Electronic Supplementary Information:

Plasma-Based Dry Reforming: Improving the Conversion and Energy Efficiency in a Dielectric Barrier Discharge

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1. Comparison of experimental and computational data

Table S1. Overview of the detailed experimental and computational results, used for the model validation; as a function of the CH_4-CO_2 ratio.

		Experimental				**Computational**			
CH_4-CO_2 Ratio	***SEI (J/cm³)***	***Conversion (%)***			***Energy Efficiency (%)***	***Conversion (%)***			***Energy Efficiency (%)***
		CH_4	***CO_2***	***Total***		***CH_4***	***CO_2***	***Total***	
10 - 90	36	62.1	27.8	**31.23**	**8.71**	97.00	16.28	**24.36**	**6.79**
10 - 90	18	37.3	15.9	**18.04**	**10.06**	67.76	10.34	**16.08**	**8.97**
25 - 75	36	50.6	27.5	**33.28**	**9.28**	57.84	20.97	**30.19**	**8.41**
25 - 75	18	28.6	16.3	**19.38**	**10.80**	37.46	10.51	**17.25**	**9.62**
50 - 50	36	40.9	26	**33.45**	**9.32**	42.00	25.38	**33.69**	**9.39**
50 - 50	18	20.4	14.2	**17.30**	**9.64**	23.20	12.93	**18.065**	**10.07**
75 - 25	36	29.7	23.3	**28.10**	**7.83**	29.93	40.39	**32.55**	**9.07**
75 - 25	18	16.1	11.7	**15.00**	**8.36**	16.24	21.52	**17.56**	**9.79**
90 - 10	36	24.1	43	**25.99**	**7.24**	23.24	67.71	**27.69**	**7.72**
90 - 10	18	12.6	28.6	**14.20**	**7.92**	13.09	42.40	**16.02**	**8.93**

Table S2. Overview of the detailed experimental and computational results, used for the model validation, as a function of the residence time and the SEI.

			Experimental				**Computational**			
CH_4-CO_2 Ratio	***SEI (J/cm³)***	***Residence Time (s)***	***Conversion (%)***			***Energy Efficiency (%)***	***Conversion (%)***			***Energy Efficiency (%)***
			CH_4	***CO_2***	***Total***		***CH_4***	***CO_2***	***Total***	
50 - 50	36	32.57	40.9	26	**33.45**	**9.32**	42.00	25.38	**33.69**	**9.39**
50 - 50	18	16.29	28.4	19.5	**23.95**	**13.35**	26.66	15.01	**20.84**	**11.62**
50 - 50	12	10.86	18.4	8.8	**13.6**	**11.37**	19.80	10.78	**15.29**	**12.78**
50 - 50	9	8.14	15.9	9.3	**12.6**	**14.05**	15.75	8.39	**12.07**	**13.46**
50 - 50	4.5	4.07	7	3.3	**5.15**	**11.48**	8.81	4.52	**6.66**	**14.86**
50 - 50	18	32.57	20.4	14.2	**17.3**	**9.64**	23.20	12.93	**18.06**	**10.07**
50 - 50	9	16.29	13.8	10.3	**12.05**	**13.44**	13.72	7.24	**10.48**	**11.68**
50 - 50	6	10.86	7.4	4.5	**5.95**	**9.95**	9.77	5.05	**7.41**	**12.40**
50 - 50	4.5	8.14	7	4	**5.5**	**12.26**	7.59	3.89	**5.74**	**12.80**
50 - 50	2.25	4.07	2.8	0.9	**1.85**	**8.25**	3.96	2.03	**3.00**	**13.37**
50 - 50	1	1					2.14	1.09	**1.62**	**16.24**
50 - 50	100	100					63.82	43.70	**53.76**	**5.39**
50 - 50	1	2					1.78	0.94	**1.36**	**13.66**
50 - 50	100	200					58.25	39.33	**48.79**	**4.90**
50 - 50	0.5	1					0.89	0.48	**0.68**	**13.73**
50 - 50	50	100					41.02	25.24	**33.13**	**6.65**

2. Computational data

When looking at the influence of the gas ratio in the entire range of conditions (see figures S1-S15), the following trends can be observed. First of all, the effect of the gas ratio seems to be different, depending on the SEI:

- At the lowest SEI of 0.01 and 0.1 J/cm³, the conversion increases upon increasing CO_2 content (10 < 25 < 50 < 75 < 90 % CO_2) for all conditions investigated.
- At an SEI of 1 J/cm³, the conversion also increases upon increasing CO_2 content (10 < 25 < 50 < 75 < 90 % CO_2) at all conditions investigated, except at the highest residence time and frequency (10 = 25 < 50 < 75 < 90 % CO_2).
- At an SEI of 10 J/cm³ the effect of gas ratio seems to vary, depending on the other conditions, and no clear trend was observed at first sight. However, when we multiply the residence time (τ) with the frequency (f), which is a measure for the number of

micro-discharges that take place within a certain residence time, we can identify the following trends:

  - When $f \cdot \tau = 10^7$, the conversion is almost constant for 10, 25 and 50 % CO_2 and then starts decreasing at 75 and 90 % CO_2.
  - When $f \cdot \tau = 10^6$, the conversion first increases from 10 to 50 % CO_2 and then decreases again at 75 and 90 % CO_2.
  - When $f \cdot \tau = 10^5$ and 10^4 , the conversion increases from 10 to 75 % CO_2 and decreases again at 90 %. Note that the experimental validation shown in the paper was performed for $f \cdot \tau = 3 \cdot 10^4$, and indeed showed the same trend.
  - When $f \cdot \tau = 10^3$, the conversion increases upon increasing CO_2 content (10 < 25 < 50 < 75 < 90 % CO_2).
  - When $f \cdot \tau < 10^3$, the conversion slightly decreases from 10 to 75 % CO_2, but then strongly increases at 90 % CO_2.

- At the SEI of 100 J/cm³ , the conversion shows the same behavior as for the SEI of 10 J/cm³, more specifically:
  - When $f \cdot \tau = 10^7 – 10^5$, the conversion first increases from 10 to 50 % CO_2 and then decreases at 75 and 90 % CO_2.
  - When $f \cdot \tau < 10^5$, the conversion is almost constant for 10, 25 and 50 % CO_2 and increases for 75 and 90 % CO_2.

To summarize, changing the gas ratio will yield different results depending on the conditions (i.e., the other parameters). Especially the SEI plays an important role, i.e., for SEI values of 0.01, 0.1 and 1 J/cm³ a higher CO_2 content in the mixture leads to a higher conversion and subsequently energy efficiency. On the other hand, for the SEI values of 10 and 100 J/cm³, also the frequency and residence time play a role, and depending on the product of both, different trends are observed.

2.1. Total Conversion as a function of residence time and frequency for each SEI value and CH_4-CO_2 ratio investigated (Figure S1-S5)

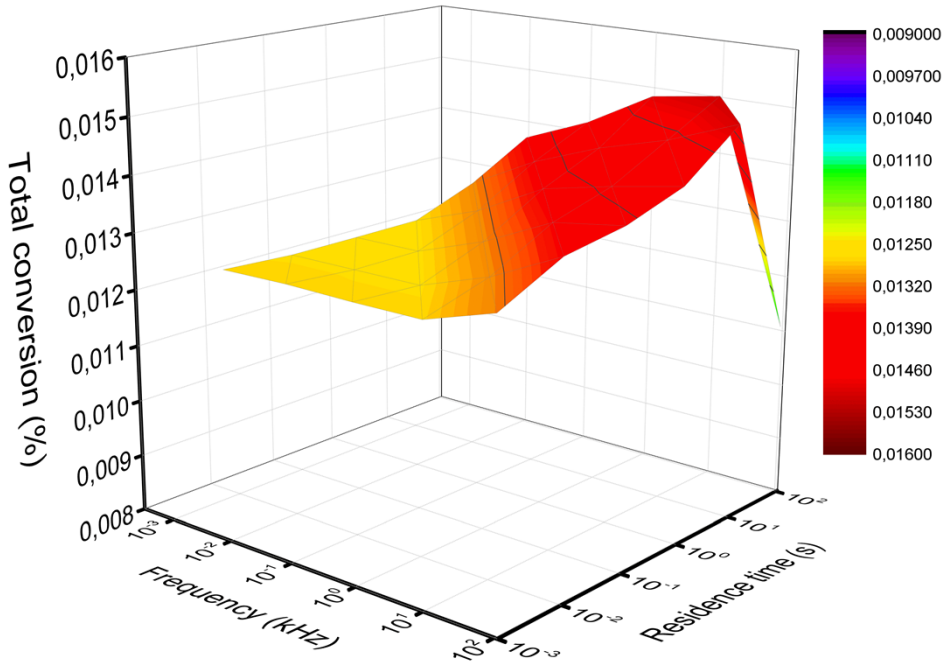

Figure S1(a). Total simulated conversion for a 10-90 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0.01 J/cm³.

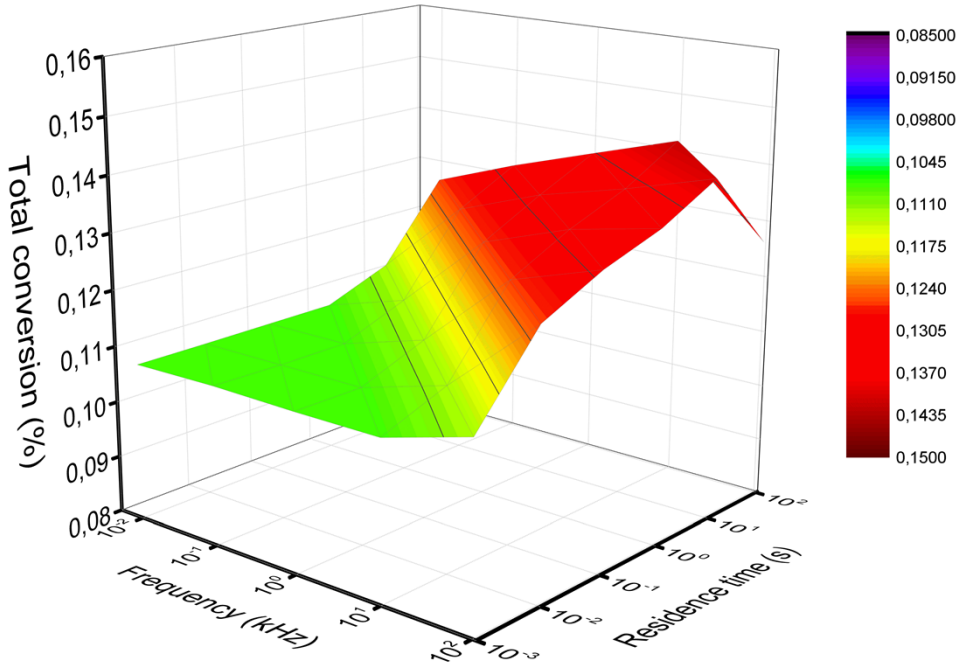

Figure S1(b). Total simulated conversion for a 10-90 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0.1 J/cm³.

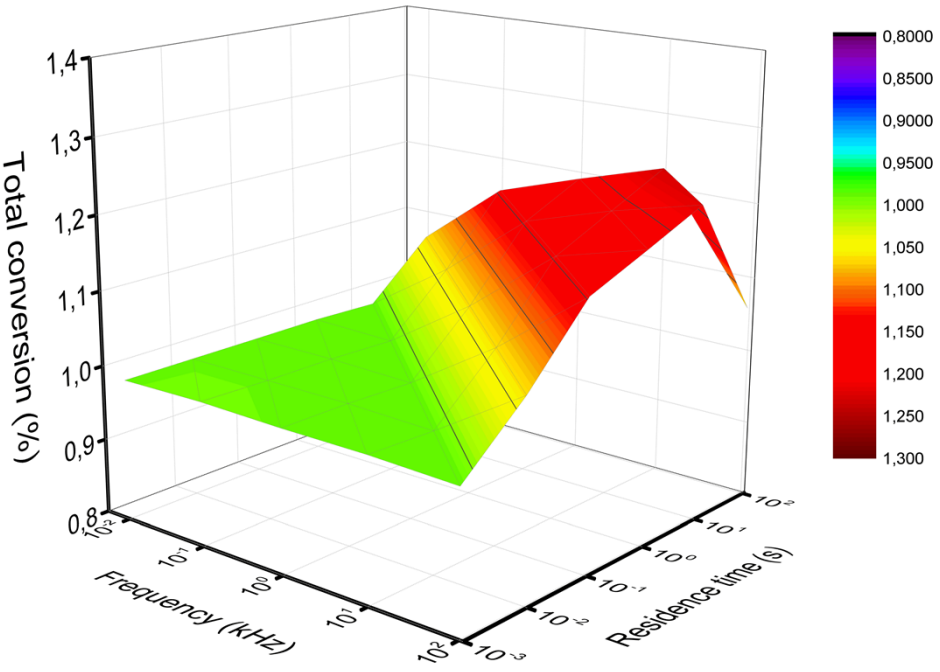

Figure S1(c). Total simulated conversion for a 10-90 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 1 J/cm³.

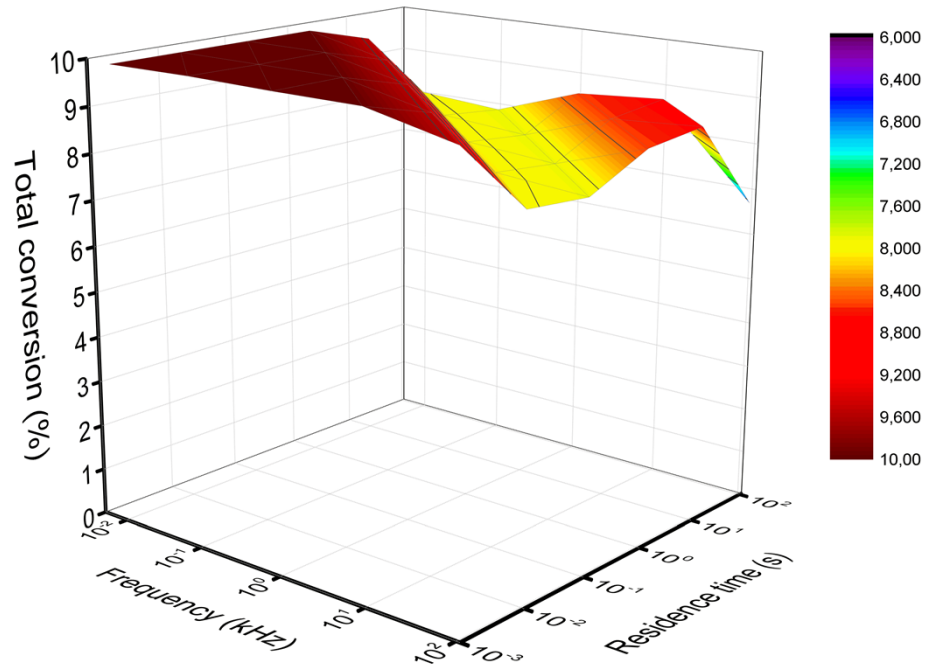

Figure S1(d). Total simulated conversion for a 10-90 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 10 J/cm³.

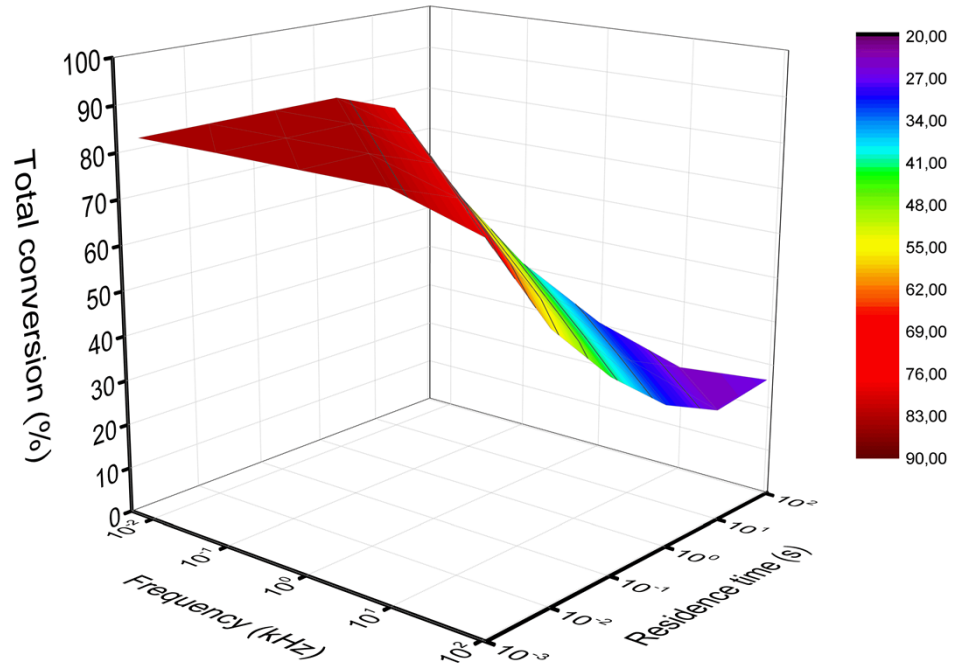

Figure S1(e). Total simulated conversion for a 10-90 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 100 J/cm³.

