

Electrochemistry and Grafting of 4-Aminothiophenol on Glassy Carbon Electrodes

Jan Marwan and Daniel Bélanger

E-mail : Jan_Marwan@yahoo.ca

Département de Chimie, Université de Québec à Montréal
Case Postale 8888, succursale Centre-Ville,
Montréal (Québec) Canada H3C 3P8

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].

In this investigation, we report the study of the electrochemical properties of 4-aminothiophenol whilst this molecule has been grafted to modify the glassy carbon (GC) electrode surface. Glassy carbon electrodes (AIMCOR, Pittsburgh, grade GC-10) were prepared from 3 mm diameter rods embodied into epoxy resin (Hysol, 56C) and were used as working electrodes. A platinum gauze and a Ag/AgCl (saturated KCl) electrode were used as counter and reference electrode, respectively. All potentials were reported versus the Ag/AgCl reference electrode. Electrochemical measurements, using an electrochemical interface SI 1287 (Solartron Instruments), on GC electrodes were carried out in acetonitrile containing 4-aminothiophenol (Aldrich) and 0.1 M NBu₄BF₄ (Aldrich) as supporting electrolyte. The 4-aminothiophenol concentration was varied from 0.1 to 5 mM. The cyclic voltammetry behavior of 4-aminothiophenol was compared to the one obtained when using thiophenol (Aldrich) and aniline (ACROS). The voltammetry was performed within a potential limit of -0.5 to 2.0 V at 50 mV/s.

The cyclic voltammogram of the 4-aminothiophenol solution shows two main peaks, one peak at lower and the other one at higher oxidative potentials. Firstly, the peak at lower potential was attributed to the oxidation of the amine functionality of 4-aminothiophenol [6]. This corresponds to the one-electron oxidation of amine to its analogous cation radical which could form chemically stable covalent linkage between the nitrogen atom of the amine and the GC electrode surface [7]. Successive grafting of 4-aminothiophenol onto GC electrodes was observed with subsequent voltammetric cycles evidenced by voltammetric studies in ferri/ferrocyanide solutions where complete blocking behaviour of the modified electrode was shown. Upon extending the electrode potential applied for the deposition of 4-aminothiophenol onto GC electrodes to more oxidative values, the electrochemical oxidation of the thiol functionality to sulfonate with its spontaneous reduction onto the GC surface appeared.

To our knowledge, this is the first approach to deposit 4-aminothiophenol onto GC electrode surfaces by

oxidizing either the amine side or thiol side containing group.

Acknowledgements

We gratefully thank the financial support of the Natural Science and Engineering Research Council of Canada (NSERC).

REFERENCES

- [1] A. T. Hubbard, *Chem. Rev.* **88**:633 (1988).
- [2] J. Y. Gui, D. A. Stern, D. G. Frank, F. Lu, D. C. Zapien, and A. T. Hubbard, *Langmuir* **7**:955 (1991).
- [3] W. A. Hayes and C. Shannon, *Langmuir* **12**:3688 (1996).
- [4] J. Lukkari, K. Kleemola, M. Meretoja, T. Ollonqvist, and J. Kankare, *Langmuir* **14**:1705 (1998).
- [5] E. Sabatani, J. Cohen-Bolakia, M. Bruening, and I. Rubinstein, *Langmuir* **9**:2974 (1993).
- [6] B. Barbier, J. Pinson, G. Desarmot, and M. Sanchez, *J. Electrochem. Soc.* **137**:1757 (1990).
- [7] J. Liu, L. Cheng, B. Lu and S. Dong, *Langmuir*, **16**: 7471 (2000).