

## PAPER

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# Can post-plasma CH<sub>4</sub> injection improve plasma-based dry reforming of methane? A modeling study

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Thermal plasma-driven dry reforming of methane (DRM) has gained increased attention in recent years due to its high conversion and energy conversion efficiency (ECE). Recent experimental work investigated the performance of a pure CO<sub>2</sub> plasma with post-plasma CH<sub>4</sub> injection. The rationale behind this strategy is that by utilizing a pure CO<sub>2</sub> plasma, all plasma energy can be used to dissociate CO<sub>2</sub>, while CH<sub>4</sub> reforming proceeds post-plasma in the reforming reactor with residual heat, potentially improving the energy efficiency compared to injecting both CO<sub>2</sub> and CH<sub>4</sub> into the plasma. To assess whether post-plasma CH<sub>4</sub> injection indeed improves the DRM performance, we developed a chemical kinetics model describing the post-plasma conversion process. We first validated our model by reproducing the experimental results of the pure CO<sub>2</sub> plasma with post-plasma CH<sub>4</sub> injection. Subsequently, we compared both strategies: injecting only CO<sub>2</sub> inside the plasma while injecting CH<sub>4</sub> post-plasma, vs. classical plasma-based DRM. Our modeling results indicate that below specific energy inputs (SEI) of 220 kJ mol<sup>-1</sup>, the total conversion slightly improves (ca. 5%) with the first strategy. However, the ECE is slightly lower due to the low H<sub>2</sub> selectivity caused by substantial H<sub>2</sub>O formation. The highest conversion and ECE are obtained at SEI values of 240–280 kJ mol<sup>-1</sup>, where both strategies yield nearly identical results, indicating the limited potential of improving the performance of DRM by pure CO<sub>2</sub> plasma with post-plasma CH<sub>4</sub> injection. Nevertheless, the approach is still very valuable to allow higher CH<sub>4</sub>/CO<sub>2</sub> ratios without problems of coke formation within the plasma, and thus, to improve plasma stability and reach higher syngas ratios, which is more useful for further Fischer–Tropsch or methanol synthesis.

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## 1. Introduction

The urgent need to mitigate greenhouse gas emissions and stimulate sustainable energy solutions has led to the exploration of novel methodologies for CO<sub>2</sub> utilization and CH<sub>4</sub> conversion. Among these, plasma-based dry reforming of methane (DRM) proved to be a promising avenue, addressing the dual challenge of greenhouse gas reduction and sustainable synthesis of value-added products.<sup>1–3</sup> In DRM, the reaction between CO<sub>2</sub> and CH<sub>4</sub> generates a mixture of H<sub>2</sub> and CO, known as syngas, which can serve as a precursor for various industrial processes, like methanol synthesis<sup>4</sup> and the Fischer–Tropsch process.<sup>5</sup> Compared to alternative strategies for syngas synthesis, such as steam reforming of methane (SRM) and partial oxidation, DRM could save half of the CH<sub>4</sub> consumption for the same amount of CO production by utilizing CO<sub>2</sub> as well.<sup>2</sup> Moreover, whereas SRM typically produces syngas with a H<sub>2</sub>/CO ratio of 3,<sup>6</sup> thereby exceeding the require-

ments for methanol synthesis and the Fischer–Tropsch process,<sup>7</sup> DRM provides more flexibility to adjust the syngas ratio by varying the CH<sub>4</sub> to CO<sub>2</sub> ratio,<sup>8</sup> or by converting the CO with H<sub>2</sub>O into H<sub>2</sub> and CO<sub>2</sub> through an additional water–gas shift reaction.<sup>9</sup>

Classical DRM is limited by severe coke formation, associated with the high temperatures needed to accommodate the strong endothermic process. The lack of commercial catalysts with sufficient resistance toward coke deposits has prevented DRM from being applied on a large scale.<sup>2</sup> To address this limitation, the combination of non-thermal plasma, particularly dielectric barrier discharges (DBD), with a catalyst has gained considerable attention in recent years.<sup>1–3,10</sup> Indeed, the unique non-equilibrium between gas and electrons in DBD can overcome the thermodynamic barrier in the DRM reaction, enabling DRM to occur at ambient conditions.<sup>11</sup> In addition, the process only requires electricity and can be instantly switched on and off, making it adaptable to irregular and intermittent renewable energy supply.<sup>12</sup>

Despite these advantages, a DBD plasma faces challenges, such as high energy costs and low energy efficiency, preventing it from achieving competitiveness with classical DRM.<sup>2,3</sup>

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Besides DBD, various other types of plasma reactors for DRM have been investigated in recent decades.<sup>3,12</sup> While promising results have been obtained, many plasma reactors exhibit limited performance due to a significant portion of the feed gas bypassing the plasma, particularly evident in gliding arc (GA) plasma, resulting in limited conversion and energy efficiency.<sup>7</sup> Snoeckx and Bogaerts<sup>3</sup> introduced a target maximum energy cost of 4.27 eV per molecule for plasma technology to be competitive with classical DRM and other emerging technologies. According to their analysis, only a spark<sup>13</sup> and an atmospheric pressure glow discharge (APGD)<sup>14</sup> were able to achieve energy costs below this target while maintaining relatively high conversions. Subsequent studies in literature have reported additional plasma reactor configurations meeting this maximum energy cost criterion and having high total conversion (>70%), including a GA setup,<sup>15</sup> a confined APGD reactor,<sup>7</sup> and four microwave (MW) plasma reactors.<sup>8,16–18</sup>

These recent studies highlight the potential of MW plasma setups for DRM, reporting excellent conversion and energy efficiency.<sup>8,16–18</sup> In addition to its impressive performance, a MW plasma offers the advantage of operating without electrodes, thereby avoiding electrode erosion, which can otherwise compromise operational longevity and introduce impurities into the plasma.<sup>19</sup> The highest reported energy efficiency, as reported by Sun *et al.*,<sup>16</sup> reaches 71%, with CO<sub>2</sub> and CH<sub>4</sub> conversion of 91% and 96%, respectively. Sun *et al.*<sup>16</sup> developed a model to support their experimental findings, consisting of two series of continuous stirred tank reactors (CSTRs) that exchange heat and mass, representing the plasma stream and surrounding stream. Their modeling results reveal that the reforming proceeds as the surrounding gas enters and diffuses out of the plasma stream due to the flow mixing, explaining the remarkably high conversion, considering that only a limited fraction of the gas passes through the plasma. It is worth noting that the maximum energy efficiency associated with thermal conversion is *ca.* 90%, as will be discussed in section 4.1 below. Hence, the best energy efficiency achieved so far, 71%,<sup>16</sup> still stays significantly below the theoretical thermal limit. This discrepancy can be attributed to various factors, such as heat losses in the reactor, possibly suboptimal mixing of the hot plasma stream with the surrounding stream, the tendency of MW plasma to overshoot the temperature required to achieve complete conversion, and the slow DRM reaction kinetics, which restricts the conversion within the limited reactor residence time. Hence, while the energy efficiency of 71%<sup>16</sup> is already remarkable, further enhancements can possibly be achieved by optimizing the reactor design.

Cho *et al.*<sup>17</sup> reported that their plasma extinguishes when they used a CH<sub>4</sub>/CO<sub>2</sub> molar ratio of 1, due to the generation of carbon particles in the MW reactor, which was also noted in ref. 20. To generate stable plasma, Cho *et al.*<sup>17</sup> opted to segregate the supply of CH<sub>4</sub> from the discharge gas (CO<sub>2</sub>) by injecting CH<sub>4</sub> at the end of the discharge. This approach offers several advantages. As demonstrated in their experiments,<sup>17</sup>

injecting CH<sub>4</sub> post-plasma enables to use a higher molar ratio of CH<sub>4</sub>/CO<sub>2</sub>, as the discharge is no longer susceptible to plasma instability caused by soot formation, leading to higher syngas ratios (H<sub>2</sub>/CO) that are better suited for the synthesis of value-added products.<sup>7</sup> We note however that by optimising the reactor design and discharge conditions, it is also possible to achieve a higher molar ratio of CH<sub>4</sub>/CO<sub>2</sub> while maintaining plasma stability and reducing susceptibility to soot formation. Indeed, two other vortex stabilised MW plasma setups<sup>8,16</sup> obtained good plasma stability for a 1 : 1 CH<sub>4</sub>/CO<sub>2</sub> ratio within a similar flow rate (*ca.* 10–30 L min<sup>−1</sup>) and SEI range (*ca.* 100–300 kJ mol<sup>−1</sup>). Furthermore, Biondo *et al.*<sup>21</sup> were able to reach even higher CH<sub>4</sub> fractions, up to pure CH<sub>4</sub> feed gas, by adopting a reverse vortex flow configuration for their MW plasma at a pressure of 100 mbar. They observed that the strong convective core-periphery transport characterising the reverse vortex flow configuration significantly reduces the formation and growth of solid carbon precursors, and inhibits their deposition at the reactor walls. Finally, Jasiński *et al.*<sup>22</sup> were able to reach a 2 : 1 CH<sub>4</sub>/CO<sub>2</sub> ratio in their MW plasma, possibly due to the high gas flow rate of 150 L min<sup>−1</sup>, stimulating the removal of carbon particles from the discharge.

In addition to the advantage of circumventing discharge instability by injecting CH<sub>4</sub> post-plasma, we assume that the tangential flow injection at the end of the discharge will create a more turbulent stream, improving the mixing between the plasma stream and the surrounding stream, thereby heating the surrounding stream and enabling conversion of the gas that did not pass through the plasma, which was proven to drive the overall conversion in ref. 16. Lastly, the authors of ref. 17 claim that the main advantage of their method is the increase in energy consumption selectivity, in which the energy injected through the plasma decomposes only CO<sub>2</sub> rather than CH<sub>4</sub>, yielding higher CO<sub>2</sub> conversion and higher syngas energy conversion efficiency (ECE) compared to other methods.

Rephrasing the hypothesis of ref. 17: when pure CO<sub>2</sub> is injected into the plasma, all plasma power goes into heating and dissociation of CO<sub>2</sub>. In contrast, when a mixture of CO<sub>2</sub>/CH<sub>4</sub> is fed to the plasma, some plasma power is absorbed by CH<sub>4</sub>, which is more easily dissociated, and less power goes to CO<sub>2</sub>, resulting in less CO<sub>2</sub> dissociation. Since CH<sub>4</sub> dissociates at lower temperatures due to the weaker C–H bonds than C=O bonds, it may be better to inject it post-plasma, as the CH<sub>4</sub> reforming can proceed in the reforming reactor with residual heat, yielding the most energy-efficient process.

In this work, we aim to examine whether directing all the energy into CO<sub>2</sub> by injecting CH<sub>4</sub> post-plasma indeed leads to better total conversion, syngas selectivity and ECE. We focus on a CO<sub>2</sub>/CH<sub>4</sub> molar ratio of 1, excluding higher ratios that would yield higher syngas ratios, to maintain a manageable scope for this study. To address this research question, we have developed a 0D chemical kinetics model that can interpret the post-plasma gas conversion process occurring when the effluent of a thermal plasma mixes with a gas stream injected post-plasma. We first validate our model by reprodu-

cing the experimental results of ref. 17. Subsequently, we conduct conceptual kinetic simulations to explore the potential benefits of selectively injecting all the plasma energy into CO<sub>2</sub>, by examining the total conversion, syngas selectivity and ECE.

## 2. Model description

To gain insight in the experimental results of ref. 17, we developed a 0D chemical kinetics model in the framework of the Chemical Reaction Engineering module of COMSOL Multiphysics.<sup>23</sup> The model solves the 0D mass balance equations for a batch reactor, given by:

$$\frac{d(c_i V)}{dt} = R_i V \quad (1)$$

where  $c_i$  is the species molar concentration,  $V$  denotes the simulation volume and  $R_i$  is the species rate expression resulting from chemical reactions. We adopt the GRI-Mech 3.0 reaction mechanism<sup>24</sup> to describe the kinetics of the DRM chemistry, as was also done in ref. 16. This chemistry contains 53 different species and 325 different reactions. However, given that the DRM process does not consider any nitrogen-containing species, we reduced the reaction mechanism to include only 34 species, as detailed in Table 1, and 218 reactions, by eliminating all nitrogen-containing species.

The reactor volume is adjusted to keep a constant pressure, balancing variations in temperature and number density:

$$\frac{dV}{dt} = \frac{V}{T} \frac{dT}{dt} + \frac{RT}{p} V \sum_i R_i \quad (2)$$

with  $R$  the ideal gas constant,  $T$  the gas temperature and  $p$  the pressure in the reactor (1 atm). We note that by considering a batch reactor, we do not capture how the gas moves along the reactor, as is done in a plug-flow model. However, our focus is primarily on determining the final composition of the product flow rather than tracking the spatial distribution of gases within the reactor.

The initial composition within the simulation represents the CO<sub>2</sub> plasma composition at the end of the discharge, *i.e.* right before CH<sub>4</sub> injection, which accounts only for a limited fraction of the total CO<sub>2</sub> flow. Indeed, since a MW plasma is strongly contracted at atmospheric pressure,<sup>25</sup> only a limited fraction of the CO<sub>2</sub> passes through the plasma and is heated to high plasma temperatures. For simplicity, we approximate the CO<sub>2</sub> discharge as a plasma stream with a constant plasma temperature ( $T_p$ ) and a surrounding stream that is preheated

to 800 K ( $T_{pre}$ ), as in the experiments of ref. 17. While the authors of ref. 17 measured the temperature in the reforming reactor, they did not determine the temperature of the CO<sub>2</sub> plasma itself. However, D'Isa *et al.*<sup>25</sup> performed temperature measurements of their CO<sub>2</sub> plasma under similar conditions (MW plasma trapped in vortex flow) and found that at atmospheric pressure, the plasma temperature is approximately 6000 K, regardless of the specific energy input (SEI), with the plasma volume increasing with SEI.<sup>25</sup> Hence, for all SEI values considered in this work, we assume  $T_p$  equal to 6000 K. Based on the SEI (J mol<sup>-1</sup>), which is an input parameter to our model, we calculate the ratio of the molar flow rate of the plasma stream to the molar flow rate of the surrounding stream, determining the molar ratio of hot CO<sub>2</sub> plasma ( $T_p$ ) to the surrounding CO<sub>2</sub> gas ( $T_{pre}$ ), according to:

$$SEI = x_p(n_{eq}H_{CO_2,eq}(T_p) - H_{CO_2}(300\text{ K})) + (1 - x_p)(H_{CO_2}(T_{pre}) - H_{CO_2}(300\text{ K})) \quad (3)$$

In eqn (3),  $x_p$  represents the molar fraction of hot CO<sub>2</sub> plasma, *i.e.* the ratio of the molar flow rate of the plasma stream to the total CO<sub>2</sub> flow rate, and  $H_{CO_2}$  is the enthalpy of pure CO<sub>2</sub> gas (J mol<sup>-1</sup>). At the plasma temperature of 6000 K, CO<sub>2</sub> is nearly completely dissociated and in chemical equilibrium. Therefore, the initial composition of the simulation, representing the CO<sub>2</sub> plasma zone, corresponds to the chemical equilibrium composition of CO<sub>2</sub> at 6000 K (*ca.* 50% O, 49% CO and 1% C (ref. 26)). In eqn (3),  $H_{CO_2,eq}$  represents the enthalpy of the CO<sub>2</sub> equilibrium mixture (J mol<sup>-1</sup>), and  $n_{eq}$  is a factor that accounts for the increase in number of particles of the dissociated chemical equilibrium mixture.