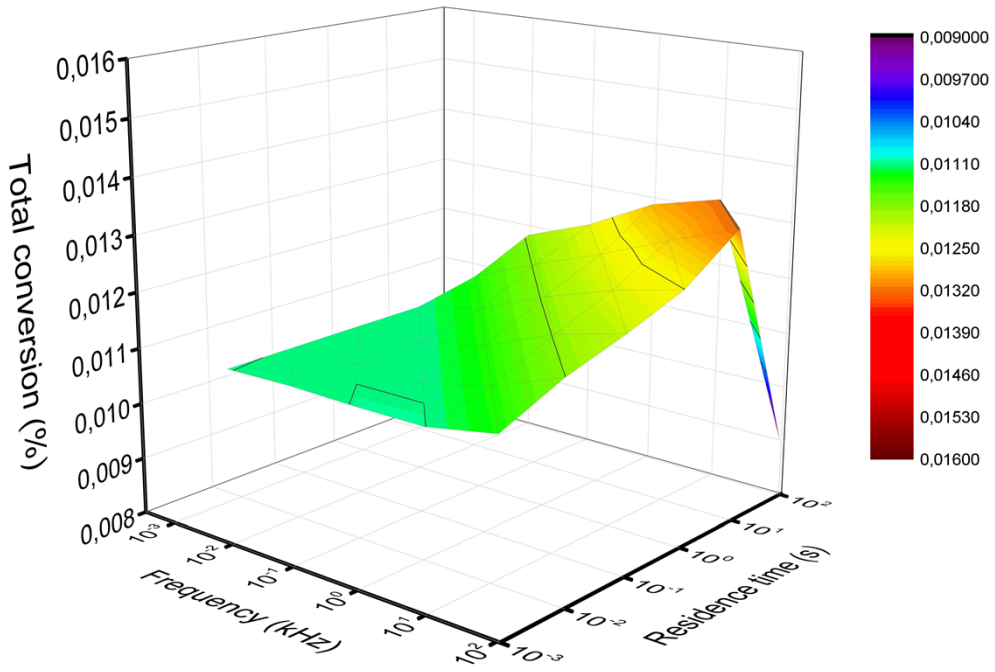

Figure S2(a). Total simulated conversion for a 25-75 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0.01 J/cm³.

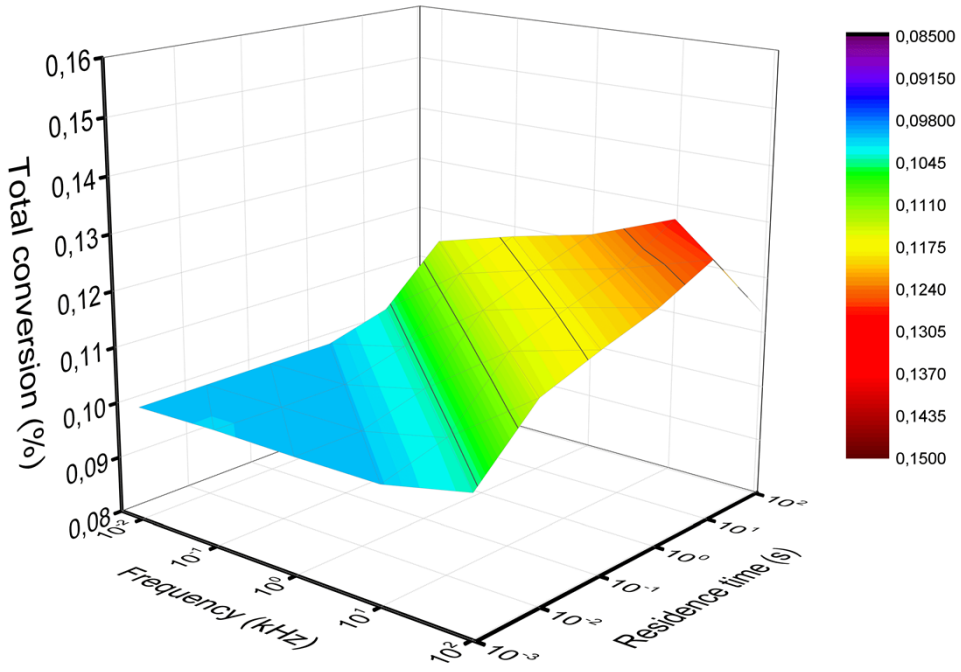

Figure S2(b). Total simulated conversion for a 25-75 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0. 1 J/cm³.

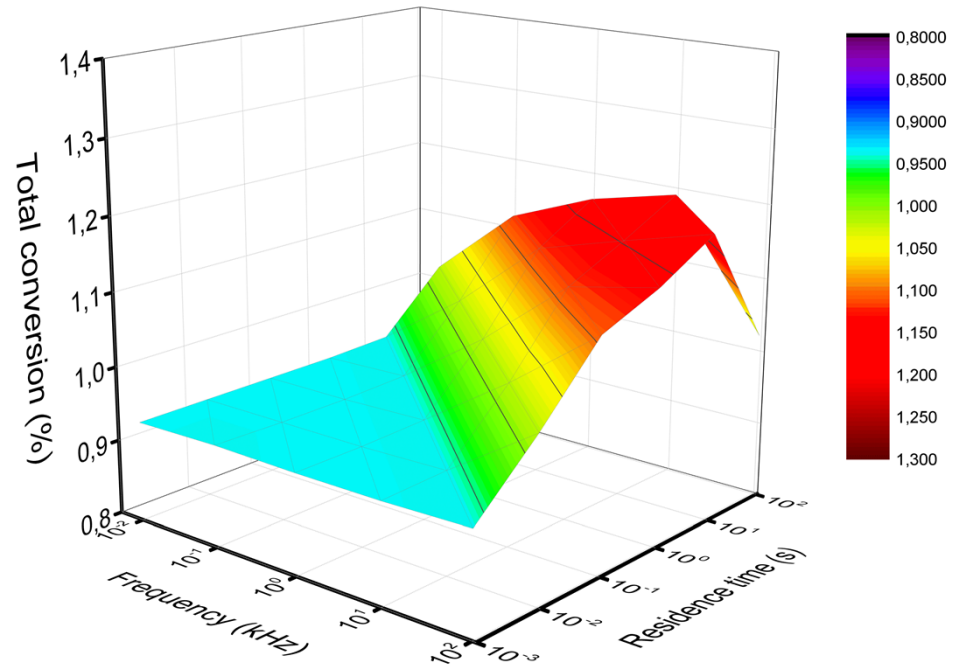

Figure S2(c). Total simulated conversion for a 25-75 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 1 J/cm³.

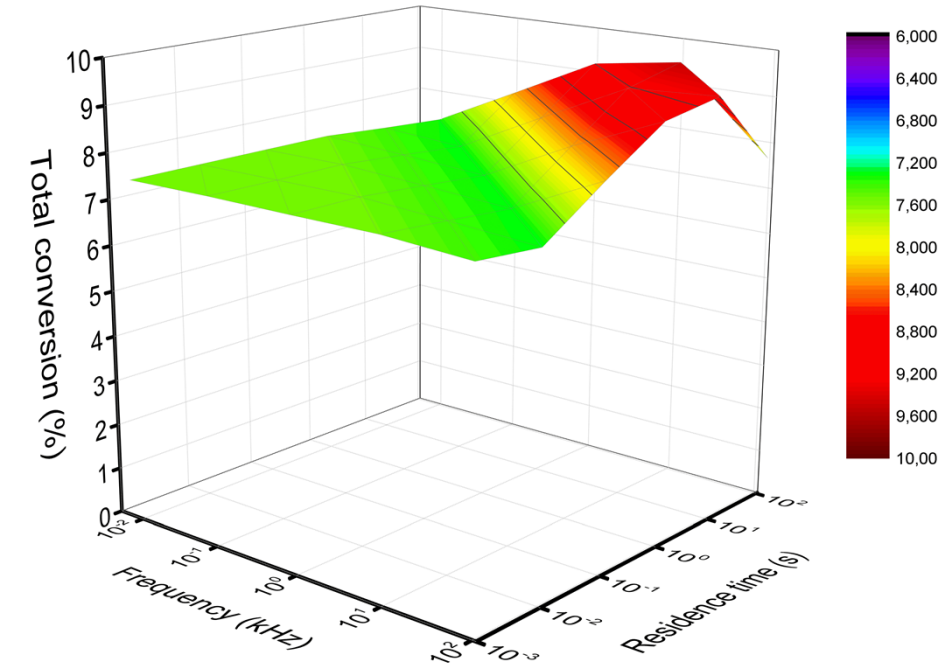

Figure S2(d). Total simulated conversion for a 25-75 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 10 J/cm³.

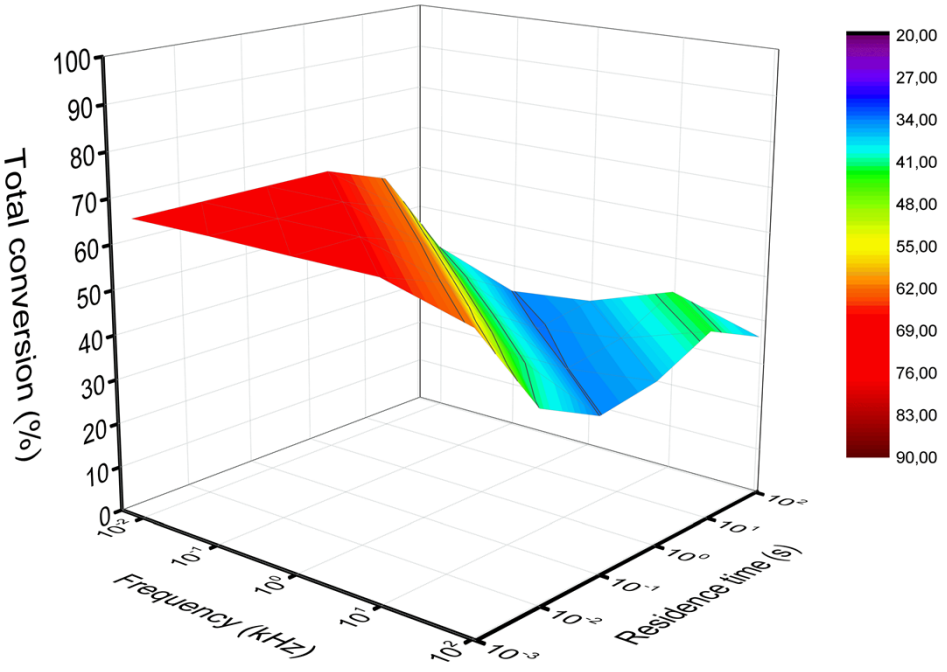

Figure S2(e). Total simulated conversion for a 25-75 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 100 J/cm³.

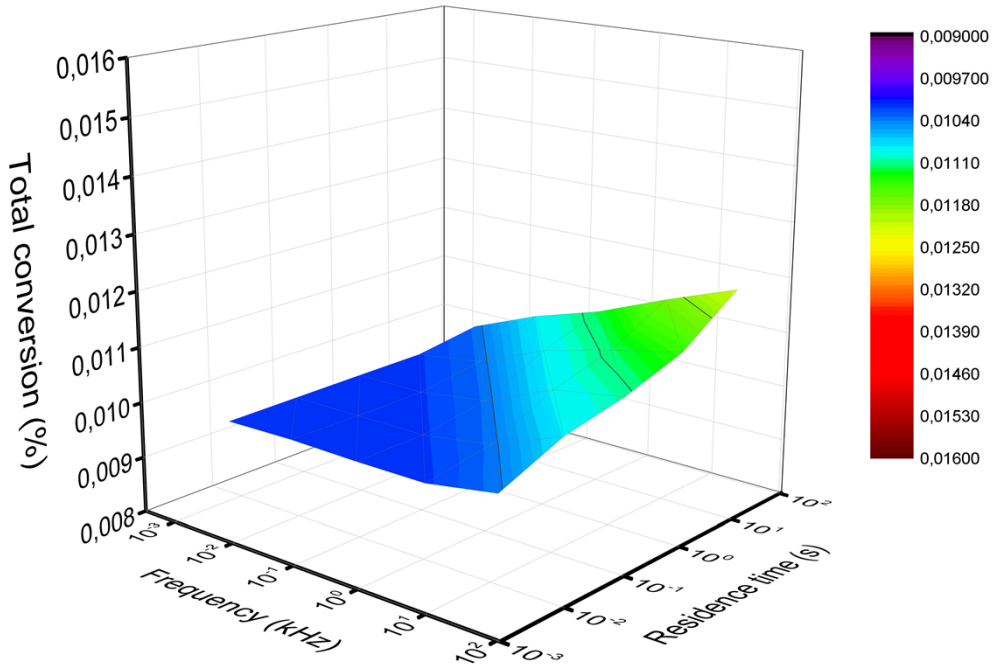

Figure S3(a). Total simulated conversion for a 50-50 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0.01 J/cm³.

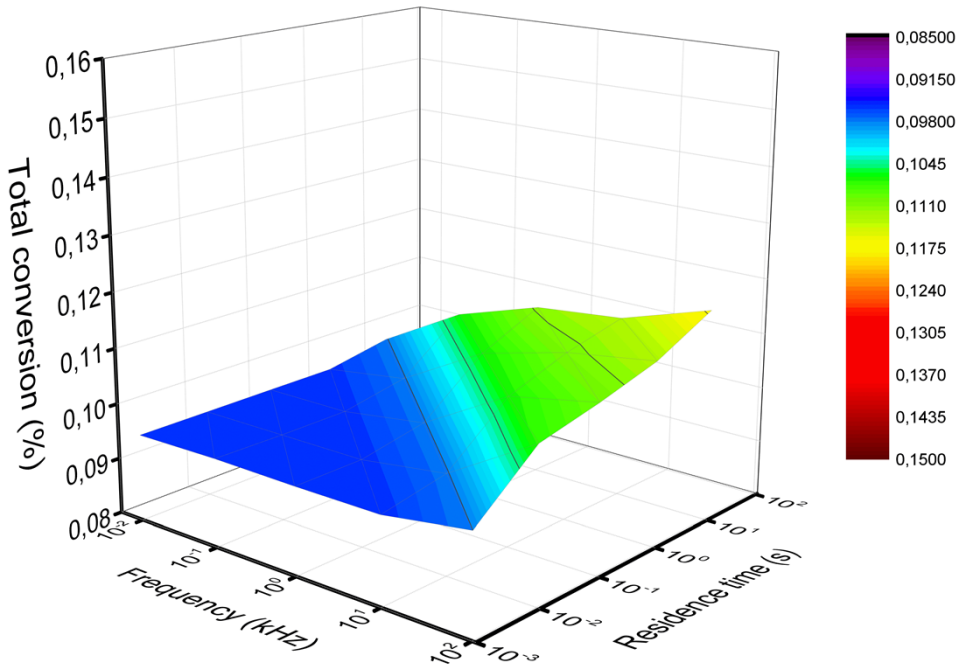

Figure S3(b). Total simulated conversion for a 50-50 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0. 1 J/cm³.

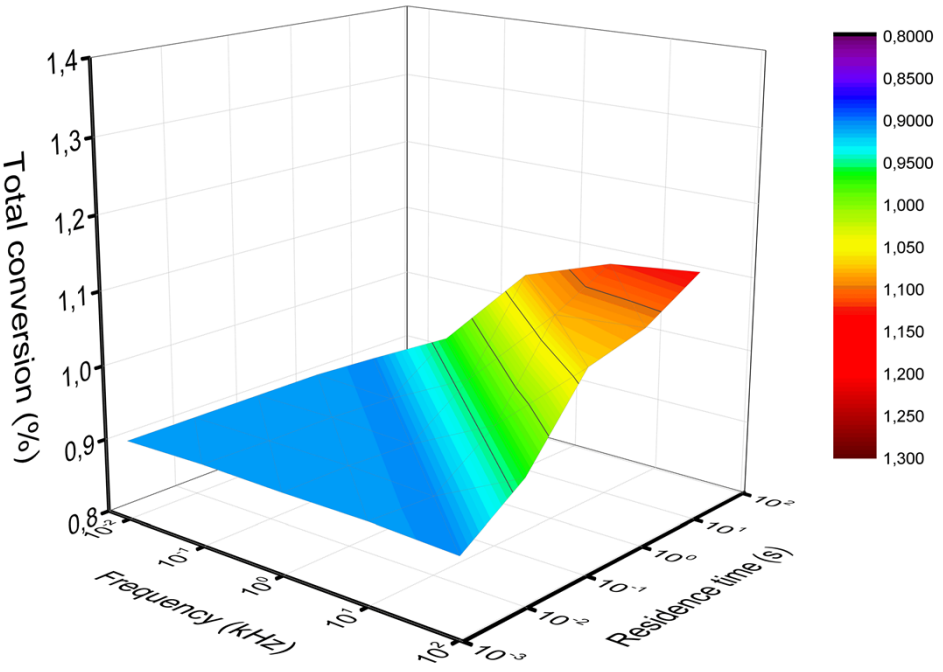

Figure S3(c). Total simulated conversion for a 50-50 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 1 J/cm³.

