Journal of CO_2 Utilization 19 (2017) 130–136

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

journal homepage: www.elsevier.com/locate/jcou

Low pressure glow-discharge methanation with an ancillary oxygen ion conductor

Friedrich-W. Speckmann [a,*], Daniel Müller [a], Jürgen Köhler [b], Kai Peter Birke [a]

[a] Department of Electrical Energy Storage Systems, Institute for Photovoltaics, University of Stuttgart, 70569 Stuttgart, Germany
[b] Laser Processing, Institute for Photovoltaics, University of Stuttgart, 70569 Stuttgart, Germany

ARTICLE INFO

Article history:
Received 26 September 2016
Received in revised form 27 February 2017
Accepted 2 March 2017
Available online 28 March 2017

Keywords:
Carbon dioxide reduction
Carbon monoxide
Solid ion conductor
Plasmolysis
Glow discharge plasma

ABSTRACT

Plasma technology is gaining increased interest for the reduction of carbon dioxide (CO_2) to carbon monoxide (CO) and oxygen (O_2). CO is a reaction partner with hydrogen (H_2) to produce gas and fuel. This paper elaborates an improved method to produce methane (CH_4) by plasma induced dissociation of carbon dioxide and H_2 in one single setup. A low pressure glow discharge plasma with an integrated zirconia based ion conductor transports oxygen ions (O^{2-}) in or out of the reaction chamber. Transporting oxygen ions into the reaction chamber is a way to have a controlled amount of water vapor for the conducted experiments. In contrast, leads the reduced amount of O_2 ions to a theoretical decrease in the recombination of CO and O_2 to CO_2 in the ionized gas and therefore increases the CO_2 conversion rate. The applied voltage to the ion conductor for the outward ion transportation and the power of the plasma source current have a major impact on the amount of extracted O^{2-} ions. The effect of these parameters on the CO production rate and the formation of methane are investigated. A positive effect of the plasma current on the amount of CO and CH_4 is detected. The influence of the temperature increase from the heated ion conductor relates to an undesired increase of the recombination rate of CO and O_2 to CO_2, but has a positive effect on the methanation.

1. Introduction

The current dependence on fossil fuels, to satisfy the increasing energy demand, has a negative effect on the overall CO_2 content in the atmosphere [1]. Similar to other greenhouse gases, CO_2 molecules absorb infrared radiation emitted from the earths surface, thus preventing radiation from leaving the atmosphere and heating up the planet. One approach to reduce the high atmospheric concentration of CO_2 is the use of a plasma source to dissociate the molecule into CO and O_2. The CO can further be used as a source for Power-to-Gas (P2G) or Power-to-Liquid (P2L) processes [2]. Especially the conversion to methane is of utmost interest:

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \quad (1)$$

A plasma is a partially ionized gas, consisting of a huge number of different species which can all interact with each other, resulting in a highly reactive chemical mix. The advantage of plasma technology for CO_2 conversion is due to the presence of energetic electrons. These electrons can activate the gas by electron impact ionization, excitation and dissociation. Therefore, the gas itself (e.g. CO_2) does not have to be heated as a whole, but can remain near room temperature.

Different types of plasma have been applied for the purpose of CO_2 conversion, the most common ones are dielectric barrier discharges [3], microwave plasmas [4] and gliding arc discharges [5]. Furthermore, the formation of methane was found after the application of pulsed corona discharges in a CO_2 atmosphere over a water film [6].

This study uses a glow discharge plasma (GDP) in combination with a solid ion conductor. The GDP is formed by the passage of electric current through a low-pressure gas (0.1–10 mbar) between two metal electrodes. As soon as the dc voltage exceeds the breakdown voltage $V_B < 2$ kV, the gas ionizes and becomes an electrically conducting plasma.

During operation the electric field forces positively charged ions to drift towards the cathode, whereas electrons are accelerated towards the anode until they loose their gained energy via ionization, excitation or dissociation of molecules or atoms. The GDP is stable as long as the positively charged ions liberate enough

* Corresponding author.
E-mail addresses: friedrich.speckmann@ipv.uni-stuttgart.de (F.-W. Speckmann), st113588@stud.uni-stuttgart.de (D. Müller), juergen.koehler@ipv.uni-stuttgart.de (J. Köhler), Peter.Birke@ipv.uni-stuttgart.de (K.P. Birke).

http://dx.doi.org/10.1016/j.jcou.2017.03.003
2212-9820/

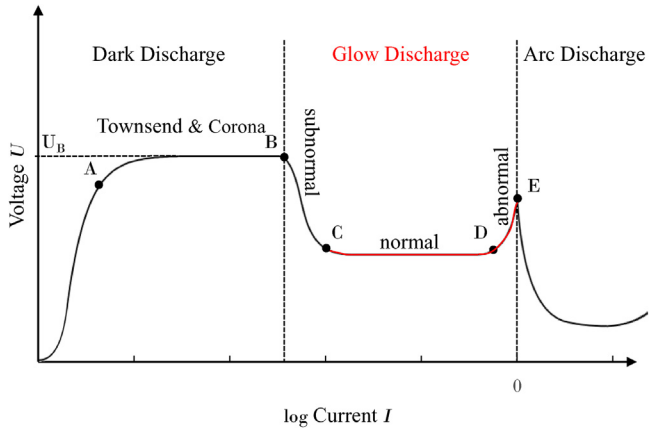

Fig. 1. Characteristic current–voltage curve of a discharge in an example gas, showing the different discharge stages. The horizontal current scale is logarithmic and the region used in the conducted experiments is marked in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

