Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary file

1. EDS data

E1_ Glasswool filter

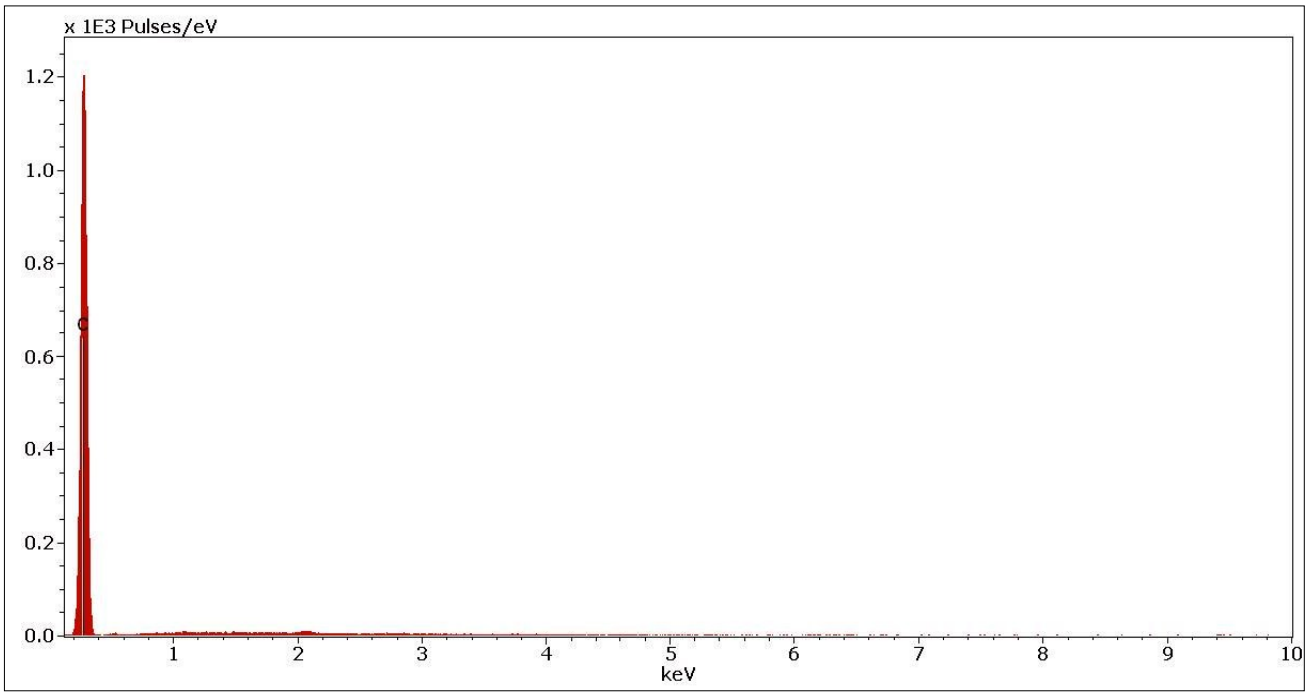


Figure S1.1: E1_ Glasswool filter

E2_VITO CORE ™

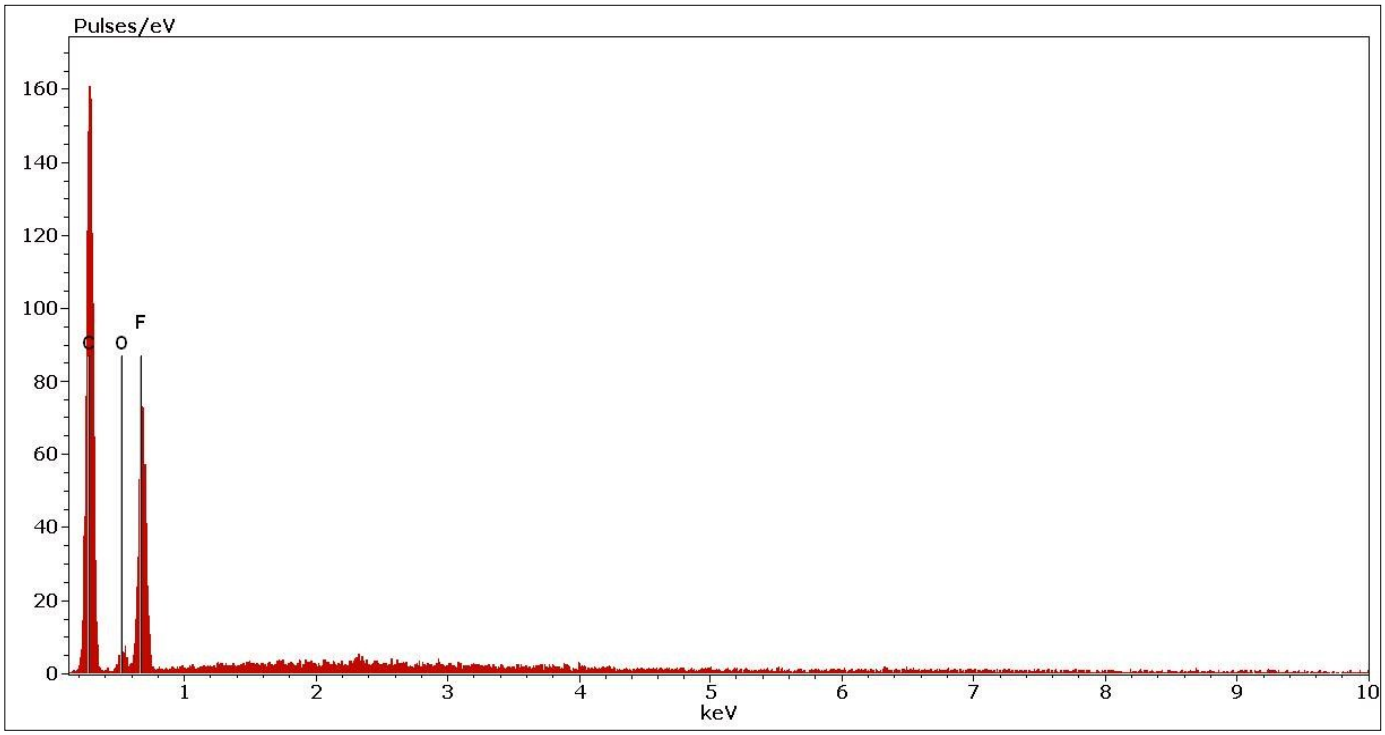


Figure S1.2: E2_VITO CORE ™

E4_ Activated carbon fleece

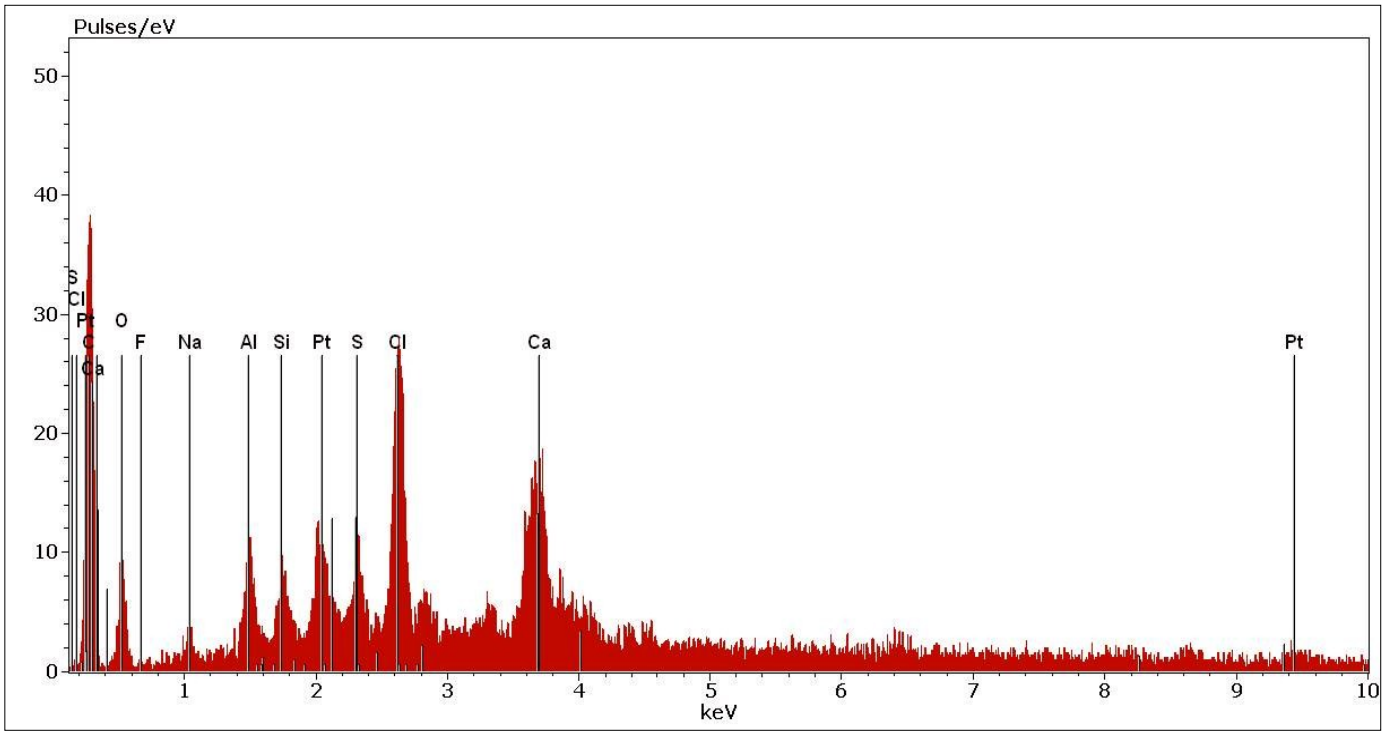


Figure S1.3: E4_ Activated carbon fleece

E5_Activated carbon fabric

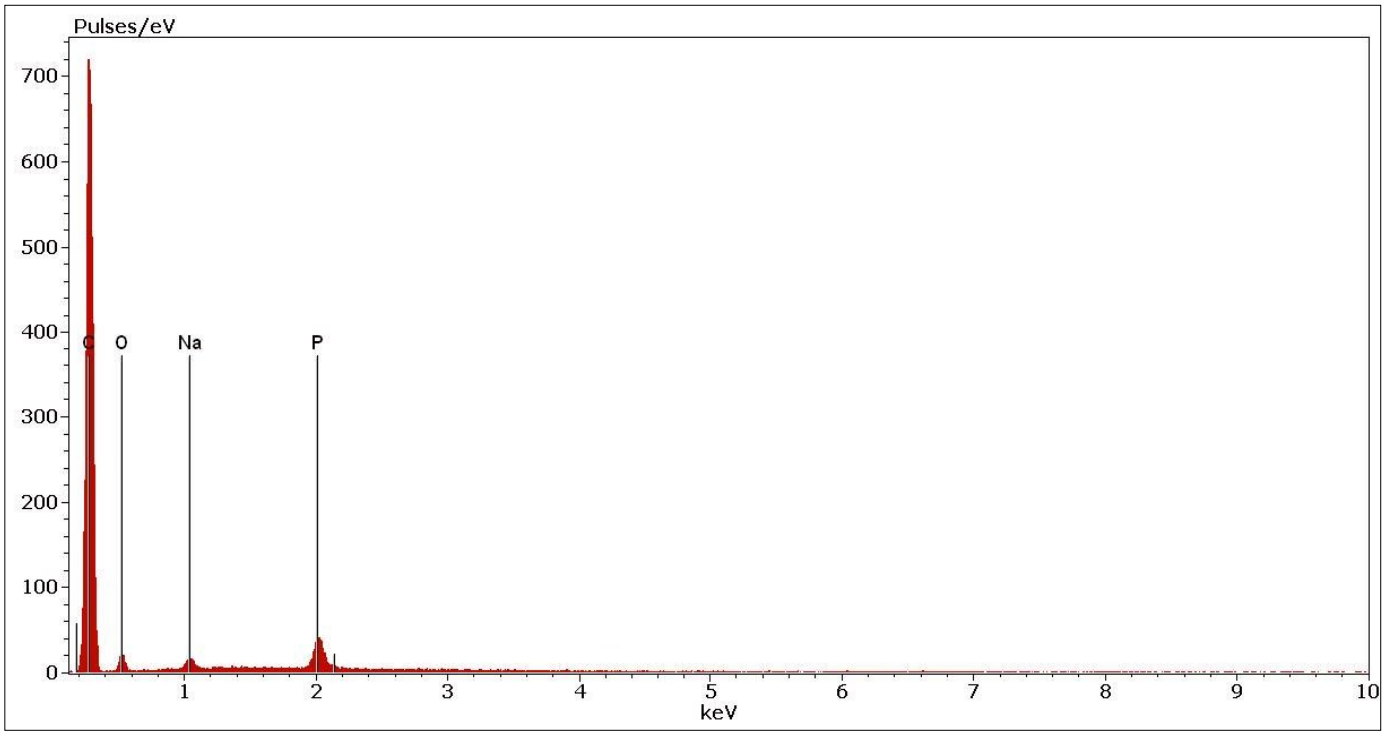


Figure S1.4: E5_Activated carbon fabric

E6_Carbon paper

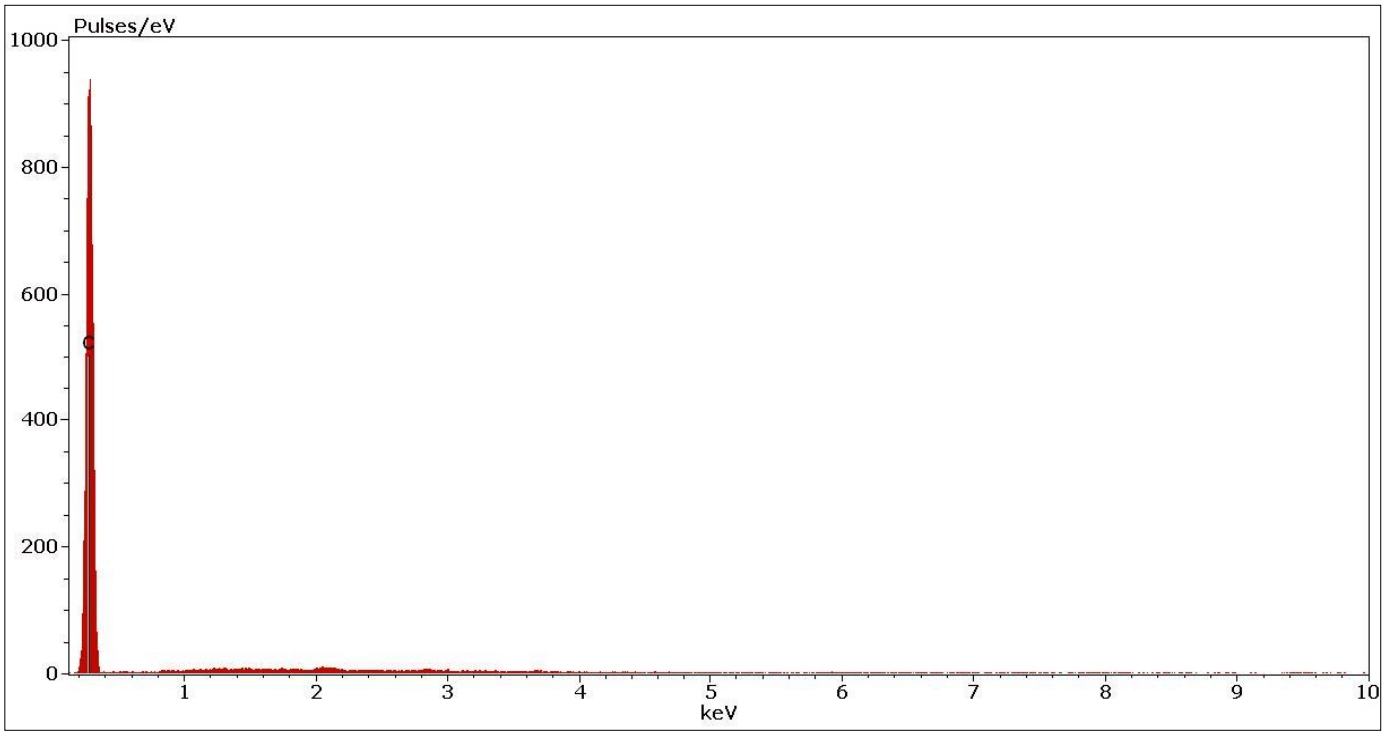


Figure S1.5: E6_Carbon paper

E7_Carbon felt

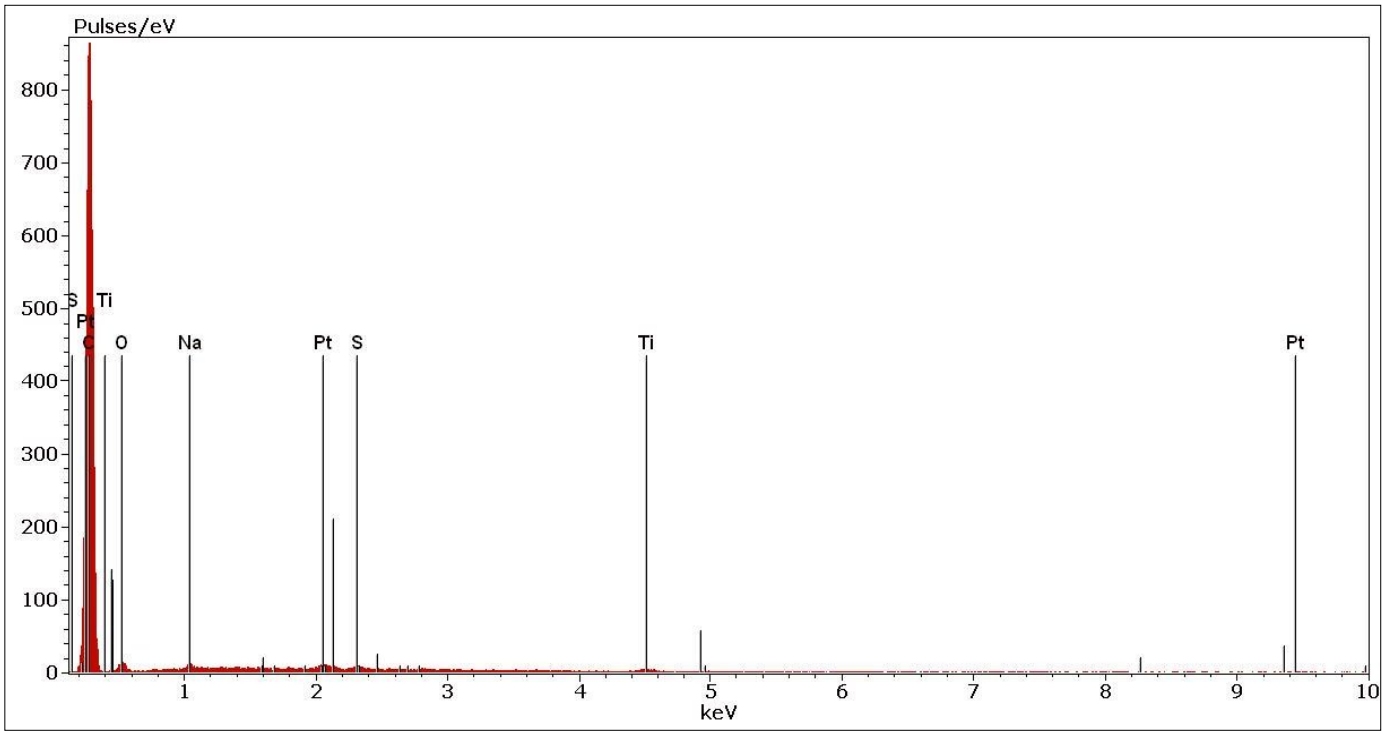


Figure S1.6: E7_Carbon felt

E8_Graphitized carbon felt

