Supporting information

Plasma activation of CO_2 in a dielectric barrier discharge: a chemical kinetic model from the microdischarge to the reactor scales

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Flow rate	Power	SEI	Residence Time	Velocity	$\Delta Z_{fil-to-fil}$	f_{pulses}	$\Delta t_{fil-to-fil}$ [1]	num_{pulses}	Δt_{fil} [2]	ΔZ_{fil}
mL/min	W	kJ/L	seconds	mm/s	mm	kHz	seconds	-	seconds	mm
25.0	**10**	24	36.8	2.72	1.33	2.0×10^{-3}	4.90×10^{-1}	76	3.68×10^{-2}	0.10
25.0	**20**	48	36.8	2.72	1.14	2.4×10^{-3}	4.18×10^{-1}	89	3.68×10^{-2}	0.10
25.0	**30**	72	36.8	2.72	1.03	2.6×10^{-3}	3.80×10^{-1}	97	3.68×10^{-2}	0.10
25.0	**40**	96	36.8	2.72	0.97	2.8×10^{-3}	3.56×10^{-1}	104	3.68×10^{-2}	0.10
25.0	**50**	120	36.8	2.72	0.92	3.0×10^{-3}	3.38×10^{-1}	109	3.68×10^{-2}	0.10
25.0	50	120	36.8	2.72	0.92	3.0×10^{-3}	3.38×10^{-1}	109	3.68×10^{-2}	0.10
31.2	50	96	29.5	3.40	0.92	3.7×10^{-3}	2.71×10^{-1}	109	3.28×10^{-2}	0.11
41.2	50	73	22.3	4.48	0.92	4.9×10^{-3}	2.05×10^{-1}	109	2.84×10^{-2}	0.13
62.5	50	48	14.7	6.80	0.92	7.4×10^{-3}	1.35×10^{-1}	109	2.29×10^{-2}	0.16
125.0	50	24	7.4	13.60	0.92	1.5×10^{-2}	6.76×10^{-2}	109	1.60×10^{-2}	0.22

1. Calculated with Kp = 0.442 and a = 0.230
2. Calculated with Kv = 0.062 and b = 0.485

Table S1 - Summary of calculation parameters.

Species				
e	CO_2	CO_2^+	CO	O
O_2	O_3	O^-	O_2^-	

Table S2 – Species in the model

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Symbol	Unit	Variable
a	-	Fitting parameter of the model
a_{ij}	-	Stochiometric coefficient of species i in reaction j
b	-	Fitting parameter of the model
dZ	mm	Differential width of the *slice* of reactor
E/N	Td	Reduced electric field
f_{pulses}	kHz	Frequency of pulses in the model (representing filaments)
K_p	W^{-1}	Fitting parameter of the model
K_v	$mm\ (mm/s)^{-b}$	Fitting parameter of the model
k_j	$cm^{-3}s^{-1}$ / $cm^{-6}s^{-1}$	Reaction rate coefficient of reaction j
L	mm	Reactor length
$Ne(t)$	cm^{-3}	Electron density as a function of time
Ne_{av}	cm^{-3}	Average electron density valid for Δt_{fil}
N_i	cm^{-3}	Number density of species i
num_{Pulses}	-	Number of pulses throughout the reactor in the model
rrt_j	s^{-1}	Reaction rate of reaction j
SEI	J/mL	Specific energy input
$\langle V \rangle$	mm/s	Average fluid velocity
Z	mm	Axial coordinate of the cylindrical reactor
$\Delta Z_{fil-to-fil}$	mm	Spacing between consecutive pulses in the model
ΔZ_{fil}	mm	Width of one filament
$\Delta t_{fil-to-fil}$	s	Period between consecutive pulses in the model, according to $\langle V \rangle$
Δt_{fil}	s	Time spent inside one filament, according to $\langle V \rangle$
$\Delta t_{micro-discharge}$	s	Duration of a micro-discharge, according to the applied voltage frequency
σ	A^2	Electron impact cross section
θ	s	Residence time

Table S3 – Variable index.