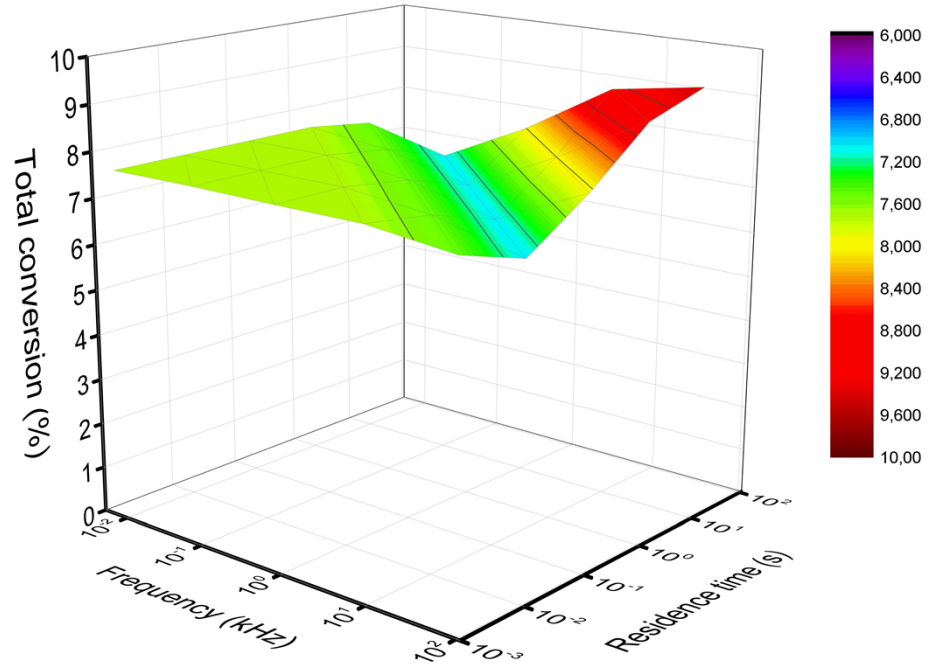

Figure S3(d). Total simulated conversion for a 50-50 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 10 J/cm³.

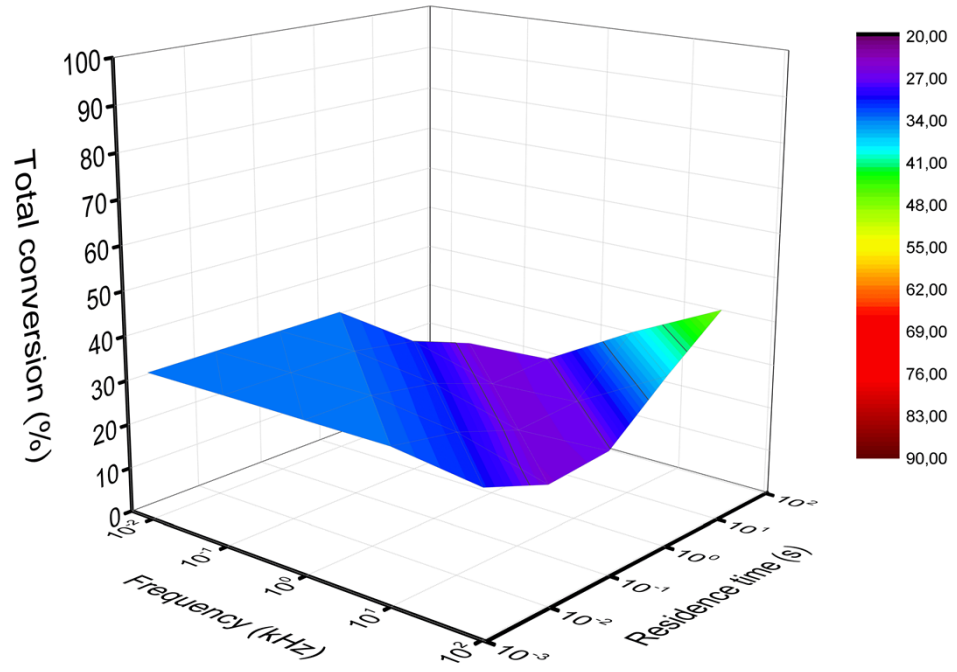

Figure S3(e). Total simulated conversion for a 50-50 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 100 J/cm³.

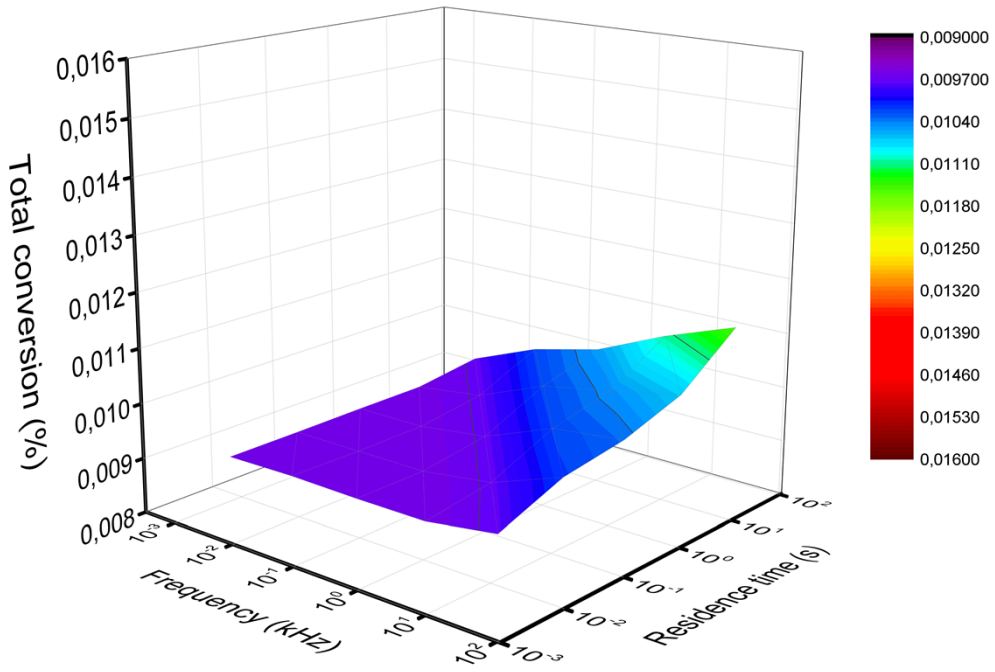

Figure S4(a). Total simulated conversion for a 75-25 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0.01 J/cm³.

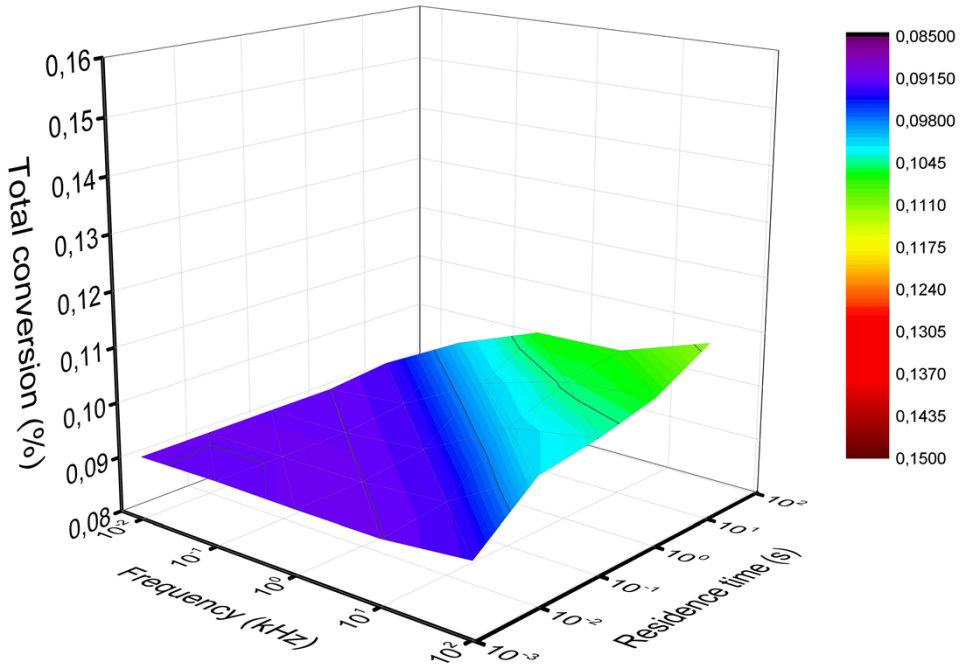

Figure S4(b). Total simulated conversion for a 75-25 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0. 1 J/cm³.

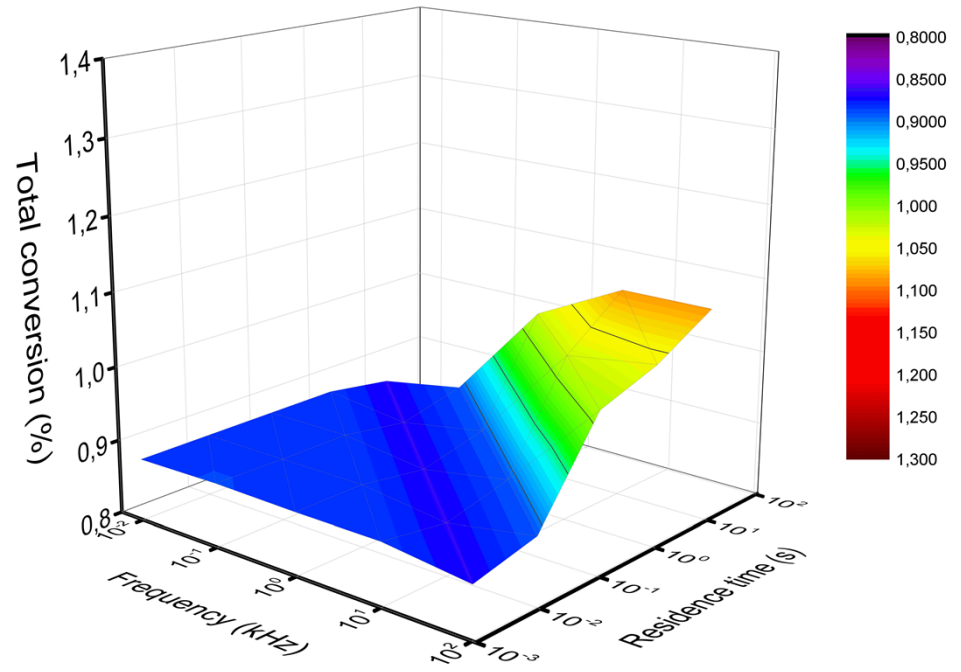

Figure S4(c). Total simulated conversion for a 75-25 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 1 J/cm³.

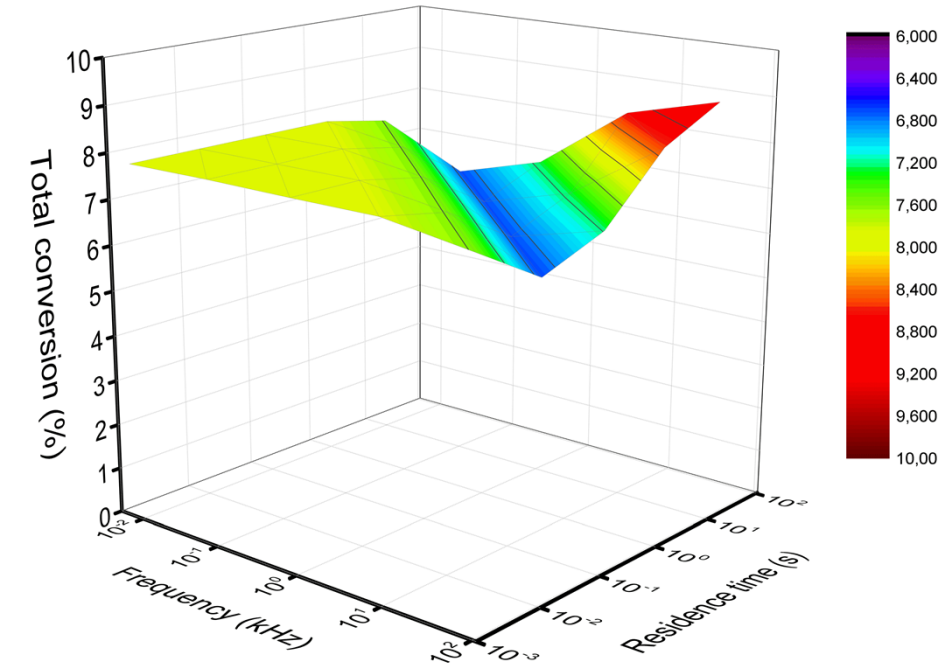

Figure S4(d). Total simulated conversion for a 75-25 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 10 J/cm³.

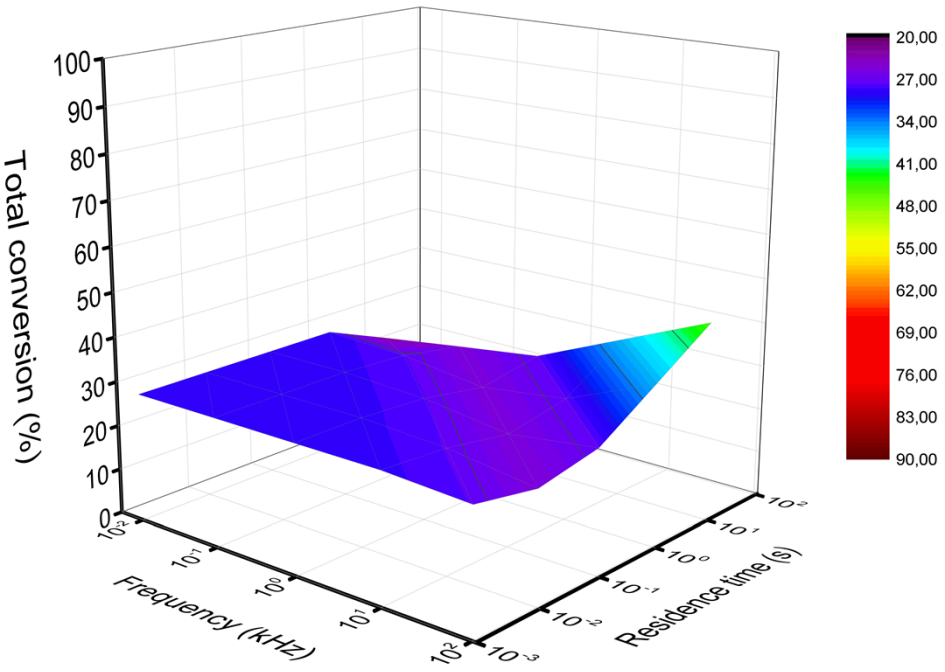

Figure S4(e). Total simulated conversion for a 75-25 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 100 J/cm³.

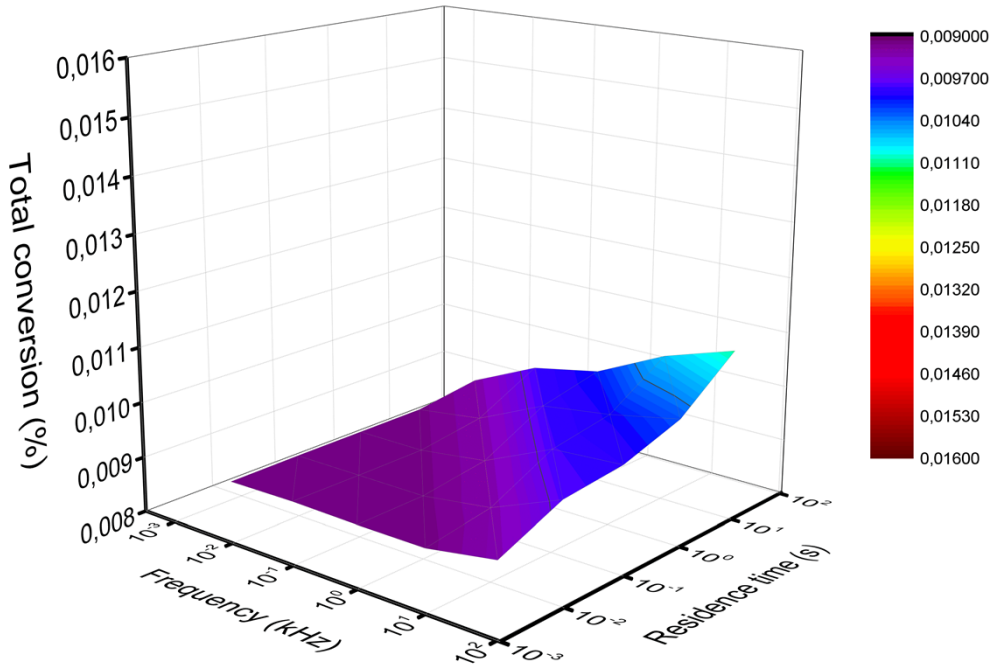

Figure S5(a). Total simulated conversion for a 90-10 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0.01 J/cm³.