When CH<sub>4</sub> is injected post-plasma, CH<sub>4</sub> (300 K) and CO<sub>2</sub> ( $T_{pre}$ ) will mix with the hot CO<sub>2</sub> plasma stream ( $T_p$ ) in the reforming reactor. We model the mixing of the gases by adding CH<sub>4</sub> (300 K) and CO<sub>2</sub> ( $T_{pre}$ ) to the simulation volume, containing only the hot CO<sub>2</sub> equilibrium mixture ( $T_p$ ) at the start of the simulation. Thus, we consider diffusive mass transfer from the surrounding CH<sub>4</sub> and CO<sub>2</sub> ( $T_{pre}$ ) stream to the inner hot gas stream, but we neglect diffusion from the latter to the surrounding stream. In this way, we can describe the system in a single kinetic simulation, assuming that conversion does not occur in the cold surrounding stream due to slow reaction kinetics.

We introduce a mixing rate  $R_m$  (mol s<sup>-1</sup>) that determines the rate at which the gases mix in the reforming reactor, *i.e.* how fast CH<sub>4</sub> and CO<sub>2</sub> ( $T_{pre}$ ) are added to the simulation. Therefore, the mixing rate is a source term ( $R_m/V_r$ ) in the species rate expression (*cf.*  $R_i$  in eqn (1)), representing the diffusive mass transfer from the surrounding stream to the

**Table 1** List of species included in the kinetic scheme<sup>24</sup>

H <sub>2</sub>	H	O	O <sub>2</sub>	OH	H <sub>2</sub> O	HO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>
C	CH	CH <sub>2</sub>	CH <sub>2</sub> (s)	CH <sub>3</sub>	CH <sub>4</sub>	CO	CO <sub>2</sub>
HCO	CH <sub>2</sub> O	CH <sub>2</sub> OH	CH <sub>3</sub> O	CH <sub>3</sub> OH	C <sub>2</sub> H	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>3</sub>
C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>6</sub>	HCCO	CH <sub>2</sub> CO	HCCOH	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>8</sub>
CH <sub>2</sub> CHO	CH <sub>3</sub> CHO						

simulation volume. Approximating the cold gas in the surrounding stream as gas contained in a volume with plane-parallel geometry and length  $R$  (radius of the reforming reactor), where the density is 0 at boundary  $x = R$ , the lowest-order diffusion solution yields an exponential decay of the average gas density:<sup>27</sup>

$$n(t) = n_0 e^{-t/\tau_0} \quad (4)$$

$$\tau_0 = \left(\frac{R}{\pi}\right)^2 \frac{1}{D} \quad (5)$$

where  $n$  is the average gas density and  $D$  is the diffusion coefficient. Therefore, we choose an exponential decay for the mixing rate  $R_m$  (mol s<sup>-1</sup>):

$$R_m = -\frac{d(n(t))}{dt} = \frac{n_{\text{tot}}}{\tau_{\text{mix}}} e^{-t/\tau_{\text{mix}}} \quad (6)$$

where  $n_{\text{tot}}$  is the total amount of gas (mol) that is added, and we name  $\tau_{\text{mix}} = \left(\frac{R}{\pi}\right)^2 \frac{1}{D}$  the characteristic mixing time. Note that the expression above integrates to  $n_{\text{tot}}$  for  $t \rightarrow \infty$ . The molar ratio of CH<sub>4</sub> to CO<sub>2</sub> ( $T_p$ ) and of CO<sub>2</sub> ( $T_{\text{pre}}$ ) to CO<sub>2</sub> ( $T_p$ ), determining  $n_{\text{tot}}$  for CH<sub>4</sub> and CO<sub>2</sub>, is equal to  $\frac{1-x_p}{x_p}$  and  $\frac{1}{x_p}$ , respectively.

The temperature of the gas mixture is calculated in the heat-balance equation:

$$\begin{aligned} \rho C_p \frac{dT}{dt} = & -\frac{R_m^{\text{CO}_2}}{V_r} (H_{\text{CO}_2}(T) - H_{\text{CO}_2}(T_{\text{pre}})) \\ & -\frac{R_m^{\text{CH}_4}}{V_r} (H_{\text{CH}_4}(T) - H_{\text{CH}_4}(300 \text{ K})) \\ & -\frac{8k(T - T_{\text{pre}})}{R_p^2} + Q_R \end{aligned} \quad (7)$$

where  $\rho$  is the gas density,  $C_p$  denotes the heat capacity,  $k$  is the thermal conductivity of the mixture,  $R_p$  is the plasma radius and  $Q_R$  is the total heat absorbed/released in chemical reactions. The first two terms on the right-hand side of the equation represent the cooling of the mixture due to mixing with CO<sub>2</sub> ( $T_{\text{pre}}$ ) and CH<sub>4</sub> (300 K), accounting for the energy needed to heat up the incoming gas to the current temperature  $T$  in the simulation volume. The third term on the right-hand side illustrates the conductive losses of the hot inner gas stream (*i.e.*, the gas mixture within the simulation volume) to the surrounding stream. Since we do not increase the temperature of the incoming CO<sub>2</sub> ( $T_{\text{pre}}$ ) and CH<sub>4</sub> (300 K), we assume that the heat gained by the surrounding stream due to the conductive losses of the inner hot gas stream is balanced by heat dissipation at the wall. The plasma radius is calculated assuming that the ratio of the cross-section of the plasma stream to the cross-section of the reactor equals the molar fraction of hot CO<sub>2</sub> plasma, and thus  $R_p = \sqrt{x_p} R$ .

The above model description applies to the experiments of ref. 17, used for our model validation. However, the model used later in this paper, for studying the performance of CO<sub>2</sub>

plasma with post-plasma CH<sub>4</sub> injection and comparing it with classical plasma-based DRM, is slightly different, as will be explained in section 4 below.

To evaluate the performance of the DRM process, a wide variety of performance metrics exists in literature.<sup>28</sup> In this work, we will focus on the CO<sub>2</sub> and CH<sub>4</sub> conversion ( $\chi^{\text{CO}_2}$ ,  $\chi^{\text{CH}_4}$ ), the CO and H<sub>2</sub> selectivity ( $S^{\text{CO}}$ ,  $S^{\text{H}_2}$ ), the total conversion  $\chi^{\text{tot}}$  and the energy conversion efficiency (ECE)  $\eta$ , to assess the potential of post-plasma CH<sub>4</sub> injection. Note that the ECE is also called simply “energy efficiency”, but we prefer the term ECE, because the expression accounts for the energy captured in CH<sub>4</sub> (high enthalpy) and evaluates how efficiently this energy, along with the applied power, is converted into the energy captured by syngas.

These performance metrics are calculated as follows:

$$\chi^{\text{tot}} = x_{\text{CO}_2} \chi^{\text{CO}_2} + x_{\text{CH}_4} \chi^{\text{CH}_4} \quad (8)$$

$$\chi^{\text{CO}_2} = \frac{[\text{CO}_2]_0 - (V_f/V_0)[\text{CO}_2]_f}{[\text{CO}_2]_0}, \quad (9)$$

$$\chi^{\text{CH}_4} = \frac{[\text{CH}_4]_0 - (V_f/V_0)[\text{CH}_4]_f}{[\text{CH}_4]_0}$$

$$S^{\text{CO}} = \frac{(V_f/V_0)[\text{CO}]_f}{([\text{CH}_4]_0 - (V_f/V_0)[\text{CH}_4]_f) + ([\text{CO}_2]_0 - (V_f/V_0)[\text{CO}_2]_f)} \quad (10)$$

$$S^{\text{H}_2} = \frac{(V_f/V_0)[\text{H}_2]_f}{2([\text{CH}_4]_0 - (V_f/V_0)[\text{CH}_4]_f)} \quad (11)$$

$$\eta = \frac{(V_f/V_0)[\text{CO}]_f \cdot \text{LHV}_{\text{CO}} + (V_f/V_0)[\text{H}_2]_f \cdot \text{LHV}_{\text{H}_2}}{\text{SEI} + [\text{CH}_4]_0 \cdot \text{LHV}_{\text{CH}_4}} \quad (12)$$

where  $x_{\text{CO}_2}$  and  $x_{\text{CH}_4}$  are the molar fraction of CO<sub>2</sub> and CH<sub>4</sub>, respectively, both equal to 0.5 since we consider a CH<sub>4</sub>/CO<sub>2</sub> molar ratio of 1,  $[\text{CO}_2]_0$  denotes the initial molar concentration of CO<sub>2</sub> plus  $n_{\text{tot}}^{\text{CO}_2}/V_0$ , where  $n_{\text{tot}}^{\text{CO}_2}$  is the number of moles of CO<sub>2</sub> added post-plasma (*cf.* eqn (6)), and  $[\text{CO}_2]_f$  denotes the final molar concentration of CO<sub>2</sub>, respectively. Similar notations apply to the other species. Similarly,  $V_0$  and  $V_f$  represent the volume at the start and end of the simulation, respectively. They are required in the equations to account for gas expansion upon reaction, because more molecules are formed after than before the reaction,<sup>28</sup> and because of a change in temperature upon reaction. Lastly,  $\text{LHV}_{\text{CO}}$ ,  $\text{LHV}_{\text{H}_2}$  and  $\text{LHV}_{\text{CH}_4}$  are the low heating values of CO, H<sub>2</sub> and CH<sub>4</sub>, respectively.

### 3. Model validation

We first model the experimental conditions of ref. 17 to validate our model, and we direct interested readers to consult<sup>17</sup> for a comprehensive description of the reactor configuration. Specifically, we try to reproduce the measured CO<sub>2</sub> conversion  $\chi^{\text{CO}_2}$  and CH<sub>4</sub> conversion  $\chi^{\text{CH}_4}$ , as well as CO selectivity  $S^{\text{CO}}$  and H<sub>2</sub> selectivity  $S^{\text{H}_2}$ , across the SEI range of 122–245 kJ mol<sup>-1</sup>. In order to compare the performance of the current process to other DRM processes, the SEI is evaluated as the plasma power

over the total gas flow rate, *i.e.* 30 slm CO<sub>2</sub> flow rate plus 30 slm CH<sub>4</sub> flow rate, as used in ref. 17. For SEI = 122 kJ mol<sup>-1</sup>, we set the characteristic mixing time  $\tau_{\text{mix}}$  equal to 0.01 s. This value corresponds to an effective diffusivity of  $1.2 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$ , which lies within the same order of magnitude as the value of  $8\text{--}16 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$  reported by Sun *et al.*,<sup>16</sup> when modelling the mixing of the plasma stream with the surrounding stream in the post-plasma region of their DRM experiments with a similar MW setup. Since the average gas temperature increases with rising SEI and the diffusion constant is proportional to  $T^{3/2}$  according to gas kinetic theory, we increase  $D$  by a factor of 1.5 (hence  $\tau_{\text{mix}} = 6.67 \times 10^{-3} \text{ s}$ ) for SEI = 245 kJ mol<sup>-1</sup>, and linearly interpolate  $D$  for intermediate SEIs. This drop in characteristic mixing time allows better agreement with the experimental results of ref. 17 compared to keeping a constant value of 0.01 s for  $\tau_{\text{mix}}$  across the SEI range.

Fig. 1(a) shows the comparison between model calculations and experimental measurements for the CO<sub>2</sub> and CH<sub>4</sub> conversion as a function of SEI. The experimental  $\chi^{\text{CO}_2}$  is perfectly

captured by the model across the complete SEI range. While the  $\chi^{\text{CH}_4}$  predicted by the model also follows the experimental trend, the values slightly exceed those measured in the experiment. The greatest relative deviation occurs at the lowest SEI of 122 kJ mol<sup>-1</sup>, where  $\chi^{\text{CH}_4} = 39\%$  predicted by the model compared to  $\chi^{\text{CH}_4} = 32\%$  in the experiment. Considering the model's simplicity and general experimental uncertainties, we find the agreement between model and experiment regarding  $\chi^{\text{CO}_2}$  and  $\chi^{\text{CH}_4}$  satisfactory.

The CO and H<sub>2</sub> selectivity predicted by the model and measured in the experiment are shown in Fig. 1(b). The CO selectivity agrees well between model and experiment, with a maximal deviation of 3.5% at SEI = 245 kJ mol<sup>-1</sup>. In contrast,  $S^{\text{H}_2}$  predicted by the model is significantly lower (*ca.* 15%) than the values obtained in the experiment. This discrepancy is primarily due to the substantial generation of H<sub>2</sub>O in the model calculations compared to the lower quantities observed experimentally. For instance, at SEI = 245 kJ mol<sup>-1</sup>, the model predicts an H<sub>2</sub>O molar fraction of 4.5%, whereas H<sub>2</sub>O was reported to account for less than 0.1% of the total product mixture in the experimental setup.

Although the absolute values for  $S^{\text{H}_2}$  predicted by the model are too low, the rising trend of  $S^{\text{H}_2}$  with increasing SEI in the experiment (75% to 87%) is also captured by the model (88% to 99%). This trend can be attributed to the higher temperatures reached at higher SEI values ( $T > 2000 \text{ K}$ ), leading to faster reaction kinetics for the conversion of H<sub>2</sub>O. Indeed, H<sub>2</sub>O is thermodynamically unfavoured above temperatures of 1200 K.<sup>29</sup> Consequently, at higher SEI levels, more H<sub>2</sub>O will be converted to H<sub>2</sub> within the limited residence time of the reactor, yielding a higher H<sub>2</sub> selectivity.