Process	Reaction	Database
Species: CO_2		
Electron attachment	e + CO2 → CO(X) + O(-,X)	*1*
Effective collision	e + CO2 → e + CO2	*1*
Vibrational excitation	e + CO2 → e + CO2(v=010)	*1*
Superelastic collision	e + CO2 (v=010) → e + CO2	*1*
Vibrational excitation	e + CO2 → e + CO2(v=020)	*1*
Vibrational excitation	e + CO2 → e + CO2(v=100)	*1*
Vibrational excitation	e + CO2 → e + CO2(v=030+110)	*1*
Vibrational excitation	e + CO2 → e + CO2(v=001)	*1*
Vibrational excitation	e + CO2 → e + CO2(v=040+120+011)	*1*
Vibrational excitation	e + CO2 → e + CO2(X,v=200)	*1*
Vibrational excitation	e + CO2 → e + CO2(X,v=050+210+130+021+101)	*1*
Vibrational excitation	e + CO2 → e + CO2(X,v=300)	*1*
Vibrational excitation	e + CO2 → e + CO2(X,v=060+220+140)	*1*
Vibrational excitation	e + CO2 → e + CO2(X,v=0n0+n00)	*1*
Electronic excitation	e + CO2 → e + CO2(e1)	*1*
Electronic excitation	e + CO2 → e + CO2(e2)	*1*
Electron impact ionization	e + CO2 → e + e + CO2(+,X)	*1*
Species: CO		
Effective collision	e + CO → e + CO	*2*
Vibrational excitation	e + CO → e + CO(V1)	*2*
Vibrational excitation	e + CO → e + CO(V2)	*2*
Vibrational excitation	e + CO → e + CO(V3)	*2*
Vibrational excitation	e + CO → e + CO(V4)	*2*
Vibrational excitation	e + CO → e + CO(V5)	*2*
Vibrational excitation	e + CO → e + CO(V6)	*2*
Vibrational excitation	e + CO → e + CO(V7)	*2*
Vibrational excitation	e + CO → e + CO(V8)	*2*
Vibrational excitation	e + CO → e + CO(V9)	*2*
Vibrational excitation	e + CO → e + CO(V10)	*2*
Electronic excitation	e + CO → e + CO*(6.22eV)	*2*
Electronic excitation	e + CO → e + CO*(6.8eV)	*2*
Electronic excitation	e + CO → e + CO*(7.9eV)	*2*

Electronic excitation	e + CO → e + CO*(10.4eV)	*2*
Electronic excitation	e + CO → e + CO*(10.6eV)	*2*
Electronic excitation	e + CO → e + C+O	*2*
Electron impact ionization	e + CO → e + e + CO+	*2*
Species: O_2		
Electron attachment	e + O_2 → O- + O	*1*
Effective collision	e + O_2 → e + O_2	*1*
Vibrational excitation	e + O_2 → e + O_2(v=0 - v=1)	*1*
Vibrational excitation	e + O_2 → e + O_2(v=0 - v=2)	*1*
Vibrational excitation	e + O_2 → e + O_2(v=0 - v=3)	*1*
Vibrational excitation	e + O_2 → e + O_2(v=0 - v=4)	*1*
Electronic excitation	e + O_2 → e + O_2(a1Dg)	*1*
Electronic excitation	e + O_2 → e + O_2(b1Sg+)	*1*
Electronic excitation	e + O_2 → e + O_2(A3Su+,C3Du,c1Su-)	*1*
Electronic excitation	e + O_2 → e + O(3P)+O(3P)	*1*
Electronic excitation	e + O_2 → e + O(3P)+O(1D)	*1*
Electronic excitation	e + O_2 → e + O_2(9.97eV)	*1*
Electronic excitation	e + O_2 → e + O_2(14.7eV)	*1*
Electron impact ionization	e + O_2 → e + e + O_2^+	*1*
Species: O		
Effective collision	e + O → e + O	*2*
Electronic excitation	e + O → e + O(1D)	*2*
Electronic excitation	e + O → e + O(1S)	*2*
Electron impact ionization	e + O → e + e + O^+	*2*
Electron impact ionization	e + O → e + e + O^+	*2*
Species: O_3		
Electron attachment	e + O_3 → O_2^-	*2*
Electron attachment	e + O_3 → O^-	*2*
Effective collision	e + O_3 → e + O_3	*2*
Electron impact ionization	e + O_3 → e + e + O_3^+	*2*

Table S4 – Processes considered for the calculation of the EEDF. Databases 1 and 2 stand for IST-Lisbon and Morgan Kinema Research & Software, both retrieved from the LXCat Project.

