Functionalization of Nickel on 4-Aminothiophenol Modified Glassy Carbon Electrodes and the Enhanced Electrochemical Activity towards the Oxidation of Ethanol

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Organized, self-assembled monolayers (SAM) on various solid supports have attracted much attention over the last decade and are commonly used to impart desired chemical or physical properties to surfaces. Monolayers of organic thiols have been intensively studied because of their stability and high degree of organization. Pioneering work on the adsorption of aromatic thiols was performed by Hubbard et al. [1, 2] who focused their studies mainly on the adsorption of thiophenol and benzyl mercaptan on platinum and silver and found the formation of complete monolayers with a low degree of long range order on Pt(111) and a higher degree on Ag(111). A relative complete picture of the self-assembled process of aromatic thiols and their resulting structure in the SAMs has emerged over the last decade [3-5].

With the use of 4-aminothiophenol, offering high electrical conductivity, particular interest has been paid to its electrochemical deposition at oxidative potentials to modify the glassy carbon electrode [6]. Using this approach nickel was functionalized onto the modified electrode, and the presence of nickel was confirmed by cyclic voltammetry and X-ray photoelectron spectroscopy, XPS. Specific attention has been directed towards the use of nickel as catalyst for the oxidation of ethanol. Comparing the cyclic voltammograms obtained for this electrochemical process on nickel foil and nickel functionalized onto modified electrodes with low nickel surface concentration $(1.8 \times 10^{-9} \text{ mol/cm}^2)$ and high $(1.4 \times$ 10^{-8} mol/cm²), striking differences were outlined. The use of the modified electrode on which a low amount of nickel has been loaded raised much interest in terms of fast kinetic processes for the ethanol oxidation even at high concentration (5 M). Comparable electrochemical activity was obtained when using almost 300 fold less quantity of nickel as catalyst material. Running the ethanol oxidation constantly at 0.5 V vs. Ag/AgCl in 1M NaOH resulted in reasonable current densities (>5 mA/cm^2).



Figure 1. Set of cyclic voltammograms at 50 mV/s in 1 M NaOH with increasing concentration of ethanol from 0.5 M a), 2

M b) to 5 M c) of nickel $(1.8 \times 10^{-9} \text{ mol/cm}^2)$ functionalised onto the 4-aminothiophenol modified GC electrode surface. 4-Aminothiophenol as surface modification agent was grafted at 2.0 V vs Ag/AgCl for 240s onto the GC electrode.

Acknowledgments

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