

NADH oxidation with hybrid polyaniline/nitrofluorenone modified electrodes

A. Kuhn*, N. Mano*, P. N. Bartlett† and E. Simon†

* Laboratoire d'Analyse Chimique par Reconnaissance Moléculaire, Ecole Nationale Supérieure de Chimie et de Physique de Bordeaux, 33406 Pessac, France;

† Department of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK.

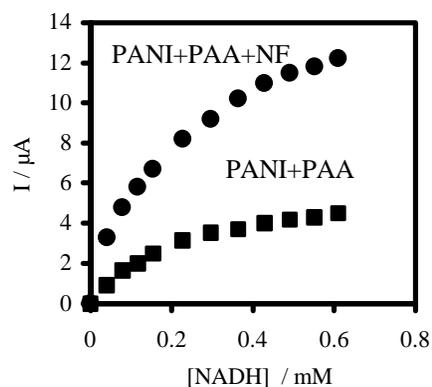
For efficient electrochemical oxidation of NADH it is necessary to use a suitable redox mediator which can undergo reduction by NADH followed by rapid electrochemical oxidation. This is because oxidation at bare electrode surfaces requires substantial overpotentials and proceeds through reactive radical intermediates which lead to electrode fouling and side reactions. In previous work published by our two groups we have shown that nitro-fluorenone derivatives (NF) are good mediators for NADH oxidation operating at low overpotentials (typically -0.05 V vs. SCE) [1, 2]. In these experiments the nitro-fluorenones were used as adsorbed monolayers on the surface of glassy carbon electrodes. This gave high currents for NADH oxidation but desorption and loss of the mediator from the electrode surface leads to a decrease in catalysis with time. In other previous work we have shown that electropolymerized films of poly(aniline) (PANI) grown in the presence of polymeric cations such as poly(vinylsulfonate) (PVS) or poly(acrylate) (PAA) can be used at pH 7 for the oxidation of NADH and that polymers of this type can be used to construct microelectrochemical transistors responsive to NADH [3-6]. The disadvantage of the using of poly(aniline) composite films is that the overpotential is higher (around $+0.05$ V vs. SCE) and one has to be careful to avoid deprotonation of the film at pH 7 and loss of electroactivity.

The use of monolayer modified electrodes suffers from two problems. First it is essential that the rate of the mediation reaction be high because the number of mediator centers present at the electrode surface is limited. Second any loss of the mediator by side reactions or through desorption will lead to a rapid loss of electrocatalytic activity. The use of multilayer modified electrodes has the advantage that there are more mediator sites present at the electrode surface, therefore the rate of reaction of the mediator need not be so great and the stability should be improved. Nevertheless these advantages are only achieved if charge transport between the mediator sites in the film is fast and mass transport of the substrate through the film is also fast so that the whole film can be accessed by the electrocatalytic reaction. Our earlier work with poly(aniline) composites has demonstrated that the poly(aniline) backbone can act as an efficient conduit for charge transport and that the electrocatalytic oxidation of NADH occurs throughout the film in this system [3-5]. The aim of the present work was to investigate whether it was possible to combine the desirable attributes of the nitro-fluorenone mediator (high rate constant for NADH oxidation at low overpotential) with the advantages of the poly(aniline) composite electrode (electrochemically deposited multilayer structure, reaction throughout the layer).

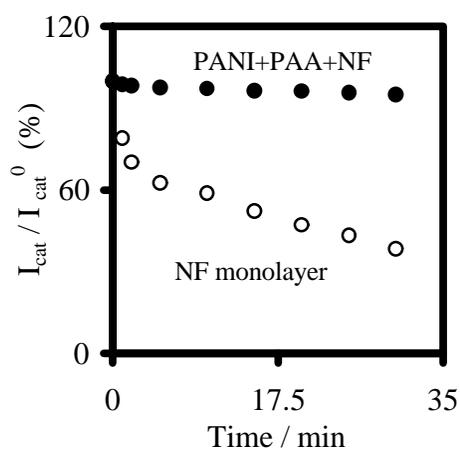
Two methods of electrode preparation have been investigated. Polymerization of aniline in the presence of

nitrofluorenone led to undesirable side effects and therefore polymerization with subsequent adsorption of the nitrofluorenone was preferred.

The response of such an electrode to increasing NADH concentrations is optimized due to the synergy of both components. Figure 1 illustrates this difference in catalytic current obtained at 0V vs. SCE and pH=7.1.



The rapid loss of catalytic activity observed for the nitrofluorenone monolayer modified electrode could be avoided using the conducting polymer as a stabilizing matrix (Figure 2).



In conclusion there is a mutual benefit when combining both compounds. This might lead to practical devices with a better overall performance.

Acknowledgements

Alliance, Region Aquitaine French Ministry of Research and Technology, ENSCPB, and the Office of Naval Research for funding,

References

1. N. Mano and A. Kuhn, *J. Electroanal. Chem.*, **477** (1999) 79.
2. N. Mano and A. Kuhn, *J. Electroanal. Chem.*, **498** (2001) 58.
3. P. N. Bartlett, P. R. Birkin and E. N. K. Wallace, *J. C. S., Faraday Trans.*, **93** (1997) 1951.
4. P. N. Bartlett and E. N. K. Wallace, *J. Electroanal. Chem.*, **486** (2000) 23.
5. P. N. Bartlett and E. Simon, *PCCP*, **2** (2000) 2599.
6. P. N. Bartlett, J. H. Wang, and E. N. K. Wallace, *J. Chem. Soc., Chem. Commun.*, (1996) 359.