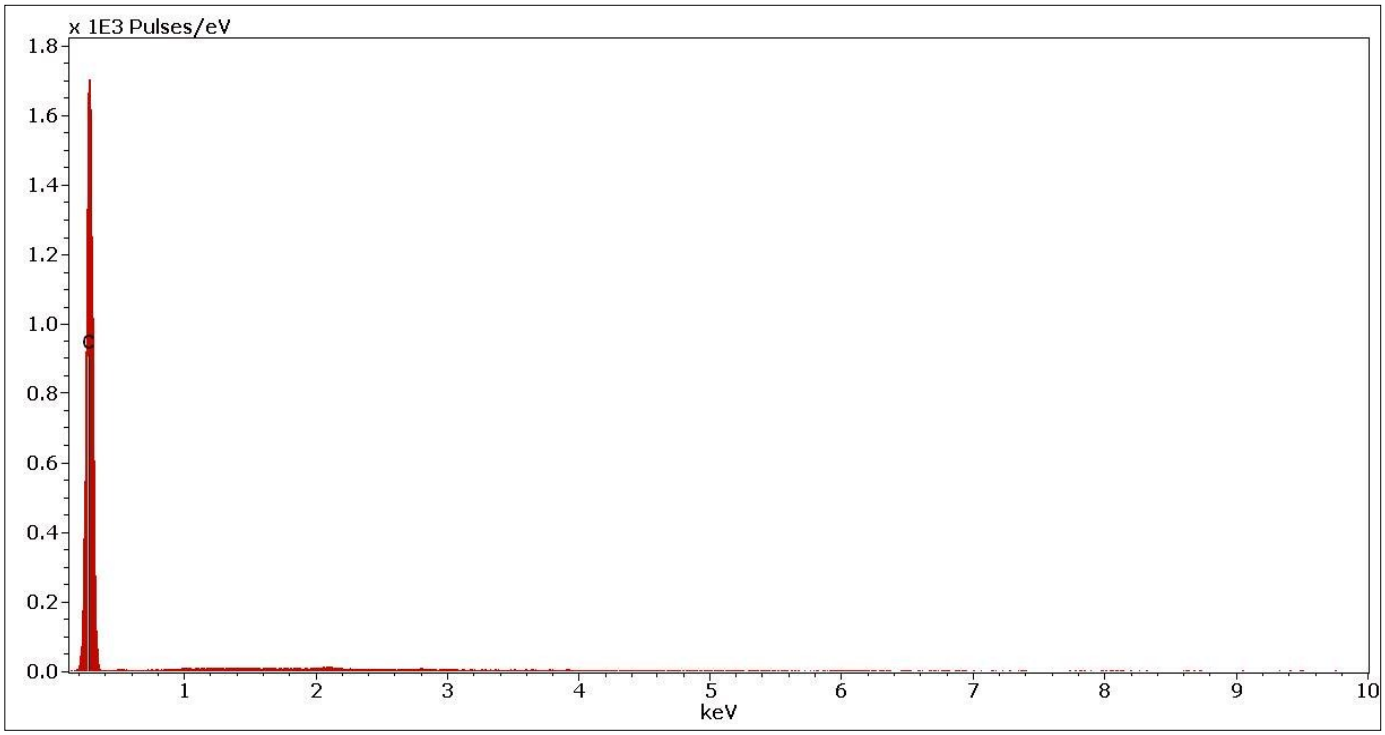


Figure S1.7: E8_Graphitized carbon felt

2. SEM image processing

Protocol used

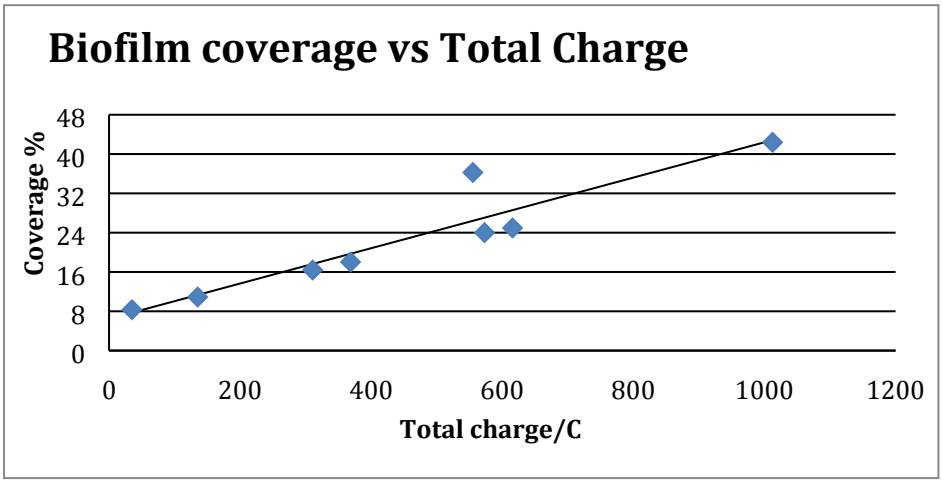
The images were processed using Gwyddion software version 2.42. Bacterial coverage was determined by considering bacterial distribution as grains. Total projected area of the grains was calculated using slope threshold method (Necas and Klapetek, 2012). Threshold value was adjusted to best fit during this area calculation. The coverage in the Table1 refers to percentage of electrode surface covered with biomass.

References

1. (Nečas, D., & Klapetek, P. (2012). Gwyddion: an open-source software for SPM data analysis. *Open Physics*, *10*(1), 181-188.).