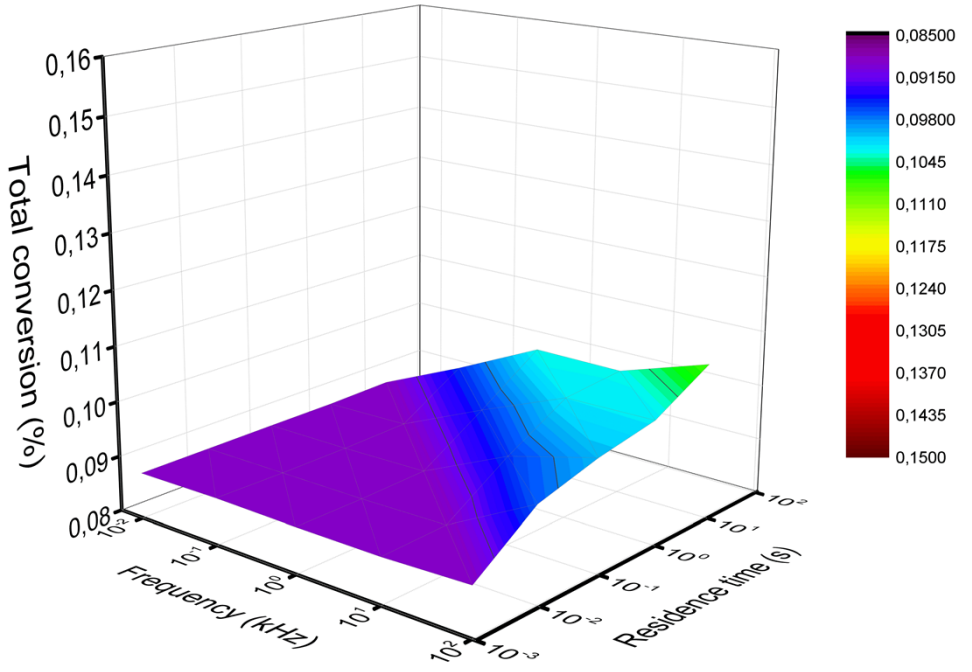

Figure S5(b). Total simulated conversion for a 90-10 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0. 1 J/cm³.

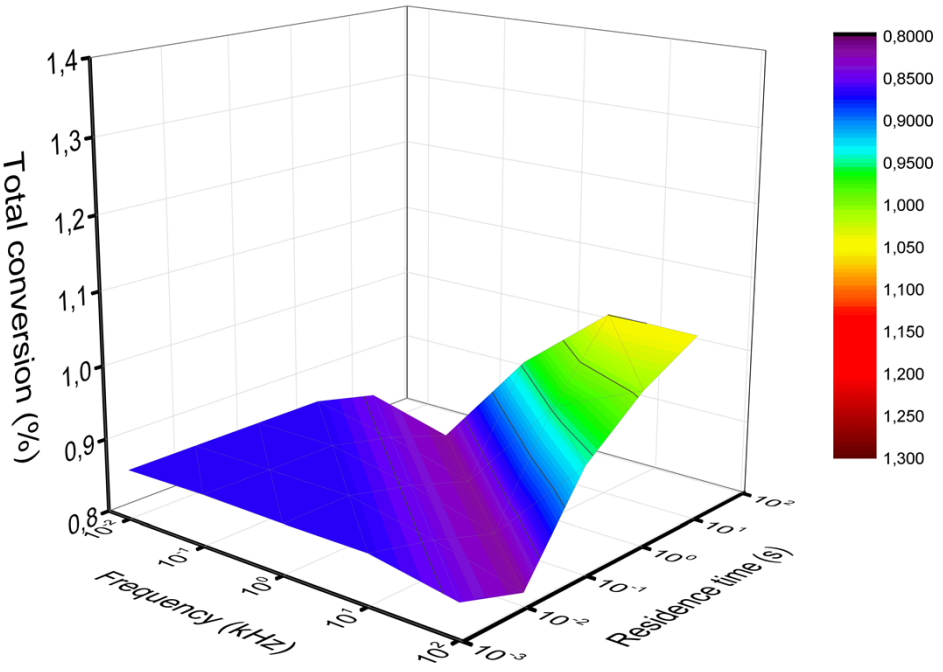

Figure S5(c). Total simulated conversion for a 90-10 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 1 J/cm³.

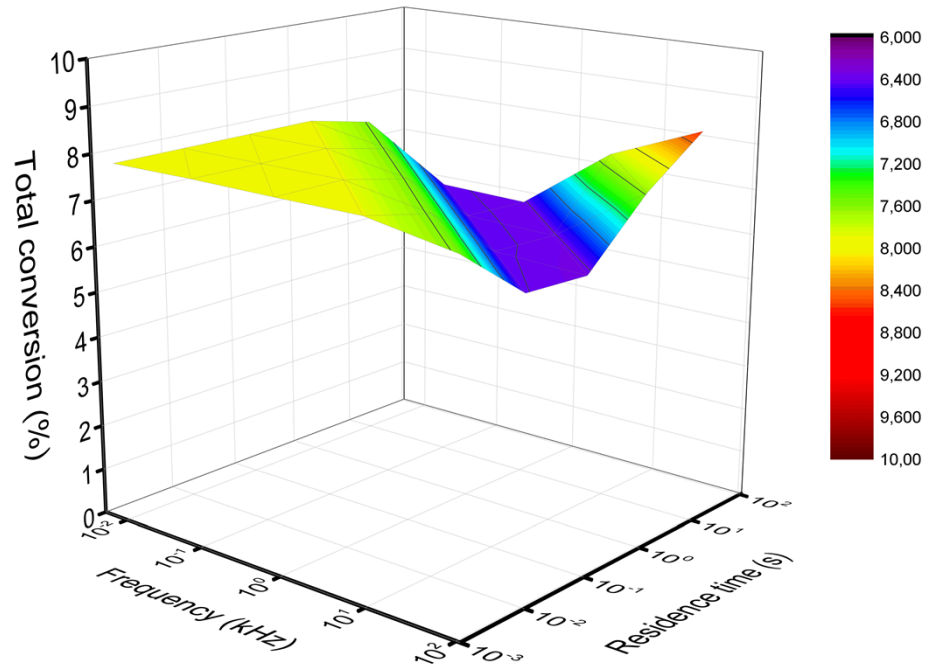

Figure S5(d). Total simulated conversion for a 90-10 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 10 J/cm³.

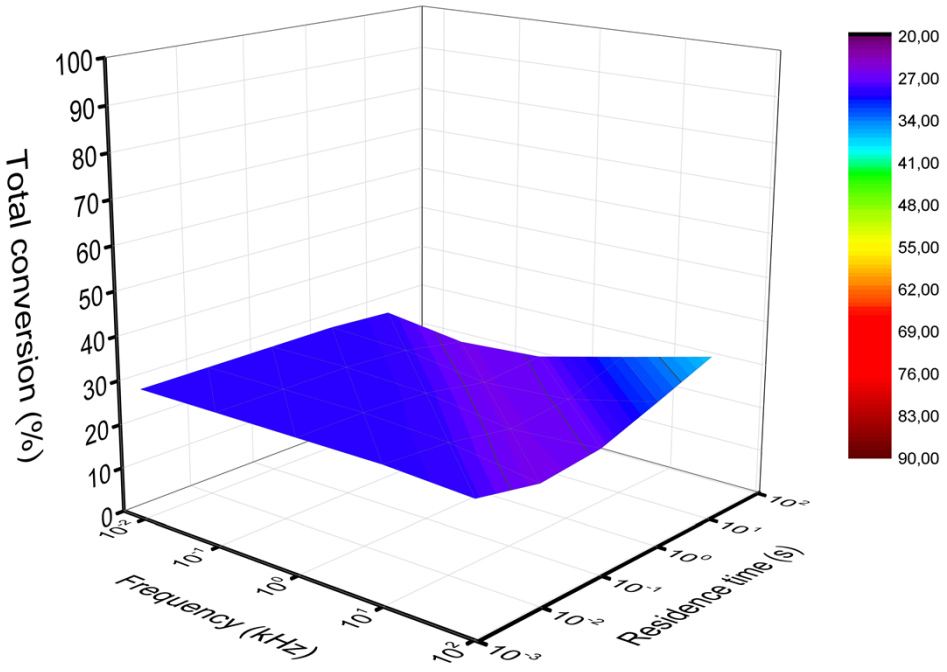

Figure S5(e). Total simulated conversion for a 90-10 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 100 J/cm³.

2.2. Energy efficiency as a function of residence time and frequency for each SEI value and CH_4-CO_2 ratio investigated (Figure S6-S10)

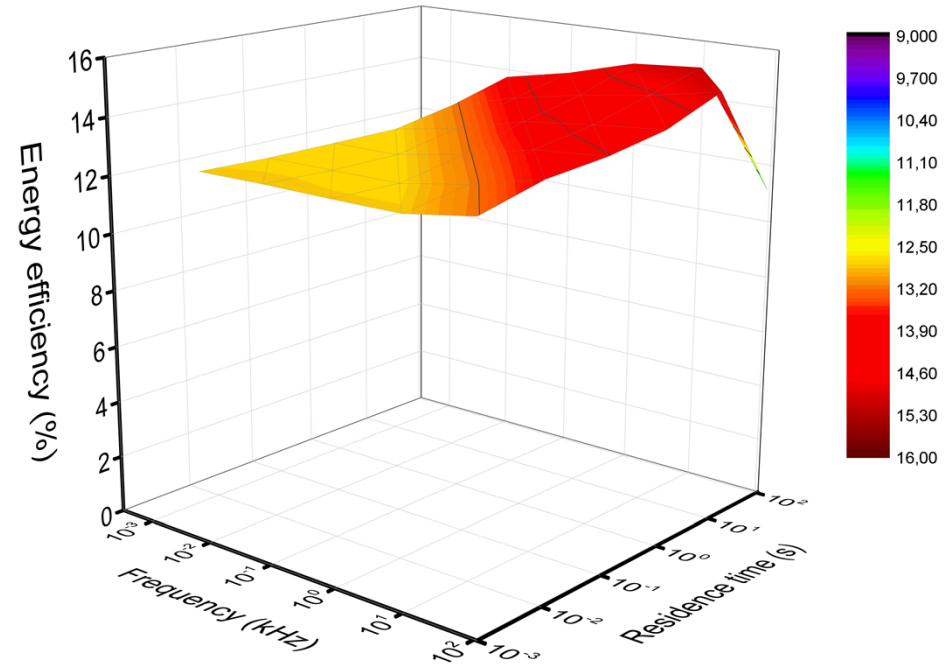

Figure S6(a). Simulated energy efficiency for a 10-90 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0.01 J/cm³.

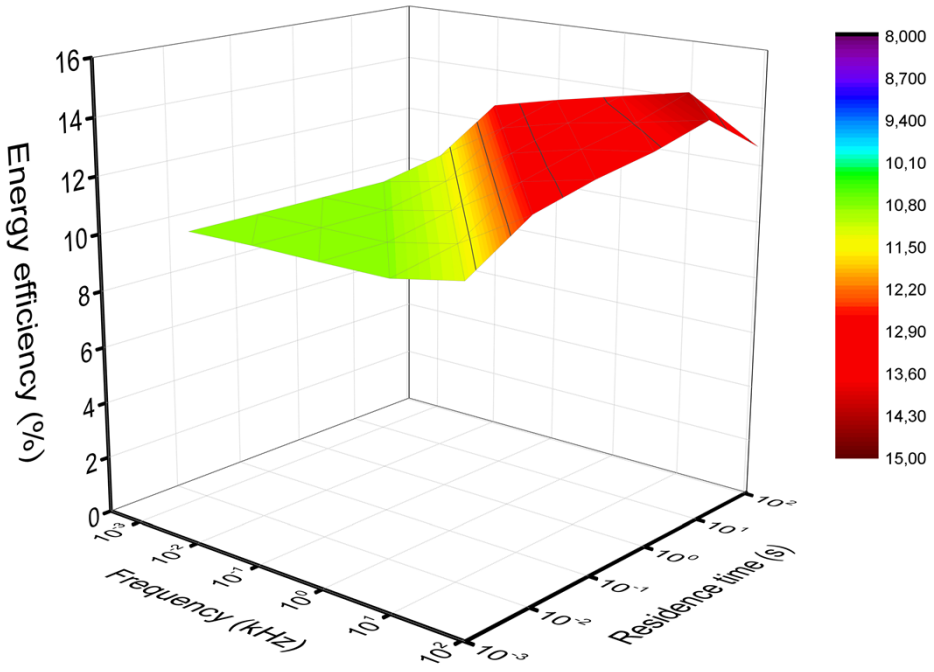

Figure S6(b). Simulated energy efficiency for a 10-90 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0. 1 J/cm³.

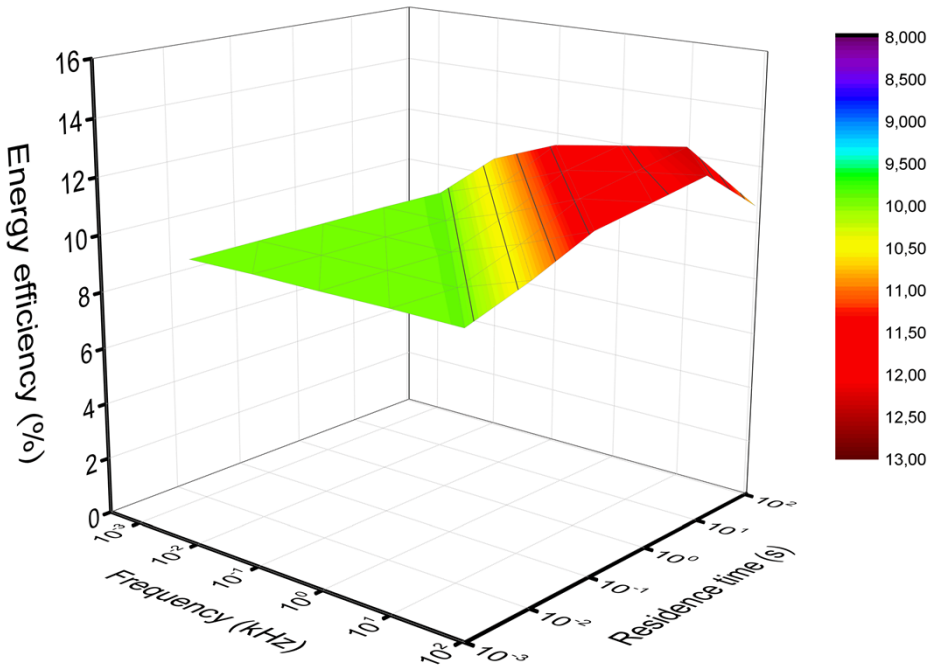

Figure S6(c). Simulated energy efficiency for a 10-90 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 1 J/cm³.

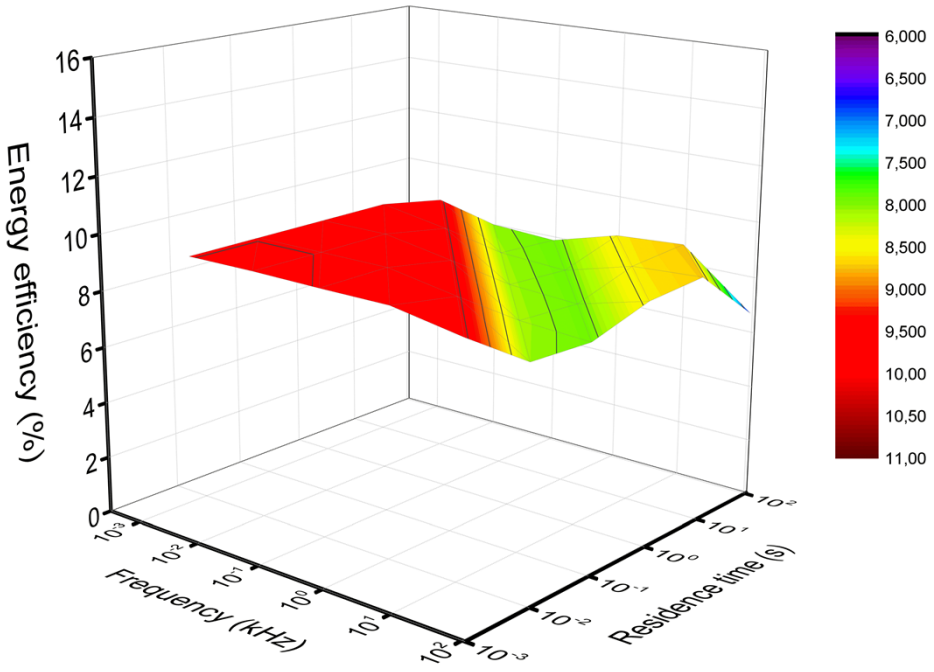

Figure S6(d). Simulated energy efficiency for a 10-90 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 10 J/cm³.

