

**Title:****Direct Electron Transfer from Adsorption-Bound Laccase to Different Carbon Based Electrodes****Authors & affiliations:**

Stefanie Rubenwolf, Arne Kloke, Sven Kerzenmacher, Roland Zengerle, Felix von Stetten

Laboratory for MEMS Applications, Department of Microsystems Engineering (IMTEK), University of Freiburg, Georges-Koehler-Allee 106, 79110 Freiburg, Germany

**Abstract:** (Your abstract must use **Normal style** and must fit in this box. Your abstract should be no longer than 300 words. The box will 'expand' over 2 pages as you add text/diagrams into it.)

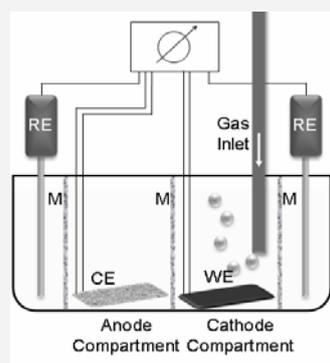
In the past direct electron transfer (DET) of laccase to different electrodes has been investigated in combination with different kinds of counter electrodes [1-4] leading to incomparable results. With a novel setup, we demonstrate measurement of DET from adsorption-bound *Trametes versicolor* laccase to cathodes, independent of their counter electrodes. We found that DET achieved with carbon nanofiber (CNF) electrodes is up one order of magnitude higher than with graphite felt electrodes.

We designed a measurement setup (Figure 1) with individual reference electrodes for anode and cathode, enabling independent electrode potential characterization. As electrolyte, 100 mM citrate buffer pH = 5.0 is used throughout the experiments. Electrodes are made from graphite felt or hydrophilized carbon nanofibers. After laccase adsorption at open circuit, load curve experiments with and without mediator allow monitoring of enzyme activity and efficiency of DET. Electrode stability is investigated by operating the electrodes at 10  $\mu$ A constant load over two days.

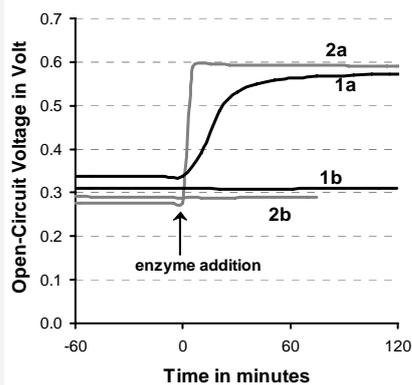
Addition of laccase to both, graphite and CNF electrodes yields comparable open circuit voltages. (Figure 2). Under load, strong polarization of the graphite-laccase electrode occurs already at 0.2 mA/g, whereas the CNF-laccase electrode tolerates more than 1 mA/g (Figure 3). Strongly reduced polarization by addition of mediator to the graphite felt electrode (Figure 4) shows that polarization is caused by poor DET and not by laccase inactivation. Operation of the electrodes at constant load indicates higher stability of laccase when adsorbed to CNFs (Figure 5).

With our novel test setup we demonstrate characterization of different biofuel cell cathodes independent of their counter electrode. We show that DET from laccase to CNFs is superior to DET to carbon fibers of graphite felt.

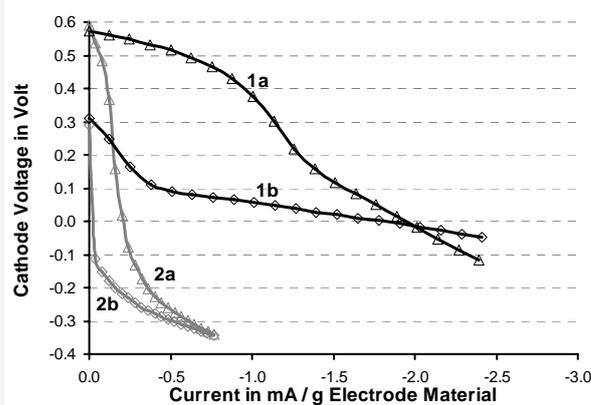
1. Brunel, L. et al., 2007. *Electrochemistry Communications* 9 (2), 331-336.
2. Habrioux, A., Sibert, E., Servat, K., Vogel, W., Kokoh, K.B., Alonso-Vante, N., 2007. *Journal of Physical Chemistry B*.
3. Kamitaka, Y., Tsujimura, S., Setoyama, N., Kajino, T., Kano, K., 2007. *Phys.Chem.Chem.Phys.* 9 (15), 1793-1801.
4. Vincent, K.A., Cracknell, J.A., Lenz, O., Zebger, I., Friedrich, B., Armstrong, F.A., 2005. *Proceedings of the National Academy of Sciences of the United States of America* 102 (47), 16951-16954.



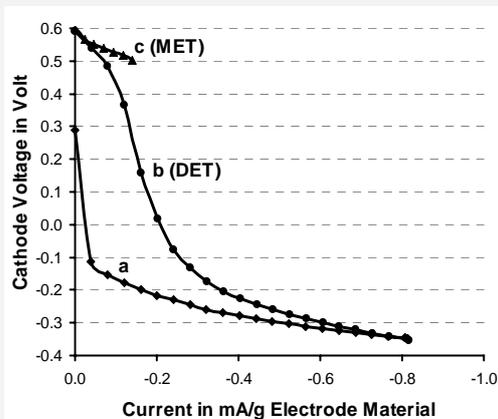
**Figure 1: Test setup for evaluation of electrodes. Working electrode (WE), platinum mesh as counter electrode (CE) and saturated calomel electrodes (SCE) as reference electrodes (RE) are in compartments separated by Fumion®-membranes (M). The cathode compartment is bubbled with air.**



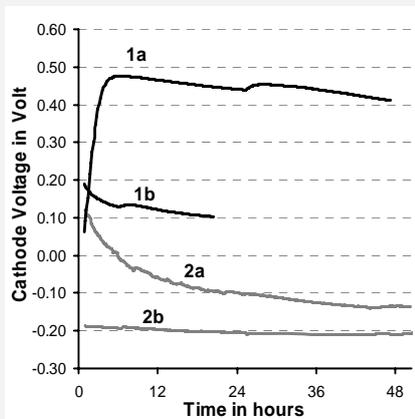
**Figure 2: Development of open circuit voltage (OCV) after laccase addition to bare electrodes. Cathode voltage of CNF (1) or graphite felt (2) cathodes is measured versus SCE. Enzyme addition: Buffer without enzyme is exchanged against a) buffer with 5 U/mL laccase b) buffer without laccase.**



**Figure 3: Galvanostatic load curves of different carbon based electrodes: CNF (1) and graphite felt (2) electrodes a) with 5 U/mL laccase b) without laccase. Load steps of 5  $\mu$ A and measurements are performed hourly.**



**Figure 4: Efficiency of direct electron transfer (DET) compared to mediated electron transfer (MET). Galvanostatic load curves with steps of 5  $\mu$ A and measurements every hour are made with graphite felt electrodes a) without addition of laccase b) with 5 U/mL laccase c) with 5 U/mL laccase and 1 mM ABTS (mediator).**



**Figure 5: Cathode stability at a constant galvanostatic load of 10  $\mu$ A. Experiments are performed with CNF (1) and graphite felt (2) electrodes a) with 5 U/mL laccase b) without laccase.**

**Do NOT write outside the boxes. Any text that is not in the boxes may be deleted.**