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# Ceramic Carbon Electrode Modified with Redox Probe and Salt Solution in Hydrophobic Polar Solvent[*]

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Ceramic carbon electrode modified with redox probe and salt solution in hydrophobic polar solvent was prepared and studied. The electrode consisting of graphite powder, homogeneously dispersed in hydrophobic silicate matrix, was prepared from the mixture of methyltrimethoxysilane based sol and graphite powder by sol-gel method. Then it was immersed in t-butylferrocene and tetrabutylammonium perchlorate solution in nitrobenzene. The electrode properties were investigated by cyclic voltammetry and chronoamperometry in $KNO_3$ solutions of different concentration. Linear polarization of the electrode towards positive potentials results in peak shaped symmetric voltammogram originating from electrooxidation of t-butylferrocene. The peak current is few times larger than that obtained when organic phase does not contain salt. It is also proportional to the concentration of the redox probe in organic phase and salt in aqueous phase, whereas the midpeak potential is almost not affected by these factors. The reasons of these effects are discussed.

**Key words**: sol-gel, carbon ceramic electrode, nitrobenzene, t-butylferrocene, ion transfer, liquid | liquid interface

Redox active molecules dissolved in small amount of organic liquid or organic liquid being redox active itself (so called redox liquid) exhibit specific electrochemistry when such organic phase is present on the surface of the electrode immersed into aqueous electrolyte [1–3]. This deposit may form droplets, drops or thin film. Its electrochemical behaviour is connected with the presence of liquid | liquid – organic | aqueous interface. When organic phase is ionically nonconductive (electrochemically unsupported case), the electrochemical reaction starts at three phase junction: electrode | organic phase | aqueous phase – typically circumference of drop or droplet deposit. This reaction involves electron transfer followed by ion transfer across liquid | liquid interface [1–3]. When organic phase containing redox active molecules is ionically conductive (electrochemically supported case), namely it contained dissolved tetraalkylammonium salt, electrochemical reaction is expected to occur at the whole electrode surface covered by drop or thin (*ca*. 30 $\mu$m) film [4–11]. Still the ion exchange between organic and aqueous phase is expected to occur. Some successful experiments with electrocatalytic redox systems show the

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[*] Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

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potentialities of supported systems for electrochemical (amperometric) sensing [10]. However, all supported systems described above are based on such solvents like nitrobenzene (NB) or benzonitrile. They exhibit stable behaviour only when aqueous phase is saturated with organic solvent, because of some solubility of the latter in water.

Recently we proposed alternative electrode material for stable redox liquid deposition. This is a composite of graphite particles and hydrophobic silicate matrix [12–18] or thin film of the latter immobilised on the surface of the metal electrode [19]. The matrix acts as resevoir of redox liquid. It also enhances stability of the redox active deposit during electrochemical experiments involving oxidation-reduction of redox active species within organic phase. Until now this approach was restricted to electrochemically unsupported systems.

The study of the electrochemical properties of so called carbon ceramic electrodes (CCE) [20–22] modified with redox probe and salt solution in hydrophobic polar solvent – NB is the subject of this paper. As a redox probe t-butylferrocene (tBuFc) was selected. It is liquid at room temperature and can be mixed with NB in any ratio allowing preparation of concentrated solution. Its electrochemical redox process in organic solvent can be described by the following reaction [23]:

$$\mathrm{tBuFc} - e \Leftrightarrow \mathrm{tBuFc}^{+} \qquad (1)$$

tBuFc and tetrabutylammonium perchlorate (TBAP) solutions in NB were used for electrode modification. The aqueous salt solution was not saturated by organic solvent. The obtained data were compared with results obtained with CCE modified with pure tBuFc [13,16] and its solution in NB [17].

## EXPERIMENTAL

*Chemicals.* Methyltrimethoxysilane (MTMOS) (99%), and NB (99+%) were from Aldrich and tBuFc (99% pure) was from Strem. They were used without further purification. TBAP was prepared by metathesis of $(C_4H_9)_4NBr$ (Fluka) with $HClO_4$ (Aldrich) in water. The product was recrystallized twice from water and dried under reduced pressure at 100°C for 24 h. $KNO_3$ (analytical grade) was from POCh. Graphite powder (MP-300, average particle size 20 $\mu$m) was obtained from Carbon GmbH. Water was purified by ELIX system (Millipore).