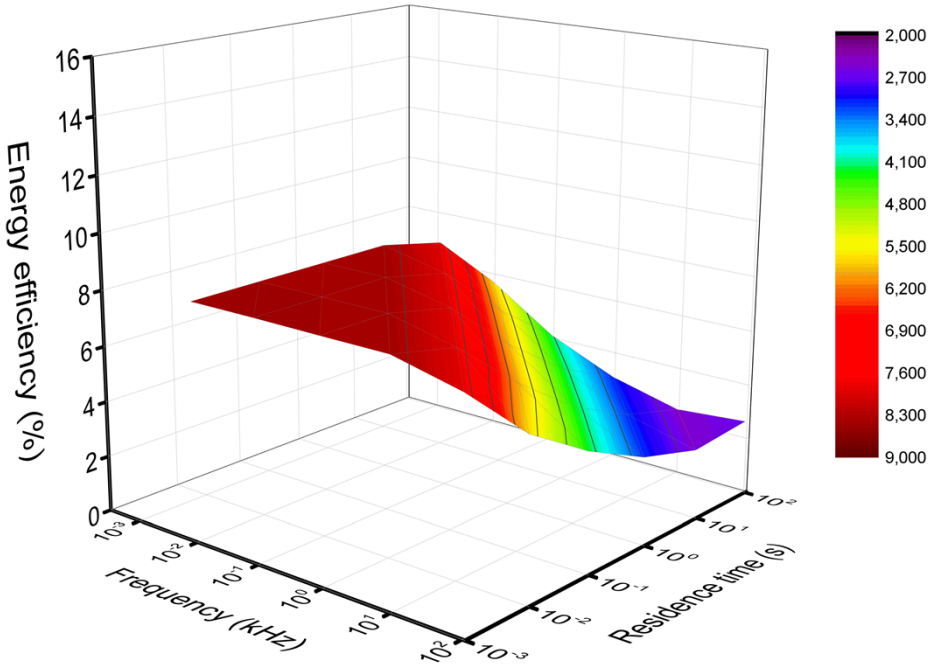

Figure S6(e). Simulated energy efficiency for a 10-90 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 100 J/cm³.

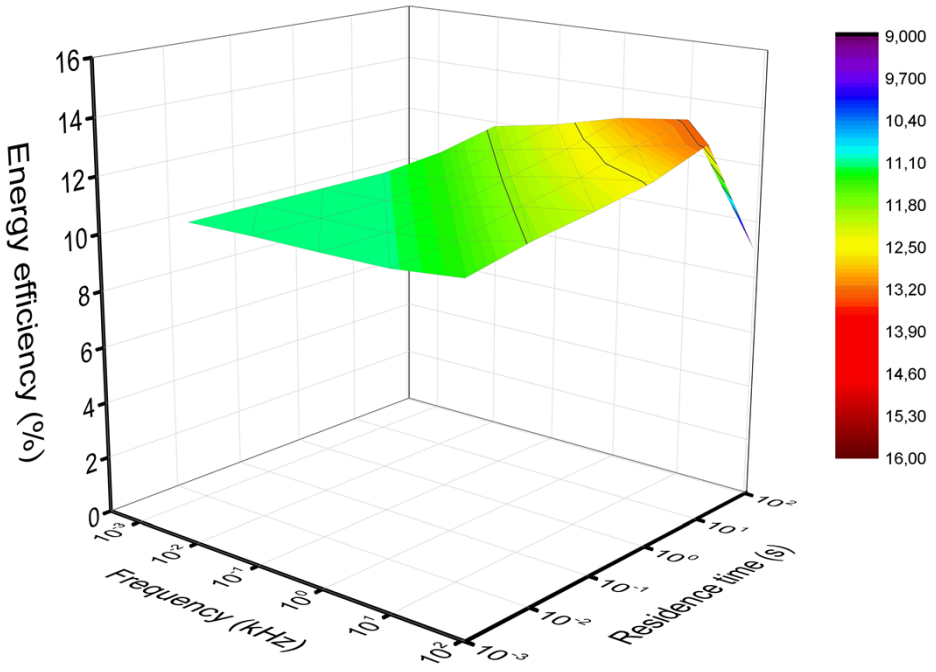

Figure S7(a). Simulated energy efficiency for a 25-75 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0.01 J/cm³.

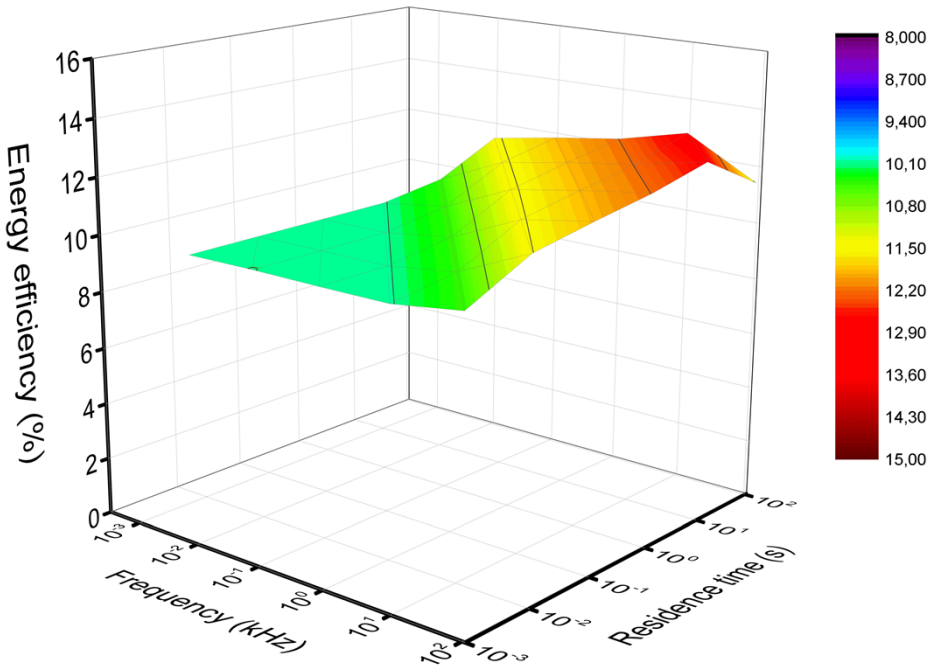

Figure S7(b). Simulated energy efficiency for a 25-75 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0. 1 J/cm³.

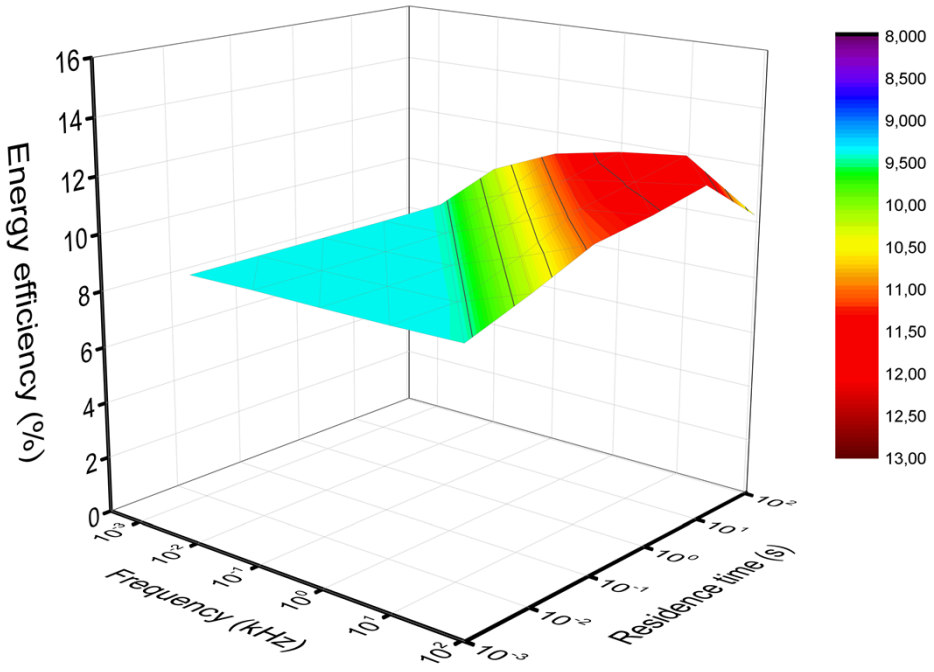

Figure S7(c). Simulated energy efficiency for a 25-75 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 1 J/cm³.

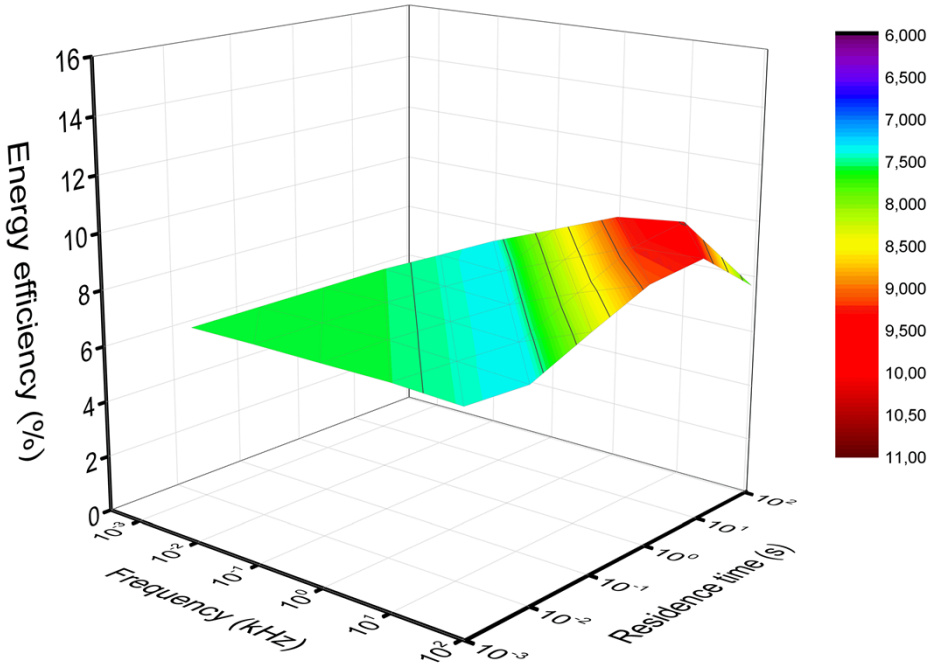

Figure S7(d). Simulated energy efficiency for a 25-75 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 10 J/cm³.

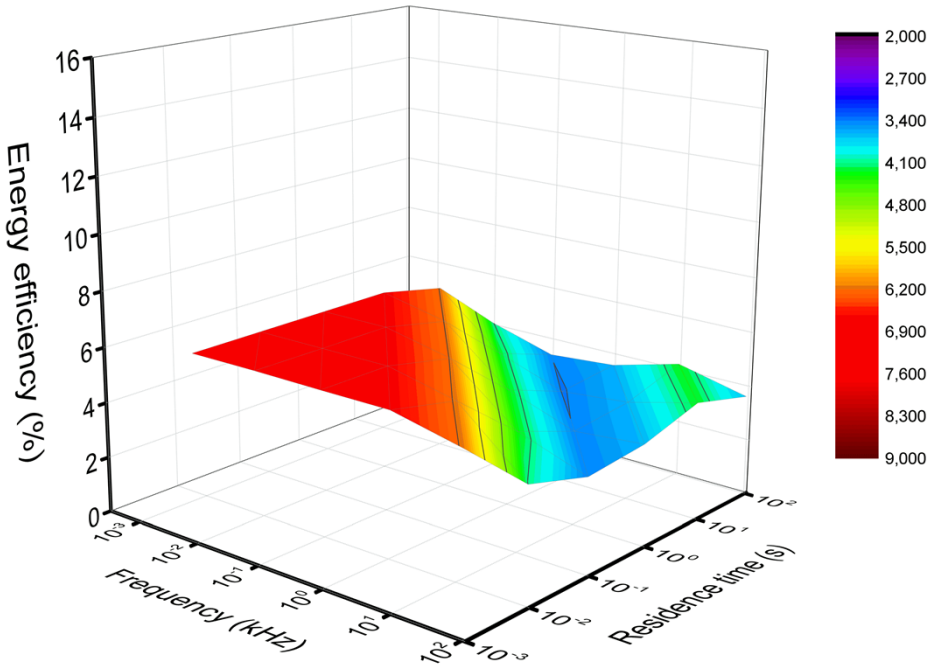

Figure S7(e). Simulated energy efficiency for a 25-75 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 100 J/cm³.

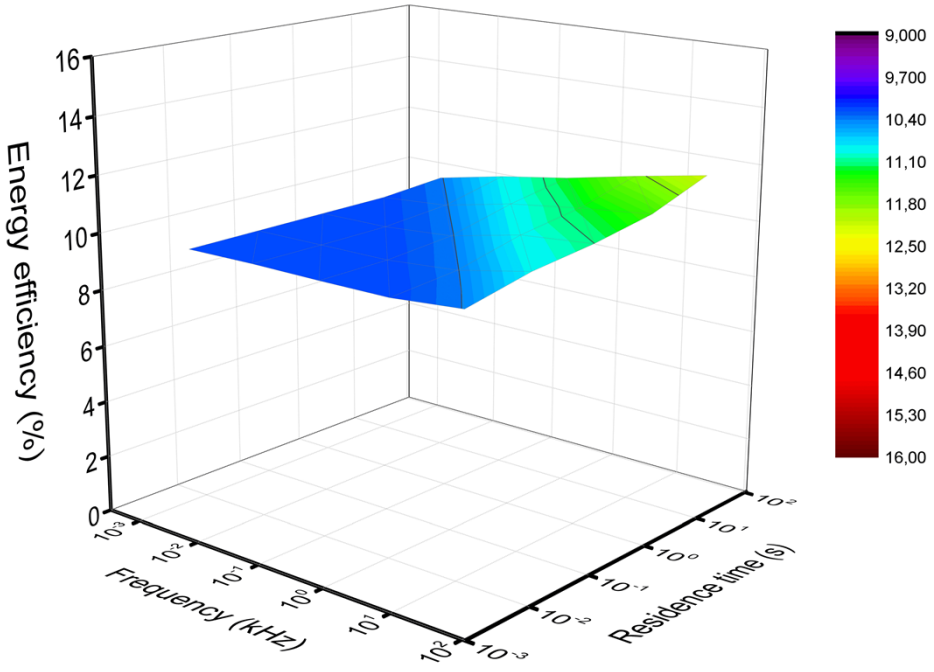

Figure S8(a). Simulated energy efficiency for a 50-50 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0.01 J/cm³.

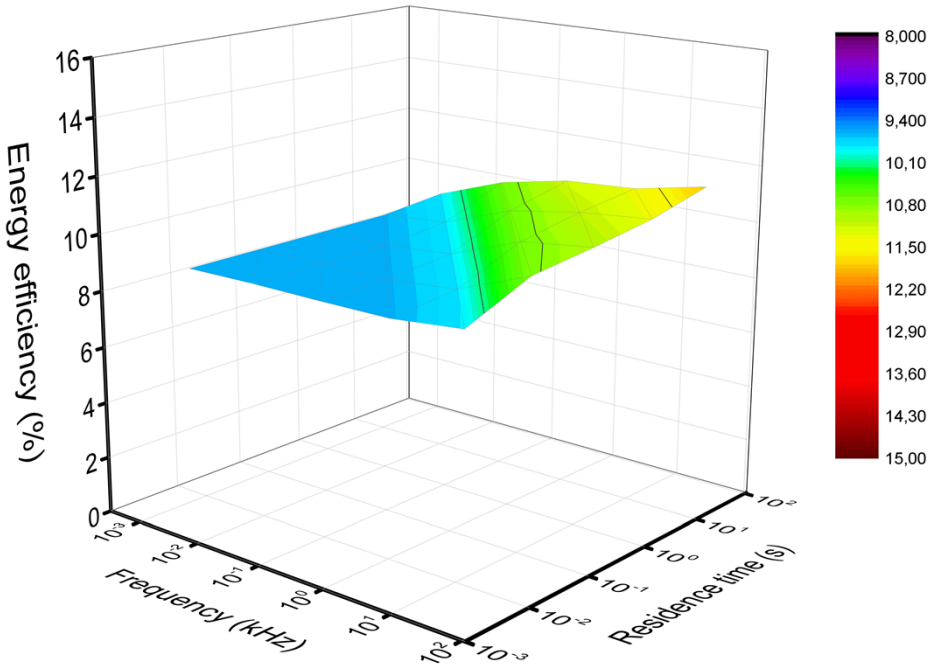

Figure S8(b). Simulated energy efficiency for a 50-50 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0. 1 J/cm³.

