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Plasma treatment of electrodes significantly enhances the development of electrochemically active biofilms

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Summary of key findings

Here we studied the effect of pre-treating carbonaceous electrodes with either an oxygen or a nitrogen plasma before reactor inoculation with a mixed microbial consortia. The plasma produces chemical modifications at the electrode surface level. X-ray photoelectron spectroscopy and water contact angle analysis showed that the plasma removes surface contamination, produces ion implantation and renders the hydrophobic surfaces highly hydrophilic. Both in the case of cathodic and anodic inoculae, plasma pre-treatment considerably accelerated the generation of a bioelectrochemical current after inoculation. Nitrogen plasma yielded the best performance, followed closely by oxygen plasma. Plasma pre-treated electrodes reached a plateau of maximum current density twice as fast as untreated electrodes. Analysis of the current development profiles suggests that the plasma pre-treatment is neither producing a preferential attachment of certain types of bacteria over others, nor accelerating the extracellular electron transfer rate. The results indicate that the plasma treatment considerably enhances the initial cell adhesion, which results in subsequently faster biofilm development. Plasma pre-treatment of electrodes is an inexpensive, fast, safe and straightforward technique to achieve more rapid start-up of bio-electrochemical processes.

Background and relevance

The viability of prospective applications of microbial bioelectrochemical systems is highly dependent on performance improvement, *i.e.* in current increase. Current production is dependent, among other factors, on the microbial consortia, bioelectrochemical reactor design, and electrode materials. One strategy to improve bacteria-electrode interaction is to apply some type of pre-treatment to the electrodes before exposing them to biofilm development. Although some pre-activation techniques proposed in the past have shown improvements in performance, they employ dangerous chemicals or extreme conditions, and sometimes even long, cumbersome, and multistep techniques. We propose the use of plasma treatment as a new pre-activation technique for carbonaceous electrode materials. Plasma treatment can be used to modify a wide variety of material surfaces in a nonspecific manner by changing the wettability, or in a more specific manner by introducing a variety of functional groups depending on the processing gas. We aim at changing the inherited hydrophobicity of carbonaceous materials, in order to increase microorganisms adhesion.

Results

Experiments were performed on glassy carbon (GC), graphite felt (GF), and graphite plates (GP). Water contact angle measurement showed that after 15 minutes of either O_2 or N_2 plasma treatment, the water contact angles were always below 5^o. XPS analysis revealed important changes in the atomic compositions at surface level after plasma treatment, attributed both to the removal of surface contamination and to effective ion implantation.

We chose to study the effect of the plasma pre-treatment on current production by electroactive biofilm developing from mixed culture inocula. This is a more relevant and broadly applicable case for real applications. We studied the current development on classical three-electrode electrochemical cells.

As a model anodic system, we used the effluent of an acclimatized BES reactor (acetate fed) in operation. Figure 1 (left) shows the catalytic current development from time of inoculation for 3 GC electrodes, oxygen plasma treated electrode (GC-O), nitrogen plasma treated electrode (GC-N), and the blank electrode (no plasma treatment, GC-blank). We observed that the current development was fastest for the nitrogen plasma treated electrode, with the oxygen plasma treated electrode following shortly after. The current for GC-O and GC-N arrives to an initial maximum plateau value at day 18 from inoculation. The current increase for the blank electrode is much slower. By the time the GC-O and GC-N electrodes have arrived at their respective maxima, the current value for the blank electrode is only 20% of the values reached by the treated electrodes. Approximately at day 32, the currents for the three electrodes became very similar. The current values were very similar for the rest of the experiment. Similar results were also observed on graphite felt electrodes. At the end of the chronoamperometry experiments, cyclic voltammograms were measured both under turnover and non-turnover conditions.

As a model cathodic system, we inoculated the reactor with a broad consortia of denitrifier organisms (feeding $NaNO_3$ and $NaHCO_3$, with no organic carbon source). Figure 1 (right) shows preliminary results for 3 graphite plates electrodes. Catalytic current development from time of inoculation is shown for oxygen plasma treated electrode (GP-O), nitrogen plasma treated electrode (GP-N), and the blank electrode (no plasma treatment, GP-blank). Once again the current development was faster for the GP-N electrode, followed by the GP-O, with the blank electrode lagging behind. These experiments are still undergoing.

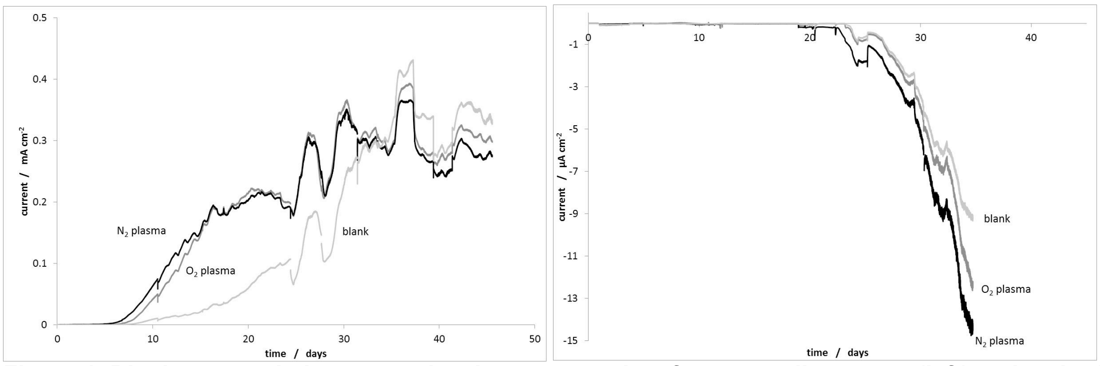

Figure 1. Bioelectrocatalytic current development vs. time for an anodic system (left) and cathodic system (right).

Discussion

For the anodic biofilms, during the first weeks after reactor inoculation, plasma treated electrodes showed considerably higher currents than non-treated electrodes. After a certain period of rapid current increase, the treated electrodes show constant current values, indicating that a mature biofilm has developed. It takes much longer for the blank electrode to reach this mature biofilm stage, but eventually, the same current densities are. Therefore, we do not believe that plasma treatment is increasing the extracellular electron transfer rate of the attached microorganisms; otherwise, we would expect a higher current density throughout the duration of the experiment. Very similar cyclic voltammetry curves both in turnover and non-turnover conditions, suggest that the plasma treatment does not seem to favour the preferential attachment of certain bacterial species over others, *i.e.* similar bacterial communities seem to be responsible for current generation in the three electrode set. This hypothesis is reinforced by a careful analysis of the logarithmic current plots. These show parallel profiles that suggest equal bacterial developing rates, suggesting once again the similarities of the bacterial communities. Therefore our results suggest that plasma treatment considerably enhances the initial cell adhesion, which results in subsequently faster biofilm development.

Preliminary results on the cathodic biofilms indicate that the effect of plasma treatment would be longer lasting that in the anodic biofilms, *i.e.* the current response would still be higher for the N_2 plasma pre-treated electrode even after development of a mature biofilm. The origin of this longer lasting effect is currently under investigation. These results are yet to be confirmed.