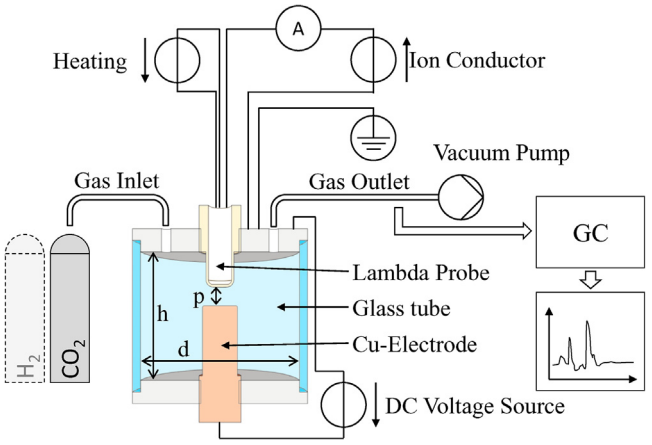

Fig. 2. Experimental setup consisting of the reaction chamber with an integrated copper electrode and a lambda probe as electrodes. The setup is further equipped with sensors for current and voltage measurements. A dc voltage source supplies the power for the plasma in the glass tube. The outlet gas is analyzed with a gas chromatograph.

electrons when they hit the surface of the cathode. The normal glow discharge is characterized by an approximately constant voltage drop between cathode and anode for a wide range of discharge current, shown in Fig. 1.

In the experimental setup, a glow discharge (area C to D) is used in order to create the plasma in a low pressure glass tube. The gas is ionized between a copper cathode and a lambda probe [7] functioning as the anode.

On one hand this technology was chosen for its simplicity, which is an advantage of the well-known glow discharge plasma technology over other plasma types. Special equipment and components are not needed for operation. Furthermore, is the discharge stable for a wide range of parameters regarding the discharge current and operating pressure. On the other hand, the operation of a DC plasma source allows the use of the protective sheath as ground potential for the plasma as well as the ion conductor. Therefore, no dedicated second electrode is needed, which leads to a simpler reactor design as well as simple wiring. This possibility is not given for plasma technologies with rotating or changing electric fields.

Conventionally, the heated (above 350 °C) ion conductor of a lambda probe conducts oxygen ions from the atmospheric site to the exhaust gas side in automobile applications, because of the difference in the partial pressures. The heating element is electrically isolated from the ion conductor ($R > 30\,M\Omega$) and has therefore no direct influence on the measured current (cf. Fig. 3).

The probe's integrated ion conductor consists of yttria-stabilized zirconia (YSZ). This ceramic material is able to conduct O^{2-} ions and thus conducts an electric current. The ion conductivity increases with temperature. In conventional automobile applications the ion flow leads to a potential difference between 25 and 900 mV. The voltage can be described by the following equation based on the Nernst equation:

$$U_{LS} = \frac{RT}{4F} \ln \frac{p_{O_2,\text{reference gas}}}{p_{O_2,\text{sample gas}}} \quad (2)$$

The probe voltage U_{LS} can be calculated with the universal gas constant R multiplied by the temperature T, divided by four times the Faraday constant F and the natural logarithm of the different oxygen partial pressures.

But regarding our experimental setup, the probe can be induced with a voltage $1\,V \leq V \leq 7.5\,V$ in order to change the direction of the ion transport through the zirconium dioxide. Therefore, negative oxygen ions are being extracted from the plasma chamber, resulting in a measurable current up to $I_{LS} = 80$ mA. The lack of oxygen ions in the gas chamber is supposed to partially prevent the back reaction of CO and oxygen molecules to CO_2, leaving CO behind, which is further used for a dynamic methanation process.

2. Experimental setup

All experiments were performed in a low-pressure glow-discharge plasma system at the Institute of Photovoltaics, University of Stuttgart. Fig. 2 illustrates the schematic experimental setup.

2.1. Glow discharge plasma system

The cylindrical reaction chamber consists of two stainless steel plates with a diameter of 75 mm and a glass tube with the length of 65 mm. The inner diameter of the chamber is $d = 68.5$ mm and the distance between the plates is $h = 55$ mm. A DC high-voltage power source (fug MCP 350-2000), with maximum output of 2 kV and 150 mA is used to generate the glow-discharge plasma at an absolute pressure of 50–100 mbar. The negative potential of the plasma generator is connected with a copper electrode, screwed into the chamber at the center of the bottom plate. The positive potential is grounded and connected with the protective sheath of the solid ion conductor, which acts as the second electrode at the opposite site of the cylinder. The distance between the flat circular tip of the copper electrode and the rounded tip of the ion conductor's casing, where the glow-discharge plasma is generated, adds up to $p = 7$ mm. Furthermore, the gas inlet and gas outlet are located on both sides of the solid ion conductor on the top plate. To maintain a steady gas flow through the chamber as well as a reasonably constant low pressure, a vacuum pump is continuously running. There are needle valves located between the gas supply and the chamber as well as between the chamber and the vacuum pump. Extraction of product gas samples, with a gas tight syringe through a septa, is possible between the gas outlet and the vacuum pump. A gas-phase chromatograph (GC) is then used to analyze the reaction products and the exhaust gas.