Plasma-assisted CO_2 processing for energy storage

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Plasma science can play a prominent role in addressing present challenges in storing sustainable energy gained from renewable sources. Non-thermal plasma-assisted processing of CO_2 at low-temperatures along with suitable catalysts may help to overcome (at least) the highly-endothermic CO_2 dissociation to provide CO for further catalytic hydrogenation steps. Fundamental requirements for such an approach are discussed in this contribution.

Sustainable energy generation from renewable sources, e.g. solar or wind power, will significantly contribute to the future energy mix. However, suitable means to store and transport the energy on a large scale are therefore highly desirable. Storing of sustainable energy in chemical fuels is a promising alternative and one of the future challenges. The talk will address how plasma science can play a prominent role in this context.

Direct conversion of CO_2 and H_2O into hydrocarbon fuels by means of artificial photosynthesis using photocatalytic materials exposed to sunlight shows rewarding prospects. It could reduce atmospheric CO_2 concentrations, while at the same time provide a source for renewable fuels that can directly be supplied to our present energy infrastructure (fig. 1). The challenge will be to achieve energy efficient dissociation of CO_2 and H_2O or both after which conventional chemical conversion into value-added hydrocarbons can take place. While water splitting has been extensively studied, traditional or catalytic routes for efficient CO_2 splitting under thermal equilibrium are absent. Hence, plasma-assisted CO_2 processing, potentially combined with suitable catalysts, is a promising non-equilibrium route to overcome the process-limiting step in the hydrogenation of CO_2.

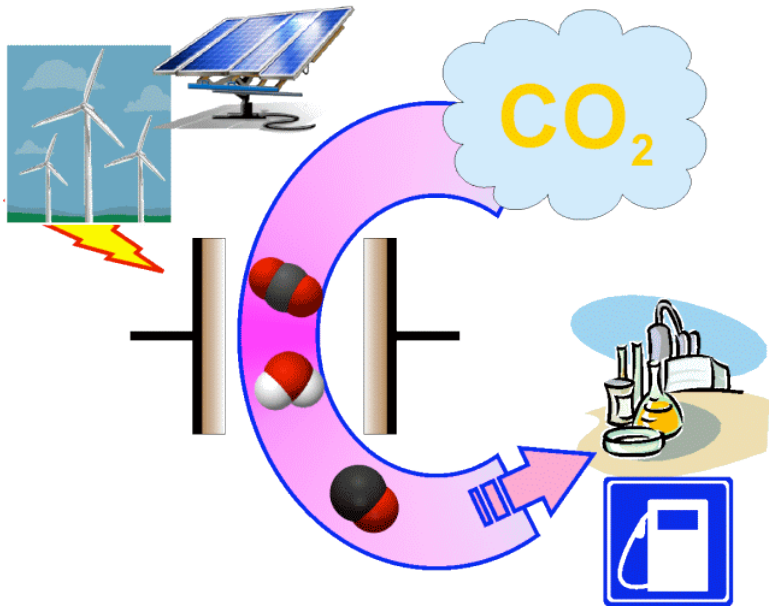

Fig. 1: Fuel processing in a closed-loop carbon cycle based on plasma-assisted CO_2 dissociation and hydrogenation assuming that electrical energy to drive the plasma source is provided from renewable sources.

This contribution will particularly provide links to two aspects of plasma processing of CO_2 namely the hydrogenation of CO_x in a non-thermal plasma using different surface materials and a direct CO_2 dissociation approach in an atmospheric pressure plasma.

At first, the direct hydrogenation of CO_2 in a low-temperature plasma expansion created from mixtures of Ar and H_2 was studied, thereby focussing on the efficiency of CO_2 depletion and the selectivity of CH_4 production. CO_x was injected into the expansion part where the dissociation mechanism might be radical- and/or ion-driven. Such conditions are ideal to study molecule formation since electron impact dissocation effects may be neglected (due to electron temperatures as low as 0.3 eV). Under argon rich conditions a CO yield of 50 % was achieved. CH_4 formation was particularly detected at high hydrogen admixtures (fig. 2). However, the obivous mismatch of conditions where significant CO and CH_4 production was observed strongly suggests a separation of the CO_2 dissociation and subsequent hydrogenation step. In other words, also in plasma-assisted CO_2 processing an inherent syngas step (i.e. a mixture of CO/H_2) is essentially required to achieve high hydrocarbon yields. This conclusion was confirmed by additional experiments where CO was injected and the CH_4 yield was increased by a factor of 10. Additionally, the expanding plasma was exposed to different metallic surfaces. Figure 2 highlights that conventional catalysts such as copper may not be beneficial in plasma-catalysis