Using the GRI-Mech 3.0 mechanism,<sup>24</sup> we were unable to reproduce the experimental H<sub>2</sub> selectivity within the existing framework of our model. This suggests that either the GRI-Mech 3.0 mechanism may not be ideally suited for our specific conditions, or that multi-dimensional effects play a role in this setup, which are not adequately accounted for in our 0D model. Therefore, we implemented the thermal chemistry set from ref. 30 to examine whether a higher H<sub>2</sub> selectivity could be achieved using a different DRM reaction mechanism. However, the results for  $\chi^{\text{CO}_2}$ ,  $\chi^{\text{CH}_4}$ ,  $S^{\text{CO}}$  and  $S^{\text{H}_2}$  are consistent within 4% between both chemistry sets, suggesting that the discrepancy between model and experiment for  $S^{\text{H}_2}$  might not be due to the gas-phase chemistry used in our model.

Note that Cho *et al.*<sup>17</sup> calculated the mass balance for H and C to determine the fraction of H<sub>2</sub>O and solid C, respectively, which could not be measured in the GC. However, considering the H<sub>2</sub>O concentration derived in this manner, they found that O atoms were missing in the O mass balance.<sup>31</sup> Therefore, they hypothesised that the missing O might be due to oxidation reactions of the stainless steel reactor walls at high temperatures.<sup>31</sup> Unfortunately, our global model cannot account for these surface processes. If oxidation of the reactor walls indeed absorbs a significant amount of O atoms, it could explain the discrepancy in H<sub>2</sub> selectivity between our model and the experiment. However, we cannot rule out the second

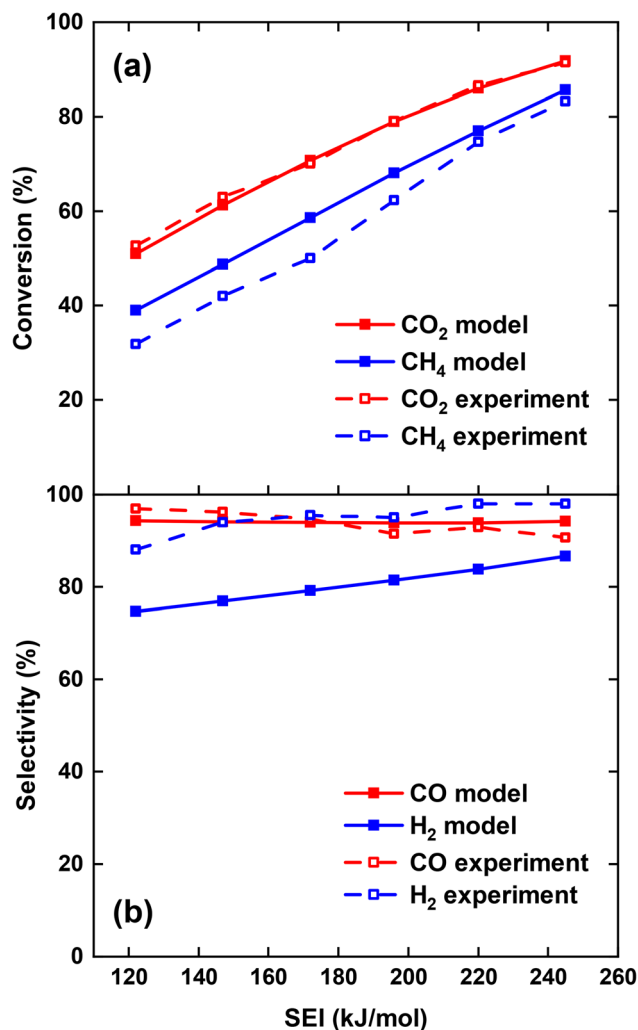


Fig. 1 Comparison of CO<sub>2</sub> and CH<sub>4</sub> conversion (a) and CO and H<sub>2</sub> selectivity (b) between model and experiment,<sup>17</sup> as a function of the SEI.



option, that a substantial amount of  $\text{H}_2\text{O}$  is formed in the experiment, as predicted by our model, which was not detected in ref. 17. In fact, this would also explain the missing O atoms in the O mass balance. Indeed, other DRM experiments in literature do report  $\text{H}_2\text{O}$  formation as major by-product (e.g., ref. 7, 20 and 32–34). Nevertheless, despite the discrepancy in  $\text{H}_2$  selectivity, our model predicts the experimental trend, and we assume that we correctly capture the  $\text{H}_2\text{O}$  formation in the DRM process when oxidation of the reactor walls is not important.

## 4. Can post-plasma $\text{CH}_4$ injection improve the DRM performance?

After obtaining reasonable agreement with experiment,<sup>17</sup> we now evaluate whether injecting all plasma energy into  $\text{CO}_2$ , with post-plasma  $\text{CH}_4$  injection, effectively leads to improved  $\text{CO}_2$  conversion and ECE.

### 4.1. DRM equilibrium calculation

Before evaluating the performance of post-plasma  $\text{CH}_4$  injection, it is useful to first calculate the DRM equilibrium, because the latter allows us to determine the maximum ECE achievable for thermal conversion, under the assumption that we do not recover the residual heat. Indeed, by comparing the performance of a specific DRM process with this thermal limit, we can assess the potential for further process improvements. Fig. 2(a) illustrates the molar fractions of the dominant species for the thermodynamic equilibrium of a  $\text{CO}_2/\text{CH}_4$  mixture with a molar ratio of 1, across the temperature range 900–3500 K. The total conversion ( $\chi^{\text{tot}}$ ), hydrogen selectivity ( $S^{\text{H}_2}$ ) and ECE ( $\eta$ ) are plotted in Fig. 2(b) across the same temperature range. The equilibrium was determined by running the GRI-Mech 3.0 mechanism until the concentrations of all dominant species remained constant for an extended duration ( $10^{15}$  s). Since all reverse processes are calculated from the equilibrium constant, this ensures the correct thermodynamic equilibrium composition. The time required to reach equilibrium (right y-axis) is determined as the point in time when the concentrations of all dominant species deviate less than 0.001% from their final value, i.e., the final timestep of the simulation where all concentrations remained constant for an extended duration.

It is clear from Fig. 2(a) that the equilibrium largely shifts towards CO and  $\text{H}_2$ , which exhibit molar fractions around 50% in most of the temperature range, while  $\text{CO}_2$  and  $\text{CH}_4$  are only present (with molar fractions of 10 and 15%) around 900 K. Note however, that the time to reach this equilibrium is very long in the lower temperature range (cf. Fig. 2(b)), so in practice, at realistic residence times, there will still be considerable amounts of  $\text{CO}_2$  and  $\text{CH}_4$  in the mixture. At 900 K, there is also about 5%  $\text{H}_2\text{O}$  present, while above 2400 K, the H molar fraction starts to rise, upon dissociation of  $\text{H}_2$ , as follows indeed from the molar fraction of the latter.

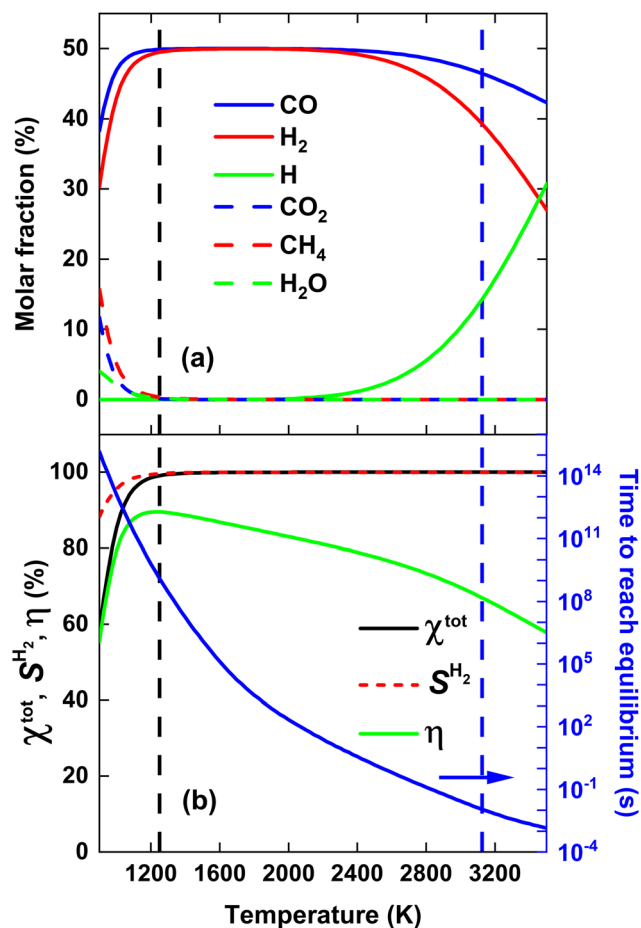


Fig. 2 Thermodynamic equilibrium calculations of a  $\text{CO}_2/\text{CH}_4$  mixture with a molar ratio of 1. (a) Molar fractions of the dominant species, and (b) total conversion  $\chi^{\text{tot}}$ , hydrogen selectivity  $S^{\text{H}_2}$  and ECE  $\eta$  (left y-axis), as well as the time needed to reach equilibrium (right y-axis). The vertical black and blue dashed line indicate the temperature at which 99% syngas yield is reached, and the temperature at which equilibrium is reached within 10 ms, respectively.

Fig. 2(b) illustrates that both  $\chi^{\text{tot}}$  and  $S^{\text{H}_2} > 99\%$  for temperatures above 1200 K.  $S^{\text{CO}}$  is not plotted, as it is close to 100% across the entire temperature range of 900–3500 K. Hence, the syngas yield is determined by  $S^{\text{H}_2}$ . Notably, the  $\text{CO}_2/\text{CH}_4$  mixture yields 99% syngas already at an average gas temperature of 1250 K (indicated by the black dashed line in Fig. 2), corresponding to  $\eta = 89.5\%$ . However, as mentioned above, reaching equilibrium at these temperatures takes more than  $10^9$  s (see right y-axis in Fig. 2(b)). To reach equilibrium within a more realistic reactor residence time of 10 ms, an average gas temperature of 3125 K is required (indicated by the vertical blue dashed line in Fig. 2), corresponding to  $\eta = 67\%$ , close to  $\eta = 71.3\%$  reported by Sun *et al.*,<sup>16</sup> where  $\text{CH}_4$  and  $\text{CO}_2$  were injected directly into the plasma.

The slow equilibrium attainment at lower temperatures is attributed to the slow  $\text{CO}_2$  dissociation process at these temperatures, which requires breaking the highly stable  $\text{C}=\text{O}$  bond.<sup>30</sup> Hence, one way to potentially lower the SEI required

for reaching a given syngas yield is by accelerating the CO<sub>2</sub> dissociation process. This could potentially be achieved by injecting all the plasma energy into CO<sub>2</sub>, while reforming CH<sub>4</sub> at lower temperatures with residual heat, effectively treating more CO<sub>2</sub> at higher temperatures for the same SEI compared to directly heating the complete CO<sub>2</sub>/CH<sub>4</sub> mixture in the plasma, as we will study in detail in the next section.

#### 4.2. Effect of post-plasma CH<sub>4</sub> injection

To verify whether directing all the plasma energy into CO<sub>2</sub> can improve the syngas yield and energy efficiency, we compare both strategies, *i.e.* (i) injecting only CO<sub>2</sub> inside the plasma while injecting CH<sub>4</sub> post-plasma, *vs.* (ii) injecting both CH<sub>4</sub> and CO<sub>2</sub> inside the plasma. To conduct this comparison, we perform two conceptual kinetic simulations, assuming uniform plasma heating and neglecting any heat losses at the wall. As it is a conceptual study, this simplification aims to ensure transparent simulation results and general modeling insights, by not focusing on plasma contraction and heat losses specific to the experimental setup of a certain plasma reactor. We note that by considering uniform plasma heating, we are effectively modeling a global diffuse plasma rather than a contracted plasma.

This modeling approach differs from the one detailed in section 2 that was used to simulate the experiments of ref. 17, as explained in the paragraph below. To ensure the most representative comparison, in scenario (ii), we inject half of the 1 : 1 CO<sub>2</sub>/CH<sub>4</sub> mixture into the plasma and the other half of the 1 : 1 CO<sub>2</sub>/CH<sub>4</sub> mixture post-plasma. In this way, the SEI within the plasma, *i.e.* the ratio of plasma power over the discharge gas flow rate, is the same for both strategies.

At the start of the simulation, the simulation volume contains the discharge gas at room temperature, which is pure CO<sub>2</sub> for case (i) and 50% of the 1 : 1 CO<sub>2</sub>/CH<sub>4</sub> mixture for case (ii). Next, the discharge gas is heated over a heating period  $t_{\text{heat}}$  of 5 ms, as this is a typical gas residence time in atmospheric pressure MW plasmas.<sup>35</sup> The power is calculated from the applied SEI (kJ mol<sup>-1</sup>):

$$P = \frac{\text{SEI} \cdot n_0 \cdot V_0}{t_{\text{heat}}} \quad (13)$$

where  $P$  (kW) is the plasma power,  $n_0$  is the initial molar density of the discharge gas and  $V_0$  is the initial volume. For simplicity, we neglect any heat losses within the discharge. While this idealized case is a reasonable approximation for vortex stabilized MW plasma,<sup>36</sup> other discharge set-ups may experience significant heat losses to electrodes and walls. We note that these losses are likely higher for the CO<sub>2</sub>/CH<sub>4</sub> plasma compared to the CO<sub>2</sub> plasma due to the higher thermal conductivity of CH<sub>4</sub>. This could potentially reduce the energy absorbed by the CO<sub>2</sub>/CH<sub>4</sub> plasma relative to the CO<sub>2</sub> plasma, thereby decreasing the syngas yield (*cf.* Fig. 5).