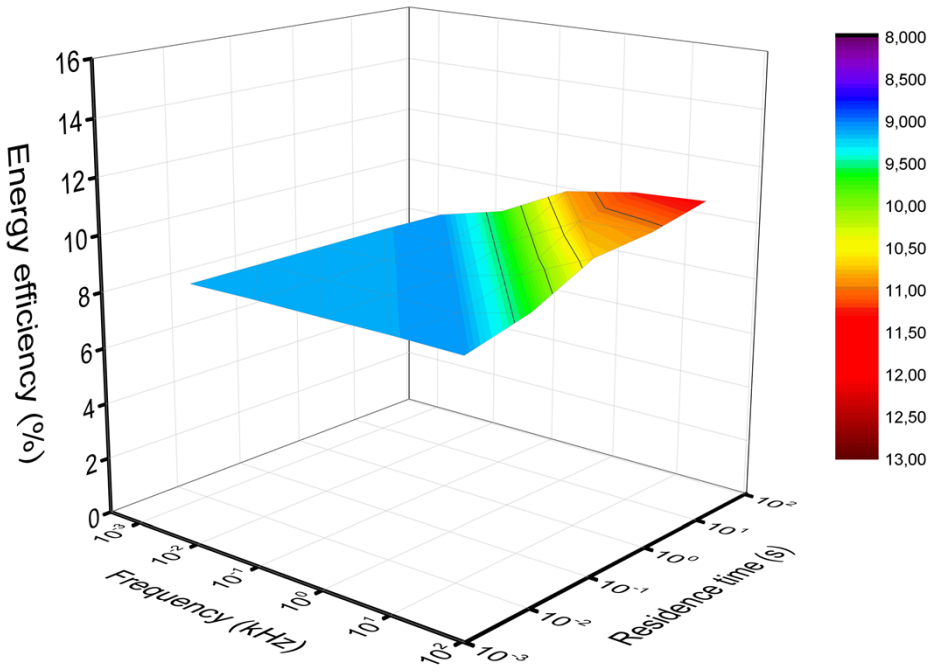

Figure S8(c). Simulated energy efficiency for a 50-50 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 1 J/cm³.

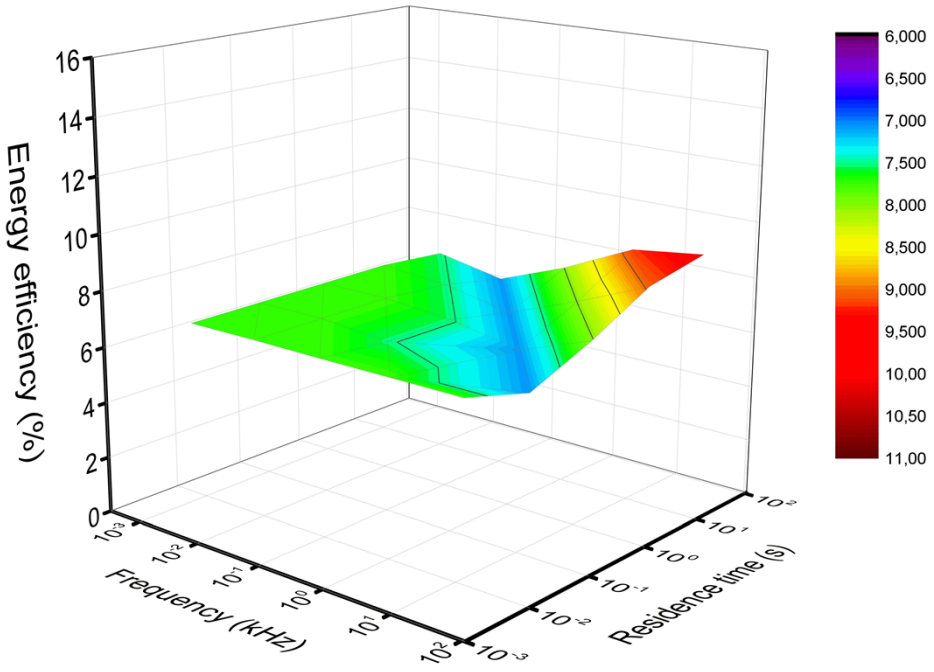

Figure S8(d). Simulated energy efficiency for a 50-50 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 10 J/cm³.

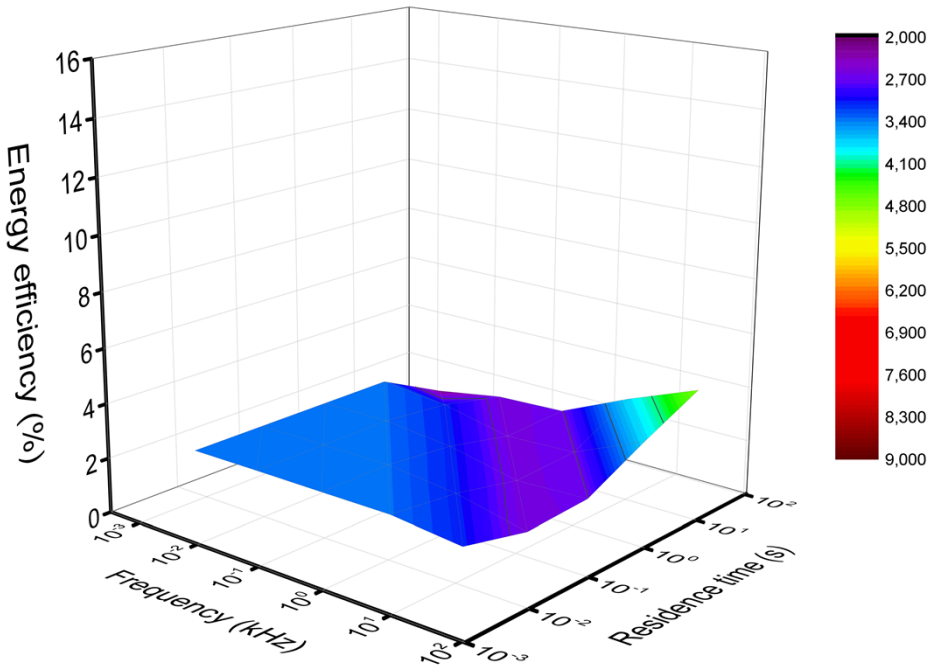

Figure S8(e). Simulated energy efficiency for a 50-50 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 100 J/cm³.

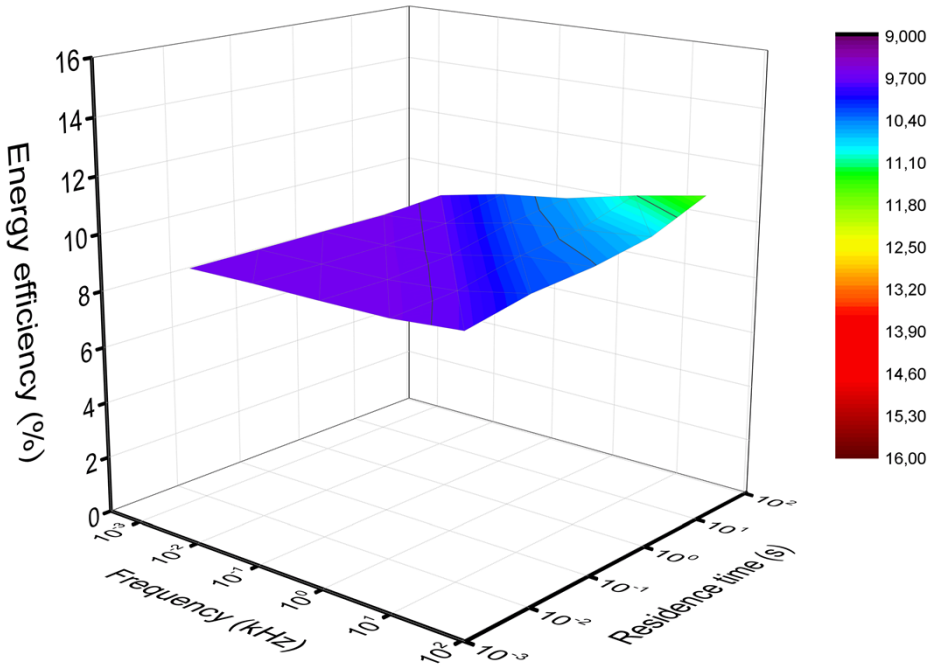

Figure S9(a). Simulated energy efficiency for a 75-25 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0.01 J/cm³.

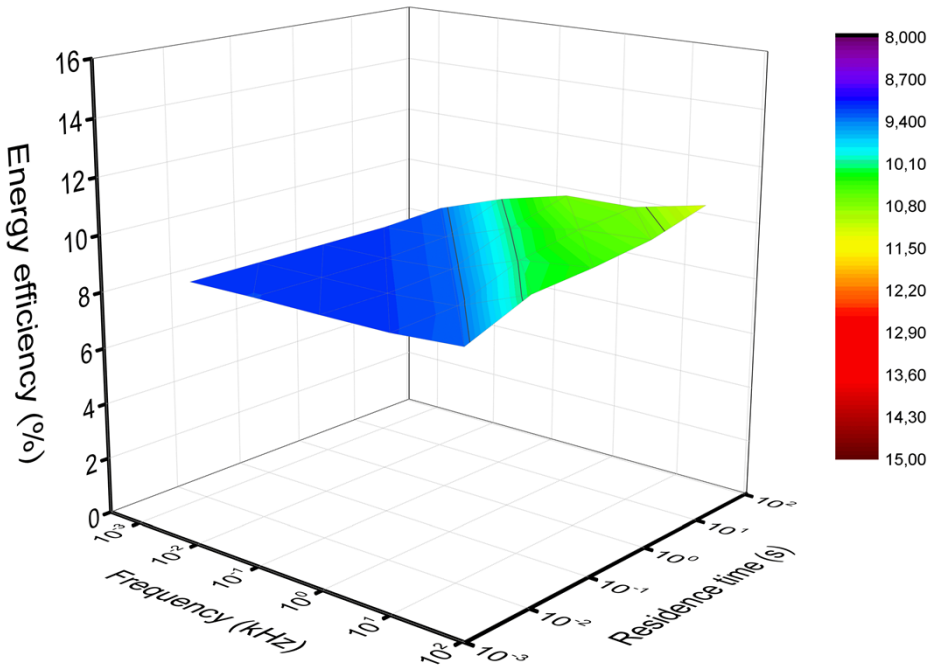

Figure S9(b). Simulated energy efficiency for a 75-25 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0. 1 J/cm³.

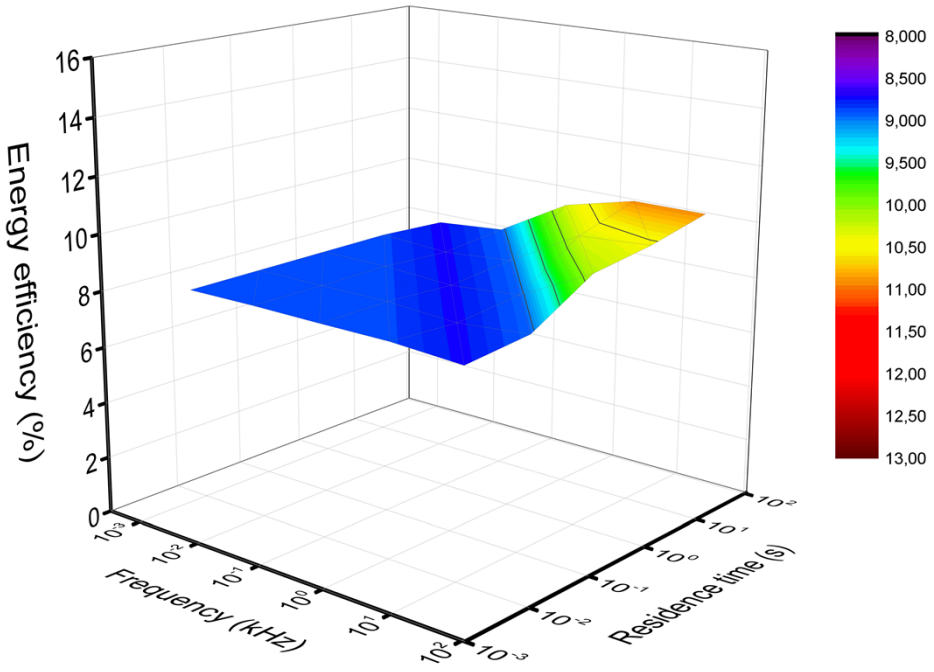

Figure S9(c). Simulated energy efficiency for a 75-25 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 1 J/cm³.

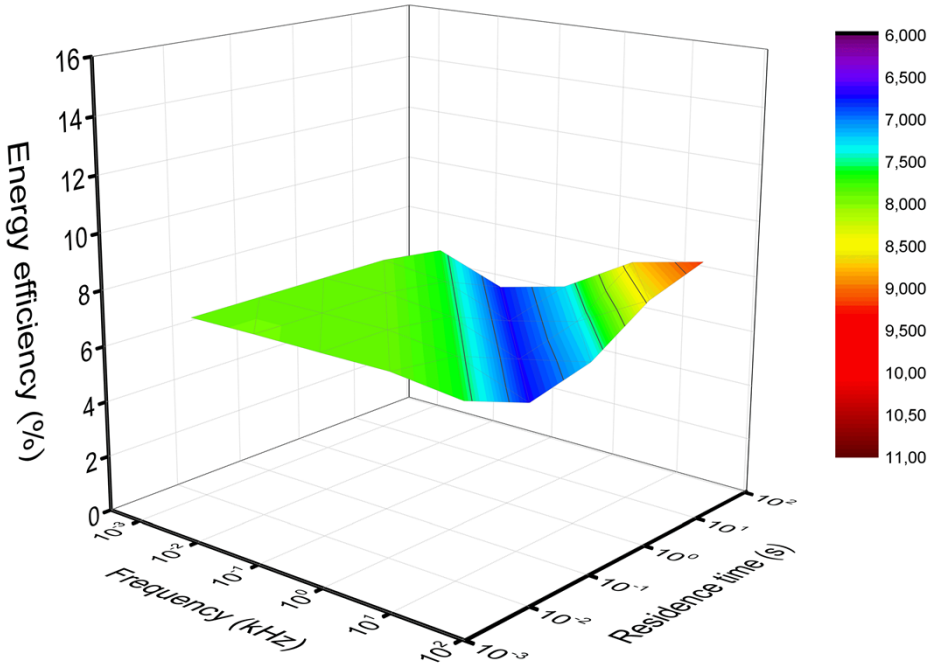

Figure S9(d). Simulated energy efficiency for a 75-25 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 10 J/cm³.

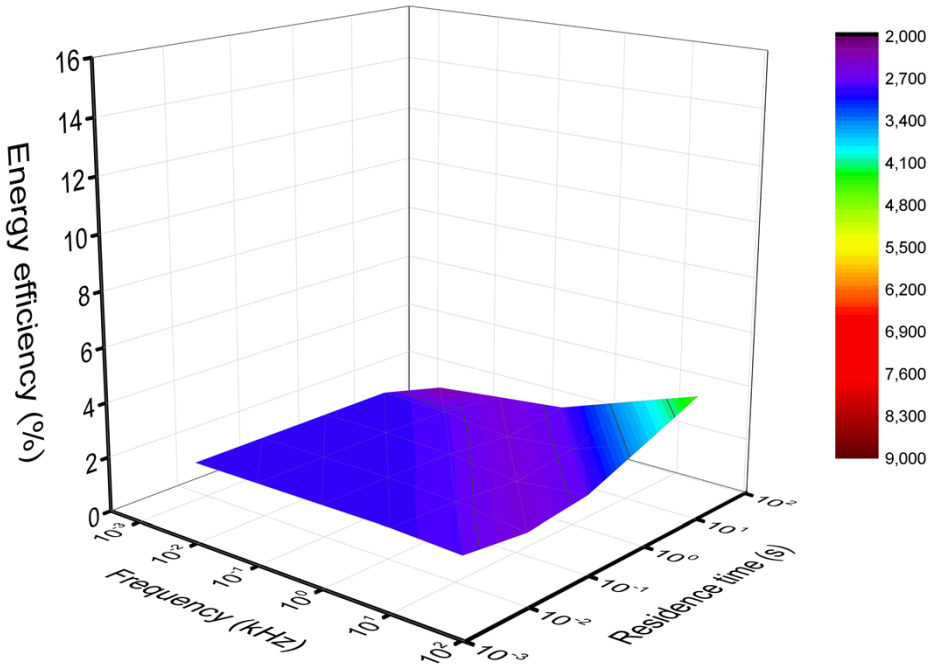

Figure S9(e). Simulated energy efficiency for a 75-25 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 100 J/cm³.

