

PREPARATION AND ION-EXCHANGE VOLTAMMETRIC CHARACTERIZATION OF COMPOSITE FILMS MADE OF CONDUCTING POLYMERS AND IONOMERS

P.Scopece, P.Ugo.

Department of Physical Chemistry, University of Venice,
S.Marta 2137, 30123 Venice, Italy

Paolo Scopece e-mail: scp@unive.it

Paolo Ugo e-mail: ugo@unive.it

Ion-exchange voltammetry is an electroanalytical technique, which employs solid electrodes modified by a thin film of an ion-exchange polymer [1]. The polymeric coating allows the selective ion-exchange preconcentration and voltammetric determination of traces inorganic and organic electroactive ions of interest for environmental, biomedical or pharmaceutical analysis. This research is aimed to introduce electrochemical control in the uptake and release of the electroactive analytes. In principle, this can be achieved by preparing a composite between an ion-exchanger with fixed anion exchange functionalities and a conducting polymer [2,3], which, in the oxidized state, can act as polycationic counter ion. Electrochemical switching of the latter polymer from the reduced (insulating) to the oxidized (conducting) form should change the composite properties from those of a cation-exchanger to those of a neutral polymer. Different composites were examined with this respect. A first series of experiments was performed by preparing a poly-3-methyl-thiophene (p3MeT) / polyester sulfonated Eastmann AQ55 composite. The composite film was prepared by electropolymerization in acetonitrile solution of 3-methyl-thiophene monomer [2] on electrodes coated with recasted AQ55 film. Fig.1 shows that such composite film keeps an electrochemical behaviour which is not too different from that of poly-3-methyl-thiophene alone even if oxidation takes place at slightly more positive potentials. Ion-exchange properties of the composite are different, since in its reduced state it can preconcentrate cations (as for instance $\text{Os}(\text{bpy})_3^{2+}$) this is a property typical of the AQ55 component of the composite [4].

A second series of composite films were prepared in aqueous solution by electropolymerization of poly-aniline on Nafion coated electrodes. In this case the influence of pH and the role of the protonation of aniline is examined in detail. The incorporation and preconcentration of both electroactive and non electroactive analyte cations was studied by electrochemical and quartz crystal microbalance measurements. Particular attention was stressed on standing the influence of the redox state of the conducting component of the composite. A key point in the successful achievement of incorporation-preconcentration and release-regeneration schemes is played by the analyte cation and competing counter-ions from the electrolyte solution. Applications to the development of electrochemically switchable sensors are discussed.

References

- [1] P.Ugo, L.M.Moretto, F.Vezzà. *Chem. Phys. Chem.*, **3**, 917(2002)
- [2] H.B. Mark Jr, N. Atta, Y.L.Ma, K.L. Petticrew, H. Zimmer, Y. Shi, S.K. Lunsford, J.F. Rubinson, A. Galal. *Bioelectrochemistry and Bioenergetics*, **38**, 229(1995)
- [3] D. Orata, D.A. Buttry. *J. Electroanal. Chem.*, **257**, 71(1988)
- [4] J.Hanzlik, P.Ugo, S.Daniele, G.A.Mazzocchin. *J. Electroanal. Chem.*, **404**, 89(1996).

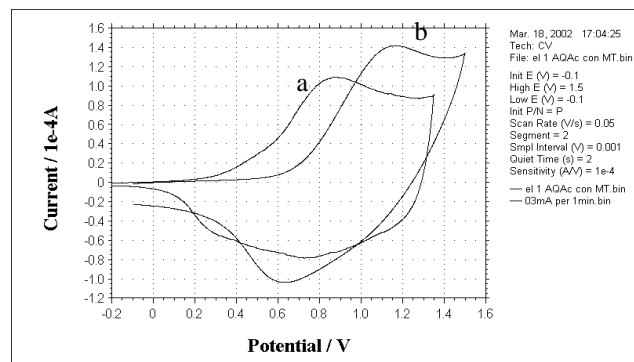


Fig.1. Cyclic voltammograms recorded in $\text{CH}_3\text{CN}/ 10^{-2} \text{ M}$ TBATFB of films of: (a) p3MeT and (b) the composite p3MeT/AQ55. The films were obtained by galvanostatic polymerization at 0.3mA for 60s on glassy carbon electrodes in CH_3CN solution containing 50mM 3-methylthiophene and 75 mM.TBATFB.