After the 5 ms heating period, the power is set to zero, and the gas injected post-plasma, *i.e.* pure CH<sub>4</sub> for case (i) and the other half of the 1 : 1 CO<sub>2</sub>/CH<sub>4</sub> mixture for case (ii), is added to the simulation, representing the mixing with the gas injected post-plasma (as explained in section 2). We set the character-

istic mixing time equal to 2.71 ms (*cf.* eqn (4) and (5)). This corresponds to a total mixing time of 10 ms, which is a reasonable estimate for the reaction time in a reforming reactor based, on our modeling results for the conditions described in ref. 17. After the total mixing time of 10 ms, 99% of the gas has been added to the simulation. Subsequently, the gas mixture is immediately quenched to 300 K, simulating its exit from the reactor. For simplicity, we assume instant quenching since our calculations indicate that the quenching rate has a negligible impact on the syngas yield. Thus, the heat-balance equation is formulated as follows:

$$t < 5 \text{ ms} : \rho C_p \frac{dT}{dt} = P + Q_R \quad (14)$$

$$5 \text{ ms} < t < 15 \text{ ms} : \rho C_p \frac{dT}{dt} = -\frac{R_m^{\text{CO}_2/\text{CH}_4}}{V} (\Delta H_{\text{CO}_2/\text{CH}_4}) + Q_R \quad (15)$$

$$t > 15 \text{ ms} : T = 300 \text{ K} \quad (16)$$

$Q_R$  is the total heat absorbed/released in chemical reactions, as explained in section 2. In eqn (15), the first term on the right-hand-side represents the cooling due to the mixing with the gas (300 K) injected at the end of the discharge. We note that the simulation results are relatively insensitive to the chosen value of the total mixing time (10 ms). For instance, dividing or multiplying the total mixing time by a factor of 2 results in only minor changes: a decrease in  $\chi^{\text{tot}}$  by approximately 1% and an increase in  $\chi^{\text{tot}}$  by approximately 2%, respectively, for both strategies.

Fig. 3 illustrates the calculated temperature profile over time for both strategies, considering an SEI of 200 kJ mol<sup>-1</sup>.

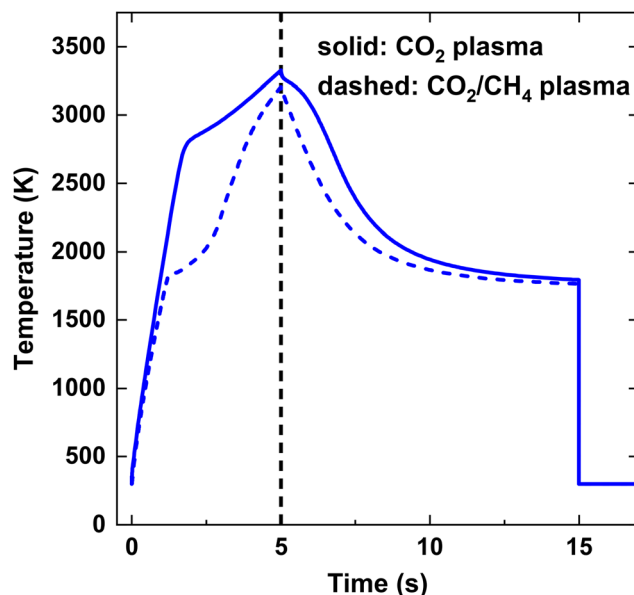


Fig. 3 Gas temperature as a function of time for SEI = 200 kJ mol<sup>-1</sup>. The black vertical dashed line at  $t = 5$  ms indicates the onset of post-plasma injection.

Initially, up to  $t = 5$  ms, the temperature rises due to the applied power, reaching its maximum temperature of  $T = 3325$  K for the  $\text{CO}_2$  plasma and  $T = 3200$  K for the  $\text{CO}_2/\text{CH}_4$  plasma. Subsequently, the temperature declines due to mixing with the cold gas injected at the end of the discharge, as illustrated in Fig. 3. At  $t = 15$  ms, the temperature immediately drops to 300 K, quenching the product mixture. In case of the  $\text{CO}_2$  plasma (i), the temperature shows a relatively linear increase up to 2800 K, beyond which the endothermic  $\text{CO}_2$  dissociation starts contributing significantly, as seen by the sudden drop in the slope of the temperature profile. Conversely, in case of the  $\text{CO}_2/\text{CH}_4$  plasma (ii), the temperature profile exhibits a kink at a lower temperature of 1800 K since the dissociation of  $\text{CH}_4$  has a much lower reaction barrier, becoming significant at much lower temperatures.

The maximum gas temperature  $T_{\text{max}}$  at  $t = 5$  ms is plotted in Fig. 4 for both strategies, across the SEI range of 80–300  $\text{kJ mol}^{-1}$ . We note that by assuming uniform gas heating, the global temperature is lower than the temperature of the hot  $\text{CO}_2$  plasma filament (6000 K) used in modeling the experimental conditions of ref. 17, within a similar SEI range, since we are no longer modeling a contracted plasma. In addition to the maximum temperature, the fractional energy consumption  $E_c$  (%) is plotted on the right y-axis in Fig. 4, defined as the fraction of plasma power absorbed in chemical reactions:

$$E_c = \int_0^{t_{\text{heat}}=5\text{ ms}} \frac{Q_R}{P} dt \cdot 100\% \quad (17)$$

At lower SEI values, the  $\text{CO}_2/\text{CH}_4$  plasma reaches significantly lower maximum temperatures compared to the  $\text{CO}_2$  plasma (see Fig. 4). For instance, at  $\text{SEI} = 100 \text{ kJ mol}^{-1}$ ,  $T_{\text{max}} =$

2730 K for the  $\text{CO}_2$  plasma and  $T_{\text{max}} = 1980$  K for the  $\text{CO}_2/\text{CH}_4$  plasma. This difference can be attributed to two factors. First, the  $\text{CO}_2/\text{CH}_4$  mixture has a higher average heat capacity, due to the higher heat capacity of  $\text{CH}_4$  compared to  $\text{CO}_2$ . Second, the energy absorbed in endothermic processes is higher for the  $\text{CO}_2/\text{CH}_4$  mixture. Indeed,  $\text{CH}_4$  is efficiently dissociated at temperatures below 2000 K, and the created H atoms accelerate the  $\text{CO}_2$  dissociation process, since the reaction  $\text{CO}_2 + \text{H} \rightleftharpoons \text{CO} + \text{OH}$  has a significantly lower energy barrier than the reaction  $\text{CO}_2 + \text{M} \rightleftharpoons \text{CO} + \text{O} + \text{M}$ , *i.e.*  $E_a = 105 \text{ kJ mol}^{-1}$  vs.  $E_a = 542 \text{ kJ mol}^{-1}$ ,<sup>24</sup> respectively, resulting in relatively high  $\text{CO}_2$  and  $\text{CH}_4$  conversion even at the lower SEI values. For example, at the end of the plasma, before post-plasma injection, at  $\text{SEI} = 100 \text{ kJ mol}^{-1}$ ,  $\chi^{\text{CO}_2} = 53\%$  and  $\chi^{\text{CH}_4} = 87\%$  for the  $\text{CO}_2/\text{CH}_4$  plasma (conversion of reactants relative to the amount of discharge gas) compared to  $\chi^{\text{CO}_2} = 20\%$  for the  $\text{CO}_2$  plasma. This is also clear from the (fractional) energy consumption, which is higher for the  $\text{CO}_2/\text{CH}_4$  plasma than for the  $\text{CO}_2$  plasma (see blue curves in Fig. 4).

Notably, at higher SEI values ( $\text{SEI} > 140 \text{ kJ mol}^{-1}$ ), the energy consumption becomes higher for the  $\text{CO}_2$  plasma compared to the  $\text{CO}_2/\text{CH}_4$  plasma (see again blue curves in Fig. 4). The reason is that  $\text{CO}_2$  dissociation is more efficient at these elevated temperatures ( $T > 3000$  K), allowing more energy to be stored in the strongly endothermic  $\text{CO}_2$  dissociation process. Indeed,  $\Delta H_{298\text{ K}} = 283 \text{ kJ mol}^{-1}$  for  $\text{CO}_2 + \text{M} \rightleftharpoons \text{CO} + \text{O} + \text{M}$  compared to  $\Delta H_{298\text{ K}} = 247 \text{ kJ mol}^{-1}$  for  $\text{CO}_2 + \text{CH}_4 \rightleftharpoons 2\text{CO} + 2\text{H}_2$ , and twice the amount of  $\text{CO}_2$  is present in the pure  $\text{CO}_2$  plasma. Nonetheless,  $T_{\text{max}}$  remains higher for the  $\text{CO}_2$  plasma across the complete SEI range due to the lower heat capacity of  $\text{CO}_2$ .

To compare the performance of both strategies, the  $\text{CO}_2$  and  $\text{CH}_4$  conversion and CO and  $\text{H}_2$  selectivity are plotted in Fig. 5(a) and (b), respectively. Fig. 5(a) illustrates that at lower SEI, the  $\text{CO}_2$  conversion is significantly higher for strategy (i), *i.e.*,  $\text{CO}_2$  plasma with post-plasma  $\text{CH}_4$  injection, *e.g.* at  $\text{SEI} = 100 \text{ kJ mol}^{-1}$ ,  $\chi^{\text{CO}_2} = 56\%$  compared to  $\chi^{\text{CO}_2} = 28\%$  for strategy (ii), *i.e.*,  $\text{CO}_2/\text{CH}_4$  plasma with post-plasma  $\text{CO}_2/\text{CH}_4$  injection. This confirms our hypothesis defined above, because in strategy (i) all plasma power goes into heating and dissociation of  $\text{CO}_2$ , while in strategy (ii) some plasma power is absorbed by  $\text{CH}_4$ , resulting in less  $\text{CO}_2$  dissociation. Note, however, that the majority of the  $\text{CO}_2$  conversion for strategy (i) occurs behind the plasma upon  $\text{CH}_4$  injection, since  $\text{CO}_2$  conversion within the plasma is limited by the dissociation equilibrium of pure  $\text{CO}_2$  gas, which will be discussed in section 4.3.1 below.

Conversely, the  $\text{CH}_4$  conversion is higher for strategy (ii) at lower SEI, which is also in line with our hypothesis, because some  $\text{CH}_4$  is already converted inside the plasma, while in strategy (i) the  $\text{CH}_4$  conversion only takes place post-plasma. However, the difference between both strategies is less pronounced compared to the  $\text{CO}_2$  conversion, *e.g.* at  $\text{SEI} = 100 \text{ kJ mol}^{-1}$ ,  $\chi^{\text{CH}_4} = 44\%$  for strategy (ii) compared to  $\chi^{\text{CH}_4} = 31\%$  for strategy (i). The difference in  $\text{CO}_2$  and  $\text{CH}_4$  conversion between both strategies decreases at higher SEI, with both strategies yielding approximately the same values for  $\chi^{\text{CO}_2}$  and  $\chi^{\text{CH}_4}$  at SEI

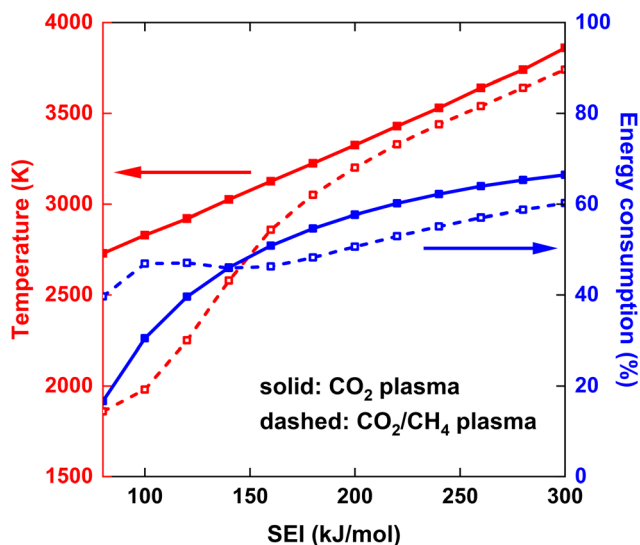


Fig. 4 Maximum gas temperature at the end of the plasma ( $t = 5$  ms) (left y-axis) and (fractional) energy consumption in the plasma (right y-axis), as a function of the SEI. The solid and dashed lines indicate the results for the  $\text{CO}_2$  plasma with post-plasma  $\text{CH}_4$  injection, and for half of the  $\text{CO}_2/\text{CH}_4$  mixture injected into the plasma and the other half of the  $\text{CO}_2/\text{CH}_4$  mixture injected post-plasma, respectively.



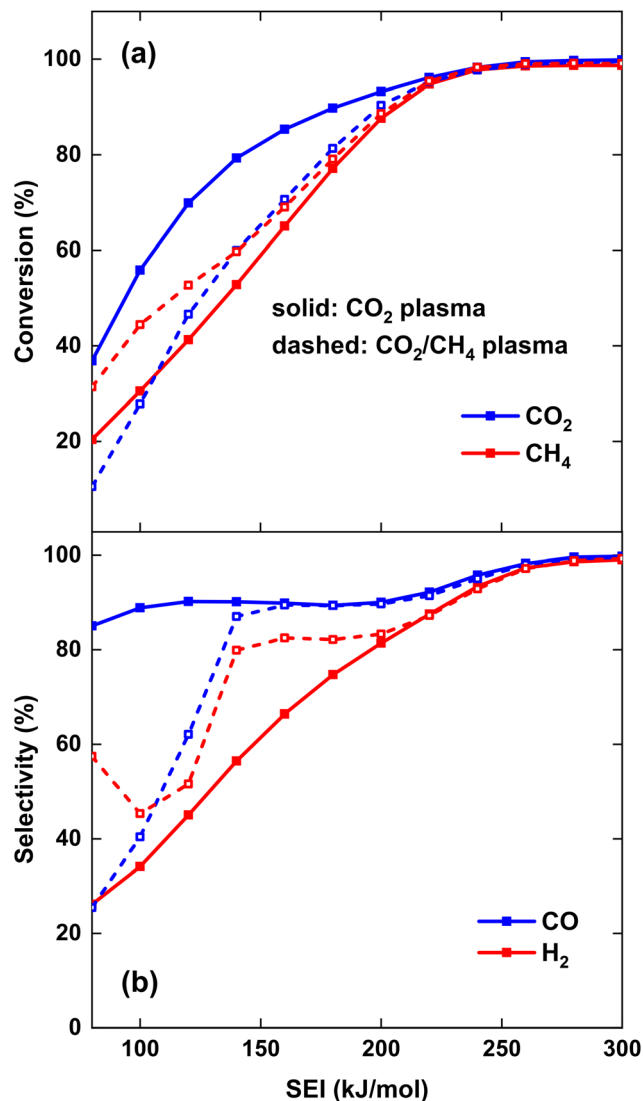


Fig. 5 CO<sub>2</sub> and CH<sub>4</sub> conversion (a) and CO and H<sub>2</sub> selectivity (b) as a function of the SEI. The solid and dashed lines indicate the results for the CO<sub>2</sub> plasma with post-plasma CH<sub>4</sub> injection, and for the CO<sub>2</sub>/CH<sub>4</sub> plasma with post-plasma CO<sub>2</sub>/CH<sub>4</sub> injection, respectively.

values above 220 kJ mol<sup>-1</sup>, reaching very good conversions above 95%. Clearly, at high enough SEI, the injection method does not matter, because the temperature behind the plasma is high enough for conversion of both CH<sub>4</sub> and the CO<sub>2</sub>/CH<sub>4</sub> mixture injected post-plasma.

