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# CO<sub>2</sub> conversion in a dielectric barrier discharge plasma: N<sub>2</sub> in the mix as a helping hand or problematic impurity?<sup>†</sup>

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Carbon dioxide conversion and utilization has gained significant interest over the years. A novel gas conversion technique with great potential in this area is plasma technology. A lot of research has already been performed, but mostly on pure gases. In reality, N<sub>2</sub> will always be an important impurity in effluent gases. Therefore, we performed an extensive combined experimental and computational study on the effect of N<sub>2</sub> in the range of 1–98% on CO<sub>2</sub> splitting in dielectric barrier discharge (DBD) plasma. The presence of up to 50% N<sub>2</sub> in the mixture barely influences the effective (or overall) CO<sub>2</sub> conversion and energy efficiency, because the N<sub>2</sub> metastable molecules enhance the absolute CO<sub>2</sub> conversion, and this compensates for the lower CO<sub>2</sub> fraction in the mixture. Higher N<sub>2</sub> fractions, however, cause a drop in the CO<sub>2</sub> conversion and energy efficiency. Moreover, in the entire CO<sub>2</sub>/N<sub>2</sub> mixing ratio, several harmful compounds, *i.e.*, N<sub>2</sub>O and NO<sub>x</sub> compounds, are produced in the range of several 100 ppm. The reaction pathways for the formation of these compounds are explained based on a kinetic analysis, which allows proposing solutions on how to prevent the formation of these harmful compounds.

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#### Broader context

Environmental and energy applications of low temperature plasmas are worldwide gaining increasing interest. The central research question is whether plasma-based solutions can yield a valuable alternative to existing thermal processes. Nowadays, the conversion of  $CO_2$  into chemicals and fuels is a hot topic. The worldwide transition to renewable energy gives plasma processes a clean electricity source, and due to their high operation flexibility, plasmas are very suitable for storing this intermittent sustainable energy in chemicals/fuels. Up to now most research is based on pure gases, however, in reality  $N_2$  will be an important impurity. This is crucial, since its presence influences the plasma properties as well as the chemical pathways and thus the chemicals formed, for example,  $NO_x$ , which have detrimental effects on air quality and human health. This paper provides the necessary understanding by combining computations and experiments. The influence of  $N_2$  on the  $CO_2$  conversion as well as the  $NO_x$  production pathways are revealed for the first time, and the observed trends are explained, based on a kinetic analysis of the reaction chemistry. This approach allows us to look further down the road and go after solutions for the encountered problems regarding *e.g.* the unwanted  $NO_x$  formation.

# Introduction

The steadily rising atmospheric concentration of  $CO_2$  over the past century has a growing detrimental effect on our climate and environment, and is a threat for our society in general.<sup>1-4</sup> This results in a booming interest for technologies which can convert  $CO_2$  into value-added products like chemicals and

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fuels,<sup>5,6</sup> as they can effectively convert waste into new feedstock, following the cradle-to-cradle principle.<sup>7</sup>

Several alternative (non-conventional) technologies are being investigated, such as photochemical, electrochemical and thermochemical pathways, either with or without catalysts, and all their possible combinations.<sup>8-14</sup>

Another new technology considered to have great potential in recent years is based on (non-thermal) plasma.<sup>15</sup> Several options are being investigated, including both pure CO<sub>2</sub> splitting into CO and  $O_2$ ,<sup>16–29</sup> as well as the reaction with other gases, like CH<sub>4</sub> (dry reforming of methane),<sup>30–47</sup> H<sub>2</sub><sup>32,48,49</sup> or H<sub>2</sub>O,<sup>32,50–53</sup> aiming for the production of syngas and valuable oxygenates, such as methanol, formaldehyde and formic acid. Most research on plasma-based CO<sub>2</sub> conversion is performed with dielectric barrier discharges (DBD),<sup>16–22,30–39,41–44</sup> microwave (MW) plasmas<sup>22–26,30–32,46,52</sup>

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and gliding arc (GA) discharges,  $^{27-31,47,54}$  with a main focus on improving the energy efficiency of the conversion, as well as the selectivity towards value-added chemicals, in combination with catalysis.  $^{21,26,32,41-46,48,55-57}$  To date, the highest energy efficiencies have been achieved with the GA and MW set-up, with values up to  $43\%^{28,29,58}$  for the GA and up to 90% for the MW plasma being reported.  $^{23,58}$  The energy efficiency of a DBD is more limited (typically up to 10%),  $^{16,30,33}$  but can be improved by inserting a packing inside the plasma,  $^{21,44,59}$  and the latter also easily allows the integration of a catalyst, for the selective production of valueadded chemicals.

However, most research studies focus on "clean" CO<sub>2</sub> gas flows, while in reality most industrial gas flows contain impurities, for which it is economically unfeasible to be further purified. In most cases nitrogen is the main impurity.<sup>9</sup> Therefore, it is of uttermost importance to study the effect of N<sub>2</sub> impurities on the plasma chemistry of CO<sub>2</sub> conversion. The questions that come to mind are: how do these impurities affect the CO<sub>2</sub> conversion and energy efficiency, and more importantly, which byproducts (useful or harmful compounds) would be formed. This allows us to find out whether pre-(N<sub>2</sub>) or post-(denox) purification steps would be needed and which one is to be preferred. Furthermore, if N<sub>2</sub>O and other NO<sub>x</sub> compounds are produced, it is important to know whether high enough concentrations might be obtained, to be considered relevant for nitrogen fixation.<sup>60</sup>

To provide answers to these important questions, we have performed experiments, supported by chemical reaction simulations, to increase the general understanding of the underlying mechanisms and pathways. We focus on a DBD as it has a very simple design and operates at atmospheric pressure, which is beneficial for up-scaling for industrial applications.<sup>16</sup> Both the effect of N<sub>2</sub> as an impurity (1 to 10%) as well as the effect of N<sub>2</sub> as an admixture or as a dilutant (10 to 98%) were studied. To our knowledge, only a few papers have reported on the effect of N<sub>2</sub> on CO<sub>2</sub> conversion, and only for a GA<sup>28</sup> and MW plasma,<sup>24,25</sup> while no papers have addressed the second question, *i.e.*, which byproducts are formed in the mixture and what are their consequences.