Table S2: Ranking of electrodes on the basis of total charge and percentage of biofilm coverage

Electrode	total charge	coverage 1	coverage 2	Average coverage
E2	1012.37	41.25	43.53	42.39
E6	615.64	23.19	26.74	24.965
E1	572.87	25	22.9	24
E8	555.11	35.12	37.39	36.255
E3	368.44	17.71	18.36	18.035
E7	310.69	15.67	17.13	16.4
E5	135.21	11.49	10.31	10.9
E4	35.03	8.92	7.73	8.325



E1_ Glasswool filter

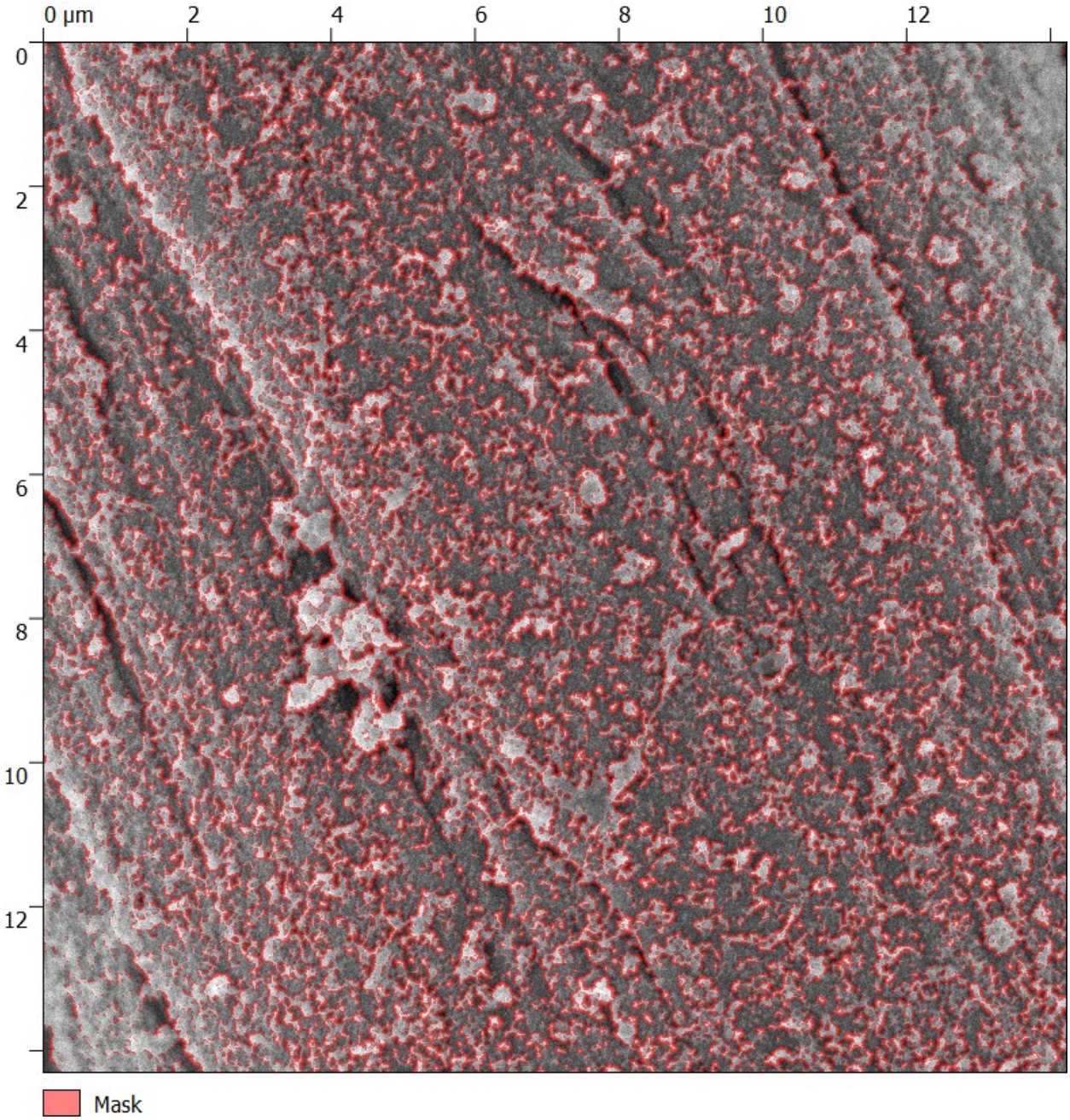


Figure 2.1: E1_ Glasswool filter (E1_131657, coverage 1)

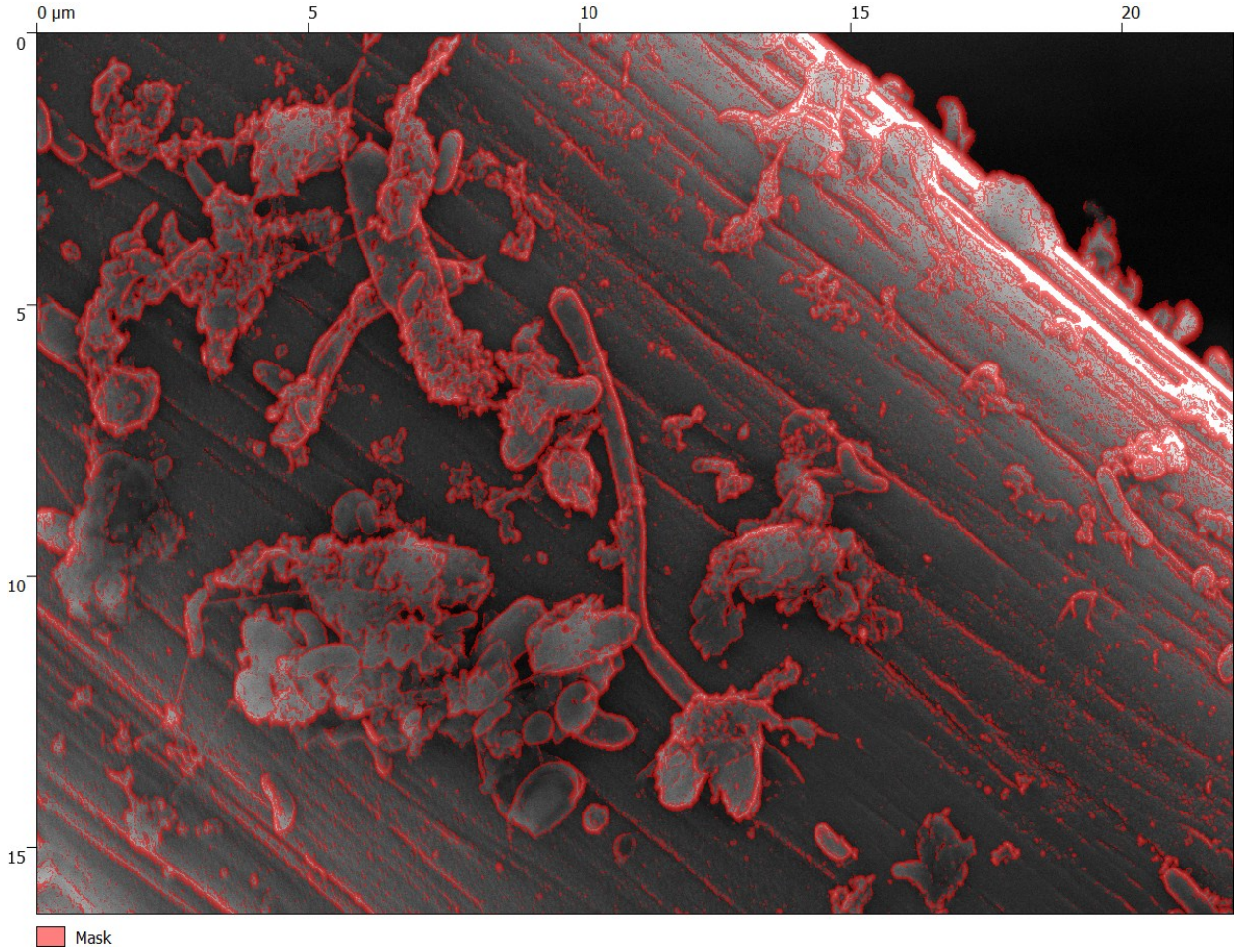


Figure S2.2: E1_ Glasswool filter (E1_132997, coverage 2)

E2_VITO CORE ™

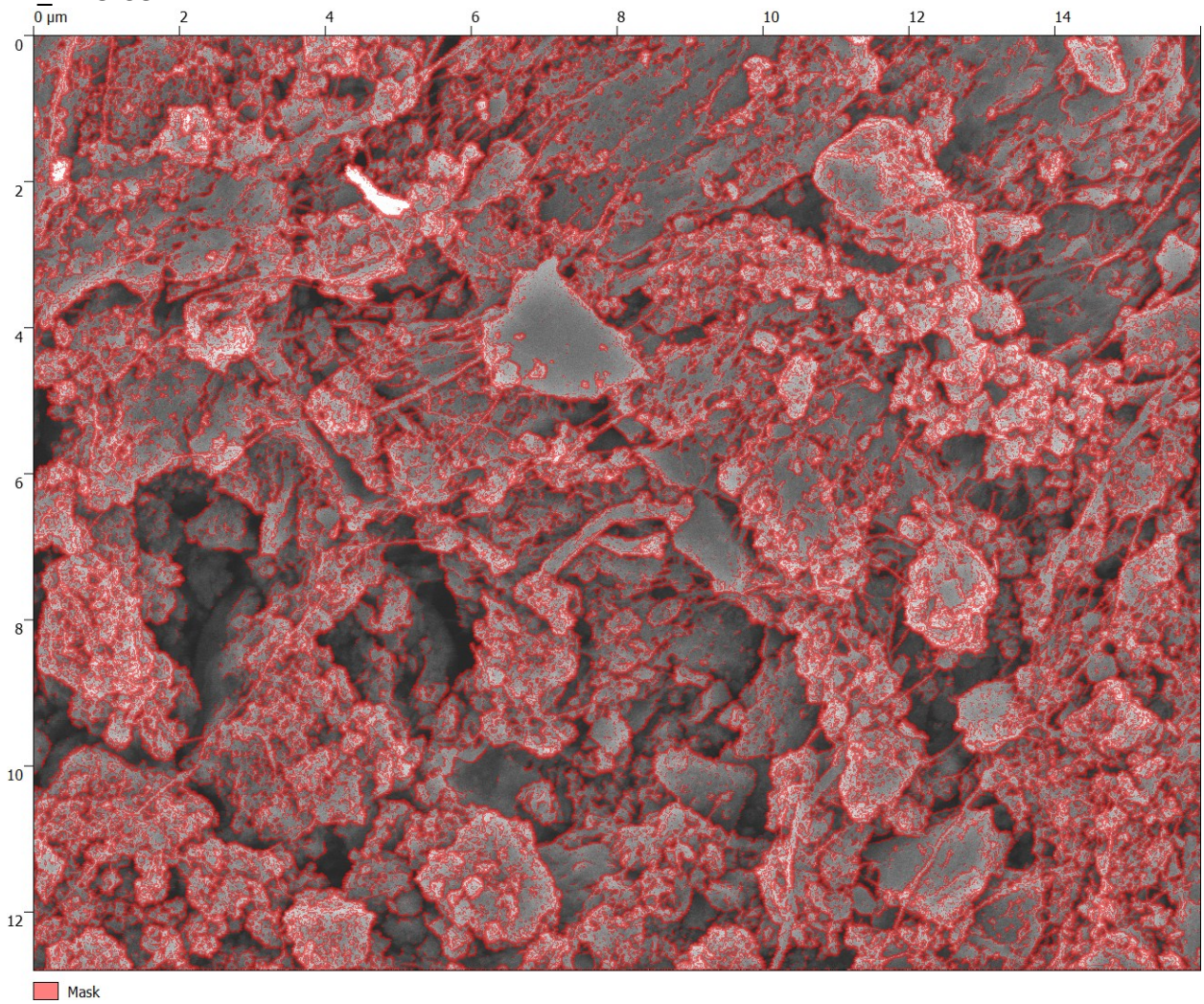


Figure S2.3: E2_VITO CORE ™ (E2_131669, coverage 1)