As depicted in Fig. 5(b), both  $S^{\text{CO}}$  and  $S^{\text{H}_2}$  are much lower than 100% at lower SEI values (<200 kJ mol<sup>-1</sup>) for both strategies, indicating that significant amounts of byproducts are formed in the DRM process. The main byproducts are C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub>O, with molar fractions around 1–8% and 1–14%, respectively, while C<sub>2</sub>H<sub>4</sub> is the next most prominent byproduct, having a molar fraction below 0.5% across the complete SEI range. While the CO selectivity remains above 85% even at the lowest SEI values for the CO<sub>2</sub> plasma with post-plasma CH<sub>4</sub> injection (i),  $S^{\text{CO}}$  is significantly lower at the lowest SEI values

for the CO<sub>2</sub>/CH<sub>4</sub> plasma with post-plasma CO<sub>2</sub>/CH<sub>4</sub> injection (ii), e.g. at SEI = 100 kJ mol<sup>-1</sup>,  $S^{\text{CO}}$  = 40%. The low CO selectivity is due to the substantial formation of C<sub>2</sub>H<sub>2</sub> in the CO<sub>2</sub>/CH<sub>4</sub> plasma at the lowest SEI values, as will be discussed in section 4.3.1 below. However, for SEI > 140 kJ mol<sup>-1</sup>, CO<sub>2</sub> dissociation becomes more favourable in the CO<sub>2</sub>/CH<sub>4</sub> plasma, and  $S^{\text{CO}}$  is approximately the same for both strategies. At SEI values below 120 kJ mol<sup>-1</sup>, the H<sub>2</sub> selectivity is rather low ( $S^{\text{H}_2}$  < 65%) since significant amounts of H<sub>2</sub>O and C<sub>2</sub>H<sub>2</sub> are formed in both strategies. In contrast to the CO selectivity,  $S^{\text{H}_2}$  is higher for the CO<sub>2</sub>/CH<sub>4</sub> plasma compared to the CO<sub>2</sub> plasma. The reason is that a substantially larger amount of H<sub>2</sub>O is formed in the CO<sub>2</sub> plasma with post-plasma CH<sub>4</sub> injection, as will be discussed in section 4.3 below. However, similar to the conversion, both strategies yield approximately the same  $S^{\text{CO}}$  and  $S^{\text{H}_2}$  values at SEI values above 220 kJ mol<sup>-1</sup>, achieving 99% syngas selectivity at SEI = 280 kJ mol<sup>-1</sup>.

Fig. 6 shows  $\chi^{\text{tot}}$  and  $\eta$  (left y-axis), as well as the energy cost (EC) of the conversion (right y-axis) as a function of the SEI for both strategies. At lower SEI values (<200 kJ mol<sup>-1</sup>), the total conversion is slightly higher for the CO<sub>2</sub> plasma with post-plasma CH<sub>4</sub> injection (i), because the increase in CO<sub>2</sub> conversion outweighs the lower CH<sub>4</sub> conversion compared to the CO<sub>2</sub>/CH<sub>4</sub> plasma with post-plasma CO<sub>2</sub>/CH<sub>4</sub> injection (ii) (see Fig. 5(a) above).

The EC is a metric for evaluating how much energy is needed for converting the reactants, particularly with the goal of energy-efficient removal of greenhouse gases. Since it is equal to the SEI divided by  $\chi^{\text{tot}}$ , the EC will be slightly lower for the CO<sub>2</sub> plasma with post-plasma CH<sub>4</sub> injection for SEI < 200 kJ mol<sup>-1</sup>. The minimum EC of 212 kJ mol<sup>-1</sup> for strategy (i) is reached at SEI = 140 kJ mol<sup>-1</sup>, corresponding to  $\chi^{\text{tot}}$  = 66%, while a slightly higher minimum EC of 224 kJ mol<sup>-1</sup> is

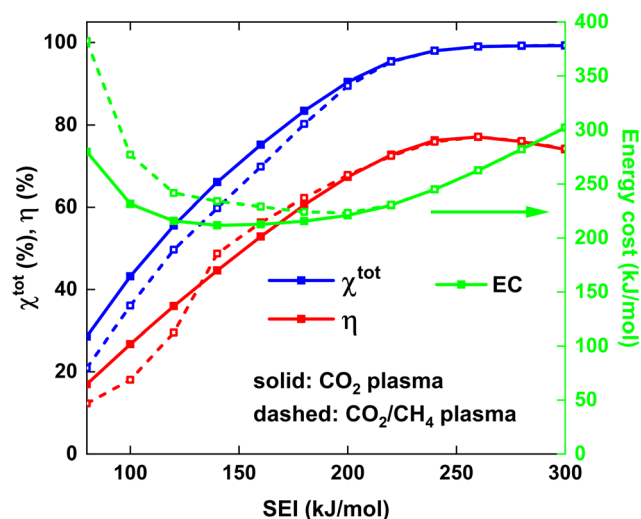


Fig. 6 Total conversion and ECE (left y-axis) and EC of conversion (right y-axis) as a function of the SEI. The solid and dashed lines indicate the results for the CO<sub>2</sub> plasma with post-plasma CH<sub>4</sub> injection, and for the CO<sub>2</sub>/CH<sub>4</sub> plasma with post-plasma CO<sub>2</sub>/CH<sub>4</sub> injection, respectively.

reached at  $\text{SEI} = 200 \text{ kJ mol}^{-1}$  for strategy (ii), corresponding to  $\chi^{\text{tot}} = 89\%$ . Although the model suggests that injecting all the energy into  $\text{CO}_2$  can slightly reduce the ECE by about 5% due to enhanced  $\text{CO}_2$  conversion at lower SEI, this reduction is not particularly significant. Furthermore, the ECE is a more critical metric for evaluating the DRM process, as it measures how efficiently syngas can be produced, which is the key objective for DRM and crucial for industrial applications.<sup>18</sup>

The trend of the ECE is more complicated. Below SEI values of  $140 \text{ kJ mol}^{-1}$ ,  $\eta$  is slightly higher for strategy (i), due to the higher values for  $\chi^{\text{CO}}$  and  $S^{\text{CO}}$ , and the product of both defines the amount of CO formed (cf. eqn (12) above). However, for  $\text{SEI} > 140 \text{ kJ mol}^{-1}$ ,  $\eta$  becomes slightly higher for strategy (ii), due to the strong increase in CO selectivity and significantly higher  $S^{\text{H}_2}$  values (cf. Fig. 5(b)), resulting in higher values for  $\eta$  despite the lower total conversion. Finally, since the  $\text{CO}_2$  and  $\text{CH}_4$  conversion and CO and  $\text{H}_2$  selectivity are approximately the same for SEI values above  $220 \text{ kJ mol}^{-1}$ , the ECE is also nearly identical in this SEI range, reaching its maximum value of 77% at  $260 \text{ kJ mol}^{-1}$ .

Remarkably, since the best performance, characterised by high conversion and ECE, is obtained at high SEI values where both strategies yield identical results, our model suggest that there is no strong advantage of considering a pure  $\text{CO}_2$  plasma with post-plasma  $\text{CH}_4$  injection. Indeed, the hypothesis that post-plasma  $\text{CH}_4$  injection results in better syngas yield and ECE holds only in the suboptimal SEI range below  $140 \text{ kJ mol}^{-1}$ , characterised by low conversion and low ECE. Our conclusion is also supported by the reported ECE values in literature, where the value of 67% reported by Cho *et al.*<sup>17</sup> is among the highest values reported in literature due to the high thermal efficiency of their particular setup, but it does not exceed the value of 71% reported by Sun *et al.*,<sup>16</sup> where  $\text{CO}_2$  and  $\text{CH}_4$  are injected directly into the plasma.

We note however that post-plasma  $\text{CH}_4$  injection might still be advantageous to increase the  $\text{CH}_4/\text{CO}_2$  ratio, by mitigating discharge instability caused by soot formation, associated with high  $\text{CH}_4$  fractions within the plasma. This could potentially lead to higher syngas ratios, more appealing for industrial applications.

### 4.3. Kinetic analysis

To gain insight into the DRM process, we perform a kinetic analysis and evaluate how the species react over time. In particular, we aim to explain why the first strategy, *i.e.* (i) injecting only  $\text{CO}_2$  inside the plasma while injecting  $\text{CH}_4$  post-plasma, fails to enhance the ECE with respect to the second strategy, *i.e.* (ii) injecting half of the 1 : 1  $\text{CO}_2/\text{CH}_4$  mixture inside the plasma and the other half of the same mixture post-plasma, within the SEI range of  $140\text{--}200 \text{ kJ mol}^{-1}$  (section 4.3.1), and why both strategies are equivalent in the optimal SEI range above  $240 \text{ kJ mol}^{-1}$  (section 4.3.2).

**4.3.1. Kinetic analysis at low SEI ( $140 \text{ kJ mol}^{-1}$ ).** Before discussing why strategy (i) fails to enhance the ECE for  $\text{SEI} > 140 \text{ kJ mol}^{-1}$ , we briefly address the region of  $\text{SEI} < 140 \text{ kJ mol}^{-1}$ , where the hypothesis that injecting all the energy into

$\text{CO}_2$  yields improved ECE holds true. For  $\text{SEI} < 140 \text{ kJ mol}^{-1}$ , in strategy (ii),  $\text{CH}_4$  is mainly converted to  $\text{C}_2\text{H}_2$ , since the O atoms resulting from  $\text{CO}_2$  dissociation are not used for oxidising  $\text{CH}_4$ . Instead, the O atoms react with  $\text{H}_2$ , resulting from  $\text{CH}_4$  dissociation, to form  $\text{H}_2\text{O}$ . For instance, at  $\text{SEI} = 100 \text{ kJ mol}^{-1}$ , the amount of CO produced is only 6% higher than the amount of converted  $\text{CO}_2$ , indicating that most of the O atoms (94%) are used to form  $\text{H}_2\text{O}$ . Consequently, the substantial formation of  $\text{C}_2\text{H}_2$  and  $\text{H}_2\text{O}$  for  $\text{SEI} < 140 \text{ kJ mol}^{-1}$  results in relatively low  $S^{\text{CO}}$  and  $S^{\text{H}_2}$  for strategy (ii). For strategy (i), the  $\text{CO}_2$  conversion is much higher, leading to higher  $S^{\text{CO}}$  since nearly every converted  $\text{CO}_2$  molecule will create a CO molecule, unlike  $\text{CH}_4$  conversion that mainly yields  $\text{C}_2\text{H}_2/\text{H}_2/\text{H}_2\text{O}$  within this SEI range. Due to the significantly higher  $\chi^{\text{CO}}$  and  $S^{\text{CO}}$  of strategy (i) compared to strategy (ii), the ECE of strategy (i) is significantly higher, *e.g.*, at  $\text{SEI} = 100 \text{ kJ mol}^{-1}$ ,  $\eta = 27\%$  and  $\eta = 18\%$  for strategy (i) and (ii), respectively. However, this SEI range ( $<140 \text{ kJ mol}^{-1}$ ) is not interesting for industrial applications due to the low conversion and ECE.

In contrast, at  $\text{SEI} = 140 \text{ kJ mol}^{-1}$ , there is a sharp increase in  $S^{\text{CO}}$  and  $S^{\text{H}_2}$  for strategy (ii) (cf. Fig. 5(b) above), since the O atoms resulting from  $\text{CO}_2$  dissociation will now primarily oxidise  $\text{CH}_4$  to CO. The reason is that, in contrast to  $\text{SEI} < 140 \text{ kJ mol}^{-1}$ , enough energy is present to convert  $\text{C}_2\text{H}_2$  and  $\text{H}_2\text{O}$ , formed during the reforming process, to CO and  $\text{H}_2$ , as indicated in Fig. 7, which is discussed below. As a result, the ECE of strategy (ii) slightly exceeds that of strategy (i) for  $\text{SEI} > 140 \text{ kJ mol}^{-1}$ , as observed in Fig. 6 above.

Fig. 7 depicts the evolution of the  $\text{CO}_2$  and  $\text{CH}_4$  conversion over time (a), as well as the molar fractions of  $\text{H}_2\text{O}$  and  $\text{C}_2\text{H}_2$  (b). The conversion is calculated as the amount of reactant consumed relative to the total amount of reactant supplied to the system, encompassing both the discharge gas and the gas injected post-plasma. Therefore, the time-dependent conversion  $\chi(t)$  is calculated for strategies (i) and (ii) as:

(i)

$$\chi^{\text{CO}_2}(t) = \frac{n_0^{\text{CO}_2} \cdot V_0 - n^{\text{CO}_2}(t) \cdot V(t)}{n_0^{\text{CO}_2} \cdot V_0} \quad (18)$$

$$\chi^{\text{CH}_4}(t) = \frac{\int_0^t R_m^{\text{CH}_4}(t) V(t) dt - n^{\text{CH}_4}(t) \cdot V(t)}{n_0^{\text{CO}_2} \cdot V_0} \quad (19)$$

(ii)

$$\chi^{\text{CO}_2/\text{CH}_4}(t) = \frac{n_0^{\text{CO}_2/\text{CH}_4} \cdot V_0 + \int_0^t R_m^{\text{CO}_2/\text{CH}_4}(t) V(t) dt - n^{\text{CO}_2/\text{CH}_4}(t) \cdot V(t)}{2n_0^{\text{CO}_2/\text{CH}_4} \cdot V_0} \quad (20)$$

where eqn (18) and (19) represent the  $\text{CO}_2$  and  $\text{CH}_4$  conversion at time  $t$  for strategy (i), and eqn (20) represents the  $\text{CO}_2$  and  $\text{CH}_4$  conversion, which have identical expressions, for strategy (ii). We note that  $n_0^{\text{CO}_2/\text{CH}_4}$  represents the initial density of  $\text{CO}_2/\text{CH}_4$  present in the simulation, *i.e.* the discharge gas, and  $n^{\text{CO}_2/\text{CH}_4}$  represents the actual density present at time  $t$ . Finally,  $R_m$  is the mixing rate, defined by eqn (6) above.