# Description of the experiments

#### Plasma reactor

The experiments are carried out in a coaxial DBD reactor. A stainless steel mesh (ground electrode) is wrapped over the outside of a quartz tube with an outer and inner diameter of 22 and 16.5 mm, respectively, while a stainless steel rod with an outer diameter of 13 mm is placed in the center of the quartz tube and used as a high voltage electrode. The length of the discharge region is 90 mm, with a discharge gap of 1.75 mm, resulting in a discharge volume of 7.4 cm<sup>3</sup>. CO<sub>2</sub> and N<sub>2</sub> are used as feed gases with a total flow rate of 611 mL min<sup>-1</sup>. The N<sub>2</sub> content is controlled using mass flow controllers (Bronkhorst), and varied between 0 and 98%, in steps of 1% (in the regions of 0–10% and 90–98% N<sub>2</sub>), while steps of 10% are used in the region between 10 and 90% N<sub>2</sub>. The DBD reactor is powered by

an AC high-voltage power supply (AFS), providing a maximum peak-to-peak voltage of 40 kV and a variable frequency of 1–90 kHz. The total current is recorded by a Rogowski-type current monitor (Pearson 4100), while a high voltage probe is used to measure the applied voltage. Furthermore, to obtain the charge generated in the discharge, the voltage on the external capacitor (10 nF) is measured. Finally, all the electrical signals are sampled by a four-channel digital oscilloscope (Picotech PicoScope 64201) and the discharge power is obtained by a control system used to calculate the area of the Q-U Lissajous Figures.<sup>16</sup> The precise experimental conditions can be found in the ESI.<sup>†</sup>

#### Product analysis: molecular gases

The feed and product gases are analyzed using a three-channel compact-gas chromatograph (CGC) (Interscience), equipped with two thermal conductivity detectors (TCD) and a flame ionization detector (FID). The first TCD channel is equipped with a Molecular Sieve 5A column for the separation of the molecular gases O<sub>2</sub>, CO and N<sub>2</sub>, while the second TCD channel contains an Rt-Q-BOND column for the measurement of CO<sub>2</sub>, C<sub>2</sub>-C<sub>4</sub> hydrocarbons and nitrogen containing compounds. The FID is equipped with an Rtx-5 column for the measurement of C<sub>1</sub>-C<sub>10</sub> and nitrogen containing compounds.

The absolute conversion,  $X_{abs}$ , of CO<sub>2</sub> and N<sub>2</sub> is calculated from the peak areas measured under the gas chromatograms:

$$X_{abs,CO_2} = \frac{\text{moles of } CO_2 \text{ converted}}{\text{moles of } CO_2 \text{ without plasma}}$$
$$= \frac{\text{moles of } CO_2 \text{ without plasma} - \text{moles of } CO_2 \text{ with plasma}}{\text{moles of } CO_2 \text{ without plasma}}$$

$$X_{abs,N_2} = \frac{\text{moles of } N_2 \text{ converted}}{\text{moles of } N_2 \text{ without plasma}}$$

$$=\frac{\text{moles of } N_2 \text{ without plasma} - \text{moles of } N_2 \text{ with plasma}}{\text{moles of } N_2 \text{ without plasma}}$$

The effective conversion,  $X_{eff}$ , is obtained by multiplying the absolute conversion,  $X_{abs}$ , with the relative gas content:

$$X_{\text{eff,CO}_2} = X_{\text{abs,CO}_2} \cdot [\text{CO}_2] (\%)$$
(3)

$$X_{\text{eff},N_2} = X_{\text{abs},N_2} \cdot [N_2] (\%) \tag{4}$$

(1)

(2)

To calculate the energy efficiency of the  $CO_2$  conversion, we define the specific energy input (SEI) in the plasma from the discharge power and the gas flow rate:

SEI 
$$(J \text{ cm}^{-3}) = \text{SEI} (kJ L^{-1}) = \frac{\text{Power} (kW)}{\text{Flowrate} (L \min^{-1})} \cdot 60 (\text{s} \min^{-1})$$
  
(5)

Subsequently, the energy efficiency ( $\eta$ ) is calculated as:

$$\eta \ (\%) = X_{\rm eff, CO_2} \cdot \frac{\Delta H_{\rm R} \ (\rm kJ \ mol^{-1})}{\rm SEI \ (\rm kJ \ L^{-1}) \cdot 24.5 \ (\rm L \ mol^{-1})} \times 100\%$$
 (6)

Note that the value of 24.5 L mol<sup>-1</sup> is calculated for 298 K and 1 atm. Furthermore,  $\Delta H_{\rm R}$  is the reaction enthalpy for CO<sub>2</sub> splitting (CO<sub>2</sub>  $\rightarrow$  CO +  $\frac{1}{2}$ O<sub>2</sub>), *i.e.* 279.8 kJ mol<sup>-1</sup> or 2.9 eV per molecule.

#### Gas expansion factor

The moles of  $CO_2$  and  $N_2$ , written in eqn (1) and (2), are as mentioned above, obtained with gas chromatography by sampling a small volume of the gas stream. Subsequently, the concentrations are deduced from a calibration curve, which is obtained for a constant gas flow. However, in a DBD the number of molecules and thus the volumetric flux increases along the reactor, as  $CO_2$  is gradually converted into CO and  $O_2$  molecules. More specifically, two  $CO_2$  molecules are split into three molecules (see eqn (7)), which increase the volume by 50%.

$$2CO_2 \rightarrow 2CO + O_2 \tag{7}$$

As will be shown in section "Effect of  $N_2$  on plasma splitting of  $CO_2$ " below,  $N_2$  is almost not converted and thus its contribution to the change in volume is minimal. However, it does act as a dilutant: when adding more  $N_2$ , the volume expansion due to  $CO_2$  splitting becomes less pronounced, since the share of  $CO_2$ in the total gas mixture decreases.

This so-called gas expansion effect is clearly not taken into account in the gas chromatography approach above, which up to now is used by almost all authors. However, depending on the gas mixture it can be quite significant, as stated by Pinhão et al.61 Therefore, in the present paper, we have properly accounted for this effect, as explained in detail in the ESI.† When neglecting this effect, the N2 conversion would be overestimated by an order of magnitude. This is the result of the very low conversion for N<sub>2</sub>, as shown below. Pinhão et al.<sup>61</sup> also reported that the relative error, and thus the overestimation, indeed increases significantly for lower values of the conversion. The CO<sub>2</sub> conversion, on the other hand, would be overestimated by a factor 1.5 for pure CO<sub>2</sub>, a factor 1.2 for a mixture with 50% CO<sub>2</sub> and a factor 1.04 in the case of 10% CO<sub>2</sub> in the mixture. Indeed, as mentioned above, the volume expansion becomes less pronounced when more N<sub>2</sub> is present in the mixture. It is thus clear that when studying the effect of different gas mixing ratios, as in the present paper, the gas expansion effect will vary, depending on the gas mixing ratio, which further complicates the situation, and stresses the importance of taking this effect properly into account. More details about the calculation of the gas expansion effect can be found in the ESI.<sup>†</sup>

#### Product analysis: N<sub>2</sub>O and NO<sub>x</sub> compounds

Gas chromatography is not a suitable technique to study the formation of  $O_3$ ,  $N_2O$  and  $NO_x$  compounds (*i.e.*, NO,  $NO_2$ ,  $N_2O_3$ )

and  $N_2O_5$ ). Therefore, we applied Fourier transform infrared spectroscopy (FTIR; Thermo Fischer Scientific, Waltham, MA). By inserting a 2 m IR gas cell in the FTIR spectrometer, we obtain an IR absorption spectrum showing all IR active vibrations. During the experiments, an FTIR resolution of 1 cm<sup>-1</sup> is used, which results in a spectrum being taken every 15 s. For basic qualitative measurements, this technique provides nearly real-time information on gas phase production of the N-containing compounds.