*Electrode preparation.* The matrix was prepared as described elsewhere [20–22]. The hydrolysed sol was prepared by mixing 1 ml of MTMOS with 1.5 ml of methanol. After addition of 50 $\mu$l of 11 M HCl it was sonicated for 2 min. Next, 1.25 g of graphite powder was added and the mixture was sonicated for another minute. The resulting mash was immediately placed into 2 mm deep cavity of the 2 mm inner diameter glass tubing filled tightly with copper wire. The electrode was left for drying for at least 48 hours at room temperature and it was polished with emery paper. The geometric surface area of the intersection was equal 0.31 cm$^2$. Modification of CCE was achieved by immersion to tBuFc and TBAP solution in NB for at least 1 min.

*Instrumentation and cell.* Cyclic voltammetry (CV) and chronoamperometry were performed with Autolab (Eco Chemie) electrochemical system with dedicated software (GPES v.4.9). The start potential in CV experiment was always equal to most negative potential. All presented results were obtained with electrodes freshly modified with organic liquid.

CCE, platinum wire and tungsten oxidized wire (both with diameter 0.5 mm) were used as working, counter and reference electrode respectively. The last electrode was prepared from freshly cut and cleaned 0.5 mm diameter tungsten wire (Aldrich) and conditioned in $KNO_3$ aqueous solution [24,25]. Its potential in 0.1 mol $dm^{-3}$ aqueous $KNO_3$ is equal –0.171 V *vs.* saturated calomel electrode. The electrodes were positioned tightly in the polypropylene cap of the cell. All experiments were done at room temperature 22–23°C.

## RESULTS AND DISCUSSION

Voltammograms obtained with the studied electrode change during first subsequent scans, namely both anodic and cathodic current decrease. However, after 5–7 scans they become stable. Similar behaviour was observed for CCE modified with tBuFc solution in NB without added salt [17].

All presented voltammograms were obtained in conditions when they were not affected by subsequent scanning. Their shape is similar to that obtained in the absence of salt dissolved in organic phase (Fig. 1). During polarization towards anodic direction the wave or not well developed peak is formed whereas during backward scan the peak shape current-potential dependence is observed. This indicates some difference in mode of reactant transport (see below). As in previous studies of related unsupported system within composite silicate based matrix [13,16,17], the redox process may be attributed to the oxidation of tBuFc within NB phase:

$$\mathrm{tBuFc}_{(NB)} - e^{-}_{(graphite)} \Leftrightarrow \mathrm{tBuFc}^{+}_{(NB)} \qquad (2)$$

However, the current obtained with the CCE modified with TBAP solution is much larger than in electrochemically unsupported case (Fig. 1).

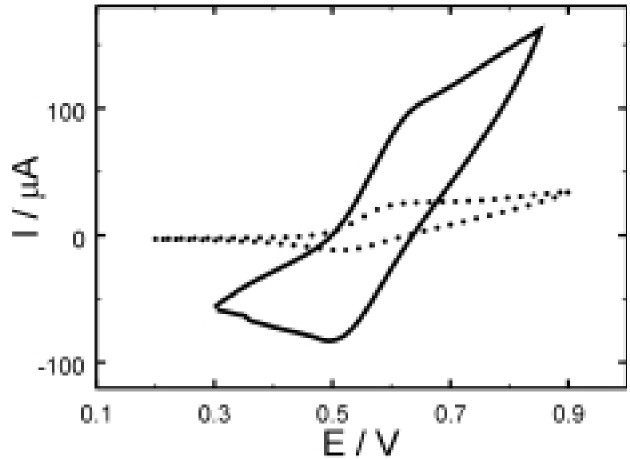

**Figure 1.** Cyclic voltammograms obtained with CCE modified with 0.45 mol $dm^{-3}$ tBuFc (dotted) and 0.45 mol $dm^{-3}$ tBuFc and 0.1 mol $dm^{-3}$ TBAP (solid) solution in NB immersed 0.1 mol $dm^{-3}$ aqueous $KNO_3$. Scan rate 0.01 V $s^{-1}$.