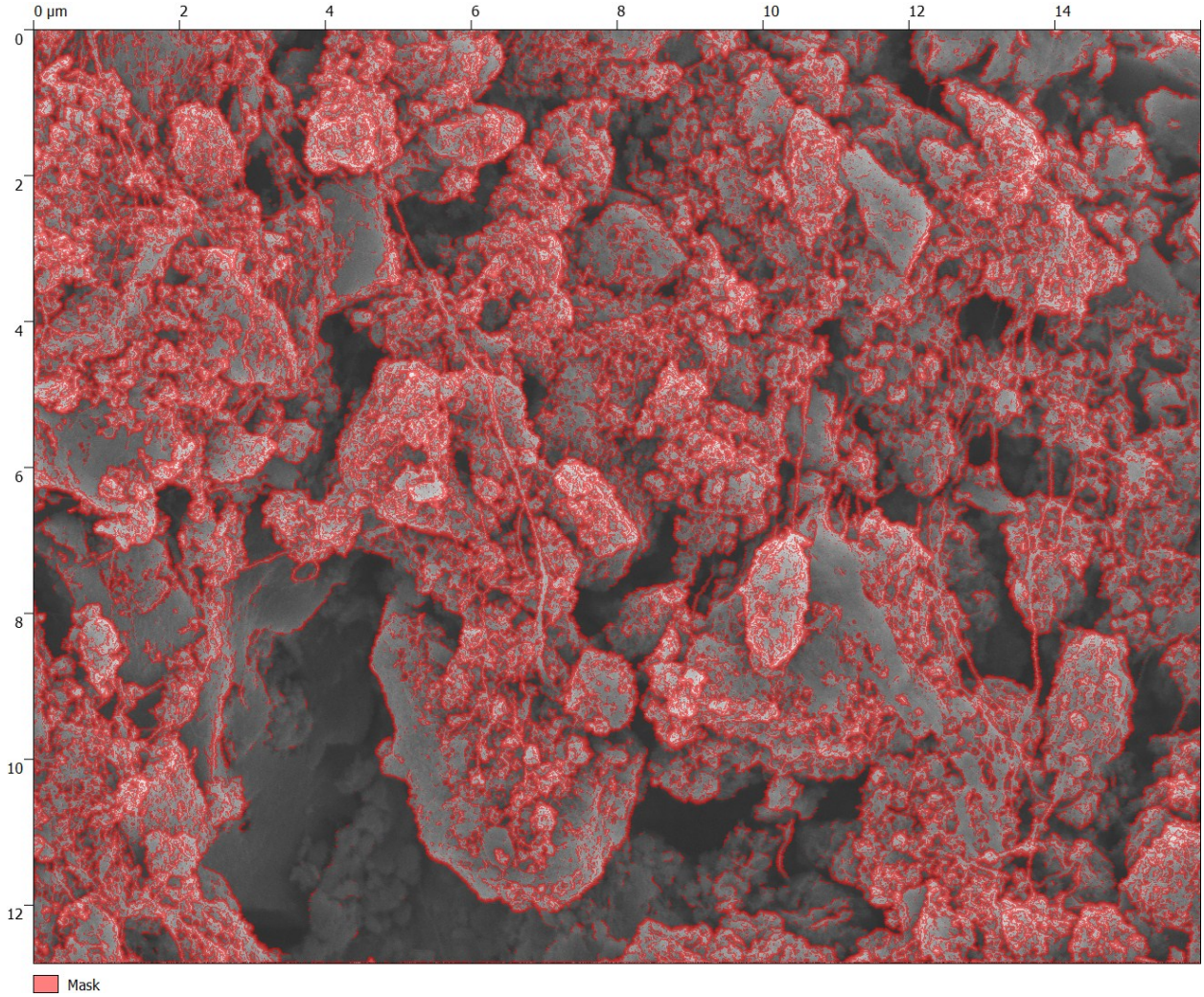


Figure S2.4: E2_VITO CORE ™ (E2_131671, coverage 2)

E3_ pre-colonized cathode prepared using VITO CORE

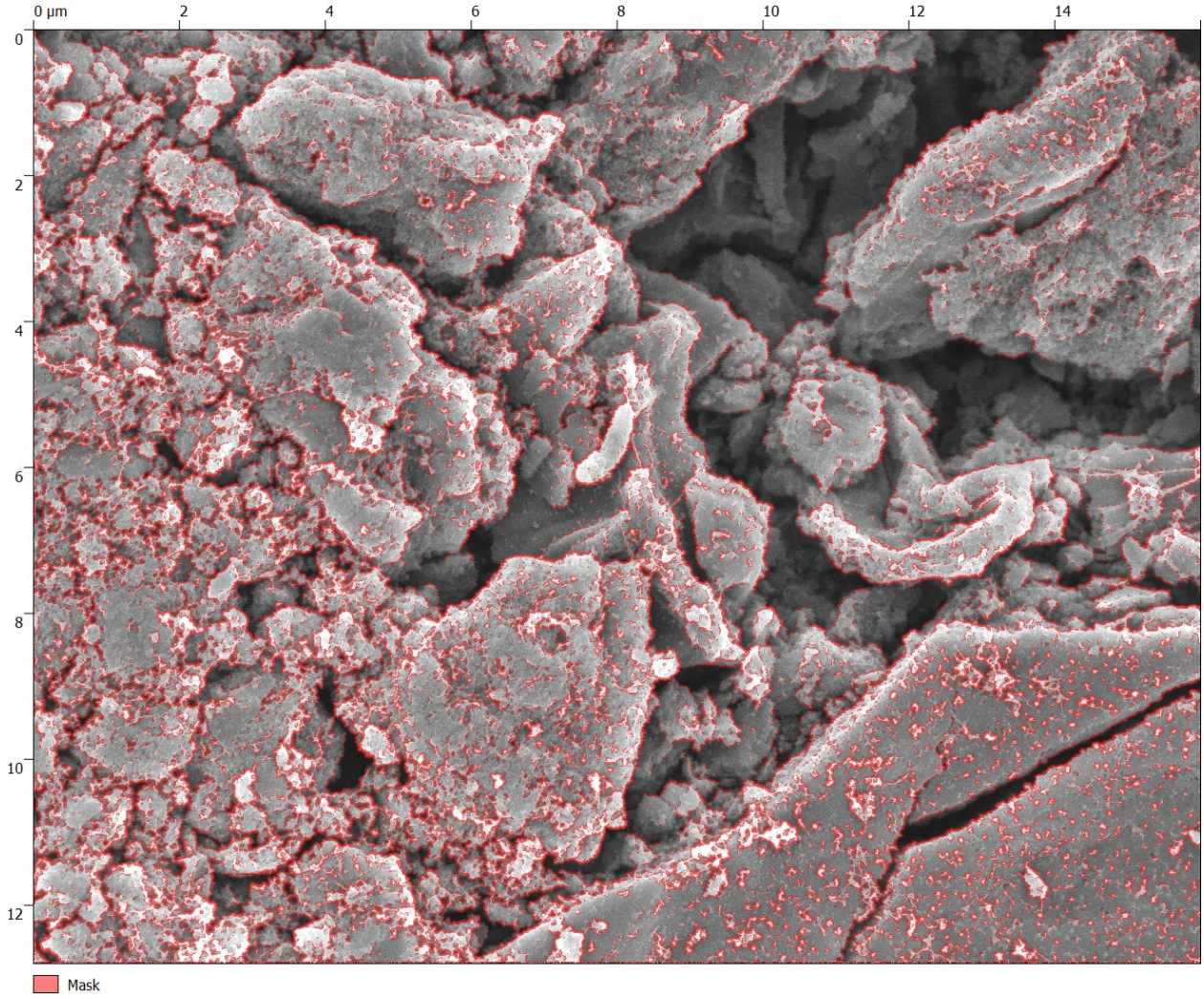


Figure S2.5: E3_ pre-colonized cathode prepared using VITO CORE™ (E3_131673, coverage 1)

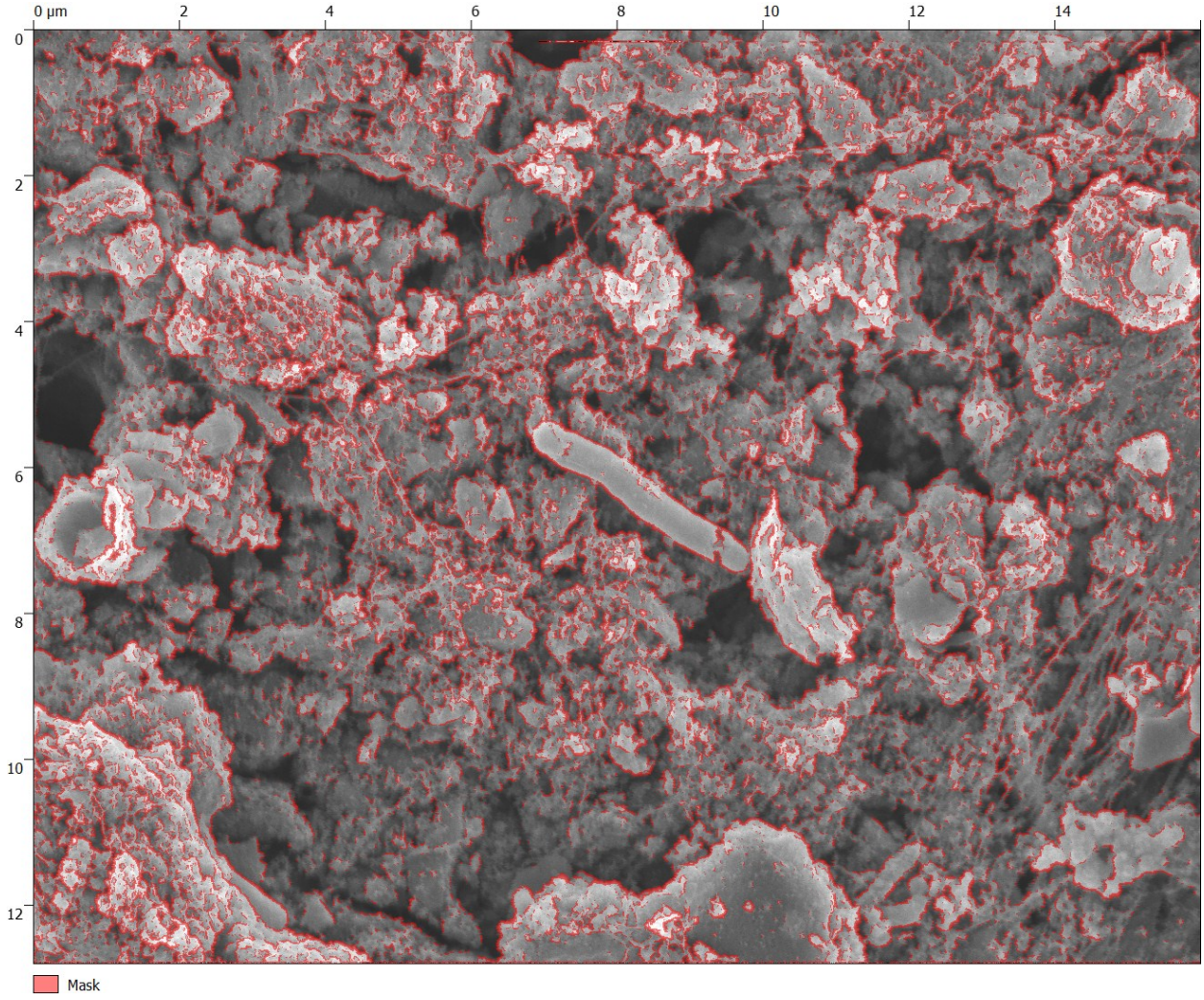


Figure S2.6 E3_ pre-colonized cathode prepared using VITO CORE™ (E3_131675, coverage 2)