## Description of the model

#### 0D chemical kinetics model

The model used in this work to explain the plasma chemistry is a zero-dimensional (0D) chemical kinetics model, called ZDPlaskin.<sup>62</sup> In this model, the time-evolution of the species densities is calculated by balance equations, taking into account the various production and loss terms by chemical reactions. Transport processes are not considered; hence, the species densities are assumed to be constant in the entire simulation volume. Although this means that the plasma is treated as a "batch reactor", we can convert this to represent a "plug-flow reactor", which is indeed close to the real situation, by translating the temporal behavior into a spatial behavior, as described below. The rate coefficients of the heavy particle reactions (*i.e.*, atoms, molecules, radicals, ions, and excited species) are assumed to be constant and adopted from the literature (see below), whereas the rate coefficients for the electron impact reactions are calculated with a Boltzmann solver, BOLSIG+,<sup>63</sup> which is integrated into ZDPlaskin. For a more detailed description of the model, we refer to the work of Pancheshnvi et al.62

#### Plasma chemistry included in the model

The chemistry set used in this model was recently developed and validated for a microwave discharge.<sup>25</sup> In short, it considers 119 different species (see Table 1), which react with each other in 339 electron impact reactions, 804 ion reactions and 2795 neutral reactions. Their corresponding rate coefficients, and the references where these data were adopted from, are listed in the ESI† of our previous work.<sup>25</sup> Some minor adjustments were made, which are explained in the ESI† of the current paper.

**Table 1** Species included in the model, besides the electrons. The symbols 'V' and 'E' stand for various vibrational and electronically excited levels of the various species, as explained in detail in the work of Heijkers *et al.*<sup>25</sup>

Molecules	Radicals	Charged species	Excited species
CO <sub>2</sub> CO	C <sub>2</sub> O, C <sub>2</sub> , C	$CO_2^+, C_2O_2^+, C_2O_3^+, C_2O_4^+, C_2^+, C^+$ $CO^+, CO_3^-, CO_4^-, CO_4^+$	CO <sub>2</sub> (Va), CO <sub>2</sub> (Vb), CO <sub>2</sub> (Vc), CO <sub>2</sub> (Vd), CO <sub>2</sub> (V1-V21), CO <sub>2</sub> (E1), CO <sub>2</sub> (E2) CO(V1-V10), CO(E1), CO(E2), CO(E3), CO(E4)
$O_2, O_3$	0	$O_2^{+}, O_2^{-}, O^+, O^-, O_4^{-}, O_4^{+}, O_3^{-}$	$O_2(V1), O_2(V2), O_2(V3), O_2(V4), O_2(E1), O_2(E2)$
N <sub>2</sub>	Ν	$N^{+}, N_{2}^{+}, N_{3}^{+}, N_{4}^{+}$	$N_2(V1-V14), N_2(C^3\Pi_u), N_2(A^3\Sigma_u^+), N_2(a'^1\Sigma_u^-), N_2(B^3\Pi_g), N(2D), N(2P)$
$N_2O, N_2O_3,$	NO, NO <sub>2</sub> , NO <sub>3</sub>	$NO^{+}$ , $N_{2}O^{+}$ , $NO_{2}^{+}$ , $NO^{-}$ , $N_{2}O^{-}$ , $NO_{2}^{-}$ ,	· · · · · · · · · · · · · · · · · · ·
$N_2O_4, N_2O_5$		$NO_{3}^{-}, N_{2}O_{2}^{+}$	
ONCN, C <sub>2</sub> N <sub>2</sub> , NCN	CN, NCO		

#### Application of the 0D model to a DBD reactor

As mentioned above, a 0D model calculates the species densities as a function of time only, and it neglects spatial variations. However, the time evolution can be translated into a spatial evolution (*i.e.* as a function of position in the DBD reactor) by means of the gas flow rate. This allows us to mimic the typical filamentary behavior of a DBD used for CO2 conversion.<sup>16,64</sup> Indeed, the gas molecules will pass through several microdischarge filaments on their way throughout the reactor. This is thus taken into account in the model by applying a large number of consecutive microdischarge pulses of 30 ns, in exactly the same way as described by Kozák et al.22 This approach has already proven to be applicable for a variety of conditions and gas mixtures.<sup>18,20,22,33,35,65,66</sup> We assume the same gas flow rate as used experimentally, *i.e.*, 611 mL min<sup>-1</sup> at atmospheric pressure, and the same DBD reactor volume of 7.4 cm<sup>3</sup> (see Section "Plasma reactor" above), which corresponds to a total residence time of 0.73 s. The temperature is assumed to remain constant at 300 K, as predicted by Aerts et al.<sup>16</sup>

## Results and discussion

First, we will show the experimental results and compare them with the model predictions, for the conversion of  $CO_2$  and  $N_2$ , the energy efficiency of  $CO_2$  conversion and the formation of  $N_2O$  and  $NO_x$  compounds, upon addition of  $N_2$  in the gas mixture. Subsequently, the underlying plasma chemistry for the  $CO_2$  and  $N_2$  conversion and the formation of the various compounds will be discussed in more detail, based on the modeling results.

#### Effect of N<sub>2</sub> on plasma splitting of CO<sub>2</sub>

Effect on conversion and energy efficiency. Fig. 1(a) illustrates the experimental and calculated absolute CO<sub>2</sub> and N<sub>2</sub> conversion as a function of the N<sub>2</sub> content. The absolute CO<sub>2</sub> conversion increases more or less exponentially with rising N2 fraction, both in the experimental data and the calculations. This indicates that N<sub>2</sub> has a beneficial effect on CO<sub>2</sub> splitting, as will be explained below. The N2 conversion, on the other hand, is very low, *i.e.*, in the order of 0.1–1% for both the experiments and the model, showing again a good agreement. The reason for the low N<sub>2</sub> conversion is that it mainly occurs through electron impact ionization of N2 molecules, followed by the reaction of the produced ions with other species, as we explained before for a CH<sub>4</sub>/N<sub>2</sub> mixture.<sup>65</sup> However, this electron impact ionization occurs at high electron energy (above 15.5 eV), which is higher than the values typically reached for our operating conditions, and this explains the low N<sub>2</sub> conversion.

