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Introduction

The use of hydrogen fuel cells for portable applications has not been widespread, because storage of a required volume of hydrogen gas has been expensive or complicated. One solution to this is the generation of hydrogen in-situ from more easily storable compounds, e.g. methanol or ethanol. Enzymes are known to oxidize these fuels at room temperature and can therefore be used in in-situ hydrogen production. In this study, the use of methanol dehydrogenase enzyme (MDH, E.C. 1.1.99.8) for electrochemical reformation of methanol is investigated. The focus is in improving the electrochemical contact between a glassy carbon electrode and MDH with carbon nanotubes (CNT).

MDH used in the study was from organism Methylobacterium Extorquens. It contains two pyrroloquinoline quinone (PQQ) coenzymes, which serve as electron acceptors when methanol is oxidized in the enzyme. PQQ is buried in the middle of the enzyme structure and if the enzyme is immobilised on a smooth electrode surface, electron transfer from the PQQ would require the electron to tunnel several nanometers. However, enzymes can absorb to CNTs so that the distance between the conductive electrode material and the redox center of the enzyme is decreased. So, by modifying a carbon electrode with CNTs, the electron transfer between the MDH and the electrode can be facilitated [1]

Experimental

The CNTs used are few-walled carbon nanotubes (FWCNT, <10 nm diam.) produced at the NanoMaterials Group (Helsinki University of Technology) by chemical vapor deposition of methane catalyzed by Co and Mo. A modified glassy-carbon disk electrode was prepared by dropping an aliquot of FWCNTs after purification in HCl and letting it dry at ambient conditions. The electrodes were then saturated with MDH by dipping the CNT-modified electrode in MDH solution overnight. MDH was from organism Methylobacterium Extorquens and purchased from Alkomohr Biotech Oy Ltd.

Electrochemical characterization of the electrodes were made in a three electrode cell. The enzyme electrode was the working electrode, platinum wire the counter electrode and saturated calomel electrode the reference electrode. Supporting electrolyte was 0.2 M phosphate buffer at pH 9.5 and measurements were made after nitrogen bubbling.

Results

CNT-MDH modified electrode shows an extra redox peak pair compared to CNT-modified electrode. Formal potential of the reaction is +40 mV vs SCE, which corresponds to the potential area where electron transfer in free PQQ takes place [2]. Also, the peak pair is absent when CNTs are replaced with carbon black (Vulcan XC72R) indicating CNTs facilitate the electron transfer.

Lowering the pH increases the electrochemical activity of the studied redox pair. Also, the formal potential shifts to a higher potential, namely to +200 mV vs SCE @ pH 6. This corresponds to the behaviour of free PQQ [2].

Increasing the potential sweep speed increases the peak currents for both the oxidation and reduction of the studied redox pair. The dependency is linear, which is typical for adsorbed species.

Attachment and electrochemical activity of MDH on CNT-modified glassy-carbon electrode is verified!

References

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