E4_ Activated carbon fleece

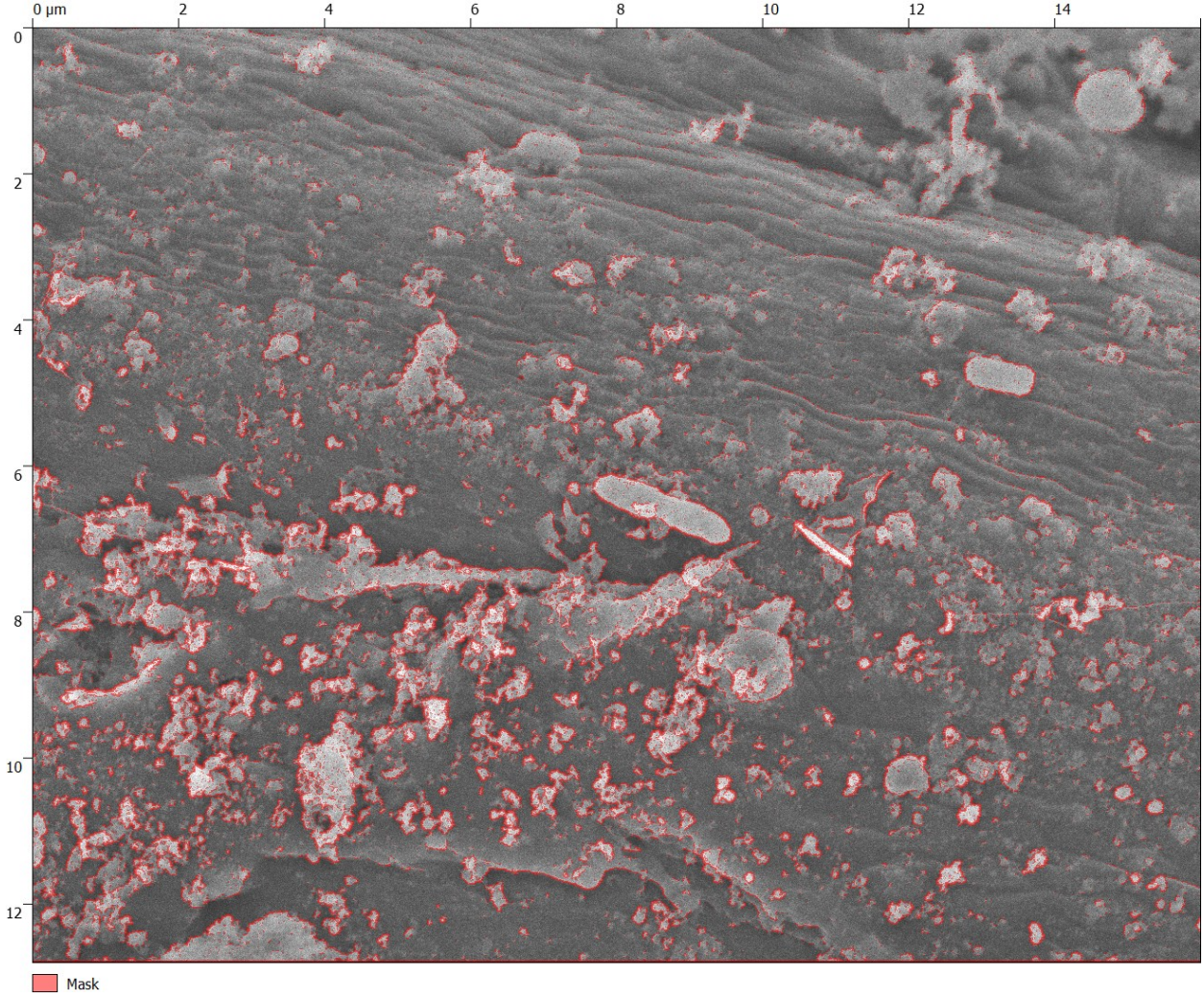


Figure S2.7: E4_ Activated carbon fleece (E4_ 131693, coverage 1)

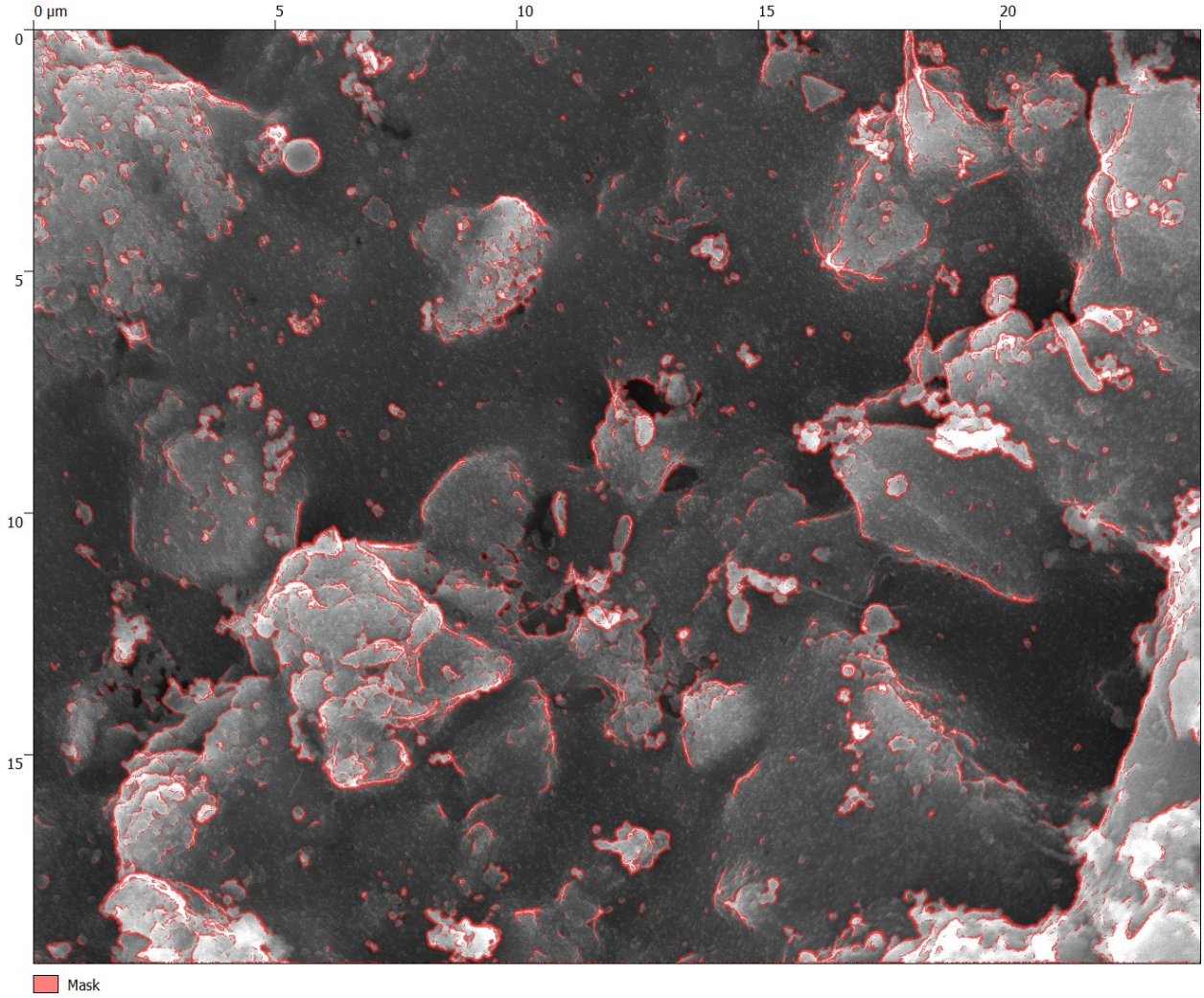


Figure S2.8: E4_ Activated carbon fleece (E4_132987, coverage 2)

E5_Activated carbon fabric

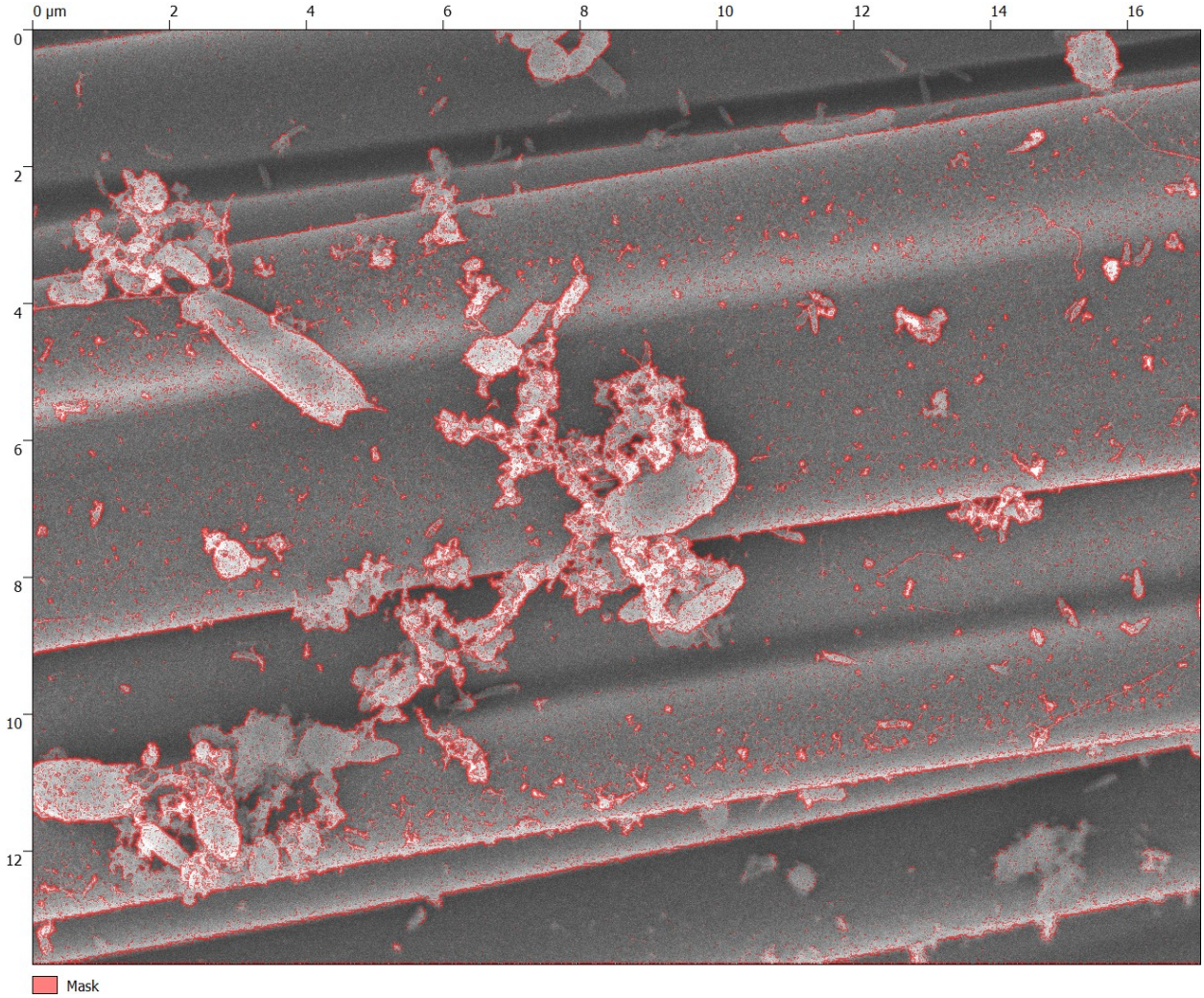


Figure S2.9: E5_Activated carbon fabric (E5_131701, coverage 1)

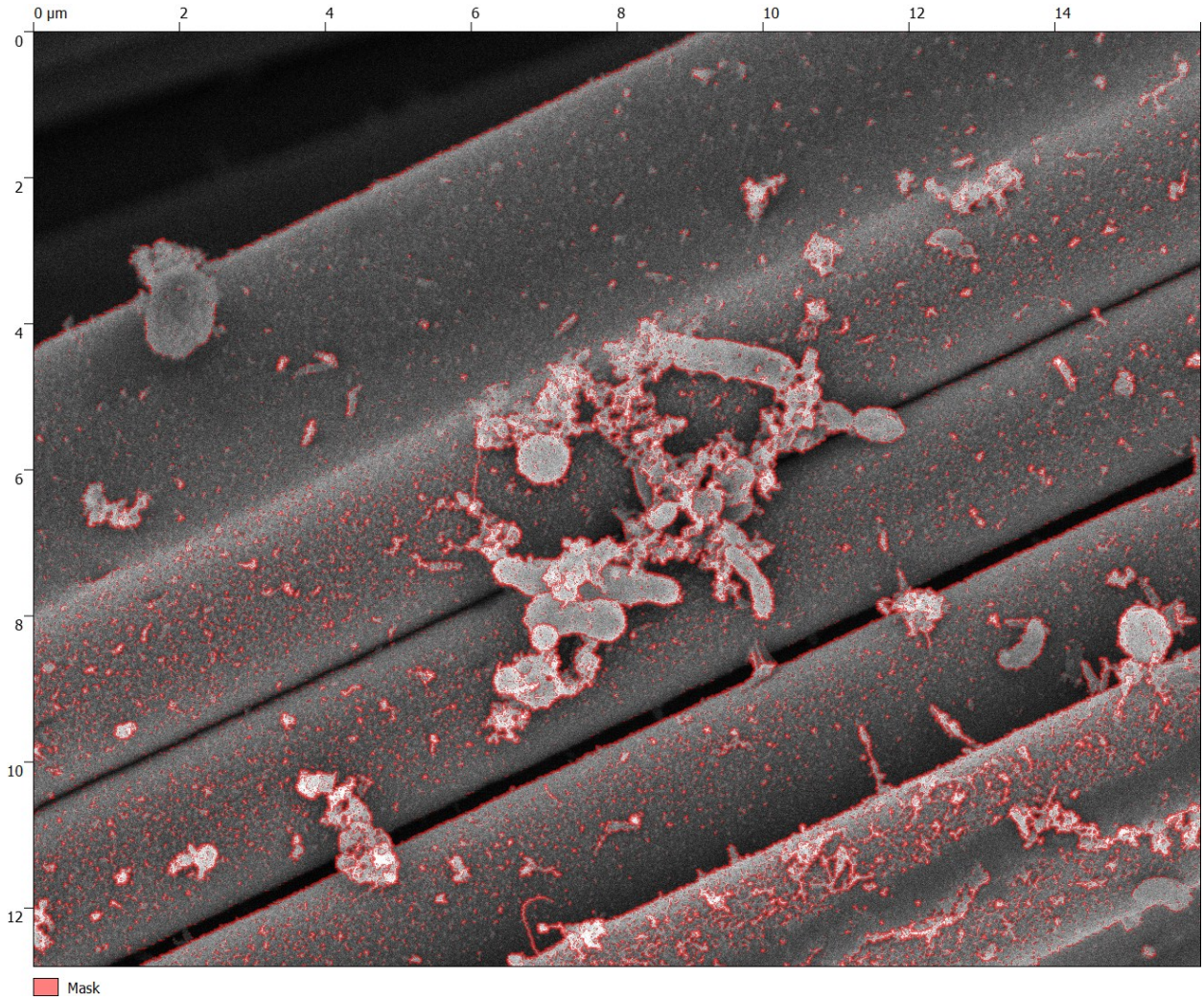


Figure S2.10: E5_Activated carbon fabric (E5_131703, coverage 2)

