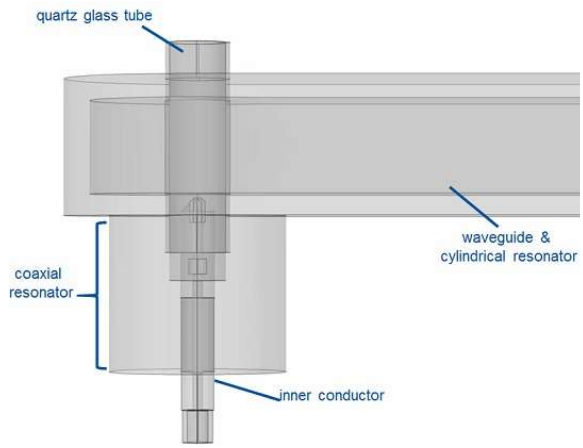

Figure 3a): Simulation model of the plasma torch

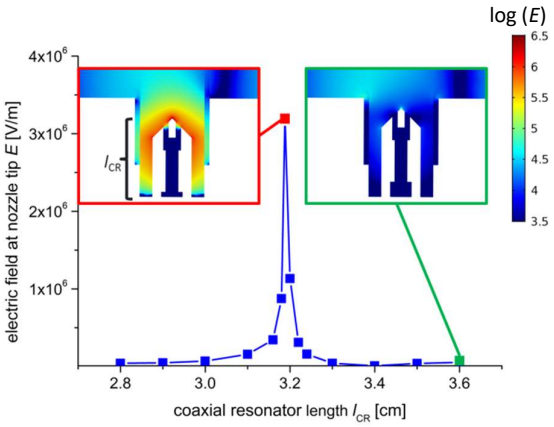

Figure 3b): Electric field at the tip of the inner coaxial resonator in dependence of its legth l_{CR}

As can be seen here, the electric field for l_{CR} = 3.2 cm ≈ λ/4 reaches a maximum of about $3 \cdot 10^6$ V/m. The insets in figure 3b) show the electric field distribution in the coaxial resonator for two different coaxial lengths in log scale. As a consequence to the sharp peak at 3.2 cm the length of the inner conductor has to be precisely adjusted to the resonance frequency in order to reach electric field strengths high enough to ignite the plasma.

Oxygen-permeation membrane reactor

In order to separate the oxygen from the gas mixture such that mainly pure CO gas can be obtained a perovskite hollow fiber had to be integrated into the system. For this purpose a tubular membrane reactor, which can be flange mounted on top of the plasma torch and incorporates a gland sealing for the hollow fiber membrane as well as spectroscopic access points, was constructed and is shown in figure 3a). The perovskite hollow fiber incorporated in the reactor has a diameter of 1.1 mm and a wall thickness of 0.15 mm. A cross section of such a perovskite hollow fiber is shown in Figure 3b). Figure 3c) shows the hollow fiber mounted in the reactor while in operation with a CO_2 plasma.

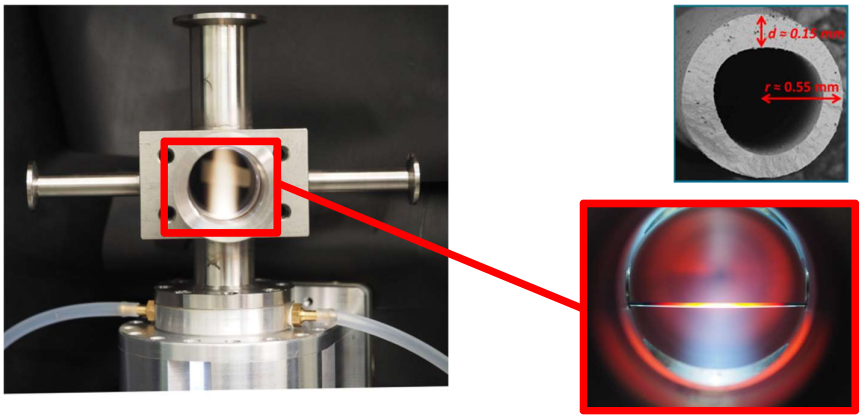

Figure 3a): Tubular membrane reactor

Figure 3b): Cross section of a perovskite hollow fiber

Figure 3c): Hollow fiber in CO_2 plasma

Hollow fiber membrane in CO_2 Plasma

Ceramic mixed ionic and electronic conductors (MIEC) become conducting for ions and electrons at higher temperatures (usually around T > 700 °C). Due to the configuration of the perovskite grid only oxygen ions can be transported through the grid by lattice vacancies. Hence such materials have a separation factor of nearly 100 %. The actual transport of the oxygen ions occurs by a transposition mechanism of the ions with an oxygen ion vacancy. The driving force for this transport is a gradient in the chemical potential of the oxygen. Dissociated and ionized oxygen is transported from the area of higher chemical potential to the area of lower chemical potential. Electrons and ion vacancies move at the same time in the opposite direction of the oxygen ions to ensure charge neutrality. Figure 4 shows a simplified schematic of the oxygen separation process in CO_2 plasma.

