

ELECTROCHEMICAL FEATURES OF PRUSSIAN BLUE/CONDUCTING POLYMER BILAYER FILMS

S. Lupu^{1*}

1. University "Politehnica" of Bucharest, Faculty of Industrial Chemistry, Department of Analytical Chemistry, Calea Grivitei 132, 78122, Bucharest, Romania.

*Present address: Ecole Normale Supérieure, Département de Chimie, 24, rue Lhomond, F-75231 Paris Cedex 05, France.

E-mail: s_lupu@chim.upb.ro; stelian.lupu@ens.fr

Keywords: Prussian Blue, Conducting polymer, chemically modified electrode, bilayer film.

During the last two decades the use of metal hexacyanoferrates for the modification of electrode surfaces has attracted much interest [1-3]. Among metal hexacyanoferrates, Prussian Blue (PB), *i.e.* iron(III) hexacyanoferrate, is one of the most extensively studied, due to its electrocatalytic activity [4-8]. However, the stability of PB is only satisfactory in acidic aqueous solutions, while at alkaline or neutral pH decomposition occurs [9].

Recently, the use of PB modified electrodes, covered on top with an outer layer of different organic polymers, has been reported [10,11]. The organic polymer layer can be a conducting polymer, such as polyaniline, or an ion-exchange polymer, such as Nafion[®]. The deposition of an outer organic polymer layer is performed with the scope of obtaining enhanced stability of the PB film in neutral or alkaline solution.

In this work, the preparation and the electrochemical behavior of bilayer films composed by PB and poly[3-methylthiophene], on a platinum electrode, are reported. The electrochemical features of the Prussian Blue/conducting polymer bilayer film are investigated in both aqueous and acetonitrile solutions. The cyclic voltammograms, recorded for the electrodes modified only with Prussian Blue in acidic aqueous solutions, present two sets of peaks corresponding to the electron transfer in the outer and inner sphere of the complex, respectively at 0.2 and 0.9 V *vs.* SCE [1, 2], while the signal recorded in acetonitrile shows that PB is still electroactive but in a lower extent. Under specific experimental conditions, the individual redox behaviour of each constituent of the bilayer is evidenced in the two solvents separately, *i.e.*, that of PB and that of poly[3-methylthiophene] in aqueous and in organic solvent, respectively. Cyclic voltammetric studies for the bilayer films show that, in acetonitrile solvent, Prussian Blue is electroactive to some extent, though the electrochemical response of the system is mainly accounted for poly[3-methylthiophene]. In aqueous solution PB exhibits good electroactivity. The bilayer films present good stability in both aqueous and organic solutions.

REFERENCES

1. K. Itaya, T. Ataka and S. Toshima, *J. Am. Chem. Soc.* 104, 4767 (1982).
2. K. Itaya, H. Akahoshi and S. Toshima, *J. Electrochem. Soc.* 129, 1498 (1982).
3. A.A. Karyakin, *Electroanalysis* 13, 813 (2001).
4. S. M. Chen, *J. Electroanal. Chem.*, 417, 145 (1996).
5. U. Scharf and E.W. Grabner, *Electrochim. Acta*, 41, 233 (1996).
6. A. A. Karyakin, E. E. Karyakina and L. Gorton, *Talanta*, 43, 1597 (1996).
7. A. A. Karyakin, E. E. Karyakina and L. Gorton, *Electrochem Comm.*, 1, 78 (1999).
8. N. Totir, S. Lupu, E. M. Ungureanu, N. Iftimie, *Rev. Chim. (Bucharest, English Edition)* 2, 23 (2001).
9. R. Koncki, O. S. Wolfbeis, *Anal. Chem.* 70, 2544 (1998).
10. K. Ogura, N. Endo, M. Nakayama, H. Ootsuka, *J. Electrochem. Soc.* 142, 4026 (1995).
11. W. Lu, G. G. Wallace, A. A. Karyakin, *Electroanalysis* 10, 472 (1998).