Reduced Electric Field (Td)	Case	Mean electron energy (eV)	R1 reaction rate coefficient (cm3/s)	R2 reaction rate coefficient (cm3/s)	R3 reaction rate coefficient (cm3/s)
1 Td	CO_2 (v_1)	0.0406	-	-	-
	No CO_2 (v_1)	0.0403	-	-	-
	Rel. error (%)	0.569%	-	-	-
5 Td	CO_2 (v_1)	0.0544	-	-	-
	No CO_2 (v_1)	0.0542	-	-	-
	Rel. error (%)	0.295%	-	-	-
10 Td	CO_2 (v_1)	0.0909	-	-	-
	No CO_2 (v_1)	0.0907	-	-	-
	Rel. error (%)	0.165%	-	-	-
20 Td	CO_2 (v_1)	0.5249	-	2.851×10^{-18}	1.25×10^{-16}
	No CO_2 (v_1)	0.5246	-	2.809×10^{-18}	1.238×10^{-16}
	Rel. error (%)	0.057%	-	1.484%	0.965%
56 Td	CO_2 (v_1)	2.2130	3.303×10^{-14}	2.123×10^{-11}	1.036×10^{-12}
	No CO_2 (v_1)	2.2130	3.297×10^{-14}	2.120×10^{-11}	1.035×10^{-12}
	Rel. error (%)	0.000%	0.182%	0.141%	0.097%

Table S5 – Mean electron energy and CO_2 electron impact reaction rates calculated with BOLSIG+ for both cases, with and without superelastic collisions $v_1 \rightarrow v_0$.

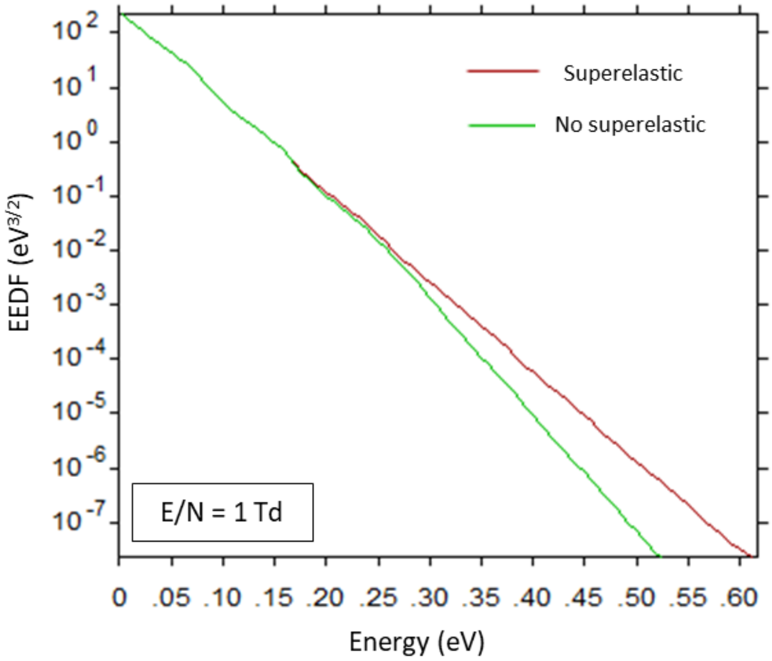

Figure S1 – BOLSIG+ calculated EEDF ($eV^{-3/2}$) at E/N = 1 Td. The red line considers a CO_2 (v_1) population of 0.076 while the green considers no vibrationally excited CO_2.

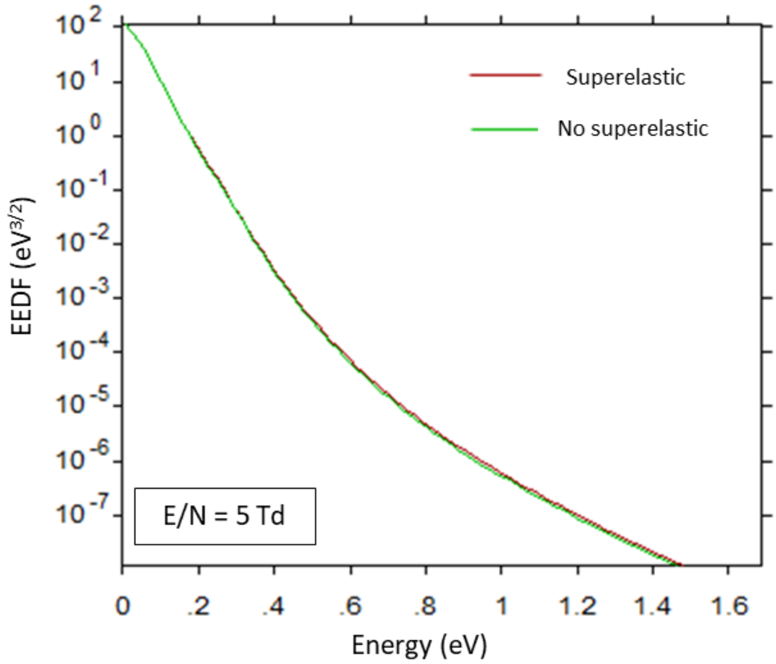

Figure S2 – BOLSIG+ calculated EEDF (eV$^{-3/2}$) at E/N = 5 Td.