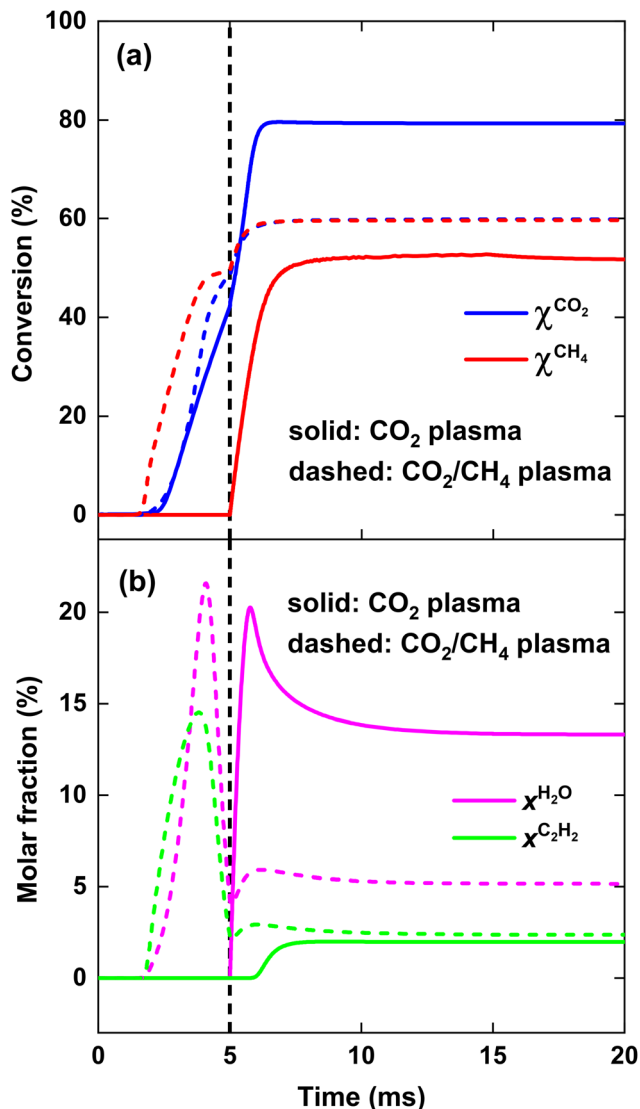


Fig. 7 CO<sub>2</sub> and CH<sub>4</sub> conversion (a), as well as H<sub>2</sub>O and C<sub>2</sub>H<sub>2</sub> molar fraction (b), as a function of time, for SEI = 140 kJ mol<sup>-1</sup>. The solid and dashed lines indicate the results for the CO<sub>2</sub> plasma with post-plasma CH<sub>4</sub> injection, and for the CO<sub>2</sub>/CH<sub>4</sub> plasma with post-plasma CO<sub>2</sub>/CH<sub>4</sub> injection, respectively. The vertical dashed line at 5 ms indicates the post-plasma mixing.

To explain the evolution of the CO<sub>2</sub> and CH<sub>4</sub> conversion shown in Fig. 7(a), we plot the net rates of conversion for CO<sub>2</sub> and CH<sub>4</sub>, *i.e.* the sum of all individual reaction rates, in Fig. 8. To account for the change in simulation volume  $V$  over time (due to gas expansion upon reaction and rise in temperature), we scale the net volumetric reaction rate  $R_i$  of reactant  $i$  (CO<sub>2</sub>/CH<sub>4</sub>) by multiplying it with the actual  $V$ , and then divide this product by the number of moles of reactant  $i$  present in the simulation, *i.e.* the initial molar density  $n_{i,0}$  times  $V_0$ , to render the rate value independent of the system size, *i.e.* the initial volume  $V_0$ :

$$R'_i(t) = \frac{R_i(t) \cdot V(t)}{n_{i,0} \cdot V_0} \quad (21)$$

where  $R'_i$  is the net rate of conversion of reactant  $i$  with unit s<sup>-1</sup>, effectively indicating how many times the initial amount of reactant reacts away per second. For instance, if  $R'_i$  has a constant value of 100 s<sup>-1</sup>, reactant  $i$  will be completely converted at  $t = 0.01$  s. The temperature along the simulation is also included in Fig. 8 (black dashed line, right y-axis).

Fig. 7(a) illustrates that at the end of the discharge ( $t = 5$  ms), a maximum CO<sub>2</sub> conversion of 42% is reached for the CO<sub>2</sub> plasma, corresponding to the dissociation equilibrium of CO<sub>2</sub> at  $T_{\text{max}} = 3020$  K (*cf.* black dashed line in Fig. 8, panel (i)). Subsequently, upon post-plasma CH<sub>4</sub> injection, the hot CO<sub>2</sub> equilibrium mixture, *i.e.*, O, O<sub>2</sub> and CO<sub>2</sub>, reacts with CH<sub>4</sub> at the elevated post-plasma temperatures. As a result, the CO<sub>2</sub> conversion sharply increases (*cf.* Fig. 7(a)), reaching a maximum value of 80%, after which the net rate of CO<sub>2</sub> conversion becomes negligible due to the slow reaction kinetics around  $T = 1800$  K (*cf.* Fig. 8(i)). Hence, the higher overall CO<sub>2</sub> conversion in scenario (i) (*cf.* Fig. 5 above) is not due to higher conversion inside the plasma (as it is even a bit lower than in scenario (ii); *cf.* Fig. 7(a)), but due to the additional CO<sub>2</sub> conversion post-plasma upon reacting with CH<sub>4</sub>, as also mentioned in section 4.2 above.

Cho *et al.*<sup>17</sup> mentioned that the O<sub>2</sub> resulting from CO<sub>2</sub> dissociation in the CO<sub>2</sub> plasma reacts with the CH<sub>4</sub> injected downstream. Since the oxidation of CH<sub>4</sub> by O<sub>2</sub> is an exothermic reaction with a low energy barrier, CH<sub>4</sub> can be efficiently oxidized by O<sub>2</sub> post-plasma using residual heat at a lower temperature. However, achieving complete CO<sub>2</sub> conversion within the plasma requires very high SEI values, *e.g.*, at SEI = 300 kJ mol<sup>-1</sup>, the CO<sub>2</sub> conversion reaches 92% by the end of the plasma. At intermediate SEI values, a substantial amount of unreacted CO<sub>2</sub> must react with CH<sub>4</sub> downstream, requiring much higher temperatures due to the lower reactivity of CO<sub>2</sub> compared to O<sub>2</sub>, similar to strategy (ii). Consequently, the total conversion for strategy (i) is only slightly higher (*ca.* 5%) than for strategy (ii) at SEI < 220 kJ mol<sup>-1</sup>.

Fig. 7(b) illustrates that when the hot CO<sub>2</sub> gas mixes with CH<sub>4</sub>, CH<sub>4</sub> is initially completely converted to CO due to the presence of reactive oxygen species (O<sub>2</sub> and O atoms) resulting from CO<sub>2</sub> dissociation, as indicated by the absence of C<sub>2</sub>H<sub>2</sub> formation for  $t < 6$  ms. Since most of the oxygen is used in the oxidation of CH<sub>4</sub>, the CH<sub>4</sub> conversion at  $t = 6$  ms, approximately 37%, is close to the CO<sub>2</sub> conversion of 42% in the plasma. Notably, the CO<sub>2</sub> conversion at  $t = 6$  ms is around 75%, which is significantly higher than the conversion at the end of the plasma, suggesting the generation of new reactive oxygen for CH<sub>4</sub> oxidation. However, most of the CO<sub>2</sub> at  $t < 6$  ms is converted to CO and H<sub>2</sub>O *via* the water-gas shift reaction (*cf.* section 4.3.3), as is clear from the substantial increase in the H<sub>2</sub>O fraction shown in Fig. 7(b). Consequently, no additional reactive oxygen is created in this manner, which explains the formation of C<sub>2</sub>H<sub>2</sub> after  $t = 6$  ms.

For strategy (ii), CO<sub>2</sub> is almost completely converted in the CO<sub>2</sub>/CH<sub>4</sub> plasma, corresponding to  $\chi^{\text{CO}_2} = 49\%$ , considering that only half of the total CO<sub>2</sub> flow passes through the plasma. When the remaining half of the 1:1 CO<sub>2</sub>/CH<sub>4</sub> mixture is

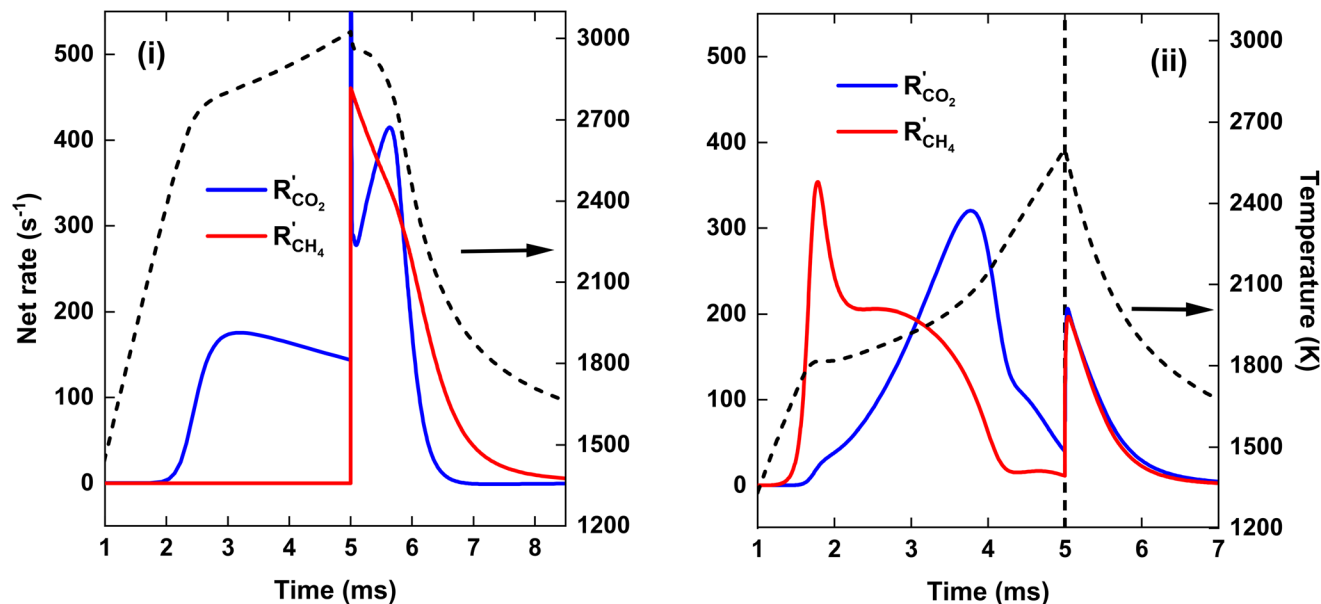


Fig. 8 Net rates of conversion of CO<sub>2</sub> and CH<sub>4</sub>, as a function of time, for SEI = 140 kJ mol<sup>-1</sup> (left y-axis). The temperature is indicated by the dashed black line (right y-axis). The left panel (i) and right panel (ii) show the results for the CO<sub>2</sub> plasma with post-plasma CH<sub>4</sub> injection, and for the CO<sub>2</sub>/CH<sub>4</sub> plasma with post-plasma CO<sub>2</sub>/CH<sub>4</sub> injection, respectively.

injected, the CO<sub>2</sub> conversion rises to its maximum value of 60%, after which, similar to case (i), the CO<sub>2</sub> conversion freezes around  $T = 1800$  K (cf. Fig. 8(ii)).

We stress that the total amount of CO<sub>2</sub> converted within the plasma is actually higher for the CO<sub>2</sub>/CH<sub>4</sub> plasma, despite the lower temperature and only half of the CO<sub>2</sub> being present, compared to the pure CO<sub>2</sub> plasma. This can be attributed to the presence of CH<sub>4</sub> that strongly shifts the equilibrium mixture to CO at lower temperatures compared to a pure CO<sub>2</sub> mixture, and the accelerated CO<sub>2</sub> dissociation due to the presence of H atoms. However, for strategy (i), when CH<sub>4</sub> is injected after the CO<sub>2</sub> plasma, the CO<sub>2</sub> conversion sharply increases and surpasses that of strategy (ii), i.e.  $\chi^{\text{CO}_2} = 80\%$  compared to  $\chi^{\text{CO}_2} = 60\%$ , respectively. This is due the fact that for strategy (i), all the remaining CO<sub>2</sub> that was not converted within the plasma is reacting at the high afterglow temperature upon CH<sub>4</sub> injection, resulting in rapid CO<sub>2</sub> dissociation kinetics, as seen in Fig. 8(i), i.e.  $R'_{\text{CO}_2} = 410 \text{ s}^{-1}$  at  $t = 5.6$  ms. In contrast, for strategy (ii), the CO<sub>2</sub> entering the simulation due to mixing with the plasma stream after post-plasma injection on average reacts at a lower temperature since the plasma afterglow is cooler (cf. Fig. 8) due to the colder plasma and the previous mixing with the incoming cold gas.