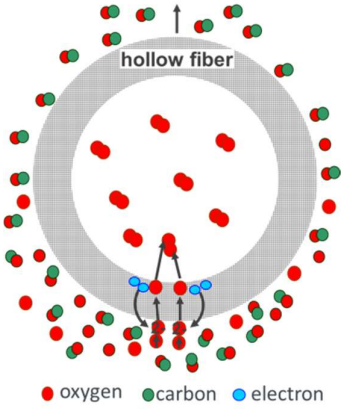

Figure 4: Schematic representation of the oxygen permeation process

In a CO_2 plasma the CO_2 dissociates in CO and atomic oxygen. Thereupon the oxygen is adsorbed at the membrane surface adjacent to the area with high chemical oxygen potential. The oxygen is then reduced to O^{2-} by absorption of two electrons from the perovskite grid and is incorporated into the grid. By diffusion over vacancies the oxygen ions reach the inner surface of the hollow fiber with lower chemical potential and release their electrons to form atomic oxygen. After recombination to O_2 and desorption from the inner perovskite surface the oxygen molecules are carried to an oxygen detector by a carrier gas.

Figure 5a) and b) exemplary illustrate the oxygen concentration measured by the detector for two different ceramic materials. In figure 5a) a common $BaCo_xFe_yZr_zO_{3-d}$ (BCFZ) hollow fiber was tested whereas figure 5b) shows the results for the newly fabricated $La_{0.6}Ca_{0.4}Co_{0.8}Fe_{0.2}O_{3-d}$ (LCCF) hollow fibers. The results clearly show that in case of the BCFZ fiber the oxygen concentration decays exponentially over time, which is attributed to the formation of barium-carbonates, whereas the oxygen concentration for the LCCF fiber remains almost constant and no carbonates are formed. Hence, the modified fiber material allows a stable operation of the oxygen separation process over time.

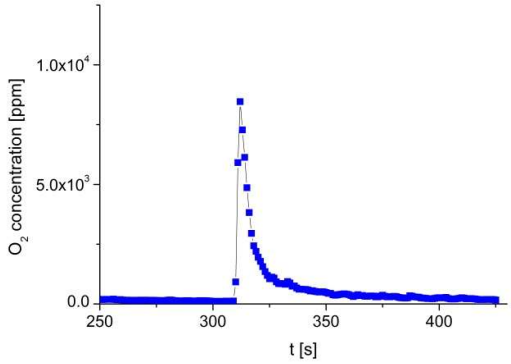

Figure 5a): $BaCo_xFe_yZr_zO_{3-d}$ hollow fiber in CO_2 plasma

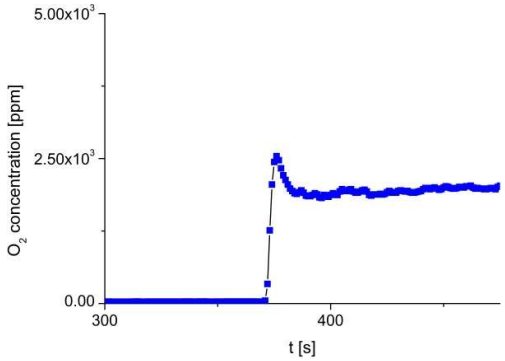

Figure 5b): $La_{0.6}Ca_{0.4}Co_{0.8}Fe_{0.2}O_{3-d}$ hollow fiber in CO_2 plasma

Summary and Outlook

In this work a modular plasma torch was designed, which enables a selfignition and a contact free operation of the plasma as well as a stable operation for a wide range of parameters. A first FEM simulation model of the plasma torch has been developed, which is in good agreement with the experimental results. Furthermore an oxygen-permeation membrane reactor was constructed, which can be connected to the plasma torch and allows the mounting of perovskite hollow fibers. Hollow fibers consisting of different materials have been tested with respect to their oxygen separation properties in CO_2 plasma and $La_{0.6}Ca_{0.4}Co_{0.8}Fe_{0.2}O_{3-d}$ fibers have been identified as stable operating in such an environment.

In the next step a bundle of hollow fiber membranes will be incorporated into the reactor in order to maximize the oxygen separation. The further procedure also includes the determination of the conversion and energy efficiency via mass spectrometry and optical emission spectroscopy respectively. Furthermore, simulations of the gas flow in the plasma torch will be included in order to improve the configuration of the plasma torch with respect to the conversion and energy efficiency.