E6_Carbon paper

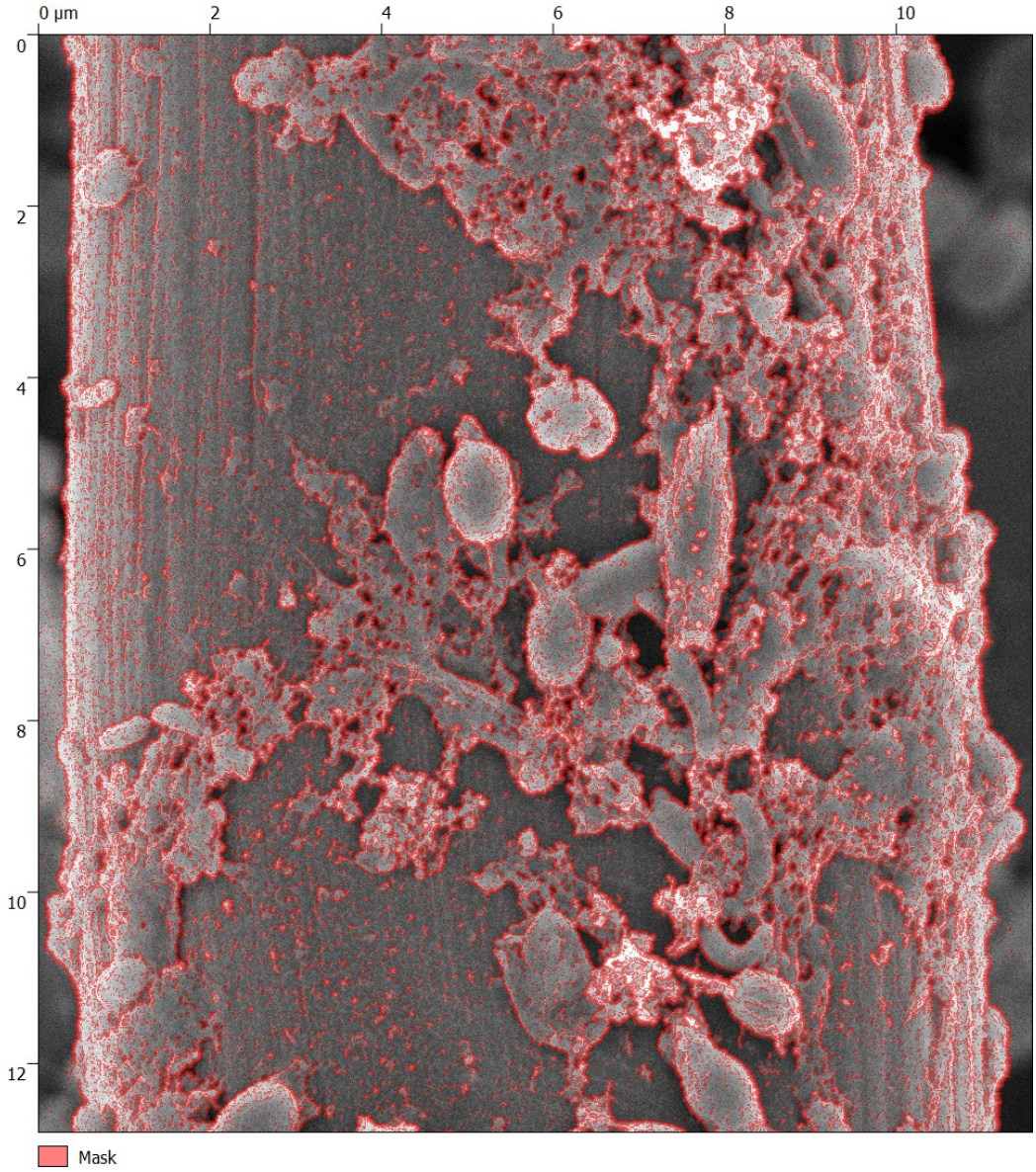


Figure S2.11: E6_Carbon paper (E6, 131711, coverage 1)

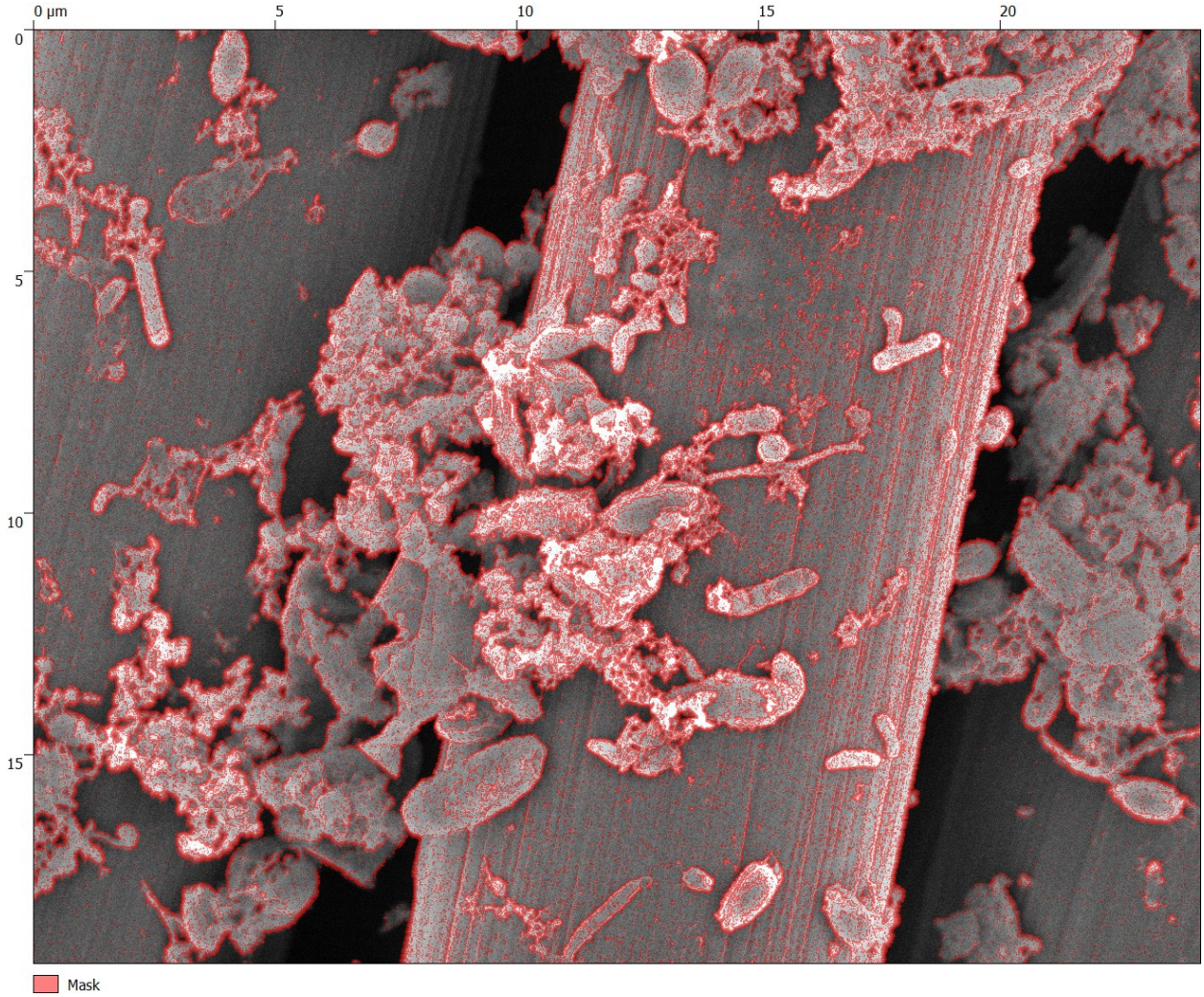


Figure S2.12: E6_Carbon paper (E6_131713, coverage 2)

E7_Carbon Felt

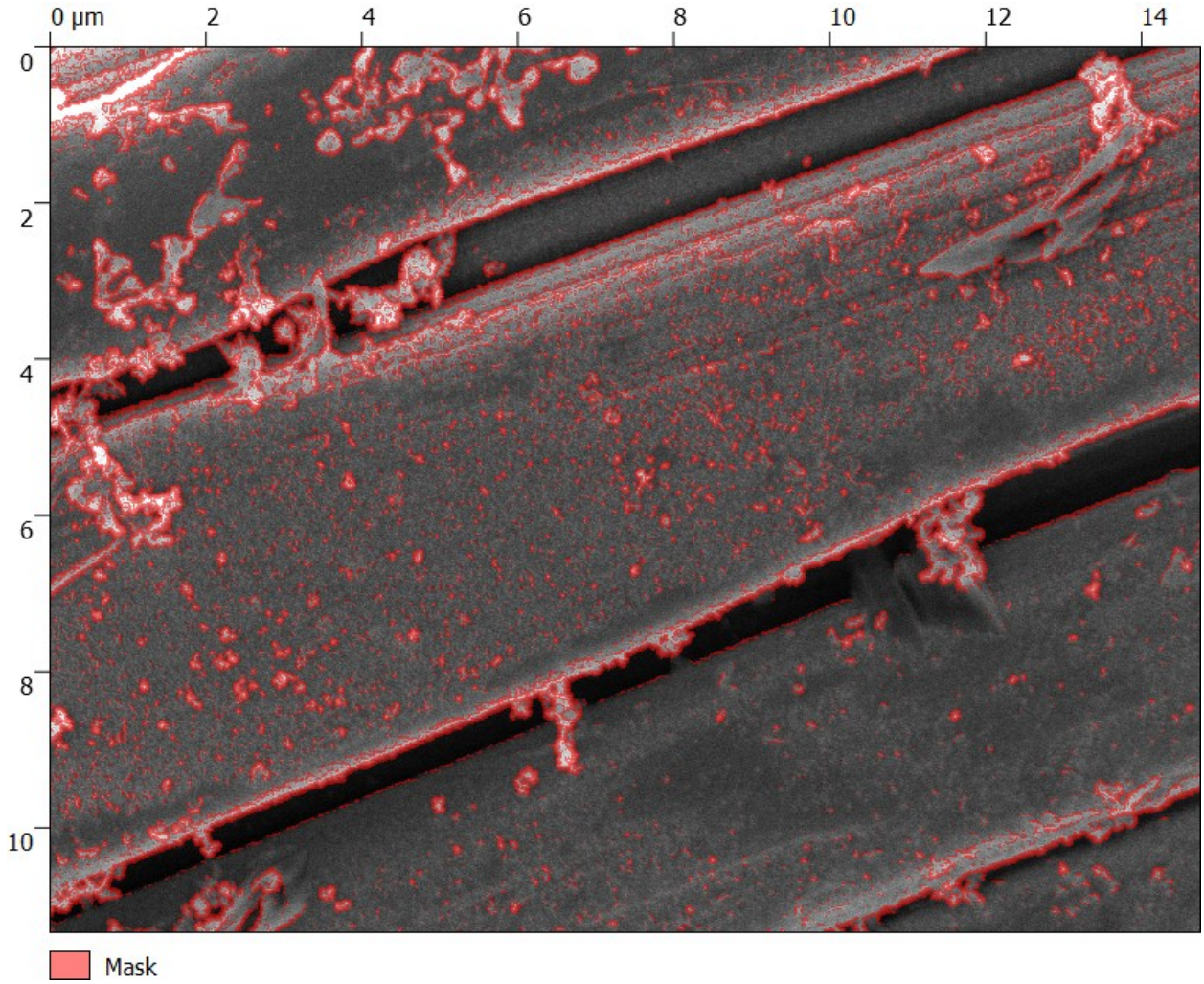


Figure S2.13: E7_Carbon paper (E7_131733, coverage 1)

