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Carbon ceramic electrode modified with redox liquid

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A carbon ceramic electrode modified with a redox liquid, butylferrocene, exhibiting in aqueous salt solution electrochemical behaviour resulting from the redox process of the modifier and ion transfer across the liquid–liquid interface has been prepared.

Originally, the idea of chemically modified electrodes (CME) was based on the immobilisation of the electron relay between the electrode surface and liquid electrolyte. At that time it was realised by chemisorption, film deposition of the electroactive substance or covalent bonding of electroactive molecules to the electrode surface.[1] The increase of the number of the redox centers has been one of the directions of the development of CME. The use of redox polymers with redox active groups covalently or electrostatically bonded to the polymer chain represents the most popular strategy.[2] Although high, the density of the redox centers is limited by synthetic requirements. The presence of other elements contributing to the volume of the polymer such as the main polymeric chain or its branches, including those connecting the redox groups, as well as solvent swelling, decreases the ‘redox density’ of the polymer.[2]

One can use pure redox active compounds in the liquid state for electrode modification. In such a case the density of redox active groups is determined by the molar volume and the mobility of the redox active molecules is much larger than in analogous solid material. The deposition of so-called redox liquids on the electrode surface exhibiting electroactivity after immersion into aqueous electrolytes was recently reported.[3,4] However, the stability of such electrodes depends strongly on the interactions between the modifier and the electrode surface. In this communication we propose the use of a sol–gel derived glass with dispersed carbon, so-called carbon ceramic electrodes (CCE),[5] as a stable matrix for the redox liquid. The hydrophobic–hydrophilic properties of the sol–gel matrix can be modified by using appropriate precursors for matrix preparation. We took advantage of strong affinity of hydrophobic liquids towards a hydrophobic silica matrix prepared from methyltrimethoxysilane (MTMOS).[6,7] Two liquid butylferrocenes (BuFc): *n*-butylferrocene (nBuFc) and *tert*-butylferrocene (tBuFc) were selected as redox modifiers. Their application leads to the concentration of the electroactive redox centers to a maximum of 4 mol dm^{-3} similar to values found for redox polymers.

For the present study the CCE was prepared by a method similar to that described in the literature.[5,8] The redox liquid modified CCE (RLCCE) was prepared by immersion of the electrode into liquid BuFc for at least 1 min. Cyclic polarization of the RLCCE in aqueous electrolyte results in voltammograms[9] which are stable during multiple potential cycling (Fig. 1). The dilution of BuFc by a hydrophobic non-electroactive solvent such as hexadecane leads to a decrease of the current. Neither anodic or cathodic peaks appear when the electrode is modified with a non-electroactive hydrophobic liquid such as a linear hydrocarbon. Therefore the specific voltammogram features can be attributed to the redox process of BuFc [eqn. (1)] with tBuFc being easier to electrooxidize than nBuFc:

$$BuFc_{(org)} - e_{(graphite)} \leftrightarrow BuFc^{+}_{(org)} \qquad (1)$$

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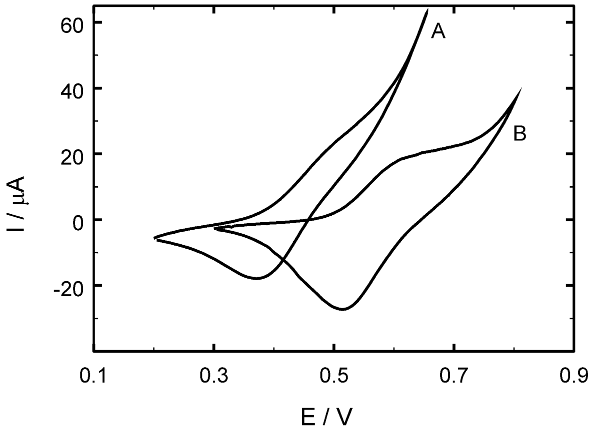


Fig. 1 Cyclic voltammograms recorded with RLCCE modified with (A) tBuFc, (B) nBuFc immersed in 0.1 M KCl aqueous solution.