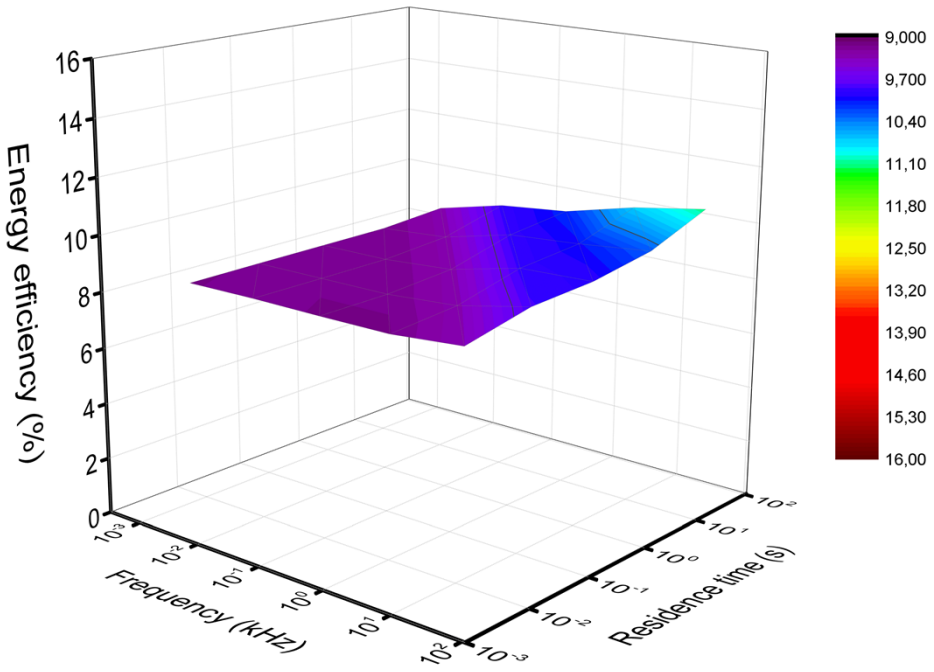

Figure S10(a). Simulated energy efficiency for a 90-10 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0.01 J/cm³.

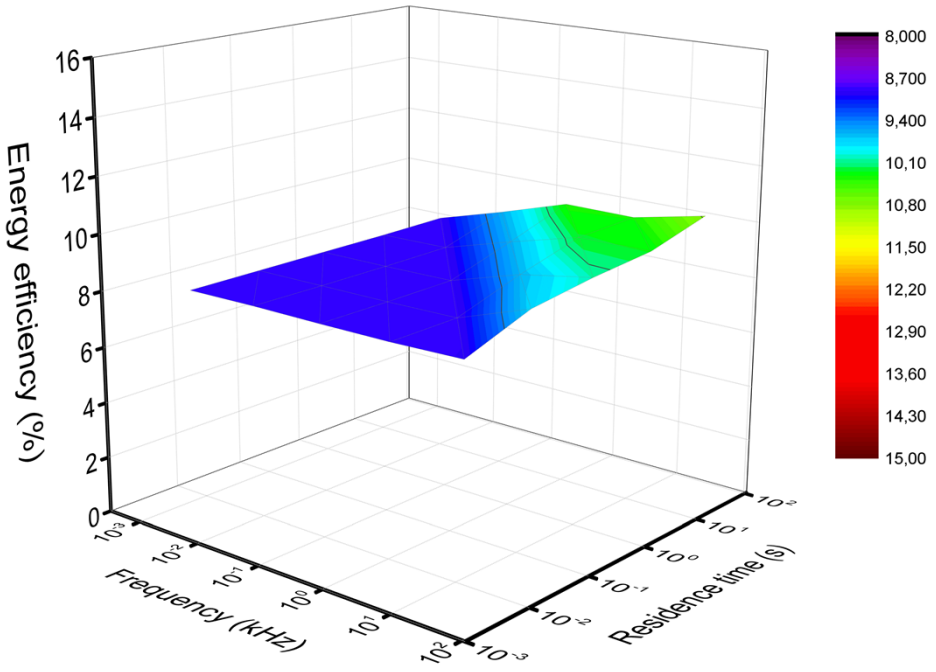

Figure S10(b). Simulated energy efficiency for a 90-10 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 0. 1 J/cm³.

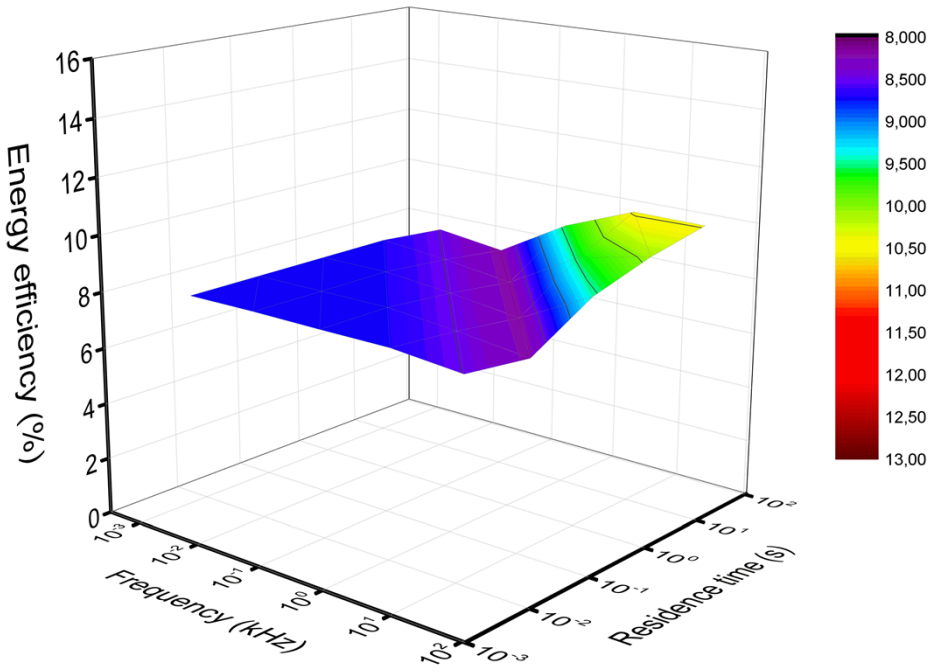

Figure S10(c). Simulated energy efficiency for a 90-10 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 1 J/cm³.

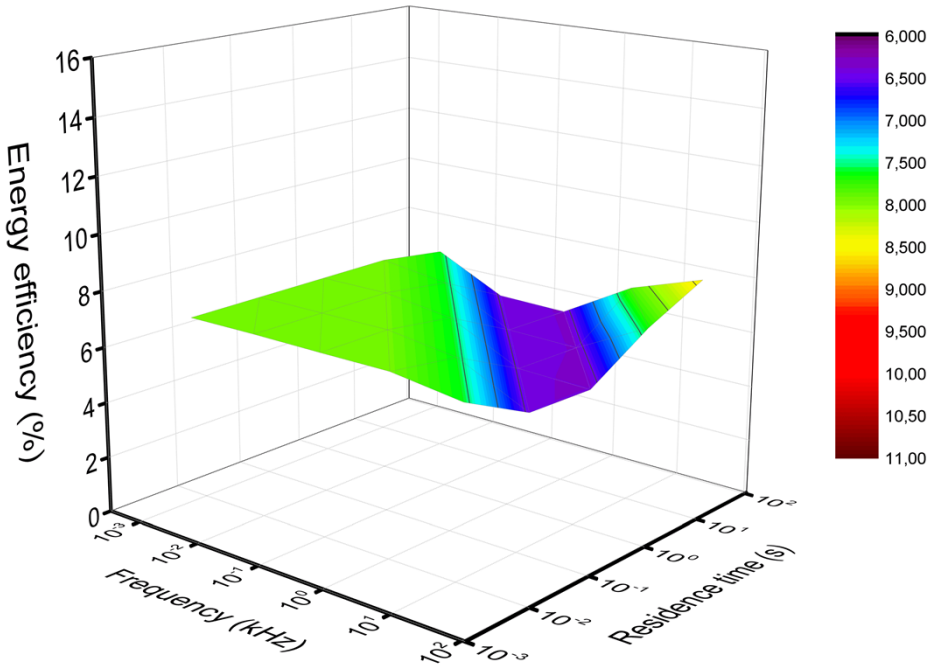

Figure S10(d). Simulated energy efficiency for a 90-10 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 10 J/cm³.

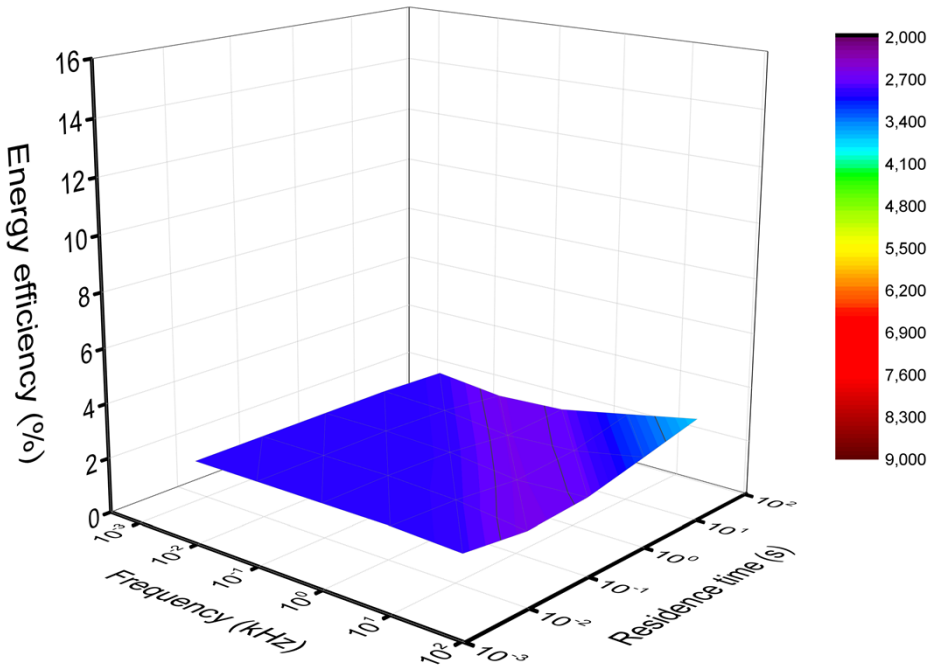

Figure S10(e). Simulated energy efficiency for a 90-10 CH_4-CO_2 ratio as a function of the residence time and frequency for an SEI of 100 J/cm³.

2.3. Calculated Maximum and Minimum Achieved Values of Energy Efficiency vs Total Conversion

Table S3. Overview of the minimum achieved values of energy efficiency vs total conversion as obtained from the calculations, for all conditions investigated.

CH_4-CO_2 Ratio	*SEI (J/cm³)*	*Conversion (%)*	*Energy Efficiency (%)*	*Residence Time (s)*	*Frequency (kHz)*
10 - 90	0.01	0.0111	11.1	100	100
25 - 75	0.01	0.00905	9.08	100	100
50 - 50	0.01	0.00886	8.89	100	100
75 - 25	0.01	0.00848	8.51	100	100
90 - 10	0.01	0.00763	7.66	100	100
10 - 90	0.1	0.108	10.8	1	0.01
25 - 75	0.1	0.100	10.1	0.001	1
50 - 50	0.1	0.0956	9.59	0.001	1
75 - 25	0.1	0.0914	9.17	0.001	1
90 - 10	0.1	0.0883	8.86	0.001	1
10 - 90	1	0.986	9.89	10	0.01
25 - 75	1	0.934	9.37	0.001	1
50 - 50	1	0.903	9.06	0.01	10
75 - 25	1	0.870	8.73	0.01	10
90 - 10	1	0.816	8.19	100	0.01
10 - 90	10	6.70	6.73	100	100
25 - 75	10	7.28	7.30	0.01	100
50 - 50	10	7.04	7.06	0.01	100
75 - 25	10	6.70	6.71	0.01	100
90 - 10	10	6.33	6.35	0.1	100
10 - 90	100	24.6	2.47	100	10
25 - 75	100	33.7	3.38	10	1
50 - 50	100	25.4	2.55	0.01	100
75 - 25	100	22.6	2.26	10	0.1
90 - 10	100	25.7	2.58	0.01	100

Table S4. Overview of the maximum achieved values of energy efficiency vs total conversion as obtained from the calculations, for all conditions investigated.

CH_4-CO_2 Ratio	***SEI (J/cm^3)***	***Conversion (%)***	***Energy Efficiency (%)***	***Residence Time (s)***	***Frequency (kHz)***
10 - 90	0.01	0.0150	15.1	100	10
25 - 75	0.01	0.0132	13.3	10	100
50 - 50	0.01	0.0122	12.2	100	10
75 - 25	0.01	0.0116	11.7	100	10
90 - 10	0.01	0.0113	11.4	100	10
10 - 90	0.1	0.142	14.2	100	10
25 - 75	0.1	0.128	12.8	100	10
50 - 50	0.1	0.119	11.9	100	10
75 - 25	0.1	0.113	11.4	100	10
90 - 10	0.1	0.110	11.0	100	10
10 - 90	1	1.23	12.3	100	10
25 - 75	1	1.19	12.0	100	10
50 - 50	1	1.14	11.4	100	10
75 - 25	1	1.10	11.0	100	10
90 - 10	1	1.06	10.7	100	10
10 - 90	10	9.99	10.0	0.001	0.1
25 - 75	10	9.49	9.52	100	10
50 - 50	10	9.63	9.66	100	10
75 - 25	10	9.32	9.36	100	10
90 - 10	10	8.75	8.78	100	10
10 - 90	100	84.2	8.45	0.001	0.1
25 - 75	100	67.0	6.72	0.001	0.1
50 - 50	100	53.5	5.37	10	100
75 - 25	100	44.7	4.49	100	10
90 - 10	100	36.9	3.70	100	10

2.4. Calculated conversion and energy efficiency as a function of the total number of micro-discharge filaments for each CH_4-CO_2 ratio investigated (Figure S11-S15)

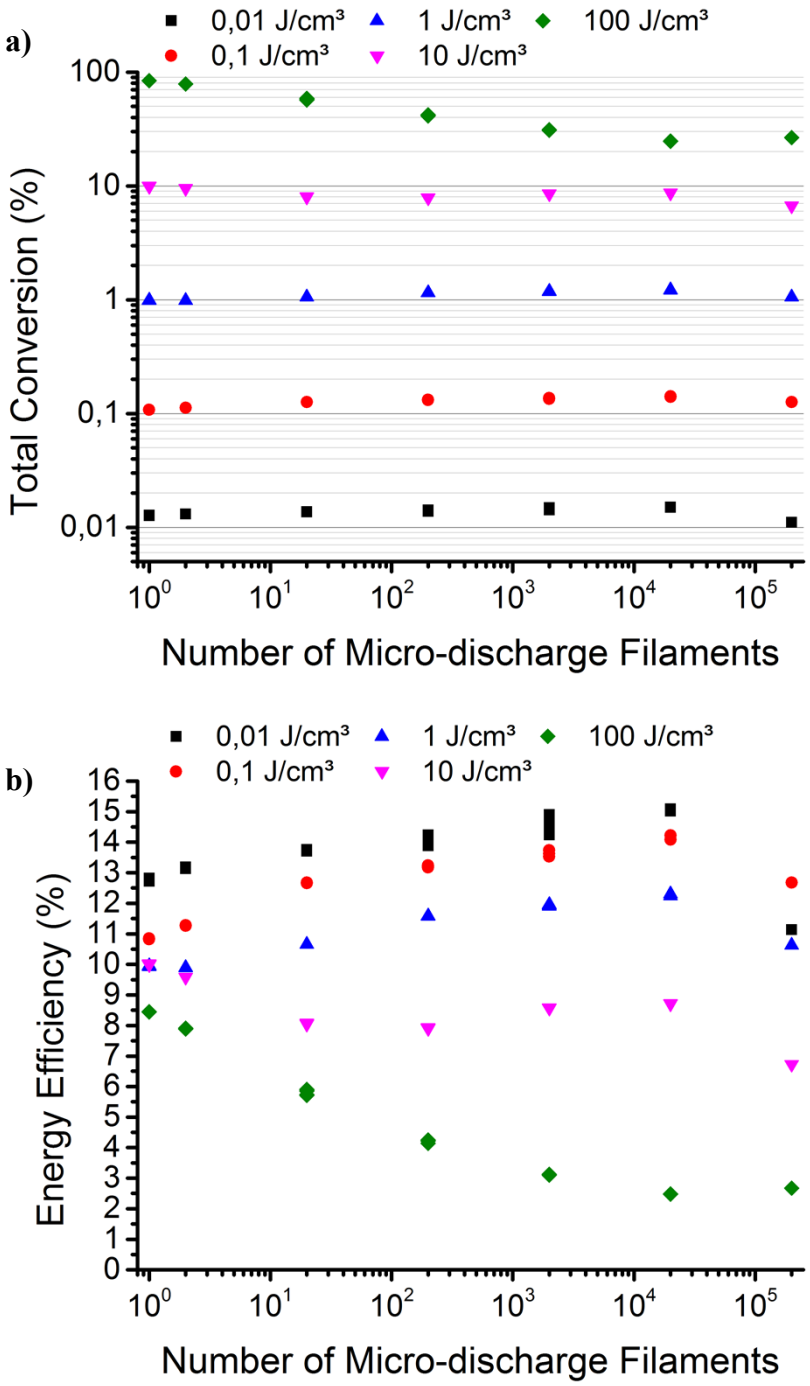

Figure S11. Calculated conversion (a) and energy efficiency (b) as a function of the total number of micro-discharge filaments (i.e., product of residence time and frequency), for all the different residence times, frequencies and SEI values investigated, for a CH_4-CO_2 mixture

of 10-90. The values corresponding to the same SEI values are indicated with the same colored symbols.