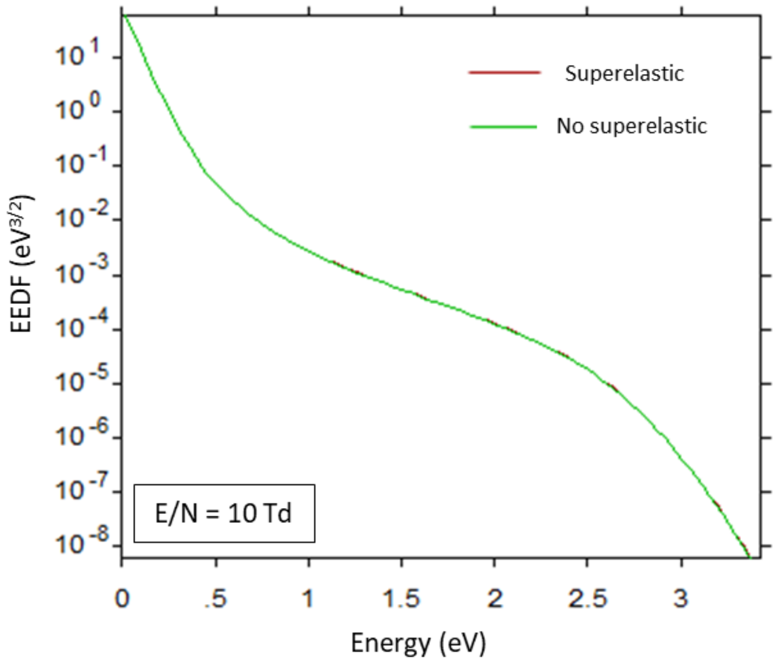

Figure S3 – BOLSIG+ calculated EEDF (eV$^{-3/2}$) at E/N = 10 Td.

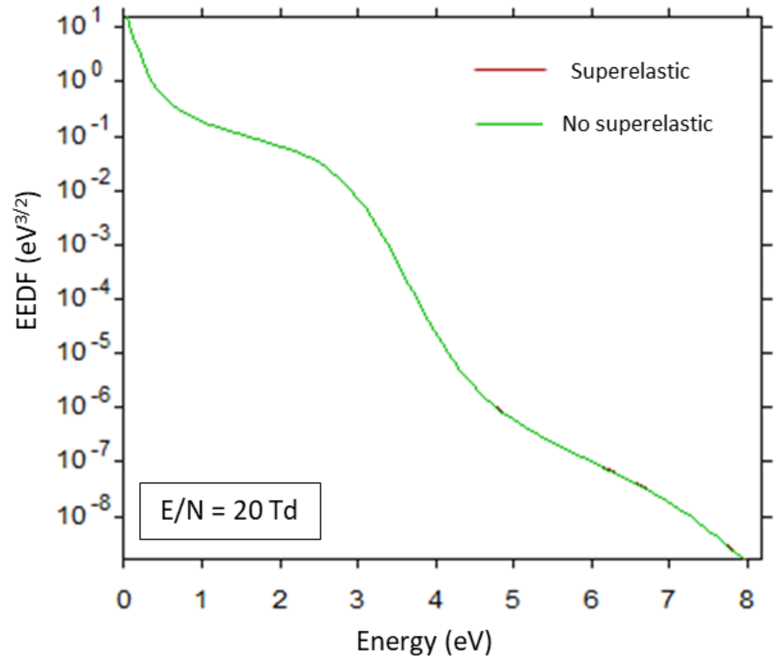

Figure S4 – BOLSIG+ calculated EEDF ($eV^{-3/2}$) at E/N = 20 Td.