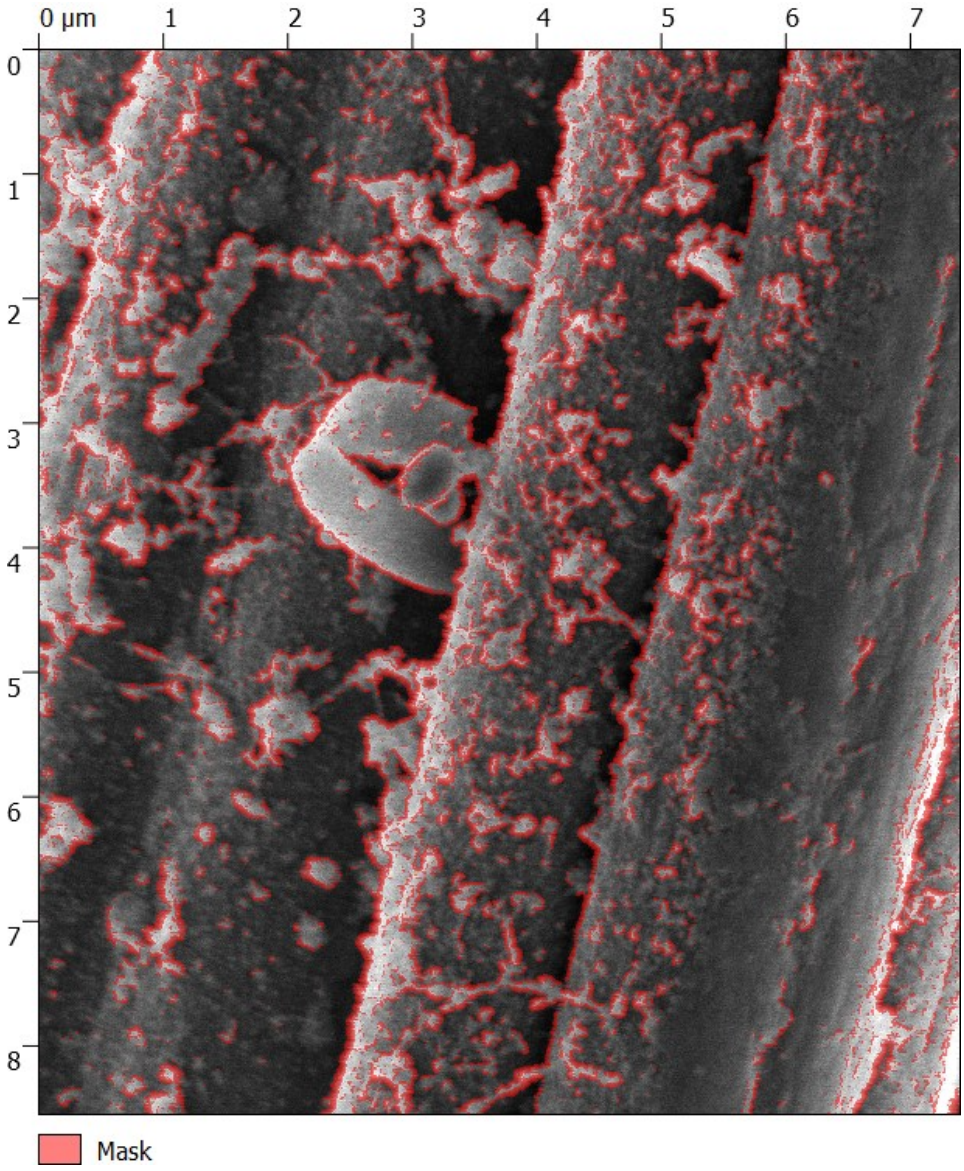


Figure S2.14: E7_Carbon paper (E7_132210, coverage 2)

E8: Graphitized carbon felt

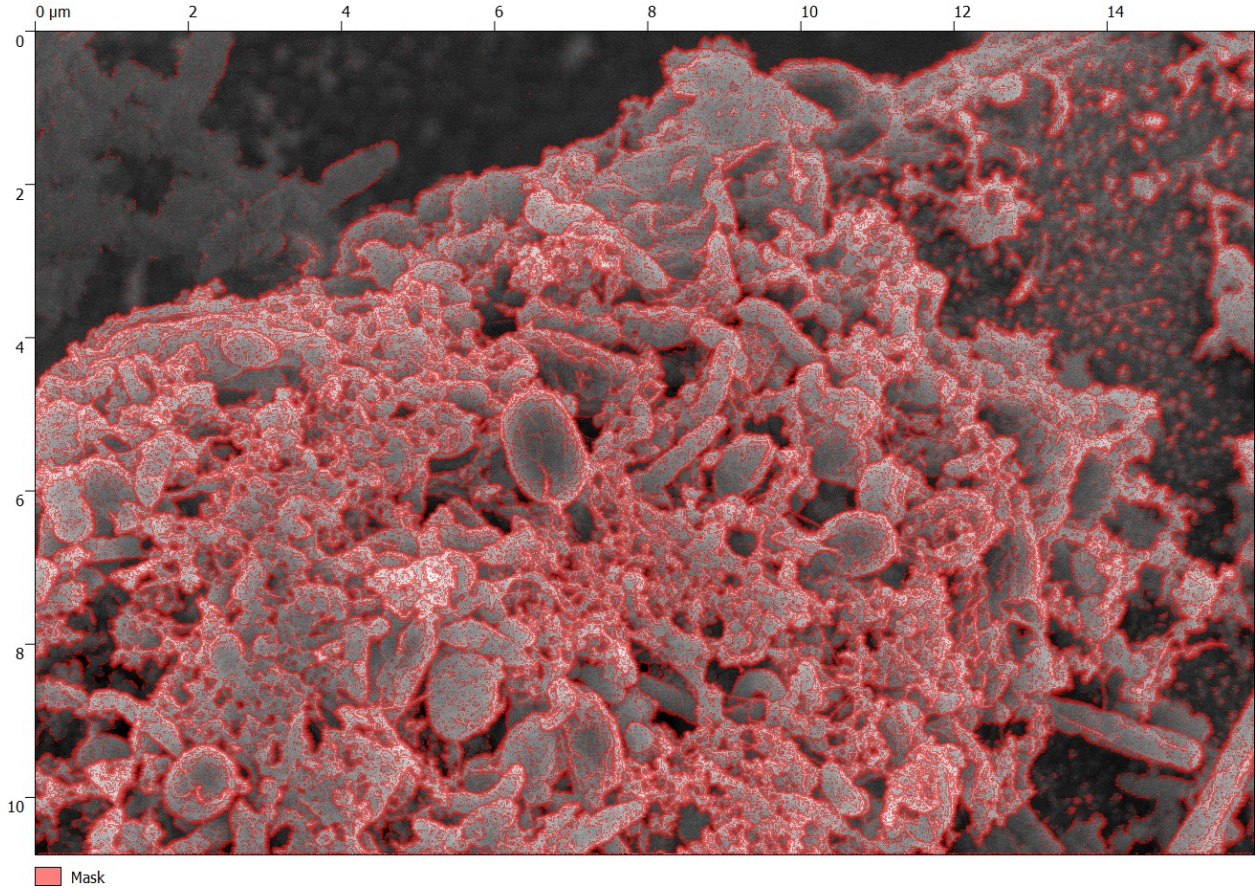


Figure S2.15: E8_Graphitized carbon felt (E8_131749, coverage 1)

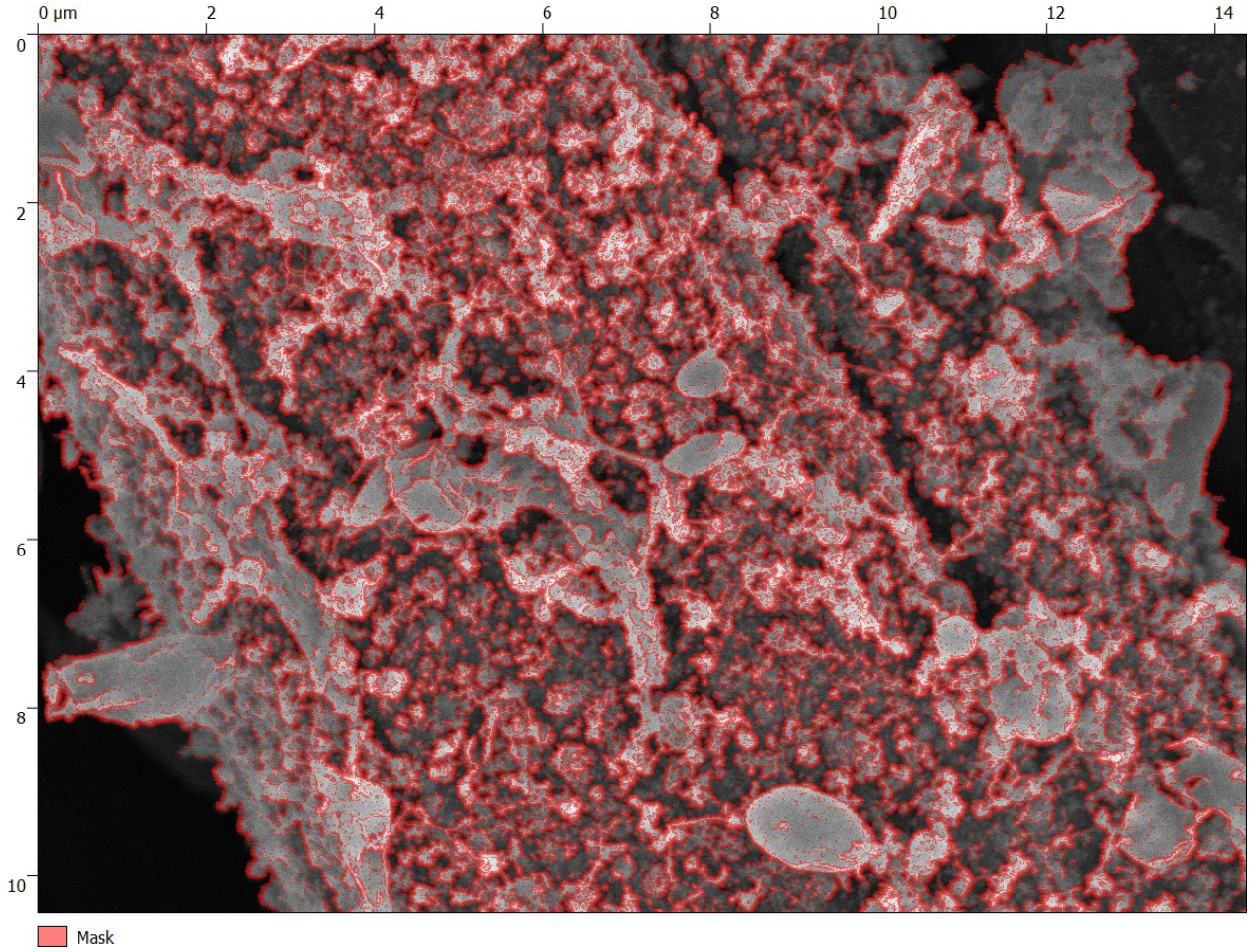


Figure S2.16: E8_Graphitized carbon felt (E8_131751, coverage 2)