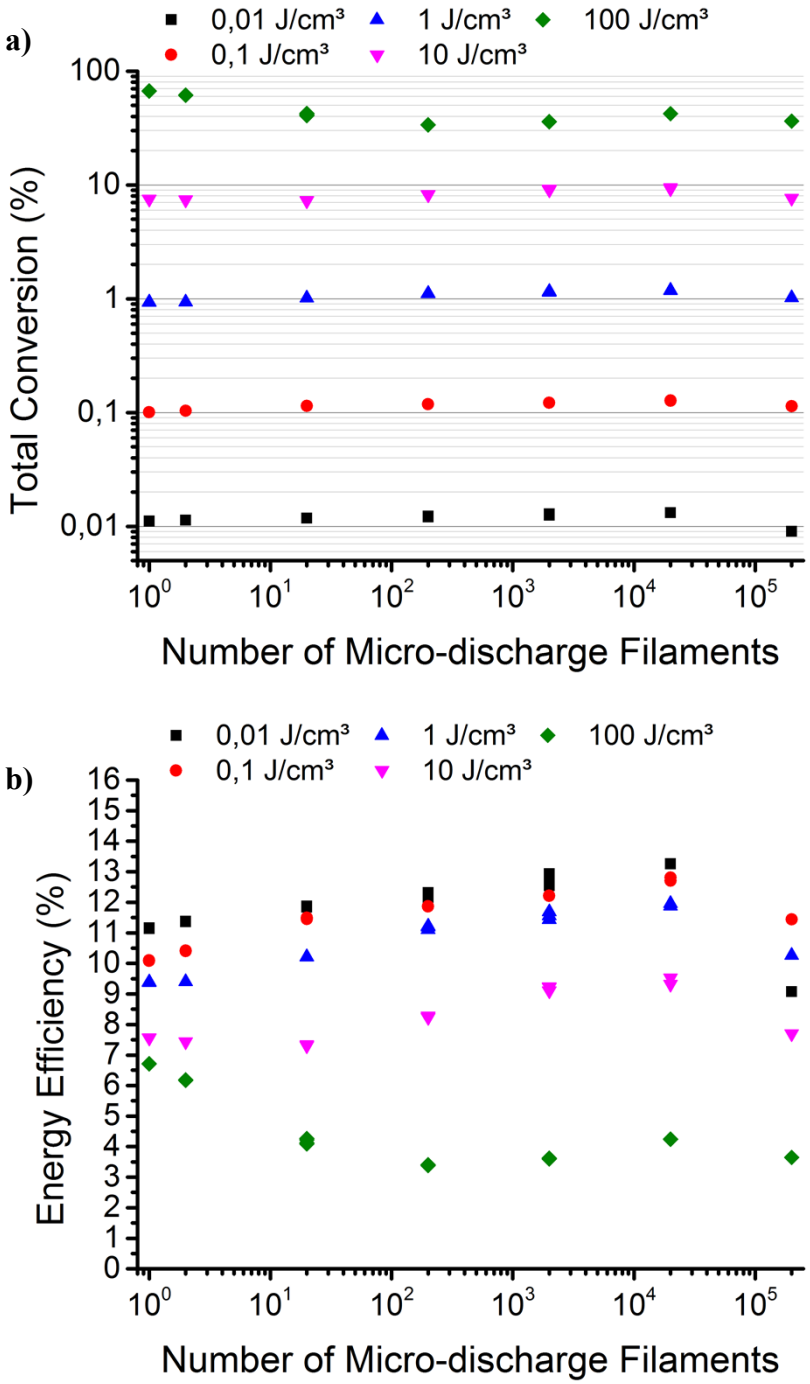

Figure S12. Calculated conversion (a) and energy efficiency (b) as a function of the total number of micro-discharge filaments (i.e., product of residence time and frequency), for all the different residence times, frequencies and SEI values investigated, for a CH_4-CO_2 mixture

of 25-75. The values corresponding to the same SEI values are indicated with the same colored symbols.

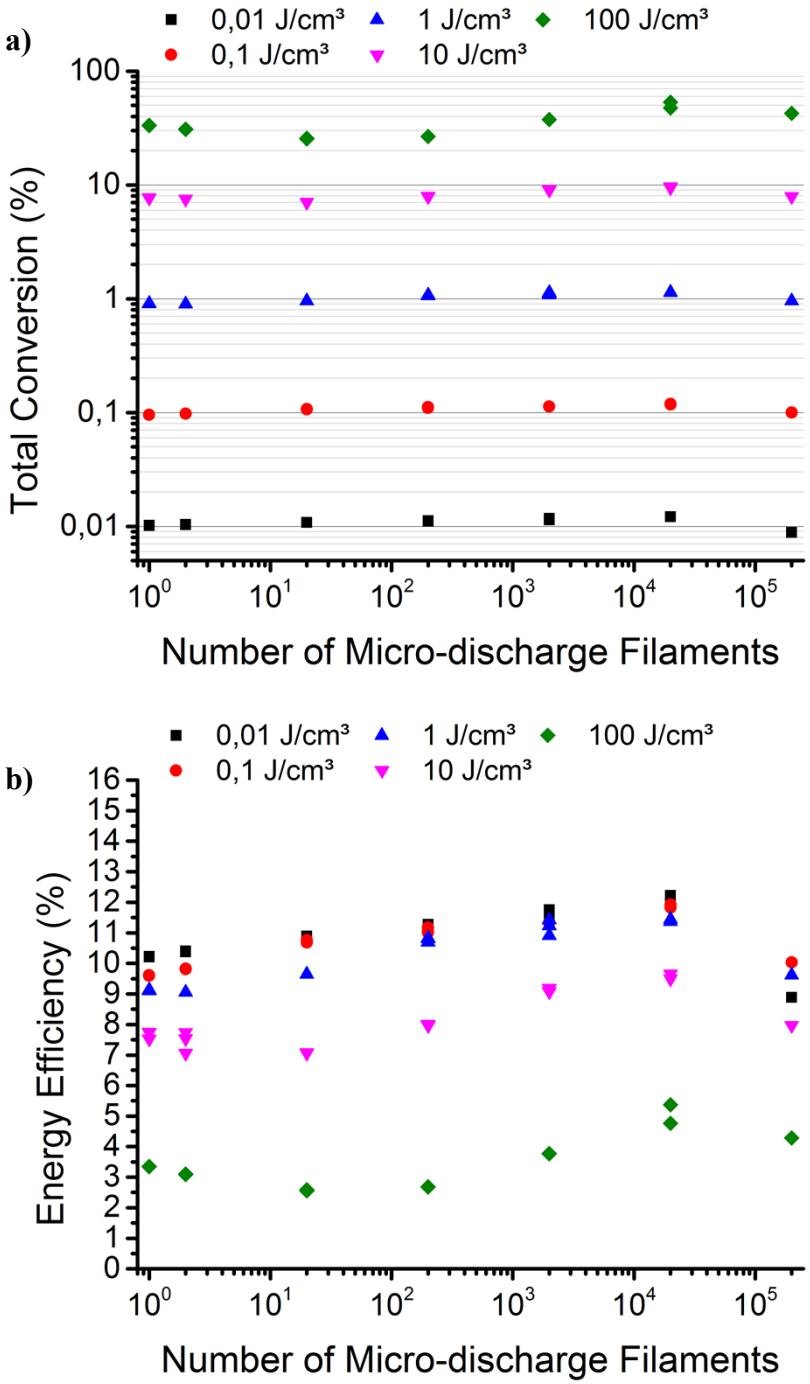

Figure S13. Calculated conversion (a) and energy efficiency (b) as a function of the total number of micro-discharge filaments (i.e., product of residence time and frequency), for all the different residence times, frequencies and SEI values investigated, for a CH_4-CO_2 mixture

of 50-50. The values corresponding to the same SEI values are indicated with the same colored symbols.

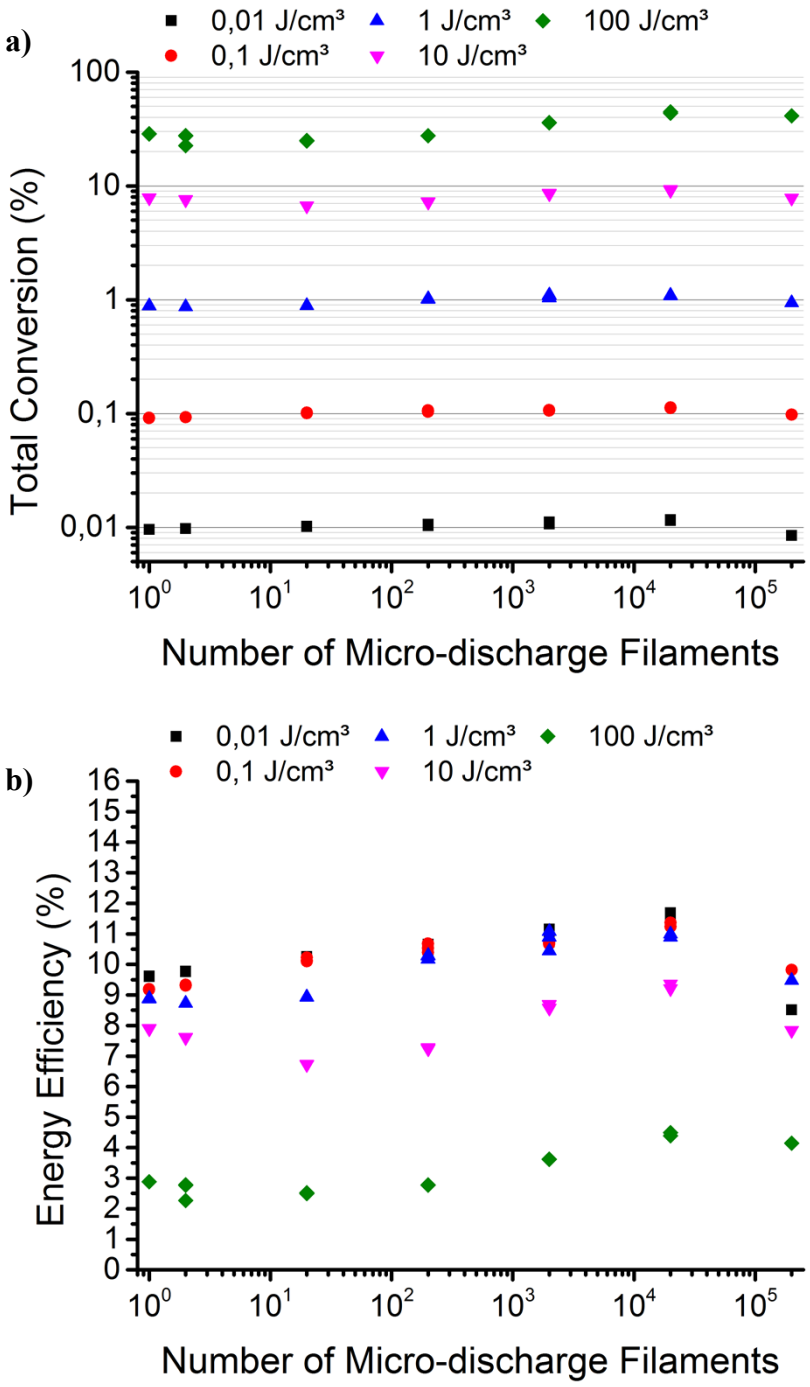

Figure S14. Calculated conversion (a) and energy efficiency (b) as a function of the total number of micro-discharge filaments (i.e., product of residence time and frequency), for all the different residence times, frequencies and SEI values investigated, for a CH_4-CO_2 mixture

of 75-25. The values corresponding to the same SEI values are indicated with the same colored symbols.

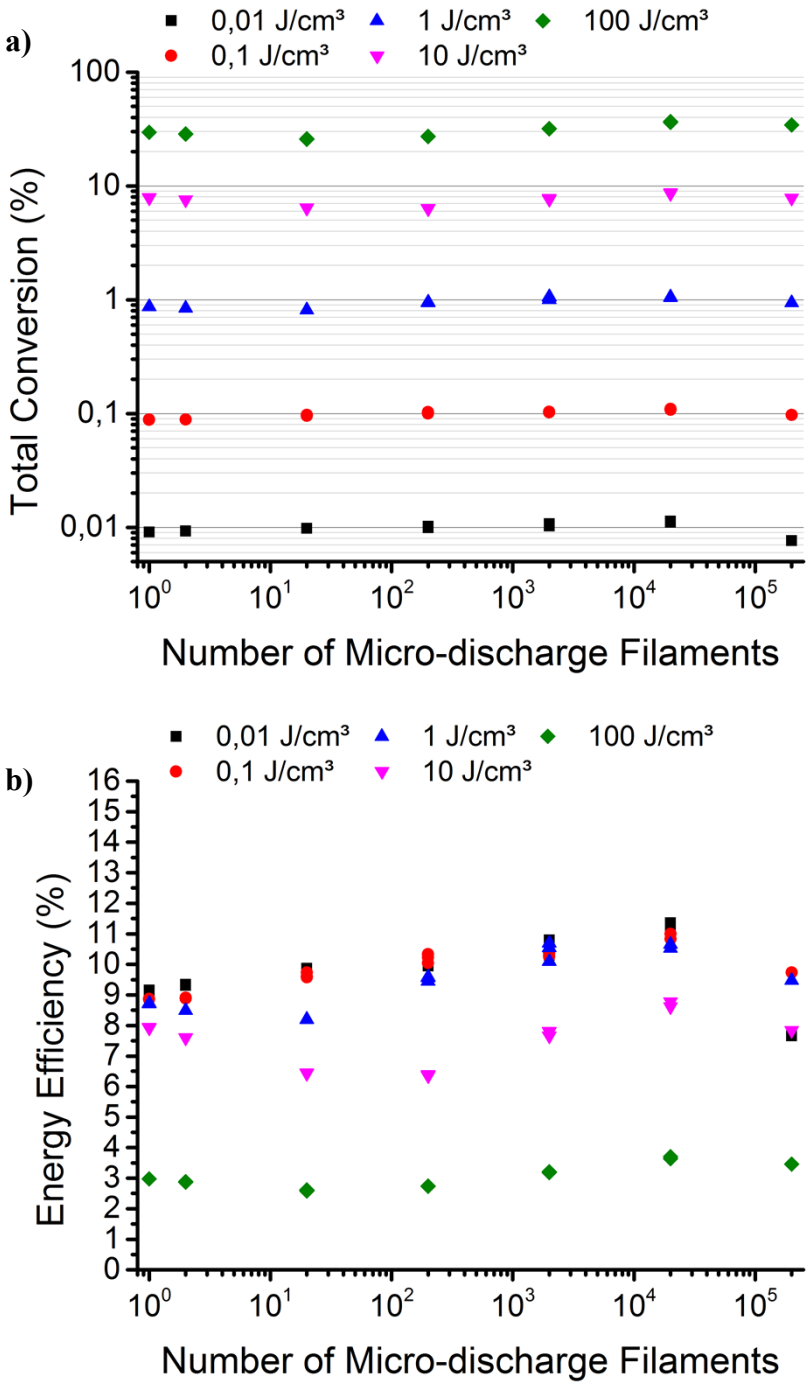

Figure S15. Calculated conversion (a) and energy efficiency (b) as a function of the total number of micro-discharge filaments (i.e., product of residence time and frequency), for all the different residence times, frequencies and SEI values investigated, for a CH_4-CO_2 mixture

of 90-10. The values corresponding to the same SEI values are indicated with the same colored symbols.