Fig. 1(b) illustrates the experimental and calculated effective (or overall)  $CO_2$  and  $N_2$  conversion as a function of the  $N_2$ content. The effective  $CO_2$  conversion remains relatively constant at around 4% when adding up to 40–50%  $N_2$ . This can be explained because the absolute conversion increases (*cf.* Fig. 1(a)), but at the same time the fraction of  $CO_2$  in the gas mixture decreases, and both effects compensate each other. In other



Fig. 1 Experimental and calculated values of absolute  $CO_2$  and  $N_2$  conversion (a), effective  $CO_2$  and  $N_2$  conversion (b) and energy efficiency of  $CO_2$  conversion (c) as a function of  $N_2$  content, for a residence time of 0.73 s and a SEI of approx. 12 J cm<sup>-3</sup>.

words, the increase in absolute conversion upon adding  $N_2$  is high enough to counteract the lower  $CO_2$  concentration in the gas mixture. When reaching 50%  $N_2$ , the effective conversion starts decreasing exponentially. This means that the increase in absolute conversion is no longer high enough to compensate for the lower  $CO_2$  concentration in the mixture. This behavior can be explained from the kinetic analysis presented in section "Underlying chemistry" below. When adding up to 50%  $N_2$ , the energy put into the plasma goes to  $CO_2$  splitting, both directly through electron impact dissociation and indirectly through electron impact excitation of  $N_2$ , which aids in the dissociation of  $CO_2$  (see below). Above 50%  $N_2$ , more energy goes into  $N_2$ excitations and it is no longer efficiently transferred to the reactions leading to  $CO_2$  dissociation (see section "Underlying chemistry" below).

Again, excellent agreement is obtained between the experimental and calculated data, except in the region between 0 and  $1\% N_2$ , where a significant rise in  $CO_2$  conversion is seen in the experiments, being absent in the model predictions. This is attributed to a change in the physical properties of the discharge when comparing a pure  $CO_2$  plasma with a  $CO_2/N_2$  plasma. Indeed, it is known that a DBD plasma in  $CO_2$  has a filamentary character,<sup>16,64</sup> while adding  $N_2$  leads to a more homogeneous and stable discharge.<sup>65,67</sup> This effect cannot be completely captured in the 0D model, explaining the slight discrepancy between experiments and model predictions.

The effective  $N_2$  conversion rises slightly (from 0.01 to 0.3% in the experiment, and from 0.005 to 0.1% in the model predictions) when adding up to 90%  $N_2$ , followed by a drop to zero for pure  $N_2$ . This behavior can again be explained by the fact that the  $N_2$  conversion occurs through ionization and the subsequent reaction of the formed ions with other species (see above), which are absent for pure  $N_2$ . The small difference in experimental and calculated values comes from the large uncertainties in the experiment, resulting from the low values and thus the large effect of the gas expansion factor, as discussed in the Experimental section above.

The energy efficiency for  $CO_2$  conversion (see Fig. 1(c)) shows exactly the same trend as the effective  $CO_2$  conversion, where it is calculated from (see eqn (6) above). Thus, the energy efficiency remains quite constant around 4% in the experiments (and slightly lower in the model predictions) until about 50% N<sub>2</sub> and then it starts decreasing rapidly, because of the lower effective  $CO_2$  conversion and the fact that more energy is consumed by the N<sub>2</sub> molecules upon increasing N<sub>2</sub> content in the mixture, and cannot be used anymore for the  $CO_2$  conversion.

Effect on product formation. CO<sub>2</sub> splitting typically yields CO and O<sub>2</sub> molecules; the latter being formed by the recombination of O atoms. Besides, also some O<sub>3</sub> can be created.<sup>18</sup> This product distribution does not change when adding N2, as revealed by our experiments and model predictions. However, the N<sub>2</sub> addition leads to the formation of some N<sub>2</sub>O and NO<sub>x</sub> compounds, which will be discussed in more detail in this section. This is very important because the production of N<sub>2</sub>O and certain NO<sub>r</sub> might be beneficial when formed in very high concentrations, as this would indicate that the process could be effective for nitrogen fixation.<sup>60</sup> However, in low concentrations (*i.e.*, below 1%), it has no economic value, and even worse, it gives a high environmental cost, since N<sub>2</sub>O and NO<sub>x</sub> have a severe negative impact on air quality, leading to restriction of their emissions and the need of denox installations.<sup>68,69</sup> Therefore, it is of crucial importance to analyze the product formation in the CO<sub>2</sub>/N<sub>2</sub> plasma, to know which of the two scenarios take place.

For NO and NO<sub>2</sub> a calibration curve is available, which allows us to express the measurement results in absolute concentrations (ppm). For  $N_2O$ ,  $N_2O_3$  and  $N_2O_5$ , however, this

is not the case and the formation of these compounds can thus only be expressed in arbitrary units (a.u.) of the measured absorbance. To maintain consistency throughout the discussion here, all experimental results will be presented in arbitrary units (a.u.) as measured absorbance with the FTIR-cell, while the calculation results will be given in ppm. For NO and NO<sub>2</sub>, we will elaborate on the comparison in absolute concentrations in the ESI,† and briefly report about it in the text below. Furthermore, to allow a detailed comparison between the experimental and calculated trends, the two *y*-axes (representing the experimental and calculated data, respectively) will be constructed so that they vary over the same range.

The measured and calculated NO and NO<sub>2</sub> concentrations are plotted as a function of N<sub>2</sub> content in the gas mixture in Fig. 2(a) and (b), respectively. Experimentally both compounds follow the same parabolic trend with a maximum at 50% N<sub>2</sub>. As will be illustrated in section "N<sub>2</sub>O and NO<sub>x</sub> formation" below, the NO<sub>x</sub> species are formed out of N (or N<sub>2</sub>(A<sup>3</sup>Σ<sup>+</sup><sub>u</sub>)) and O atoms, which originate from N<sub>2</sub> and CO<sub>2</sub>, respectively. Thus, it is not unexpected that the maximum of the NO<sub>x</sub> concentration is achieved when both reactants are present in approximately equal concentrations. The calculated results follow more or less the same trend for NO<sub>2</sub> but a left-skewed trend for NO with respect to the experimental values. Nevertheless, in both cases, the profiles first rise and then drop with increasing N<sub>2</sub> content, so we believe that the model can be used to explain the observed trends (see section "N<sub>2</sub>O and NO<sub>x</sub> formation" below).



Fig. 2 Experimental and calculated concentrations of NO (a) and NO<sub>2</sub> (b) as a function of N<sub>2</sub> content, for a residence time of 0.73 s and a SEI of approx. 12 J cm<sup>-3</sup>.