For SEI = 140 kJ mol<sup>-1</sup>, the pure CO<sub>2</sub> plasma yields better CO<sub>2</sub> conversion, as more CO<sub>2</sub> is heated to the elevated plasma temperatures compared to case (ii), where half of the CO<sub>2</sub> is injected post-plasma. However, there is not enough residual heat to facilitate sufficient CH<sub>4</sub> reforming, since a maximum CH<sub>4</sub> conversion of 53% is reached around  $T = 1700$  K (cf. Fig. 8), beyond which the CH<sub>4</sub> dissociation freezes. Moreover, as shown in Fig. 7(b), a large amount of H<sub>2</sub>O is formed in the

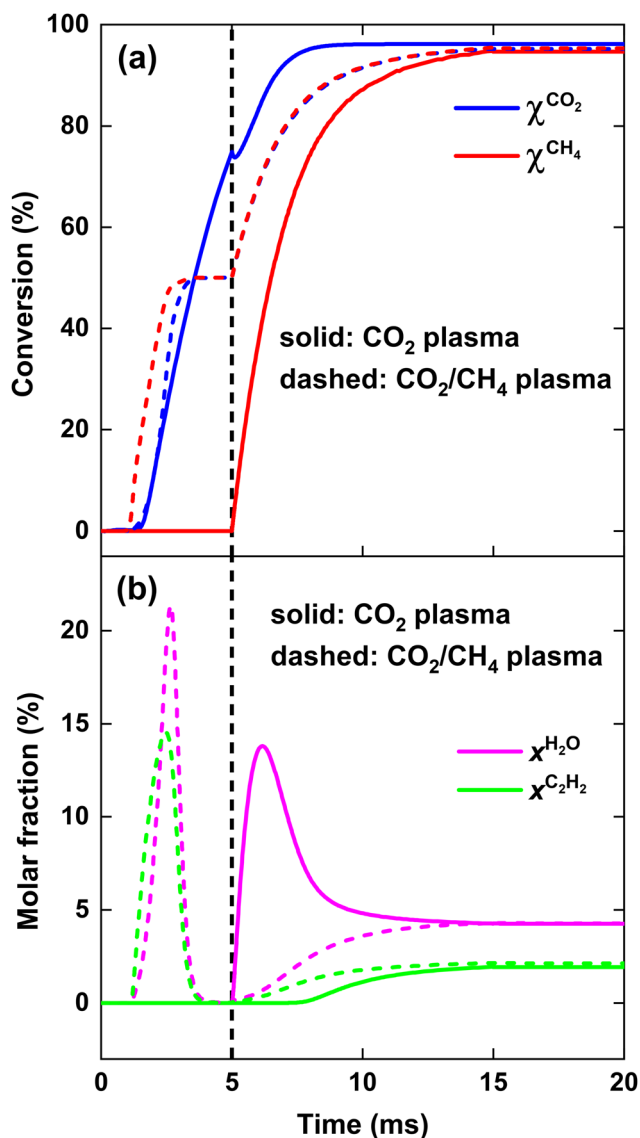
plasma afterglow (up to 20%), resulting in the low H<sub>2</sub> selectivity of 56% (cf. Fig. 5(b)). For strategy (ii), a higher CH<sub>4</sub> conversion of 60% is achieved, since half of the CH<sub>4</sub> is completely converted within the discharge, and ca. 20% of the CH<sub>4</sub> injected post-plasma (equivalent to 10% of the total CH<sub>4</sub>) can be converted with residual heat. Moreover, as illustrated in Fig. 7(b), strategy (ii) produces only 5% H<sub>2</sub>O, almost a factor 3 lower than in strategy (i), resulting in the significantly higher H<sub>2</sub> selectivity of 80% (cf. Fig. 5(b)). The disparity in H<sub>2</sub>O production between the two strategies can be attributed to the equilibrium of the water-gas shift reaction, which will be discussed in detail in section 4.3.3.

Although the pure CO<sub>2</sub> plasma with post-plasma CH<sub>4</sub> injection yields higher CO<sub>2</sub> conversion for SEI values under 220 kJ mol<sup>-1</sup>, resulting in slightly higher total conversion with respect to strategy (ii), the H<sub>2</sub> selectivity is significantly lower due to substantial H<sub>2</sub>O formation. As a result, the ECE is lower for the pure CO<sub>2</sub> plasma with post-plasma CH<sub>4</sub> injection within the SEI range of 140–200 kJ mol<sup>-1</sup> (cf. Fig. 6). Therefore, our model suggests that it is not possible to improve the performance of the DRM process by considering a pure CO<sub>2</sub> plasma with post-plasma CH<sub>4</sub> injection, within this SEI range of 140–200 kJ mol<sup>-1</sup>. Furthermore, Fig. 6 indicates that the optimal performance, characterized by high conversion and ECE, is achieved at SEI values between 240–280 kJ mol<sup>-1</sup>, where both strategies yield identical results.

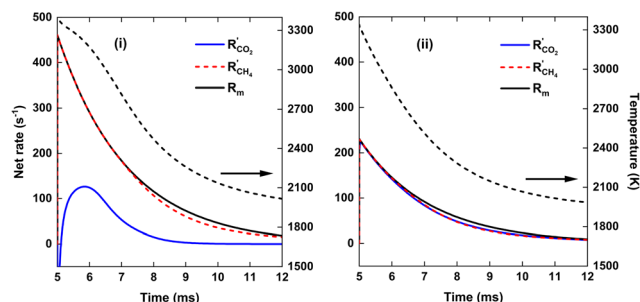
**4.3.2. Kinetic analysis at high SEI (220 kJ mol<sup>-1</sup>).** To gain deeper insights into why both strategies yield nearly identical results for SEI values above 220 kJ mol<sup>-1</sup>, we analyse the temporal evolution of CO<sub>2</sub> and CH<sub>4</sub> conversion for SEI = 220 kJ mol<sup>-1</sup>, as well as the molar fractions of H<sub>2</sub>O and C<sub>2</sub>H<sub>2</sub>, as



plotted in Fig. 9(a and b). In addition, we examine the net rates of conversion of  $\text{CO}_2$  and  $\text{CH}_4$ , using the same scaling approach as in Fig. 8, as plotted in Fig. 10. Here, we focus on the mixing process after post-plasma injection, starting from  $t = 5$  ms, because we aim to evaluate whether sufficient residual heat is present to completely convert the fraction of gas injected post-plasma, unlike the case at low SEI ( $140 \text{ kJ mol}^{-1}$ ) discussed in section 4.3.1. This is true when the rate of  $\text{CH}_4$  conversion for strategy (i) and the rate of  $\text{CO}_2$  and  $\text{CH}_4$  conversion for strategy (ii) equal the mixing rate  $R_m$ , *i.e.* the rate of  $\text{CH}_4$  addition for strategy (i) and the rate of  $\text{CO}_2$  and  $\text{CH}_4$  addition for strategy (ii). Therefore, we also plot  $R_m$  in Fig. 10,



**Fig. 9**  $\text{CO}_2$  and  $\text{CH}_4$  conversion (a), as well as  $\text{H}_2\text{O}$  and  $\text{C}_2\text{H}_2$  molar fraction (b), as a function of time, for  $\text{SEI} = 220 \text{ kJ mol}^{-1}$ . The solid and dashed lines indicate the results for the  $\text{CO}_2$  plasma with post-plasma  $\text{CH}_4$  injection, and for the  $\text{CO}_2/\text{CH}_4$  plasma with post-plasma  $\text{CO}_2/\text{CH}_4$  injection, respectively. The vertical dashed line at 5 ms indicates the post-plasma mixing.



**Fig. 10** Net rates of conversion of  $\text{CO}_2$  and  $\text{CH}_4$  and mixing rate (solid black line) as a function of time, for  $\text{SEI} = 220 \text{ kJ mol}^{-1}$  (left y-axis). The temperature is indicated by the dashed black line (right y-axis). The left panel (i) and right panel (ii) show the results for the  $\text{CO}_2$  plasma with post-plasma  $\text{CH}_4$  injection, and for the  $\text{CO}_2/\text{CH}_4$  plasma with post-plasma  $\text{CO}_2/\text{CH}_4$  injection, respectively.

scaled in the same manner as the net rates of  $\text{CO}_2$  and  $\text{CH}_4$  conversion.

As is clear from Fig. 9, for strategy (i), in contrast to the previous case at  $\text{SEI} = 140 \text{ kJ mol}^{-1}$ , enough residual heat is present to almost completely convert the  $\text{CH}_4$  injected post-plasma, yielding  $\chi^{\text{CH}_4} = 95\%$ . Indeed, the temperature post-plasma is above 3000 K in the first 1.5 ms, and only drops below 2000 K after 7 ms post-plasma (*cf.* Fig. 10, panel (i)), while at  $140 \text{ kJ mol}^{-1}$ , the temperature post-plasma drops below 2000 K already after 2 ms for strategy (i) and after 1 ms for strategy (ii) (*cf.* Fig. 8, panel (ii)). The nearly 100%  $\text{CH}_4$  conversion is also clear from Fig. 10(i), where the rate of  $\text{CH}_4$  addition due to mixing is nearly balanced by the net rate of  $\text{CH}_4$  conversion (*cf.* black solid and red dashed line). Similarly, at this high  $\text{SEI}$  of  $220 \text{ kJ mol}^{-1}$ , strategy (ii) also achieves near-complete conversion of  $\text{CO}_2$  and  $\text{CH}_4$  since enough residual heat is present to convert the other 50% of the 1 : 1  $\text{CO}_2/\text{CH}_4$  mixture post-plasma. This is again illustrated in Fig. 10(ii), where the net rates of  $\text{CO}_2$  and  $\text{CH}_4$  conversion closely match their rate of addition due to mixing.

We stress again that high  $\text{SEI}$  values above  $220 \text{ kJ mol}^{-1}$  are needed for the pure  $\text{CO}_2$  plasma to have complete conversion of  $\text{CH}_4$  downstream. However, at these  $\text{SEI}$  values, the DRM kinetics are fast enough to also completely convert the 1 : 1  $\text{CO}_2/\text{CH}_4$  mixture injected post-plasma for strategy (ii). Consequently, our modeling results indicate that it is not possible to improve the ECE of the DRM process by using a pure  $\text{CO}_2$  plasma with post-plasma  $\text{CH}_4$  injection.

**4.3.3. Water-gas shift reaction to explain the  $\text{H}_2\text{O}$  formation and  $\text{H}_2$  selectivity.** Remarkably, Fig. 9(b) illustrates that at  $220 \text{ kJ mol}^{-1}$  both strategies converge to the same  $\text{H}_2\text{O}$  fraction (reached around  $t = 13$  ms), despite the reaction kinetics being completely different. Indeed, in strategy (i),  $\text{H}_2\text{O}$  is initially formed post-plasma at high temperatures ( $T > 3100 \text{ K}$ ) and is subsequently decomposed when the mixture cools down and cold  $\text{CH}_4$  is added, while in strategy (ii),  $\text{H}_2\text{O}$  is gradually formed as the mixture cools down and cold  $\text{CO}_2$  and  $\text{CH}_4$  are added to the simulation. This convergence suggests

that some sort of equilibrium is reached for the H<sub>2</sub>O fraction. However, at these temperatures the H<sub>2</sub>O fraction at thermodynamic equilibrium is negligible (*cf.* Fig. 2(a)).

The reason is that the H<sub>2</sub>O fraction follows the equilibrium of the water-gas shift (WGS) reaction:

$$[\text{H}_2\text{O}] = \frac{[\text{CO}_2] \cdot [\text{H}_2]}{[\text{CO}] \cdot K_{\text{eq}}}$$

where  $K_{\text{eq}}$  is the equilibrium constant of the WGS reaction, declining with temperature due to the negative Gibbs free energy of the reaction ( $\Delta G_0 = -28.6 \text{ kJ mol}^{-1}$ ), as shown in Fig. 11. At temperatures surpassing 1200 K, CO<sub>2</sub> will eventually convert entirely to CO over a sufficiently extended period, as is clear from the DRM equilibrium calculations in section 4.1, reaching a negligible H<sub>2</sub>O fraction, in accordance with the WGS equilibrium. However, the time required to attain equilibrium at the temperatures under consideration exceeds the total residence time of 15 ms (5 ms heating + 10 ms mixing). For instance, at  $T = 2500 \text{ K}$ , more than a second is needed to reach DRM equilibrium (*cf.* Fig. 2). Consequently, CO<sub>2</sub> is not fully converted yet, allowing for a significant H<sub>2</sub>O fraction. The WGS equilibrium explains why both strategies converge to the same H<sub>2</sub>O fraction, as nearly equivalent CO<sub>2</sub> and CH<sub>4</sub> conversions are achieved (*cf.* Fig. 5(a)) due to the rapid reaction kinetics at the elevated temperatures associated with SEI > 220 kJ mol<sup>-1</sup>. We stress that we did not impose the WGS equilibrium in the kinetic simulations. Instead, by analyzing the species concentrations, we found that the kinetics of the WGS reaction are sufficiently fast, allowing the WGS equilibrium to be attained throughout the complete simulation until the temperature drops below *ca.* 1800 K.

We now explain the H<sub>2</sub>O formation, determining  $S^{\text{H}_2\text{O}}$ , for strategy (i) and (ii) at 140 and 220 kJ mol<sup>-1</sup>, by means of the

WGS equilibrium. For strategy (i), comparing Fig. 9(b)–7(b), the H<sub>2</sub>O fraction reaches a lower maximum value at SEI = 220 kJ mol<sup>-1</sup>, with  $x^{\text{H}_2\text{O}} = 14\%$  for SEI = 220 kJ mol<sup>-1</sup> vs.  $x^{\text{H}_2\text{O}} = 20\%$  for SEI = 140 kJ mol<sup>-1</sup>. The lower H<sub>2</sub>O fraction at SEI = 220 kJ mol<sup>-1</sup> is due to the substantially higher CO<sub>2</sub> conversion compared to SEI = 140 kJ mol<sup>-1</sup>, outweighing the lower value for  $K_{\text{eq}}$  associated with the higher afterglow temperature. In addition to the lower maximum H<sub>2</sub>O fraction at SEI = 220 kJ mol<sup>-1</sup>, H<sub>2</sub>O is able to react away more effectively, yielding a significant lower final H<sub>2</sub>O fraction of 4% compared to  $x^{\text{H}_2\text{O}} = 13\%$  for SEI = 140 kJ mol<sup>-1</sup>. When CH<sub>4</sub> is injected after the CO<sub>2</sub> plasma, the H<sub>2</sub>O fraction initially increases until it reaches its maximum value, after which it decreases due to dilution of the H<sub>2</sub>O fraction through CH<sub>4</sub> addition, as well as further conversion of CO<sub>2</sub> to CO and the cooling of the gas mixture, which shifts the WGS equilibrium to CO<sub>2</sub> and H<sub>2</sub>. The reason that the decline in H<sub>2</sub>O fraction is much smaller at SEI = 140 kJ mol<sup>-1</sup> is that the mixture cools to temperatures where the kinetics of the WGS reaction are too slow ( $T < 1800 \text{ K}$ ; *cf.* Fig. 8(i)), effectively freezing the H<sub>2</sub>O concentration. Indeed, the drop in H<sub>2</sub>O fraction is mainly due to dilution. This is illustrated in Fig. 12, where the calculated H<sub>2</sub>O fraction as a function of time decouples from the theoretical H<sub>2</sub>O fraction predicted by the WGS equilibrium around  $t = 7 \text{ ms}$ , in contrast to the case of SEI = 220 kJ mol<sup>-1</sup> where the calculated H<sub>2</sub>O fraction perfectly aligns with the equilibrium prediction.