3. Confocal images

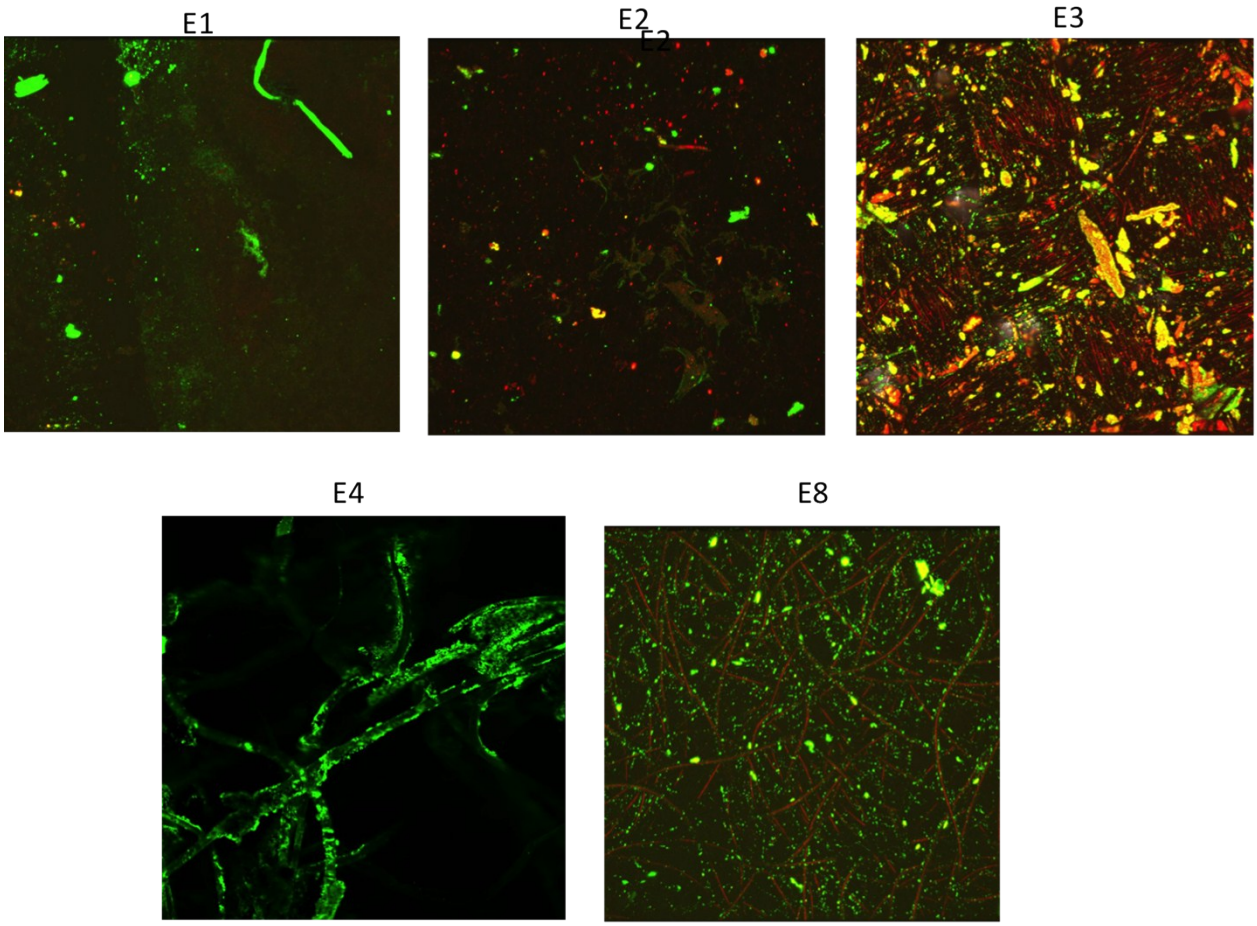
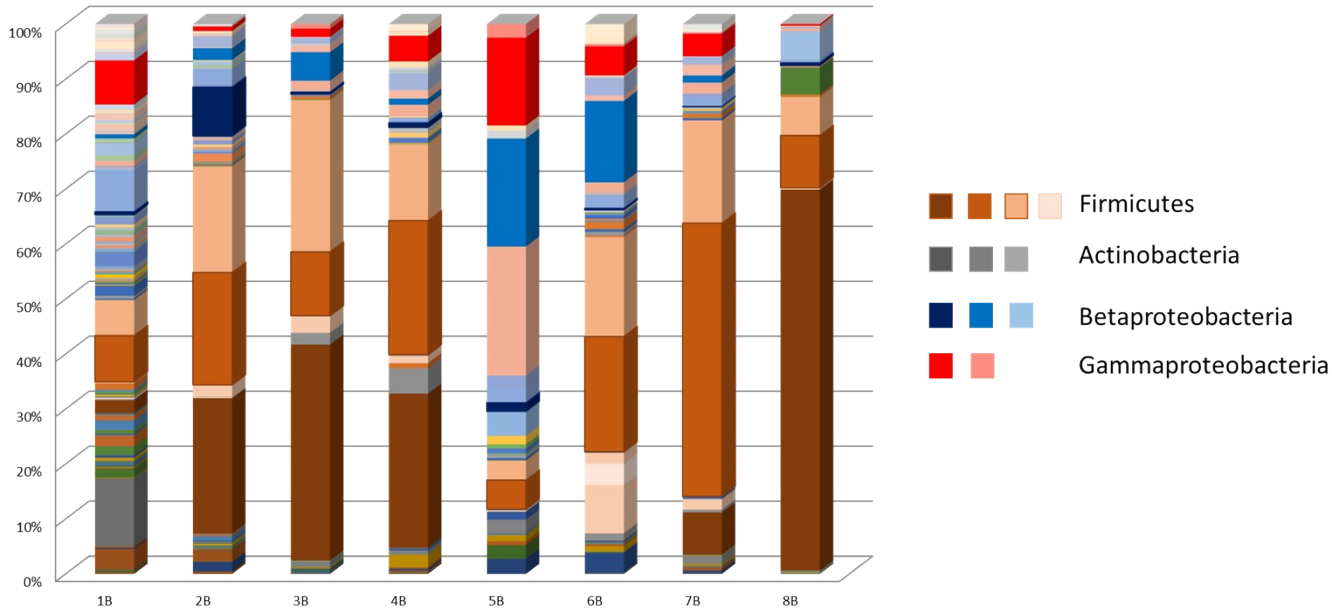


Figure S3:. Confocal microscopy was performed on a 0.25-cm2 section of electrode labeled with SYTO®9 Green Fluorescent Nucleic Acid Stain (Invitrogen), using a Fluoview FV10i (Olympus) automatic confocal microscope. Green-tagged cells were imaged using an excitation at 489 nm and an emission at 510 nm. Carbon fibers were red-imaged using an excitation at 645 nm and emission at 620 nm (Rousseau et al., 2016).

4. Microbiological diversity data



Relative abundance of bacteria at OTUs level of biofilms developed on biocathodes made from various materials

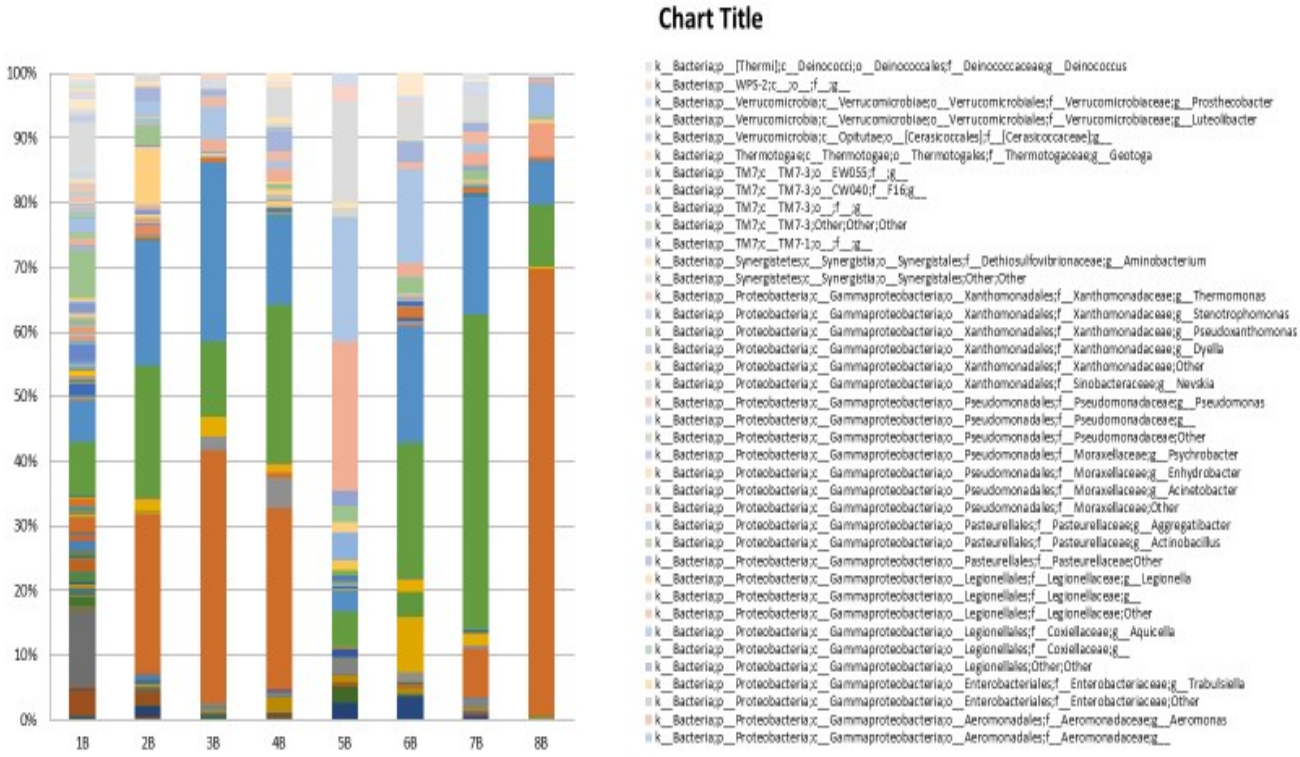


Table S4: Sample coverage, species richness and species diversity indices

	1B	2B	3B	4B	5B	6B	7B	8B
Observed species	268,00	182,00	123,00	136,00	73,00	127,00	143,00	117,00
alpha_rarefaction_1110_9.txt	536,28	420,56	262,33	316,00	136,00	246,17	317,79	278,00
PD_whole_tree	16,60	11,37	8,45	8,63	5,85	8,43	9,17	7,13
Shannon index	6,59	4,72	3,58	4,40	4,16	4,66	4,21	3,29

5. Electrochemical Impedance Spectroscopy Analysis

Electrochemical impedance spectroscopy (EIS) responses are commonly analyzed to an equivalent circuit model, due to the straightforwardness of this approach. However, this is often misused, as referred in our authoritative previous work:

- Dominguez-Benetton et al. (2012) Chem Soc Rev 41(21):7228–7246.

Besides, it is far from being the only possibility, even less the only valid or meaningful alternative to analyze EIS data. A graphical representation of impedance data is not only possible, but it has been the primary option emphasized by some of the most renown EIS experts, for instance:

- Orazem, Pébère and Tribollet (2006). Journal of The Electrochemical Society 153(4):B129-B136.

Graphical methods provide the first step toward interpretation and evaluation of impedance data. As described in our manuscript, we have chosen the graphical representation of impedance concerning the negative imaginary measurement (-ZIm) against the frequency (ω), both parameters in logarithmic scale, to determine the well-identified slope of the curves above the relaxation frequency, which directly corresponds to the magnitude of the CPE parameter α. Note that in this case we do not derive magnitudes for the CPE and we only discuss the α parameter, which can be ascribed to the distributed nature of the electrochemical properties of the interface. We do see a good agreement with such interpretation with the biofilm development and final distribution over the electrodes. Thus, even if this is not as extended as the use of equivalent circuits, this analysis allows us to deduce the extent of distribution of the electrochemical interface (i.e., see reference above of Orazem et al.), which in turn has an impact on the performance of the electrodes.

We have widely employed this approach in previous works regarding microbial electrochemical systems (some of them published in highly renowned RSC journals), where we show that a meaningful interpretation can be achieved, even when equivalent circuits are not at all employed:

- Dominguez-Benetton et al. (2012) Chem Soc Rev 41(21):7228–7246.
- Sharma et al. (2013) Chem Comm 49:6495.
- Sharma et al. (2015) RSC Advances 5(49): 39601-39611.
- Sevda et al. (2015) Bioelectrochemistry 106(A):159–166.

Note that in some works we do employ an equivalent circuit analysis, e.g.:

- Castaneda and Dominguez-Benetton (2008) Corrosion Sci. 50 (4):1169-1183.
- Lepage et al. (2014) RSC Advances 4 :23815.
- Gonzalez-Gamboa et al. (2018) Sustainability 10(7):2446.

Yet, we use such approach only when we think it can bring in relevant, non-ambiguous information and meaningful conclusions for our analysis, beyond what a graphical method alone could provide. Our preferred approach would be to use fundamental equations to describe the EIS response, but we do not have sufficient information so far to construct a valid model for the specific cases investigated here, plus we consider it far from our intended scope.

The same is valid for the charge transfer resistance. This parameter can be directly obtained from the graphical representation of the impedance modulus Bode plot, which his a common practice on the analysis of EIS data. This is described in text books such as:

- Orazem and Tribollet. Electrochemical Impedance Spectroscopy. John Wiley & Sons, Inc. 2008. DOI:10.1002/9780470381588.