Influence of Carbon Fiber Morphology on Direct Electron Transfer

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Direct electron transfer (DET) from Laccase to carbon fiber electrodes was compared for two different fiber morphologies, graphite felt (GF) macrofibers, and carbon nanofibers (CNF). Weight-related current density is increased eight fold if nano- instead of macrofibers are used. We show that this effect is rather caused by a higher fiber surface area of the CNF-laccase electrode than by a better DET. However, voltage decay of CNF-laccase electrodes is nearly two fold lower for GF-laccase electrodes.

Efficiency of DET is dominated by the distance between enzyme active site and surface of the electrode[1]. Therefore morphology of the electrode material should play an important role. Here we compare the performance of GF macrofibers and CNF as cathodes with adsorption-bound laccase.

In a two compartment test cell cathode potential is measured against a saturated calomel electrode (SCE). 100 mM citrate buffer pH = 5.0 is used as electrolyte throughout the experiments. Electrodes are fabricated from graphite felt, and hydrophilized carbon nanofibers respectively. After laccase adsorption at open circuit, load curve experiments with and without mediator allow monitoring of enzyme activity and efficiency of DET. Long-term stability is investigated at continuous load.

Adsorption process of laccase at both, GF and CNF electrodes, is similar and yields comparable open circuit voltages (Figure 1).

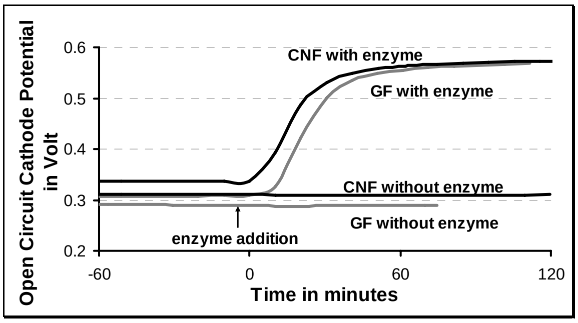

Fig. 1: Influence of enzyme adsorption on open circuit voltage (OCV). Cathode voltage is measured with carbon nanotubes (CNF) or graphite felt (GF) as cathode.

The load curve in Figure 2a shows that at a voltage of 0.3 V weight-related current density of the CNF-laccase electrode is about eight times higher than that of the GF-laccase electrode. Figure 2b shows this effect is not caused by a better DET of CNF-laccase electrodes but rather by a higher surface area of the nanomaterial: Fiber-surface-related current density at 0.3 V is actually three times lower for CNF-laccase electrodes than for the GF-laccase electrodes. First tests with untreated CNF show even better current densities than CNF-laccase electrodes but still a lower fiber-surface-related current density than GF-laccase electrodes (data not shown).

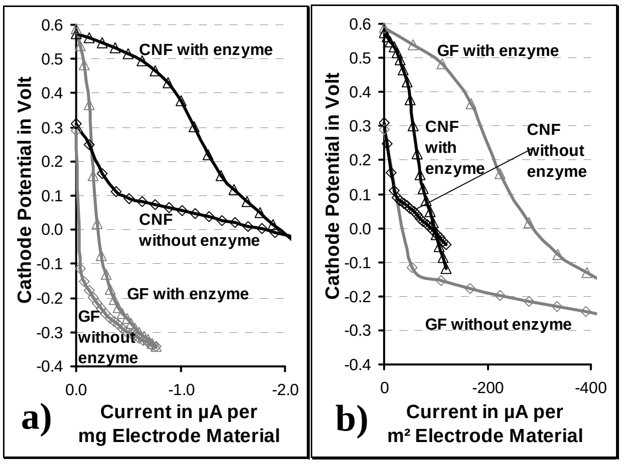

Fig. 2: Load curves of carbon nanofiber (CNF) and graphite felt (GF) electrodes a) related to electrode weight, b) related to the surface area of the electrode fibers.

Strongly reduced polarization by addition of mediator to GF- and CNF-laccase electrodes (Figure 3) shows that polarization is caused by poor DET rather than by insufficient laccase activity or diffusion.

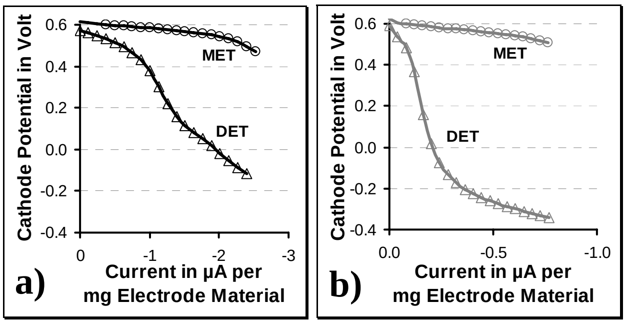

Fig. 3: *Load curves of a) carbon nanofiber (CNF) and b) graphite felt (GF) electrodes showing direct (DET) and mediated electron transfer (MET) related to electrode weight.*

Operation of the electrodes at a constant load of 10 µA for two days indicates nearly two fold higher stability of laccase when adsorbed to CNFs (Figure 4). CNF-laccase electrode potential decreases by 0.05 mV compared two 0.08 mV for the GF-laccase electrode.

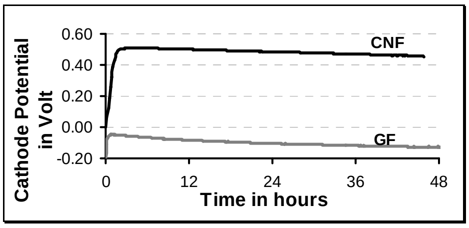

Fig. 4: Cathode potential of graphite felt (GF) and carbon nanofiber electrodes (CNF) at a constant load of 10 µA.

Results show that weight-related current density of a laccase cathode can be increased eightfold when carbon nano- instead of macrofibers are used. Reason for this effect is their higher surface area rather than better DET. Furthermore carbon nanofibers enhance laccase electrode lifetime.

1. J. Kim, H. F. Jia, and P. Wang, *Biotechnology Advances*, 2006, **24**, 296-308.