CCE is composed of relatively large (20 $\mu$m) graphite particles forming percolation paths within mesoporous (pore diameter equal *ca.* 10 nm [26]) silicate matrix [27]. NB solution fills the matrix pores and they can be easily penetrated by individual tBuFc molecules or $tBuFc^+$ cations as well as $TBA^+$ and $ClO_4^-$ ions. Eventually, organic liquid covers the rough surface of the sol-gel material facing aqueous phase as well as the surface of the most outer graphite particles not covered by silicate matrix. It has been proven that in system composed of drop of redox probe solution in organic polar solvent deposited on hydrophobized graphite this type of process commences at the three phase junction: electrode | organic liquid drop | aqueous electrolyte [28]. Analogous situation is expected to occur at CCE filled with unsupported organic phase. The electrode process should start at junction: graphite particle | organic liquid immobilized within silicate matrix | aqueous electrolyte [13,16–18].

When the organic liquid phase is ionically conductive as in the present study, one would expect that electrode reaction is not restricted to three phase junction. This is because the third – aqueous phase acting as a source of counterions may not be placed close to the graphite particles – source or sink of electrons. Therefore one would expect that the real electrode surface corresponds to the surface of all graphite particles composing percolation paths within the electrode body. If this reasoning is correct the current obtained with CCE modified with supported organic phase should be two orders of magnitude larger than unsupported CCE which is not the case (Fig. 1). This indicates that the difference between the active surface of "supported" or "unsupported" electrode is not large. Therefore only particles being close to the liquid | liquid interface participate in electrode reaction as a source or drain of electrons. This may be because ion transport across this interface follows electron transfer reaction, being the rate limiting step. Interestingly, no substantial difference between voltammetric behaviour of glassy carbon electrode modified with drop of ferrocene solution in NB containing and not containing TBAP was observed [29]. The authors pointed out the extension of the reaction domain to the whole electrode surface covered by organic phase [29,30], however they did not consider kinetic effects of ion transfer across liquid | liquid interface. The covering of graphite by silicate matrix making most of them inaccessible for redox active molecules represents alternative explanation of small difference between currents obtained in "supported" and "unsupported" electrode.

The shape of voltammogram and the current magnitude depend on both $c_{tBuFc(org)}$ and concentration of salt in aqueous phase ($c_{KNO_3(aq)}$) (Figs. 2, 3).

The voltammograms are wave shaped with noticeable exception of these obtained for smallest concentration of tBuFc ($c_{tBuFc(org)}$). For a given $c_{KNO_3(aq)}$ the magnitude of the current is proportional to $c_{tBuFc(org)}$. However this dependence is not linear. Although the shape of the voltammogram does not allow determination of redox potential one may conclude that it is not much affected by the concentration of salt in aqueous phase. The current is also proportional to the aqueous electrolyte concentration as it was observed for CCE modified with analogous unsupported NB