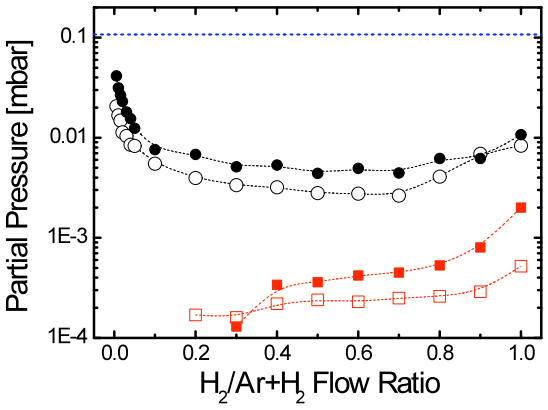

Fig. 2: CO (circles) and CH_4 (squares) partial pressures measured in the expansion of an arc plasma created from Ar/H_2 mixtures (full symbols). The intial CO_2 concentration is indicated (dotted). Note the logarithmic scale. CO_2 dissociation up to 50 % in Ar is detected. Using copper as wall material the CO concentration was significantly reduced and so was the CH_4 production (open symbols).

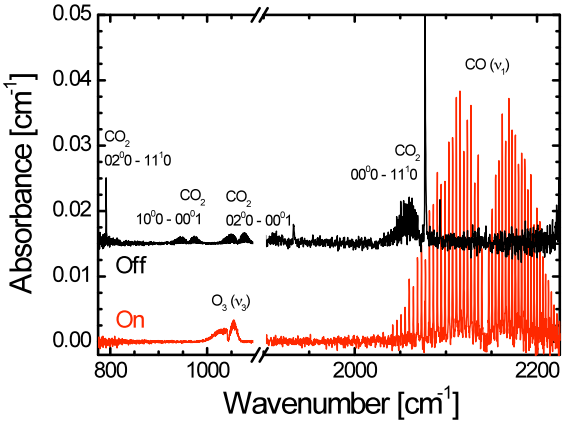

Fig. 3: FT-IR spectra recorded from the exhaust of a flow-tube DBD in CO_2 for plasma-off (upper trace) and plasma-on (lower trace, differential spectrum) conditions. In the upper trace different vibrational transitions are labelled. The lower trace shows the main products: CO and O_3.

Along these lines the CO_2 splitting was separated into an individual plasma-assisted step to increase the overall efficiency of fuel formation and to tackle the most energy demanding chemical process. In view of throughput and future up-scaling capability a dielectric barrier discharge (DBD) configuration was chosen. Furthermore, vibrational pumping of CO_2 at elevated pressures is known to increase the energy efficiency of dissociation.

A flow tube reactor was designed to facilitate the application of (optical) plasma diagnostic methods. Provided the plasma actively stabilised DBDs have been shown to be operated in high-current glow-like modes at high frequencies in the kHz range. Such conditions can provide the energies required to dissociate CO_2 (> 12.5 kJ/l). First experiments under unstabilised conditions (fig. 3) yielded an energy efficiency of the order of a few percent which is comparable to sother present approaches at atmospheric pressure. A main challenges remains that the energy efficiency usually increases at the expense of high gas flow rates.

Future studies need to focus on the efficiency of injecting energy to non-equilibrium plasmas at atmospheric pressure thereby particularly maximising the vibrational heating of CO_2 to accomplish energy efficiencies as high as 80 % (as reported for especially designed microwavesources operated at reduced pressure). Tuning the plasma-chemistry to recycle oxygen formed during the dissociation will help increasing the overall efficiency, but may require plasma-catalytic approaches using materials which are specifically tailored for a non-equilibrium environments.