Plasma dissociation of water for CO₂ conversion

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Abstract: Direct utilization of H₂O and CO₂ for the production of syngas (H₂ + CO) or hydrocarbons is appealing from a sustainability perspective. It can be carbon neutral when driven by renewable energy and coupled to processes that capture CO₂ from the air. We present preliminary results of plasma-induced dissociation of H₂O in inductively-coupled plasma (ICP) as a preliminary step on the way to an integrated conversion process.

Keywords: H₂O, plasma-induced dissociation, CO₂ conversion, syngas, solar fuels

Introduction

Production of syngas (H₂ + CO) or hydrocarbons from H₂O and CO₂ using a thermo-chemical cycle offers a path for converting renewable energy (solar, wind) into a storable form. Utilization of H₂O and CO₂ for fuel production as a storage solution is the most appealing option from a sustainability perspective. It can be a carbon neutral when coupled to processes that capture CO₂ from the air.

Water dissociation by plasma for hydrogen production involves conversion of electricity into chemical energy. Other approaches such as electrolysis, thermo-chemical and thermo-catalytic cycles, radiolysis [1], and thermal decomposition [2] are possible. However, there are drawbacks associated with each. For instance, the complexity of reaction kinetics, phase separation and corrosion phenomena in electrolysis; and high temperature around 3000 K required to produce radicals and molecules - OH, H₂, O₂, H and O - during thermal decomposition [2].

Fridman [1] has reported direct dissociation of water in plasma can be more efficient than aforementioned processes for hydrogen production, according to equation (1) with high specific productivity.

\[ H₂O → H₂ + \frac{1}{2}O₂ \quad ΔH = 2.6 \text{ eV/mol} \] (1)

It also potentially allows for in-situ production of reactive hydrogen intermediates that are essential in any CO₂-based hydrocarbon production process. Since plasma can also be used to activate CO₂ molecules, the approach has the potential to allow for development of an integrated reaction process.

Quite apart from its potential as a hydrogen source, the presence of water has been demonstrated to have a beneficial influence on the performance of several CO₂-capture materials. The extent to which this influence can be modified by plasma-activation of the water molecules remains an open question.

This work presents preliminary results from an experimental setup that is designed for investigation of plasma-activation of H₂O and CO₂ both in the gas phase and in conjunction with relevant solid CO₂-capture materials. It represents part of the commissioning and validation of a new experimental setup. Plasma-induced activation and dissociation of H₂O is achieved by means of inductively-coupled plasma (ICP). The reactor performance is monitored in real time by means of Mass Spectrometry, Optical Emission Spectroscopy and total pressure response measurements. In case of plasma-material interaction studies, pre- and post-exposure analysis is available ex-situ. This work is part of longer term efforts to develop an integrated plasma process for CO₂ conversion.

Experimental procedure

The experimental setup used is depicted in Figure 1. It consists of three different sections with different pressure ranges. The first section had a Quadrupole Mass Spectrometer (QMS) attached in a high vacuum region (~10⁻⁹ mbar base pressure), separated from a second section by 3 mm aperture. The base pressure in the second section is typically ~10⁻⁸ mbar to ~10⁻⁷ mbar. A valve separates these two high vacuum sections from the third (medium-low vacuum: ~10⁻³ mbar-10 mbar working pressure range) region. A 1 mm aperture is mounted before the valve, to limit the pressure rise in the QMS region during system operation. A heating stage is mounted in this section for resistive heating target material. The introduction of water vapour and plasma generation is via a quartz tube of 30 cm length and 2 cm in diameter attached

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![Fig. 1. Schematic of setup for dissociation of water by plasma.](image-url)
to this section. An Optical Emission Spectrometer (OES) is connected via fiber optic cable to measure plasma light (200-1100 nm) through the top of the quartz tube.

Figure 2 illustrates the two possible configurations of the quartz tube: either horizontally for direct sampling of the plasma species, or vertically for plasma-exposure of a material sample that can be heated independently using a resistive heating plate. For the current experiments the former configuration was used.

![Fig. 2. Orientation of the quartz tube for direct plasma sampling and for material exposure.](image)

Deionised water is subjected to several freeze-pump-thaw cycles before use. Water vapour is introduced via a needle valve to achieve a target pressure in the quartz tube. To ignite ICP inside the tube, RF power is applied to the load coil and an alternating current oscillates inside the coil at a rate corresponding to the frequency (13.56 MHz) of the RF generator. Dissociation of water as a function of input power and tube pressure can be monitored by the QMS. During water dissociation, the input powers typically ranging from 50 W to 275 W from the RF generator were established while minimizing the reflected power to zero by adjusting the capacitances of matching box.

Results

QMS signals of various species, such as H₂O, H₂, O₂, and OH, were monitored as a function of input power. For example, Figure 3 shows the water plasma response generate an initial (no plasma) 0.55 mbar pressure for different input powers. The dominant species produced are H₂ and O₂.

The generation of H₂ and O₂ from water is more clearly illustrated in Figure 4 which shows both increasing with input power. The ratio of O₂ to H₂ varies somewhat at low power, but becomes effectively constant at higher values.

![Fig. 4. Ratios of different species as a function of input power. Initial H₂O pressure ~0.55 mbar.](image)

Data for dissociation of water in ICP plasma at different pressures as a function of input power is depicted in Figure 5. Water dissociation decreased with increasing pressure in quartz tube. The dissociated fraction appears to stabilize at ~69 %.

![Fig. 5. Normalized counts for dissociation of water as a function of input power for different initial pressures.](image)
In addition to QMS measurements, OES studies, employing Ocean Optics HR 4000 Spectrometer, have been carried out to monitor changes of plasma species. The emission spectra of the plasmas were monitored in the range 200-1100 nm. The important lines for water emission were oxygen radicals at 775.14 nm and 842.5 nm, OH radicals at 307.3 nm and Balmer series ($H_\gamma=432.16$ nm, $H_\beta=484.2$ nm and $H_\alpha=654.15$ nm) as plotted in Figure 6 (a-d) for 0.29 mbar pressure and input power from 50 W to 200 W. Those values are about ~2 nm less than the values given in [2, 3, 4, 5]. The intensities of the emissions increase with increasing input power, consistent with the increased plasma dissociation of water at higher input powers.

Additional OES investigation of 100 W water plasma at 0.64 mbar and 0.91 mbar initial pressure shows less excitation of the hydrogen and oxygen lines at the higher pressure [Figure 7 (a-b)]. The intensity of $H\alpha$ also decreased for the higher pressure (not shown).

Summary
Initial measurements from a new plasma setup intended for the study of plasma-induced $H_2O$ and $CO_2$ have been presented. The system is intended to track the evolution of species during plasma-phase and plasma-material interactions. The measurement capabilities have been applied to track the power and pressure dependencies of a water plasma.

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References