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Author(s)	Zu, Y; Li, F
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NADH Oxidation at Fluorosurfactant-Covered Metal Electrodes

Yanbing Zu, Feng Li

Department of Chemistry, the University of Hong Kong, China

NADH is a common redox cofactor in bio-systems, acting as carriers of two electrons and one proton. The oxidation of NADH at electrodes is the interest of a lot of studies, aiming at fabricating electrochemical biosensors and bioreactors. In aqueous solution at pH 7.0, the thermodynamic redox potential (E°) for NAD^+/NADH is -0.561 V versus SCE. It has been known that the overpotential of NADH oxidation is very large at bare metal electrodes (ca. 0.7 V and 1 V vs. SCE at Pt and Au electrodes, respectively). Strong adsorption of NADH and its oxidation products on these electrodes generally poisons the electrode surface and inhibits the oxidation process. The differences in activity of electrode materials mainly originate from adsorption phenomena. For the efficient electro-oxidation of NADH, mediated electrocatalysis has been studied. Some organic compounds immobilized on electrode surface demonstrate very high rates for the mediated oxidation of NADH. However, the deactivation usually remains a question for these electrodes.¹

Here, we describe a new method of reducing the overpotential of NADH oxidation and improving the reproducibility at a fluorosurfactant-covered gold electrode. The adsorption behavior of fluorosurfactants at the electrode/electrolyte interface has been studied and compared with their hydrocarbon analogues recently.² We found that, in neutral solution, the initial growth stage of the surface oxides at a gold electrode could be inhibited significantly by a nonionic fluorosurfactant, Zonyl FSN, as shown in Figure 1. However, the adsorption layer may promote some electrochemical reactions. For example, the oxidation rate of tripropylamine at an FSN-covered gold electrode can be significantly enhanced.³ Interestingly, the adsorbed FSN on gold may also reduce the overpotential of NADH oxidation. Figure 2 shows that no oxidation of NADH occurred before the growth of surface oxides at a bare gold electrode. It has been proposed that the surface oxides could catalyze NADH oxidation. However, at FSN-covered gold electrode, a NADH anodic wave appeared at around 0.55V, well before the onset of surface oxide growth, as shown in Figure 3. Similar result was also obtained at a Pt electrode. Since the modification of the electrodes is base on the physical adsorption of fluorosurfactant species, the regeneration of the active surfaces is facile. We believe the adsorbed FSN inhibited the adsorption of NADH molecules on the electrodes, and therefore, decreased the overpotential and enhanced the oxidation process.

Reference

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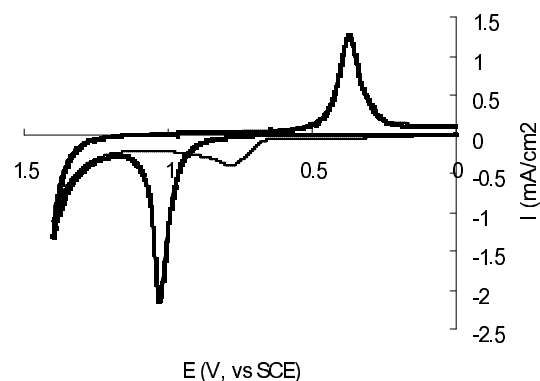


Figure 1. Cyclic voltammograms of a 2-mm-diameter gold electrode in 0.15 M PBS (pH 7.6) in the absence (thin line) and presence of 0.1 wt % FSN (bold line). Scan rate, 0.1 V/s.

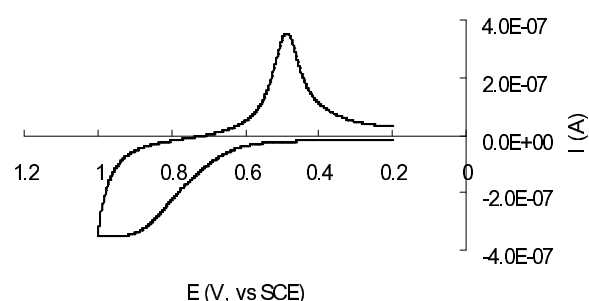


Figure 2. Cyclic voltammogram of a 2-mm-diameter gold electrode in 0.15 M PBS (pH 7.6) containing 50 μM NADH. Scan rate, 0.1 V/s.

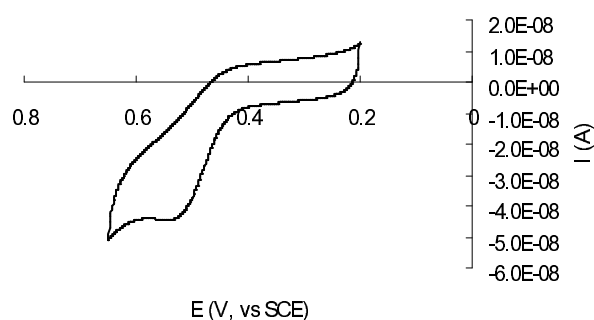


Figure 3. Cyclic voltammogram of a 2-mm-diameter gold electrode in 0.15 M PBS (pH 7.6) containing 50 μM NADH and 0.05 wt % FSN. Scan rate, 0.01 V/s.