Furthermore, even the absolute values of the concentrations are in reasonable agreement, as elaborated in the ESI.†

Experimentally, the obtained NO concentration is about an order of magnitude higher than the NO<sub>2</sub> concentration, with maximum values of 550 and 54 ppm, respectively (see ESI<sup>+</sup>). Even at 1% N<sub>2</sub> the measured concentrations are already 40 and 10 ppm, respectively. To put these values in perspective, when converting them to emissions in the common units of  $g \text{ km}^{-1}$ in the automobile sector,<sup>70</sup> they are  $\sim 3000$  times higher than that currently allowed under European emission standards for passenger cars (EURO 6 norm, 80 mg km<sup>-1</sup>).<sup>71</sup> Compared with industrial emissions, when converting them to the industrially used units of mg  $m^{-3}$ , they are in the order of 10–20 times higher than the current BAT-AELs (Best Available Technique Associated Emission Levels) for coal fired power plants with a capacity of > 300 MW in Europe, which allow NO<sub>x</sub> emissions of 50–200 mg m<sup>-3,<sup>72</sup> The calculated NO and NO<sub>2</sub> concentrations</sup> are somewhat lower, but in the same order of magnitude, with a maximum of 115 and 34 ppm, respectively.

These NO<sub>x</sub> compounds react in the air, resulting in smog formation and acid rain. Thus, these high concentrations will have a negative effect on air quality and the environment.<sup>73</sup> At the same time, however, the concentrations are too low to be considered useful for nitrogen fixation.<sup>60</sup> Indeed, the current industrial processes for nitrogen fixation, *i.e.*, the Haber–Bosch process (for making ammonia) and the Ostwald process (for making nitric acid starting from ammonia) can achieve overall yields of 99%.<sup>74</sup>

The other NO<sub>x</sub> compounds detected in the experiments are  $N_2O_3$  and  $N_2O_5$ , for which the concentrations (again in a.u.) are plotted in Fig. 3(a) and (b), along with the model predictions (in ppm). Again, a reasonable agreement is obtained in the experimental and calculated trends, especially for  $N_2O_5$  (note the same variation in the orders of magnitude of both *y*-axes).

The N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> concentrations vary over two and three orders of magnitude, respectively, within the entire range of N<sub>2</sub> contents in the gas mixture. According to our calculations, concentrations up to 1000 ppm are found for N<sub>2</sub>O<sub>5</sub>, while the calculated N<sub>2</sub>O<sub>3</sub> concentrations do not exceed 0.05 ppm. Unfortunately, we were not able to deduce the absolute values for the experimental concentrations, because of lack of suitable detectors to create a calibration curve. Since N<sub>2</sub>O<sub>5</sub> can be considered as the anhydride of nitric acid, this would indicate that if the calculated concentrations are realistic, these concentrations would contribute heavily to the formation of acid rain if emitted to the atmosphere. Regarding the  $N_2O_3$  emission, this appears not to be a problem, since the calculations predict negligible amounts to be formed. This is in agreement with the fact that at room temperature the dissociation into the constituent gases NO and NO<sub>2</sub> is favored over the formation of N<sub>2</sub>O<sub>3</sub>.<sup>75</sup>

Finally, the measured and calculated  $N_2O$  concentrations are presented in Fig. 4. Again the same parabolic trend as a function of the  $N_2$  content in the gas mixture is observed as for the  $NO_x$  compounds, with a maximum at 50–60%  $N_2$ . The calculated maximum concentration is about 55 ppm, but experimentally it was again not possible to obtain absolute values of



Fig. 3 Experimental and calculated concentrations of  $N_2O_3$  (a) and  $N_2O_5$  (b) as a function of  $N_2$  content, for a residence time of 0.73 s and a SEI of approx. 12 J cm<sup>-3</sup>.

the concentration. Nitrous oxide is a very potent greenhouse gas, with a global warming potential (GWP) of 298  $CO_{2,equivalent}$ . Keeping in mind that for the conditions under study, we effectively convert about 4%  $CO_2$  (see Fig. 1(b) above), this means that if the N<sub>2</sub>O concentration would exceed 130 ppm, the reduction in GWP would be equal to zero. Hence, the production of nitrous oxide is voiding the greenhouse gas mitigation potential of our technology (by up to 40% for N<sub>2</sub>O concentrations up to 55 ppm) if we do not add a denox purification step



Fig. 4 Experimental and calculated concentrations of N<sub>2</sub>O as a function of N<sub>2</sub> content, for a residence time of 0.73 s and a SEI of approx. 12 J cm<sup>-3</sup>.

afterwards. Denox technology mainly includes Selective non-Catalytic Reduction (SNCR), Selective Catalytic Reduction (SCR) and a combination of both. Although these are already mature technologies with high  $NO_x$  reduction efficiencies (70–95%), they are also prone to high operational costs.<sup>76,77</sup> This is no surprise since in general, end-of-pipe clean-up technology is always more expensive.

It becomes clear from both the measurements and the calculations that  $N_2O$  and several  $NO_x$  compounds are produced. Although their concentrations remain in the ppm range, this is certainly not negligible, since they give rise to several environmental problems. Hence, it appears to be crucial to separate the  $CO_2$  gas from  $N_2$  impurities (or gas fractions) before plasma treatment, to avoid the formation of  $NO_x$  compounds and thus the need to install expensive denox installations afterwards.

#### Underlying chemistry

In the following sections, the underlying plasma chemistry, as predicted by the model, will be discussed in more detail, for the  $CO_2$  conversion in the presence of  $N_2$ , as well as for the formation of  $NO_x$  compounds and  $N_2O$ . Indeed, a better insight into the underlying chemical reactions might help to steer the process, to improve the  $CO_2$  conversion and energy efficiency, and to reduce the  $NO_x$  and  $N_2O$  formation.

 $CO_2$  conversion. The reactions responsible for the  $CO_2$  conversion are presented in Fig. 5, as a function of the  $N_2$  content in the gas mixture. At low  $N_2$  contents, the most important reaction is electron impact dissociation of  $CO_2$  into CO and O, while at high  $N_2$  contents, the reaction with metastable  $N_2(A^3\Sigma_u^+)$  molecules, yielding the same splitting products (CO and O) and leaving  $N_2$  in its ground state, is mainly responsible for the  $CO_2$  conversion. Indeed, upon higher  $N_2$  contents, the electron energy is gradually being used for  $N_2$  excitation instead of  $CO_2$  dissociation, explaining the drop in electron impact dissociation rate and the corresponding increase in the dissociation rate by  $N_2$  metastable molecules. The former reaction is dominant during the microdischarge filaments of the DBD, as is illustrated



Fig. 5 Relative contribution of the main processes leading to  $CO_2$  conversion as a function of  $N_2$  content, for a residence time of 0.73 s and a SEI of approx. 12 J cm<sup>-3</sup>.

in the ESI,<sup>†</sup> while the latter reaction is more important in the time between the filaments, *i.e.*, the so-called afterglows. Other reactions that play a minor role towards CO<sub>2</sub> dissociation (~5%) are electron impact ionization of CO<sub>2</sub> and electron impact dissociation from vibrationally excited CO<sub>2</sub> (*i.e.*, CO<sub>2</sub>(V)) (see Fig. 5).

