Carbon Nanotube Powder Microelectrodes for NADH Oxidation

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Selective determination of nicotinamide redox coenzymes such as NADH and NAD(P)H is a key to developing electrochemical dehydrogenase sensors and investigating the electron transport in relevant biological systems. Because of the high oxidation overpotential of NADH at bare electrodes, such as glassy carbon electrodes, a number of mediator modified electrodes have been reported to accelerate the NADH oxidation reaction [1,2]. However, these mediator modified electrodes suffer more or less the leaching out problem which causes instability of the modified electrodes. In this work a carbon nanotube powder microelectrode (CNTPME) is reported for NADH oxidation. The powder microelectrode was originated from our laboratory. It features a tiny amount of powder material filled in the cavity formed by etching the tip of a Pt micro disk electrode. The powder microelectrode exhibits characters of both microelectrodes and porous electrodes. The details of preparation of powder microelectrodes have been reported elsewhere[3].

Though the powder microelectrode generally exhibits much higher apparent activity compared to the smooth electrode made of the same material, this work shows that the carbon nanotube behaves differently from other commonly used high surface area carbon materials for NADH oxidation.

The CNPME showed a pair of very stable cyclic voltammetric (CV) current peaks near 0.0 V (*vs.* SCE) in pH 7 background solution, ascribable to surface quinone groups (Fig.1a). The peak potential was found to change with pH by ca. 59 mV/pH in the pH range 1-7, in agreement with the anticipated Nernrstian behavior for a reaction involving two electrons and two protons. According to the charge under the current peak, the concentration of quinone groups was estimated to be about 4.5×10^{-8} mole per cm^2 apparent surface area and the coverage of quinone groups on the real surface area of the nanotubes was about 20%. Assuming the first electron transfer being the rate determining step, from the scanning rate dependence of the peak separation the heterogeneous rate constant for the redox reaction of the surface quinone groups was calculated to be 6 s^{-1}.

Fig. 1b and Fig. 2 show the CV and steady state polarization curve, respectively, of NADH oxidation at the CNTPME in pH 7 buffer solution containing 1 mM NADH. Unlike those often reported in literature, both CV and steady state polarization showed no sign of poisoning due to the products or intermediates of NADH oxidation. The two waves in Fig. 2 show approximately the same height, attributable to the two one-electron steps of oxidation. The overpotential of the first wave is negatively shifted for ca. 750 mV compared to that for the glassy carbon electrode. The apparent plateau current density of the first wave was ca. 7.5×10^{-5}A cm^{-2} and the rate constant for this step was approximately 3.8×10^5 M^{-1} S^{-1}. For comparison, the behaviors of NADH oxidation at the powder microelectrode made of high surface area activated carbon (KB carbon, $950m^2g^{-1}$) were investigated. Compared with the CNTPME, the current response of KB carbon powder microelectrode was an order of magnitude lower; besides, the response was unstable so that no steady state polarization curve could be recorded successfully.

The CNTPME showed a good linear response to NADHA concentration in the range 5 μM to 1 mM with a sensitivity 33 mA $cm^{-2}M^{-1}$, 90% response time 30 s and temperature coefficient $1.3\%/^0C$ (in the range $15\text{-}40^0C$). In view of the simple preparation and the stable and sensitive response, the CNTPME appears to be good sensing electrode for detecting NADH and the substrates of dehydrogenases which need NADH as the cofactor.

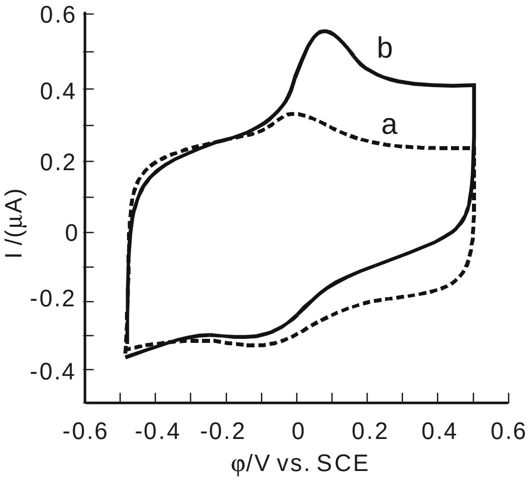

Fig. 1 CV of CNTPME in (a) pH 7 phosphate buffer; (b) buffer containing 1 mM NADH, at 50 mV s^{-1}.

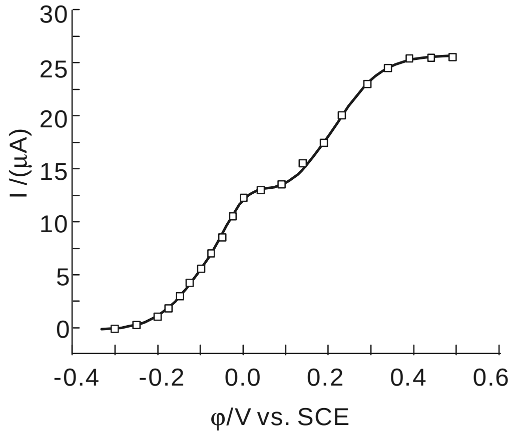

Fig. 2 The steady state polarization curve of NADH oxidation at the CNTPME in pH 7 phosphate buffer containing 1mM NADH

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