The position of the voltammogram on the potential scale also depends on the anion of the aqueous electrolyte (Fig. 2). The corresponding midpotentials are 0.33, 0.45 (approximate value) and 0.55 V for Br$^-$, Cl$^-$ and F$^-$ solutions, respectively for tBuFc. It is easier to electrooxidise tBuFc with less hydrated anions present in the aqueous phase.[10] Additionally, for a given anion, the magnitude of the peak current is proportional to the salt concentration in the aqueous phase. Thus the electrooxidation of BuFc is thermodynamically more favorable in the presence of weakly hydrated anions. Although a slight solubility of BuFc$^+$ in water was suggested,[3] the result presented above indicates that the formation of this cation in the organic phase is followed by anion transfer from the aqueous phase [eqn. (2)]:

$$BuFc^{+}_{(org)} + X^{-}_{(aq)} \leftrightarrow BuFc^{+}\cdots X^{-}_{(org)} \qquad (2)$$

This is also expected in terms of fulfillment of the electroneutrality condition. The existence of separately solvated cations or anions in weakly polar media such as butylferrocene is unlikely and the formation of ion pairs is expected.

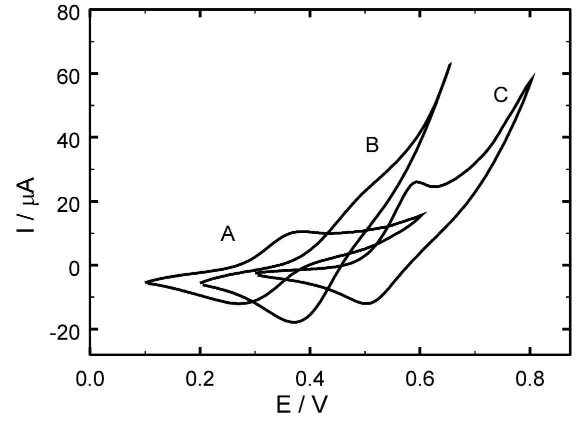
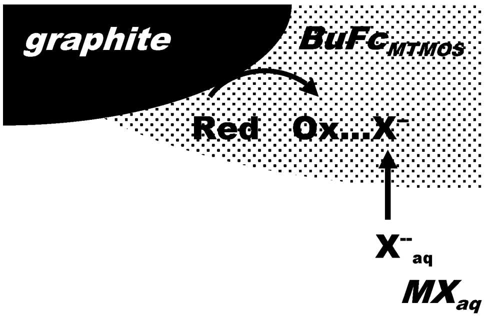


Fig. 2 Cyclic voltammograms recorded with RLCCE modified with tBuFc immersed in 0.1 M aqueous solutions: (A) KBr, (B) NaCl, (C) KF.

One can expect that the heterogeneous structure of the electrode (Scheme 1) plays an important role in the mechanism of the electrode process. At the beginning of the potential scan the electrooxidation of the BuFc molecule is expected to occur only close to the three-phase junction: graphite/organic phase/ aqueous phase, because of the lack of supporting electrolyte in the organic phase. The sigmoidal, ultramicroelectrode like anodic wave or weakly developed anodic peak supports this view. The short time ($t \leq 10$ s) linear part of Cottrell plot (i *vs.* $t^{-0.5}$) (not shown) obtained from the potential step experiment is positive which also indicates ultramicroelectrode like behaviour of graphite particles. Back electroreduction of $BuFc^+$ may not be limited to the three phase-junction, because ions or ion pairs are already present as a result of the electrode process and indeed a cathodic peak is observed. It has to be emphasized that BuFc not only fills the hydrophobic MTMOS based matrix but it may eventually cover some part of graphite particles in contact with the aqueous phase.

The magnitude of peak current densities obtained with RLCCE are comparable or larger than these obtained with a thin layer of ferrocene polymer immobilised on the electrode surface.[2,11,12] Obviously, this parameter depends not only on the concentration of redox active molecules, but also on other factors such as viscosity of the redox liquid, structure of the interface, the rate of ion transfer through the interface, the solubility of the product of the electrode reaction in both phases and probably many other factors. It has to be emphasized that we did not remove the polymer matrix, however, it plays different role than in the case of polymer modified electrodes.[2] It supports both an electronic conductor (graphite particles) and a redox active compound (redox liquid) together as well as providing a liquid–liquid interface. The redox liquid fills > 10 nm pores of the matrix[13] rather than being connected to the polymeric chain.



Scheme 1 Schematic representation of the electrode reaction site.

In summary, we have reported stable immobilisation of redox liquids in CCE. First, this is an example of a different approach in modification of the electrode/electrolyte interface. Also it represents another application of gels solvated with organic solvent[14] as well as another method of CCE modification.[5] The prospective application of this electrode as a sensor can be envisaged. Mechanistic studies of the performance of RLCCE are being conducted.

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