Up to 60–70% N<sub>2</sub>, the sum of the rates due to electron impact dissociation and dissociation by N<sub>2</sub> metastable molecules drops only slightly upon increasing N<sub>2</sub> content, explaining why the effective CO<sub>2</sub> conversion drops only slightly, as shown in Fig. 1(b). In other words, upon adding N<sub>2</sub>, the N<sub>2</sub> metastable molecules provide an extra dissociation mechanism for CO<sub>2</sub>, explaining why the absolute CO<sub>2</sub> conversion rises (Fig. 1(a)), but this is compensated by the lower CO<sub>2</sub> content in the mixture, leading to a slight drop in effective CO<sub>2</sub> conversion. Above 70% N<sub>2</sub>, however, both rates start decreasing due to the lower CO<sub>2</sub> concentration, which is not compensated by the higher N<sub>2</sub> concentration (and thus higher dissociation by N<sub>2</sub> metastable molecules), leading to a drop in the effective CO<sub>2</sub> conversion.

 $N_2O$  and  $NO_x$  formation. The most important formation and destruction processes for NO,  $NO_2$  and  $N_2O$  are presented in Fig. 6, 7 and 8, respectively. Our calculations predict that NO is mainly formed during the afterglows, *i.e.*, in between the microdischarge filaments, because it is dictated by heavy particle reactions (see ESI<sup>†</sup>). The dominant formation mechanism of NO is the reaction between O radicals and  $NO_2$  molecules, forming NO and  $O_2$  molecules.

This reaction is by far the most important for  $N_2$  fractions below 95% (see Fig. 6(a)). Above 95%, the reaction between N radicals and ozone, yielding the same products, becomes slightly more important.

The dominant NO loss mechanism is the recombination with O atoms into NO<sub>2</sub> through a three-body reaction. This third body can be either CO<sub>2</sub> (mainly important for N<sub>2</sub> contents below 40%) or N<sub>2</sub> (for N<sub>2</sub> contents between 40 and 90%). For N<sub>2</sub> contents above 95% the reaction with N atoms, yielding the formation of O and N<sub>2</sub>, becomes most important. Other loss mechanisms are the formation of N<sub>2</sub>O<sub>3</sub> (mainly at N<sub>2</sub> fractions below 70%) and the reaction with electronically excited N<sub>2</sub>(a'<sup>1</sup>\Sigma<sub>u</sub><sup>-</sup>), forming N<sub>2</sub>, N and O (at higher N<sub>2</sub> fractions). However, these reactions do not contribute to more than ~5–20%.

It is thus clear that there is an interplay between NO and NO<sub>2</sub>, as was also observed in other modeling work, albeit for other conditions (*i.e.*, a plasma jet expanding in humid air).<sup>78</sup> NO<sub>2</sub> is the main source of NO production and *vice versa*, as will be shown in Fig. 7. This will also become clear from the reaction scheme in Fig. 9 below.

The NO<sub>2</sub> production also occurs mainly in between the filaments, attributed to heavy particle reactions. The only important process for NO<sub>2</sub> production is the three-body recombination between NO and O, with either CO<sub>2</sub> or N<sub>2</sub> as a third body (at N<sub>2</sub> contents below and above 40%, respectively; see Fig. 7(a)). These are also the main loss mechanisms of NO, as is illustrated in Fig. 6(b). Some other processes, like the dissociation of N<sub>2</sub>O<sub>3</sub> into NO and NO<sub>2</sub>, the reaction between NO<sub>3</sub> and NO, forming two NO<sub>2</sub> molecules, or between NO<sub>3</sub> and O, forming NO<sub>2</sub> and O<sub>2</sub>, also play a minor role (~5–20%) in the production of NO<sub>2</sub>.



Fig. 6 Relative contributions of the main formation (a) and loss (b) mechanisms of NO as a function of N<sub>2</sub> content, for a residence time of 0.73 s and a SEI of approx. 12 J cm<sup>-3</sup>.

As is clear from Fig. 7(b), the dominant loss mechanism of NO<sub>2</sub>, for all N<sub>2</sub> fractions, is the reaction with O atoms, forming NO and O<sub>2</sub>, which is also the most important formation mechanism of NO, see Fig. 6(a) above. Some other loss mechanisms are the formation of N<sub>2</sub>O<sub>3</sub> through three-body recombination with NO, the formation of NO<sub>3</sub> through three-body recombination with O (and  $N_2$  as a third body), and the formation of  $N_2O_5$ through three-body recombination with NO<sub>3</sub>, but they clearly play a minor role, as seen from Fig. 7(b). Note that the rates of formation of  $N_2O_5$  (by the three-body recombination reaction between  $NO_2$  and  $NO_3$ ; the pink curve in Fig. 7(b)) and its dissociation into NO<sub>2</sub> and NO<sub>3</sub> (upon collision with a neutral particle; the blue curve in Fig. 7(a) are almost equal to each other. This indicates that these molecules are equally converted into each other, as will also be visible from the reaction scheme in Fig. 9 below.

Finally, in Fig. 8(a) and (b) we show the main N<sub>2</sub>O formation and loss processes, respectively. The dominant formation mechanism of N<sub>2</sub>O is the reaction between N and NO<sub>2</sub>, forming N<sub>2</sub>O and O. Only at N<sub>2</sub> fractions below 5%, N<sub>2</sub>O is mainly formed by the reaction between NCO and NO, forming N<sub>2</sub>O and CO. Finally, the reaction between the metastable N<sub>2</sub>( $A^{3}\Sigma_{u}^{+}$ ) molecules and O<sub>2</sub>, forming N<sub>2</sub>O and O, also makes a minor contribution (~5–20%).

The main loss mechanism of  $N_2O$  is the reaction with  $N_2(A^3\Sigma_u^+)$ , forming  $N_2$ , N and NO. Only at low  $N_2$  fractions, the



Fig. 7 Relative contributions of the main formation (a) and loss (b) mechanisms of NO<sub>2</sub> as a function of N<sub>2</sub> content, for a residence time of 0.73 s and a SEI of approx. 12 J cm<sup>-3</sup>.

charge transfer reactions with  $N_2^+$  ions, forming either  $N_2O^+$ and  $N_2$ , or  $NO^+$ , N and  $N_2$ , play a minor role (up to 30% at 1%  $N_2$ fraction), while electron impact ionization also has a small, yet non-negligible contribution towards the destruction of  $N_2O$ (~5–10% at 1%  $N_2$  fraction).