For strategy (ii), Fig. 7(b) and 9(b) illustrate that H<sub>2</sub>O reacts away at the end of the plasma and is slowly formed during the reforming of CH<sub>4</sub> when the cold 1:1 CO<sub>2</sub>/CH<sub>4</sub> mixture is added post-plasma, reaching a final value of  $x^{\text{H}_2\text{O}} = 5\%$  and  $x^{\text{H}_2\text{O}} = 4\%$  for SEI = 140 kJ mol<sup>-1</sup> and SEI = 220 kJ mol<sup>-1</sup>,

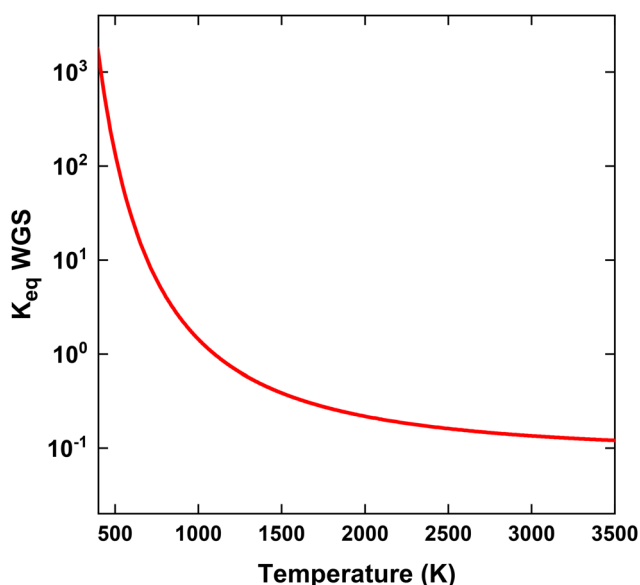


Fig. 11 Equilibrium constant of WGS reaction as a function of temperature.

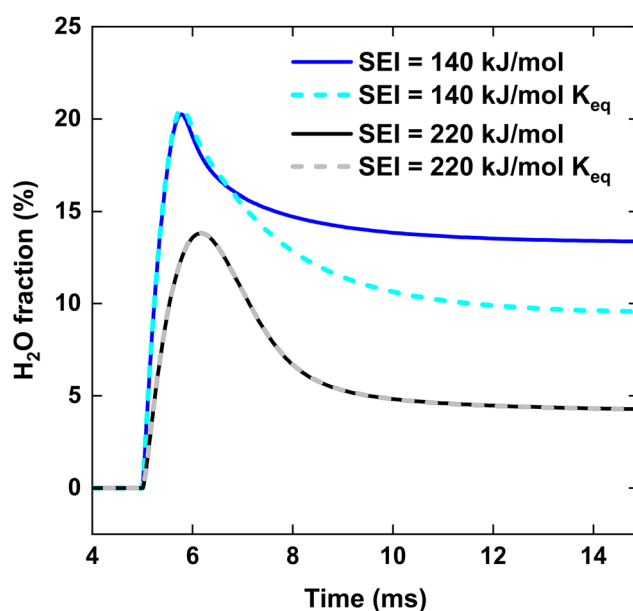


Fig. 12 H<sub>2</sub>O fraction as a function of time, for the CO<sub>2</sub> plasma with post-plasma CH<sub>4</sub> injection, at SEI = 140 kJ mol<sup>-1</sup> and SEI = 220 kJ mol<sup>-1</sup>. The dashed lines indicate the H<sub>2</sub>O fraction predicted by the WGS equilibrium.

respectively. For  $\text{SEI} = 140 \text{ kJ mol}^{-1}$ , following the WGS equilibrium,  $\text{H}_2\text{O}$  is almost completely converted near the end of the plasma, since near-complete conversion of  $\text{CO}_2$  is achieved inside the plasma, as seen in Fig. 7(a) and (b). However, in contrast to the WGS equilibrium that predicts a high final  $\text{H}_2\text{O}$  fraction of 28% due to the relatively low  $\text{CO}_2$  conversion of 60%, the  $\text{H}_2\text{O}$  fraction reaches a rather low value of 5% after complete addition of the cold  $\text{CO}_2/\text{CH}_4$  mixture. Indeed, similar to the injection of cold  $\text{CH}_4$  after the  $\text{CO}_2$  plasma (i), the WGS reaction kinetics quickly get frozen when the gas mixture cools down due to mixing with the cold  $\text{CO}_2/\text{CH}_4$  mixture, explaining the low final  $\text{H}_2\text{O}$  fraction.

From the discussion above, it is clear why the  $\text{CO}_2$  plasma with post-plasma  $\text{CH}_4$  injection (i) yields a significantly lower  $S^{\text{H}_2}$  at lower SEI ( $<200 \text{ kJ mol}^{-1}$ ) compared to the  $\text{CO}_2/\text{CH}_4$  plasma with post-plasma  $\text{CO}_2/\text{CH}_4$  injection (ii). For strategy (ii), most of the  $\text{H}_2\text{O}$  formed during the reforming process within the plasma is decomposed due to the high  $\text{CO}_2$  and  $\text{CH}_4$  conversion at the end of the plasma. When the cold  $\text{CO}_2/\text{CH}_4$  mixture is injected post-plasma, the mixture cools down and the  $\text{CO}_2$  concentration will eventually increase since there is insufficient heat to immediately convert the added  $\text{CO}_2$  gas. Consequently, the  $\text{H}_2\text{O}$  concentration will increase according to the WGS equilibrium. However, at these temperatures where the rate of  $\text{CO}_2$  conversion is significantly lower than the rate of  $\text{CO}_2$  addition due to mixing ( $T < 2000 \text{ K}$ ), the kinetics of the WGS reaction are also too slow to follow the WGS equilibrium. As a result, the  $\text{H}_2\text{O}$  fraction will slightly increase during the reforming process post-plasma, but is frozen at a relatively low concentration. In contrast, for strategy (i), a substantial amount of  $\text{H}_2\text{O}$  is formed during the reforming process following post-plasma  $\text{CH}_4$  injection, since a significant fraction of  $\text{CO}_2$  remains after the  $\text{CO}_2$  plasma due to incomplete conversion within the plasma at lower SEI ( $<200 \text{ kJ mol}^{-1}$ ).

Lastly, we note that if complete  $\text{CO}_2$  dissociation is reached within the  $\text{CO}_2$  plasma for strategy (i),  $\text{CH}_4$  will be completely converted to  $\text{CO}$  by  $\text{O}_2$  and  $\text{O}$  resulting from the completely dissociated  $\text{CO}_2$  plasma, and no  $\text{H}_2\text{O}$  will be formed according to the WGS equilibrium. However, this is not an energy efficient approach for DRM since the energy required to completely dissociate the  $\text{CO}_2$  gas is much higher than the energy needed to reach near 100% syngas yield from a 1 : 1  $\text{CO}_2/\text{CH}_4$  mixture. This is evident from Fig. 9(a) and (b), which show that 100% syngas yield (full conversion with no byproducts) is achieved at the end of the plasma for strategy (ii), whereas the  $\text{CO}_2$  conversion at the end of the  $\text{CO}_2$  plasma in strategy (i) reaches only 75%.

## 5. Conclusions

We have developed a 0D chemical kinetics model to describe the post-plasma gas conversion process occurring when the effluent of a thermal plasma mixes with a gas stream injected post-plasma, and we applied this model here to plasma-based DRM. Specifically, our model aims to investigate the potential

benefits of injecting all the plasma energy into  $\text{CO}_2$  for the thermal plasma-driven DRM process, by considering a pure  $\text{CO}_2$  plasma with post-plasma  $\text{CH}_4$  injection. The rationale behind this strategy is that when a  $\text{CO}_2/\text{CH}_4$  mixture is fed to the plasma, some of the plasma power is absorbed by  $\text{CH}_4$ , which is more easily dissociated, thereby reducing the power available for  $\text{CO}_2$  dissociation compared to a pure  $\text{CO}_2$  plasma. As  $\text{CH}_4$  dissociates at lower temperatures, injecting it post-plasma allows  $\text{CH}_4$  reforming to proceed in the reforming reactor with residual heat, potentially improving the energy efficiency of the process compared to injecting both  $\text{CO}_2$  and  $\text{CH}_4$  into the plasma.

We first validated the model by reproducing the experimental results of ref. 17, achieving reasonable agreement for the  $\text{CO}_2$  and  $\text{CH}_4$  conversion and  $\text{CO}$  selectivity, but underestimating the  $\text{H}_2$  selectivity by *ca.* 15%. The lower  $\text{H}_2$  selectivity predicted by the model is due to the significantly higher  $\text{H}_2\text{O}$  fraction calculated by the model compared to that measured in the experiment, possibly due to the lack of oxidation reactions of the metal reactor walls in the model, which was hypothesized to play a role in the experiment of ref. 17, or due to undetected  $\text{H}_2\text{O}$ .

Subsequently, to verify whether directing all the plasma energy into  $\text{CO}_2$  can improve the syngas yield and energy efficiency, we compared both strategies, *i.e.* (i) injecting only  $\text{CO}_2$  inside the plasma while injecting  $\text{CH}_4$  post-plasma, *vs.* (ii) injecting half of the 1 : 1  $\text{CO}_2/\text{CH}_4$  mixture into the plasma and the other half of the 1 : 1  $\text{CO}_2/\text{CH}_4$  mixture post-plasma. Our conceptual kinetic simulations assume uniform plasma heating and neglect any heat losses, to make the modeling results as transparent as possible.

Our modeling results indicate that for SEI values below  $220 \text{ kJ mol}^{-1}$ , the  $\text{CO}_2$  conversion can be increased by considering a pure  $\text{CO}_2$  plasma with post-plasma  $\text{CH}_4$  injection (i). The enhanced  $\text{CO}_2$  conversion arises from the greater fraction of  $\text{CO}_2$  subjected to high temperatures conducive to efficient  $\text{CO}_2$  dissociation, compared to strategy (ii), where half of the  $\text{CO}_2$  is injected post-plasma. For instance, at  $\text{SEI} = 140 \text{ kJ mol}^{-1}$ ,  $\chi^{\text{CO}_2} = 80\%$  *vs.*  $\chi^{\text{CO}_2} = 60\%$  for strategy (ii). While the  $\text{CH}_4$  conversion is slightly lower for strategy (i), *e.g.* at  $\text{SEI} = 140 \text{ kJ mol}^{-1}$ ,  $\chi^{\text{CH}_4} = 53\%$  *vs.*  $\chi^{\text{CH}_4} = 60\%$  for strategy (ii), the higher  $\text{CO}_2$  conversion outweighs the lower  $\text{CH}_4$  conversion, resulting in a slightly higher (*ca.* 5%) total conversion for  $\text{SEI} < 220 \text{ kJ mol}^{-1}$ . Consequently, the minimum EC of conversion is slightly lower, *i.e.*,  $212 \text{ kJ mol}^{-1}$  *vs.*  $224 \text{ kJ mol}^{-1}$  for strategy (i) and (ii), respectively. For  $\text{SEI} > 220 \text{ kJ mol}^{-1}$ , both strategies yield nearly identical results, due to the rapid reaction kinetics at the elevated temperatures ( $T > 2000 \text{ K}$ ), with  $\chi^{\text{tot}} > 95\%$ .

For  $\text{SEI} < 140 \text{ kJ mol}^{-1}$ , strategy (i) yields a lower ECE (5–9%) due to the significantly higher  $\chi^{\text{CO}_2}$  and  $S^{\text{CO}}$  compared to strategy (ii). However, this SEI range is not particularly interesting for applications because of the relatively low conversion ( $<60\%$ ) and ECE ( $<50\%$ ). Notably, strategy (i) causes substantial  $\text{H}_2\text{O}$  formation when  $\text{CH}_4$  is injected post-plasma, which is only partially decomposed within the limited reactor residence time for  $\text{SEI} < 220 \text{ kJ mol}^{-1}$ . For instance, at  $\text{SEI} = 140 \text{ kJ}$

$\text{mol}^{-1}$ , the final  $\text{H}_2\text{O}$  molar fraction is 13%, resulting in a low  $\text{H}_2$  selectivity of 56%. For strategy (ii), at  $\text{SEI} \geq 140 \text{ kJ mol}^{-1}$ ,  $\text{H}_2\text{O}$  formed during the reforming process inside the plasma is almost completely converted at the end of the discharge, yielding significantly higher  $\text{H}_2$  selectivity, e.g. at  $\text{SEI} = 140 \text{ kJ mol}^{-1}$ ,  $S^{\text{H}_2} = 83\%$ . As a result, for SEI values ranging between 140 and  $200 \text{ kJ mol}^{-1}$ , although the total conversion is slightly higher (1–6%), the  $\text{CO}_2$  plasma with post-plasma  $\text{CH}_4$  injection yields a slightly lower ECE (1–4%). In other words, the substantial  $\text{H}_2\text{O}$  formation, leading to a lower  $\text{H}_2$  selectivity, explains why there is no clear benefit of the  $\text{CO}_2$  plasma with post-plasma  $\text{CH}_4$  injection for SEI values between 140 and  $220 \text{ kJ mol}^{-1}$ .

For the  $\text{CO}_2$  plasma with post-plasma  $\text{CH}_4$  injection, high SEI values above  $200 \text{ kJ mol}^{-1}$  are needed to ensure that enough residual heat is present post-plasma to have efficient  $\text{CH}_4$  conversion ( $\chi^{\text{CH}_4} > 80\%$ ), and significantly convert the  $\text{H}_2\text{O}$  formed during the DRM process, resulting in good  $\text{H}_2$  selectivity ( $S^{\text{H}_2} > 80\%$ ). However, at these SEI values, the  $\text{CO}_2/\text{CH}_4$  plasma with post-plasma  $\text{CO}_2/\text{CH}_4$  injection yields similar results, as sufficient residual heat facilitates the efficient conversion of the injected  $\text{CO}_2/\text{CH}_4$  mixture post-plasma.

Our model predicts the best performance for SEI values ranging from 240 to  $280 \text{ kJ mol}^{-1}$ , where both strategies yield nearly identical results, reaching a total conversion of 99% and ECE of 77%. Consequently, our model suggests that, although enhanced  $\text{CO}_2$  conversion is feasible at lower SEI values by directing all the energy into  $\text{CO}_2$ , improving the ECE of the DRM process is not possible through a pure  $\text{CO}_2$  plasma with post-plasma  $\text{CH}_4$  injection. Nonetheless, such a configuration might still be useful to increase the  $\text{CH}_4/\text{CO}_2$  ratio, by circumventing plasma instability resulting from soot formation attributed to high  $\text{CH}_4$  fractions within the plasma. This could potentially yield higher syngas ratios, more appealing for industrial applications.

## Author contributions

Conceptualization, M. A., I. T. and A. B.; methodology & investigation, M. A., I. T. and A. B.; writing – original draft, M. A. and A. B.; writing – review & editing, M. A. and A. B.; funding acquisition, A. B.; supervision, A. B.

## Data availability

All data that support the findings of this study are included within the article.

## Conflicts of interest

There are no conflicts to declare.

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