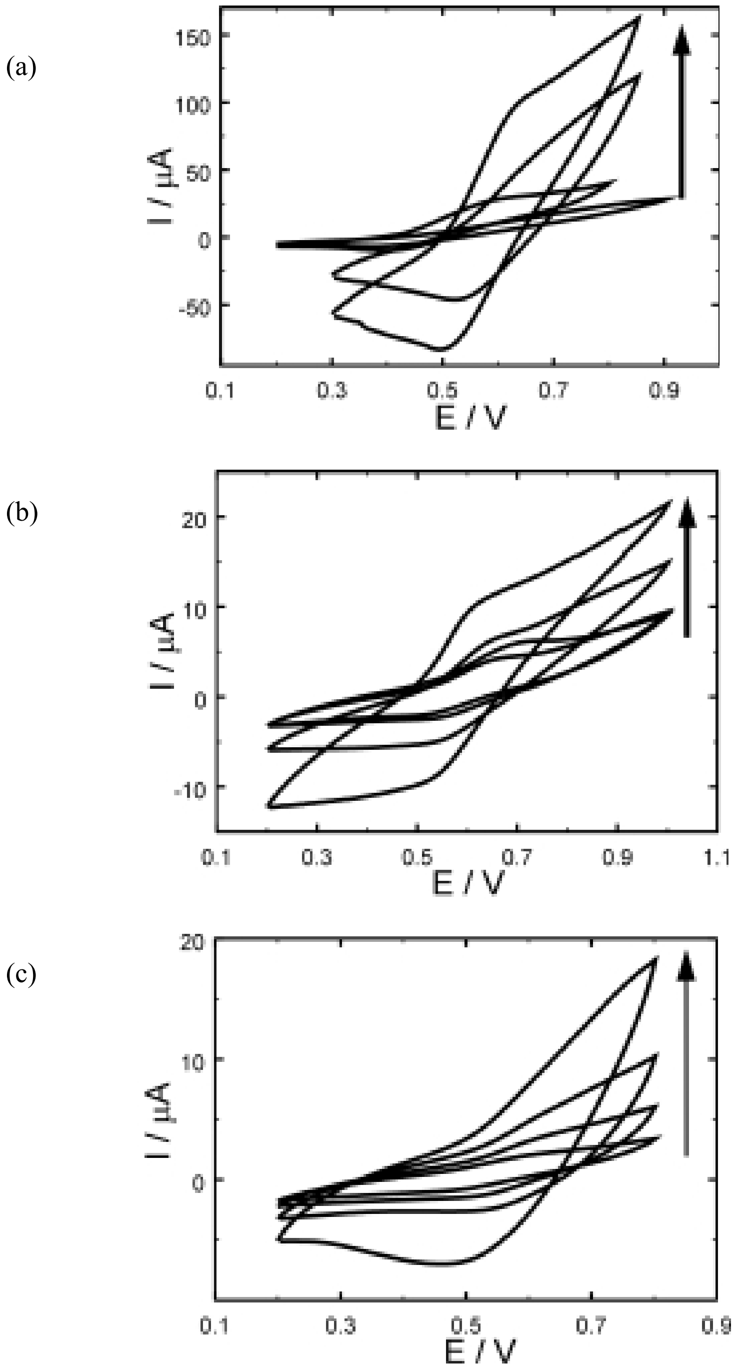

**Figure 2.** Cyclic voltammograms obtained with CCE modified with (a) 0.45, (b) 0.045 and (c) 0.0045 mol dm$^{-3}$ tBuFc in 0.1 mol dm$^{-3}$ TBAP solution in NB immersed in 0.001, 0.01, 0.1 and 1 mol dm$^{-3}$ aqueous $KNO_3$. Scan rate 0.01 V s$^{-1}$. The arrow shows $KNO_3$ concentration increase.

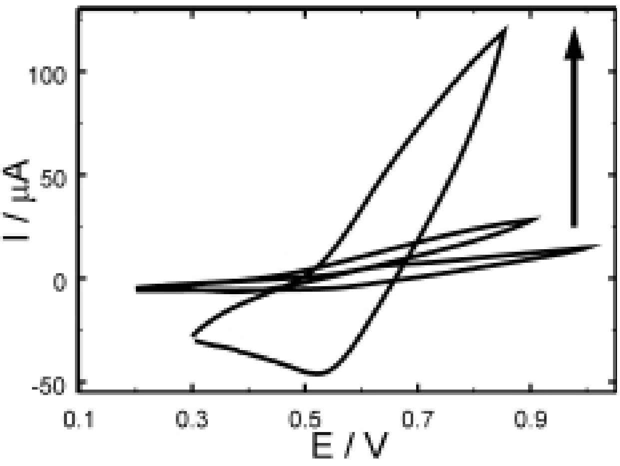

**Figure 3.** Cyclic voltammograms obtained with CCE modified with 0.45, 0.045 and 0.0045 mol dm$^{-3}$ tBuFc solution in 0.1 mol dm$^{-3}$ TBAP solution in NB immersed in 0.01 mol dm$^{-3}$ aqueous $KNO_3$. Scan rate 0.01 V s$^{-1}$.

phase [17] or by pure redox liquid [16]. This clearly indicates that the transfer of $NO_3^-$ from aqueous to organic phase occurs in order to fulfil electroneutrality condition:

$$NO_{3\ (aq)}^- \rightarrow NO_{3\ (NB)}^- \qquad (3)$$

For studied electrode this reaction can be only generated electrochemically. This is because $NO_3^-$ exhibits moderate standard Gibbs energy of transfer from $H_2O$ to NB [31] and partition coefficient of $KNO_3$ between NB and $H_2O$ is extremely low ($1.37\times10^{-4}$ [32]).