With these data, we can compose an overall reaction scheme, as presented in Fig. 9. The width of the full arrows is scaled according to the values of the time integrated reaction rates. Fig. 9(a) illustrates the main products arising from  $CO_2$ , which will subsequently react with the N-compounds presented in Fig. 9(b) and (c). Below the most important processes will be described. Initially, N<sub>2</sub> will be excited to its metastable state  $N_2(A^3\Sigma_u^+)$ , which will react with O atoms in the formation of NO, or with O2 creating N2O. Upon electron impact dissociation, N2 will also be split into N atoms, which can react with both O and O<sub>3</sub> yielding NO. Subsequently, NO can be converted into NO<sub>2</sub> through a reaction with O, but NO2 will also react back into NO upon reaction with O. This makes NO2 the main source of NO production and vice versa, as is clear from Fig. 9(b). Furthermore, the N atoms, which are directly formed from N<sub>2</sub> dissociation, also play a role in the conversion between NO and NO2. From NO there is also a pathway back to N2 upon reaction with N or  $N_2(a'^1\Sigma_u)$ , and a pathway back to N upon reaction with  $N_2(a'^1\Sigma_u)$ . Furthermore, N2O can also react back to N2 and N upon reaction with  $N_2(A^3\Sigma_u^+)$  and  $N_2^+$ . NO<sub>2</sub>, on the other hand, has no significant



Fig. 8 Relative contributions of the main formation (a) and loss (b) mechanisms of  $N_2O$  as a function of  $N_2$  content, for a residence time of 0.73 s and a SEI of approx. 12 J cm<sup>-3</sup>.

pathway back to  $N_2$  or N. This is all illustrated in Fig. 9(b), which represents the start of the different chemical pathways. This will be important to keep in mind in the further discussion below, as it will allow us to see whether we can intervene in the chemistry taking place.

Subsequently, a loop between NO, NO<sub>2</sub> and N<sub>2</sub>O<sub>3</sub>, as well as a loop between NO<sub>2</sub>, NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>, is created, as presented in Fig. 9(c). Furthermore, some of the NO<sub>2</sub> is also lost to N<sub>2</sub>O through reaction with N radicals. The only way out of these loops, as mentioned above, is through the reaction of NO with N or N<sub>2</sub>(a'1 $\Sigma_u^-$ ), yielding either N or N<sub>2</sub> and an O atom, or through the reaction of N<sub>2</sub>O with N<sub>2</sub>(A<sup>3</sup> $\Sigma_u^+$ ) or N<sub>2</sub><sup>+</sup>, leading to N<sub>2</sub>, NO and a N atom, or to NO<sup>+</sup>, N<sub>2</sub> and N or N<sub>2</sub>O<sup>+</sup> and N<sub>2</sub>, respectively.

From these reaction schemes it becomes obvious that, with respect to the plasma chemistry, there are two possibilities to prevent the formation of N<sub>2</sub>O and NO<sub>x</sub> compounds. The first one is to prevent the formation of the N-species involved in these reactions, *i.e.* metastable N<sub>2</sub>( $A^3\Sigma_u^+$ ) and N. This would only be possible in a plasma set-up in which all the electrons have an energy lower than 6.2 eV, which is the excitation threshold energy for the formation of N<sub>2</sub>( $A^3\Sigma_u^+$ ) through electron impact, while the dissociation threshold of N<sub>2</sub> into N lies at 9.75 eV. These conditions are not possible with a classic DBD. Set-ups which operate at lower average electron energies than a DBD are gliding arcs and microwave discharges. Indeed, in the



**Fig. 9** Reaction scheme to illustrate the main pathways of the N<sub>2</sub>O and NO<sub>x</sub> chemistry as predicted by the model. Reaction pathways starting from  $CO_2$  (a), initiation of the NO<sub>x</sub> chemistry (b), complete overview of the N<sub>2</sub>O and NO<sub>x</sub> chemistry (c). The thickness of the arrows corresponds to the importance of the reactions.

model for the  $CO_2/N_2$  microwave plasma by Heijkers *et al.*<sup>25</sup> it was shown that metastable  $N_2(A^3\Sigma_u^+)$  is of minor importance. Nevertheless, the formation of  $NO_x$  was also observed, albeit through a different mechanism. Indeed, in a microwave plasma, the lower energy of the electrons causes vibrational excitation to become more important than electronic excitation and dissociation, and the vibrationally excited  $N_2$  molecules react with O atoms to form N and NO, instead of the electronically excited  $N_2$  in a DBD.

The second, more realistic option is to prevent the reaction between the N-species  $(N_2(A^3\Sigma_u^+) \text{ and } N)$  and the O-species

#### Paper

 $(O, O_2 \text{ or } O_3)$ , which is the initial pathway for the formation of NO and  $N_2O$  (cf. Fig. 9(b) above). In order to achieve this, one should look for quenching mechanisms of the  $N_2(A^3\Sigma_u^+)$  metastable molecules, or possible scavengers, catalyst interactions or separation membranes for the N atoms and the O-species. Quenching of metastable molecules can be realized upon collision with other molecules. Although possible in theory, this will not be easy to realize in practice. Moreover, it is even not advisable, because exactly these metastable  $N_2(A^3\Sigma_u^+)$  molecules aid in the conversion of CO<sub>2</sub> upon increasing N<sub>2</sub> content, as shown in Fig. 5. With respect to the O-species, it is important to notice that in a DBD plasma operating in CO<sub>2</sub> all O<sub>2</sub> and O<sub>3</sub> are originating from O (cf. Fig. 9(a)). Thus, when eliminating O, we automatically eliminate O2 and O3. Furthermore, from Fig. 9(c) it becomes clear that if we only succeed in eliminating  $O_2$  and  $O_3$ , but not the O atoms, there is still a pathway from NO<sub>2</sub> to N<sub>2</sub>O upon reaction with N atoms. This stresses the importance of trying to eliminate especially the O atoms.