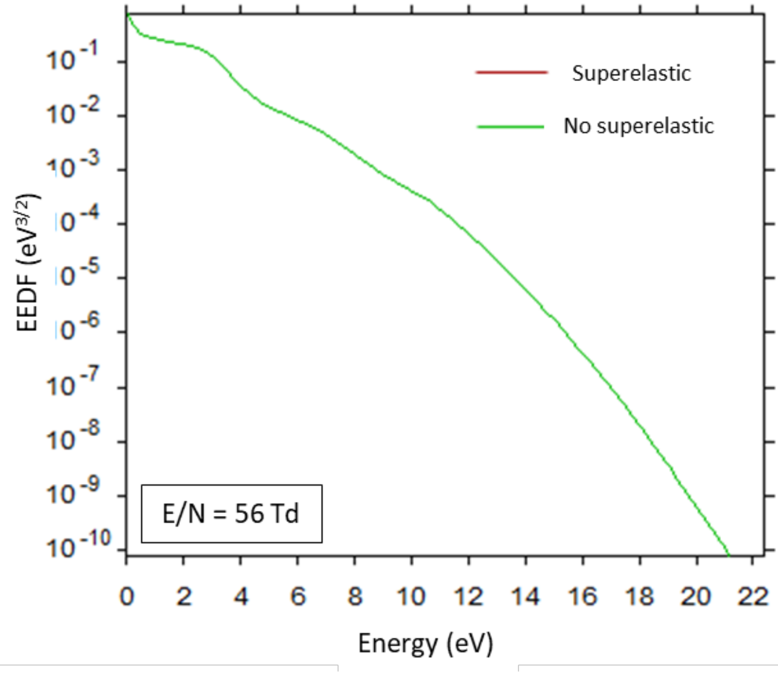

Figure S5 – BOLSIG+ calculated EEDF ($eV^{-3/2}$) at E/N = 56 Td.

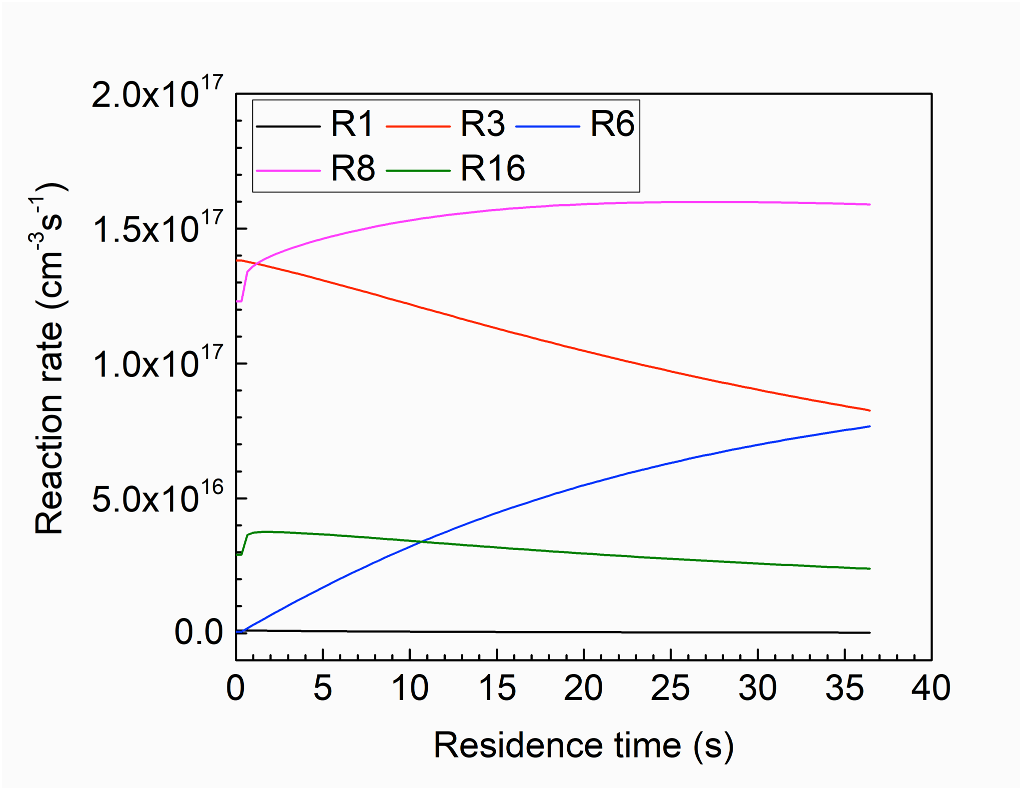

Figure S6 - Reaction rate of minor contributing reactions (25 mL/min and 50 W)