The shape of voltammogram, especially anodic scan indicates significant contribution of radial diffusion. To answer the question whether this is the case we performed potential step experiments. The current *vs*. time dependence obtained for anodic step is going to stabilize at some positive value of the current, whereas that obtained in cathodic step tends to go to zero (Figs. 4a,b). The shape of anodic step Cottrell plot for longer time is linear with positive intercept. This indicates ultramicroelectrode like behaviour [33]. The positive deviation from this dependence at shorter times may be connected with transition from linear to semiinfinite diffusion regime. On the other hand the deviation from linearity observed for cathodic step at longer times is typical for diffuse layer depletion in ultramicroelectrode assembly [34–38] and it was observed for CCE modified with pure redox liquid [16]. The ultramicroelectrode like behaviour is connected with the small size of graphite particles forming percolation paths within silicate matrix. They probably act as an assembly of microelectrodes having not well defined geometry and size distribution.

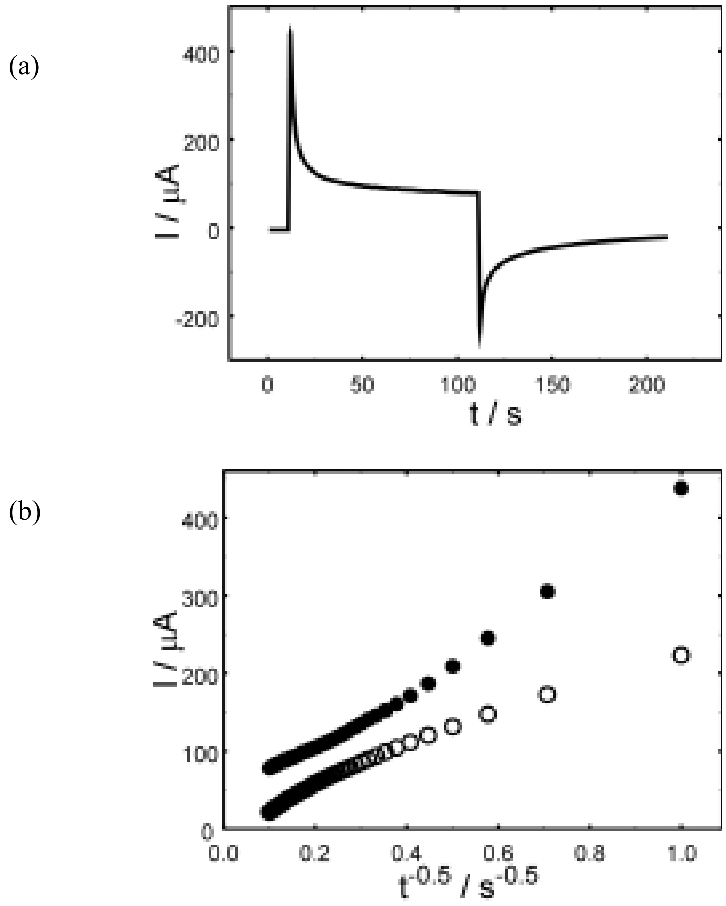

**Figure 4.** (a) The current, I, vs. time, t, plot obtained from the potential step experiment with CCE (solid) modified with 0.45 mol dm$^{-3}$ tBuFc in 0.1 mol dm$^{-3}$ TBAP solution in NB immersed in 0.1 mol dm$^{-3}$ aqueous $KNO_3$. (b) The Cottrell plot of anodic (●) and cathodic current (○) obtained from experiment described above.

## CONCLUSIONS

The features of voltammograms obtained with CCE impregnated with redox probe solution and salt solution in hydrophobic polar solvent were presented and analysed. Only small part of carbon particles act as electronic conductor for the studied reaction. It seems to that the oxidation of redox probe is followed by anion insertion into the organic phase impregnating the electrode body. Further refinement of the mechanism requires systematic change of hydrophobic/hydrophilic properties of redox probe and counteranion. Research in this direction is performed.

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