

Carbon ceramic electrode modified with redox liquid

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The immobilisation of large number of redox centers on the electrode surface, is most often realised by deposition of a thin layer of redox polymer [1]. Quite recently proposed immobilisation of random ensemble of redox liquid (hydrophobic redox active compound being liquid at room temperature) droplets represent alternative way of electrode modification [2,3]. This strategy is highly versatile, because almost any organic or organometallic compounds can be turned into a liquid by modification with suitable lipophilic substituents. However, the resulting electrode seems to be not very stable from the point of view of practical applications.

Application of sol-gel derived hydrophobic porous glass may solve stability problems, because of strong hydrophobic interactions between liquid and solid. The carbon ceramic electrode (CCE) composed of hydrophobic silicate matrix containing graphite particles [4], filled with decamethylferrocene solution in various hydrophobic solvent exhibits stable behaviour in aqueous solution [5,6].

CCE modified redox liquid - t-butyloferrocene (tBuFc) was prepared and studied. It was obtained by immersion in tBuFc or its diluted solution in volatile solvent (hexane). These procedures result in bulk or microphase modification of the electrode material. Its properties were investigated by cyclic voltammetry and chronoamperometry in aqueous salt solution of different concentration. The preliminary results of this work were already published [7].

The cyclic polarization of CCE modified with redox liquid in aqueous electrolyte results in peak shaped voltammogram. Its shape depends on the procedure of modification and composition of aqueous phase. For electrode modified with pure redox liquid the anodic wave is followed by sharp current increase and cathodic peak is well developed (Fig. 1). The cyclic voltammogram recorded with tBuFc microphases modified electrode is peak shaped (Fig. 2) and for slow scan rate some decrease of current is observed during first few scans. The specific voltammogram features were attributed to the redox process of tBuFc. The dependence of voltammogram position on potential scale indicates that electrooxidation of tBuFc is followed by anion insertion. This is different than the oxidation of n-butyloferrocene droplets deposited on pyrolytic graphite followed by expulsion of cation into aqueous phase [8]. It can be ascribed to larger hydrophobicity of tBuFc and to the ability of polar hydrophobic matrix to accommodate tBuFc⁺ with corresponding counterion. However, experiments done with second working electrode positioned close to the CCE surface as well the appearance of bluish colour in aqueous phase indicate that prolonged electrolysis or electrode polarization at more positive potentials results in expulsion of tBuFc⁺ cations into aqueous phase. This effect is more pronounced in the presence of more hydrated anions like SO₄²⁻.

The magnitude of the current is proportional to the aqueous electrolyte concentration (Fig.1). The shape of current-potential dependences obtained with bulk modified electrode indicates that electrode process starts at the three phase junction formed by graphite particles and liquid organic-aqueous interface supported by hydrophobic silicate.

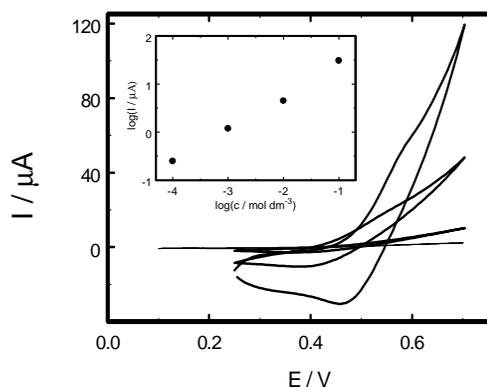


Fig. 1. Cyclic voltammograms obtained with CCE modified with tBuFc and immersed in aqueous KNO₃ with different concentration (0.1, 0.01, 0.001 and 0.0001 mole dm⁻³ going from larger to smaller current magnitude). Scan rate 0.01 V s⁻¹. The insertion shows logarithmic plot of anodic peak currents, I vs. salt concentration, c in aqueous phase.

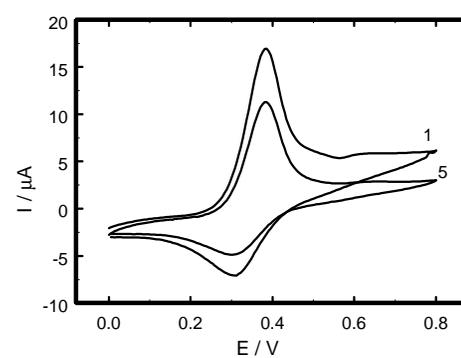


Fig. 2. Cyclic voltammograms obtained with CCE modified with tBuFc microphases and immersed in 0.1 mole dm⁻³ aqueous KNO₃ Scan rate 0.01 V s⁻¹. First and fifth scan are presented.

References

1. R.W. Murray (Ed.) Molecular Design of Electrode Surfaces, Wiley, New York, (1992).
2. F. Marken, R.D. Webster, S.D. Bull, S.G. Davies, *J. Electroanal. Chem.*, **437**, 209 (1997).
3. U.Schroder, R.G. Compton, F. Marken, S.D. Bull, S.G. Davies, S. Gilmour, *J. Phys. Chem. B*, **105**, 1344 (2001).
4. M. Tsionsky, G. Gun, V. Glezer, O. Lev, *Anal. Chem.*, **66**, 1747 (1994).
5. M. Opallo, M. Saczek-Maj, *Electrochem. Commun.*, **3**, 306 (2001)
6. M. Saczek-Maj, M. Opallo, *Electroanalysis*, **14**, 1060 (2002).
7. M. Opallo, M. Saczek-Maj, *Chem. Commun.*, 448 (2002).
8. J.D. Wadhavan, N.C. Evans, R.G. Compton, *J. Electroanal. Chem.*, **533**, 71 (2002).