In the three cases suggested above to eliminate the O-species, the main idea is the same, *i.e.*, to find an interaction which makes the O atoms or O<sub>2</sub> and O<sub>3</sub> molecules no longer available as reactants, and most importantly, this interaction has to be significantly faster than the reaction between  $N_2(A^3\Sigma_u^+)$ and O or O2; and between N and O or O3. An example of a scavenger in the case of O is H, which reacts very fast with O to form OH and subsequently to H<sub>2</sub>O. This effectively traps the O atoms, as was proven to be possible by a combined experimental and computational study of Aerts et al.<sup>20</sup> Another well-known scavenger of O is O2, reacting to O3. However, since the latter product reacts again to form O and O2, and furthermore O3 is also unwanted, it is not a suitable choice in this case. Furthermore, the advantage of H as a scavenger is that the scavenged product, H<sub>2</sub>O, can be easily separated from the gas mixture. For the second option, *i.e.*, catalyst interactions, the idea of using a catalyst with a high surface interaction with O atoms, allowing the recombination reaction to  $O_2$  on its surface,<sup>79</sup> is not a good choice. Indeed, in this way O2 would be released in the plasma and it could undergo reactions again. A more advanced catalytic process that could be an option is an alternative form of chemical looping,<sup>80,81</sup> in which the O (or O<sub>2</sub>) is captured in the plasma set-up and then used as an oxidizing agent in a second set-up. The third method, based on separation membrane technology, could be considered as similar to the catalyst, but instead of recombining the O to O<sub>2</sub> on the surface, the O atoms (or O<sub>2</sub> molecules) would be transported away from the reaction mixture. A last option could be the combination of a solid oxide electrolyser cell with a plasma set-up.82 It should be realized, however, that the options mentioned above for catalysts, membranes and electrolyser cells, have only been applied up to now to separate O<sub>2</sub> from the gas mixture, and not the O atoms, while it is clear, as mentioned above, that in order to avoid the formation of all NO<sub>x</sub> compounds, we need to be one step ahead and thus, we need to be able to trap already the O atoms, which is still a challenge.

If one of these concepts could be realized, it would eliminate the need for a pre-purification  $(N_2)$  or post-purification (denox)

step, and thus reduce the cost of the overall process. Indeed, besides the N<sub>2</sub>O and NO<sub>x</sub> formation, the presence of N<sub>2</sub> in the gas mixture has no detrimental effect, as the effective CO<sub>2</sub> conversion remains more or less constant up to a N<sub>2</sub> fraction of 50%, as shown in Fig. 1(b), because the lower CO<sub>2</sub> fraction in the mixture is compensated for by the higher absolute CO<sub>2</sub> conversion due to the N<sub>2</sub>(A<sup>3</sup> $\Sigma_{u}^{+}$ ) metastable molecules.

Future work should also address other impurities such as noble gases (*e.g.* He and Ar) or molecular gases such as  $H_2$  and hydrocarbons. The presence of He and Ar should not affect the chemical pathways and products. They will mainly influence the electrical characteristics of the plasma. More specifically, their presence will lower the breakdown voltage. This was demonstrated in previous work by our own group and others.<sup>17,83</sup> Only for very high concentrations, the addition of noble gases would lead to a diluting effect.<sup>84</sup>

 $H_2$  and hydrocarbons, on the other hand, will have an important influence on the chemical pathways and products. For example, we expect  $H_2$  and  $CH_4$  to have the same influence as reported in our previous work.<sup>20</sup> Both will be split in H atoms upon electron impact reactions, and the latter will react very fast with the O atoms present, leading to OH and subsequently to  $H_2O$ . As mentioned above, this might eliminate the production of  $NO_x$  compounds. Furthermore, this might lead to a slightly increased  $CO_2$  conversion, since the O atoms are being directed to a liquid product.

# Conclusions

The purpose of this work was to obtain a better understanding of the effect of  $N_2$  (in the range between 1 and 98%) on the  $CO_2$ splitting in DBD plasma, by means of an extensive combined experimental and computational study. We focused on the effect on  $CO_2$  conversion, both absolute and effective, and the energy efficiency, as well as on the formation of N-containing byproducts, like  $N_2O$  and  $NO_x$  compounds.

We made a comparison between the measured  $CO_2$  and  $N_2$  conversions and the energy efficiency for  $CO_2$  conversion, and the corresponding values calculated by means of a 0D chemical kinetics model, for the entire range of  $N_2$  fractions. A good agreement was reached between the experimental data and the model predictions, indicating that the model includes the correct plasma chemistry and can be used to describe the main production and loss pathways for the various compounds. This allows us to gain sufficient insight into the entire process, and to propose solutions for improving the process in the future.

Our study clearly reveals that the presence of N<sub>2</sub> in the gas mixture up to 50% barely influences the effective CO<sub>2</sub> conversion and the corresponding energy efficiency, in spite of the lower CO<sub>2</sub> fraction in the mixture (and thus the lower CO<sub>2</sub> amount available for conversion). The reason is that N<sub>2</sub> enhances the absolute CO<sub>2</sub> conversion, due to the dissociation of CO<sub>2</sub> upon collision with N<sub>2</sub>(A<sup>3</sup> $\Sigma_u^+$ ) metastable molecules, and both effects compensate each other. On the other hand, N<sub>2</sub> admixtures above 50% result in an exponential drop in the effective CO<sub>2</sub> conversion and energy efficiency, because more and more energy is consumed by  $N_2$  molecules, and not used anymore for  $CO_2$  conversion. This means that, for mixtures containing up to 50%  $N_2$ , no pre-separation steps are necessary with respect to the effective conversion and energy efficiency.

On the other hand, the presence of  $N_2$  in the mixture leads to the formation of  $N_2O$  and several  $NO_x$  compounds, with concentrations in the range of several 100 ppm. While these concentrations are too low to be considered useful for nitrogen fixation, they will give rise to several environmental problems.  $N_2O$  is an even more potent greenhouse gas than  $CO_2$ , with a GWP of 298  $CO_{2,equivalent}$ , while NO and  $NO_2$  are responsible for acid rain and the formation of ozone and a wide variety of toxic products. Thus, from the point of view of byproduct formation, it would be necessary to use either a pre-purification ( $N_2$ ) or post-purification (denox) step.

Our detailed chemical kinetics analysis tells us that the production of these N<sub>2</sub>O and NO<sub>x</sub> compounds starts through a reaction between metastable  $N_2(A^3\Sigma_u^+)$  molecules and either O or  $O_2$  and between N atoms and either O or  $O_3$ ; yielding the formation of NO or N2O. Subsequently, the N is trapped in three reaction loops between the various NO<sub>r</sub> compounds and N<sub>2</sub>O, and the only way out is through the reaction of NO or  $N_2O$  with either N or  $N_2(A^3\Sigma_u^+)$ , yielding the formation of either N or N<sub>2</sub> and O atoms. On the plasma chemistry level, we believe that the only option to prevent the formation of  $N_2O$  and  $NO_x$ compounds is by inhibiting the reaction between the N-species  $(N_2(A^3\Sigma_u^+) \text{ and } N)$  and the O species  $(O, O_2 \text{ or } O_3)$ . To realize this, we should search for possible scavengers, catalyst interactions or separation membranes, especially for the O atoms, since this would also inhibit the formation of O<sub>2</sub> and O<sub>3</sub>. If this could be successful, it would effectively eliminate the need for a prepurification  $(N_2)$  or post-purification (denox) step.

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